PETROPHASE 2017

Le Havre, France, June 11-15

PetroPhase 2017

The 18th International Conference on Petroleum Phase Behavior and Fouling

Table of contents

Welcome to PetroPhase 2017 4

History of conferences and locations 6

Le Havre overview 7

Le Havre 500th anniversary 9

Committees 10

Sponsors 11

Exhibitors 12

Programme overview 14

Programme 16

- Petroleum Chemistry Orals 25
- Petroleum Chemistry Posters 43
- Emulsions Orals 105
- Emulsions Posters 113
- Flow Assurance Orals 133
- Flow Assurance Posters 143
- Upgrading and Fouling Orals 181
- Upgrading and Fouling Posters 191
- Shale Oil & Gas and Enhanced Oil Recovery Orals 203
- Shale Oil & Gas and Enhanced Oil Recovery Posters 213
- Petroleum Properties and Phase Behaviour Orals 227
- Petroleum Properties and Phase Behaviour Posters 237
- Asphaltene 2017 285

Authors index 319

Welcome to PetroPhase 2017

Dear conference participants,

On behalf of the Technical and Organizing Committees, we welcome you to the 18th International Conference on Petroleum Phase Behavior & Fouling – PetroPhase 2017.

PetroPhase is a conference dedicated to the study of the properties and chemistry of petroleum fluids and their effect on producing, processing, and refining in the upstream, mid-stream, and downstream industries. The conference was first started in 1999 as "The International Conference on Petroleum Phase Behavior & Fouling" and has since evolved into an annual event alternating venues among international cities. It has been fortunate to have enjoyed financial and organizational support from many academic and industrial partners through the years.

Total, the University of Pau and the University of Rouen-Normandy are proud to organize the 18th PetroPhase conference, in the city of Le Havre, that will celebrate at the same time the 500th birthday of its foundation.

The conference is traditionally organized each year by different volunteer organizations, and the C2MC joint lab is proud to continue the tradition this year.

Our joint laboratory C2MC was created in 2014 on the basis of two analytical groups from the universities of Pau and Rouen and a part of the Analytical Department from the Research Direction of TOTAL RC. The addition of skills and synergies arising from these three groups is already generating a creative ambiance in cutting-edge research into the molecular characterization of complex matrices such as petroleum. Including members from the Complex Fluids Laboratory of Pau University, C2MC research programs are closely related to the scientific fields covered by PetroPhase.

In addition to the technical presentations (poster or oral) the conference receptions and social events allow attendees ample opportunity to interact with colleagues working in or in the support of the petroleum industry. The conference dinner on Wednesday evening will be held in “Le Grenier à sel” in the village of Honfleur across the river from Le Havre, on the left bank of the seine.

We thank the technical and organizing committees for their work, without which a conference of this size would not be possible. We would like to thank our sponsors: government, private and industrial. Finally, we wish to thank the presenters and attendees of the conference – you are the reason that PetroPhase exists and thrives.

So, enjoy all aspects of the conference and we hope your stay will be a memorable one.

Dr. Pierre Giusti - Chair, Total Refining & Chemicals, Le Havre, France

Pr. Brice Bouyssiere - Co-chair, University of Pau, France

Pr. Hervé Carrier - Co-chair, University of Pau, France

Pr. Carlos Afonso - Co-chair, University of Rouen-Normandy, France

From left to right: Hervé, Carlos, Pierre and Brice

History of conferences

17th – 2016, Elsinore, DENMARK

16th – 2015, Riviera Maya, MEXICO

15th – 2014, Galveston, USA (Texas)

14th – 2013, Rueil-Malmaison, FRANCE

13th – 2012, St Petersburg, USA (Florida)

12th – 2011, London, UNITED KINGDOM

11th – 2010, Jersey City, USA (New Jersey)

10th – 2009, Rio de Janeiro, BRAZIL

9th – 2008, Victoria, CANADA (British Columbia)

8th – 2007, Pau, FRANCE

7th – 2006, Asheville, USA (North Carolina)

6th – 2005, Amsterdam, The NETHERLANDS

5th – 2004, Banff, CANADA (Alberta)

4th – 2003, Trondheim, NORWAY

3rd – 2002, New Orleans, USA (Louisiana)

2nd – 2000, Copenhagen, DENMARK

1st – 1999, Houston, USA (Texas)

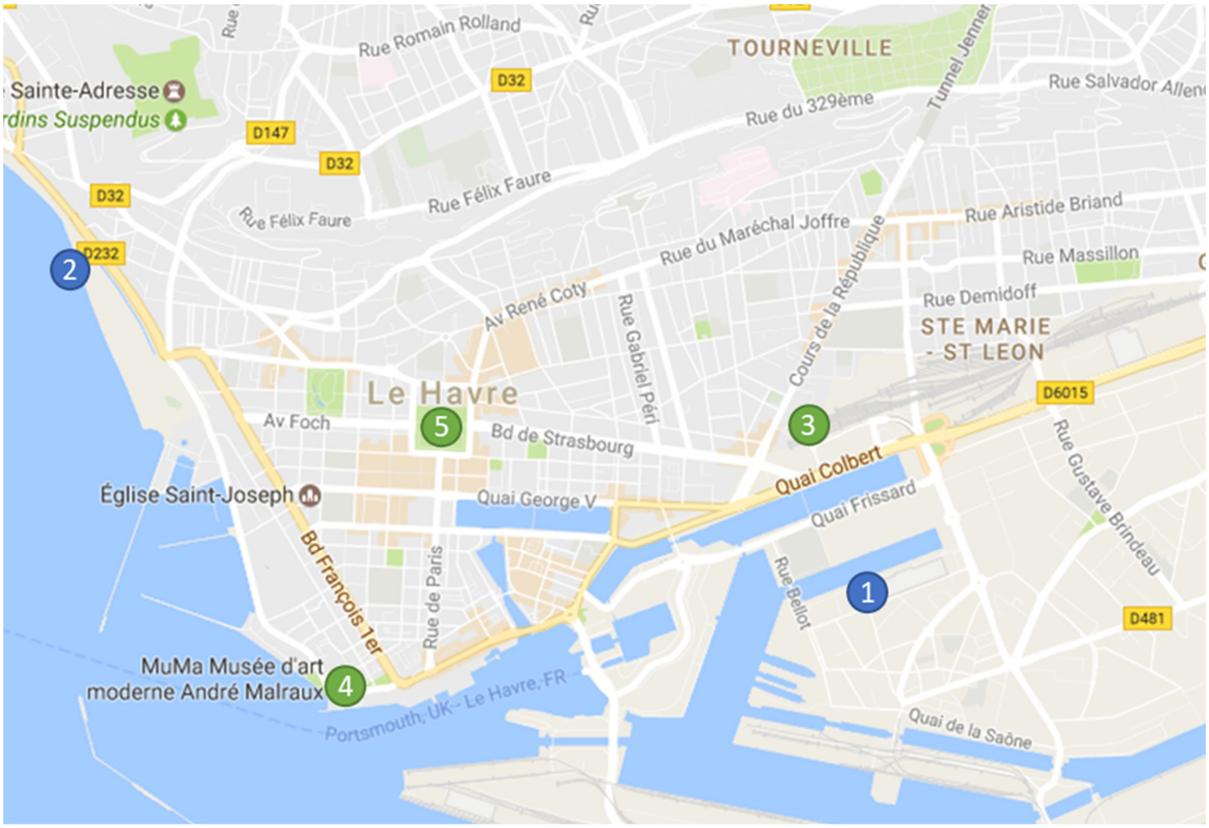
Le Havre overview

The city of Le Havre is situated on the right bank of the estuary of the river Seine on the Channel southwest of the Pays de Caux.

Modern Le Havre remains deeply influenced by its employment and maritime traditions. Its port is the second largest in France, after that of Marseille, for total traffic, and the largest French container port. The name Le Havre means "the harbour" or "the port".

The city and port were founded by King Francis I of France in 1517. It was from the end of the 18th century that Le Havre started growing and the port took off with international trade. After the 1944 bombings the architectural firm of Auguste Perret began to rebuild the city in concrete.

In 2005 UNESCO inscribed the central city of Le Havre as a World Heritage Site.



① Conference Center

② Beach Restaurants

③ Train Station

④ MuMa art museum

⑤ Le Havre City Hall

Le Havre 500th anniversary

In spring 2017, as Le Havre marks its 500th anniversary, visual artists, designers, graphic artists, stage directors, novelists, will follow in the wake of the architect Niemeyer and the painter Monet to reinterpret this surprising city, to reveal it to Europe… and perhaps even to itself. When you arrive in the city, on the Volcan Theater side, you enter an open-air monument with Porte Océane located at the west end; here the beach is frequented by relaxing bathers gazing at the horizon as the biggest container ships in the world go by.

Celebrating a city's foundation and 500 years of history is a rare opportunity. An opportunity to take a fresh look at our city — a look that might surprise us. A chance to show the world what we are and what we can do. This anniversary is a historically unique occasion to show what this surprising city is really like.

Four cultural tours have been designed around the city: discover the works of art created and installed in the public space to celebrate Le Havre's 500th anniversary - visit the prestigious exhibitions held to mark the event - admire the emblematic monuments that make up Le Havre's architectural landscape, from the city center area listed as a UNESCO world heritage site, to the harbor basins and the heights above the city

Committees

Technical Committee

Alberto Di LULLO	ENI, Italy
Andrew YEN	Nalco, USA
Ben SMITH	BP, UK
Carlos LIRA-GALEANA	IMP, Mexico
Daniel MERINO GARCIA	Repsol, Spain
David JENNINGS	Baker Hugues, USA
Harvey YARRANTON	University of Calgary, Canada
Honggang ZHOU	Total EP, France
Irv WIEHE	Soluble Solutions, USA
Isabelle MERDRIGNAC	IFPEN, France
Jean François ARGILIER	IFPEN, France
Jean-Luc DARIDON	University of Pau, France
Jianxin WANG	Chevron, USA
Johan SJØBLOM	NTNU, Norway
John SHAW	Univesity Of Alberta, Canada
Michael HOEPFNER	University of Utah, USA
Murray GRAY	Univesity Of Alberta, Canada
Nicolas PASSADE-BOUPAT	Total EP, France
Nicolas VON SOLMS	Technical University of Denmark
Peter KILPATRICK	University of Notre Dame, Indiana, USA
Peter SEIDL	Federal university of Rio de Janeiro, Brazil
Ryan RODGERS	Florida State University, Tallahassee, USA
Ryuzo TANAKA	Idemitsu Kosan, Japan
Simon ANDERSEN	Asphalteam, Denmark
Steven ROWLAND	Future Fuels Institute, USA
Sunghwan KIM	Kyungpook National University, South Korea
Sylvain VERDIER	Haldor-Topsøe, Denmark
Wanderson ROMAO	Federal University of Espírito Santo, Vitoria, Brazil
Wei YAN	Technical University of Denmark
Yajaira COMBARIZA	University of Santander, Colombia

Conference Co-Chairs

Pierre GIUSTI, Chair	Total, France
Hervé CARRIER	Université de Pau et des Pays de l’Adour, France
Brice BOUYSSIÈRE	Université de Pau et des Pays de l’Adour, France
Carlos AFONSO	Université de Rouen, France

Sponsors

Platinium Sponsors

TOTAL

Silver Sponsors

energy&fuels

Bronze Sponsors

VUV ANALYTICS

ifp Energies nouvelles

ExxonMobil

INSTITUT CARNOT ISIFoR

TREMPLIN CARNOT I2C

UNIVERSITÉ DE PAU ET DES PAYS DE L'ADOUR

UNIVERSITÉ DE ROUEN

BYK
Additives & Instruments

Exhibitors

Oilfield Production Additives
Refining Additives
Performance Additives
Industrial Fuels
Racing Fuels
Services & Support

TOTAL ADDITIFS & CARBURANTS SPÉCIAUX

VUV ANALYTICS

Waters
THE SCIENCE OF WHAT'S POSSIBLE.®

Leco®
Delivering the Right Results

PROMAT Sécurité

Formulaction
Smart scientific analysis

TOP INDUSTRIE
High Pressure Engineering

Agilent Technologies

ThermoFisher
SCIENTIFIC

BRUKER

VINCI
TECHNOLOGIES

Programme

Programme Overview

Sunday, June 11th	Monday, June 12th	Tuesday, June 13th
	Keynote 8:30 – 9:10	**Keynote** 8:30 – 9:10
	Petroleum Chemistry I 9:10 - 10:25	**Flow Assurance I** 9:10 - 10:25
	Coffee Break 10:25 – 10:55	Coffee Break 10:25 – 10:55
	Petroleum Chemistry II 10:55 – 12:10	**Flow Assurance II** 10:55 – 12:10
	Lunch 12:10 – 13:30	Lunch 12:10 – 13:30
	Keynote 13:30 – 14:10	**Petroleum Chemistry III** 13:30 – 15:35
	Emulsions 14:10 – 15:25	
Registration 16:00 – 18:00	Coffee break + Poster session I 15:25 – 16:30	Coffee break + Poster session II 15:35 – 16:40
Opening address and Reception 18:00 – 22:00	**Asphaltene 2017** 16:30 – 18:30	**Asphaltene 2017** 16:40 – 18:40
	Dinner at Le Havre Beach – Restaurant l'Amarino 19:00	

Wednesday, June 14th	**Thursday, June 15th**
Keynote 8:30 – 9:10	**Keynote** 8:30 – 9:10
Upgrading & Fouling I 9:10 - 10:25	**Petroleum Properties I** 9:10 - 10:25
Coffee Break 10:25 – 10:55	**PetroPhase 2018 announcement** 10:25 – 10:35
	Coffee Break 10:35 – 10:55
Upgrading & Fouling II 10:55 – 12:10	**Petroleum Properties II** 10:55 – 12:10
12:10 – 12:15 E&F (ACS) Poster price announcement	Lunch 12:10 – 13:30
Lunch 12:15 – 13:30	
Keynote 13:30 – 14:10	D-day trip Visit of the D-Day Landing Beaches (with additional fees) 13:30 – 17:00
Shale Oil & Gas and Enhanced Oil Recovery 14:10 – 16:50	
Departure to Honfleur Bus trip 17:00 – 17:30 Visit of Honfleur 17:30 – 19:00	
Gala Dinner at Le Grenier à Sel in Honfleur 19:00 – 23:00 23:00 Return to le Havre	

Sunday, June 11th

16:00	Registration - Registration at the conference center
18:00 - 22:00	Opening address and Reception

Monday, June 12th

Petroleum Chemistry I

Chairs : Peter Kilpatrick, Christian Blanco-Tirado

08:30	**PC-K**	**› Contributions of High Resolution Mass Spectrometry to the Field of Petroleomics** Ryan Rodgers, *Future Fuels Institute, Florida State University, National High Magnetic Field Laboratory*
09:10	**PC-O1**	**› Development of a petro-informatics platform for the characterization of heavy petroleum fractions** Ryuzo Tanaka, *Technology & Engineering Center, Idemitsu Kosan Co., Ltd.*
09:35	**PC-O2**	**› Asphaltenes' and porphyrins' molecular cartography and the aggregation properties studied by molecular dynamics simulations** Hugo Santos Silva, *Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux*
10:00	**PC-O3**	**› Elucidating Structures of Compounds in Crude Oil Based on Tandem Mass Spectrometry Combined with Ion Mobility Mass Spectrometry** Sunghwan Kim, *Department of Chemistry, Kyungpook National University*

10:25 - 10:55	Coffee break

Petroleum Chemistry II

Chairs : Ryan Rodgers, Sunghwan Kim

10:55	**PC-O4**	**› Molecular Insights into Petroleum Resid Composition through Advanced Mass Spectrometry Techniques** Amrit Jalan, *ExxonMobil Research and Engineering*
11:20	**PC-O5**	**› Determination of Interaction and Complexation among Asphaltene to Understand their Aggregation and Precipitation** Sébastien Simon, *Ugelstad Laboratory, Norwegian University of Science and Technology*
11:45	**PC-O6**	**› Direct Characterization of Aliphatic and Aromatic Contributions to Chemical Classes of Four Crude Oils using Tunable Vacuum Ultraviolet Photoionization** Jeremy Nowak, *UC Berkeley*

12:10 - 13:30	Lunch

Emulsions

Chairs : Maurice Bourrel, Dominique Langevin

13:30	**E-K**	**› Crude oil emulsions and behaviour of asphaltenes at oil-water interfaces** Dominique Langevin, *Laboratoire de Physique des Solides*
14:10	**E-O1**	**› Demulsifier structure-performance relationship in water-in-oil systems** Craig Davies, *Croda Europe Ltd., University of Bristol*
14:35	**E-O2**	**› Advantage of using Multiple light scattering technique for the new safe demulsifier efficiency analysis for oil production** Christelle Tisserand, *Formulaction*
15:00	**E-O3**	**› A lattice gas model for asphaltenes adsorption at water/oil interface** Vincent Pauchard, *Energy Institute and Chemical Engineering Department City College of New York, New York, USA*
15:25 - 16:30		Coffee break + Poster session I
16:30 - 18:30		**Asphaltene 2017** Chairs : Marianny Y. Combariza, Simon Andersen, Ryan Rodgers, Pierre Giusti
19:00 -21:00		Dinner at Le Havre Beach – Restaurant l'Amarino

Tuesday, June 13th

Flow Assurance I

Chairs : Nicolas Passade-Boupat, Simon Andersen

08:30	**FA-K**	**› Flow Assurance - New solutions for the same old problems** Daniel Merino-Garcia, *Repsol, Madrid, Spain*
09:10	**FA-O1**	**› Influence of Al2O3/SiO2 ratio on asphaltenes precipitation in a packed-bed microreactor with in situ analytics** Bruno Pinho, *New York University - Tandon School of Engineering*
09:35	**FA-O2**	**› An insight View on Asphaltene Stability Measurement** Jens Pfeiffer, *PSL Systemtechnik GmbH - Alfred Hase, NALCO Champion*
10:00	**FA-O3**	**› Asphaltenes destabilization and deposition assessment by acoustic resonator** Ezequiel Orlandi, *Laboratoire des Fluides Complexes et leurs Réservoirs*
10:25 - 10:55		Coffee break

Flow Assurance II

Chairs : Daniel Merino-Garcia, Hervé Carrier

10:55	**FA-O4**	**› Decoding cool-down test on wet insulation for flow assurance through full scale validation using advanced technologies** Bo Xu, *Shawcor Ltd*
11:20	**FA-O5**	**› Cold flow solutions for wax challenges** Claire Ward, *Croda Europe Ltd*
11:45	**FA-O6**	**› Large Scale Wax Deposition Experimental Study and Model Performance Evaluation** Shuxin Hou, *Statoil ASA*
12:10 - 13:30		Lunch

13:30 - 15:35

Petroleum Chemistry III

Chairs : Ryuzo Tanaka, Douglas Kushnerick

13:30	**PC-O7**	**› On the Many Competing Mechanisms in Gel Permeation Chromatography of Petroleum Fractions** Simon Andersen, *Asphalteam*
13:55	**PC-O8**	**› Automated SPE and LC-HRMS for optimized tetraprotic acid quantification in crude oil** Matthieu Loriau, *TOTAL Exploration Production*
14:20	**PC-O9**	**› The Effects of Macrocycle Type and Exocyclic Oxygen on Petroporphyrin Properties and Behavior in Bulk and at Interfaces** Peter Kilpatrick, *University of Notre Dame*
14:45	**PC-O10**	**› Understanding the Molecular Structure of Asphaltene in a Geochemical Perspective** Quan Shi, *China University of Petroleum-Beijing*

15:10	**PC-O11**	**› Correlations between molecular composition and the adsorption/aggregation behavior of Arabian asphaltenes** Deisy Giraldo, *Universidad Industrial de Santande*
15:35 - 16:40		Coffee Break + Poster session II
16:40 -18:40		**Asphaltene 2017** Chairs : Marianny Y. Combariza, Simon Andersen, Ryan Rodgers, Pierre Giusti

Wednesday, June 14th

Upgrading & Fouling I

Chairs : Irv Wiehe, Pierre Giusti

08:30	**UF-K**	› **Optimizing slurry hydrocracking unit performances via a deep characterization of heavy products** Nicoletta Panariti, *Eni S.P.A.*
09:10	**UF-O1**	› **Delayed coker coke characterization: correlation between process conditions, coke composition and morphology** Naydu Zambrano Urrutia, *Universidad Industrial de Santander*
09:35	**UF-O2**	› **Increased Asphaltenes Stability in Conventional Crude Oils When Blended With a Bio-Crude Oil** Sai Reddy Pinappu, *Baker Hughes Inc*
10:00	**UF-O3**	› **Characterization and upgrading of catalytic fast pyrolysis oils from pine tree** Sylvain Verdier, *Haldor Topsoe A/S*
10:25 - 10:55		Coffee break

10:55 - 12:10

Upgrading & Fouling II

Chairs : Nicoletta Panariti, Sylvain Verdier

10:55	**UF-O4**	› **Fouling phenomena when processing light crudes** Marco Respini, *Baker Hughes*
11:20	**UF-O5**	› **Crude Oil Fouling using a Multi-celled Batch Autoclave and a New Flow through Fouling Apparatus** Jeramie Adams, *Western Research Institute*
11:45	**UF-O6**	› **Molecular Characterization and Modeling for Crude Oil and Reactors** Shu Wang, *AspenTech Inc.*
12:10 – 12:15		E&F (ACS) Poster price announcement
12:15 - 13:30		Lunch

Shale Oil & Gas and Enhanced Oil Recovery

Chairs : Jean-Pierre Korb, Henrik Sørensen

13:30	**SO-K**	› **Crude oil surface active species: Consequences for emulsion stability and Enhanced Oil Recovery** Maurice Bourrel, *Total E&P*
14:10	**SO-O1**	› **Influence of adsorption and capillary pressure on phase equilibrium in shale reservoirs** Diego Sandoval, *Technical University of Denmark*
14:35	**SO-O2**	› **The Combined Electromagnetic Methods for Enhanced Heavy Oil Recovery: Experimental and Theoretical Proofs** Victor Kireev, *Bashkir State University*

15:00	**SO-O3**	**› CT scannings of core floods: Quantitative analysis of saturation without dopant** Amalia Halim, *The Danish Hydrocarbon Research and Technology Centre*
15:25	**SO-O4**	**› Molecular simulations of the micro-porous organic matter in shales** Guillaume Galliero, *Laboratoire des Fluides Complexes et leurs Réservoirs*
17:00 - 17:30		Departure to Honfleur - Bus trip
17:30 -19:00		Visit of Honfleur
19:00 - 23:00		Gala Dinner at the Grenier à Sel in Honfleur
23:00 - 23:30		Return to le Havre - Bus rotations to the hotels

Thursday, June 15th

Petroleum Properties I

Chairs : Guillaume Galliero, Socrates Acevedo

08:30	**PP-K**	**› Strange Brew – Mixtures of Heavy Oil and Solvent** Harvey Yarranton, *University of Calgary*
09:10	**PP-O1**	**› Atomic force microscope as a tool to detect asphaltene particles in crude oil** Watson Loh, *University of Campinas (UNICAMP)*
09:35	**PP-O2**	**› Contribution of molecular simulation to systematic thermophysical property prediction for upstream and downstream applications** Philippe Ungerer, *Materials Design SARL*
10:00	**PP-O3**	**› Quartz Crystal Microbalance Enables Selection of the Right Asphaltene Inhibitor for Application in a Real Field Condition** Edris Joonaki, *CFAR, Institute of Petroleum Engineering, Heriot-Watt University*
10:25 - 10:35		**PetroPhase 2018 announcement**
10:35 - 10:55		Coffee break

Petroleum Properties II

Chairs : Harvey Yarranton, Michael Hoepfner

10:55	**PP-O4**	**› Extraction and molecular-level characterization of soluble organics in produced water from a Gulf of Mexico platform** Andrew Yen, *Nalco Champion*
11:20	**PP-O5**	**› Direct Observation Of Asphaltene Nanoparticles On Model Mineral Substrates** Gijo Raj, *New York University Abu Dhabi*
11:45	**PP-O6**	**› Ultra-Small-Angle Scattering Investigation of the Structure and Precipitation Mechanism of Asphaltenes in Solvent Mixtures** Yuan Yang, *Department of Chemical Engineering, University of Utah*
12:10 - 13:30		Lunch
13:30 -17:00		D-day beaches trip - Visit of the D-Day Landing Beaches (with additional fees)

Abstracts

ORALS
Petroleum Chemistry

Contributions of High Resolution Mass Spectrometry to the Field of Petroleomics

Ryan Rodgers*†[1,2,3], Steven Rowland[1,3], Donald Smith[3], Greg Blakney[3], Martha Chacon[3], Jonathan Putman[2], Amy Mckenna[3], Yuri Corilo[1,3], David Podgorski[3], Priscila Lalli[1,3], Amy Clingenpeel[3], Jie Lu[1], Alan Marshall[2,3], and Christopher Hendrickson[3]

[1]Future Fuels Institute, Florida State University (FFI) – 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, United States, United States

[2]Department of Chemistry and Biochemistry, Florida State University – 95 Chieftain Way, Tallahassee, FL 32306, United States

[3]National High Magnetic Field Laboratory, Florida State University – 1800 East Paul Dirac Drive, Tallahassee, FL 32310, United States

Abstract

Over the past 20 years, advances in modern high resolution / ultra-high resolution mass spectrometry have forever changed the expectations of complex mixture analysis. Aided by advances in ionization methodologies that facilitate the molecular-level analysis of high boiling/polar species, ultra-high resolution mass spectrometry routinely resolves and identifies (at the level of elemental composition assignment), tens-of-thousands of species that comprise each of the acidic, basic, aromatic, and aliphatic components of petroleum samples. These analytical capabilities have been used to revisit, and ultimately support a decades old theory of the composition of petroleum (the Boduszynski Continuum) and expose the compositional constraints (in class, type, and carbon number) imposed by boiling point. Such compositional information, combined with knowledge of the Boduszynski Continuum, facilitate the accurate boiling point prediction of individual elemental compositions based on mass measurement alone, and is now poised to push forward to the molecular-level modeling of heavy ends (Petroleomics). Furthermore, discontinuities in the continuum expose species that disproportionately contribute to production issues such as emulsions, deposits, and asphaltene aggregation. Downstream, the detailed molecular analysis of boiling point defined fractions, coupled to chromatographic separation (online and offline) based on aromatic ring number(s), and further structural analysis by tandem mass spectrometry, have exposed the structural, compositional, and hetero-atom dependence of the petroleum continuum with boiling point. Here, we highlight the petroleum continuum revealed by ultra-high resolution FT-ICR mass spectrometry to date, and expose the underlying island and archipelago structural motifs that exist in the heavy ends. Notable discoveries in the past two decades of research at the National High Magnetic Field Laboratory will be discussed. Work supported by NSF Division of Materials Research through DMR-11-57490, State of Florida, and the Future Fuels Institute.

---

*Speaker

†Corresponding author: rodgers@magnet.fsu.edu

Development of a petro-informatics platform for the characterization of heavy petroleum fractions

Tanaka Ryuzo*†[1] and Nakamura Tsutomu[2]

[1]Technology Engineering Center, Idemitsu Kosan Co., Ltd. – Japan
[2]Advanced Technology and Research Institute, Japan Petroleum Energy Center – Japan

Abstract

An informatics system was developed to obtain the chemical structure, physical properties, and reactivity of petroleum molecules, and also to evaluate their usefulness in the oil industry. The system, called the "petro-informatics platform: PIP," integrated three fundamental technological disciplines of petroleomics, namely, detailed composition and structure analysis, molecule-based kinetic modeling, and petro-informatics.

An analytical technique that used FT-ICR-MS (Fourier transformation ion cyclotron resonance mass spectrometry) was developed to clarify the composition of heavy petroleum fractions in detail. The identification of the chemical structures of molecules in the fractions was performed deterministically with a newly developed data analysis program. Based on the chemical information, a molecule-based kinetic model of RDS (residuum desulfurization) was constructed using the JKMT (kinetic modeler's toolbox for JPEC) modeling tool. An attribute-based reaction modeling technique (ARM) was utilized to reduce the model size of the complex reaction system. Rate parameters in the model were derived from the data of a series of high-throughput experiments. The reaction experiments, analytical data, and model input and output, were all handled and analyzed through the PIP.

Additionally, an asphaltene aggregation model called the "multi-components aggregation model: MCAM," was also developed. The developed model could predict the quantities of solution, aggregation, and solid phases. The averaged aggregation degree of the aggregation phase in a heavy oil molecular system could also be predicted based on the structure and properties of all the molecules in the system. The model is applicable to various problems encountered by the oil industry from upstream or downstream, such as asphaltene precipitation in a wellbore, the presence of storage tank sludge, and the sediment present in a heat exchanger. The molecule-based aggregation model would make a powerful tool that could predict and analyze the above mentioned asphaltene related problems.

---

*Speaker

†Corresponding author: ryuzo.tanaka@idemitsu.com

sciencesconf.org:petrophase2017:145065

Asphaltenes' and porphyrins' molecular cartography and the aggregation properties studied by molecular dynamics simulations

Hugo Santos Silva*†1, Ana Carolina Sodero , Brice Bouyssiere , Hervé Carrier , Jean-Pierre Korb[2], Ahmad Alfarra , Didier Bégué , Germain Vallverdu , and Isabelle Baraille‡

[1]Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux (IPREM) – CNRS : UMR5254, Université de Pau et des Pays de l'Adour [UPPA] – Hélioparc Pau Pyrénées 2 av. P. Angot 64053 PAU CEDEX 9, France

[2]Physique de la matière condensée (PMC) – CNRS : UMR7643, Polytechnique - X – Route de Saclay 91128 PALAISEAU CEDEX, France

Abstract

The challenges faced by the oil and oil shale industries comprise the comprehension of the physical-chemical behaviour of the heavy-weight phases. These phases have a high tendency to aggregate and this is mainly due to the presence of asphaltenes whose constitution is fairly unclear up to now. The chemical composition of this phase is one of the driving forces of this behaviour and the structure-property relation for these systems is a key point to the development of refining techniques displaying more performance, including the designing of new catalysts. In this presentation, the aggregation of asphaltene molecules is studied upon the light of their molecular cartography screened by classical molecular dynamics techniques. In a recent work, our group has used some of the experimentally-identified asphaltene molecules by Schuler *et al.*[1] to study the effect of the heteroatom substitution on the aggregation pattern and energies of nano-aggregates. We have been able to show that the heteroatom substitution on the aromatic core does not change the type of the aggregation in the nano-structures but changes considerably the energies of interaction[2]. Moreover, we presented solid arguments towards the identification of the role of these heteroatoms on the shape of the aggregates when they are found in the lateral chains: oxygen, mainly, can induce strong H-bond interactions and completely change the aggregation scenario of these molecules. Sulphur can also induce the appearance of new H-bond and S-O interactions as it was also shown by our group recently[3]. Besides this, another striking result of these works is that the aggregation strength depends strongly on the shape of the aromatic core: larger aromatic cores tend to aggregate more easily than smaller ones.

We also present the follow-up of these results in order to give hints towards answering the following questions: 1 - what is the influence of the size of the conjugated core on the aggregation pattern of any given asphaltene molecule?; 2 - what is the influence of the lateral chain length on this same aggregation pattern?; 3 - can these two effects be coupled among

---

*Speaker

†Corresponding author: hugo.santos-silva@univ-pau.fr

‡Corresponding author: isabelle.baraille@univ-pau.fr

sciencesconf.org:petrophase2017:144818

them?; 4 - how can temperature and pressure change them?; 5 - are they consistent for different aggregation clusters sizes?; and 6 –what is the effect of the presence of porphyrins on the aggregation pattern of these molecules?

Schuler, B., Meyer, G., Pena, D., Mullins, O. C., & Gross, L. (2015). Unraveling the molecular structures of asphaltenes by atomic force microscopy. *Journal of the American Chemical Society*, *137*(31), 9870-9876.

Silva, H. S., Sodero, A. C., Bouyssiere, B., Carrier, H., Korb, J. P., Alfarra, A., ... & Baraille, I. (2016). Molecular Dynamics Study of Nanoaggregation in Asphaltene Mixtures: Effects of the N, O, and S Heteroatoms. *Energy & Fuels*, *30*(7), 5656-5664.

Sodero, A. C., Santos Silva, H., Guevara Level, P., Bouyssiere, B., Korb, J. P., Carrier, H., ... & Baraille, I. (2016). Investigation of the Effect of Sulfur Heteroatom on Asphaltene Aggregation. *Energy & Fuels*, *30*(6), 4758-4766.

PC-O3

Elucidating Structures of Compounds in Crude Oil Based on Tandem Mass Spectrometry Combined with Ion Mobility Mass Spectrometry

Sunghwan Kim*[1], Ha Jihyun , Cho Eunji , Ahmed Arif , and Lim Dongwan

[1]Department of Chemistry, Kyungpook National University – South Korea

Abstract

Tandem mass spectra obtained from 25 standard compounds at normalized collision energy (NCE) of 50 were used to investigate structures of compounds comprising crude oil. Product ion distributions observed in tandem mass spectra of standards were dependent on the number and length of alkyl side chains. Long alkyl side chains (CnH2n, n≥5) were easily lost and methyl group attached to aromatic group was left after collision. In addition, compounds with short interlinking alkyl chain (CnH2n, n≤1) were not significantly fragmented and decrease of double bond equivalence (DBE) was observed especially when compounds had saturated ring. Based on the observations, possible structures of S1 class compounds having DBE value of 6, 7, 8, and 9 were suggested. It is also determined that, in tandem mass spectra of crude oils, 1) the series of peaks separated by CH2 observed from crude oils are generated from isomers having different number of alky side chains, 2) distribution of peaks produced by tandem mass spectrometry is dependent on the number and length of alkyl side chains attached to aromatic cores, and 3) significant fragmentation does not occur for aromatic cores with short alkyl chains (CnH2n, n≥2) and hence archipelago structures with short alkyl linkage can't be excluded based on tandem mass spectra alone. To further verify the assigned structures, ion mobility mass spectrometry was also applied. Ions were fragmented and product ions were subject to ion mobility analysis. Collisional cross section (CCS) values were obtained from the product ions and they were compared to theoretically calculated CCS for structural verification.

---

*Speaker

Molecular Insights into Petroleum Resid Composition through Advanced Mass Spectrometry Techniques

Amrit Jalan*†[1], Kathleen Edwards[1], Doug Kushnerick[1], Anthony Mennito[1], Kuangnan Qian[1], and Helen Wellons[1]

[1]ExxonMobil Research and Engineering – Annandale, NJ 08801, United States

Abstract

Crude oil refining processes involve an intricate set of chemical and thermodynamic transformations spanning several orders of magnitude in both the temporal and spatial domains. As a result, process models based on a molecular understanding of petroleum composition are necessary to understand/optimize these processes. The Structure-oriented Lumping (SOL) formalism for process models advanced by Quann and Jaffe captures molecular characteristics of petroleum mixtures as vectors of 24 structural increments and enables efficient crude valuation and refinery optimization.

Molecule-based compositional modeling is also the primary driver for high-detail petroleum analysis and characterization. Analytical techniques for determining the composition and chemical structure of petroleum fractions with boiling point below 1000 ◦F have been largely established. However, extension of these tools to resid (boiling point $>$ 1000 ◦F) has been challenged due to analytical difficulties and extreme combinatorial complexity associated with these materials. This contribution will discuss molecular insights into resid composition obtained from a combination of analytical measurements comprising Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS), Field desorption mass spectrometry (FD-MS) and Collision-induced dissociation (CID). These state-of-the-art measurements provide the first insights into the ”multi-core” nature of resid as well as its constituent building blocks that are similar to ”single-core” structures in VGO. In addition, strategies to estimate physical/chemical properties of these components and capture these qualitative insights in the SOL modeling framework will also be discussed.

---

*Speaker

†Corresponding author: amrit.jalan@exxonmobil.com

PC-O5

Determination of Interaction and Complexation among Asphaltene to Understand their Aggregation and Precipitation

Sébastien Simon*†1, Sreedhar Subramanian , Duo Wei , and Johan Sjöblom

1Ugelstad Laboratory, Norwegian University of Science and Technology – N-7491 Trondheim, Norway

Abstract

Asphaltene is a fraction of petroleum crude oil responsible for numerous problems during crude oil production, processing and transport such as emulsion formation and deposition/precipitation. To solve these problems, it is important to understand the properties of asphaltene. However, the complexity of asphaltene fraction, composed of thousands of molecules polydisperse in molecular weight, structure and functionalities, makes this understanding difficult. To simplify this task, the fractionation of asphaltene [1] or the development of model molecules with well-defined structures similar to "average" asphaltene molecules [2] are powerful strategies.
In this study, the self-association properties of asphaltene model compounds either acidic C5PeC11 or aliphatic BisAC11 as well asphaltene fractions have been studied by isothermal titration calorimetry (ITC) and compared with real asphaltenes [3]. It is shown that mixtures of model compounds displaying different self-association patterns can well quantitatively mimic polydisperse asphaltene systems probed by ITC. In addition, it is found that asphaltene fractions present different self-association properties as well. This means asphaltene is composed of compounds displaying very different association properties.

Then the influence of interactions between asphaltene model compounds on their solubility is determined. It is found that BisAC11 can increase the maximum solubility of C5PeC11 in mixtures of xylene and heptane. This effect is attributed to the formation of a soluble complex between C5PeC11 and BisAC11 for which the association constant is experimentally determined. This association energy corresponds to a DG of ≈ -16 kJ/mol.

References:

(1): Subramanian, S.; Simon, S.; Gao, B.; Sj´oblom, J. Asphaltene fractionation based on adsorption onto calcium carbonate: Part 1. Characterization of sub-fractions and QCM-D measurements. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2016**, *495*, 136-148.

(2): Sj´oblom, J.; Simon, S.; Xu, Z. Model molecules mimicking asphaltenes. *Advances in Colloid and Interface Science* **2015**, *218*, 1-16.

(3): Simon, S.; Wei, D.; Barriet, M.; Sjoblom, J. An ITC and NMR study of interaction

---

*Speaker

†Corresponding author: sebastien.simon@chemeng.ntnu.no

and complexation of asphaltene model compounds in apolar solvent I: Self-association pattern. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2016**, *494*, 108-115.

(4): Wei, D.; Simon, S.; Barriet, M.; Sj'́oblom, J. An ITC study of interaction and complexation of asphaltene model compounds in apolar solvent II: Interactions with asphaltene inhibitors. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2016**, *495*, 87-99.

PC-O6

Direct Characterization of Aliphatic and Aromatic Contributions to Chemical Classes of Four Crude Oils using Tunable Vacuum Ultraviolet Photoionization

Jeremy Nowak*[1] and Allen Goldstein

[1]UC Berkeley – United States

Abstract

The chemical complexity and diversity of crude oil challenges chromatographic and mass spectrometric techniques to characterize petroleum hydrocarbons. Recent advances in two dimensional gas chromatography (GCxGC) and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) can identify hydrocarbons as a function of heteroatom composition or double bond equivalent (DBE) chemical class, but provide limited structural characterizations or have difficulty distinguishing between aromatic and aliphatic components of a single DBE class that do not differ significantly in polarity.

Here we present a technique for direct characterization of aliphatic and aromatic contributions to the same DBE class without the need for prior chromatographic separation. Aliphatic compounds, including alkanes and cycloalkanes, have ionization energies above 9.0 eV while aromatic compounds, including alkylbenzenes and polycyclic aromatic hydrocarbons, have ionization energies below 9.0 eV. We combine GCxGC with tunable vacuum ultraviolet soft photoionization high-resolution time-of-flight mass spectrometry (GCxGC-VUV-HTOF) at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory (LBNL) to characterize the composition of four oils from different reservoirs (North Sea, Azerbaijan, Texas, and the Gulf of Mexico). When the VUV beam was tuned to 10.5 eV, both aromatic and aliphatic hydrocarbons were ionized to reveal the complete chemical composition of C9-C30 hydrocarbons of DBE=0-10. When the VUV beam was tuned to 9.0 eV, only aromatic hydrocarbons were ionized. The DBE=4, 5, and 6 compound classes include both aromatics and cycloalkanes, therefore GCxGC combined with tunable VUV photoionization allows the characterization of aliphatic and aromatic fractions of each compound class in all four oils. The DBE=8 compound class consists of both aromatics and aliphatic fragments, thus we can distinguish how aromaticity of this compound class also differs amongst the four oils.

In all four oils, aliphatic contributions to the DBE=4, 5, and 6 compound classes increase as molecular weight increases. From C15-C25, the Gulf of Mexico oil was _˜80-100% aromatic in the DBE=4 class, _˜50-100% aromatic in the DBE=5 class, and _˜70-100% aromatic in the DBE=6 class, making this oil the most aromatic of the four oils. The Azerbaijan oil was the most aliphatic, with only _˜30-60% of the C15-C25 hydrocarbons of the DBE=4, 5, and 6 classes possessing aromaticity. C15-C25 hydrocarbons of the DBE=4 class in the Texas oil were _˜40-90% aromatic, while the respective hydrocarbons in the North Sea oil were _˜30-60% aromatic. However, the C15-C25 hydrocarbons of the DBE=6 class in the North Sea oil were _˜60-80% aromatic, while the respective hydrocarbons in the Texas oil were only _˜30-60% aromatic. C15-C25 hydrocarbons of the DBE=8 class were _˜40-80%

---

*Speaker

sciencesconf.org:petrophase2017:146300

aromatic in the North Sea and Gulf of Mexico oils, while the same species were _˜20-30% aromatic in the Texas and Azerbaijan oils.

The combination of GCxGC with tunable soft ionization can be used to better understand aliphatic and aromatic contributions to petroleum hydrocarbon classes, identify crude oils based on their source, and examine environmental weathering or biodegradation pathways of crude oil components.

PC-O7

On the Many Competing Mechanisms in Gel Permeation Chromatography of Petroleum Fractions.

Simon Andersen*[1]

[1]Asphalteam – Denmark

Abstract

The use of Gel Permeation Chromatography (GPC) or Size Exclusion Chromatography (SEC) in the analysis of petroleum material has been surrounded by controversy due to non-size effects and lack of proper calibration standards. Hence quantitative data in terms of molecular size distributions and absolute values is often perceived as prone to large errors. Therefor some researchers have discarded the method as worthless. Despite this in many cases the use of GPC can provide significant insight into changes and differences in materials as regularly successfully reported in the literature. The technique is affected especially by the solute-solvent interactions impacting in theory the solute-stationary phase adsorptive interaction. This is manifested in mainly adsorption to the stationary phase overriding the size effect and retarding the elution. This leads to a shift to lower molecular weights. The association of molecules in poor solvents could lead to early elution giving too high MWs. Most often for heavy fractions the total excluded volume is almost reached for ordinary solvents such as THF and Toluene, with a significant tailing beyond a retention corresponding to a molecular weight of zero. When applying the solvent NMP (N-methyl pyrrolidone) a peak may be observed eluting before the total excluded volume expected from elution in toluene. The prevailing mechanisms cannot explain the occurrence of these peaks, which were also the center of much discussions in the literature regarding especially analysis of asphaltenes. However, often overlooked is the hydrodynamic effects that may lead to separation due to formation of microphase droplets with completely different behavior. This mechanism can explain the occurrence of the early peak in NMP, due to the peculiar phase behavior of NMP-asphaltene systems which renders the asphaltenes partially insoluble in NMP. While a decreasing solvent power of the eluent normally leads to increased column adsorption more dominant than e.g. association, there is a turning point where the occurrence of micro phases will start to behave as non-interacting particles. These particles will separate according to hydrodynamics and will travel at the maximum linear velocity through the column. As total exclusion is generally determined by the average velocity the particles will penetrate the column earlier leading to a new peak. Nano-aggregates would not behave this way (shown by elution in heptane-toluene blends) and hence in NMP the front peak indicates that larger particulate matter constituting a separate phase has been formed. The reduced adsorption in NMP is due to the strong NMP-aromatics interaction, while the particulate micro phase matter is formed by non-aromatic asphaltenes. These mechanisms will be dealt with in detail concluding that GPC or SEC indeed provides very valuable information on the nature of the material analyzed which can be useful in both petroleum geochemistry, flow assurance and processing in refinery operations.

---

*Speaker

sciencesconf.org:petrophase2017:145680

Automated SPE and LC-HRMS for optimized tetraprotic acid quantification in crude oil.

Matthieu Loriau*[1], Sandrine Lescoulie[1], Beatrice Martin , Jean-Philippe Gingras , and Nicolas Passade-Boupat

[1]TOTAL Exploration Production – TOTAL – France

Abstract

In a context of crude oil volatility, it is important to rationalize methods and measurements to reach robust and cost efficient risk assessments. This principle is also available in research. As an example, calcium naphthenates deposits, due to tetra-protic acids (TPA), are a tricky subject for surface installation due to their potential implications [1] : the risk of occurrence is low (few field cases reported), but when it occurs, it leads to production stoppage for significant periods. TPA, also called Arn, was isolated by Conocco and Statoil in the early 2000's in field deposits. Since then, several other deposits issues in the world were attributed to TPA. On the other hand, TPA have been qualitatively detected in a quite large number of oils compared to the number of fields where deposit issues happened. The quantification of this risks relies on a quantitative measurements of the TPA in crude oil samples. None easy to use method are available today on the market. Very often this quantification is treated by R&D structures, in internal research centers or external research laboratories (universities). The TPA quantification implies multi-step extraction by solid phase extraction whose number can vary from two to four, with solvent vent steps and is ended in most of the case by chemical derivatization for quantification [2, 3, 4]. In this paper, an automated SPE sequence is presented for a two step extraction with reliable results in correlation with time saving and robustness brought. The second part is linked to the quantification itself. To save time again, a direct LC-HRMS method is developed without any derivatization step. Several recommendations are given to obtain a direct negative ESI quantification of TPA. The overall results of these developments is an optimum of "fit for purpose" research methodology where manual steps are reduced to the minimum, without compromise with the quality of the result.

---

*Speaker

The Effects of Macrocycle Type and Exocyclic Oxygen on Petroporphyrin Properties and Behavior in Bulk and at Interfaces

Peter Kilpatrick*[1,2], Mckay Rytting[1,2], Yunlong Zhang[3], Steven Rucker[3], Anthony Mennito[3], and Michael Harper[3]

[1]Department of Chemical and Biomolecular Engineering (Notre Dame, USA) – United States
[2]University of Notre Dame – United States
[3]ExxonMobil Research and Engineering (Annandale, NJ) – United States

Abstract

Petroporphyrins are the heavy metal (V, Ni) containing hydrocarbon molecules in petroleum, accounting for as much as 0.2-0.4% of heavy petroleum. Having previously described a separation and purification procedure used to recover a small variety of petroporphyrins from crude oil at purities up to 95%, we now report the purification and characterization from a North American heavy crude residue of a very wide variety of vanadyl petroporphyrins with intense Soret bands ranging from 405-423 nm. The purity and identity of these materials was determined through metal analysis by x-ray fluorescence spectroscopy; porphyrin Soret, alpha, and beta band absorbance by UV/visible spectrophotometry; and molecular weight distribution and porphyrin types by LDI-TOF and FT-ICR mass spectrometry. These porphyrins, purified from the vacuum residue of a North American heavy crude oil, comprise 10 differing porphyrin base types (including DPEP, Etio, and Rhodo forms and their combinations). We also have observed an entire class of porphyrins that contain an exocyclic oxygen, i.e. with molecular formula CnHmN4O2V. They have previously been observed and identified in crude oil samples but never isolated in meaningful quantities or characterized as thoroughly as we describe here.

We have utilized small-angle neutron scattering (SANS) to investigate the aggregation behavior of these petroporphyrins, measuring nanoaggregate size of several different petroporphyrins in toluene and 60-40 toluene-hexane mixtures at multiple concentrations and temperatures. We have also used PFGSE-NMR to estimate nanoaggregate size to corroborate and complement our SANS results. Additionally, SANS has allowed us to measure the thickness of the petroporphyrin films that form at oil/water interfaces by emulsifying water/toluene mixtures with dissolved petroporphyrin, allowing the films to form, then washing away residual petroporphyrin in solution and measuring the scattering profile of the remaining petroporphyrin films, which can be used to estimate its thickness.

Using an oscillating drop rheometer, we have measured the tension and elasticity of the isolated petroporphyrins and have seen that despite significant variation in molecular structure, the tension and elasticity of petroporphyrin interfacial films is remarkably consistent, with tensions steadying at around 15 mN/m (about 10 mN/m less than asphaltenes) and

---

*Speaker

elasticities tending to plateau around 40 mN/m (about 15 mN/m greater than asphaltenes). Interestingly, while asphaltenes exhibit molecular rearrangement at the interface, indicated by a decrease in elasticity beginning sometime between 24 and 48 hours, we have observed no such behavior with petroporphyrins. Even after several days, the elasticity continues to slowly increase while the tension remains fairly consistent.

Finally, we have performed these same characterizations (aggregate size, film thickness, interfacial tension and rheology) with asphaltenes as well, both with and without added petroporphyrins of several different classes, to better understand the relationship between these two families of hydrocarbons.

PC-O10

Understanding the Molecular Structure of Asphaltene in a Geochemical Perspective

Quan Shi*[1], Linzhou Zhang , Zhentao Chen , and Yehua Han

[1]China University of Petroleum-Beijing (CUPB) – China

Abstract

Molecular composition and structure of petroleum asphaltenes are the most common topics in petroleum chemistry which usually aroused controversy. Although the argues such as the "archipelago" vs "island" seems subsided recently, the structure of asphaltenes are still unclear. If we explain the molecular structure of asphaltenes in a geochemical perspective, most controversy in petroleum chemistry would be meaningless: the asphaltenes just a description in property instead of a chemical definition. It is destined that no definite conclusion when we discuss the chemical structure of asphaltenes from different geochemical origins, because we could be studying different chemical substances. Each molecule of asphaltenes is the product of its biological precursors with complex chemical reactions in the long geological history, it should can be explained in chemistry. This presentation will investigate the molecular composition of asphaltenes with large chemical dispersity and explain the geochemical origin, discuss controversial issues such as the molecular size and structure of petroleum asphaltenes.

---

*Speaker

Correlations between molecular composition and the adsorption/aggregation behavior of Arabian asphaltenes

Deisy Giraldo*[1], Martha Chacon-Patiño[1], Cristian Blanco-Tirado[1], and Marianny Combariza Montanez†[1]

[1]Universidad Industrial de Santander [Bucaramanga] (UIS) – Cra 27 Calle 9 Ciudad Universitaria
Bucaramanga-Santander-Colombia, Colombia

Abstract

Asphaltenes are considered the least valuable fraction of crude oil because they are responsible for serious problems during production, transporting, and upgrading. Changes in petroleum composition, such as diluent addition, or physical conditions like pressure or temperature dropping, can produce asphaltene deposits, causing formation damage, pipeline plugging, and catalysts poisoning in refining processes. In this sense, understanding the link between molecular composition and stability of dispersions from asphalntenes and its fractions is fundamental to improve production and processing of heavy oils. In this contribution we studied the relation between chemical composition and stability of HepTol (heptane: toluene) dispersions of asphaltenes from Arabaian heavy crude oil and its fractions, obtained by preparative thin layer chromatography (TLC), using NIR radiation scattering via Turbiscan and ultra high resolution mass spectrometry FT-ICR (+) APPI. For this purpose, we fractioned arabian asphaltene using preparative TLC SiO2 plates into alkyl-aromatics, polars, and non-eluted fractions. We established trends between compound retention characteristics and molecular features such as aromaticity, heteroatom/C ratios, and degree of alkylation. Additionally, we show that fractionation of asphaltene samples on silica surfaces expose many species not observed when analyzing the whole asphaltene mixture by APPI-FT-ICR-MS. On the other hand, we performed aggregation tests in Hep:Tol solutions of whole asphaltene samples, and their preparative TLC fractions, and registered in all cases backscattering profiles typical of samples undergoing flocculation. We observed a clear link between fraction polarity (or retention on silica) and aggregation: the more a fraction is retained on the silica plate, the faster it aggregates in HepTol. Along the same lines, the aggregation behavior of the preparative TLC fractions is quite interesting: the TSI profiles show that asphaltenic species most prone to aggregation are concentrated in the non-eluted fraction on the silica plate. In contrast, the polar and alkyl aromatic fractions are much more stable in HepTol solutions. The observed trend is quite similar for all tested asphaltene sample and its fractions. We believe, based on previous observations, that molecular features responsible for asphaltene adsorption on SiO2 play also important roles in asphaltene aggregation in Hep:Tol solutions. In other words, synergistic effects between high aromaticity, heteroatom content, and polar group accessibility, in particular molecular compositions, seem to drive the aggregation processes in a similar way as they do adsorption. We also show that asphaltene fractionation on SiO2 can isolate challenging asphaltenes (-or the ones more prone to aggregate and deposit) from a complex asphaltene mixture.

---

*Speaker

†Corresponding author: marianny@uis.edu.co

POSTERS
Petroleum Chemistry

The Effect of Surfactant on Selectivity in the Extraction of Aromatic Hydrocarbons from the Lube Oil

Hidaya Izza*[1]

[1]Lab. Dynamique, Interactions et Réactivité des Systèmes – Algeria

Abstract

An investigation was conducted in order to examine the effect of the addition of surfactant to the fraction of the light lubricating oil (spindle) during the solvent extrac- tion process. The solvent power and selectivity can be fur- ther increased by using surfactant as an additive. This could facilitate the separation phase and increase the yield of the raffinate. In this study, we suggested the use of ethoxylated anionic surfactant (sodium lauryl ether sulfate). The aromatics in the lube oil were extracted at different tempera- tures (ranging from 333.15 to 343.15 K) with different con- centrations of surfactant (ranging from 0.01 to 0.1 wt%). The extraction temperature and the amount of surfactant in furfural were systematically investigated to determine their optimum values. Compositions in monoaromatics, diaromat- ics, polyaromatics, and saturates were determined by using UV–Vis spectrophotometry. When surfactant was added, the solvent acquired the ability to preferentially extract polyaromatics instead of the monoaromatics. This directly affects the required oil quality. It was found that using 0.01 wt% of surfactant at 343.15 K yields the optimum extraction conditions.

---

*Speaker

Characterization of asphaltenes precipitated at different solvent power conditions using Ultrahigh-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Matthias Witt*[1] and Estrella Rogel†[2]

[1]Bruker Daltonik GmbH – Fahrenheitstrasse 4, 28359 Bremen, Germany
[2]Chevron – 100 Chevron Way Richmond, CA 94801, United States

Abstract

Heptane was used to induce precipitation at room temperature using heptane/crude oil ratios from 1 to 100. The precipitated material was recovered by filtration and analyzed with ultrahigh resolution FT-ICR mass spectrometry using laser desorption ionization (LDI) and atmospheric pressure photoionization (APPI). Relative responses indicate changes in the distribution of molecules showing an increase in the DBE as well as aromaticity (DBE/C) as heptane concentration increases. In terms of class distributions in the precipitated material, it was found that the relative response of the hydrocarbon class and classes containing just one heteroatom decreases as the heptane concentration increases, while the relative response of classes containing two or more heteroatoms increases. The increase in DBE and in classes with several heteroatoms as the solvent power decreases seems to contradict the general believe that the first molecules to precipitate when the flocculation onset is reached are those considered more polar and less soluble, characteristics associated with larger aromaticity and larger heteroatom content. Change of aromaticity was confirmed by increases in the 1600 cm–1/2900 cm–1 ratio (aromatic/aliphatic signal ratio) obtained by FT-IR.

---

*Speaker

†Corresponding author: ERGC@chevron.com

OIL VEGETABLE BASED MICROEMULSION CLEANER FLUID FOR APPLICATION IN PETROLEUM WELLS

Fabiola Curbelo*†1, Alfredo Ismael Curbelo Garnica*‡2, Julio Cézar Freitas*§3, Elayne Araújo2, Evanice Paiva2, and Edson Araujo2

1Federal University of Paraiba, Departament of Chemical Engineering (UFPB) – Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil
2Federal University of Paraiba, Department of Chemical Engineering (UFPB) – Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil
3Federal University of Rio Grande do Norte, Chemical Institute (UFRN) – Cidade Universitária, Natal, RN, 59078-970, Brazil

Abstract

After drilling phase, a good completion of wells is necessary. The cementing of wells seeks to guarantee the union of wellbore wall - column of coating, being able to avoid the appearance of deviations in drilling. In the well drilling stage, the solids present in drilling fluid are deposited on the walls of the well, due to the penetration of the aqueous phase (filtrate) of drilling fluid into porous medium, forming filter cake. Many deepwater fields are being drilled with synthetic or oil based drilling fluid. the filter cake and drilling fluid residue left on all the well surfaces after the drilling phase is a water-impermeable layer. Remove these residues is necessary to avoid high costs in operation, for this properly-designed clean-up fluids, called flushing liquid, are used, such as microemulsion fluids. Certain formulations of microemulsions can cleanup in a broad range of temperature, density, and salinity. They restore the water-wet condition of the rock and increase injectivity or productivity of the wells. This work presents laboratory evaluations of microemulsion used, like flushing liquid, to cleanup (removal test) of oil based drilling fluid and alteration of the wettability of the rock (inversion test), from oil-wet to water-wet, were performed. Formulations of microemulsioned systems, with different weight fractions, were evaluated, and they were composed of three phases: an aqueous phase, an oily phase (vegetable oil) and a nonionic surfactant. Firstly, a ternary diagram was developed, and, in the microemulsion region, the best composition for the development of microemulsion was chosen. The removal test, carried out in up to 10 minutes and at 88 oC, was done in a becker, where in walls of the becker, corresponding to an area of 66 cm2, was distributed 4 mL of the drilling fluid, forming a fluid film. Subsequently, 200 mL of the microemulsion were added to this becker and the removal test was started on a rotary viscometer. The inversion tests were carried out by electrical conductivity measurements in Wettability equipment. In the removal tests, two formulations were effective because it was possible to remove the fluid film completely in 1 min and 43s,

---

*Speaker

†Corresponding author: fabioladias@yahoo.com

‡Corresponding author: alfredocurbelo@yahoo.com

§Corresponding author: juliofreitasj@hotmail.com in both samples. In order to reduce the volume of microemultion used for removal, water dilution was performed in a volume ratio of 1: 1, with favorable results of 100% removal, in which formulation 1 (40% FO, 55% T and 5% FA) spend about 6 min 35 s for total removal and formulation 2 (50% FO, 45% T and 5% FA) about 3min 27s. For wettability inversion tests, in which 200 mL of the drilling fluid is used in test, being allowed to use up to 200 mL of the microemulsion (cleanup fluid), it was verified that the formulations were efficient, requiring only 50 mL for formulation 1 and 30 mL for formulation 2. This results showed the efficiency of oil vegetable based microemulsion to cleanup and wettability inversion of wellbore wall.

Application of Molecular Dynamic Simulation to improve the CCS calculation accuracy of aromatic compounds with long alkyl chains commonly found in crude oil

Arif Ahmed*[1], Dongwan Lim[2], Young Hwan Kim[3], and Sunghwan Kim†[1]

[1]Kyungpook National University – South Korea
[2]Kyungpook National University – South Korea
[3]Korea Basic Science Institute – South Korea

Abstract

Structural elucidation of compounds in crude oils still remains a great analytical challenge. The combination of two well established MS techniques (ion mobility mass spectrometry IM-MS and ultrahigh-resolution mass spectrometry) with theoretical collisional cross-section (CCS) calculations already shown very effective to increase the amount of information gained as well as to determine the molecular structures of aromatic compounds from such a complex sample like crude oils.1 However, mentioned approach was restricted to determine non-alkylated and short alkyl chains aromatic compounds. In this study, we performed temperature and time dependent molecular dynamic (MD) simulation to improve the CCS calculation accuracy, especially for long alkyl chain containing aromatic compounds.

In this study, two types of calculation program (GAMESS and Hyperchem) has been used to compare the theoretical results. Both program can produce pretty similar computational results. However, Molecular Dynamic Simulation by GAMESS is expensive. More specifically, MD simulation using DFT method along with high basis set takes couple of days for a certain temperature by GAMESS. On the other hand, Hyperchem takes only 1 hour and 40 minutes to perform a 100-picosecond calculation. Another important point is, GAMESS allows parallel calculation submission but Hyperchem does not. Therefore, considering all the options still Hyperchem is an effective calculation program to perform MD simulation for long alkyl chain containing aromatic compounds. Reaction time and temperature dependence MD simulation was performed by using Hyperchem. Molecular Dynamic Simulation results using Hyperchem clearly states that the difference between theoretical and experimental CCS values reduces at high temperature. Therefore, it is clear from the computational results that, high temperature especially at 700 K, computational results correlate better with experimental results. Therefore, 700 K might be the effective experimental temperature for long alkyl chain containing aromatic compounds. MD Simulation results for rigid structures using HyperChem clearly states that the difference between theoretical and experimental CCS values reduces at high temperature. Therefore, it is clear from the computational results that, high temperature especially at 500K and 700 K, computational results correlate better with experimental results. Therefore, this technique is also effective for compounds with rigid structure.

---

*Speaker

†Corresponding author: sunghwank@knu.ac.kr

sciencesconf.org:petrophase2017:143730

- Ahmed, A., Cho, Y., Giles, K., Riches, E., Lee, J.W., Kim, H.I., Choi, C.H., Kim, S.: Elucidating molecular structures of nonalkylated and short-chain alkyl [n< 5, (CH(2))n] aromatic compounds in crude oils by a combination of ion mobility and ultrahigh-resolution mass spectrometries and theoretical collisional cross-section calculations. Anal. Chem. 86, 3300–3307 (2014).

Comprehensive two-dimensional gas chromatography for analysis of distillate fraction from waxy crude oil: An attempt to explain flow assurance related properties data

Marcia Oliveira*[1], Cleber Ursini[1], Bruno Couto[1], Lenise Vieira[1], and Daniele Miranda[1]

[1]Petrobras Research Center (PETROBRAS) – Brazil

Abstract

Waxy crude oil production in deep and ultra-deep offshore areas poses unique related challenges. These conditions often lead to the precipitation and deposition of waxes on surfaces or increase the effective viscosity of the flowing fluid. The net effect is an increase in pressure drop for a given rate through reduction in flowing fluid area or viscosity change. For all aspects of petroleum production, it is necessary to understand the properties and the petroleum fluids (oil, gas, and water) behavior through production systems under consideration.
The compositional analysis of petroleum fractions is an important tool in the search for improved methods for crude oil production related to flow assurance issues. The knowledge of the composition of petroleum fractions facilitates the evaluation and data interpretation of fluid properties and flow behavior.

As petroleum contains thousands of different chemical compounds, in order to obtain a more accurate description of petroleum fractions composition, multidimensional comprehensive systems are gaining importance. By the combination of two chromatographic columns with different separation mechanisms, the overall peak capacity is increased, offering a decisive advantage in relation to current analytical methods. Comprehensive two-dimensional gas chromatography analysis (GCxGC) is the most applied comprehensive chromatographic mode and the majority of applications of GCxGC in the oil industry refer to petroleum fractions obtained from refining. The classical configuration using a non-polar column connected to a second fast semi-polar column leads to structured chromatograms where hydrocarbons are arranged according to their chemical group and their number of carbon atoms. Middle distillates are interesting samples to be analyzed by this analytical tool. The complexity of these samples practically impedes their detailed analysis in conventional gas chromatography (GC) and their final boiling point is compatible with maximum temperatures of columns.

In this study, GCxGC analysis were performed for middle distillate fractions with boiling point range between 150 and 400○C from Brazilian waxy crude oils in order to check the applicability of this method to analyze these kind of fluid. The experiments were carried out using a 2D chromatograph equipped with a CO2 dual jets modulator, a split injector and a flame ionization detector (FID). Helium was used as a carrier gas. The column system consisted of a combination of a non-polar (dimethyl polysiloxane) and a mid-polar (diphenyl

---

*Speaker

dimethyl polysiloxane) configuration placed in the same oven. The system was operated in programmed temperature conditions and the modulation period was set to 18 s. The data processing was performed by using GC Image 2.3 (Zoex Corporation).

The instrumentation and methodology improvement presented in this study enables us to distinguish normal paraffins, branched paraffins, naphthenes and mono and multi-rings aromatics compounds from diesel cuts of four waxy crude oils. The data obtained was processed allowing the quantification by families and number of carbon atoms.
The objective of our analytical efforts is a better understanding of the chemistry of petroleum middle fractions mapping hydrocarbons types as an attempt to explain the differences in waxy crude oil flow assurance related properties.

Study of heavy oil asphaltene samples aggregation by dynamic and static light scattering

Vladimir Kuryakov*[1], Igor Yudin[1], Victor Dechabo[1], Victor Kosov[1], and Dmitrii Yudin[1]

[1]Oil and Gas Research Institute of RAS (OGRI RAS) – Russia, 119333, Moscow, Gubkina Str. 3,
IPNG (OGRI RAS), Russia

Abstract

The asphaltenes were often investigated as responsible for the high viscosity level in the heavy crude oils as well as a source of a serious production problems for their *habit* to create deposits in the pipelines with the consequent need of expensive maintenance operations (aimed to keep constant the production rate). In this paper we present the study of asphaltene samples obtained from heavy oil originated in the Tatarstan region (Republic of Tatarstan, Russian Federation), via Dynamic Light Scattering (DLS) and Static Light Scattering (SLS) measures. The solutions of asphaltenes in toluene were investigated for different concentration of heptane. The DLS method permits to measure the particle sizes in liquids within the range from half nanometer to several micrometers. We measured the dependence of the average size of asphaltene aggregates on time and at different concentrations of the heptane. It was observed the stability limit of the asphaltene suspension in toluene and the aging of its aggregation with series of measurements each one carried out during a week and with an interval of several weeks among the series. The solutions of toluene-asphaltene at various concentrations of asphaltenes were investigated also by Static Light Scattering (SLS scattering indicatrix) and correlated with the effect of small amount of additives (heptane). Our results show that for small heptane concentrations the DLS method may not provide a complete description and the results should be integrated by the SLS ones. Moreover we investigated the behavior of the secondary aggregation for the asphaltenes previously precipitated after the addiction of heptane and treated by ultrasonic dispersion (re-aggregation). Our studies of re-aggregation after ultrasonic dispersion performed with the use of various additives were able to reveal the most effective inhibitor of aggregation. The study was supported by the Russian Foundation for Basic Research, Grant no. 15-08-07727-a.

---

*Speaker

Structural Determination of Polycyclic Aromatic Hydrocarbons by Ion Mobility Mass Spectrometry

Priscila Lalli*[1,2], Yuri Corilo†[1,2], Martha Chacon[1], and Ryan Rodgers‡[1,2,3]

[1]National High Magnetic Field Laboratory (MagLab) – 1800 East Paul Dirac Drive, Tallahassee, FL 32310, United States
[2]Future Fuels Institute (FFI) – 1800 East Paul Dirac Drive, Tallahassee, FL 32310, United States
[3]Department of Chemistry, Florida State University, (FSU) – 95 Chieftain Way, Tallahassee, FL 32306, United States

Abstract

INTRODUCTION
Polycyclic aromatic hydrocarbons (PAH) are a class of compounds that consist of fused conjugated aromatic rings. They are present in crude oil as products from aromatization of natural products such as steroids. Their characterization has received enormous interest due to their toxicity when released to the environment. Large PAHs also act as coke precursors in catalytic cracking leading to catalyst deactivation and lower conversion. Knowledge of the position of the aromatic rings (and naphthenic rings when present) is important because they dictate the compounds' reactivity. Here, we use ion mobility mass spectrometry (IM-MS), post-ion mobility collision-induced dissociation (CID), theoretical CCS calculation and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to determine the structures of PAH in petroleum samples.

METHODS

VGO cuts from Canadian bitumen were fractionated by HPLC (Waters Alliance e2695) per aromatic ring number with a 2,4-dinitroanilinopropyl silica (DNAP) and silver modified strong cation exchange (Ag-SCX) stationary phases. (+) APPI IM-MS experiments were performed with a Synapt G2Si HDMS (Waters Corp.) equipped with a time-of-flight (TOF) mass analyzer. The traveling wave IM cell was calibrated with polyalanine to obtain experimental collision cross section (CCS) values. Theoretical CCS calculations were performed with Mobcal (Trajectory Method) and structures optimized with Gaussian (DFT B3LYP/6-31G(d)). (+) APPI FT-ICR MS were acquired with a custom-built 9.4 tesla FT-ICR mass spectrometer at an average mass resolving power of m/m50% $>$ 600,000 at *m/z* 500 and 100-400 ppb mass error.

PRELIMINARY DATA

IM-MS and CID experiments were performed on a variety of PAH standard compounds, including isomeric sets and PAHs containing naphthenic rings. Theoretical CCS calculations

---

*Corresponding author: lalli@magnet.fsu.edu

†Speaker

‡Corresponding author: rodgers@magnet.fsu.edu

were also performed for these structures and agreed with the experimental CCS values.

Because of the high complexity of petroleum samples and fractions, it is important to be aware of possible non-resolvable isobars when using a TOF mass analyzer due to insufficient resolving power. The most common isobaric interference for hydrocarbon species is sulfur-containing compounds (C3 vs. SH4, 3.4 mDa). PAHs containing 5 aromatic rings or more elute in the last fraction (5+-ring) of the aromatic ring separation, whereas sulfur containing species elute in earlier fractions because they have a lower number of aromatic rings.

The 5+-ring fraction collected from VGO cuts from Canadian bitumen was then analyzed by (+) APPI FT-ICR MS and (+)APPI IM-TOF MS. FT-ICR data confirmed that no isobaric species are present for the PAH compounds in this fraction. Experimental CCS values for individual ions in the sample were compared to those obtained for the respective standard compounds (when available). For example, the ion at m/z 252.0935 (C20H12) was found to correspond to benzo[e]pyrene and not benzo[b]fluoranthene. For other ions, structures were assigned by comparison between the experimental CCS value and theoretical CCS calculated for hypothetical structures. The compositional space from FT-ICR data gives an indication of the possible structures; therefore, it was used along with CID spectra to guide the choice of the hypothetical structures.

Work supported by NSF DMR-11-57490, the FSU Future Fuels Institute, and the State of Florida.

UNDERSTANDING ASPHALTENE AGGREGATION INHIBITORS. A MOLECULAR DYNAMICS STUDY

Jennifer De León*†[1] and Bibian Hoyos[1]

[1]Universidad Nacional de Colombia (COLOMBIA) – Colombia

Abstract

In this work, the radial distribution function (RDF) and the distance between centers of mass (COM) of asphaltenic systems in *n*-heptane in presence and in absence of four proposed asphaltene aggregation inhibitors were calculated using molecular dynamic simulations. Five different systems were constructed: one without treatment used as reference, using 30 asphaltene molecules at 30% wt in n-heptane, and four systems in which 10% wt of treatment was added for each of the four inhibitors evaluated. The evaluated inhibitors consisted of a three-ring aromatic core, with one or two chains of one or nine carbon atoms in each case. The asphaltene representation was obtained from experimental data from Maya asphaltenes following a stochastic algorithm [1]. The inhibitor molecules were selected in order to stablish a correlation between the molecular structure of the proposed treatment, and the effect over asphaltene aggregation at a molecular level. In particular, the effect of the number and length of aliphatic chains in the molecular structure of the proposed inhibitors was evaluated. For an aromatic core consisting of three rings, the presence of one aliphatic chain with a single carbon atom, an increase of the distance between COM of asphaltene was observed in the RDF curve with respect to the reference line in absence of treatment, which is a clear indicator of inhibition of aggregation. However, in this case the system still exhibits indications of cluster formation. When the number of substituents was increased to two, a reduction in the distance between asphaltene molecules was observed, as well as the formation of large aggregates in the simulation box. This behavior indicates that increasing the number of aliphatic substituents favors the aggregation, contrary to what was expected. It appears that the presence of additional chains entangles the asphaltene aggregates, preventing them from separating.

When the length of the aliphatic chain was increased from 1 to 9 carbon atoms, a clear shift in the RDF curve, along with the results of distance of the COM of asphaltenes, indicate a marked increase in the separation between the molecules. Also, the RDF curve depicts a smooth behavior, more associated with liquid systems, which indicates minimum aggregation in these systems. This indicates that the long aliphatic chains act as bridges between asphaltene molecules, forming viscoelastic structures that behave like a liquid phase.

Molecular dynamic simulation has proved to be an effective tool towards understanding the mechanism behind asphaltene aggregation, and as presented in this work, can give valuable information when selecting an appropriate course of treatment for complex problems,

---

*Speaker

†Corresponding author: jde@unal.edu.co

such as asphaltene aggregation.

References

J. De León and B. A. Hoyos, "A stochastic method for asphaltene structure formulation from experimental data: Avoidance of implausible structures," *Proceedings of Petrophase Annual Conference*. p. 28, 2015.

SEARCHING FOR THE MOLECULAR REPRESENTATION OF ASPHALTENES FOR AGGREGATION AND VISCOSITY EVALUATION

Ana Velásquez[1], Jennifer De León*†[1], and Bibian Hoyos[1]

[1]Universidad Nacional de Colombia (COLOMBIA) – Colombia

Abstract

Molecular dynamics simulations were used to evaluate the effect of the molecular representation of the asphaltene fraction on the viscosity and the average aggregate size calculations of asphaltene/solvent systems. Asphaltene aggregation was studied in vacuum and in solvents of a paraffinic (n-heptane) and an aromatic nature (toluene) at concentrations of 18.6 and 30.0 wt.%. Three different asphaltene representations were evaluated, namely, a mixture of four molecules and systems with the asphaltene phase represented exclusively with island-type molecules or archipelago-type molecules, constructed from experimental data from Maya asphaltenes following a stochastic procedure [1].

The average aggregate size for pure asphaltene systems was independent to the molecular representation used. However, for the island-type representation, the presence of short aliphatic chains allows for the formation of extremely large aggregates in a vacuum, whereas for the mixture and archipelago representations, the long aliphatic chains increase steric hindrance and stop the growth of asphaltene aggregates, limiting the size of the aggregates to up to four molecules.

For asphaltene/solvent systems, aggregation results with the mixture representation were consistent with the expected solubility behavior of asphaltenes in both n-heptane and toluene. With this representation, the final configuration in n-heptane consisted of up to four-molecule aggregates, whereas in toluene, the aggregates were dimers at most. For the island and archipelago representations, the average aggregate size was significantly lower than with the mixture representation. The structural configuration of the island-type molecule selected misrepresented the aggregation behavior of the asphaltenic phase and produced higher deviations in viscosity results. The representation of the asphaltene phase exclusively with the archipelago architecture also fails to correctly describe the asphaltene aggregation since practically no aggregation was observed.

For all three representations, an increase in viscosity with asphaltene concentration was observed. In n-heptane, the asphaltene aggregates were compact and stable with time, and their behavior resembled that of solid particles suspended in a fluid phase. In toluene, the aggregates were of a porous nature forming viscoelastic networks and reducing the mobility of the fluid phase.

---

*Speaker

†Corresponding author: jde@unal.edu.co

The combined results of aggregation and viscosity indicate that the mixture representation is a more appropriate choice for the evaluation of the behavior of asphaltenic systems. In addition, by having both island-type and archipelago-type structures, the mixture representation of the asphaltene phase allows the study of different scenarios for asphaltenic systems.

References

J. De León and B. A. Hoyos, "A stochastic method for asphaltene structure formulation from experimental data: Avoidance of implausible structures," in *The Sixteenth International Conference on Petroleum Phase Behavior and Fouling.*, 2015, pp. 1–10.

The Use of NIR for Study the Asphaltene Precipitation in a Multicomponent System with Carbon Dioxide

Monique Amaral*†[1], João Coutinho[2], Gustavo Borges[1], Elton Franceschi[1], and Claudio Dariva[1]

[1]Tiradentes University – Brazil
[2]University of Aveiro – Portugal

Abstract

The asphaltene particle instability and precipitation during the exploration of carbonate oil reservoirs continues to be a challenge for scientists and petroleum industry. The phase behavior of asphaltenes in carbonaceus reservoirs is important to understand the flocculation phenomena at high pressure. New approaches and technologies have been developed, and the near infrared spectroscopy (NIR) has becoming a promising technique in this direction. This study was focused on the investigation of the phase behavior of systems composed by carbon dioxide+asphaltene+cyclohexane+ toluene at high pressure, by using visual and NIR detection of the phase transitions. The asphaltenes were precipitated from a Brazilian crude oil using standards procedures. The phase behavior experiments were performed in a high-pressure variable volume view cell in the temperature range from 30 to 70°C, and pressures up to 200 bar. Specific conditions of temperature, pressure, carbon dioxide and asphaltene compositions were selected to analyze the application of the NIR spectroscopy for the asphaltene flocculation detection. The results obtained indicated that asphaltene miscibility curves are strongly dependent of the carbon dioxide concentration, whereas temperature and pressure presented a smaller influence on the phase transitions in the range investigated. The results obtained also suggested that the NIR technique with chemometric applications can be a robust technique to describe the phase behavior of multicomponent systems with asphaltenes.

---

*Speaker

†Corresponding author: moniquej.amaral@yahoo.com.br

A Versatile Mass Spectrometry Method with Plasma Ionization Technique for Direct Analysis of Hydrocarbons in Petroleum

Yehua Han*†[1], Zhaoyang Fan , and Yanfen Zhang

[1]State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing – China

Abstract

There are numerous hydrocarbons in Petroleum, saturated and unsaturated, linear, branched, cyclic and polyaromatic. Different types of hydrocarbons contribute quite diversely to the nature of crude oil, as well as the final quality of petroleum products. Therefore, molecular-level characterization of petroleum hydrocarbons in complex matrix is of great significance for crude oil evaluation and process optimization.

Gas chromatography mass spectrometry (GC MS) is widely used in hydrocarbon analysis. However, for hydrocarbons beyond gasoline range, GC MS clips its wings. Ultra-high resolution mass spectrometry, especially Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), is a promising tool in petroleumomics study. It has been proven to be powerful in the analysis of polar components in petroleum. But it's still quite challenging to characterize nonpolar hydrocarbons using FT-ICR MS due to the limitation of proper soft ionization techniques.

Here we present a plasma based ionization method for direct and simultaneous analysis of all typical classes of petroleum hydrocarbons including paraffins, naphthenes and aromatics. Hydrocarbons could be ionized gently into molecular ions or pseudo-molecular ions, so that complex can be resolved by FT-ICR MS and identified by precise molecular composition. Paraffins, naphthenes and aromatics were demonstrated to have different ionization behaviors by careful control of ionization parameters, therefore they could be further classified and discriminated. In this developed method, paraffins (including linear and branched alkanes) existed as oxidized form [M-3H+O]+ after ionization, and cycloalkanes and aromatics exhibited as molecular ion M+. Ionization mechanism were investigated using model compounds. It has been applied to the analysis of crude distillates and heavy oil, demonstrated to be a versatile method for molecular level characterization of petroleum hydrocarbons.

---

*Speaker

†Corresponding author: hanyehua@cup.edu.cn

PC-P12

Increasing Flexibility in Two-Dimensional Liquid Chromatography by Pulsed Elution of the First Dimension (Pulsed-elution 2D-LC)

Simon Jakobsen*[1,2], Sylvain Verdier[2], Nikoline Nielsen[1], and Jan Christensen[1]

[1]University of Copenhagen, Department of Plant and Environmental Science (UCPH - PLEN) –
Thorvaldsensvej 40, 1871 Frederiksberg, Denmark
[2]Haldor Topsoe A/S (HTAS) – Haldor Topsøes Allé 1, 2800 Kgs. Lyngby, Denmark

Abstract

The interest in online comprehensive two-dimensional liquid chromatography (LC × LC) have increased as it offers ways to improve the performance of separations in terms of peak capacity and selectivity compared to one-dimensional liquid chromatography. However, the price for greater resolving power in LC × LC is a more complex system, where parameterization of the first dimension constrains the second dimension and vice versa. In this study a way to release these constrains is presented.

The developed method addresses several of the challenges encountered in LC × LC. This includes in particular: loss of peak capacity due to undersampling of the first dimension, limited peak capacity in the second dimension due to short second dimension analysis time and limitations in selection of column dimensions and flow rates.

The method is based on a strategy where the sample is eluted of the first dimension column by pulses of increasing eluotropic strength and width. In between the pulses the first dimension is kept in a no-elution state by applying a flow of mobile phase with weak eluotropic strength. The eluate from the first dimension is diluted with a make-up flow of water to lower the eluotropic strength of the transferred fraction before it is trapped on trap columns in the modulator and re-injected onto the second column.

It is demonstrated that the LC system is capable of delivering the required pulses of strong solvent and by tuning the length and eluotropic strength of these pulses, analytes with retention factors in water kw above 150 can be manipulated to elute in 3-4 pulses. In between the pulses the first dimension can be kept in a no-elution state for up to 10 minutes without changes in which pulse and the pulse number analytes with kw above 350 elutes in. For analytes with $kw = 150$ minor changes in the pulse position of elution was observed when the no-elution time was increased from 1 to 10 min. The developed method was tested using 27 nitrogen containing aromatic compounds and applied to the analysis of vacuum gas oils. Peak capacities of 4018 and 4610 (corresponding to a peak production rate of 7.4 peaks/min and 4.5 peaks/min) was obtained for a 540 min and 1040 min analysis, respectively. The pulsed elution approach combined with a refocussing step between the two dimensions offers great potential with respect to increasing the flexibility of LC × LC.

---

*Speaker

Applying SFC-ESI-MS for the non-targeted analysis of pyrolysis oils

Josephine Lübeck*[1], Linus Malmquist[1], Giorgio Tomasi[1], Sylvain Verdier*[2], Asger Hansen[2], David Dayton[3], Ofei Mante[3], and Jan Christensen†[1]

[1]University of Copenhagen – Department of Plant and Environmental Sciences, University of Copenhagen, Thorvaldsensvej 40, 1871 Frederiksberg, Denmark
[2]Haldor Topsoe A/S – Nymollevej 55, 2800 Kgs. Lyngby, Denmark
[3]RTI International – RTI International, Research Triangle Park, NC 27709 USA, United States

Abstract

Pyrolysis oils are produced from miscellaneous bio-crudes as an alternative energy resource for petroleum. However, due to their composition, e.g. high oxygen and water content, acidity etc., upgrading is a required process. In order to upgrade in the most profitable sense, characterisation of the oxygenated species is a necessity. Herein, the application of supercritical fluid chromatography-negative electrospray ionisation-mass spectrometry (SFC-ESI(-)-MS) for monitoring different catalytic upgrading techniques of pyrolysis oils is shown. A fractionation method was developed to attain organic and water phases in order to facilitate the analysability. Optimisation of the SFC method was performed to increase selectivity and eliminate carry over. Several feeds were examined, and group-type separation was achieved. Data treatment involved chemometric processing to visualise oxygenated species and to illustrate the variation between the feeds. Based on mass spectra and elution order, compound suggestions were accomplished.

---

*Speaker

†Corresponding author: jch@plen.ku.dk

Analysis of Crude Oils and Asphaltenes with Thermal Analysis coupled to Photoionization Mass spectrometry

Christoph Grimmer*[1], Christopher Rüger[1], Thorsten Streibel[1,2], Anne Ulbrich[1], and Ralf Zimmermann†[1,2]

[1]University of Rostock – Dr.-Lorenz-Weg 1 18059 Rostock, Germany
[2]Helmholtz Zentrum München – Germany

Abstract

Introduction: The characterization of heavy petrochemical fractions is a challenging analytical problem as heavy crude oils, oil sands, asphaltenes etc. are extremely complex mixtures. Thus insight into these complex molecular systems will only be possible by combining results from different high-end methodologies such as LC-MS/MS, ultra-high mass resolution MS or IMS-MS. This is particularly true if molecular motives are targeted, that cause certain physical properties such as unwanted precipitation or viscosity. In this context thermal analysis coupled to laser photoionization mass spectrometry represents a novel tool for characterization of heavy petrochemical fractions.
Method: A thermal analyzer (TA) is coupled to a photoionization time-of-flight mass spectrometer (TA-PIMS, File 1). Ionization is performed by laser generated VUV-light pulses (118 nm, 10.5 eV) in a single photon ionization process (SPI, universal soft ionization) or with 266 nm UV-photons in a resonance enhanced multi photon process (REMPI, selective soft ionization for aromatic compounds). During the TA-temperature program, the vaporizable compounds (e.g. the atmospheric distillable fractions of crude oils) are subsequently released and detected in the MS. At temperatures of 300-350 ∘C the non-volatile sample constituents start to pyrolyze (i.e. simulating thermal cracking of non-volatile residues) leading to a shift towards molecules of lower weight. Chemical information on sample properties are obtained via the different REMPI- and SPI-mass spectra.

Results: The investigated crude oils show two distinct regions (e.g. survey view in File 2). From 30 to 300 ∘C evaporation of volatile compounds takes place. At 300 ∘C evaporation of semivolatile compounds continues, while thermal fragmentation of nonvolatile substances occurs, resulting in overlapping signals especially for aromatic species with m/z ratios between 200 and 350. Under inert gas atmosphere, the heating induces thermal fragmentation (i.e. pyrolysis) of high-molecular structures. Typical degradation pathways, such as alkylated aromatic substances decomposing into alkenes and aromatic cores, can be easily detected by SPI (blue) and REMPI (red).

For characterization of different petrochemicals, e.g. crude oils or asphaltenes, a substance class assignment, based on literature knowledge and selectivity, can be done either time resolved (resolution of 1 s with a heating rate of 10 K/min) or as sum parameters (File 3).

---

*Speaker
†Corresponding author: ralf.zimmermann@helmholtz-muenchen.de

Another approach to investigate underlying processes during evaporation and pyrolysis are data analytical methods such as non negative matrix factorization (NMF). The resulting simplified spectra can help to determine relevant masses for specific pathways.

Conclusion: Soft and selective photoionization is well suited for the investigation of complex mixtures. Thus TA-PIMS, together with sophisticated data analytical methods show great potential for characterization of heavy petrochemical fractions.

PC-P15

Computer-aid Gasoline Molecular Composition Reconstruction on the Basis of GC-FID data

Linzhou Zhang*†[1], Chen Cui[1], Quan Shi[1], and Suoqi Zhao[1]

[1]China University of Petroleum-Beijing – China

Abstract

Nowadays, there are two major methods to obtain gasoline composition, which are experimental method (GC-FID or GC-MS) and computer-aid reconstruction method based on bulk property data. Computer-aid reconstruction method transforms bulk properties to virtual molecular composition in a rapid way. However, the previous work in our lab has proved that composition produced by this method is unstable. Unstable composition will result in unstable prediction of properties, especially octane number. Experimental method is capable of obtaining more accurate result with good consistency. Although the composition analyzed by GC-FID is much more accurate than simulation method until carbon number reaches 8, the amount of isomers increases exponentially and exceed the separation capacity of gas chromatography column for C8+ components. Here, a new method is proposed to solve this problem. Firstly, molecules in gasoline were categorized into different chemical families based on their structure. In the same chemical family, molecules with the same carbon number will be lumped together. Lump composition below C8 (C8-) can be directly obtained from GC FID while that of C8+ is incomplete. On the basis of the hypothesis that the content of each chemical family against carbon number in gasoline follows a certain statistic distribution, the parameters of the distribution was tuned by fitting C8- component distribution curve. Content of C8+ is used as constraint during this optimization process and new composition was obtained. The method that combines GC-FID and computer-aid reconstruction shows better accuracy and wider application than merely GC-FID method. Several gasoline samples had been tested by this method. The predictions are in good agreement with experimental data.

---

*Speaker

†Corresponding author: lzz@cup.edu.cn

PC-P16

Delta 13C values for heteroatom classes derived from ESI-FTICRMS data

Peter Arisz*†[1], Jos Pureveen[2], and Ron Heeren[1]

[1]Maastricht University (M4I) – Universiteitssingel 50;6229 ER Maastricht, Netherlands
[2]Shell (Netherlands) – Netherlands

Abstract

Classification of oils by high resolution FTICRMS can nowadays be done in many labs on a routine basis. Although high resolution spectra of oil are supercomplex and rich in data, a key element of FTICRMS is that the very high mass resolution allows the measurement of accurate mass peaks with unique atomic compositions. Special software packages such as PetroOrg are designed to rapidly unravel spectra. The software groups the mass peaks into classes that are characterized by the number of heteroatoms as well as by the number of 13C isotope atoms in their structure.
Under favorable conditions both monoisotopic and their first 13C-isotope peaks are completely separated from other isobaric mass peaks. In theory this allows to derive delta 13C values from FTICRMS data by the comparison of the peak intensities of monoisotopic peaks and their first 13C isotope peak.

A requirement for high resolution measurements is that the number of ions in the FTICR cell is limited to about 10e6. This limit, combined with the vast number of organic structures in oil makes that the measurement is prone to a significant statistical error (measured intensity is x ± /x). Consequently, the error in the 13C/12C peak ratio of individual pairs is large. However, the number of 13C-monoisotopic pairs per heteroatom class can be large too and therefore the error in the mean value converges to about ±10 to ±30 per mil for the most abundant classes.

13C/12C-Isotope ratios can reveal information about the biological origin and history of crude oils. Common delta 13C values for crude oils range between -35 and -21 per mil. Negative ESI-FTMS of one particular oil shows delta 13C values of about -22 per mil for all O and SO classes. Any of the N containing class, however, show exceptionally depleted 13C values of -70 per mil or more which values are significantly different from the O and SO classes. Presently we test the robustness of the method and investigate if any systematic error might influence the result.

---

*Speaker

†Corresponding author: p.arisz@maastrichtuniversity.nl

PC-P17

Analysis of heavy petroleum fractions and solid fuels via thermal analysis (TA) coupled to ultra-high resolution mass spectrometry (FT-ICR MS)

Christopher Rüger*[1], Anika Neumann[1], Martin Sklorz[1], Stephan Dörk[1], and Ralf Zimmermann[1,2]

[1]University of Rostock – Dr.-Lorenz-Weg 1 18059 Rostock, Germany
[2]Helmholtz Zentrum München German Research Center for Environmental Health (HMGU) – Germany

Abstract

Introduction: With the extensive usage of crude oil, accessible reservoirs containing petroleum of high quality will become rare and will lead to an increasing exploration of sources containing petroleum of lower quality. Such sources include oil sand, bitumen, shale oil and extra heavy crude oils. They can contain a high content of the so-called asphaltenes, a highly aromatic and complex fraction. Asphaltenes are known to cause a number of serious flow assurance challenges. Their characterization on molecular level can help to understand and solve aggregation processes. In this study we present thermal analysis coupled to ultra-high resolution mass spectrometry with soft atmospheric pressure chemical ionisation (APCI) for the investigation of solid fuel samples, bitumen and heavy oils as well as their asphaltene fractions.

Method: For evolved gas analysis (EGA), a thermo balance was hyphenated to APCI. Ultra-high resolution mass spectrometry was conducted utilizing a FT-ICR MS equipped with a 7 T magnet (File 1). Alternating, intact mass spectra as well as fragment spectra (collision induced dissociation - CID) were recorded. Besides other a SARA heavy fuel oil fractionation, several heavy crude oils, their asphaltene fractions (precipitated with different solvents) as well as a coalification series (peat, brown-, black- and anthracite-coal) were investigated. The time resolved high resolution mass spectra were pre-processed and exported using the vendor software. Self-build MATLAB algorithms were utilized for identifying features. Elemental compositions were assigned to these filtered data within 2 ppm error range.

Results: Increasing temperature leads to emission of higher boiling point species with a m/z up to 650. At higher temperatures (_˜ 300-350 ◦C), pyrolysis changes the pattern. All SARA fractions and the parent oil exhibit specific molecular characteristics, e.g. CHOx-class species are highly abundant in the resin fraction, whereas the CH- and CHS-class is predominant in the aromatics fraction. Additionally, the temperature trend of the classes is significantly different (File 2). The asphaltenes showed low signal in the thermo desorption and revealed high abundance in the pyrolysis step. For the CH-class at higher temperatures relatively low aromatic pyrolysis decomposition structures as well as high aromatic species were found (File 3). Distinct differences, such as the ratio between the two phases and the elemental composition of the evolved species, were found between the different parent heavy oils. Furthermore, there was decreasing contribution of the desorption phase when applying heavier alkanes

---

*Speaker

for precipitation. The coalification series reveals a clear trend: higher coal-grade leads to a decreasing desorption phase, whereas the pyrolysis phase become predominant. Moreover, in the CID spectra the stable polycyclic aromatic hydrocarbons increase in abundance.
Conclusion: Thermal gravimetry coupled to soft ionization high resolution mass spectrometry, is a suitable and powerful tool for the characterization of high complex petroleum samples on the molecular level. Solid samples, such as asphaltene fractions or coal, can be investigated directly without prior sample treatment. The time/temperature resolved processing allows the investigation of individual molecular species or compound classes. Pyrolysis fragments and/or CID of high molecular weight compounds allow structural elucidation on the chemical core structures.

A Multiscale Simulation Approach towards Understanding the Behaviour of Asphaltenes in Crude Oils

Jason Law*[1], Guadalupe Serratos[1], Thomas Headen[2], Carmelo Moreno[3], Edo Boek[4], and Erich Mueller†[1]

[1]Department of Chemical Engineering, Imperial College London – Imperial College London, South Kensington Campus, London SW7 2AZ, UK, United Kingdom
[2]ISIS Neutron and Muon Source, Science and Technology Facilities Council, Rutherford Appleton Laboratory – Rutherford Appleton Laboratory, Harwell Campus, Didcot OX11 0QS, UK, United Kingdom
[3]Department of Chemical Engineering, University of Bath – Department of Chemical Engineering, University of Bath, Bath BA2 7AY, UK, United Kingdom
[4]Department of Applied Mathematics and Theoretical Physics / Centre for Mathematical Sciences (DAMTP/CMS) – DAMTP, Centre for Mathematical Sciences, Wilberforce Road, Cambridge CB3 0WA, UK, United Kingdom

Abstract

The modelling of the behaviour crude oils is particularly challenging due to inherent uncertainty concerning the chemical characterization of the system, and also due to the diverse length and time scales involved. This work focuses on the particular problem of the characterization of the asphaltene aggregation process. Here we describe a framework that spans multiple time, size and complexity scales to provide a richer description of the problem.
At the bottom of the size/complexity scale, we start with an experimentally-based description of plausible molecular structures of asphaltenes and resins; the Quantitative Molecular Representation (QMR) approach [1] is used to generate structures based on experimental data from crude oils. These structures are optimised to select a small subset of molecules that give the best match with the experimental data input, consisting of elemental analysis parameters, and both 1H and 13C NMR-spectroscopy parameters.

The behaviour of the model asphaltene structures generated by QMR in heptane, toluene and heptol solvents was then determined using a fully atomistic description employing the OPLS-AA force field in classical molecular dynamics (MD) simulations. The simulations shed light on the incipient clustering mechanisms and the size and distribution of asphaltenes in simple solvents. While simulations at this level of detail are enlightening, it has been shown [2] that no level of current computational resources is sufficient to cover the real times required to represent the clustering process, hence the need to recourse to a lower level of fidelity.

At the next level of scale, we built coarse-grained (CG) models, in which beads representing

---

*Speaker
†Corresponding author: e.muller@imperial.ac.uk

multiple atoms are used, significantly reducing the number of particles and calculations involved in the simulation. We use here the SAFT-γ Mie approach [3,4], where the parameters describing the intermolecular forces are obtained from fitting the properties of molecules and molecular segments to macroscopic thermophysical properties, and produce CG models of the asphaltenes, resins and different components (aromatics, waxes, non-condensables, etc.) of a typical live oil. The output of selected atomistic MD simulations is used to validate the robustness of the CG model. Complex systems composing of realistic mixtures of solvents, resins and multiple asphaltenes in wide ranges of pressures and temperatures are then explored using CG models in large-scale parallel MD simulations. Preliminary results suggest ways in which the polydispersity and complexity of the crude help maintain the larger asphaltene molecules from segregating and precipitating.

References

Neurock, M.; Nigam, A.; Trauth, D.; Klein, M. T. Chem. Eng. Sci. 1994, 49, 4153–77 . for a recent application see Boek, E.S., Yakovlev, D.S., Headen, T. 2009. Energy & Fuels 23, 1209-1219.

Headen, T. F. et al. (2017). Energy & Fuels, 31, 1108–1125.

M´uller, E. A., Jackson, G. 2014. Annu. Rev. Chem. Biomolec. Eng., 5, 405-427

Jiménez-Serratos G. et al. *Coarse-graining polycyclic aromatic hydrocarbons using SAFT-γ force fields: application to molecular simulations of asphaltenes* , Petrophase 2017

PC-P19

The Application of Direct Inlet Probe in combination with High Resolution Time-of-Flight Mass Spectrometry for the Characterization and Comparison of Heavy Petroleum Products.

Uwe Käfer[1,2], Thomas Groeger[*†2], Christopher Rüger[1], Jürgen Wendt[3], Thomas Wilharm[4], and Ralf Zimmermann[1,2]

[1]University of Rostock (Chair for Analytical Chemistry) – Germany
[2]Helmholtz-Zentrum München (CMA) – Germany
[3]LECO European Application Technology Centre – Germany
[4]Analytik Service-Gesellschaft mbH – Germany

Abstract

Intorduction: The characterization and specification of heavy petroleum products and bitumen for industrial usage is mostly based on physical properties like penetration, softening point, breaking point and viscosity. However these parameters are often not sufficient to predict in-service performance or aging behavior. High resolution-mass spectrometry can deliver accurate mass information, which is needed for a better investigation of the chemical composition that determines chemical properties of heavy petroleum fractions. In this work a laboratory aging procedure is applied to different bitumen samples, which are afterwards fractionated in a SARA-type LC separation. To determine chemical features and molecular differences, a direct insertion technique is used to make the high boiling fractions accessible to high resolution time-of flight mass spectrometry.
Experimental: Bitumen samples of different origins and varying physical properties were artificially aged with a modified rotating flask test (RFT), resulting in three samples of different aging state for each bitumen. The samples were afterwards separated into SARA fractions (saturates, aromatics, resins, asphaltenes) by heptane precipitation and a preparative medium pressure LC method. For the Mass spectrometric analysis a High Resolution TOF, equipped with a direct inlet probe (DIP) and EI/PI source, was used. The DIP-unit allows direct introduction of the sample into the ion source, where it is vaporized under heavily reduced pressure, which makes the technique suitable for high boiling samples. Furthermore the possibility of applying a temperature gradient adds another dimension of separation.
Results & Discussion: Measurements showed increasing asphaltene contents and decreasing penetration depths for aged samples. However the severity of the changes, caused by the aging treatment, varies massively between the different bitumen samples. In order to reduce the complexity of the matrix all samples were fractionated into SARA groups. The SARA composition also showed differences between the bitumen samples and mostly the aromatics and resins fraction were influenced by the aging procedure. For the DIP-MS measurements, a linear temperature gradient from 50 to 400 ◦C was applied to vaporize the samples directly in the ion source under high-vacuum. This technique results in boiling curve-type

---

[*] Speaker
[†] Corresponding author: thomas.groeger@helmholtz-muenchen.de

total ion chromatograms and allows separation according to volatility. The application of EI and PI allow a comparatively uniform ionization and analysis of such complex matrices. EI-fragmentation and molecular peaks could be discriminated through their time profile. The resolution of over 50.000 and mass accuracy of better than 1 ppm enabled the assignment of sum formulas to the majority of the mass traces. By using kenrick-plots, classification groups and advanced data mining techniques, the chemical character of the samples were visualized and some aging mechanisms were revealed SARA fractions showed major differences regarding the aromaticity of their components and their heteroatom distribution. In combination with LC separation a multi-dimensional comprehensive characterization was possible in respect to volatility, polarity, molecular mass and aromaticity. Homemade chemo metric algorithm also allows a direct relative comparison of samples and first quantitative results.

PC-P20

The application of high temperature comprehensive two-dimensional gas chromatography for simulated distillation of light crude oils

Maximilian Jennerwein[1,2,3], Thomas Groeger*[2], Markus Eschner[1], Thomas Wilhram[1],
Jürgen Wendt[4], and Ralf Zimmermann†[2,3]

[1]Analytik Service-Gesellschaft mbH – Germany
[2]Helmholtz-Zentrum München (CMA) – Germany
[3]University of Rostock (Chair for Analytical Chemistry) – Germany
[4]LECO European Application Technology Centre – Germany

Abstract

Introduction: The distillation behavior of crude oil is a key parameter for the later refining process. The feedstock could be either investigated by a down-scaled real distillation process, which is separated into an atmospheric and a vacuum procedure, or by a so called simulated distillation (SimDist). The SimDist is based on a gas chromatographic investigation with a non-selective flame ionization detector. While relative quantitative information are gained by the comparison of the FID - response to a reference sample and alkane standard material, no deeper qualitative information is gained about the boiling point distribution of the sample. We will introduce a concept for a two-dimensional simulated distillation (2D-SimDist) for light crude oil. The virtual boiling point cuts from GC×GC-TOF MS were evaluated versus real boiling point cuts as well as the corresponding 1D SimDist quantitatively and a detailed qualitative information was derived from GC×GC-TOFMS by classification and scripting of compound classes. By this approach 98% of the compounds could be classified to compound classes and distillation cuts.
Experimental: CPC Blend (light crude oil) was distillated according to ASTM D2892 and D5236 with 30○C boiling point cuts. 3 sets of distillation cuts were generated with an offset of the start temperature of 10○C. starting at 70○C, 80○C and 90○C. In additional also complete crude oil from different origin (Arabian light crude oil, Norwegian Troll crude oil, Nigerian Furcado crude oil, Mittelplate crude oil and a blend of North African crude oils) was investigated. The samples were investigated by 1D SimDist according to ASTM D7169 and GC×GC-TOFMS. GC×GC-TOFMS was equipped with an reversed phase column combination and adopted to high temperatures (HT-GC×GC). Compound classes were identified by classification (GC×GC pattern) in combination with scripting (investigation of fragmentation pattern). GC×GC-high resolution TOFMS was applied for evaluation and identification of additional compound classes.
Results&Discussion: The scripting and classification approach based on nominal mass EI fragmentation pattern was already applied for specified middle distillates and was successfully extended to higher boiling point ranges and unprocessed crude matrices. Especially heteroatomic species were added. Accurate mass information from high resolution TOFMS

---

[*]Corresponding author: thomas.groeger@helmholtz-muenchen.de
[†]Speaker

allowed a validation of inconclusive classifications and the targeting of additional compound classes. The boiling point range was also extended to > C 65. In total > 20 compound classes were used to classify the different crude oils, which allowed an classification of about 98% of the detectable peaks. The investigation of real boiling point cuts by GC×GC-TOFMS and 1D SimDist showed a good comparability. It also reveals some weakness of the applied distillation approach. Start as well as end points of the distillation cuts were contaminated by the previous and following cut. Due to this approach the one dimensional simulated distillation could be transferred to a two dimensional set up and the information ained by SimDist could be extended by an detailed qualitative inspection for each 10◦C virtual boiling point cut.

APPLICATION OF 1H-NMR ANALYSIS TO THE STUDY OF ASPHALTENES FRACTIONS FROM COLOMBIAN CRUDE OILS AND THEIR BEHAVIOR IN SOLVENT DEASPHALTING

Lina Navarro*†[1], Fernanda Barbosa[2], Peter Seidl‡[3], Carlos Lizcano[4], and Jhon Peñaloza[5]

[1]Lina Constanza Navarro Quintero (Lina Navarro) – Km 7 Via Piedecuesta. Colombian Petroleum Institute. Piedecuesta, Santander., Colombia
[2]Fernanda Barbosa (Fernanda Barbosa) – Ilha do Fundao. CETEM, Rio de Janeiro, Brazil
[3]Peter Seidl (Peter Seidl) – Ilha do fundão, Escola de Quimica, Rio de Janeiro, Brazil
[4]Carlos Eduardo Lizcano Pimiento (Carlos Lizcano) – Km 7 Via Piedecuesta. Colombian Petroleum Institute. Piedecuesta, Santander., Colombia
[5]Jhon Iván Peñaloza Bueno (Jhon Peñaloza) – Km 7 Via Piedecuesta. Colombian Petroleum Institute. Piedecuesta, Santander., Colombia

Abstract

Asphaltenes continue to attract much attention although there have been considerable advances in their description and characterization in the recent literature. Their tendency to flocculate and precipitate during both oil production and refining is a strong incentive for the development of more efficient processes for the mitigation of the effects of asphaltenes on petroleum fractions. Adequate knowledge of the chemical structures that are present in a fraction and their behavior under certain conditions is essential for an understanding of their behavior in different stages of petroleum processing
In the present work, Asphaltene samples were extracted from three Colombian heavy crude oils (C1, C2 and C3) and fractionated by a new method based on solvent blends [1]. The asphaltene fractions were monitored by hydrogen nuclear magnetic resonance (1H-NMR). Chemical characterization of the crude oils showed that, according to the API classification, all of them are heavy crudes with similar asphaltene content, however the resin fraction reveal a dramatic reduction for crude C3, reflecting a lower resin/asphaltene ratio for this crude oil.

The percentage of asphaltenes extracted from three crude oil samples using the solvent blends technique showed that the three crude oils are rich in asphaltene content, within a range between 10-15% and their values are similar to the percentage obtained by IP-143 method.

1H-NMR analysis revealed that the chemical species extracted, exhibited some differences in structure. Asphaltenes from C1 and C2 (A-C1 and A-C2) crude oils showed similar 1H-NMR

---

*Speaker
†Corresponding author: lina.navarro@ecopetrol.com.co
‡Corresponding author: pseidl@eq.ufrj.br

parameters while asphaltenes from C3 (A-C3) exhibit different structural parameters. Aromatic hydrogens for A-C3 show a decrease (7.13%) compared with A-C1 and A-C2 (27.3% and 29.5%). A-C3 also show high level of Hβ, suggesting molecules with larger side chains as well as minor substitution on the aromatic ring. The same behavior can be observed for Hα and Hγ. The A-C3 samples showed a higher percentage of total saturated hydrogens and significant differences in β and γ hydrogens compared with A-C1 and A-C2, which correspond, respectively, to CH2 or CH hydrogens neighboring saturated groups and terminal or branched CH3 hydrogens in aliphatic chains.

A-C3 asphaltenes resemble asphaltene archipelago structures and the C3 crude oil has been characterized by its special behavior in some refining processes, like solvent deasphalting. This crude oil cannot be deasphalted under normal conditions and requires larger quantities of solvent for aggregation, precipitation and subsequent separation from deasphalted crude oil. This physical behavior must to be related to their chemical structure. It is possible than A-C3, having the least amount of aromatic species compared with A-C1 and A-C2, makes the aggregation process more difficult, resulting in difficulty with aggregation and susequent separation in a pyysical process, like solvent deasphalting.

SILVA F.B., *et al.* BRAZILIAN JOURNAL OF PETROLEUM AND GAS, v. 7 n. 3, p. 107-118, 2013.

PC-P22

Comparisons of Fractionation and Characterization Methods for Asphaltenes

Paula Fiorio[1], Fernanda Silva[2], Peter Seidl*†[1], Maria José Guimarães[1], Lina Quintero[3], érika Chrisman[1], and Sônia Menezes[4]

[1]Federal University of Rio de Janeiro (UFRJ) – Brazil
[2]Center of Mineral Technology (CETEM) – Brazil
[3]Ecopetrol – Colombia
[4]Petrobras (CENPES) – Brazil

Abstract

Solid deposition is one of the most serious problems that arise in the production of crude oils. Well and oil pipeline clogging may result in interruptions of oil production and very significant cost elevations. The precipitation of asphaltenes has been attributed to changes in P, T and composition of a crude oil, mixing crudes with other oils or diluents, or the presence of insoluble material such as inorganic salts or paraffins. The tendency of certain oils to flocculate and form deposits is attributed to asphaltenes and their respective molecular interactions.
Asphaltene composition and behavior are important issues for production, transportation, storage and refining of petroleum. Problems such as flocculation, aggregation and precipitation are frequently associated with asphaltenes in different stages of petroleum processing. Even at low concentrations, they have a strong tendency to aggregate and precipitate causing major damage in the oil industry.

The knowledge of the chemical structure of asphaltenes is very important in these studies, since the chemical structure reflects the chemical properties of these components and provides a basis for molecular modeling studies. Much attention has been paid to the determination of physical, chemical and structural properties of asphaltenes using a great variety of conventional and advanced characterization techniques. The adoption of fast and reliable asphaltene extraction procedures provides a more comprehensive understanding of asphaltene molecular structure and the mechanisms that lead to their precipitation.

This work compares three different methods of asphaltene fractionation in order to provide reliable data of asphaltene structural properties for modeling studies. The precipitation of asphaltenes was carried out by the IP-143 standard method, a IP-143 modified method using mixtures of heptane and toluene (heptol) in different concentrations and a method based on the selective extraction of the constituents using mixtures of a naphthenic (N) and a paraffinic solvent (P1 or P2). The asphaltenes obtained by different techniques were characterized by elemental analysis and NMR. Elemental analysis reveals the C/H ratio and reflects the degree of condensation of the aromatic rings. The NMR analysis gives the functionalities of the chemical species of the hydrocarbons that are extracted.

---

*Speaker

†Corresponding author: pseidl@eq.ufrj.br

sciencesconf.org:petrophase2017:145326

These methods were applied to vacuum residues that have been analyzed in our characterization and modeling studies and to the samples that were provided for the asphaltene session. Fractionation of asphaltenes using the solvent blends showed that the total percentage of saturated hydrogen is higher with the NP1 mixture, which favors constituents with higher amount of Hγ which corresponds to the hydrogens on the terminal CH3 or branched aliphatic chain. In samples of asphaltenes obtained by NP2 there is a greater amount of Hβ suggesting larger side chains than those obtained with NP1 and also a lower degree of substitution on the aromatic ring. The fractionation of asphaltenes using heptol showed that aromatic species are concentrated in the more soluble sub-fraction and also suggested that this subfraction may be mainly responsible for the association of these molecules.

PC-P23

SUBFRACTIONATION AND STRUCTURAL CHARACTERIZACTION OF ASPHALTENES DERIVED FROM COLOMBIAN HEAVY CRUDE OIL

Lina Morantes[1] and Juan Carlos Poveda*†[2]

[1]Universidad Industrial de Santander – Colombia
[2]Universidad Industrial de Santander (UIS) – Colombia

Abstract

Asphaltenes, which are the most polar and heaviest molecules in crude oils, are responsible of many problems occurring during petroleum production due to changes in thermodynamic variables such as temperature, pressure and oil composition. A better understanding of asphaltenes depends on the development of a more accurate description of its solution behavior both in crude and solvents. In this work, Dynamic Light Scattering (DLS) and 1H Diffusion-Ordered Spectroscopy (DOSY) were used to studied the polydispersity, the tendency to form aggregates and the aggregated structures in a hydrocarbon solvent of different asphaltenes sub-fractions. These techniques, recently applied in the petroleum industry, appeared as a key tool to investigate the behavior of asphaltenes diluted in solvents over a wide range of concentrations and temperatures.
Asphaltenes were extracted from a Colombian heavy crude oil according to the ASTM D6560-12 standard method. The yield of asphaltenes (precipitate) was 15 %wt. Asphaltene sub-fractions were obtained by the flocculation method using mixtures of toluene (solvent) and n-heptane (flocculant). Three sub-fractions were obtained at the following toluene/heptane volume ratios: 60/40, 40/60 and 20/80. Asphaltenes that remained in solution were fully recovered as a fourth sub-fraction.

The size of the asphaltene aggregates in toluene and in solutions containing toluene/heptane mixtures was investigated by laser scattering (scattering angle of 90∘) in a Malvern Zetasizer Nano ZS90 instrument. DLS measurements were carried out varying the asphaltene concentration from 0.01 to 0.5 g/L and also varying the temperature between 30–80 ∘C. A 0.5 g/L solution was prepared by dispersing the appropriate amount of solid asphaltenes in the solvent by sonication; less concentrated solutions of asphaltenes were prepared from this solution by successive dilutions. All samples were allowed to stand overnight before any experiment and then were sonicated for 10 min immediately before the measurement. Asphaltene sub-fractions showed different behaviors at the same temperature and with the same solvent medium. However, some general tendencies were founded: *i*) an increase in asphaltene average sizes as a function of concentration when dissolved in toluene at the same temperature; *ii*) a significant raise in the mean particle sizes after flocculant addition; and *iii*) the size of asphaltenes aggregates decreased as temperature increased, particularly in

---

*Speaker

†Corresponding author: jcpoveda@uis.edu.co

systems containing *n*-heptane.
DOSY experiments were performed at the Nuclear Magnetic Resonance Laboratory (Parque Tecnológico UIS-Guatigurá, Bucaramanga, Colombia) using a Bruker Advance III spectrometer. The effect of sample concentration and temperature on the diffusion coefficients was analyzed for solutions of asphaltenes ranging from 1 to 10 g/L and temperatures between 30–80 $\circ$C. Experiments were carried out on the different asphaltene sub-fractions diluted in toluene. Results showed that asphaltene structures are temperature- and concentration-dependent: *i*) when asphaltene concentration is increased, the self-diffusion coefficient decreases slightly; and *ii*) the diffusion of the asphaltenes species increase as temperature is raised.

THEORETICAL-EXPERIMENTAL STUDY OF ASPHALTENE PROPERTIES

Lyzette Moura*†[1], Auro Tanaka , and Jaldyr Varela Junior

[1]Universidade Federal do Maranhão (UFMA) – Cidade Universitária Dom Delgado, Avenida dos Portugueses, 1966, Vila Bacanga, São Luís, Maranhão, CEP 65065-545, Brazil

Abstract

Asphaltenes are structures mainly constituted by polycondensed aromatic rings, also presenting aliphatic lateral chains, some functional groups containing oxygen, nitrogen, and sulfur, in addition to trace quantities of metals as vanadium and nickel. The heteroatoms (N, O, and S) are strongly involved in the interactions (hydrogen bond, charge transfer, etc.) responsible for the asphaltene self-association. This work aim to investigate a serie of properties (thermodynamics, structurals, and electronics) of asphaltenes and the intermolecular interactions of this fraction in the crude oil medium, such as, energy bonding, charge distribution, HOMO-LUMO gap, π-π interaction, vibration frequency, heat of formation, enthalpy, and free energy, focusing on the determination of characteristics such as molar mass and volume, based on the density functional theory, DFT. This will make possible to propose stable structural conformations that will be validate comparing data from literature and experimental results of characterization of asphaltenes from Brazilian crude oils. Preliminary experimental data obtained from LDI-MS provided a molar mass value of approximately 760 Da (n-heptane insoluble asphaltenes) and results from RMN indicated the presence of nitro group (-NO2) and aromatic rings, information that conducted to the minima molecular formula C51H100NO2. These data were used to propose two kinds of structures (an island and an archipelago) that are being evaluated and optimized employing the functional B3LYP; the basis set 6-311++G(d,p), LANL2TZ(f) and Aug-cc-pVDZ will be applied to the determination of thermodynamics, structurals, and electronics parameters.

---

*Speaker

†Corresponding author: lgmdemoura@gmail.com

PC-P25

Evaluating the Novel UniSpray Ion Source for the Analysis of Petroleum Samples

Eleanor Riches*†[1] and Steve Bajic[1]

[1]Waters Corporation – Stamford Avenue, Altrincham Road, Wilmslow, Cheshire. SK9 4AX, United Kingdom

Abstract

A novel UniSpray® ionization source has been developed that uses a unique approach to generating ions for mass spectral analysis. This atmospheric pressure ionization source comprises a grounded capillary from which analyte solution elutes that is nebulized by high velocity nitrogen gas. The eluent spray impacts on a cylindrical, stainless steel target rod held at high voltage, typically _˜0.5 - 4.0 kV, offering the potential to ionize analytes with greater efficiency. In this work, ions produced by UniSpray ionization are compared with ions produced by ESI, APCI, APPI, and ASAP ionization sources for a range of petroleum related samples.
Solvent standard solutions were prepared at suitable analytical concentrations using appropriate solvents: _˜0.5 mg/mL for crude oil fractions, PAH standards, and naphthenic acid standards, and _˜0.1% for engine oils. For ESI, APCI, APPI, and UniSpray, solutions of samples were infused directly. In the case of ASAP, the glass capillary tube was dipped directly into the solutions and the samples were volatilized by a stream of high temperature nitrogen gas followed by ionization via APCI. The high resolution ion mobility data were processed using PetroOrg software to identify the most significant classes of compounds ionized by each different source.

Typical classes of compounds were ionized by the established sources, for example the N1 class by ESI, S1 class by APPI and HC class by ASAP. UniSpray also showed ionization of similar classes but the presence of water appears to play a vital role in the efficiency of the UniSpray source, which poses a challenge when optimizing conditions for samples that are immiscible with water. However, UniSpray does offer greater class coverage on a single source platform compared with the typical sources used, although it does not appear to provide full universal ionization coverage for all typical petroleum samples.

---

*Speaker

†Corresponding author: eleanor_riches@waters.com

Dimerization of acyl pyrene derivatives as a model for asphaltenes aggregation.

Suyane Alvarenga*[1], Rodrigo Correa†[2], Josué Bello Forero[2], Simon Garden[2], Raquel Teixeira[2], Rodrigo Souza[2], and Vinicius Ribeiro[2]

[1]Centro Federal de Educação Tecnológica Celso Suckow da Fonseca (CEFET/RJ) – Brazil
[2]Universidade Federal do Rio de Janeiro (UFRJ) – Brazil

Abstract

Acylpyrene derivatives with acyl chains varying from two to twelve carbon atoms were prepared and their respective excimer formations were followed by Fluorescence emission spectroscopy and the respectives dimerization enthalpies. Our results show that the dimerization enthalpy energy reduces while the acyl side chain increases from two to twelve carbon atoms (1.4 - 7.2 kcal/mol). This result indicates that the π-stacking formation in acylpyrene series is difficulted by the acyl chain and the same behavior could be occuring during asphaltenes aggregation.

---

*Speaker

†Corresponding author: rodrigojosecorrea@gmail.com

An in-depth study of sulfur using imaging XANES with synchrotron radiation

Sudipa Mitra-Kirtley*[1], Sirine Fakra[2], Andrew Pomerantz[3], and Justin Birdwell[4]

[1]Rose-Hulman Institute of Technology (RHIT) – 5500 Wabash Avenue Terre Haute IN 47803, United States
[2]Lawrence Berkeley Laboratory (LBL) – Lawrence Berkeley National Lab 1 Cyclotron Road Mail Stop ??? * Berkeley, CA 94720, United States
[3]Schlumberger-Doll Research (SDR) – 1 Hampshire St, Cambridge, MA 02139, United States
[4]United States Geological Services (USGS) – 103 Sheppard Dr 110, Durango, CO 81303, United States

Abstract

The sulfur chemistry of shale organic matter (bitumen and kerogen) and shale-derived products (oil and gas) can impact the extent of petroleum generation and petroleum migration (Bolin et al, 2016). Understanding sulfur is therefore, important for understanding petroleum geochemistry in general and valuable to the petroleum industry. Here we investigate different oil shales from around the world representing a diverse range of sedimentary rock formations as well as a 2017 Petrophase asphaltene sample. Hard X-ray microprobe measurements, performed at the Advanced Light Source (ALS) beamline 10.3.2, Lawrence Berkeley National Laboratory, will be presented. We used micro X-ray fluorescence (μXRF) elemental and chemical mapping, sulfur K-edge X-ray absorption near-edge structure (μXANES) spectroscopy and X-ray diffraction (μXRD) to localize and determine the speciation of sulfur present in these samples. Additional bulk S K-edge XANES data obtained at Argonne National Laboratory, Advanced Photon Source (APS), beamline 9-BM, on the 2017 asphaltene sample will also be presented. Earlier S K-edge XANES measurements on bitumens extracted from the oil shales show remarkable differences between immature samples from different formations representing lacustrine and marine depositional environments (Bolin et al, 2016), which is also reflected in the subset of kerogens. Although generally dominated by commonly occurring sulfur moieties, such as sulfide, sulfoxide and thiophene, the distribution of these and other sulfur forms vary significantly among the samples. Comparison between bulk and microprobe data will be stressed, and differences in sulfur distribution and chemistry for samples from different depositional environments and varying organic sulfur content will be the primary focus of this presentation.

Bolin, T. B., Birdwell, J. E., Lewan, M. D., Hill, R. J., Grayson, M. B., Mitra-Kirtley, S., Bake, K. D., Craddock, P. R., Abdallah, W., and Pomerantz, A. E., *Energy & Fuels,* 2016, 30, 6264–6270.

---

*Speaker

COMPARATIVE STUDY OF DIFFERENT VEGETABLE OILS FOR THE PREPARATION OF MICROEMULSIONS USED AS CLEANER FLUIDS OF BASED OIL DRILLING FLUID

Fabiola Curbelo*†[1], Anna Cabral‡[1], Gustavo Lopes§[1], Elayne Araújo¶[1], Rafael Ungarato*‖[2], Julio Cézar Freitas***[3], and Alfredo Ismael Garnica*††[1]

[1]Federal University of Paraiba, Departament of Chemical Engineering (UFPB) – Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil
[2]Oxiteno – Brazil
[3]Federal University of Rio Grande do Norte, Chemical Institute (UFRN) – Av Sen Salgado Filho, S/N Caixa Postal 1524 - Campus Universitario - Lagoa Nova CEP 59072-970 / Natal - RN, Brazil

Abstract

Cleaner fluids are used in the drilling activity, to displace the layer created by the drilling fluid on the well surface. Most of the drilling fluids are synthetic or oil-based fluids, thus, the layer formed is water-impermeable. If this layer is not removed properly, the cementing operation is compromised, since the cement adheres to water-wet surfaces. Well formulated microemulsions using vegetable oils and used as cleaner fluids, have been a promisor field of study, since it has shown high removal of drilling fluids, improvement their rheological parameters, and ability to water-wet surfaces. The objective of this work was to develop microemulsions composed of two different vegetable oils (VO1 and VO2), equal aqueous phase (water and glycerin 1:1) and non-ionic surfactant (Ultranex NP100); and compare their capacity to displace a non-aqueous drilling fluid, thermal stability measured by cloud temperature of system, rheological parameters, and inversion tests. Two ternary diagrams, differing only the oily phase, were elaborated to determine the microemulsion region. From this region, the system: 40% VO1 or OV2, 5% aqueous phase and 55% surfactant in wieght, was chosen to formulate the microemulsions. The methodology to obtain the cleaning capacity of microemulsions was to create a thin layer of drilling fluid in a predefined area of becker, introduce 200 mL of heated microemulsion (88oC), place the becker in a Fann viscosimeter and set a 300 rpm rotation, and calculate the area that was cleaned by the microemulsion in a maximum of 10 minutes. The cloud temperature of the system was obtained by heating the microemulsion under agitation. The inversion tests were carried out by electrical conductivity measurements in Wettability equipment. The rheology analysis was performed in

---

[*] Speaker
[†] Corresponding author: fabioladias@yahoo.com
[‡] Corresponding author: annagcabral@gmail.com
[§] Corresponding author: gustavosantos_lopes@hotmail.com
[¶] Corresponding author: elaynea_@hotmail.com
[‖] Corresponding author: rafael.ungarato@oxiteno.com
[**] Corresponding author: juliofreitasj@hotmail.com
[††] Corresponding author: alfredocurbelo@yahoo.com

a Brookfield DVIII Ultra rheometer that measured the viscosity of the microemulsions from 30oC to 70oC. The results showed that the microemulsion with VO1 has a higher capacity to remove a non-aqueous fluid, cleaning over 96% of drilling fluid more than VO2 (81,8%). The cloud temperature of the system with VO1 was not reached even at high temperatures (tested until 118oC), while the system with VO2 was blurred at 42oC. Finally, the rheology analysis showed that both microemulsions are Newtonian fluids, for all the temperatures analyzed, which is the ideal behavior for cleaner fluids. Therefore, the microemulsions with VO1 and VO2 present appropriate properties to be used as cleaner fluids, but the microemulsion with VO1 had better results regarding the removal of drilling fluids, cloud temperature, and to cleanup and wettability inversion of wellbore wall to water wet surface.

Calorimetric study of asphaltenes and their sub-fractions obtained by column fractionation with silica

Rubia Mariath*†[1], Agnes Scheer[1], Carlos Yamamoto[1], and Sebastien Simon[2]

[1]Universidade Federal do Parana [Curitiba] (UFPR) – Av. Cel. Francisco H. dos Santos, 210, Brazil
[2]Norwegian University of Science and Technology - NTNU (NORWAY) – Norway

Abstract

Asphaltenes are the heaviest fractions of crude oil, and give rise to phenomena of organic deposition in reservoirs, wells, pipes and equipment. The deposition of these asphaltenes leads to production flow restrictions and unplanned outages. To better understand the deposition process we study the calorimetric behavior using DSC analysis. But the asphaltene is a very complex compound, so we fractionate the asphaltenes in three sub-fractions using a column with silica to have more information about the whole structure of this material. To analyze the effect of the calorimetric study and related it with the of the sub-fractions, they were characterized with FTIR. The results indicated that the third sub-fraction shows more saturated compounds than the other two sub-fractions, which may indicate the precursor group in the precipitation and deposition of asphaltenes.

---

*Speaker

†Corresponding author: rubiamariath@gmail.com

Effects of microwave irradiation on the wettability characteristics of heavy oils

Jaber Taheri-Shakib[1], Ali Shekarifard*[1], Hassan Naderi[2], and Seyedahmad Hosseini†[3]

[1]Institute of Petroleum Engineering, School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran – Iran

[2]Research Institute of Petroleum Industry, Department of Research and Technology of the rock and fluid reservoirs, Tehran, Iran – Iran

[3]Department of Environment, Land and Infrastructure Engineering, Politecnico di Torino, Turin, Italy – Italy

Abstract

One of the most critical parameters in oil reservoirs is wettability. The wettability is a significant phenomenon for fluid flow in porous media. In this study, the effect of microwave radiation on a crude oil sample YAD of Iran south-west reservoir (API: 18.96) is addressed. 150 ml of a sample placed in a microwave oven (Fischer assay extended by microwave) in time durations of 2, 4, 6, 8 and 10 minutes radiated with a power of 600 w and a frequency of 2450 KHz. The measured contact angle of crude oil samples with limestone reservoir rock reveal that by increasing the time of microwave irradiation, the wettability tends from entire oil-wet to water-wet. Resins and Asphaltenes (polar compounds of oil) are primary factors of wetting the oil to the surface. SARA experimental results show that asphaltene content of sample reduces 16% and 7% in time ranges of 2, 4 minutes, respectively. In two minutes radiation, the most optimum reduction takes place. While increasing the time of microwave irradiation, resin content decreases 27% at 10 minutes. Furthermore, Sulphur contents of crude oil that are also polar compounds decline when increasing irradiation time that eventually falls 19% which can be considered as upgrading. Along with desulfurization, the percentage of light carbon fractions (C1-C10) in time durations of 2, 4 minutes increases around 17% and 9% which enhances the upgrading process. Reduction in the polar resin and sulphur contents cause the oil to lose its wettability characteristics. This reflects the importance of these compounds in wettability phenomenon that has high capability to absorb microwaves which diminish their contents due to cracking. The contents of polar compounds are high in heavy oils, and since the efficacy of microwave irradiation is a function of oil polar compounds, thus absorption capacity of microwave radiation would be high in heavy oils. Using microwave irradiation technology in heavy oil reservoirs is one of the fundamental and practical methods in wettability alteration and increasing the production which can be an efficient alternative to the existing chemical solvents and surfactants causing higher cost and lower efficiency in these reservoirs.

---

*Corresponding author: ali.shekarifard98@gmail.com

†Speaker

ADSORPTION STUDY AND OIL RECOVERY BY ANIONIC AND NONIONIC SURFACTANTS IN SANDSTONE BOTUCATU - BRAZIL

Fabiola Curbelo*†[1], Mariana Vale‡[1], Julio Cézar Freitas*§[2], Rafael Ungarato*¶[3], and Alfredo Ismael Garnica*‖[4]

[1]Federal University of Paraiba, Departament of Chemical Engineering (UFPB) – Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil
[2]Federal University of Rio Grande do Norte (UFRN) – Av Senr Salgado Filho, S/N Caixa Postal 1524 - Campus Universitario - Lagoa Nova CEP 59072-970 / Natal - RN, Brazil
[3]Oxiteno – Brazil
[4]Federal University of Paraiba, Department of Chemical Engineering (UFPB) – Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil

Abstract

Surfactant flood tertiary oil recovery schemes have been employed for more than 35 years and has proved to be effective in reducing the saturation of residual oil (RO) in laboratory experiments and field projects through the reduction of the interfacial tension and mobility ratio between the oil and water phases. Which may render them less efficient or ineffective in EOR techniques is adsorption of surfactants onto reservoir rock surface. Nevertheless, nowadays, because of the high oil price, this technology has experienced increased interest. In this work, the performance of two different surfactants, saponified coconut oil (SCO) (anionic) and Alkest TW 80 (T80) (nonionic) were investigated during the adsorption and oil recovery in sandstone coreflood from the Botucatu geological formation in Brazil. Both sets of tests were carried out in a surfactant flooding apparatus using 30 psi as pressure gradient. The critical micelle concentration (c.m.c.) of the surfactant solutions was determined by surface tension measurements. The concentration of the solutions injected in adsorption and oil recovery tests were 50%, 100%, 200%, and 500% above (c.m.c.) to ensure micelle formation. An experimental of dynamic adsorption investigations were carried out to examine the adsorption equilibrium, in room temperature (27○C) and high temperature (60○C) in 50% above the c.m.c. The surfactant adsorption experiments in the rock were carried out in shake using 250 mL erlenmeyer flasks. Each experiment was carried at with eight different amounts of adsorbent and at a constant volume of 200 mL of solution with a known initial concentration. The erlenmeyers were taken to Dubnoff shake under constant agitation with the objective of reaching the equilibrium. The experimental results showed a poor adsorption for both surfactants, according to the equilibrium isotherm. The T80 adsorbed less than the

---

*Speaker
†Corresponding author: fabioladias@yahoo.com
‡Corresponding author: marianamartinsv@hotmail.com
§Corresponding author: juliofreitasj@hotmail.com
¶Corresponding author: rafael.ungarato@oxiteno.com
‖Corresponding author: alfredocurbelo@yahoo.com

SCO, since it is nonionic and has little interaction with the rock. Both surfactants reached equilibrium time at 6 hours. The results of oil recovery in coreflood showed that the two surfactants, SCO and TW 80, yielded a good additional recovery factor, above 75%, and that the increase in the injected concentration, from 200% to 500% cmc, did not have significant results in the oil recovery factor

PC-P32

Asphaltenes are a Continuum of Island and Archipelago Structural Motifs

Martha L. Chacon[*,1], Steven Rowland[1,2], and Ryan Rodgers[†,1,2]

[1]National High Magnetic Field Laboratory (NHMFL) – 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, United States, United States
[2]Future Fuels Institute, Florida State University (FFI) – 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, United States, United States

Abstract

Asphaltenes are enigmatic compounds, best known for their tendency to clog wells/pipelines, damage reservoirs, stabilize emulsions, and foul refinery equipment. Understanding molecular structure is the first step to establish composition-function correlations that help solve asphaltene related problems. The molecular characterization history of these materials is full of controversy, and past efforts initially focused on determining the "correct" molecular weight distribution. Today there is agreement that asphaltenes, in their monomeric form, are species with masses between _˜250-2000 g/mol; but disagreement remains over the molecular architecture. There are two schools of thought about the organization of aromatic cores within asphaltenes. The island model, which describes asphaltenes as single aromatic cores with peripheral alkyl side-chains, is widely accepted. Comprehensive reports by mass spectrometry (MS) suggest that islands are the dominant structures in asphaltenes. However, this model is not consistent with certain asphaltene properties, such as the nature of thermal cracking products and heterogeneous aggregation. The need for a model that agrees with the composition of asphaltene upgrading products gave rise to the archipelago model, which proposes the existence of several aromatic cores linked by alkyl- or cycloalkyl- bridges. FT-ICR MS is uniquely suited to determine molecular composition and may also be used to gain insight into molecular architecture. However, special attention is required; mass spectral data can be biased by the ionization efficiency and aggregation tendencies of asphaltene molecules.

The work presented here focuses on unlocking differences in structural motifs that correlate to solubility and ionization efficiency. Asphaltenes were precipitated and analyzed without Soxhlet extraction, with Soxhlet extraction (according to ASTM D6560-12), and with maceration and 20 hours extended Soxhlet washing as described for the Petrophase 2017 asphaltene. Results reveal that the unwashed asphaltenes more closely resemble petroleum maltenes and are dominated by HC and S classes. However, an increase in N-, O-, and S-containing compounds was observed after Soxhlet washing and extended purification. Asphaltenes were precipitated with *n*-pentane (C5) and *n*-heptane (C7) and analyzed along with the C5 insoluble but C7 soluble compounds (C5-7 asphaltenes) by FT-ICR MS. The C5 and C5-7 asphaltenes were shown to be essentially identical by FT-ICR MS analysis. This is likely due to the fact that C5-7 asphaltenes, considered the compositional bridge between maltenes and asphaltenes, have a greater ionization efficiency compared to C7 asphaltenes.

---

[*] Speaker
[†] Corresponding author: rodgers@magnet.fsu.edu

sciencesconf.org:petrophase2017:146480

Structural characterization was performed with infrared multiphoton dissociation (IRMPD) fragmentation and revealed distinctly different fragmentation patterns for C5-7 and C7 asphaltenes. Fragment ions from C5-7 asphaltenes consist predominately of ions with double bond equivalents (DBE) greater than 16; whereas fragments from C7 asphaltenes consist primarily of ions with DBE$<$ 16. These differences indicate that the more easily ionizable C5-7 molecules are enriched in island-type compounds and that C7 asphaltenes are likely a mixture of island and archipelago type compounds. Likewise, there is a direct correlation between Soxhlet washing time and the abundance of low DBE, IRMPD fragments. Thus, removal of the asphaltenic species that have the highest ionization efficiency (mostly island) exposes asphaltenic species that are increasingly archipelago-type structures.

Analysis of Petroleum Products by Gel Permeation Chromatography (GPC) Online with Inductively Coupled Plasma Mass Spectrometry (ICP MS) and Offline with Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS)

Jonathan Putman*†[1,2,3,4], Sara Gutiérrez Sama[3,4,5], Caroline Barrère-Mangote[3,4], Ryan Rodgers[2,6,7], Ryszard Lobinski[3,4], Brice Bouyssière‡[3,4,5], and Pierre Giusti[3,4]

[1]National High Magnetic Field Laboratory, Florida State University – 1800 East Paul Dirac Drive, Tallahassee, FL 32310, United States

[2]Department of Chemistry and Biochemistry, Florida State University – 95 Chieftain Way, Tallahassee, FL 32306, United States

[3]TOTAL RC – CNRS Joint Laboratory C2MC, Complex Matrices Molecular Characterization – Centre national de la recherche scientifique - CNRS (France) – BP 27, 76700 Harfleur, France

[4]TOTAL Raffinage Chimie, TRTG – TRTG – BP 27, 76700 Harfleur, France

[5]Laboratoire de Chimie Analytique Bio-Inorganique et Environnement (LCABIE) – CNRS : UMR5254, Université de Pau et des Pays de l'Adour – HELIOPARC - 2 Avenue du Président Angot 64000 PAU, France

[6]National High Magnetic Field Laboratory (NHMFL) – 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, United States, United States

[7]Future Fuels Institute, Florida State University (FFI) – 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, United States, United States

Abstract

Heavy metals in crude oils and petroleum distillates can wreak havoc in refinery processes due to the deactivation of hydrotreatment and hydrocracking catalysts. The most abundant metals such as vanadium, nickel, and iron exist as heterocyclic macrocycles containing four modified pyrrole subunits called porphyrins. Results from previous studies show that porphyrins are involved in macromolecular aggregation with asphaltenes.1 Knowledge of the size distributions of the metalloporphyins enables better optimization strategies in the refinery process, rather than relying solely on total metal concentration.2 Gel Permeation Chromatography (GPC) with elemental detection by Inductively Coupled Plasma Mass Spectrometry (ICP MS) provides the size profile of species that contain heavy metals. A typical GPC profile can be divided into four main fractions that vary in aggregation state. These fractions were collected for a typical refinery atmospheric residual feedstock. FT-ICR MS results show

---

*Speaker

†Corresponding author: jputman@magnet.fsu.edu

‡Corresponding author: brice.bouyssiere@univ-pau.fr

a surprisingly strong correlation between decreased aromaticity and aggregation potential. As aggregate size increases, the molecular composition of the fractions becomes increasingly aliphatic. For each of the seven most abundant heteroatom classes, the high molecular weight fraction (as measured by GPC) had the highest average H/C ratio (most saturated). For the two most abundant heteroatom classes, hydrocarbons (HC) and sulfur (S1), the most aggregated fraction had the lowest average double bond equivalence (DBE) and at the same time the average carbon number was almost two times greater than that of the whole sample. Contrary to expectations, aggregation dependence was not correlated with an increase in the relative abundance of polar or polyaromatic species. Thus, the results suggest that aggregation is more correlated to weaker, non-polar intermolecular forces between saturated, long-chain alkyl substituents. Ongoing work is focused on determining the significance of this with regards to asphaltene precipitation. Analyses of the asphaltene fractions should also reveal the distributions of metal containing petroporphyrins as a function of aggregate size. Work supported by NSF Division of Materials Research through DMR-11-57490, Conseil Régional d'Aquitaine (20071303002PFM), and FEDER (31486/08011464).

(1) Acevedo, S.; Guzmán, K.; Labrador, H.; Carrier, H.; Bouyssiere, B.; Lobinski, R. *Energy Fuels* 2012, *26*, 4968.

(2) Desprez, A.; Bouyssiere, B.; Arnaudguilhem, C.; Krier, G.; Vernex-Loset, L.; Giusti, P. *Energy Fuels* 2014, *28*, 3730.

Gel Permeation Chromatography (GPC) and Advanced Polymer Chromatography (APC) Inductively Coupled Plasma High Resolution Mass Spectrometry (ICP HR MS) Study in Petroleum Product Analysis

Sara Gutiérrez Sama*[1,2,3], Alain Desprez[1,2,4,5], Peter Hancock[6], Damian Morrison[6],
Gabriel Krier[5], Charles-Philippe Lienemann[7], Jérémie Barbier[7], Ryszard Lobinski[1,4],
Caroline Barrère-Mangote[1,2], Pierre Giusti[1,2], and Brice Bouyssiere[1,4]

[1]TOTAL RC – CNRS Joint Laboratory C2MC, Complex Matrices Molecular Characterization – Centre national de la recherche scientifique - CNRS (France) – BP 27, 76700 Harfleur, France
[2]TOTAL Raffinage Chimie, TRTG – TRTG – BP 27, 76700 Harfleur, France
[3]Laboratoire de Chimie Analytique Bio-Inorganique et Environnement (LCABIE) – CNRS : UMR5254, Université de Pau et des Pays de l'Adour – HELIOPARC - 2 Avenue du Président Angot 64000 PAU, France
[4]Laboratoire de Chimie Analytique Bio-Inorganique et Environnement (LCABIE) – CNRS : UMR5254, Université de Pau et des Pays de l'Adour [UPPA] – HELIOPARC - 2 Avenue du Président Angot 64000 PAU, France
[5]UL, LCP-A2MC – Université de Lorraine – Technopôle Metz, Metz, France
[6]Waters Corporation – Wilmslow, United Kingdom
[7]IFP Energies Nouvelles (IFPEN) – IFP Energies Nouvelles – Solaize, France

Abstract

Heavy fractions (with high boiling point) of crude oil, such as Atmospheric Residues (AR) or Vacuum Residues (VR), must be transformed into light products for use as fuels. Any V and Ni present can cause the deactivation of refining catalysts so they must be extracted by expensive hydrocracking steps. Information on the chemical environment of these species (speciation) is important to improve such processes.

GPC was used to separate these aggregates by their hydrodynamic volume and multi-elemental detection by ICP HR MS was done to obtain the aggregates size profiles. The most important parameters and the evolution over time were studied. An AR and a VR were analyzed in stabilized and non-stabilized tetrahydrofuran (THF). Two long term kinetic studies of the aggregation state of the samples in these different solvents were done with several solutions prepared from D-254 to D-0 of the study, and analyzed the same week. An ICP HR MS instrument (ELEMENT XR, Thermo Scientific) was coupled to different sets of GPC columns at several flow rates. The time of analysis and high solvent consumption present significant barriers to GPC so APC was tested to obtain size profiles of undesirable

---

*Speaker

metal macromolecular aggregates in petroleum products, as it provides accurate and repeatable molecular weight information faster than GPC. Four VR samples were studied with two APC XT columns of 125 and 450 Å (4.6 x 150 mm, 2.5 μm). The APC system enabled different solvents to be used and tested for sample preparation and elution.

Multimodal profiles for V- and Ni-containing aggregates were obtained for both GPC and APC ICP HR MS, indicating the presence of different types of aggregates having different molecular weights. The APC IPC MS profiles obtained show V and Ni aggregates with bimodal distribution, while trimodal profiles were observed using GPC columns, although more than 6 times slower. This could mean that higher shear rate degradation occurs when using APC columns compared to GPC ones.

Significant differences were found depending on the solvent flow rate and the GPC columns used, which seem to have an influence on the size distribution of V, Ni and S aggregates, unlike the presence of a stabilizer in the solvent. These differences could be caused by a degradation phenomenon which converts High Molecular Weight aggregates into aggregates of lower molecular weight. In this case, this phenomenon needs to be avoided to study the native aggregation state of the aggregates in the sample. Moreover, an evolution of the size distribution was observed over time, with re-aggregation of V and Ni aggregates into higher molecular weight aggregates, mainly during the first month after the sample preparation, so samples must be freshly injected to study their native aggregation state. APC allowed the mapping of petroleum samples faster than GPC in order to establish the structure/properties relationship. Significant differences of the APC ICP MS profiles were found depending on the origin of the sample as well as the solvent used, which seem to have an influence on the aggregation state.

Analysis of pyrolysis oils by GCxGC-qTOF with online derivatization

Mette Kristensen*[1], Asger Hansen[2], Peter Christensen[1], Jan H. Christensen[1], and Sylvain Verdier†[2]

[1]University of Copenhagen – Department of Plant and Environmental Sciences, University of Copenhagen, Thorvaldsensvej 40, 1871 Frederiksberg, Denmark
[2]Haldor Topsoe A/S – Nymollevej 55, 2800 Kgs. Lyngby, Denmark

Abstract

During fast pyrolysis, pyrolysis oils are produced by fragmentation and depolymerization of large biomolecules, mainly lignin, cellulose and hemicellulose. The composition of pyrolysis oils depend on the feed and the pyrolysis conditions but can in general be put into five broad categories: hydroxyaldehydes, hydroxyketones, sugars and dehydrosugars, carboxylic acids and phenolic compounds. The large water content and the high fraction of oxygenated compounds, especially acids and sugars, give rise to complication in storage, transportation, use and in the refinery process. The analysis of these oxygenated compounds are therefore of high importance in the production of pyrolysis oils.
In this study, online derivatization with N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) was proved to be a useful method for the analysis of acids and sugars in pyrolysis oils. Online derivatization combined with comprehensive two dimensional gas chromatography (GCxGC) with accurate mass time-of-flight mass spectrometry (TOF-MS) was used to improve compound separation and sensitivity and for compound identification in five pyrolysis feeds.

Water and diethylether/dichloromethane extracts of five pyrolysis feeds were analysed and the distinct chemical composition of the feeds were related to differences in deactivation of the catalyst during production.

---

*Corresponding author: mkri@plen.ku.dk
†Speaker

PC-P36

Critical concentration for the aggregation of asphaltene solutions follow by Diffusional Spectroscopy

Juan Carlos Poveda-Jaramillo*[1], Lina Morantes , Mary Torres , and Daniel Molina

[1]Parque Tecnológico Guatiguara - Universidad Industrial de Santander (RMN - PTG - UIS) – Colombia

Abstract

Diffusional NMR spectroscopy is a powerful analytical tool to analysis translational motion of molecules in solution which are strongly affected by thermodynamic conditions. In this work, we report the analysis of critical concentrations to the formation of molecular aggregates of Colombian asphaltenes using DOSY 1H-spectroscopy. Samples from different heavy crude oils: Castilla, Rubiales, Chichimene, and Suria, were extracted using the ASTM 6560-12 standard method. To eliminate occluded resins into the samples it's were washed extensively with heptane. Diffusional behaviors of samples were analyzed as well the concentration of asphaltenes was increased progressively, resulting in the spectra new signals as a result of the aggregation processes. The effect of temperature was analyzed in the range from 298 K up to 353K.

To understand the aggregation processes and changes detected in the critical concentrations, we make an approach to the molecular structure of samples using the average molecular parameters, AMPs were calculated using data from different spectroscopic techniques as: 1H-13C-NMR, Raman and Infrared, MALDI mass spectrometry and elemental analysis. Very important to understand the aggregation processes by a π- π mechanism is the knowledge of molecular parameters, p.e. diameter of aromatic layers La, and the average length of the saturated aliphatic side-chains. The size of nano aggregates and clusters was calculated by using a calibration curve constructed with a set of more than ten standard compounds with molecular weights between 120 and 1200.

From our experiments, we observe that experimental conditions as concentration and temperature should be well controlled to obtain data with a high confidence. Also, we try to obtain a relationship using average molecular parameters and the concentration and temperature of samples.

Authors thanks to Vicerectoria de Investigaciones of the Universidad Industrial de Santander, Grant 1871.

---

*Speaker

THERMAL DEGRADATION OF CASTILLA AND MAYA ASPHALTENES ANALYZED BY X-RAY DIFFRACTION

Juan Carlos Poveda-Jaramillo*[1] and Keyla Ortiz

[1] Parque Tecnológico Guatiguara - Universidad Industrial de Santander (RMN - PTG - UIS) – Colombia

Abstract

Asphaltenes are the heaviest fraction of crude oils. Which contain poly-condensed aromatic compounds associated with heteroatoms and metals. The thermal decomposition of petroleum asphaltenes has received attention because at high temperatures, asphaltenes polymerize and cause plugging of the catalyst bed and the downstream lines and equipment. Furthemore, asphaltenes act as a coke precursor which in turn leads to catalyst deactivation. The aim of this work was to study the structural changes and possible transformations of the Castilla and Maya asphaltenes. Those were evaluated in range of temperature from 100 a 550 ◦C by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and X-ray diffraction (DRX).

TGA analysis showed three stages, the first corresponding to temperatures of 40-400 ◦C when presents a weight loss of around 5%, this could be attributed to the loss of volatile fractions as chain hydrocarbons. The second stage corresponds to temperatures between 400-500 ◦C with a drastic loss of mass of 45% and 50% for Castilla and Maya, respectively. This thermal decomposition can be set down to the conversion of asphaltenes into coke. The third stage corresponds to temperatures between 500-700 ◦C where a mass loss of about 6% is observed. On the other hand, DRX allowed to calculate the crystal parameters of the asphaltenic aggregates, such as the average height of the stack of aromatic sheets perpendicular to the plane of the sheet (Lc), aromaticity factor (fa) and the number of aromatic sheets in a stacked cluster (M). For a temperature range 100-400 ◦C, when the temperature increases, there is a decrease in Lc from 16,64 to 13,91 ◦A and a decrease in M going from 5,56 to 4,67 for Castilla asphaltenes. Also, the Maya asphaltenes present the same behavior of the parameters evaluated where Lc decreases from 19,77 to 14,14 A ◦ and M from 4,54 to 4,02. The structural modification could be attributed to the conversion of asphaltenes to coke and the cleavage of C-S and C-C bonds occurring in the 350-410 ◦ C range. For temperatures higher than 400 ◦C an increase of the values of Lc and M is observed, this behavior could be attributed to the stabilization by resonance structures of the aromatic rings and these, in turn, participate in the abstraction of hydrogens and structural rearrangements. In addition, as the temperature increased, the asphaltenes aromaticity factor also increased from 0,65 to 0,80 for Castilla and from 0,43 to 0,83 for Maya asphaltenes, which is due to the loss of peripheral aliphatic chains. The results show that around 400 ◦ C a high thermal degradation and a structural reorganization in the study asphaltenes occurs.

Authors thanks to Vicerectoria de Investigaciones of the Universidad Industrial de Santander.

---

*Speaker

Aggrgation and Asphaltene Adsorption in presence of Nanoparticles

Jimmy Castillo*[1], Neidy Hernandez , Vicmary Vargas , and Manuel Bernadas

[1]Universidad Central de Venezuela – Ciudad Universitaria, Los Chaguaramos Caracas, Venezuela.
Código Postal: 1050, Venezuela

Abstract

The use of nanoparticles in the crude oil industry has been increased in the last years. The principal use of the nanoparticles is focused in the adsorption of asphaltenes in order to deasphalt for enhance oil recovering. Other applications are in catalysis or viscosity reduction. The self-association of the asphaltenes in solution is a well-known phenomenon, the asphaltenes tend tor aggregates in solution but few works have been done to understand the thermodynamic equilibrium of the asphaltene self-association and simultaneous adsorption onto nanoparticles.The superficial area of the nanoparticle, area and the active sites number is of great importance in the adsorption process, in the case of asphaltene the size of the sorbent particularly play an important role in the adsorption process due to the size of the smallest asphaltene unity. The reported size for the asphaltene nanoaggregate is around 3 nm, with this size the interaction with nanoparticles of 30 to 90 nm is considerably different to the interaction of these nano-aggregates with the bulk sorbent. The possibility to adsorb multilayers onto nanoparticles diminish strongly due to the relative size effect. In the present work, we study the asphaltene aggregation and adsorption onto nanoparticles. Two series of experiments were conducted. The first is induced the aggregation o asphaltenes in presence of nanoparticles as a sorbent.In a second experiment the aggregation is induced and after the aggregation, the solutions are kept in contact with aggregated asphaltenes. The results showed that nanoparticles adsorb preferably the smallest aggregates diminishing the asphaltene aggregation. Other phenomena observed during asphaltenes adsorption in macroscopic raw material as multilayer or aggregated adsorption were not observed using nanoparticles.

---

*Speaker

sciencesconf.org:petrophase2017:152488

PC-P39

High Resolution Accurate Mass GC/Q-TOF with Low Energy Electron Ionization for Identification of Sulfur-containing Compounds

Nathan Eno*[1], Sofia Nieto[1], Laurent Pascaud[2], Sabrina Marceau[3], Benoit Paupy[3], and Pierre Giusti[3]

[1]Agilent Technologies, Inc. – 5301 Stevens Creek Blvd. Santa Clara, CA 95051, United States
[2]Agilent Technologies France SAS – Agilent Technologies France SAS – PARC TECHNOPOLIS – BATIMENT OLYMPE ZA COURTABOEUF 3 AVENUE DU CANADA 91940 LES ULIS, France
[3]TOTAL RAFFINAGE CHIMIE (TRTG) – Total Raffinage Chimie – Département Analyse BP 27 - 76700 Harfleur, France

Abstract

Determining the presence and amount of sulfur-containing compounds in petrochemical feedstock is a primary concern for refinery operations due to the potential negative consequences these compounds can have on downstream equipment. Several analytical techniques exist to selectively measure these compounds, but such techniques generally do not provide further qualitative information that may be desirable in determining chemical formulae or structures of the sulfur containing compounds for investigative purposes. In this work, qualitative evaluation by GC/MS of pre- and post- hydrotreated gas oil samples from a diesel hydroprocessing unit was performed with an Agilent 7890B GC system coupled to a novel, high resolution accurate mass 7250 GC/Q-TOF equipped with a low energy capable EI source.

Individual analytical fingerprints for components within the gas oil samples were obtained using the SureMass peak detection algorithm of Agilent MassHunter Unknowns Analysis. Differential analysis between the samples was performed with Agilent Mass Profiler Professional (MPP) software. Compound identification of the statistically relevant differential compounds was performed with Agilent ID Browser software.

Many sulfur containing compounds were identified in the pre-hydrotreatment sample using library matching against the NIST 14 GC/MS library. Compounds with no library hit or inconclusive match against the NIST 14 GC/MS library were further evaluated using low energy EI spectra acquired between 9 and 15 eV. Low energy EI spectra were used to create molecular ion candidates for the unidentified sulfur containing compounds. Subsequent analysis by quadrupole isolation and CID fragmentation of the candidate molecular ions to create high resolution accurate mass product ion spectra narrowed the list of candidate molecular ions to propose chemical formulae for the compounds. Molecular Structure Correlator (MSC) was used to further propose chemical structures to the now putatively identified sulfur containing compounds.

---

*Speaker

Selective extraction of naphtenic acid from crude oil using magnetic nanoparticles

Marcin Sawczuk*[1,2], Cristian Blanco Tirado†[1], and Marianny Combariza Montanez[1]

[1]Universidad Industrial de Santander [Bucaramanga] (UIS) – Cra 27 Calle 9 Ciudad Universitaria Bucaramanga-Santander-Colombia, Colombia
[2]Technical University of Denmark [Lyngby] – Anker Engelunds Vej 1 Building 101A 2800 Kgs. Lyngby, Denmark

Abstract

Functionalized magnetic nanoparticles (MNPs) are possible effective means for removing naphthenic acid (NA) from crude oil. In this work, magnetite nanoparticles functionalized with amine-containing ligands were used to selectively extract NA from model oil and from the heavy crude solution.
Nanoparticles were synthesized in the sonochemical process, by coprecipitation from the Fe2+ and Fe3+ solution in the basic pH. Further on, they were capped in the oleic acid (OA) to ensure proper dispersion of the material and functionalized with (3-Aminopropyl)triethoxysilane (primary amine) and N-[3-(Trimethoxysilyl)propyl]ethylenediamine (primary-secondary diamine). Two ligands varying in number of amine groups were used to assess the influence of the active sites concentration on the NA extraction. Non-functionalized nanoparticles were used as a reference.

Extraction procedure included dispersion of 1000 mg of nanoparticles in 100 ml of 4000 mg/l NA solution in heptane or 5% (vol.) solution of a South American heavy crude. Such suspension was then sampled over time to show decrease of the free NA concentration due to the acid-binding action of the MNPs. Subsequently, nanoparticles were removed from the NA solution using a permanent magnet and the acids were desorbed in DCM-MeOH-NH3(aq) (10:10:1 vol.). MNPs were then recycled for further removal of NA from the initial solution. Solutions were sampled after each extraction cycle to assess the effectiveness of the procedure.

Nanomaterials were characterized for their specific surface area, particle size, crystalline phases and thermal decomposition pattern. Moreover, synthesised particles were subject to FT-IR ATR to show effectiveness of the functionalization and titrated with HCl to ascertain concentration of the amine groups on the material surface. Liquid FT-IR using 0.1 mm NaCl cell was a principal technique for NA quantification. Readings for the model oil were calibrated using commercial NA mixture, whilst readings for the crude solutions give only relative values, taking initial concentration of acids as a reference.

Nanoparticles showed to be effective means for NA removal. MNPs functionalized with diamine turned out to be the most efficient type. Capacity of the acid extraction for this material reached up to 105 mg/g for the commercial NA mixture. Moreover, these results

---

*Corresponding author: m.sawczuk@yahoo.com
†Speaker

were repeatable when the nanomaterial was reused, proving that the MNPs are suitable for the reuse. Trials with the heavy crude solution showed that 4 extraction cycles are sufficient to lower the NA concentration to the quantification limit of the analytical method.

Measurements of the adsorption kinetics showed that, under proper agitation and initial NA concentration of 4000 mg/l, 3 minutes are sufficient for saturating 90% of the total NA binding capacity of the material. In such conditions, 30 minutes of agitation at 1500 RPM leads to complete stabilization of the NA levels in the liquid phase, so that they do not change significantly even after 24 hours.

ORALS
Emulsions

Crude oil emulsions and behaviour of asphaltenes at oil-water interfaces

Dominique Langevin*[1] and Jean-François Argillier[2]

[1]Laboratoire de Physique des Solides (LPS) – CNRS : UMR8502, Université Paris XI - Paris Sud – Bat. 510 91405 Orsay cedex, France
[2]Institut Français du Pétrole Energies Nouvelles – IFPEN – France

Abstract

Crude oil emulsions are frequently created during oil recovery and processing. The stability of these emulsions is closely related to the behavior of asphaltenes at the interface between oil and water. The presentation will focus on this behavior and on its caracterisation using interfacial tension, interfacial rheology and interfacial thickness measurements.The role of water pH and added surfactants will be discussed and the data correlated with emulsion stability. The question of adsorption reversibility, the role of asphaltene aggregation and the influence of asphaltene separation methods will be addressed.

---

*Speaker

sciencesconf.org:petrophase2017:153934

Demulsifier structure-performance relationship in water-in-oil systems

Craig Davies*[1,2] and Julian Eastoe[2]

[1]Croda Europe Ltd. – Cowick Hall, Snaith, Goole, East Yorkshire, DN14 9AA, United Kingdom
[2]University of Bristol – School of Chemistry, Cantock's Close, Bristol, BS8 1TS, United Kingdom

Abstract

Crude oil is found in reservoirs beneath the Earth's surface in association with brine, which is inevitably coproduced with the oil. Indigenous surfactants present in crude oils (i.e. asphaltenes) adsorb at the oil-water interface forming viscoelastic films thereby stabilising the water-in-crude oil (w/o) emulsions. Chemical demulsification has long been established as the most effective method of breaking w/o emulsions. This chemical demulsification process is thought to involve decreasing the interfacial tension gradient and interfacial viscosity, which in turn increases the rate and efficiency of flocculation and coalescence. The hydrodynamic interactions between droplets depend on capillary pressure (dynamic interfacial tension) and interfacial rheological properties (interfacial elasticity). The aim of this research is to understand how different demulsifiers affect the structural behaviour and destabilisation of model w/o microemulsion systems.
Interfacial studies of optically dense w/o emulsions are experimentally challenging. Therefore, transparent w/o microemulsion systems have been developed as proxies for practical crude oil emulsions. The optimisation of microemulsion systems to study the demulsification of w/o emulsions has previously shown good correlation to macroemulsion systems. Using these w/o microemulsions, a number of different amphiphilic poly(propyleneoxide)-poly(ethyleneoxide) (PPO-PEO) block copolymer demulsifiers have been evaluated. The first stage was to determine the phase behaviour and for a family of PPO-PEO polymers containing a common level of PEO (10 wt.%) a structure-performance relationship was seen which induced destabilisation of the microemulsions. Therefore, non-amphiphilic homo-polymers (pure PEO or PPO) were also studied but showed no effect on microemulsion phase stability. This suggests that only amphiphilic additives adsorb at the oil-water interface and exhibit a demulsification effect.

Dynamic light scattering (DLS) studies have shown the addition of demulsifying amphiphilic polymers increased the microemulsion droplet size. In contrast, adding non-amphiphilic homo-polymers had only minor effects on droplet size. Hence, it appears that only the amphiphilic PPO-PEO demulsifiers significantly affect droplet structure and/or interactions, which leads to destabilisation.
Small-angle neutron scattering (SANS) studies have been conducted using contrast matching in order to determine how the polymers organise in microemulsions. This technique made it possible to study the interfacial films in isolation and follow changes as demulsifiers of different chemical structures were added. Microemulsions containing polymers were seen to scatter the neutrons differently compared to the blank microemulsion indicating different

---

*Speaker

interactions within the system. SANS studies will also help to determine if the polymers form micelles or aggregate in the bulk solvent phases. Putting together the SANS, DLS and phase behaviour results will help to elucidate the mode of action and operation of these demulsifiers.

Advantage of using Multiple light scattering technique for the new safe demulsifier efficiency analysis for oil production

Christelle Tisserand*[1], Christine Dalmazzone[2], A Mouret[2], C Noïk[2], and Gérard Meunier[3]

[1]Formulaction – Formulaction – 3-5 Rue Paule Raymondis, 31200 Toulouse, France
[2]IFP Energies nouvelles – IFP Energies Nouvelles – 1 et 4 Avenue de Bois-Préau 92852 Rueil-Malmaison, France
[3]Formulaction – formul – 3-5 Rue Paule Raymondis 31200 Toulouse, France

Abstract

The formation of stable water-in-crude-oil emulsions during oil production poses significant challenges during oil/water separation in surface production facilities. These emulsions can be very stable because of the presence of rigid films formed by polar compounds, such as asphaltenes and resins, and other fine solids.
Effective separation of crude oil and water is an essential operation in order to ensure the quality of crude oil but also of separated water phase at the lowest cost. Chemical demulsification appears as an essential step in crude oil dehydration. Demulsifiers are generally polymeric surfactants (copolymers ethylene oxide, propylene oxide, polymeric chain of EO/PO of alcohols, ethoxylated phenols, nonylphenols, alcohols, amines, resins, sulphonic acid salts...). Commercial demulsifiers are formulated in solvents like short-chain alcohols, aromatics or heavy aromatic naphtha and can contain a mixture of several active matters. Most of these products are not safe from an environmental point of view. The increase of environmental constraints makes therefore necessary the development of safer formulations in order to replace toxic chemicals like aromatics or nonylphenols.

Several methods are used to evaluate the efficiency of demulsifiers by measuring the separated phases properties with bottle tests, microscopy, rheology, differential scanning calorimetry... This study will show advantage of using Multiple light scattering technique which consists in sending photons (NIR light source, 880nm) into the sample. These photons, after being scattered many times by the particles (or droplets) in the dispersion emerge from the sample and are detected by the 2 detectors placed in backscattering and transmission. These light intensities are measured versus the sample height every 40 microns. By repeating these measurement versus aging of the sample, the operator can detect **particle size** change (coalescence, flocculation) and **phase separation** (sedimentation, creaming). The optical device based on this MLS technique (Turbiscan) enables to measure and elucidate instability phenomena in liquid colloidal dispersions from 0 to 95% in volume fraction, with particles from 10 nm to 1 mm, up to 200 times quicker than the naked eye.
We will first present MLS theory and principle of measurement of Turbiscan® device. Then we will show application examples extracted from different studies in IFPEN laboratory on

---

*Speaker

the evaluation of demulsifiers efficiency. The results will show that compared to classical bootle tests, MLS enables to determine quickly and objectively all the demulsification process from flocculation/coalescence to phase separation. The technique permits to quantify the separation kinetics, the amount of extracted water and the clarity of the separated water.

A lattice gas model for asphaltenes adsorption at water/oil interface

Vincent Pauchard*[1], Shaghayegh Darjani[1], and Nelya Akhmetkhanova[1]

[1]Energy Institute and Chemical Engineering Department City College of New York, New York, USA – United States

Abstract

A recent set of articles proposed that asphaltenes adsorbed at the water/oil interface would behave as surfactants and hence would follow an equation of state [1-2]. This equation of state (relating surface pressure to surface coverage) was approximated by a Langmuir model yielding an estimate of molecular interfacial area around 0.3 nm2. Such a low value could correspond to the area of an average asphaltenes aromatic core oriented parallel to the water surface, in line with Sum Frequency Generation (SFG) spectroscopy observations [3] and Density- Functional based Tight-Binding (DFTB) calculations [4]. The caveat of this approach is that the Langmuir model does not predict any transition to a solid interface at high coverage as observed experimentally by shear rheology [5]. On the other hand, the use of a surfactant molecular area larger than the area of an adsorption site (a water molecule, in this case) contradicts the localized adsorption assumption of the Langmuir model. These discrepancies can be resolved using ideal adsorption models accounting for the relative size of adsorbate and adsorption site, i.e. Lattice Gas models. It is here reported the comparison between asphaltenes experimental data and a Lattice Gas model of hexagonal molecules covering 3 adsorption sites on a triangular lattice. The choice of this model was dictated by the original estimate of asphaltenes molecular area (i.e. 3 to 4 times the area of a water molecule) and the geometry of their aromatic core (peri-condensed). With respect to dilatational rheology, the Lattice Gas model very well captures the relationship between high frequency modulus and surface pressure, which is also a trace of the equation of state. The same applies to the relationship between surface pressure and area of droplet suddenly contracted or expanded. The Lattice Gas model also predicts a transition from a fully fluid to a fully solid interface between 65 and 85% relative coverage. The corresponding surface pressure values almost exactly match the experimental values at which a contracted droplet loses it Laplacian shape. Finally the Lattice Gas model predicts some dynamic frustration within the dense interfacial layers: if coverage increases fast compared to interfacial diffusion, either during spontaneous adsorption or during interfacial area reduction, the interfacial layer would enter into a metastable glass state that would slowly relax towards a crystalline state with time. Such a scenario is perfectly consistent with the observation of Soft Glass rheology features during interfacial shear experiments on asphaltenes laden surfaces [6]. It is also consistent with the observation of birefringence within asphaltenes laden interfaces upon aging of a contracted droplet [7].

J. P. Rane et al, Langmuir (2013)

J. P. Rane et al, Energy and Fuels (2015)

---

*Speaker

A. Ballard et al, Langmuir (2011)

A. Simon et al, *Petrophase 2016*.

Y. Fan et al, *Colloids and Surfaces A* (2010)

J. R. Samaniuk et al, *Dispersion Science and Technology* (2015)

R. Varadaraj et al, *Energy & Fuels* (2012).

POSTERS
Emulsions

Operational Cost-saving Effort in Industry Downturn by Managing Asphaltene-stabilized Emulsion Issue in Onshore Field

Hideharu Yonebayashi*[1], Takaaki Uetani[1], Naoto Furuichi[1], Hirokazu Yorozu[1], Kazuyo Sasaya[1], Takehiro Shibuya[1], and Narihito Kiminami[1]

[1]INPEX Corporation – Japan

Abstract

To be survived in the recent industry downturn, all cost impacted efforts have been applied into operations and production. This paper describes a laboratory case study and practical field application for minimizing operational cost and maximizing oil production in a domestic onshore oil field experienced severe asphaltene-stabilized emulsion problems after switching production scheme from natural depletion to artificial lift by installing jet pump. The best demulsifier designed for natural depletion scheme at the commencement of production was no longer effective for jet pumping operational scheme. Accordingly, the daily oil production rate was forced to drop from the target rate (100%) to 75% for satisfying export oil specification (i.e. sufficient level of water content in the export oil). Because of the tight emulsion generated with less than 10μm average of water droplet diameter, the export oil was lowered its quality from water specification point of view. The main objective of the study was to urgently achieve the target daily oil production rate with satisfactory export specification by mitigating the emulsion problems.

Two approaches were taken: First, the demulsifier injection scheme was revised by moving the injection point from the downstream to the upstream of the well. However, no clear improvement was observed. Second, it was decided to newly find the best alternative demulsifier through an extensive laboratory test. A number of chemical products were gathered from various suppliers and all were tested for their efficiency to break the emulsion. All screening works were performed in in-house laboratory because a fair comparison was needed with the same testing procedure and experimental conditions. If such screening tests were conducted in each chemical supplier's laboratories, all suppliers might propose their best chemicals, anyhow showing good results by means of their own various procedures. Some chemicals showing good results might have unpractical volume of additives, and chemical costs were concerned to be higher. Such situations that were just convenient for chemical suppliers should be avoided.

The laboratory test showed that the current demulsifier (DM1), which had been dosed since the production start-up, made the emulsion problem even worse. DM1 was selected as the best chemical and worked well during the natural depletion scheme. However, we found out that it was not effective for the artificial lift operation. Eventually, DM1 was replaced with the new best demulsifier (DM2) because of the highest score in the laboratory test, as a result, the emulsion problem could be solved. The well production rate was successfully

---

*Speaker

sciencesconf.org:petrophase2017:127809

increased from the current control value to the target one, while maintaining the quality of the export oil specification.

A lesson learned from this successful field case study was that the use of a demulsifier should be reviewed as necessary: for example, when its effectiveness was lost and when the operational condition/scheme was changed. The best demulsifer selected for a particular production condition may not be best anymore, and possibly deteriorate the quality of the oil, when the production condition changes, as seen in our field.

STUDY OF THE REOLOGICAL BEHAVIOR OF A MICROEMULSION BASED DRILLING FLUID

Fabiola Curbelo*†[1], Roxana Sousa[2], Julio Cézar Freitas*‡[3], Renata Braga*[4], Glauco Braga[5], and Alfredo Ismael Curbelo Garnica*§[1]

[1]Federal University of Paraiba, Departament of Chemical Engineering (UFPB) – Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil

[2]Federal University of Paraiba, Departament of Chemical Engineering (UFPB) (UFPB) – Cidade Universitária, João Pessoa, Paraiba, 58051-900, Brazil

[3]Federal University of Rio Grande do Norte, Chemical Institute (UFRN) – Campus Universitário, Natal, Rio Grande do Norte, 59078-970, Brazil

[4]Federal Universityof Rio Grande do Norte, Agricultural School of Jundiaí (UFRN) – Campus Universitário, Macaíba, Rio Grande do Norte, 59280-000, Brazil

[5]Federal University of Paraiba, Department of Chemical Engineering (UFPB) – Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil

Abstract

During drilling wells, rocks are drilled by rotation and weight action applied to the drill bit. The rock fragments are continuously removed through a drilling mud. Looking for a sustainable and economic perspective for the petroleum and natural gas industry, the reduction of environmental effects is necessary, as well as cost reductions, directly related to drilling fluids formulation. Microemulsion systems are widely applied in industry because they are spontaneous, thermodynamically stable and easily prepared. Oil-based drilling fluids are often costly and fairly toxic, and water-based drilling fluids can cause some problems in drilling in reservoirs with water-sensitive rocks. Oil in water microemulsion (O/W) or water in oil micromulsion (W/O) based drilling fluids can replace these two types presented because they have high lubricity, low water, stability, low toxicity, low cost, higher density than the oil based fluids, allows addition of salt, formation of a smooth and thin filter cake and hinders the gas influx. This work presents laboratory developing of microemulsion based drilling fluid possibly applicable to petroleum drilling wells. For this, a microemulsioned system composed of three phases: an aqueous phase (water and glycerin), an oily phase (vegetable oil) and a non-ionic and biodegradable surfactant was used. Firstly, a ternary diagram was developed, and, in the microemulsion region, the best possible composition for the development of microemulsion based drilling fluid was chose. Posteriorly, the additivation of microemulsion was realized with densifying agents, viscosifiers, filtration controllers and salt, so that the microemulsion based drilling fluid obtained properties of a drilling fluid. Finally, physical and chemical properties of the obtained microemulsion based drilling fluid were studied through rheological and filtration tests, chemical tests, aging, degradation and

---

*Speaker

†Corresponding author: fabioladias@yahoo.com

‡Corresponding author: juliofreitasj@hotmail.com

§Corresponding author: alfredocurbelo@yahoo.com lubricity. From the results obtained, were verified that the (O/W) type microemulsion based drilling fluid presented: adequate viscosity; gel strength; low fluid loss, only 4.5 mL; low solids content, 6%; besides being low cost, stable in a large range of salinity conditions; desirable lubricity characteristics of 0.07638, reducing friction and increasing equipment life and reducing working temperature of developed fluid; and high concentration of water is supported.Based on the key performance indicators, it was observed that the microemulsion system added stability to developed drilling fluid, thereby during circulation stops, the microemulsion based drilling fluids can keep the cuttings (broken pieces of rock) in suspension for longer. In addition, the use of surfactants can reduce torque (moment of force) and increase the drill bit effective power, and glycerin presents itself as a bactericidal and densifying agent. The high viscosity of O/A microemulsion based drilling fluids has particular utility in reservoirs at high temperatures, where the microemulsion remains stable. The fluid presented a pseudoplastic behavior and it was shown that the Herschel-Bulkley rheological model described a developed drilling fluid.

Interfacial properties of asphaltenes in EOR and in oil separation

Susanna Lauren*[1] and Jyrki Korpela[1]

[1]Biolin Scientific – Finland

Abstract

Understanding oil-water interface is crucial in different stages of oil recovery and separation. In oil recovery stage, different enhanced oil recovery methods such as CO2 flooding are used to increase the recovery rates. After CO2 is being injected into an oil reservoir, it contacts and interacts with the reservoir oil and thus changes both reservoir equilibrium conditions as well as fluid properties. This may lead to precipitation and deposition of the heavy organic solids, primarily asphaltenes. These phenomena result in wettability alteration and permeability reductions of the reservoir rock which consequently leads to a decrease in oil recovery. As oil is recovered, complex oil-water emulsions are formed. Adsorbed asphaltenes at oil-water interface tend to increase the stability of these emulsions. Stable oil-water emulsions are generally unwanted as they increase pumping and transportation expenses and corrode pipes, pumps and distillation columns.

Wettability and interfacial tension measurements between oil, fluid and rock can offer useful information for enhanced oil recovery optimization. Optical wettability analysis has been widely utilized to study the oil-water interface [1]. Interfacial tension and contact angle measurements offer a possibility to do measurements also at high pressures and temperatures mimicking the reservoir conditions. We have previously presented the effect of surfactants on interfacial tension between CO2 and brine [2].

Another widely utilized approach is to study the interfacial rheology at the oil-water interface. The elasticity at the interface is known to correlate with the stability of the oil-water emulsion. Interfacial rheology of an adsorbed asphaltene layer has been previously studied by the pulsating drop method. [3]. An alternative method which allows interfacial shear rheology (ISR) characterization as a function of asphaltene packing density is based on a floating needle rheometry [4]. This method has already been utilized to study several polymers, biological and nanoparticle systems but its use in oil-water emulsion studies has not yet been recorded. Here we present the ISR measurement at crude oil-water interface. The data shows clear increase of interfacial shear elasticity as a function of time. This indicates the evaporation of the light crude oil components stabilizing the interfacial layer further.

The above-mentioned methods provide valuable information needed for in-depth understanding of the interfacial properties at different stages of oil recovery and separation. Together they are able to provide a large view over the effect of asphaltenes at oil-water interfaces.

Yu, G. et.al., "Interfacial behavior and water solubility of various asphaltenes at high temperature", Colloids and Surfaces A: Physicochemical and Engineering Aspects 441 (2014)

---

*Speaker

378.

Lauren, S. and Ohlsson, G., "Effect of surfactants on interfacial tension between CO2 and brine – application to enhanced oil recovery", Petrophase 2015, Riviera Maya, MX.

Rane, J.P. et. al., "Interfacial rheology of asphaltenes at oil – water interfaces and interpretation of the equation of state", Langmuir 29 (2013) 4750.

Bhamla, M.S. et. el.,"Influence of interfacial rheology on drainage from curved surfaces", Soft Matter 10 (2014), 6917.

Alternative techniques for the destabilization of W/O emulsions with electric field

Maria Rodriguez*†[1], José Sorrentino[1], Luz Pita[1], and Carlos Carrillo[1]

[1]Universidad Central de Venezuela. Facultad de Ingeniería. Escuela de Ingeniería Química. Laboratorio de Separaciones Mecánicas (UCV) – Ciudad Universitaria, Los Chaguaramos Caracas, Venezuela. Código Postal: 1050, Venezuela

Abstract

In the oil industry, W/O emulsions tend to generate problems such as corrosion in lines and equipment, as well as the increase in energy consumption in the transport of emulsified fluids. This is why the process of separation of phases (water and hydrocarbon) is fundamental after the process of extraction of the oil from the production well. To this end, the study on the destabilization of the W/O emulsions is proposed, in view of the application of different techniques based on the application of electric field, without the incorporation of dehydrating chemistry. The application of electric field as accelerator of coalescence in the dehydration of crude, is a common practice in the surface installations, when using electrostatic separators. The present study considers as cases of analysis: 1) only application of electric field, 2) electric field combined with coalescer media in fixed bed, 3) electric field combined with coalescer media in suspension. For this, the characterization of the W/O emulsion was carried out according to density, viscosity, water content and accumulated drop size distribution. In the electric field treatments the application of 400V was maintained in a cell of flat electrodes of copper with a volume of 4cm3, at 25°C and atmospheric pressure, for an average time of 13min. As a coalescer media, 4mm glass rings were used. The cases combining the electric field with coalescer media consider: a) a fixed bed of glass rings between the electrodes of the cell and b) the application of electric field to a suspension (emulsion + glass rings at a concentration of 2% in volume). The quantification of the destabilization reached was done through the destabilization factor (FD), defined as the amount of water in drops of a certain reference size present in the sample after the treatment was applied, between the amount of water in drops Same size present in the sample before the treatment was applied. The FD is determined based on the analysis provided by the Image Pro Plus software, obtained by the Nikon ME-600 optical microscope. The results show that the combination of the electric field with a hydrophilic coalescing medium potentiates the destabilization of the W/O emulsion, the use of the medium in the form of suspension being more efficient, since it increases the destabilization achieved by applying the electric field . In this work it is evident that phase separation is possible using these techniques, without the addition of dehydrating chemistry.

---

*Speaker

†Corresponding author: rodriguezreyesmar@gmail.com

Development of chemicals to improve the flocculation in crude oil desemulsification

Rafael Ungarato*[1], Fabiola Rezende[1], Paulo Filho[1], and Guilherme Fonseca[1]

[1]Oxiteno S.A. – Brazil

Abstract

Development of new molecules based on amine derivatives in order to obtain a product able to improve the flocculation in the demulsified process of water in oil emulsions. Increasing the flocculation process is critical to reducing the amount of water in the treated oils. Some molecules are capable of acting in order to promote the very rapid breaking of the emulsions, but without the desired water limit for the treated oil. In this sense, the development of molecules capable of increasing the flocculation of water droplets is essential for drier oils.
It was performed a DOE to obtain different physical and chemical properties for amine derivatives, such as RSN, surface tension, and others. All the products were evaluated regarding their capacity to reduce the water content in crude oil after the demulsifying process. For this, it was used bottle test followed by assessments of the quality of the separated water and the water-oil interface. These data were also correlated with physical chemical properties. After the first trial, the selected molecules have their performance evaluated for different crude oils at different temperatures and concentrations. In this case it was also evaluated the desalination of these products.

Combining the techniques described, it was possible to identify the best product for different types of oil in different conditions (temperature and dosage). It was possible to observe correlation between physical chemical properties (RSN, surface tension, IFT) and the results of performance (bottle test). The results obtained from the DOE give information to choose the best product to be used in relation to the type of crude oil (ie. API grade, BSW). The desalination of the crude oil was also evaluated and it was possible to affirm that the use of these molecules has impacts in this process, improving the crude quality after the demulsification process. These results led to the development of a series of products capable of promoting flocculation efficient enough for different oils, giving them very low values of residual water in the treated oils.

---

*Speaker

Study of paraffin/water emulsion by dynamic and static light scattering

Vladimir Kuryakov*[1] and Pier Giorgio De Sanctis Lucentini[2]

[1]Oil and Gas Research Institute of RAS (OGRI RAS) – Russia, 119333, Moscow, Gubkina Str. 3, IPNG (OGRI RAS), Russia
[2]Gubkin Russian State University of Oil and Gas (National Research University) – 119991, Moscow, Leninskii prospect 65, Russia

Abstract

By means of ultrasonic dispersion the emulsions of various pure paraffin (C19-C28), some of their mixtures and sample of paraffin mixture from crude oil were prepared in water with and without the use of surfactants. The sizes of paraffin emulsions function of the power of the ultrasonic dispersion and the type of surfactant were measured by means of dynamic light scattering (DLS) technique. The zeta potential of emulsion droplets were measured and the stability of the emulsions in time was experimentally analyzed. The emulsions properties, the crystallization and the melting temperatures of the paraffins in the emulsions were determined with a good accuracy from the DLS and the intensity of scattered light measurements at heating and cooling. For the pure paraffins it has been observed a good agreement with the literature data. The melting and crystallization phase transitions in the emulsions are accompanied with bright imprints on the temperature dependence of the scattered light intensity associated with a change in the refractive index of paraffin. The crystallization and the melting of paraffins in the DLS-measured temperature dependences of the emulsions size are connected with a change in the average size of the emulsion due to the difference of the paraffin densities between the liquid and the solid state. DLS and SLS are powerful experimental methods for studying phase transitions in emulsions, allowing to investigate the influence of the various factors on the resulting temperature of the phase transitions (factors as the size of the emulsion, the additives in the dispersion and in the dispersed media...). The study was supported by the Russian Foundation for Basic Research, Grant no. 16-03-00895-a

---

*Speaker

Synthesis and evaluation of gallic acid derivatives in heavy oil-water emulsions

Ariana Margarita Vazquez Almaguer*†[1], Nancy Diaz Zavala*‡[1], Nohra Gallardo Rivas*§[1], Jose Melo Banda¶[1], and Jose Dominguez[2]

[1]Instituto Tecnologico de Ciudad Madero (ITCM) – Av. 1o. de Mayo esq. Sor Juana Inés de la Cruz s/n Col. Los Mangos C.P.89440 Cd. Madero Tamaulipas,, Mexico

[2]Instituto Mexicano del Petróleo (IMP) – Eje Central Lázaro Cárdenas Norte 152, San Bartolo Atepehuacan, Ciudad de México. C.P. 07730, Mexico

Abstract

The presence of heavy oil in the fields of Mexico represents a great technical and scientific challenge. The decay of national light crude production demands to design and use new technology in order to improve its recovery; therefore, the use of chemical agents that are able neutralize the binding effect of asphaltenes, seems to be an important research area. These chemicals should be amphiphilic so that they can interact with both oil and water. For example, organic molecules synthetized from gallic acid can be applied in emulsion stabilization due to the dipolar effect induced by the presence of heteroatoms, besides their appropriate molecular structure that combines both chemical affinities (hydrophilic and hydrophobic).
In this paper, it is reported the synthesis and evaluation of the emulsion-stability effect of two molecules derived from gallic acid, 3,4,5-tributoxy benzoic acid (AG-4) and 3,4,5-tributoxy ethyl gallate (EG-4). They were characterized by means of gas chromatography coupled to mass spectrometry (GC-Mass) by Perkin Elmer, Fourier transform infrared spectroscopy (FTIR) Spectrum One Perkin Elmer using the Attenuated Total Reflectance accessory (ATR), and Ultraviolet-Visible Spectrophotometer, model GBC Cintral 303 (UV-vis) which corroborated the desired chemical structure of the molecules.

The affinity of these molecules with oil and water congenital emulsions was evaluated using an ultrasonic sonifier, Hielscher brand, Up200Ht model, as homogenizer. Samples of 100 ml of congenital water-heavy crude emulsions (15:85) were prepared, varying the amount of stabilizer added: 10 μl and 20 μl of AG-4 or 8.5 mg and 17 mg of EG-4. Both tests included a reference emulsion without stabilizer.
EG-4 molecule achieved the best results because it was able to keep and stabilize 50% of the congenital water volume, in contrast to the 40% got by AG-4. The analysis of Scanning Electron Microscopy with Energy Dispersive microanalysis (SEM-EDS) model JSM-6390LV, JEOL and X ray microanalyzer of X-ray incax-sight, OXFORD INSTRUMENTS, showed fibers in the form of dendrites.

---

*Speaker

†Corresponding author: ariana_vazquez@hotmail.com

‡Corresponding author: npatdiaz@hotmail.com

§Corresponding author: nohvigari@itcm.edu.mx

¶Corresponding author: melobanda@yahoo.com.mx

Microwave: deshydratation and desalting of crude oil heavy

Ariana Margarita Vazquez Almaguer*†[1] and Arturo Lopez Marure*‡[1]

[1]Centro de Investigacion en Ciencia Aplicada Tecnologia Avanzada del Instituto Politecnico Nacional (CICATA-Altamira IPN) – Carretera Tampico-Puerto Industrial Altamira Km 14.5, 89600 Altamira, Tamps., Mexico

Abstract

Microwave irradiation is an alternative demulsification process of water-oil (w / o) and oil-water (o / w) emulsions. A heating of materials at a microwave frequency depends of the frequency of the electromagnetic wave and the dielectric properties of materials. In this way, a precise knowledge of the rheological properties of water-oil Maya-salts system is needed to understand the behavior under the influence of a electromagnetic field.
The objective of this research is to optimize the rheological parameters of the water-oil Maya-salts that contribute to a reduction of energy consumption in crude oil dehydration and desalting using microwave radiation. For this purpose, were selected sampling points in the circuit extraction Tamaulipas Field Constituciones and Cacalilao, in the area of Altamira of PEMEX Exploration and Production. Protocols for preparation of prototype emulsions were determined in laboratory, varying water concentrations (50%, 20%, 10%) and different types of crude oil (crude Altamira 14.7 ◦API, Cacalilao 7.2 ◦API and Tamaulipas 13.6 ◦ API).

The charactetization of the physical, chemical and rheological properties of the water-Maya crude-salts systems wash established. The results show, a wide spectrum of information about the behavior of emulsions obtained before and after microwave irradiation, which is to be used to design microwave applicators.
This paper concludes that the best rate of dehydration is the obtained by a 20/80 water-oil dilution for crudes kind different three. The decrease in the density of oil which is evidenced by an increase in degrees API. The microwave irradiation alters the main functional groups of the crude, but there is a fragmentation of the hydrocarbon chains. In the case of 50/50 oil-water emulsions, the hydrocarbons dissolved in the congenital water are recovered.

---

*Speaker

†Corresponding author: ariana_vazquez@hotmail.com

‡Corresponding author: drmarure@hotmail.com

Thermohydrodynamic processes in water-in-oil emulsions under MW impact

Regina Iulmukhametova*[1], Elmira Tukhbatova[1], Airat Musin[1], and Liana Kovaleva[1]

[1]Bashkir State University (BashSU) – Russia, the Republic of Bashkortostan, Ufa, Zaki Validi street, 32, Russia

Abstract

One of the negative factors in the oil extraction and processing, as well as in the elimination and recycling of oil-sludge barns is the formation of a high stability of water-in-oil emulsions. In the case of frequently encountered high water cut of oil products gravity is usually used. The acceleration of the droplet sedimentation can be effected by microwave (MW) irradiation. In this case, the thermoconvective flow arising in the surrounding fluid create hydrodynamic flows that can prevent the emulsion destruction.

In this paper a water-in-oil emulsion is considered in the gravitational field under the influence of MW irradiation. The dissipation of the energy of the MW field occurs predominantly in water droplets. Under the influence of the field the medium begins to warm, and thermal convection of the liquid arises. The inhomogeneity of the medium leads to an uneven absorption of the field energy. The intensity of energy absorption in the medium depends on the content of water droplets in the emulsion. The mathematical model of the process of microwave electromagnetic effects on water-in-oil emulsions is formulated in the diffusion approximation with allowance for free-convective fluid flows arising in the medium while it changes its temperature and the concentration of water droplets in the carrier phase. The mathematical model of the process includes a system of thermal convection equations in the Boussinesq approximation supplemented by the diffusion equation. The energy dissipation of the microwave EM field is modeled in the form of distributed heat sources, the values of which depend on the electric field strength and on the concentration of water droplets in the emulsion. The dependence of the viscosity of a hydrocarbon liquid on temperature is taken into account.

The algorithm for the numerical solution of the problem in three-dimensional form is implemented in an open source numerical simulation software OpenFOAM. It is found that the velocity of convective mixing for colloid-dispersed systems and microemulsions exceeds the velocity of gravitational droplet deposition. Simulation without taking into account the enlargement of the droplets shows that the thermal convection in the liquid leads to mixing of the emulsion. The temperature of the medium eventually equalizes, thermal convection is gradually damped. This process continues until the thermal and concentration flows in the liquid are leveled out. It is shown that the nature of the flow varies with time, which is associated with a redistribution of water droplets in the emulsion and a change of temperature gradient in the system. The results obtained can be useful for establishing the regimes of effective application of the microwave method for the destruction of water-in-oil emulsions.

This research is supported by the Grant of President of the Russian Federation MK-9398.2016.1.

---

*Speaker

Analysis of asphaltenes dynamic interfacial tension data using a diffusion limited mixture model

Vincent Pauchard[1], Fang Liu*[2], and Nelya Akhmetkhanova[2]

[1]Energy Institute and Chemical Engineering Department City College of New York, New York, USA – United States

[2]Energy Institute and Department of Chemical Engineering, City College of New York, New York, NY, 10031, USA – United States

Abstract

Asphaltenes samples are well known to be composed of a wide array of molecular structure (size, aromaticity, the presence of heteroatoms, etc.), which should lead to a wide distribution of interfacial activities. In particular adsorption coefficients are believed to vary tremendously with slight changes in molecular structure, which should impact significantly the asphaltenes adsorption kinetics. It was recently shown that a binary mixture model for diffusion limited adsorption would describe qualitatively all the features of asphaltenes dilatational rheology [1]. Furthermore, the parameters extracted from the quantitative fit between the binary model and experimental rheology data could further be used to fairly predict dynamic interfacial tension for the same asphaltenes solution past the first seconds. In terms of surface activity, it appears that less than 10% of asphaltenes are much more surface-active than the bulk of them. A tiny fraction of them ($< 0.5\%$) even seems to be responsible for an "everlasting" interfacial tension decay. Extending this analysis to a ternary mixture would require experimental rheology data over a frequency range larger than what are usually available. This limitation can be alleviated by directly analyzing the dynamic interfacial tension data as will be presented. Performing such an analysis requires a complex parametric optimization procedure involving the Ward-Tordai equation. The outcome is that a mixture model of three components is sufficient to capture experimental dynamic interfacial decay from less than 1 second up to 24 hours. At low bulk concentration (below the critical nanoaggregate concentration, i.e. CNAC), the total concentration of the three pseudo-components systematically falls close to the nominal concentration of the solution (as calculated with an average molecular weight of 750 g/mol). Around 90% of asphaltenes have a low surface activity whereas less than 0.5% almost behave as insolubles. As bulk concentration increases, the concentration of the less surface-active fraction keeps increasing proportionally, whereas the concentration of the most surface-active concentration levels-off. This can be interpreted in terms of electrostatic interactions. If both nanoaggregation and adsorption are driven by PI interactions, then the most surface-active asphaltenes would also be the components that are most prone to aggregate. Such a scenario would explain qualitatively the bilinear curves obtained around the CNAC for NMR signal [2,3] or conductivity [4] versus asphaltenes concentration.

Liu, F., Darjani, S., Akhmetkhanova, N., Maldarelli, C., Banerjee, S., & Pauchard, V. (2017)

---

*Speaker

Mixture effect on dilatation rheology of asphaltenes laden interfaces. Langmuir, 33(8), 1927–1942.

Lisitza, N. V., Freed, D. E., Sen, P. N., & Song, Y. Q. (2009). Study of asphaltene nanoaggregation by nuclear magnetic resonance (NMR). Energy & Fuels, 23(3), 1189-1193.

Durand, E., Clemancey, M., Quoineaud, A. A., Verstraete, J., Espinat, D., & Lancelin, J. M. (2008). 1H diffusion-ordered spectroscopy (DOSY) nuclear magnetic resonance (NMR) as a powerful tool for the analysis of hydrocarbon mixtures and asphaltenes. Energy & Fuels, 22(4), 2604-2610.

Goual, L., & Abudu, A. (2009). Predicting the adsorption of asphaltenes from their electrical conductivity. Energy & Fuels, 24(1), 469-474.

INFLUENCE OF GLICERYN AND XANTHAM GUM IN RHEOLOGICAL PROPRIETY OF MICROEMULTION DRILLING FLUID

Fabiola Curbelo*†[1], Caio Nesello[1], Julio Cezar Freitas*‡[2], Glauco Braga[3], Rafael Fernando Ungarato*§[4], and Alfredo Ismael Garnica*¶[1]

[1]Federal University of Paraiba, Departament of Chemical Engineering (UFPB) – Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil
[2]Federal University of Rio Grande do Norte, Chemical Institute (UFRN) – Campus Universitário Lagoa Nova CEP 59078-970, Brazil
[3]Federal University of Paraiba, Department of Chemical Engineering (UFPB) – Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil
[4]Oxiteno – Brazil

Abstract

The environmental laws regarding industrial activity have been stricter with time, and the petroleum industry needs to adapt to this new perspective. The main challenge for this industry is to keep or increase the ratio between the performance and price while respecting these new laws. One of the key components that needs to be improved is the drilling fluid. This fluid is used while drilling the oil or gas well and has several functions: lifting rock cuttings to the surface, cleaning the well, overcoming the pressure of the fluids so they don't enter the well, helping with the stabilization of the wellbore and cooling and lubricate the drill bit; but it can have one of the most negative impact in the environment among the fluids and materials used in the oil well perforation. Oil-based fluids show a satisfactory performance, they tend to be expensive and cause a non-desirable impact on the environment, which is the reason their use has been forbidden in many areas of the world. Water-based fluids often damage rock formations and hardly ever have the specifications for drilling in horizontal wells, which are known for their ability to deliver high production rates and large reserve volume. Microemulsions have been widely used in this field because of its stability and properties that are suitable for the drilling operation. This work has focused on the formulation and prepare of drilling fluids based microemulsions, which consisted of these three components: glycerin and water (aqueous phase-AP) in proportion 1:1 and 3:7, respectively; vegetable oil (oily phase- OP) and a non-ionic and biodegradable surfactant (S). The weight ratio of 3 components of ternary phases diagram was: 40% (AP), 15% (OP) and 45% S. Xanthan gum was used in aqueous phase (AP) with two proportions, 1.5 wt% and 0.75 wt% of microemulsion. For each of these fluids, it was evaluated its rheological behavior, and, also, it was performed a comparative study regarding the effect of the xanthan gum and

---

*Speaker
†Corresponding author: fabioladias@yahoo.com
‡Corresponding author: juliofreitasj@hotmail.com
§Corresponding author: rafael.ungarato@oxiteno.com
¶Corresponding author: alfredocurbelo@yahoo.com

the proportion of glycerin in the aqueous phase of the microemulsions. The results showed that the experimental data of four fluids studied fitted in the Herschel-Bulkley rheological model. The fluid A, with 1.5 wt% xanthan gum and 1:1 (glyceryn:water) and The fluid B, 1.5 wt% xanthan gum with 3:7 presented higher (11.8 and 12.1, respectively) than the fluid C, 0.75 wt% xanthan gum and 1:1 and fluid D, 0.75 wt% and 3:7 (4.97 and 6.9, respectively). It was observed that the amount xanthan gum influenced more than the glycerin, however the glycerin enhanced consistency of fluids (fluid B 0.58 to fluid A 0.78) and (fluid D 0.56 to fluid C 0.78). Drilling fluids studied presented characteristics similar to commonly used by oil industries and showed advantages as: possibility of use in directional wells due to lubricity promote by oily phase (15% OP) and reduction in the probability of generating damage to the formation (emulsion) during drilling of producers zone when compared to water based fluid.

Effect of Sec-butanol on the crude oil/cyclohexane interphase

Victor Perez*†1, Ingrid Velasquez[1], Juan Sykora[2], Patrick Bouriat[3], Christophe Dicharry[3], and Juan Pereira[1]

[1]Laboratory of Petroleum, Hydrocarbon and Derivates (PHD), University of Carabobo, Valencia, Venezuela – Venezuela
[2]Químicos de Mantenimiento C.A. Venezuela. (QUIMAINCA) – Venezuela
[3]Complex Fluids Laboratory (UFR), de PAU (UPPA) University, France. – Université de Pau et des Pays de l'Adour - UPPA (FRANCE) – France

Abstract

Asphaltenes and resins are the most important fractions of petroleum, determining the behavior of most crude oils, exerting great influence on its properties, from its extraction, transportation and its refining. Water in oil (W/O) emulsions are formed in most crude oils which are as stable as is the resistance of the interfacial film formed by asphaltenes. The viscoelastic properties of the film that separates the phases, depend on the soluble or insoluble surfactants (asphaltenes/resins) present in the crude oil and their interactions. On the other hand, solvents influence the asphaltene adsorption. This research work studies the influence that Sec-Butanol has on the formed film of w/o interphase, determined by the modifications that suffer the rheological parameters of the systems under study. Crude oil diluted in cyclohexane in a 10% w/w solution, allowed to study the viscoelastic properties of the monolayer formed by asphaltenes, using a drop tensiometer (TECLIS). Later, was studied the effect that alcohol has on the interfacial film, in its diffusion from the aqueous and organic phase to the interphase, at a 1% w/w concentration. Sec-Butanol influences the viscoelastic behavior of the interphase, causing to move, counterclockwise, the cross point between the elasticity curves of module and the phase angle in function of time, so it can be used as an additive in commercial demulsifiers.

---

[*] Speaker

[†] Corresponding author: vmperezuc@gmail.com

sciencesconf.org:petrophase2017:145348

E-P13

Effect of the HepTol blend on the rheology of a crude oil with a high asphaltene content.

Victor Perez*[1], Ingrid Velasquez[1], Juan Sykora[2], Patrick Bouriat[3], Christophe Dicharry[3], and Juan Pereira[1]

[1]Laboratory of Petroleum, Hydrocarbon and Derivates (PHD), University of Carabobo, Valencia, Venezuela – Venezuela

[2]Químicos de Mantenimiento C.A. (QUIMAINCA) Venezuela. – Venezuela

[3]Complex Fluids Laboratory (UFR), de PAU (UPPA) University, France. – Université de Pau et des Pays de l'Adour - UPPA (FRANCE) – France

Abstract

The oil industry uses organic solvents to treat, handle or move crude oil; as diluents to extract and/or transport it, characterization (SARA method) and classification (ACSI method). Asphaltenes are soluble in toluene and insoluble in heptane, the latter being used for their precipitation and separation from crude oil. When the asphaltene molecules are dispersed in a crude oil, there is a competitiveness for being adsorbed on the interphase (W/O or O/W). However, due to the precipitation and formation of aggregates caused by heptane influence, the number of molecules in the media will be smaller, although at the interphase level, will be the same. Modification of the media causes changes of the interfacial film characteristics. This research shows the effect a HepTol blend has on water in oil emulsions (W/O) in a crude oil with a high content of asphaltenes. The test consists of diluting the crude oil with HepTol (Heptane/Toluene ratio from 0 to 100% respectively) and study the viscoelastic properties of the monolayer formed by asphaltenes, using a drop tensiometer. Results show a close relationship between the influence of the HepTol relationship and the rheological interfacial parameters with the stability of the formed water in oil (W/O) emulsions, demonstrating the importance of the interactions between the components with interfacial activity and the solvent. The study yielded a maximum value in the elasticity module and the stability of emulsion time, for HepTol with a 55/45% Heptane/Toluene ratio.

---

*Speaker

sciencesconf.org:petrophase2017:145350

Effect of water-soluble indigenous crude oil surfactants on w/o interfacial properties and emulsion stability

Leticia Ligiero*[1,2], Christophe Dicharry[3], Brice Bouyssière[4], Nicolas Passade-Boupat[2], and Patrick Bouriat[1]

[1]Laboratoire des Fluides Complexes et leurs Réservoirs (LFC-R) – Université de Pau et des Pays de l'Adour, TOTAL, Centre National de la Recherche Scientifique : UMR5150 – BP 1155 - 64013 Pau, France

[2]Total EP – Total EP – France

[3]Laboratoire des Fluides Complexes et leurs Réservoirs (LFCR) – Université de Pau et des Pays de l'Adour, Centre National de la Recherche Scientifique : UMR5150 – BP 1155 - 64013 Pau, France

[4]CNRS/UPPA, UMR 5254, LCABIE (LCABIE) – LCABIE – Hélioparc - 2 av. Pr. Angot, 64053 Pau, France

Abstract

Crude oil recovery and refining operations are based on high consumption water processes. During production and refining, oil and water are constantly mixed together, and stable water-in-oil (w/o) emulsions may be formed, which must be broken in order to respect environmental legislation, avoid corrosion problems, and to increase process yield. Both emulsion stability and w/o interfacial properties depend on crude oil composition and on its indigenous natural surfactants. When water and petroleum are mixed together, some amphiphilic components of the crude oil can migrate into the water phase. The molecules that are transferred from the oil to the water change the aqueous phase properties, the w/o interfacial behavior and emulsion stability. Identifying these molecules and understanding their impact on the w/o interfacial properties are key points to optimize crude oil dehydration operations. In this study, the effect of the water-soluble species of one crude oil (named AD) on the w/o interfacial properties and emulsion stability was investigated by means of recycling experiments. First, 10 consecutive emulsions using the same oil phase and a fresh water phase were formed, and the stability and the interfacial rheological properties were evaluated. Second, 3 consecutive emulsions using the same water phase and a fresh new oil phase were performed and submitted to same physicochemical tests. The main objective was to evaluate whether the compositional change of the water phase has a beneficial or detrimental effect on the oil dehydration. Analytical tests (High Resolution Mass Spectrometry and Total Organic Carbon analysis) were performed in some of the resolved to waters to quantify and identify some of the water-soluble species. Results indicate that the transferred oil-to-water species during the emulsification process impact the w/o interfacial properties. The recycling experiments confirmed that AD water-soluble species favor crude oil dehydration. Finally, some of these water-soluble species were identified (O2, O3, S1) but much effort is still necessary to identify more species in order to match the system composition to its physicochemical properties.

---

*Speaker

ORALS
Flow Assurance

Flow Assurance - New solutions for the same old problems

Daniel Merino-Garcia*[1]

[1]Repsol, Madrid, Spain – Spain

Abstract

The day-to-day activities of a Flow Assurance engineer span all phases of field development: the decisions related to fluid quality start in prospect phase, peak during the development phase and are also very relevant during operation, as many factors may lead to potential problems even in the best-designed field.
Oil producers have basically dealt with the same reservoir fluids for more than a century; what has changed is the knowledge of composition and behavior, as well as the understanding of the heterogeneities in reservoir composition.

This led to the capacity (or necessity) to expand the operating envelope to lower temperatures, higher pressures, and the allowance of solid presence in production lines.

The discipline of Flow Assurance gained relevance with time, as it became more critical to predict and prevent solid formation and flow instabilities in areas with difficult access for remediation actions (deepwater, arctic, long distance tie backs, etc). It is now playing a major role in the definition of field architecture. The engineer has at hand a number of experimental techniques, models, inhibition strategies and remediation options, to tackle each and every one of the flow assurance challenges.

The presentation will describe the workflow of flow assurance analyses that are typically done at each stage of development, with special emphasis on the areas where further developments (experimental, modeling, control / mitigation strategy) are required.

---

*Speaker

sciencesconf.org:petrophase2017:155617

Influence of Al2O3/SiO2 ratio on asphaltenes precipitation in a packed-bed microreactor with in situ analytics

Bruno Pinho*[1], Nikhil Joshi[2], Andrew Yen[3], and Ryan Hartman†[1]

[1]New York University - Tandon School of Engineering (NYU) – 6 MetroTech Center, Brooklyn, NY 11201, United States
[2]Anadarko Petroleum Corporation – The Woodlands, TX 77380, United States
[3]Nalco Champion – An Ecolab Company, Sugar Land, TX 77478, United States

Abstract

The outcomes of stimulation chemistry on asphaltenes-damaged reservoirs are not yet well understood[1,2], due to a lack of available information in the field[3] and limited laboratory techniques for the discovery of asphaltenes-reservoir interactions[4]. Hydrocarbon reservoirs are complex in their mineralogy and chemistry[5]. Microfluidics offer an effective platform for rapid, *in situ* characterizations[6,7] at experimental conditions that simulate sandstone reservoirs[8,9]. We have begun to examine the influence of the Al2O3:SiO2 ratio (an important characteristic of reservoir mineralogy[10]) on asphaltenes damage in quartz packed-bed microreactors using *in situ* Raman spectroscopy (1D to 3D mapping), UV-vis spectroscopy, and pressure sensors. Our devices were damaged by injecting 300 nm ZSM-5 zeolite nanoparticles (a model aluminosilicate available with Al2O3/SiO2 ratios of 1/91 and 1/26) before any damage by asphaltenes.The new methodologies aresensitive enough to identifythe effect of the chemicalinteractions at the molecularlevel, giving insights toasphaltenes' sheet size(nm), and bed occupancyvariations. Our results showthat in the precipitationprocess, an Al2O3/SiO2 ratioof 1/26 leads to 10% higher asphaltenes' sheet size and 325% higher bed occupancy than a bed with only SiO2. When increasing the ratio, the number of pore volumes required to reach maximum bed damage also increases. Our findings support that the Al2O3 content delays asphaltenes nanoaggregation[11,12]. Consequently, lower asphaltene-SiO2 and lower asphaltene-asphaltene interactions are expected in presence of Al2O3, which is consistent with the acidity playing an important role. In preliminary tests, damaged devices with Al2O3/SiO2 ratios of 1/26 require three-times as much xylenes to restore permeability than devices without Al2O3 content.

A future with online and automated feedback of the laboratory investigations described above could revolutionize client support and stimulation designs by high-throughput understanding of the damage mechanism, rapid formulation and selection of the appropriate chemicals, and the generation of data for predictive modelling used by geochemical simulators.

References:

X. Qin, P. Wang, K. Sepehrnoori, G. A. Pope, *Ind. Eng. Chem. Res.* **2000**, *39*, 2644–2654.

---

[*] Speaker

[†] Corresponding author: ryan.hartman@nyu.edu

K. Gonzalez, H. Nasrabadi, M. Barrufet, *J. Pet. Sci. Eng.* **2016**, DOI 10.1016/j.petrol.2016.09.010.

O. C. Mullins, *et al.*, *Energy & Fuels* **2012**, *26*, 3986–4003.

T. Pernyeszi, Á. Patzkó, O. Berkesi, I. Dékány, *Colloids Surfaces A Physicochem. Eng. Asp.* **1998**, *137*, 373–384.

J. Wang, A. L. Ferguson, *J. Phys. Chem. B* **2016**, *120*, 8016–8035.

M. H. Schneider, V. J. Sieben, A. M. Kharrat, F. Mostowfi, *Anal. Chem.* **2013**, *85*, 5153–60.

V. J. Sieben, A. K. Tharanivasan, J. Ratulowski, F. Mostowfi, *Lab Chip* **2015**, *15*, 4062–4074.

C. Hu, A. Yen, N. Joshi, R. L. Hartman, *Chem. Eng. Sci.* **2016**, *140*, 144–152.

C. Hu, R. L. Hartman, *AIChE J.* **2014**, *60*, 3534–3546.

N. N. Nassar, *Energy and Fuels* **2010**, *24*, 4116–4122.

C. A. Franco, N. N. Nassar, M. A. Ruiz, P. Pereira-Almao, F. B. Cortés, *Energy and Fuels* **2013**, *27*, 2899–2907.

M. Mohammadi, M. Akbari, Z. Fakhroueian, A. Bahramian, R. Azin, S. Arya, *Energy & Fuels* **2011**, *25*, 3150–3156.

An insight View on Asphaltene Stability Measurement

Jens Pfeiffer*[1] and Alfred Hase*†[2]

[1]PSL Systemtechnik GmbH (PSL) – Baumhofstrasse 116 37520 Osteroder am Harz, Germany
[2]NALCO Champion – Bundrat Tech Centre, Peterseat Drive Aberdeen, AB12 3HT, United Kingdom

Abstract

The precipitation of asphaltenes during production, transport and storage of crude oils, respectively products of crude oils, leads to technical and economics problems. One of the major issues is to predict and prevent such a flocculation's to minimize the risk in the pipeline. Current state of research, Asphaltene stability under upstream and refinery conditions is still only partially studied due to limited capabilities of test equipment on high temperature and high pressure measurement. To overcome these restrictions of test equipment, measurement are typically performed at reduced temperature and/or pressure conditions and are often run with diluted samples, using Toluene or Xylene, in order to provide better translucency for optical detection of asphaltene flocculation.

Due to this lack of alternative measurement, the effect of temperature/pressure/dilution is widely ignored or just empirically corrected by rules of thumb.

However, sometimes there are more side-effects than those rules of thumb which have to be taken into consideration .
The authors will demonstrate in this comprehensive study the kinematic impact of various solvents for Asphaltenes and how high pressure and high temperature will effect the onset of Asphaltene instability under extreme conditions. They will also provide detailed data and give recommendations on how to compare the obtained data under different test conditions and how to achieve best accuracy.

---

*Speaker

†Corresponding author: Alfred.Hase@CHAMP-TECH.com

Asphaltenes destabilization and deposition assessment by acoustic resonator

Ezequiel Orlandi*[1], Jean-Luc Daridon[1], and Hervé Carrier[1]

[1]Laboratoire des Fluides Complexes et leurs Réservoirs (LFC-R) – Université de Pau et des Pays de l'Adour [UPPA], CNRS : UMR5150, TOTAL – BP 1155 - 64013 Pau, France

Abstract

A methodology of analysing crude oil asphaltenes destabilization and deposition is presented. In this method, asphaltenes are destabilized from crude oil in contact with an acoustic wave sensor by continuous n-heptane injection. During the titration experiment, the responses in resonant frequency and bandwidth from three harmonics of resonance are continuously monitored. From these measurements, the onset of asphaltene destabilization is estimated and deposition mechanism is investigated. Asphaltene deposition from crude oil is compared with deposition of extracted asphaltenes, diluted crude oils and model asphaltenes compounds. The technique opens new perspectives on assessing asphaltenes destabilization and the structure of asphaltenes deposits obtained under smooth and continuous crude oil solubility change. The validity of the utilization of quartz crystal resonator under such condition is discussed along with the implications that this technique can have to the flow assurance science.

---

*Speaker

Decoding cool-down test on wet insulation for flow assurance through full scale validation using advanced technologies

Bo Xu*[†][1], Heydrich Marcus , and Mark Redmond

[1]Shawcor Ltd – 25 Bethride Rd, Toronto, ON, Canada

Abstract

As one of flow assurance methods, thermal insulation of pipelines has played a very significant role for the offshore oil & gas production. High cost and significant technical challenges are unavoidable for cleaning a plugged flowline/pipeline in the deep sea. This makes it very desirable to verify and qualify pipeline performance through testing. Simulated Service Vessel (SSV) tests have been the main technology used in the oil & gas industry for full scale validation of insulated offshore pipelines. Cool-down tests on the insulated pipe are often required by clients along with the Overall Heat Transfer Coefficient (OHTC) measurement. The cool-down time is crucial information for the operators to design response plans for managing the risk of flowline plugging due to hydrate or wax formation. However, due to the heating method used in tests, the measured cool-down time would be misleading without considering the thermal effect from test components including pipe mounting parts. This paper will analyze the transient heat transfer process during the cool-down test on the second generation SSV test facility at Shawcor, which has conducted more than 30 SSV tests on various insulated pipes. A validation of the finite element analysis (FEA) model is conducted by comparing the FEA modeling results with the SSV test data. A correlation between the cool-down time from SSV tests and that from simulation for the same pipe will be established. This will provide a better understanding of the SSV test data on the cool-down time and translate the cool-down test data to the real application.

---

*Speaker

[†] Corresponding author: bo.xu@shawcor.com

Cold flow solutions for wax challenges

Claire Ward*[1], Helen Sarginson[1], Natalie Hodgson[1], Creasey Julia[1], Joshua Middleton[1], and Craig Davies[1]

[1]Croda Europe Ltd (Croda) – Croda Europe Ltd, Cowick Hall, Snaith, Goole, East Yorkshire, DN14 9AA, England, United Kingdom

Abstract

Maintaining flow in the production and transportation of crude oil is a critical challenge in both on-shore and off-shore environments. Problems such as wax deposition and flow restriction from gelling can occur with changes in temperature and pressure during production, as well as changes in crude oil composition when oil streams are combined. Traditionally, solvent, thermal and mechanical methods have been used as wax remediation treatments. However, chemical treatments are now increasingly employed to mitigate flow assurance problems caused by the naturally occurring paraffins in crude oil. Due to the unique composition of every crude oil, there is no single product capable of treating all flow assurance problems. This paper discusses how subtle changes in chemistry can give diverse cold flow improver product performances, making them suitable for use in different global crude oils. The physical properties, application performance and environmental impact of the products were evaluated in this work. Varying the chemistry of these high activity cold flow improvers led to improved low viscosity profiles, especially at sub-zero temperatures, facilitating a wider temperature operating window for users in off-shore applications and cold weather climates. The high and low temperature stability of these products was also investigated by thermal gravimetric analysis.

The application performance in crude oil was measured by pour point and cold finger test methods, and the cold flow improver additives were employed before the fluid temperature dropped below the wax appearance temperature. Small variations in the chemistry of the products were shown to give significant differences in pour point depression and viscosity profiles in a North American and a Latin American crude oil, therefore helping to minimise flow restrictions. These structural variations also led to similar differences in performance in cold finger wax deposition studies on other crude oils from around the globe.

To add to the benefits of the physical attributes and application performance, these products were also designed to have a very low environmental impact and have achieved CEFAS gold certification with no substitution warnings. The study of these cold flow improvers is a key building block for further rationalised product design to improve flow assurance.

---

*Speaker

sciencesconf.org:petrophase2017:144822

Large Scale Wax Deposition Experimental Study and Model Performance Evaluation

Shuxin Hou*†[1] and Hans Petter Rønningsen[1]

[1]Statoil ASA – Norway

Abstract

Wax deposition for a Norwegian continental shelf waxy oil was experimentally investigated using Statoil in-house large scale flow loop. The waxy oil was first characterized, with special focus on wax precipitation and rheological properties. The experimental work was carried out at flow and heat transfer conditions, which are designed to simulate the subsea oil transportation scenario of project development significance. The wax deposition evolving process was captured, and the wax thicknesses were measured. The porosity of the wax deposits was also analyzed. These experimental data are vital to understand wax deposition mechanism, and contribute to improved wax deposition modelling.

The performance of several available wax deposition models is also comprehensively investigated. Generally, model overpredictions are found when compared against the experimental findings. Aside from molecular diffusion, the other mechanisms influencing the wax deposition process, such as supersaturation, deserves special attention.

The effect of wax inhibitor was also experimentally investigated. As contrary to expectations, quicker wax layer growth was found. The addition of wax inhibitor tends to influence wax particle appearance and the waxy oil behavior, as evidenced by both large scale flow loop study and laboratory characterization using Differential Scanning Calorimetry.

---

*Speaker

†Corresponding author: shou@statoil.com

sciencesconf.org:petrophase2017:138806

POSTERS
Flow Assurance

RHEOLOGICAL ANALYSIS OF GAS HYDRATES FORMATION IN CRUDE OIL USING PRESSURE CELL

Edson Soares*†[1], Gustavo Samdoval[2], Rafhael Andrade[1], Renato Siqueira[3], Roney Thompson[2], Flávio Campos[4], and Adriana Teixeira[4]

[1]Universidade Federal do Espírito Santo (UFES) – Av. Fernando Ferrari 514 - Vitória - ES, Brazil
[2]Universidade Federal do Rio de Janeiro (UFRJ) – Brazil
[3]Instituto Federal do Espírito Santo (IFES) – Brazil
[4]Centro de Pesquisa e Desenvolvimento da Petrobras (PETROBRAS/CENPES) – Brazil

Abstract

Gas Hydrates are crystalline solids composed of water and gas. The gas molecules are trapped in water cavities, if a specific thermodynamic condition of high pressure and low temperature is attained. Such condition is typical in deep water, which causes a huge problem for oil transportation, when the pipelines can be totally blocked. In fact, this phenomenon is one of the most challenging problems in flow assurance. One reason for that is the level of complexity to conduct careful analyses, since the hydrate formation is a stochastic phenomenon. In fact, it is very time- and apparatus-dependent. In addition to the chemical and thermodynamic complexities, nucleation and growth of crystals, the oil with gas hydrates is a very Non-Newtonian material, which exhibits an elasto-visco-plastic-thixotropic behaviour. A reliable measurement of the viscosity and yield stress of hydrates are quite important for flow assurance but very difficult to be attained, since these values are highly influenced by shear and temperature history and also the composition of the waxy crude oils. Besides that, the experiments must be performed at very controlled high-pressure and low temperature. In this work, a magnetic pressure cell is used to rheologically analyse the properties of gas hydrates in water-in-crude oil emulsions. The cell is connected to a booster that permits to set up high pressures to saturate the emulsion with carbon dioxide and methane. The desired temperature is controlled using a heating/cooling thermostatic bath. The viscosity behaviour was studied during the induction, growth and dissociation of the crystals along the time. We investigated the water volume fraction, shear rate and two different geometries: a concentric-cylinder and a vane rotor. The hydrate viscosity increases with time until it reaches a maximum plateau and then begins to reduce due to the break down of the hydrates structures. The concentric-cylinder geometry seems to be a better choice to measure the rheological properties of gas hydrates formation.

---

*Speaker

†Corresponding author: edson.soares@ufes.br

sciencesconf.org:petrophase2017:143624

Usage of Water Fugacity to Manage Margin for Flow Assurance

Nevin Gerek Ince*†[1], Seiya Hirohama‡[2], Gang Xu[1], Prasad Narasimhan[1], Francisco Brana-Mulero[1], and David Bluck[1]

[1]Schneider Electric Software – United States
[2]Schneider Electric – Johnston Island

Abstract

Real time optimization (RTO) has been successfully applied to downstream units to maximize profit of plant operations. Typical an RTO is equipped with a process simulator and an optimizer, which are connected with advanced control systems of plants. The process simulator runs repeatedly during actual plant operations and matches the actual operation by periodically tuning parameters. Applying the tuned simulation model, the optimizer seeks a set of operating conditions to maximize a specified objective function which is typically the economic profit of the process of interest. The optimization utilizes the Langmuir multiplier approach under process constraints such as capacities of devices that are mathematically described as sets of equations in the simulator. The obtained optimum operating conditions are then transferred to set points of the actual plant control systems, so that the real operation eventually achieves the optimum performance. The same technology can bring huge benefits to upstream applications and processing of natural gas, so that the operating conditions, such as production rate of each well and booster compressor powers, can be optimized to maximize profit. Hydrate occurrence in flow assurance defines an important process constraint for gas processing facilities and it should be considered as a process constraint in optimization. Furthermore, because a certain margin in operating conditions should be kept and reflected in the RTO, a practical methodology to define margin against hydrate occurrence is also required.

This work defines the margin as the difference between water fugacity of a hypothetical hydrate cage (*fH2O,hy*) and the water fugacity in the fluid at real conditions (*fH2O,f*). Apparently, a hydrate is supposed to occur if *fH2O,hy* is less than *fH2O,f*. A necessary value for the margin (*fH2O,hy* - *fH2O,f*) should be appropriately determined based on the information on fluctuation of process conditions and expected error in fugacity. We employ Solid Solution Theory to predict *fH2O,hy* and a simple empirical mixing rule with a Cubic Equations of Sate (CEoS) to accurately predict *fH2O,f*. Although there are known limitations to CEoS, a CEoS with proper mixing rules can provide the fidelity and performance in a wide variety of applications. Even for mixtures containing polar components like water or glycols, the approach works well with low cost computer resource which is important in dynamic simulations and rapid optimizations. Furthermore, we determine binary interaction parameters for all major pairs of hydrate inhibitor and components in typical natural gas. As components for natural gas, we consider 20 hydrocarbons, water, carbon dioxide and

---

*Speaker

†Corresponding author: nevin.gerek@schneider-electric.com

‡Corresponding author: seiya.hirohama@schneider-electric.com

hydrogen sulfide. For pairs that have missing experimental data, we use a correlation for binary interaction parameters based on a group contribution approach. We confirm that the ”margin” for water fugacity (*fH2O,hy* - *fH2O,f*) was successfully calculated to avoid hydrate occurrence at a given composition, temperature and pressure.

In summary, a thermodynamic base is established to model fluid mixtures of hydrocarbons, hydrate inhibitors, and water. The model is applied to calculate a margin in water fugacity to avoid hydrate occurrence, which is applicable to RTO of gas processes, securing flow assurance.

Novel Algorithm for Constructing Complete Asphaltene PT and Px Phase Diagrams

Christian Agger*†[1] and Henrik Sørensen[1]

[1]Calsep A/S – Parallelvej 12 2800 Kgs. Lyngby, Denmark

Abstract

Objectives/Scope
A novel algorithm is presented for constructing complete asphaltene PT and Px phase diagrams in a fast and robust manner. The algorithm tracks the phase boundaries between oil, gas and asphaltene phases. This allows a complete overview of phases present under production of reservoir fluids containing asphaltenes. The algorithm can also be used at high temperatures as for example to visualize at what conditions asphaltenes will precipitate in refineries.

Methods, Procedures, Process

The algorithm employs a trajectory tracking principle using the phase envelope tangent vector, expressing sensitivity, for extrapolation and interpolation and for fast and robust mapping of the phase envelope with no performance decline while mapping critical and semi-critical regions. The mapping is performed while continuously surveying stability of incipient and existing phases using modified tangent plane analysis.

In our implementation the algorithm models asphaltene precipitation as a liquid-liquid split using either classic cubic-, CPA- or PC-SAFT EoS-es for all phases including gas, but is not prejudice in this respect, and is equally well suited for activity coefficient- or Flury-Huggins models.

Results, Observations, Conclusions

It is demonstrated that the algorithm can be modified to take an injection gas amount as specification, allowing for construction of isothermal phase diagrams showing the mixtures response on asphaltene stability pressure to gas injection, i.e. construction of Px phase diagrams in addition to PT phase diagrams.

Examples of complete asphaltene PT and Px phase diagrams are shown illustrating the multitude of behaviors possible with different types of fluids when seen over a broad range in temperature and compositions.

It is often a challenge to carry out automatic tuning to experimental asphaltene onset conditions when the initial parameters are not close to the optimum values. The usage of the

---

*Speaker

†Corresponding author: ca@calsep.com

algorithm to properly initiate and direct procedures for automatic tuning to asphaltene data in such cases is exemplified. Further the high performance and stability of the algorithm makes it well suited for use in such automatic tuning procedures.

Novel/Additive Information
The novelty lies in the ability of the presented algorithm to construct complete asphaltene PT and Px phase diagrams in a fast and robust manner.

A new approximate method for modelling the effects of temperature, pressure and oil compositions on asphaltene instability in live crudes and stabilised oils with CPA

Xiaohong Zhang*†[1], Nuno Pedrosa[1], and Richard Szczepanski[1]

[1]KBC Advanced Technologies Ltd (A Yokogawa Company) (KBC) – Unit 1, 93 Great Suffolk Street,
London SE1 0BX, United Kingdom

Abstract

Asphaltenes are the heaviest, most highly polarisable and polydisperse fractions in crude oils. Their complex nature and continuous changes of chemical structures due to self-aggregation bring in many challenges and problems to the oil and gas, petro-chemical, processing and refining industries. The stability of asphaltene in crudes oils can be easily disturbed with the changes of temperature, pressure or composition of the petroleum fluids owing to fluid commingling and blending or gas injection. Once the instability of asphaltenes in crude oils is triggered, asphaltenes start to precipitate and deposit in reservoirs, well tube, and process facilities, causing significant damages and having substantial economic impact to the industries. Understanding the complex phase behaviour of asphaltenes in crude oils, therefore, is essential for the industries, so that correct strategy and remediation can be implemented to prevent the problems.

Thermodynamic models have been playing an important role in understanding the phase behaviour of asphaltenes. However, because of the complex nature of asphaltene phase behaviour all thermodynamic models rely on substantial experimental asphaltene onset data to validate and optimise the model parameters so that the models are able to capture the correct trends in phase behaviour with change of temperature, pressure and oil composition. This study investigates the possibilities of using a limited amount of experimental data to estimate the model parameters with the Cubic-Plus-Association (CPA) model [1,2]. The new approximate method simplifies the treatment of asphaltene-asphaltene self-association and asphaltene-resin cross association in order to reduce the adjustable model parameters from four to two, therefore decreasing the requirement for asphaltene onset data.

The new approximate approach is validated with various types of crude oils and blends and gas injection data. A comprehensive comparison is be carried out for the cases with detailed asphaltene onset data.

References:

: Xiaohong Zhang, Nuno Pedrosa and Tony Moorwood, Energy Fuels 2012, 26, 2611–2620.

. Nuno Pedrosa, Richard Szczepanski, Xiaohong Zhang, Fluid Phase Equilibria, vol. 359, 15 December 2013, Pages 24–37

---

*Speaker

†Corresponding author: xzhang@kbcat.com

Novel demulsifiers based on acrylic random copolymers for heavy crude oils

Flavio Vazquez*†[1], Edgar Hernández , Edgar Zamora[1], Alfonso López[1], Fernando álvarez , and César Flores[1]

[1]Instituto Mexicano del Petróleo (IMP) – Eje Central Lázaro Cárdenas Norte 152 Col. San Bartolo Atepehuacan, México D.F. C.P 07730, Mexico

Abstract

Most common surfactants employed to remove water and salts from petroleum are polyether block copolymers. However, along heavier crude oils, with high asphaltene contents, are extracted more stable water in oil emulsions are formed. The efficiency of conventional demulsifiers to eliminate such emulsions is limited. In addition, polyethers and polymeric resins suffer a strong chemical degradation when operations of acid stimulation of wells are performed, producing a sensible reduction of their demulsification capacity. Considering all these problems, a series of random acrylic copolymers were synthesized, varying their composition and average molecular weight. These copolymers could be easily dispersed in a series of crude oils (from light to extra-heavy crude oils). It could be stablished that their dehydrating efficiency depends strongly on their comonomers composition and the polymer chain length. Acrylic random copolymers are resistant to chemical degradation induced by acid. It was also observed that for every kind of petroleum there is a specific copolymer molecular weight which produces a maximal water removal. The clarification of the extracted water depends specially on the copolymer composition. The random acrylic copolymers exhibited a performance better than those of commercial formulations of demulsifier agents. This behavior could be explained in terms of the mechanism of emulsion destabilization, which was studied by Dissipative Particle Dynamics (DPD). Whereas polyethers in petroleum start the drop coalescence by tunneling, acrylic random copolymers induce a direct and fast drop approach. These new demulsifiers are prepared by an environmentally friendly and low cost process.

---

*Speaker

†Corresponding author: fvmoreno@imp.mx

Scaling-up and industrial evaluation as petroleum demulsifiers of bifunctionalized block copolymers

Flavio Vazquez*[1], Alfonso López†[1], Fernando Alvarez[1], and César Flores[1]

[1]Instituto Mexicano del Petróleo (IMP) – Eje Central Lázaro Cárdenas Norte 152 Col. San Bartolo
Atepehuacan, México D.F. C.P 07730, Mexico

Abstract

The extraction along the time of heavier crude oils, with greater contents of asphaltenes, makes more difficult to remove their water emulsions. Conventional demulsifiers, such as polyethers, show a limited efficiency to remove salts and water dispersed in heavy petroleum. Most common polyethers are propylene oxide (PO)-ethylene oxide (EO) block copolymers with OH-groups at the chain ends. This chemical groups can react with H+ and induce the polymer degradation at low pH, which implies that the demulsification in triphasic separators reduces its rate or even stopped after operations of acid stimulation of wells. An alternative to increase the demulsifying efficiency of PO-EO block copolymers is to graft amine groups at the end of the polymer chains. In addition, the amines at the end of the polymer chains cannot be attacked at low pH conditions. A series of block copolymers of different composition and molecular weight were synthesized and, afterwards, functionalized with different amines. These molecules were evaluated in different kinds of petroleum, from light to heavy crude oils. In all the cases, the functionalized block copolymers exhibited a dehydrating efficiency greater than those of commercial demulsifiers. Once the high performance of these novel dehydrating agents was stablished, their synthesis process was optimized in order to scale up the preparation of these functionalized block copolymers and fabricate several tons of the product. The PO-EO block copolymers, bifunctionalized with amines, were dosed during several hours in a stream of heavy crude oil (50 000 bbl/d), in an interval of temperatures between 40 and 60 $\circ$C. It could be observed an efficiency of the new demulsifiers higher than that of commercial polyethers. When operations of acid stimulation were performed, the demulsification was not stopped but, on the contrary, their efficiency increased sensibly because the chemical protonation of the amines at the copolymer ends.

---

*Speaker

†Corresponding author: alopezo@imp.mx

Novel silicon-free antifoaming agents evaluated at laboratory and industrial level

Flavio Vazquez*[1], César Flores†[1], Edgar Hernández[1], Enrique Cevada[1], Alfonso López[1], and Fernando álvarez[1]

[1]Instituto Mexicano del Petróleo (IMP) – Eje Central Lázaro Cárdenas Norte 152 Col. San Bartolo Atepehuacan, México D.F. C.P 07730, Mexico

Abstract

Silicone are often employed to suppress petroleum foams in biphasic separator, producing contamination of crude oils and severe problems of catalyst deactivation during refining stages. Commercial alternatives to silicon defoamers show very low efficiencies to control foaming. A series of acrylic polymers were developed as a low-cost alternative to silicon based defoamers. The chemical composition and chain length were varied. The different acrylic chains were dosed into gasified heavy crude oil and their capacity to suppress foam was evaluated. It was observed that there is a strong influence of the chemical composition and molecular weight on the defoaming efficiency of the polymers. For each kind of petroleum there is an optimal polymer length to suppress the foam formation. The new acrylic defoamers exhibited a performance better than silicone and free silicone commercial defoamers. Afterwards, the synthesis procedure was scaled up in order to fabricate an acrylic defoamer at industrial level. The acrylic defoamer was dosed into a biphasic separator which process 50 000 bbl/d. It could be shown than the new IMP acrylics are more efficient defoamers than conventional silicone polymers.

---

*Speaker

†Corresponding author: caflores@imp.mx

Study of the demulsification mechanisms of acrylic copolymers employed as dehydrating agents of heavy crude oils

Flavio Vazquez*[1], Fernando Alvarez† , Edgar Hernández[1], Edgar Zamora[1], Alfonso López[1], and César Flores[1]

[1]Instituto Mexicano del Petróleo (IMP) – Eje Central Lázaro Cárdenas Norte 152 Col. San Bartolo Atepehuacan, México D.F. C.P 07730, Mexico

Abstract

The influence of a series of new petroleum demulsifiers, based on acrylic copolymers, on the coalescence stage of water/crude oil emulsions was studied by Dissipative Particle Dynamics (DPD). To analyze the effect of the copolymer, blank simulations and simulations including the copolymer were developed. These simulations were developed in NVT ensemble in a two-drops and two-dimensional model at a temperature of 353 K (80 ∘ C) for a period of 5x106 simulation steps. It was observed that irrespective of the composition of crude oil the aliphatic regions linked to asphaltic, saturated and resin fractions are located on the oil water interface, stabilizing it. Coarse-grained models employed in the generation of meso-molecules could mimic the structural properties of aliphatic and aromatic regions present in asphaltenic, aromatic and resin fractions. The simulations were carried out under periodic boundary conditions cells with reduced and physical densities of 0.98 and 3 g/cm3 respectively. In the blank system, the coalescence of the drops was not observed throughout the simulation. On the other hand, for the simulation in the presence of the acrylic copolymer, the acrylic copolymer is localized in the oil/water interface displacing both resins and asphaltenes from the interface and accelerating the process of coalescence.

---

*Speaker

†Corresponding author: falvarez@imp.mx

Size Exclusion Chromatography of Crude Oils: from Asphaltene Determination to Modelling.

Estrella Rogel*†[1], Kyle Hench , and Richard Dutta

[1]Chevron – 100 Chevron Way Richmond, CA 94801, United States

Abstract

Since the development of gels for use in organic solvent systems, size exclusion chromatography has been used extensively for characterization of asphalts, asphaltenes, crude oils and their fractions. The usefulness of this technique is based on the assumption that the elution volume of a particular compound is related to its molecular size or to some size-related parameter. In this work, we analyzed the elution behavior of dozens of crude oils and developed a methodology that allows the determination of asphaltene content by using SEC. This technique uses a simple calibration and takes around 12 min to evaluate asphaltene content. Analysis of the elution patterns using different detectors as well as molecular modeling of asphaltene molecules shed light on the elution mechanism. In particular, we will present the evaluation of molecular sizes of asphaltene molecules and their comparison with polyethylene molecules commonly used to calibrate SEC columns.

---

*Speaker

†Corresponding author: ERGC@chevron.com

FA-P10

Boiling and aphroicity of oil mixtures

Mélanie Arangalage*[1], Laurence Talini , and François Lequeux

[1]Laboratoire de Physico-Chimie des Polymères et des Milieux Dispersés (PPMD) – CNRS : UMR7615, Université Pierre et Marie Curie (UPMC) - Paris VI, ESPCI ParisTech – 10, Rue Vauquelin 75231 Paris Cédex 05, France

Abstract

After extraction of crude oil, undesirable foaming can occur within the gas/oil separators leading to unwanted production shutdown: risks of liquid carry-over and gas carry-under interfere with the gas/oil separation process. The objective of my PhD is to understand the role played by asphaltenes on the formation and the stability of oil foams. To this end, several experiments are conducted. To understand the foam stability, a set up has been designed to study the lifetime of single bubbles generated in alkane/toluene mixtures in the presence of asphaltenes. We observe that the lifetime of the bubble depends dramatically on the asphaltenes presence. However, this phenomenon is intricate with the evaporation of the solvent – that can also increase the lifetime of bubbles. We will discuss these phenomena in the frame of Marangoni effect.

---

*Speaker

Crystal Growth of Clathrate Hydrate from Water Drops in Cyclopentane

Jorge Peixinho*[1], Valentin Ageorges[1], and Benoît Duchemin[1]

[1]Laboratoire Ondes et Milieux Complexes, CNRS and Université Le Havre Normandie – CNRS : UMR6294, Université du Havre – France

Abstract

Clathrate hydrates are icelike crystalline compounds with encaged guest molecules trapped inside the cages of hydrogen bonded water molecules. Hydrate growth is visualized for cyclopentane molecules within water drops of two microliter on glass (hydrophilic) and polytetrafluoroethylene (hydrophobic). The drops experience a temperature cycle where they freeze into ice balls, form hydrates and dissociate to liquid drops. Their morphology is tentatively related to the interfacial tension between water and cyclopentane, which is measured for different temperatures and for different concentrations of an oil-soluble surfactant: sorbitan monooleate (Span 80). This study describes cyclopentane hydrate crystal characteristics during the lateral surface growth and demonstrates the effect of the oil-soluble surfactant sorbitan monooleate (Span 80) on the hydrate crystal growth. The morphology seen here could be relevant for explaining the behavior of hydrate emulsions, that could be used as model systems for flow assurance studies.

---

*Speaker

ON THE STRUCTURE-SOLUBILITY RELATIONSHIP OF ASPHALTENES IN IONIC LIQUIDS USING COSMO-RS

Jose Manuel Dominguez*[1], Raiza Hernandez-Bravo[1], Alma Delia Miranda[1], and Omar Martinez-Mora[2]

[1]Instituto Mexicano del Petróleo (IMP) – Eje Central Lázaro Cárdenas Norte 152 Col. San Bartolo Atepehuacan, México D.F. C.P 07730, Mexico
[2]Universidad Veracruzana (UVer) – Mexico

Abstract

A computational study was made to determine the solubility behavior of 17 ionic liquids with asphaltenes and a quantum chemical DFT approximation with a triple valence polarized atomic basis set (def-TVZP) and the Perdew-Burke-Ernzerhof (PBE) density functional. The conductor-like screening model for real solvents (COSMO-RS) was used to determine the density, molar volume, viscosity and heat capacity by means of a statistical thermodynamic treatment of interacting surface charge of the single molecules. The solubility parameter of ionic liquids and asphaltenes was determined using the relationship of density and solubility parameters proposed by Panuganti et al. The results of thermodynamic properties and solubility parameters were compared with the experimental data, then a close agreement was verified. The relative solubility of the asphaltenes in ionic liquids was determined using the calculated δ values and the Hansen's sphere method. It was found that the structure and size of the cation (including the cationic ring head and the alkyl chain length) of ILs have an influence on their ability for dispersing asphaltenes according to the molecular interactions that govern miscibility behavior of ionic liquids and asphaltenes i.e., van der Waals, $\pi - \pi$, cation-π, hydrophobic interactions.

---

*Speaker

ON THE MOLECULAR INTERACTIONS OF IONIC LIQUIDS WITH HEAVY OILS ASPHALTENES

Jose Manuel Dominguez*[1], Alma Delia Miranda[1], and Raiza Hernandez-Bravo

[1]Instituto Mexicano del Petróleo (IMP) – Eje Central Lázaro Cárdenas Norte 152 Col. San Bartolo Atepehuacan, México D.F. C.P 07730, Mexico

Abstract

A theoretical study was performed using COSMO-RS, Turbomole using the Kohn-Sham Hamiltonian with the gradient-corrected Perdew-Becke-Ernzerhof (PBE)12 exchange-correlation functional and the Double Numerical plus D- function basis set (DND) were used in the calculations on molecular interactions of ionic liquids (ILs) with asphaltenes from heavy oil. The main purpose consisted on describing the flowing behavior of heavy crude oils, with respect to relevant parameters such as viscosity and surface tension. It was found that upon proper conditions ILs promote disaggregation of asphaltenic dimmers, which is significant for the modification of viscosity and interfacial tension of the heavy oils during transport and handling. The molecular interactions between ionic liquids and asphaltenes may occur by a combination of cation-π pair with dispersive forces (London), which promote disaggregation of the asphaltenic lumps, by lowering viscosity and IFT, which in turn improves the flowing behavior of the heavy oils.

Keywords: Ionic Liquids, Oil Viscosity reducers, π-cation interactions.

---

*Speaker

Convergence of a thermodynamic and a chemiometric approach to model asphaltene stability

Sebastiano Correra*[1] and Silvia Pavoni[1]

[1]ENI – via Emilia, 1 - 20097 San Donato Milanese, Italy

Abstract

Asphaltene precipitation and deposition is a problem that may affect various stages of the process of oil production. It may happen as a consequence of live oil depressurization, in the producing string, and as consequence of blending of different stock tank oils in storage tanks.
The different contexts and different type of available data induced to the development of different tools to predict and afford asphaltene deposition. Asphaltenes stability and their behavior have been faced by two different explaining approaches in Eni: a thermodynamic approach, used for describing aspect related to molecular environment and physical conditions, and a chemiometric approach used for determining the probability of asphaltenes unstability/stability and the related possibility of having compatibility issues in crudes at stock tank conditions.

After statistical analysis, both approaches appear to be correlated and their integration can offer interesting developments, depending on the available data necessary for the evaluation of the stability/compatibility of crudes and their blends.

---

*Speaker

sciencesconf.org:petrophase2017:145103

FA-P15

Model hydrates vs. methane hydrates: a quantitative comparison of adhesion force

Sebastiano Correra*[1], Pier Zonta[2], Alberto Pontarollo[2], and Bernardo Molinas[2]

[1]ENI – via Emilia, 1 - 20097 San Donato Milanese, Italy
[2]EniProgetti – Via Pacinotti, 4, 30175, Venezia Marghera, VE, Italy

Abstract

Formation of hydrate deposits in pipelines and sealines is one of main risks to be addressed in natural gas transport. Relatively small amounts of connate water may give rise, under appropriate conditions, to formation of deposits, and then to production losses. For this reason, in design for subsea development it is always necessary to provide for storage, transport and injection of chemicals, with huge costs.
In order to mitigate or avoid formation of hydrate deposits, it could be possible to avoid hydrate adhesion through an appropriate internal coating. A literature review showed that empirical tests with gas, until now, have given ambiguous and not reproducible results. Slightly better results were obtained with model systems (able to form hydrates at atmospheric pressure), but always doubts remain in this case about the actual representativeness of findings. For these reasons, a new tool has been developed, allowing adhesion stress measurements on true natural gas hydrates.

Several different coatings were selected to mitigate hydrate adhesion, and have been characterized by means of roughness (with different methods), water contact angle and diiodomethane contact angle. Screening tests were then performed, to evaluate adhesion force/energy of model hydrates to these materials. A dynamometer (adhesion tester) was employed to measure the force requested to detach a cuvette, stuck to the tested material by means of THF hydrates.

In order to obtain a quantitative and reliable comparison of better performing materials, methane hydrate adhesion testing was performed by using the new instrument. It is a torsional balance installed inside an autoclave, where it is possible to form methane hydrates. The system may work up to 100 bar, and allows to measure the torque needed to detach methane hydrate from the sample surface. Comparison of results show that some surfaces behave differently with respect to the type of hydrate.
It is possible to conclude that tests performed with THF hydrates at room pressure could not be representative of the behavior of natural gas hydrates at high pressure. Only tests in real operating conditions guarantee reliable results.

---

[*] Speaker

Improving Thermodynamic Asphaltene Modelling

Xiaohong Zhang*[1], Nuno Pedrosa , Richard Szczepanski , and Jean-Luc Daridon

[1]KBC Advanced Technologies Ltd (A Yokogawa Company) (KBC) – Unit 1, 93 Great Suffolk Street, London SE1 0BX, United Kingdom

Abstract

Asphaltenes are the heaviest, most highly polarisable and polydisperse fractions in crude oils that can precipitate and deposit when their solubility limit is reached due to the change of pressure, temperature and/or fluid compositions. Such precipitation and deposition phenomenon can lead to decline in permeability, blockage of well and surface facilities, finally production decrease or termination which has substantial economic impact. Understanding the complex phase behaviour of asphaltenes in crude oils, therefore, is essential for the industries, that both thermodynamic modelling and experimental measurements play a very important role.
Reliable thermodynamic modelling relies on high quality experimental data. This study is to address how the thermodynamic models such as Cubic-Plus-Association (CPA)[1] can be improved and extended with the asphaltene onset data of live crudes measured by Quartz crystal resonator techniques under pressure. The principle of the Quartz crystal resonator technique [2] is based on a direct recording of the dissipation and the frequency of a quartz crystal resonator immersed in the fluid, therefore it is very sensitive and can accurately detect both the upper and lower onset of asphaltenes in crude oils. The experimental measurements can cover a wide range of temperature and pressures which also provide a quality data to assess the predictability of the CPA approach varying with temperature and pressure.

Various types of crude oils are considered in the study including gas injections and crude blending to investigate the effect of the change of temperature, pressure and oil compositions on asphaltenes stability in crude oils. The performance and predictability of the CPA approach is assessed with experimental data.
References:

: Xiaohong Zhang, Nuno Pedrosa and Tony Moorwood, Energy Fuels 2012, 26, 2611–2620.

: Jean Luc Daridon, Marc Cassiède,Djamel Nasri, Jerome Pauly, and Hervé Carrier, Energy Fuels 2013, 26, 4639–4647

---

[*] Speaker

FA-P17

Viscosity of water-in-oil emulsions from different API gravity Brazilian crude-oils

Marcia Oliveira*[1], Luise Miranda[1], and Alexandre Carvalho[1]

[1]Petrobras Research Center (PETROBRAS) – Brazil

Abstract

Water in oil (w/o) emulsions are formed during crude oil production, mainly due to high shear rates near wellbore or equipment, like pumps and valves, during the crude oil flow from reservoir to production facility. The emulsion viscosity is affected by a number of factors, such as: water content, oil viscosity, temperature, droplet size and presence of solids. Although literature has reported that when the water content exceeds a certain value, the dispersion changes to oil in water (o/w) emulsion type, with water as the continuum phase. However, it has not been observed in Brazilian fields. Above a specific water cut value, the oil becomes "water saturated" and the excess of water flows as free water. Thus, two flowing phases can be notice: free water and w/o emulsion. Therefore, the prediction of emulsion stability and its rheological behavior is considered an important parameter in flow assurance fluid characterization. Those data are essential already in production system design phase. This paper in based on a large set of experimental viscosity data for emulsions of Brazilian crude oils, with gravity ranging from 13 to 35 ◦API. The w/o emulsions of crude oils with gravity higher than 35 ◦API and lower than 13 ◦API are not likely to be stable, especially for higher water fractions. On the other hand, intermediate gravity crude oils incorporate up to 70% of water.

Analyzing experimental data obtained for 128 crude oils and their emulsions at different temperatures and dispersed phase volume fractions, it can be concluded that depending on the fluid composition, the emulsion viscosity and stability can vary a lot, being difficult to correlate typical black oil parameters with the emulsion relative viscosity. Emulsions prepared with different crude oils with the same API gravity, for example, show relative viscosity about 6 to 90 at 70% water cut. It was observed that the largest increase in viscosity occurs with crude oil gravity between 20 and 30◦API. These results are largely missed by the available correlations in the literature.

These results show that a better understanding of the rheological behavior and stability of these emulsions is required to predict the pressure drop during the field life.

---

*Speaker

Kinetic Precipitation of Asphaltenes with the Presence of Inorganic Solids

Chaisoontornyotin Wattana*[1], Jingzhou Zhang[1], Samson Ng[2], and Michael Hoepfner*†[1]

[1]University of Utah – United States
[2]Syncrude Canada Limited – Canada

Abstract

This work investigated the influence of inorganic solids on the rate of kinetic precipitation of asphaltenes from diluted bitumen. At a fixed amount of precipitated asphaltenes, higher solid contents significantly enhanced the rate of asphaltenes precipitation, resulting in no significant observable kinetics under certain conditions. The results suggested a heterogeneous precipitation mechanism for asphaltenes exists when inorganic solids are present in bitumen or petroleum samples. A combined homogeneous aggregation and heterogeneous nucleation model was developed to analyze the results. The rate of heterogeneous nucleation was observed to be upwards of 90% faster than the rate of homogeneous aggregation, but as the quantity of precipitated asphaltenes increased, the rate of homogeneous aggregation could exceed that of heterogeneous nucleation. Scanning Electron Microscope with Energy-Dispersive X-ray Spectroscopy was used to investigate the inorganic solid properties. The results suggest that kaolinite is likely the mineral present in the studied samples that exhibit the heterogeneous precipitation mechanism; however, other materials may also behave similarly. This investigation leads to a better understanding of asphaltene aggregation in systems with inorganics solids and provides a simple model that can estimate the rate of asphaltene precipitation under different conditions. Moreover, this work provides a potential new tool to increase the rate of the often-slow kinetic precipitation of asphaltenes using inorganic solids as nucleation sites to reduce experimental time.

---

*Speaker

†Corresponding author: michael.hoepfner@utah.edu

Comparison of Asphaltenes Obtained by Decompression and by CO2 Injection

Marcus Cardoso[1], Fabio Gozzo[1], Daniel Merino-Garcia[2], Watson Loh[1], and Paulo Rosa*†[1]

[1]University of Campinas (UNICAMP) – Brazil
[2]Repsol-Sinopec – Brazil

Abstract

The precipitation of asphaltenes can occur due to the changes in pressure and temperature during the oil ascension from the reservoir or due to composition variation of the system. One example of the composition variation is observed when CO2 is added to increase the oil recovery from the reservoir. In this work, we present some results of asphaltene precipitation from a recombined oil induced by both decompression at constant temperature and CO2 injection. The used dead oil had 3.6% of asphaltene, density of 0.86 g/mL and its asphaltene precipitation onset induced by *n*-heptane was determined as 0.6 mL of *n*-heptane/g of oil. The high-pressure experiments were conducted in a 20 mL (2 cm of inside diameter) variable volume cell equipped with 2 sapphire windows displaced at 180 degrees. At these windows, a solid detection system with a laser at 1550 nm and a transmitted light power detector was mounted in order to detect the onset of asphaltene precipitation. The dead oil was recombined with a natural gas at a gas to oil (GOR) ratio of 120. The system was equilibrated for 24 hours at 84.5 ◦C and 450 bar. For the precipitation induced by pressure reduction, a decompression rate of 1 bar/min was used. After the precipitation onset (380 bar), the pressure was further decreased by 40 bar in order to induce higher amounts of precipitated material. The system was kept at this condition for 3 hours and, after that, an isobaric filtration (filtration medium of 0.5 mm) was conducted to recover the precipitated matter. The filter was rinsed with CO2 to remove the oil phase in contact with the precipitated. The precipitated matter was recovered with toluene and was analyzed by mass spectrometry (LDI-MS). For the precipitation induced by CO2 injection, the recombined oil was equilibrated and the system was decompressed to 405 bar and the CO2 was inject at 1 mL/min. After the precipitation, the system was kept for 3 h at constant conditions and, after that, the isobaric filtration was conducted. The appearance of these recovered asphaltenes were quite different. The material precipitated by CO2 injection was a paste-like and the one recovered from the decompression experiment appeared as a dry powder. In spite of that, the LDI-MS analyses were similar for the two precipitated materials, indicating their similar mass distribution.

---

*Speaker

†Corresponding author: paulorosa@iqm.unicamp.br

sciencesconf.org:petrophase2017:145278

Evaluating Wax Inhibitors Additives in Crude Oils

Jeramie Adams*†1, Frederic Tort‡2, and Jean-Pascal Planche1

1Western Research Institute (WRI) – 3474 North 3rd Street Laramie, WY 82072, United States
2TOTAL Additives and Special Fuels (TOTAL ACS) – TOTAL ACS – 3, Place du Bassin 69700
Givors, France

Abstract

A waxy Wyoming crude oil was treated with two different wax inhibitors additives, a commercial additive (CA) and one provided by TOTAL ACS (WIEP 1503). The oil was treated with the additives at the same wt% of active material, and the performance of the additives was determined from cold finger tests and centrifuging. Cold finger tests clearly showed that the WIEP 1503 additive was significantly better at reducing the amount of wax that adhered to the cold finger. Likewise, centrifuge experiments showed that the volume of the wax plug that concentrated at the bottom of the centrifuge tube was consistent with the results of the cold finger tests. Insight into the wax dispersion mechanism between the two additives was gained from the Waxphaltene Determinator (WD) separation profile. The CA significantly reduced the amount of microcrystalline enriched wax in the system by making them become more soluble, which was also verified by centrifuge experiments. On the other hand, the WIEP 1503 additive behaved more like a particle dispersant, possibly due to steric stabilization, since it doesn't reduce the amount of microcrystalline wax to the same level as the CA. However, the WIEP 1503 additive does keep the waxes from concentrating during centrifuging and sticking to the cold finger. The two additives were also evaluated on a West African crude oil which contained significantly more wax, and on a lower wax containing tight oil, both of which are solidified at ambient temperatures. At the dosage level tried, the additives had little impact on the highly waxy West African crude oil, but were effective at reducing the pour point of the tight oil. The reduction in the pour point of the tight oil was also confirmed by WD profile, which showed that as the amount of microcrystalline enriched waxes were reduced the pour point was likewise reduced. Additionally, the WD profile showed that the more microcrystalline-oil-insoluble waxes-are more concentrated in the WD fraction that is obtained by dissolving precipitated material in heptane at 60 ◦C (Waxy B). High temperature GC-MS also shows that these oil-insoluble waxes are more concentrated in higher molecular weight alkanes than the waxes contained in the maltenes fraction. WD analyses of waxes that deposited on the cold finger were also demonstrated to be more concentrated in the microcrystalline enriched Waxy B fraction.

---

*Speaker
†Corresponding author: Jeramie.adams@uwyo.edu
‡Corresponding author: frederic.tort@total.com

EVALUATION OF ASPHALTENE INHIBITION BY MOLECULAR MODELING

Peter Seidl*[1] and Peter Seidl*†

[1]Escola de Química da Universidade Federal do Rio de Janeiro (EQ/UFRJ) – Brazil

Abstract

Solid deposition is one of the most serious problems that arise in oil production. Well and oil pipeline clogging can lead to operational delays and result in very significant cost elevations. The precipitation of asphaltenes is caused by a number of factors, including changes in P, T and composition of a crude oil, mixing crudes with other oils or diluents, or the presence of insoluble material such as inorganic salts or paraffin/wax crystals. The tendency of certain oils to flocculate and form deposits is attributed to asphaltenes and their respective molecular interactions.

The efficiency of an asphaltene deposition inhibitor may be evaluated by molecular modeling. This technique allows the interaction of asphaltenes with the inhibitors to be tested and thus ensure economy in the process synthesis of these compounds. The knowledge of the chemical structure of asphaltenes is very important in computational studies, since the chemical structure reflects the quality of the estimates of the chemical properties of these components. Molecular mechanics and molecular dynamics have shown that due to the large conjugated π-electronic system, the dispersion interaction is fundamental to the strength of the aggregation interaction among asphaltene molecules

The present study evaluates asphaltene stability in the presence of inhibitors and compares the efficiency of different types of potential inhibitors for the depositon of certain asphaltene structures. The importance of distinct features of the inhibitor is investigated in the process of asphaltene-inhibitor interaction by Molecular Modeling using the COMPASS force field. Specific interactions of selected asphaltenes and inhibitors were studied by DFT SVWN/6-31G(d,p) melhod with corrections for *BSSE- (Basis Set Superposition Error)*. The roles of aromatic rings and unsaturated sections are discussed.

---

*Speaker

†Corresponding author: pseidl@eq.ufrj.br

Development of a Novel Dynamic Asphaltene Deposition Simulator Coupled with Computational Fluid Dynamics

Aliakbar Hassanpouryouzband*[1], Edris Joonaki†[1], Vahid Taghikhani[2], Ramin Bozorgmehry Boozarjomehry[3], Antonin Chapoy[1], and Bahman Tohidi[1]

[1]Centre for Flow Assurance Research Studies (CFAR), Institute of Petroleum Engineering, School of Energy, Geoscience, Infrastructure and Society, Heriot-Watt University – Riccarton, Edinburgh, EH14 4AS, UK, United Kingdom

[2]Department of Chemical and Biomolecular Engineering, Rice University – Houston, USA, United States

[3]Chemical and Petroleum Engineering Department, Sharif University of Technology – P.O. Box 11365-9465, Tehran, Iran, Iran

Abstract

Asphaltene deposition is a serious concern in the oil production and often during refining processes. Many oil reservoirs containing asphaltenes can be produced without any asphaltene deposition problem until the oil stability is disturbed or destabilized due to pressure depletion, temperature variations, flow variations, mixing with other crude streams and addition of gas or gas & liquids. When conditions change and equilibrium is disturbed, asphaltene nano-aggregates can form larger aggregates and might stick to the rock/pipeline surfaces. Asphaltene deposition is a complex phenomenon and depends on many factors, and the goal of this research study is to shed lights on the underlying physics of asphaltene deposition and take them into account for development of a new model. There are several attempts in the past to develop asphaltene deposition models to simulate the deposition profiles along a flow path. However, there is still lack of a comprehensive simulator to forecast the possibility of asphaltene deposition and quantify the amount of deposited asphaltenes in a flow line with consideration of all respective parameters and mechanisms.

In this study, a novel dynamic simulator for asphaltene deposition along the wellbores based on object oriented programming method has been developed. Computational structure of the simulator, i.e. back-end code, was designed using an improved hierarchical model which is divided into three main parts: 1- Thermodynamics 2-Fluid dynamics. 3-Mass and heat transfer. Regarding the thermodynamics part, the PC-SAFT equation of state was used to predict the fluid phase behaviour using Gibbs minimization method. In fluid dynamics part, the k- turbulence model using finite volume formulation was utilized to simulate the fluid flow along the wellbore. For the mass and heat transfer part, 2-D transfer models along the z and r axis were employed. In addition, asphaltene particles were classified in different particle sizes of which were determined using calculating kinetics of asphaltene aggregation along the wellbore in mass transport module. Kinetics of asphaltene precipitation and deposition also

---

*Corresponding author: ah63@hw.ac.uk

†Speaker

were considered as boundary conditions in mass transport module. All calculations were explicitly linked to each other at each time step. A user-friendly front-end was designed which is connected to the computational back-end via a strong data binding structure.

This dynamic asphaltene deposition simulator, as a new tool, provides a framework to investigate the relative sensitivity and importance of various physical and chemical processes linked to asphaltene deposition. For a quantitative analysis of all simulation results, the asphaltene dynamic behaviour was investigated in a defined wellbore system, all parameters of which were defined according to realistic data. Furthermore, for validation of the simulator, results of this modelling study were compared with real well data and excellent agreement was obtained.

FA-P23

RGB Image Analysis as a promising tool for studies involving wax deposition in the petroleum industry

João Cajaiba*†[1], Allan Belati‡[1], Alex Queiroz§[1], and Lucas Pimentel[1]

[1]Federal University of Rio de Janeiro – Brazil

Abstract

The deposition of paraffin on equipment that occurs during oil production is a common difficulty for the oil industry. When pipelines are located in cooler environments, paraffin crystallizes and forms solid deposits, resulting in economic loss due to flow blockage. One crucial indicator of the potential for oil to deposit paraffin is the wax appearance temperature (WAT), the temperature at which crystals are first detected. This study evaluated the possibility of using image analysis to determine the WAT. Red, green, and blue (RGB) image analysis is a technique that uses a camera as a sensor that converts the light intensity values detected by the sensor into storable, digital bit values. A graph is then generated showing the RGB color pattern variation during a specific process, comparing to the original image. This study also compared RGB image analysis with other techniques, such as Focused Beam Reflectance Measurement and Heat Flow Calorimetry, as well as with gas chromatographic evaluation of the paraffin composition throughout the crystallization process. RGB image analysis was able to determine the WAT in both batch and flow modes. RGB Image analysis, a cheaper, faster and easier technique, proved to be efficient and accurate once the values of the WAT for a given cooling rate were validated through other techniques. The results of this study open the door to the possibility of comparative testing of the chemical inhibitors used to reduce wax deposition.

---

[*] Speaker

[†] Corresponding author: cajaiba@iq.ufrj.br

[‡] Corresponding author: allanbelati@yahoo.com.br

[§] Corresponding author: alex.queiroz@live.com

sciencesconf.org:petrophase2017:145331

Influence of hydrodynamic parameters on the performance of a wax inhibitor evaluated in a Rotating Cold Finger device.

Guilherme Lima*[1,2], Felipe Fleming[1,2], Lilian Padula[3], and Luis Azevedo[2]

[1]Centro de Pesquisa e Desenvolvimento da Petrobras – Brazil
[2]Departamento de Engenharia Mecânica da Pontifícia Universidade Católica - Rio de Janeiro – Brazil
[3]Nalco Champion - An Ecolab Company – Brazil

Abstract

Paraffin inhibitors are chemicals formulated with the aim of retarding the deposition rates of the system. Its efficiency evaluation is usually performed in the laboratory by inducing the deposition of paraffins on a cold surface.
In the so called "cold finger" apparatus, a metal cylinder kept at a temperature lower than WAT (Wax Appearance Temperature) is introduced into an oil sample, which is maintained above the WAT. The precipitation of paraffins at the cold surface leads to the formation of a deposit that can then be measured. Tests with inhibited oils allow evaluating the ability of the chemical to reduce the deposition rate, or to provide morphology changes in the deposit, making it more susceptible to mechanical removal.

Besides the imposed temperature gradient, other parameters such as the bulk viscosity and the flow regime may influence in the deposition process. The diffusivity of the medium is a function of its viscosity. In addition, the crystallization of paraffins promotes important changes in the rheological character of the fluid, introducing non-Newtonian flow behavior. Several published experimental data also indicate that the rate of deposition is correlated with the Reynolds number of the flow.

In the present work, a rotating cold finger apparatus was used. In this type of equipment the cylinder immersed in the oil sample rotates with a constant angular speed, inducing a Taylor-Couette type flow in the sample containing vessel. Two model fluids were prepared with equal concentrations of the same paraffins (same n-alkane distribution). Only the solvent was changed so that the fluids presented different viscosities.

Cold finger tests were performed by varying the viscosity of the fluid and the Reynolds number with and without the presence of an inhibitor. Two values of the Reynolds number were evaluated. The Reynolds number was calculated based on the cylinder rotational speed and on the gap space, as it is usually done to characterize Taylor-Couette flows. Thus, a set of experiments was conducted under the same Reynolds number, but varying the fluid viscosity, while a second set of experiments was performed under the same bulk viscosity and varying the flow Reynolds number.
The results obtained lead to the conclusion that, for a constant value of the imposed temperature gradient, the chemical inhibition is a function of the operating conditions imposed

---

*Speaker

sciencesconf.org:petrophase2017:145356

on the cold finger. Analysis of the paraffin content of the deposits obtained by HTGC (High Temperature Gas Chromatography) shows reduction of porosity in the presence of the inhibitor, a fact already observed in other published studies. The observed dependence of wax deposit formation and inhibition on the flow hydrodynamic parameters is an indication that further studies are necessary to clarify the performance of inhibitors under different hydrodynamic conditions. In fact, due to the significant differences between the complex flow structures present in Taylor-Couette flows and those in pipe flows encountered in field applications, further inhibition studies under field flow conditions are highly recommended and will be performed.

Effects of pH and temperature on the properties of Langmuir film containing asphaltenes

Ronaldo Gonçalves*†1 and Clara Kabbach

1Fundação Inaciana Pe Saboia de Medeiros (FEI) – Brazil

Abstract

Crude oil asphaltenes represent an oil fraction extracted with base on its solubility in aliphatic organic solvents, which is constituted by a wide series of chemical species, including the most polar and the most interface active compounds from the petroleum. Asphaltenes have also been involved in oilfield problems related to the phase behaviour and solid deposition that are able to make unfeasible the oil flow in pipes and to damage the displacement process through the reservoir-rock porous. Besides, asphaltenes are also participants of the stabilization process of oil-in-water emulsions proposed to pipeline heavy oils. In emulsion formulation processes, asphaltene fraction is able to interact with several others components added into emulsion composition to improve its properties. In this study, asphaltenes were extracted from a light crude oil using n-pentane as flocculating. Asphaltene films in the air–water interface were investigated using a Langmuir trough. The films were prepared from dichloromethane spreading solution and their properties were evaluated by means of constant compression rate at different temperatures and pH of the subphase. Surface pressure - area and surface potential - area isothermal curves were built. Results were interpreted from mathematic modelling and determination of the model parameters. Data shows the compression dynamic of films depends on the both temperature and pH. Gaseous phase was not identified. However, the films presented extensive region for liquid-expanded and liquid-compressed phases and a well-defined transition point in-between. At 10 Celsius degrees, the lower surface pressure was found to be 36 mN/m at pH 2. The higher surface pressure was 52 mN/m at pH 8, at the same temperature. Properties of asphaltene Langmuir films showed to be affected by the ionization of acid and basic groups on the asphaltene structure. The curve analysis indicated different phase transition points for surface pressure and potential pressure curves.

---

*Speaker

†Corresponding author: rgsantos@fei.edu.br

sciencesconf.org:petrophase2017:145367

Experimental and Modeling Methods to Predict Asphaltene Deposition Tendency

Mohammad Tavakkoli[1], Fei Wang[1], Sara Rezaee[1], Sai Panuganti[1], Jun Kuang[1], and Francisco Vargas*†[1]

[1]Chemical and Biomolecular Engineering Department, Rice University – 6100 Main St., MS-362, Houston, Texas, 77005., United States

Abstract

It is well accepted that asphaltene precipitation is a necessary but not a sufficient condition for its deposition, which is a severe problem in oil production. Although, we fully agree with this statement, it is a common misunderstanding that thermodynamic modeling can only predict the onset of asphaltene precipitation and therefore, it is unable to predict the actual deposition tendency. While the kinetics and hydrodynamic effects play key roles on determining the rate of asphaltene deposition, the sticking and spreading tendency can be estimated using the effective Hamaker constant in the Lifshitz theory (Gonzalez, 2008). The Hamaker constant can be expressed as a function of refractive indices and, through the one-third rule (Vargas and Chapman, 2010), as a function of the density of the asphaltene lean and rich phases. Therefore, the Hamaker constant can be estimated from equations of state that can predict accurate liquid densities, such as the PC-SAFT EOS. Furthermore, the asphaltene rich and lean phases formed upon addition of a normal alkane to a dead oil sample, can be analyzed at ambient conditions and the asphaltene rich-phase sticking and spreading tendency at the wellbore conditions can be estimated using the proposed thermodynamic modeling framework. The relationship between the Hamaker constant and the asphaltene deposition tendency is being validated through deposition experiments using a packed-bed column at various temperatures and oil/n-heptane ratios. Although using this simulation approach may not be feasible to quantify the rate of asphaltene deposition, we intend to provide a simple discrimination method between potentially problematic and non-problematic wells, by looking at the sticking and spreading tendencies of the precipitated asphaltene-rich phase. Furthermore, we also intend to estimate the performance of coated surfaces on their ability to reduce asphaltene deposition under more realistic conditions.
Keywords: Asphaltene Deposition, PC-SAFT EOS, Hamaker Constant.

References

Gonzalez, Doris L. 2008. "Modeling of Asphaltene Precipitation and Deposition Tendency Using the PC-SAFT Equation of State." Ph.D. Thesis, Rice University.

Vargas, Francisco M., and Walter G. Chapman. 2010. "Application of the One-Third Rule in Hydrocarbon and Crude Oil Systems." *Fluid Phase Equilibria* 290 (1–2): 103–8. doi:10.1016/j.fluid.2009.12.004.

---

*Speaker

†Corresponding author: fvargas@rice.edu

Asphaltene and wax precipitation measurements in live crude oils under high pressure

Hervé Carrier*[1] and Jean-Luc Daridon[1]

[1]Laboratoire des Fluides Complexes et leurs Réservoirs (LFC-R) – Université de Pau et des Pays de l'Adour [UPPA], CNRS : UMR5150, TOTAL – BP 1155 - 64013 Pau, France

Abstract

Direct observation of phase transitions are hard to achieve in live oils under pressure due to the high level of opacity of crude oils. Because of this difficulty, various methods have been proposed to detect indirectly phase changes by monitoring physical properties such as volumetric, calorimetric, and dielectric properties and by noting the point of discontinuity in these properties during scanning experiments. However, in some crude oils, the discontinuity is not so pronounced and phase changes only result in small variations in physical properties. For such fluids, an interesting alternative consists in using acoustic measurements which can be carried out with a high degree of accuracy including at high pressure, and which presents the advantage of giving access to various derived properties.

Acoustic sensors are conveniently small, very sensitive and capable of measuring a variety of input quantities depending on the wave mode and the configuration chosen. It is because of these far-reaching characteristics that acoustic sensors have been more and more used in chemical and biochemical sensing as well as in measuring physical properties. All these potentialities have been exploited here for the development of an acoustic technique for probing both liquid-vapour and liquid–solid phase separations. The experimental setup used to determine phase changes by such acoustic technique involves an automatic PVT cell containing a quartz crystal resonator connected to a network analyzer and an additional syringe pump. It allows carrying out constant mass expansion measurements and isobaric cooling (or heating) experiments. It is also able to perform high pressure titration experiments by injecting at fixed rate liquid or gas solvents within the PVT cell.

The proposed technique was used here to determine the full P, T phase diagram of a north sea crude oil in the pressure range 0.1 to 100 MPa for temperature between 293 to 393 K. The bubble points were measured by constant mass expansion experiments whereas waxy solid appearance temperatures were determined during isobaric cooling measurements. Finally, the asphaltene instability domain was estimated by doing pressure scanning experiments at fixed temperature. The upper asphaltene onsets were determined during expansion measurement whereas the lower asphaltene thresholds were measured during compression experiments starting from the liquid vapour domain.

---

*Speaker

sciencesconf.org:petrophase2017:146516

FA-P28

Development of a Paraffin Inhibitor Suitable for Subsea Applications

Abhishek Golchha*[1], Michael Newberry[1], Paul Stead[1], and Emanuel Marsis[1]

[1]Baker Hughes (BHI) – United States

Abstract

Paraffin Inhibitors are routinely used in oil and gas fields to prevent wax deposition in flow lines and pipelines. In many applications in offshore deepwater fields, paraffin inhibitors are injected subsea at wellheads via umbilicals. The work presented in this paper is related to the development of a paraffin inhibitor that can withstand the conditions of deepwater application and enable the operator to inject the chemical reliably through an umbilical.
The different formulations were tested using a low-temperature centrifuge test to determine if the product is thermally driven to separation at lower temperatures. Viscosity measurements using a temperature ramp on a rheometer were also conducted to identify the approximate temperature where a product would begin to form precipitates and gel. Furthermore, a high-pressure umbilical qualification test was conducted on the formulations to determine their suitability under higher pressures and seabed temperatures.

Injection through an umbilical exposes the chemicals to low seabed temperatures (_˜4◦C) and high pressures at injection locations. Under these conditions, paraffin inhibitors have a tendency to form precipitates that can deposit and, ultimately, result in the loss of an umbilical. This work includes the study of several different formulations using the active component of a paraffin inhibitor, different solvent systems, and additives that can allow the formulation to be stable at lower temperatures. The final formulation passed all the above tests and was stable up to 8,000psia (maximum pressure tested) on the umbilical loop test. In this test, a test sample is transported through a tube maintained at _˜4◦C, and the pressure is increased step-wise to measure properties like differential pressure, density change, etc. to determine if the product is suitable at a particular pressure. This was achieved primarily through the use of a novel mixture of organic solvents and additives that enhances the solubility of the active component in the solution, making it more stable at lower temperatures. In addition, the performance of the product was not compromised because benchmark cold finger testing showed comparable levels of inhibition with the new product as with the original paraffin inhibitor.

The need to develop production chemicals that can sustain extreme temperatures and pressures is increasing. This study illustrates the development of a paraffin inhibitor that can be delivered reliably under conditions mentioned above without losing any performance benefits. This work addresses issues faced in offshore deepwater fields with paraffin issues and takes measures to ensure no umbilicals are lost due to blockage of paraffin inhibitors at low seabed temperatures.

---

*Speaker

Evaluation of Asphaltene Deposition – A Systematic Study and Validation of Online Focused Beam Reflectance Measurement FBRM® at Reservoir Conditions

Erika Koroishi*[1], Eddy Ruidiaz†[1], Nilo Kim‡[1], Osvair Trevisan§[1], Gabriel Soares-Bassani¶[2], and Daniel Merino-Garcia‖**[3]

[1]Center for Petroleum Studies, CEPETRO/UNICAMP, Campinas, São Paulo, Brazil – Brazil
[2]Repsol Sinopec Brasil, Rio de Janeiro, Brazil – Brazil
[3]Repsol, Madrid, Spain – Spain

Abstract

The production of crude oil from a reservoir is by no means an easy task. One of the greatest challenges operators may face during the life of a field is the handling of solids. These solids range from inorganic material, such as salts and sand, to organic material that comes from the crude oil (waxes, asphaltenes, hydrates, and naphtenates). Apart from sand, the rest of the solids usually precipitate due to changes in composition (Commingling of fluids), temperature, or pressure.

The aim of this work consists in the evaluation of kinetics of solid formation with Focused Beam Reflectance Measurement (FBRM®) at high pressure conditions, working with live oil.

The first stage of the experimental study was the evaluation of asphaltene precipitation in a batch system, using crude oil at room conditions and heptane. The second one consisted in dynamic test carried out in a loop able to support pressures ca. 300 bar and temperatures up to 70○C. Additionally, an experimental methodology was developed to charge live oil into loop system. The measurements were followed by online Focused Beam Reflectance Measurement FBRM®. The fluid was depressurized in steps, from 300 to bubble point (ca. 50 bar). A greater count of asphaltene particles can be seen for range of 100 – 75 bar. FBRM measurements allowed monitoring asphaltene particle appearance and growth for each stage of depressurization.

---

[*] Corresponding author: erika@cepetro.unicamp.br

[†] Corresponding author: eddy@cepetro.unicamp.br

[‡] Corresponding author: nilo@cepetro.unicamp.br

[§] Corresponding author: trevisan@cepetro.unicamp.br

[¶] Corresponding author: gabriel.soares@repsolsinopec.com

[‖] Speaker

[**] Corresponding author: dmerinog@repsol.com

FA-P30

Obtention of Ionic Copolymer and Terpolymer for barium sulphate scale prevention

Suzanny Carvalho*†[1], Ken Sorbie , Elizabete Lucas , Palermo Luiz Carlos , and Lorraine Boak

[1]Institute of Macromolecules (IMA), Federal University of Rio de Janeiro (UFRJ) – Brazil

Abstract

In oilfield production systems, inhibitors are widely used to prevent mineral scale formation and the most common and efficient way to apply inhibitors downhole is by using squeeze treatments. Scale inhibitors (SI) are able to act to prevent/inhibit mineral scale through two main mechanisms, i.e., nucleation inhibition and crystal growth inhibition. It is well known that phosphonates operate mainly as crystal growth inhibitors and polymeric species work principally, as nucleation inhibitors. Work on the development of polymeric inhibitors has increased over the years, given the very wide range of potential co- and terpolymeric species that are possible. An effective polymeric scale inhibitor would commonly contain one or more of the following functional groups: carboxyl, -COOH; sulphonic, - HSO3; ester, -COOR; phosphonic acid, -PO3H2, etc. In this work, we examine some copolymers and terpolymers containing the **amide** monomer unit; i.e. acrylamide would the apropriate monomer, CH2=CHCONH2.
The aim of this current work was to synthesise and evaluate polymeric inhibitors which are copolymers and terpolymers based on acrylamide, maleic acid and vinyl sulphonic acid monomers. These polymeric *potential* scale inhibitors were synthesized in the Institute of Macromolecules (IMA), Federal University of Rio de Janeiro (UFRJ), and the synthesised polymers were evaluated in the FAST laboratories, Heriot Watt University.

In this current work, two types of test were carried out on the synthesised polymeric products: viz. static BaSO4 inhibition efficiency (IE) tests and static adsorption/compatibility tests. The static BaSO4 inhibition efficiency tests were carried out at 95◦C, pH 5.5 for two different seawater (NSSW)/formation (NFFW) water volume ratios, i.e. 10/90 (NSSW/NFFW) and 60/40 (NSSW/NFFW). The former volume ratio (10/90) gives a much milder barite scaling brine and both of these brine mixes were used for the copolymer and terpolymer testing. Static adsorption/compatibility tests were carried out at pH 6, in a solution volume V = 0.04L of solution, at T = 50◦C using m = 5, 10 and 20g of dolomite (100-315μm) over a range of active SI concentrations from 0- 500ppm.
The IE results show that the terpolymers had better BaSO4 inhibition efficiency when compared to the copolymers for both mixing ratios and it was found, that the –COOH groups had an important role on copolymers/terpolymers performance. During adsorption tests using dolomite mineral substrate, the terpolymers showed a relatively low level of pure adsorption (not precipitation) for both tepolymers POL 3-B and POL 5-B. The pure adsorption mechanism was confirmed in 3 ways, (i) by noting the absolute level of adsorption which was in

---

*Speaker

†Corresponding author: suzannypc@ima.ufrj.br

the region $\simeq$ 0.1 – 0.6 mg/g, which is in the pure adsorption range, (ii) by looking at the pH trends on adsorption, and (iii) by showing that there was no significant changes in either divalent ions or SI concentration before and after the test.

Sand Particle Behaviour in Multiphase Pipeline

Ezzidene Zorgani*†1, Hameed Al-Awadi‡2, Yan Wei§3, and Hoi Yeung¶3

[1]Libyan Petroleum Institute (LPI) – Tripoli, Libya
[2]College of Technological Studies, Public Authority for Applied Education and Training, Kuwait – Kuwait
[3]Cranfield University – United Kingdom

Abstract

Solids transport in oil and gas pipeline is organized under the umbrella of "flow assurance." Unlike issues such as waxes and hydrates. Solids problems have received relatively little interest to date; this is especially true for solids transport in high-viscosity fluids. Operators are to face technical issues some time during crude oil production from a reservoir. There are three technical issues that are critical to sand production for oil and gas operating companies need to address in order to maximize reservoir production while maintaining the integrity of the production facility. These are sand erosion due to high velocity, sand settling due to low velocity and sand monitoring.

In conjunction with oil companies, Cranfield University has embarked on a programme of research to investigate sand transport issues in single and multiphase pipelines. The effects of fluid properties and pipe orientations are being quantified.

---

[*] Speaker

[†] Corresponding author: zorgani@hotmail.com

[‡] Corresponding author: zorgani@hotmail.com

[§] Corresponding author: zorgani@hotmail.com

[¶] Corresponding author: zorgani@hotmail.com

ORALS
Upgrading and Fouling

Optimizing slurry hydrocracking unit performances via a deep characterization of heavy products

Nicoletta Panariti*[1], Luciano Montanari†[1], Francesca Bazzano[1], Lucia Bonoldi[1], Claudio Carati[1], Cristina Flego[1], Stefania Guidetti[1], Alberto Landoni‡[1], and Erica Montanari[1]

[1]Eni S.p.A. – Italy

Abstract

In the upcoming years residue conversion processes will become ever more important in refining industry, mainly due to higher-quality fuels increasing demand and fuel oil reduction: environmental and economic factors are the main driving force for heavy feedstock upgrading. One of the main challenges to face with residue conversion is the capability to handle the asphaltenes contained in the feedstock.
In this paper we present our experience in asphaltene characterization aimed at supporting EST (Eni Slurry Technology) unit operation. EST process objective is maximized yield of light and middle ditillates avoiding formation of coke deposits, inside and outside the reactor. Improvements in the operability and efficiency of this unit requires control or management of coke formation, which can only be achieved through a better understanding of the fundamental mechanisms involved. A deep knowledge of the asphaltene molecular structure and their evolution during the hydrocracking reactions is extremely important in order, to optimize operating conditions and to improve the efficiency of EST process.

Samples from the industrial unit located in Eni's Sannazzaro refinery have been characterized in our laboratories, in order to compare the molecular structure of the asphaltenes after hydrotreating with the asphaltenes contained in the feedstock. In particular, MW measurements have been carried out applying different techniques, since the results are strongly dependent on the analytical methods employed. The data obtained by the more common Gel Permeation Chromatography (GPC) have been compared with the results achieved through more recent techniques: Atmospheric Pressure Photoionization-MS (APPI-MS) and Time-Resolved Fuorescence Depolarization (TRFD). The comparison of the MW values obtained provides some insight into the advantages and limitations of the techniques. All techniques show the reduction of asphaltene MW after hydrotreating, in accordance with the expected reduction of alkyl chains. The same asphaltene samples studied by total scanning fluorescence (TSF) showed a transformation of their aromatic cores during the EST process.

A detailed characterization was performed also on slurry particles recovered from industrial unit samples (Elemental Analysis, XRD and HREM), showing not only the state of EST catalyst but also of the carbonaceous material/coke intrinsically linked to molybdenite and other metals sulphides.

---

*Speaker

†Corresponding author: luciano.montanari@eni.com

‡Corresponding author: alberto.landoni@eni.com

sciencesconf.org:petrophase2017:157269

This work will also focus on some lessons learned from EST unit operation, mostly related to residue stability after hydrocracking. We have developed in house procedures aimed at evaluating the behaviour of the vacuum bottom and other slurry streams in order to better understand the conditions that can promote asphaltene precipitation and fouling, mainly in the fractionation section.

Delayed coker coke characterization: correlation between process conditions, coke composition and morphology

Naydu Zambrano Urrutia*[†1], Martha Niño Gómez[‡1], Hector Picón Hernandez[§2], and Fernando Martinez Ortega[1]

[1]Universidad Industrial de Santander [Bucaramanga] (UIS) – Cra 27 Calle 9 Ciudad Universitaria Bucaramanga-Santander-Colombia, Colombia

[2]Instituto Colombiano del Petróleo (ICP) – Km 7 Autopista a Piedecuesta, Santander, Colombia

Abstract

Coking process offers a solution for heavy and extra-heavy oil treatment, however, the high percentages of coke formed during the process have encouraged the opening of new research towards the analysis and classification of the different morphologies obtained, the purpose is to increasing its value and usage. It is already known that chemical composition of the feedstock and processing conditions influence in the coke morphology: sponge, shot, needle and transition coke. The understanding of nature and factors that control the morphology of delayed coker coke is necessary to avoid the formation of "transition coke". The transition coke increase cycle time and operative risks, however, the knowledge in the case of transition coke is few. The purpose of this study is to shed additional insight in the correlation between surface chemical composition and morphology of delayed coker coke with variables of the process such as: temperature, pressure and elemental analysis of the feedstock. A total of twenty cokes from five vacuum bottoms were provided by ICP-ECOPETROL S.A; four samples per each vacuum bottom were collected taking into account two different temperatures and pressures, the samples were processed in a pilot plant under delayed coking conditions. Analytic results by FT-Infrared spectroscopy showed a decrease of the content of asphaltene and resin phases after a pre-treatment with toluene and n-heptane, which were contaminants of the raw material. By X-ray Photoelectron Spectroscopy (XPS) was possible identify heteroatoms as N, S, Si and O on the surface of the samples, each one associate with some characteristic compounds in coke: pyrrole and pyridine, thiophene and silicon dioxide. Metals were not found in the surface of the solids, however characterization by Atomic Absorption (AA) showed elements as Ni and V in the bulk, this observation confirms the physical segregation of metal entities within coke. Surface specific area between 2-3 m2/g implies the lack of porosity in the material. Morphological classification by SEM showed a mix of associated shot-type, transition and sponge coke. The results of this work allow to verify that low metals amount in the samples are relate to not well-defined shot coke, in agreement with previous reports that associate this morphology with high quantities of Ni and V. In this case, it is possible that this fact in combination with the amounts of nitrogen

---

*Speaker

[†]Corresponding author: naydu_zambrano@hotmail.com

[‡]Corresponding author: marthan@uis.edu.co

[§]Corresponding author: hector.picon@ecopetrol.com.co

sciencesconf.org:petrophase2017:145318

and sulphur on the surface could be influence the formation of transition coke. Finally, a study is needed to determine the effect of Si presence in the samples, the origin of this element is related to the Fluid Catalytic Cracking process. The preparation of carbon derived is possible due to the delayed coker coke characteristics observed.

Increased Asphaltenes Stability in Conventional Crude Oils When Blended With a Bio-Crude Oil

Sai Reddy Pinappu*[1] and Koushik Gumaste*†[1]

[1]Baker Hughes Inc (BHI) – 12645 West Airport Blvd Sugar land, Texas 77478, United States

Abstract

Bio-crudes or green crudes produced from the hydrothermal treatment of biomass such as algae, wood, etc. have the potential to substitute for or be partially mixed with conventional crudes and supplied as a viable feedstock for refining processes. Thus, the effect of blending bio-crude into conventional crude oils has to be studied to evaluate its influence on feedstock quality.

This paper describes the effect of bio-crude on asphaltenes stability when blended with conventional crude oils. Baker Hughes Field ASIT ServicesTM technology was used to study the effect of bio-crude on asphaltenes stability when blended with conventional crude oils at various blend ratios. It was observed that, by increasing the amount of bio-crude added to the conventional crude blend, the overall blend stability with respect to asphaltenes increased compared to the conventional crude oils. Thus, it was discovered that bio-crude addition has a positive stabilizing effect with respect to asphaltenes and can be considered a potentially viable feedstock.

---

*Speaker

†Corresponding author: Koushik.Gumaste@bakerhughes.com

sciencesconf.org:petrophase2017:145217

Characterization and upgrading of catalytic fast pyrolysis oils from pine tree

Sylvain Verdier*[1], Ofei Mante[2], Asger Hansen[1], Josephine Lübeck[3], Jan Christensen[3], Mette Kristensen[3], Kristoffer Poulsen[3], Giorgio Tomasi[3], Jostein Gabrielsen[4], and David Dayton[2]

[1]Haldor Topsoe A/S – Nymollevej 55, 2800 Kgs. Lyngby, Denmark
[2]RTI International – RTI International, Research Triangle Park, NC 27709 USA, United States
[3]University of Copenhagen – Department of Plant and Environmental Sciences, University of Copenhagen, Thorvaldsensvej 40, 1871 Frederiksberg, Denmark
[4]Haldor Topsoe A/S – Nymollevej 55, 2800 Kgs. Lyngby, Denmark

Abstract

Production of biocrudes from wood using catalytic fast pyrolysis (CFP) was successfully investigated by RTI International over the last few years. Using a novel single-step process, biocrudes with low oxygen content were produced in a large-scale CFP unit.

In this study, five biocrudes were produced from loblolly pine at different CFP severities. Each of these feeds was subsequently hydrotreated in a once-through hydrotreating pilot plant unit. The various feeds and related products were thoroughly analyzed using the following methods with special emphasis on oxygenates:

Standard ASTM analyses such as Sim. Dist., elemental analysis, viscosity, MCR, etc.,

GC×GC-FID and GC×GC-TOFMS,

Derivatization followed by GC×GC-TOFMS, and

SFC-TOFMS

These different analytical tools allow us to compare the five feeds and identify key compounds influencing the hydroprocessing step. The characterization of the products enables the identification of the most refractory compounds as well as the understanding of the impact of catalyst deactivation on product composition and properties.

---

*Speaker

Fouling phenomena when processing light crudes

Marco Respini*[1] and Gavin Medine

[1]Baker Hughes (BHI) – Baker Hughes Incorporated 17021 Aldine Westfield Houston, TX 77073, United States

Abstract

Light, paraffinic crude oils appear, at first glance, to carry a low risk of refinery fouling. These crude oils are low in asphaltene content and give the appearance of high stability due to the absence of a well defined flocculation onset in stability tests. Contrary to expectations, refinery processing of these light, paraffinic crudes has often resulted in severe fouling of crude preheat exchangers due to asphaltene deposition and co-deposition of other crude components. This paper presents data from laboratory tests and from modeling analysis of preheat exchanger fouling rates to help explain the fouling associated with light crudes. Mechanisms that can lead to fouling when processing light crudes include the impact of temperature on stability, the compatibility of light crudes and heavy crude blends, shear stress on deposits impacting the rate of removal versus deposition, and the role of waxes on asphaltene precipitation. Field experience confirms the tendency of light crudes to destabilize with increased temperature. Thermodynamic modeling based on Flory Huggins theory shed light on the impact of temperature on stability. The impact of incompatibility of light and heavy crude blends was confirmed by fouling data from refinery units. Higher shear stresses correlate to reduced aggregation of asphaltenes in both laboratory tests and in analysis of heat exchanger fouling factor data. Light crudes high in wax content exhibit asphaltene precipitation even in the absence of light paraffins, with the asphaltenes incorporated into precipitated wax crystals. This paper also discusses mitigation steps to address the fouling risks associated with light, paraffinic crudes. These include modeling to establish improved blending practices and the benefits provided by additives to improve compatibility and reduce rates of fouling.

Understanding the many mechanistic drivers that lead to fouling, and the mitigation options to manage fouling are critical elements for processing these light, paraffinic crudes.

---

*Speaker

sciencesconf.org:petrophase2017:144913

Crude Oil Fouling using a Multi-celled Batch Autoclave and a New Flow through Fouling Apparatus

Jeramie Adams*†[1,2], R. Grimes[2,1], John Schabron[3], and Paul Eaton[4]

[1]Western Research Insitute – United States
[2]Western Research Institute (WRI) – United States
[3]Western Research Institute – United States
[4]Hill Country Labs, LLC – United States

Abstract

Crude oils consisting of a tight oil, Canadian dilbit, Canadian dilbit blended with hydroconverted bottoms, a Wyoming crude, and other crude oil refinery blends were tested for their fouling behavior using a hot wire autoclave type fouling apparatus, with a wire temperature of 320 ◦C-to approximate heat exchanger heating within the preheat train. Fouling experiments revealed that there was unpredictable redistribution of volatiles in the system after the fouling experiments. Despite the sample losing some volatiles into the void space of the autoclave, correlations were found between the amount of foulant deposited on the wire and the asphaltene stability of the crude oils as determined from the saturates, aromatics, resins-Asphaltene Determinator (SAR-AD) separation profile and from the Automated Flocculation Titrimeter (AFT) data. Due to the volatiles loss in the autoclave type fouling unit, a new flow through crude oil fouling unit was assembled at WRI, in which fouling was detected as increased pressure drop through a heated flow loop. Fouling tests with a control crude oil with different blends of heptane showed that fouling increased with added amounts of heptane. Additional fouling experiments with other crude oils, which were also used in the autoclave fouling experiments, showed a correlation between fouling and asphaltene stability.

---

*Speaker

†Corresponding author: jadams32@uwyo.edu

sciencesconf.org:petrophase2017:144608

UF-O6

Molecular Characterization and Modeling for Crude Oil and Reactors

Shu Wang*[1], Suphat Watanasiri†[1], Darin Campbell[1], and Zhen Hou[1]

[1]AspenTech Inc. (AspenTech) – 20 Crosby Drive Bedford, Massachusetts 01730 USA, United States

Abstract

Simulation of refinery-wide processes helps the petroleum industry to design, optimize and operate refineries profitably and safely, while meeting all necessary regulatory requirements. The traditional pseudo-component approach developed over 30 years ago is still widely used today to represent the feedstocks and products in these process models. This approach uses correlations and heuristics to provide thermodynamic and other properties required in the simulation. For refinery reactor models, kinetic lumps are used to represent molecular classes that undergo reactions to produce the desired products. These kinetic lumps are determined from either finger-print data of the feed or correlations that are based on other properties (such as PNA or sulfur contents) of the feed. Both the pseudo-component and kinetic lump representations contain limited molecular level information. Due to the increasing demands of environment regulations, changing feedstocks, higher margins, etc., the petroleum industry is very interested in improving the accuracy and understanding of the refinery process models and has been exploring the use of molecular information for quite some time. In this presentation, we will describe a framework recently developed to leverage molecular knowledge to increase the accuracy of characterization of crude oil and process simulation. The molecular method was applied to characterize crude oils using traditional laboratory assay data as well as analytical data such as GC-MS (Gas Chromatography), GC/MS-TOF (Time-Of-Flight), and FT-ICR-MS (Fourier Transform Ion Cyclotron Resonance). The resulting molecular compounds, compositions and associated properties are then used to calculate the properties of the process streams. The molecular information is also used directly to represent kinetic lumps composition used in refinery reactor models.

---

*Speaker

†Corresponding author: Suphat.Watanasiri@aspentech.com

POSTERS
Upgrading and Fouling

Photocatalysis & nanomaterials: a clean and economic way to improve asphaltene

Maria Luiza Pereira*†[1], Daniel Grasseschi[2], and Henrique Toma[1]

[1]University of Sao Paulo (IQ-USP) – Brazil
[2]MackGraphe - Mackenzie Presbiterian University (MackGraphe) – Brazil

Abstract

Asphaltene are well known for forming hard scales, difficult to remove that can obstruct pipelines, compromising the flow assurance and also lead to the well shut down.1Their currentlyconversion into asphalt and coke after destructive distillation during oil refinig are an expensive method to eliminate them, requiring very high temperatures.Along with the concern about environment and the limitation of natural and finite sources of energy scientists are pushed to find innovative ways to improve them by converting into valuable raw materials, reducing the environmental impact and the expenses.Metallic nanoparticles are notable for their remarkable optical properties. In conjunction withthe chemically derived graphene, an excellent catalyst emerges, coupling enhanced electronic andthermal conductivity, plasmonic properties, biocompatibility and inertness. Photocatalysis onto this kind of materials can provide a clean and economic option for asphaltene removal and oil recovery. In this study,the interactions between nanomaterials and asphaltenes were evaluated by hyperspectral darkfield microscopy and then photocatalysis experiments were performed according to the electronic response observed on the former analysis. Asphaltene are deposited onto films of gold nanoparticle@reduced graphene oxide (AuNP@RGO), AgNP@RGO (silver) and gold nanorods (AuNR).The electronic spectra indicatesthe occurrence of charge transfer betweenasphaltene and the nanomaterials in all the cases, .Photocatalysis efficiency dependes on charge separation and transport efficiency mainly2, and those results indicate that this class of nanomaterialscan act as photocatalysts forasphaltene's cracking. Using the plasmon excitation for the photooxidation of a model molecule forasphaltene (Fig 1), catalyst in water suspension or film, halogen lamp source, and synthetic air, 90 % of bis(2-ethylhexyl) phthalate (Fig 1) was obtained when the AuNP@RGO was used as catalyst, and a good yield was achieved also with AuNP, 76%, and without catalyst no important product was formed.We propose that the asphaltene'scracking, in room temperature,occurs via generation of reactive oxygen species driven by the photo-excited electrons from the AuNP and the RGO, leading to less toxic and most valuable products.

1. Kamran Akbarzadeh, Ahmed Hammami, Abdel Kharrat, Dan Zhang, Jeferson Creek, Shah Kabir, A Jamal Jamaluddin, Alan Marshal, Ryan Rodgers, Oliver Mullins, T. S. Asphaltenes - Problematic but Rich in Potential. *Oilf. Rev.* (2007).
2. Li, X., Yu, J., Wageh, S., Al-Ghamdi, A. A. & Xie, J. Graphene in Photocatalysis: A Review. *Small* 12, 6640–6696 (2016).

---

*Speaker
†Corresponding author: malupereira@usp.br

EVALUATION OF HYDROTREATMENT OF THE EXTRA HEAVY CRUDE OIL ASPHALTENES

Henry Labrador*†[1], Andrea Nardi[2], Miguel Luis*‡[3], and Ligia Llovera*[4]

[1]Laboratorio de Petróleo, Hidrocarburo y Derivados. Departamento de Química, Facultad Experimental de Ciencias y Tecnología. Universidad de Carabobo. Naguanagua, Edo. Carabobo. Codigo Postal 2001 – Venezuela

[2]Lab, de Resonancia Magnética Nuclear, Instituto Investigaciones Cientificas – Venezuela

[3]2Lab. de Catalisis y Metales de transición. Departamento de Química, Facultad Experimental de Ciencias y Tecnología. Universidad de Carabobo. Naguanagua, Edo. Carabobo. – Venezuela

[4]Lab, de Resonancia Magnética Nuclear, Instituto Investigaciones Cientificas (IVIC) – Venezuela

Abstract

In this investigation, a variation of four different catalytic beds was performed in a continuous flow tubular reactor using CoMo/γ-Al2O3 and NiMo/γ-Al2O3 catalysts. The position of the catalysts and the asphaltenes in the catalytic bed was modified for each reaction. The catalysts were activated by a sulfurization process at 350○C for 4 hours and then hydrotreatment (HDT) reactions were carried out at 300○C for 5 hours. A hydroconversion of the asphaltenes of more than 90% was obtained for all the catalytic beds. In the FTIR and RMN studies, the variation of the average structures of the asphaltenes was observed.

---

*Speaker

†Corresponding author: hjlabrad@uc.edu.ve

‡Corresponding author: maluis62@yahoo.es

Crude Oil Fouling using a Multi-celled Batch Autoclave and a New Flow through Fouling Apparatus

Jeramie Adams*†[1,2], R. Grimes[2,1], John Schabron[3], and Paul Eaton[4]

[1]Western Research Insitute – United States
[2]Western Research Institute (WRI) – United States
[3]Western Research Institute – United States
[4]Hill Country Labs, LLC – United States

Abstract

Crude oils consisting of a tight oil, Canadian dilbit, Canadian dilbit blended with hydroconverted bottoms, a Wyoming crude, and other crude oil refinery blends were tested for their fouling behavior using a hot wire autoclave type fouling apparatus, with a wire temperature of 320 ◦C-to approximate heat exchanger heating within the preheat train. Fouling experiments revealed that there was unpredictable redistribution of volatiles in the system after the fouling experiments. Despite the sample losing some volatiles into the void space of the autoclave, correlations were found between the amount of foulant deposited on the wire and the asphaltene stability of the crude oils as determined from the saturates, aromatics, resins-Asphaltene Determinator (SAR-AD) separation profile and from the Automated Flocculation Titrimeter (AFT) data. Due to the volatiles loss in the autoclave type fouling unit, a new flow through crude oil fouling unit was assembled at WRI, in which fouling was detected as increased pressure drop through a heated flow loop. Fouling tests with a control crude oil with different blends of heptane showed that fouling increased with added amounts of heptane. Additional fouling experiments with other crude oils, which were also used in the autoclave fouling experiments, showed a correlation between fouling and asphaltene stability.

---

*Speaker

†Corresponding author: jadams32@uwyo.edu

sciencesconf.org:petrophase2017:144608

UF-P4

Durability of iron oxide catalyst for catalytic cracking of heavy oil with steam

Eri Fumoto*[1], Shinya Sato[1], and Toshimasa Takanohashi[1]

[1]National Institute of Advanced Industrial Science and technology (AIST) – Japan

Abstract

Upgrading of heavy oil such as petroleum residual oil is strongly demanded. We had examined catalytic cracking of atmospheric residual oil (AR) using iron oxide-based catalyst in a steam atmosphere. The catalyst consisted of iron oxide, zirconia and alumina. Heavy oil fractions reacted with lattice oxygen of iron oxide to produce light fractions and carbon dioxide. Then consumed lattice oxygen was supplemented with oxygen species generated from steam. Zirconia promoted the generation of oxygen species and addition of alumina inhibited the structural change of iron oxide.

To investigate the catalytic durability, we conducted catalytic cracking of AR for 2-6 h in a steam atmosphere. The catalyst was prepared by a coprecipitation method. The catalyst was loaded in a laboratory scale fixed-bed reactor. The feedstock solution of AR derived from Middle East crude diluted with toluene was fed to the reactor. The reaction temperature was 748 K, the pressure was 0.1 MPa, the ratio of catalyst to feedstock flow rate was 1.3 h, and the ratio of steam to feedstock was 3.0 g/g. Liquid and gas products were analyzed by gas chromatographs and the used catalyst was analyzed by elemental analysis, X-ray diffractometry, and nitrogen adsorption.

Heavy oil fractions were decomposed with the iron oxide-based catalyst to produce light fractions, carbon dioxide, and carbon residue on the catalyst. Conversion of heavy oil decomposition was almost constant for 4 h, and the conversion slightly decreased after 6 h of reaction. When lattice oxygen of iron oxide is consumed during the reaction, the structure of iron oxide catalyst changes from hematite to magnetite. The structure of 2 h used catalysts showed the mixture of hematite and magnetite. The result indicated that oxygen species were supplied to iron oxide lattice from steam although part of lattice oxygen was consumed during the reaction. The hematite and magnetite structure were maintained after 4 h and 6 h of reaction. The nitrogen adsorption analysis showed that pore of the used catalyst decreased after 4 h of reaction. The carbon residue on the catalyst may cause pore plugging and catalytic activity decrease after 6 h of reaction. Accordingly, combustion of carbon residue on the catalyst could reactivate the catalyst.

---

*Speaker

Enhancing the Efficiency of Scale Inhibitor Squeeze for Mature Fields of the Campos Basin – RJ

Giuseppe Cardoso[1], Francisca Rosário[2], Alexandre Vaz[3], and Joao Silva[*†1]

[1]Federal University of Rio de Janeiro (UFRJ) – Brazil
[2]CENPES/PETROBRAS – Brazil
[3]NORTH FLUMINENSE STATE UNIVERSITY – Brazil

Abstract

The Seawater is used as a method of oil recovery, to maintain the reservoir pressure, ensuring the wells production of producing fields *offshore*. In the oil fields at sea (offshore), it is used seawater. The formation water associated with oil reservoirs may present metal ions concentration in solution which are chemically incompatible with the sulphate concentration in seawater, when this result in a supersaturated mixture of saline water, which may precipitate barium sulfates, strontium and calcium generating scale. Sulfates and other inorganic salts formed can deposit in the pores of the reservoir rock, especially surrounding the producing well, reducing rock permeability and productivity index, besides damaging the well systems and generate additional costs for treatments to restore the equipaments and well productivity.

The main technologies used for control sulfates scales in the nearbore producing wells of oil fields with sea water injection is referred to scale inhibitor squeeze, which constitutes in the sequential injection of treatment fluids through the production well. The scale inhibitor is retained in the pores of the reservoir rock, and then released gradually, when the well returns production, avoiding the scale formation for a certain period of time. Currently, we seek to understand the mechanisms of action of additives that can increase the treatment efficiency and the lifetime threof.

The objective of this study is to assess the calcium ion and a commercial polymer, as additives for increasing the lifetime of inhibiting scale from increasing the ratio of release / retention of inhibitor in the pores of reservoir rock from a specific field in. The experimental results show that both additives have resulted in higher efficiency. The experimental results besides providing a study of a mechanism were used as input data to simulate treatments that result in lifetime extension for a real scale of an oil production well.

---

[*]Speaker
[†]Corresponding author: jfcajaiba@gmail.com

sciencesconf.org:petrophase2017:145001

USE OF SOLVENT DEASPHALTING FOR THE TREATMENT OF OIL SANDS FROM COLOMBIA

Lina Navarro*†[1], Jhon Peñaloza[2], John Arias[3], and Carlos Lizcano[4]

[1]Lina Constanza Navarro Quintero (Lina Navarro) – Km 7 Via Piedecuesta. Colombian Petroleum Institute. Piedecuesta, Santander., Colombia
[2]Jhon Iván Peñaloza Bueno (Jhon Peñaloza) – Km 7 Via Piedecuesta. Colombian Petroleum Institute. Piedecuesta, Santander., Colombia
[3]John Edwar Arias (John Arias) – Colombia
[4]Carlos Eduardo Lizcano Pimiento (Carlos Lizcano) – Km 7 Via Piedecuesta. Colombian Petroleum Institute. Piedecuesta, Santander., Colombia

Abstract

Currently, Colombia is the sixth country largest in daily production of oil in Latin America. For this reason and to the importance of this resource for the economy, the government and oil companies have been interested in the search and exploitation of unconventional sources of oil. In Colombia there are five oil sands deposits (unconventional sources) located in the center and south of the country. However, the extraction and separation of bitumen from oil sands is relatively expensive and poses several environmental challenges. Roughly two tons of oil sands are required to produce a barrel of oil, and the separation of the bitumen from sand and clay requires significant amounts of energy and the use of large quantities of water [1].

In the present work, a methodology was developed, in order to perform simultaneously: solvent deasphalting and the non-aqueous extraction of the improved crude oil associated to Oil Sand. The experiment was completed in four stages. In the first stage, the mineral sampling was realized in the municipality of Pesca, Boyacá, Colombia. In the second stage the material characterization was performed. In the third stage, solvent extraction (solvent deasphalting) was developed and in the final stage, the heat of combustion of residual mineral containing asphaltenes was evaluated. It was found that the Oil Sand analyzed could be classified as Oil-Wet because it had a lower moisture to 2%, and a higher oil impregnation (8%) giving half-defining impregnation. The mineral associated to the Oil Sand, present a quartz and clay content of 95% and 5% respectively, behavior favorable for the extraction process. During the extraction methodology, the recovery yield of deasphalted oil was higher than 70% and solvent recovery above 98% was achieved. The evaluation of the residual material calorific showed near 2000 kJ / kg values.

Performance of Solvent Mixtures for Non-aqueous Extraction of Alberta Oil Sands Energy Fuels, 2015, 29 (4), pp 2261–2267.

---

*Speaker

†Corresponding author: lina.navarro@ecopetrol.com.co

Characterization of Coke as a Spectrum: An Industrial Approach

Roxanne Shank*†[1] and Thomas Mccartney‡[1]

[1]Clean Harbors Energy Industrial Services – Canada

Abstract

The understanding of coke deposit composition in industrial processes is something of a fleeting concept. Coke, in and of itself, is defined as carbonaceous material, yet that is where the definition tends to fall short. For an industrial chemical cleaner, who is charged to remove such deposits from a fouled piece of equipment, defining the material as coke does little in the way of describing the nature of the problem. Coke comes in many different forms, including needle coke, honeycomb coke, sponge coke, shot coke, black powder, and coke fines. Coke can be 'green', or unprocessed, calcined or uncalcined, fuel grade or anode grade. The chemical and physical properties of the coke depend greatly on the hydrogen and oxygen content, as well as the presence of other elements, such as sulfur, iron, copper, magnesium, manganese, vanadium, and nickel. The temperatures, pressures and length of time used in the refining processes also have a large impact on the crystal form and reactivity of the material. Over 30 different coke samples were analyzed with large variations in chemical composition, wettability and crystal structure. These variations in composition lead to the beginning of a definition of the coke spectrum. Where a particular deposit falls on this spectrum will help determine the physical and chemical characteristics of the material, and determine the best course of action for the removal of problem cokes deposits on refinery equipment within the industry.

---

*Speaker

†Corresponding author: shank.roxanne@cleanharbors.com

‡Corresponding author: mccartney.thomas@cleanharbors.com

sciencesconf.org:petrophase2017:145293

Isolation and Characterization of Asphaltenic Species that Disproportionately Contribute to Aggregation

Steven Rowland*†[1,2], Martha Chacón-Patiño[2], and Ryan Rodgers[1,2]

[1]Future Fuels Institute (FFI) – 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, United States, United States

[2]National High Magnetic Field Laboratory (NHMFL) – 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, United States, United States

Abstract

Asphaltene precipitation and deposition play major roles in fouling concerns for both upstream and downstream applications. The propensities for extensive self-association and adsorption to mineral surfaces are the driving forces behind deposition in reservoirs, pipelines, and refinery processes. These aggregates have also proven to stabilize emulsions and poison upgrading catalysts. The remarkable complexity of asphaltene samples has proved to be a barrier to the complete understanding of aggregation tendencies, and the ”true” composition of asphaltenes is still widely debated. It is universally accepted that the structure of asphaltenes plays a pivotal role in describing asphaltene precipitation and aggregation; however there is currently no agreement on the structural motifs present in asphaltenes. The classic ”island” model depicts asphaltenes consisting of one poly-nuclear aromatic core with peripheral alkyl side chains; whereas, the more recent ”archipelago” model includes bridged aromatic moieties that may contain multiple polar functionalities. Given the complexity of asphaltenes, it is likely that both island and archipelago compounds are present in most crude oils. The work presented here focuses on the development of an extrography fractionation to extend the molecular understanding of asphaltenes and to provide further insight asphaltenes that are most responsible for aggregation. Asphaltenes were adsorbed to a silica gel stationary phase and soxhlet extracted with a series of solvents designed to selectively remove aphaltenes based on structural features and solubility. A total of eight fractions were collected, and it was observed that the earliest eluting fraction (fraction 1) resembled the whole asphaltene when analyzed by FT-ICR MS. The analysis of fractions 3-8 revealed chemical compositions that were not observed in the whole asphaltene, and thereby greatly extended the number of ionized and assigned species by greater than two-fold. An increase in the number of heteroatom containing compounds was also observed with increasing fraction number, and the most polar compounds appear to elute latest in the extraction. The analysis by positive-ion atmospheric pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry [(+) APPI FT-ICR MS] of fractions 5-8 proved much more difficult due to limited solubility/aggregation, and ion accumulation times were greater than one order of magnitude longer when compared to fraction 1. Further analysis was conducted by size-exclusion chromatography in 100% toluene. The chromatographic elution of fractions 1 and 6 (the fractions with the greatest mass %) were compared to the elution profile of the whole asphaltene. Fraction 1 revealed a tri-modal distribution in size where less than half

---

*Speaker

†Corresponding author: rowland@magnet.fsu.edu

of the sample appears to be in an aggregated state. However, fraction 6 showed extensive aggregation at the same concentrations. This suggests that the compounds most responsible for asphaltene self-association are not typically observed by direct infusion mass spectrometry alone and that the extractive pre-fractionation developed in this work is able to separate asphaltenes based on aggregation tendencies. Thus, the extraction allows for more complete analysis of the asphaltenes that disproportionately contribute to aggregation/precipitation. Work supported by NSF Division of Materials Research through DMR-11-57490.

UF-P9

High Resolution Mass Spectrometry Provides Insight into the Products of Hydroprocessed Pyrolysis Biocrudes

Steven Rowland*[1,2], Rebecca Ware[3], Ryan Rodgers[2,4,5], Ofei Mante[6], David Dayton[6], and Sylvain Verdier†[7]

[1]Future Fuels Institute (FFI) – 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, United States, United States
[2]National High Magnetic Field Laboratory (NHMFL) – 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, United States, United States
[3]Florida State University Department of Chemictry and Biochemistry (FSU) – 95 Chieftain Way, Florida State University, Tallahassee, FL 32306, USA, United States
[4]Future Fuels Institute, Florida State University (FFI) – 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, United States, United States
[5]Department of Chemistry and Biochemistry, Florida State University – 95 Chieftain Way, Tallahassee, FL 32306, United States
[6]RTI International – RTI International, Research Triangle Park, NC 27709 USA, United States
[7]Haldor Topsoe A/S (HTAS) – Haldor Topsøes Allé 1, 2800 Kgs. Lyngby, Denmark

Abstract

Over the past few decades, biofuels have become a key component in the quest for alternative fuels. However, these biocrudes are enriched in compounds that contain high levels of oxygen, which drastically increases viscosity and may lead to refinery corrosion. Effective use of biocrudes for alternative fuels is dependent on the removal of oxygen prior to refining. Hydrotreatment may be utilized to reduce the level of oxygen in biocrudes; however, optimal catalysts and process parameters are currently unknown and thus, an active research area. An understanding of the products of hydrotreatment provides insight into the reaction pathways, quality, and efficiency of upgrading processes. Here, we provide a comparison of a catalytic fast pyrolysis oak-derived biocrude and its hydrotreated products by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). FT-ICR MS provides the unique ability to assign the molecular formulae to thousands of biocrude compounds and allows for unique insight into oxygen-containing products. FT-ICR MS analysis shows that oxygen distributions in oak-derived pyrolysis biocrude range from 1-14 oxygen atoms per molecule. Whereas, hydrotreated oak biocrudes showed 1-6 oxygen atoms per molecule. The average number of oxygen atoms per molecule was reduced from _˜ 8 to 2 oxygens per molecule after hydrotreatment. Structural features were also highlighted by plots of double bond equivalents (DBE) vs. number of carbon atoms (C#). It was observed that after hydrotreatment, oxygen-containing compounds showed phenol type structural motifs when compared to the unprocessed biocrude, which resembles lignin and cellulose type compounds.

---

*Speaker

†Corresponding author: sylv@topsoe.com

Thus, FT-ICR MS proved to be extremely useful for the understanding of pyrolysis biocrudes and their hydrotreated analogs unattainable by other analytical techniques.

ORALS
Shale Oil & Gas and Enhanced Oil Recovery

Crude oil surface active species: Consequences for emulsion stability and Enhanced Oil Recovery

Maurice Bourrel*[1]

[1]Total EP – Total EP : TotalEP Consultant – Pau, France

Abstract

Asphaltenes and naphthenic acids have attracted a great deal of interest from the scientific community concerned by issues experienced in crude oil production.
Problems are encountered in bulk phases handling (asphaltenes deposits, compatibility between crude oils, calcium naphthenates precipitation...), as well as at the water-oil interface.

This presentation aims at discussing the competition between asphaltenes, naphthenic species and possibly synthetic surfactants for adsorbing at the water-oil interface. The consequences on the behavior of the oil, water, surfactant mixtures in areas such as flow assurance (flow assurance) and Chemical Enhanced Oil Recovery (surfactant solution formulation, low salinity water flooding) are investigated.
Literature data are reviewed and some new experimental results are provided

---

*Speaker

sciencesconf.org:petrophase2017:153647

Influence of adsorption and capillary pressure on phase equilibrium in shale reservoirs

Diego Sandoval*[1], Erling Stenby[1], Michael Michelsen[1], and Wei Yan†[1]

[1]Technical University of Denmark – Denmark

Abstract

Production of oil and gas from shale reservoirs has gained more attention in the last decades due to its increasingly econimical feasibility and size of potentital sources around the world. Shale reservoirs are characterized to have a more tight nature in comparison to the conventional reservoirs, having pore size distributions ranging in the nanometer scale. Such nature introduces new challenges in the flow and phase behavior of the fluids inside. High capillary forces can be experienced between the liquid and vapor. Adsorption of components into the rock becomes relevant due to the large specific surface areas and low porosities. The combined effect of capillary pressure and adsorption can change the properties and compositions of the bulk phases considerably. The impact of these effects are of great importance to understand the storage of hydrocarbons inside the reservoir and to forecast its production. In this study, we provide a phase equilibrium calculation algorithm for multicomponent mixtures inside porous media with both capillary pressure and adsorption effects, and apply it to analyze the influence of capillary pressure and adsorption for different types of fluids.

The new calculation algorithm needs to include capillary pressure in stability analysis. For flash involving an adsorbed phase and capillary pressure, it can be designed as a nested loop where the inner loop solves the equilibrium between bulk phases with capillary pressure and the outer loop updates the overall composition of the bulk phases and the adsorbed amount. It is found that updating inner and outer loops together can be more efficient. The inner loop flash can be solved using a second order method while the update in the outer loop is currently successive substitution. The modified stability analysis is always used in the end to confirm the final solution. A comparison of several adsorption models shows that the ideal adsorbed solution theory and the extended Langmuir model are generally satisfactory for the available literature data while more complicated adsorption models like the multicomponent potential theory of adsorption can be useful for extrapolation to different temperatures.

The results show a considerable difference from those without capillary pressure and adsorption. Capillary pressure plays an important role close to the phase boundary shifting the bubble and dew points. The vapor-liquid region is greatly affected by the adsorbed phase due to high selectivity towards specific components which modifies the composition of the fluid bulk phases. Heavier components are adsorbed in the gas region and close to the dew point, yielding a lighter mixture for the fluid bulk phases which is reflected in the increase of the lower dew point. The fact that the adsorbed amount is comparable and sometimes higher than the amount contained in the bulk space of the nanopores makes the adsorbed phase play an important role.

---

*Speaker

†Corresponding author: weya@kemi.dtu.dk

sciencesconf.org:petrophase2017:145184

The Combined Electromagnetic Methods for Enhanced Heavy Oil Recovery: Experimental and Theoretical Proofs

Liana Kovaleva*[1], Alfred Davletbaev[1], Rasul Zinnatullin[1], Victor Kireev†[1], and Ruslan Sultanguzhin[1]

[1]Bashkir State University – 32 Zaki Validi Str., 450076 Ufa, Russia

Abstract

Electromagnetic treatment of bottomhole formation zone is considered as promising effective enhanced oil recovery method for extraction of high-viscosity, heavy and bituminous oils, as well as for development of low-permeability and shale oil deposits.
From the physical point of view, when electromagnetic waves are propagated in an oil-saturated rock, the electromagnetic field energy is dissipated due to orientational polarization of polar oil molecules (such as asphaltenes and their compounds). This leads to destruction of asphalt-resin-paraffin compounds and heating of oil up to the temperatures above the crystallization temperature of paraffin, thereby increasing oil mobility. The most significant heating effect is observed in the case when the electromagnetic waves frequency is close to the natural resonant frequency of polar oil molecules, which is determined individually for each oil and lies in the range 1–100 MHz. In addition to mentioned effects of electromagnetic treatment, there is also important additional effect of oil polar components desorption from the rock surface.

In this paper the results of theoretical, numerical and experimental analysis of the features of heating oil-saturated rocks under the influence of radio-frequency electromagnetic field are presented.

The dependences of dielectric parameters on electromagnetic field frequency and temperature for various samples of oils, oil-saturated and water-oil-saturated rocks with different degree of water saturation are experimentally determined. It is established that an increase in water content in the rock leads to an increase in the relative permittivity and the dielectric loss tangent.

The heating dynamics of oil-saturated and water-oil-saturated porous media at various frequencies and intensities of electromagnetic impact was studied using specially designed experimental setup that is modeled an oil well with bottomhole formation zone. It is shown that "rock-oil-water" systems are heated more intensively than "rock-oil" systems. This result can be explained by increasing of the dielectric parameters values for the first case.

The mathematical model of the radio-frequency electromagnetic field treatment of a producing oil well bottomhole zone is developed. The comparison of the results of numerical

---

*Corresponding author: liana-kovaleva@yandex.ru

†Speaker

modeling of the temperature fields in the bottomhole formation model with the experimental data demonstrated good agreement between them.

On the basis of numerical modeling, it has been shown that for development of low-permeability deposits, the most effective technologies are those in which electromagnetic influence on bottomhole formation zone is carried out jointly with other enhanced oil recovery methods, such as hydrofracturing or solvent injection. Depending on the attitude of deposit, oil and reservoir properties, various impact methods can be carried out either simultaneously or in step-by-step manner.
Using the original computer simulator, several impact techniques were compared. The total efficiency of each impact technique was determined by calculating energy balance and economic efficiency (payback period). In particular, the production dynamics of heavy oil from a well with fracture was simulated with step-by-step electromagnetic treatment and simultaneous solvent injection. The efficiency of combined electromagnetic technology in comparison with the "cold" extraction method has been shown, and the fact that the greatest efficiency is achieved for relatively "short" (5-10 m) fractures has been proved.

CT scannings of core floods: Quantitative analysis of saturation without dopant

Amalia Halim*[1], Anders Christensen†[1,2], Sidsel Nielsen‡[1], and Erling Stenby[3]

[1]The Danish Hydrocarbon Research and Technology Centre (DHRTC) – Elektrovej, b 375, DTU oil and gas, Kongens Lyngby-2800, Denmark

[2]Department of Applied Mathematics and Computer Science (DTU Compute) – Richard Petersens Plads, b 324, DTU, Kongens Lyngby-2800, Denmark

[3]DTU Chemistry (DTU Chemistry) – Kemitorvet, 207, DTU Chemistry, Kongens Lyngby-2800, Denmark

Abstract

Core flooding experiments are used for testing enhanced oil recovery strategies (EOR) on a laboratory scale. In a typical core flooding experiment, a core plug is saturated with oil, water and EOR agents. It is of importance to understand the multiphase flow of these liquids inside the porous rock formation. The combination of X-ray CT scanning and image analysis has been used to study multiphase flow in porous media for a few decades. However, in low permeable rocks, the interpretation of multiphase flow experiments is still a challenge. Previous experiments have been conducted with the aid of dopants in oil or water phase, but this has been shown to be problematic in chalk, as the dopants bind to the surface. In addition, the dopants might change the water-oil interactions. Our goal is to develop a method to visualize oil and water inside the rock without dopants.

A CT scanner works by taking conventional X-ray images from all around an object. These images can then be mathematically transformed to yield a 3D image of the object. By calibrating the images and precisely aligning consecutive scans of dry and wet cores, the porosity and saturation images can be obtained in 3D. This is done by subtracting the CT-value of the dry core from the wet core and normalizing with the difference in CT-value of air and liquid. When the porosity map is known, the saturation can be quantified by considering the difference between a mono-liquid saturated core and bi-liquid saturation. The main advantage of this approach is the saturation can be quantified, even though the scanner cannot resolve the pore space directly.

In practice, there are several challenges before the 3D images can be obtained. The X-ray tube in the scanner produces heat; this may lead to a small shift of the x-ray focus point which changes the CT-values of the images. To compensate for the fluctuations, materials with known CT-values were used as a reference, eg: the core holder and the sleeve. In each slice, the image-values could then be corrected using the reference values. The correction for change in core position was done by co-registration of the images using the SPM toolbox developed for medical imaging. It uses the small variations in the core sample, e.g. change of density to align the scans precisely. The noise inherent in the images from the CT-scan

---

*Speaker

†Corresponding author: anym@dtu.dk

‡Corresponding author: sman@dtu.dk

needs to be reduced before a subtraction of images yield sensible results. This is done by Gaussian smoothing for quantitative results or non-linear filters for visualisation.
Methodology and software has been developed in MATLAB to perform these steps automatically, with minimal user input, yielding quantitative porosity and saturation maps in 3D. The current results are promising, and it is possible to visualize 3D image of water and oil movement in the core plug at specific pore volume injections. For validation, the material balance is used as the reference. The saturation profiles from the CT scanner matches very well with the material balance of the collected fluids.

SO-O4

Molecular simulations of the micro-porous organic matter in shales

Julien Collell[1], Romain Vermorel[2], and Guillaume Galliero*[3]

[1]TOTAL SA – TOTAL – Centre Scientifique et Technique Jean-Féger, Avenue Larribau, 64018 PAU, France

[2]Laboratoire des Fluides Complexes et leurs Réservoirs (LFC-R) – Université de Pau et des Pays de l'Adour [UPPA], CNRS : UMR5150, TOTAL – BP 1155 - 64013 Pau, France

[3]Laboratoire des Fluides Complexes et leurs Réservoirs (LFCR) – CNRS : UMR5150, TOTAL – Université de Pau et des Pays de l'Adour BP 1155 64013 Pau, France

Abstract

Hydrocarbon production from shales has significantly increased during the last decade. However, the actual recovery mechanisms are largely unknown, which hinders the sustainability of such resources. In particular, hydrocarbons in shales are mostly located in micro-porous nodules of organic matter, the so-called kerogen, which are likely to act both as hydrocarbons micro-reservoirs and selective barriers to flow. Because of the nature of kerogen (complex micro-porous soft material), experiments are quite challenging and many of its physical properties, be it static or dynamic, are difficult to assess.
To overcome the aforementioned difficulties, we used Molecular Simulations to investigate various physical properties of the organic matter (kerogen + fluid content) contained in shale source rocks. Using characterization data, we have generated molecular structures mimicking the total organic matter under reservoir conditions [1-2]. Then, molecular simulations have been employed to quantify both static (adsorption ...) [3] and transport (diffusion ...) properties [4] in various conditions.

Our results prove that molecular simulations efficiently supplements experiments with regard to the quantitative description of the organic matter in shales. First, it provides a handy alternative to estimate physical properties of the organic matter under quasi-experimental conditions [2]. Second, it can be used to assist researchers with the theoretical modeling of adsorption and transport phenomena in kerogen at the nanometer scale [3-4].

Ungerer, P., Collell, J., Yiannourakou, M. Molecular modeling of the volumetric and thermodynamic properties of kerogen: Influence of organic type and maturity, (2014) Energy and Fuels, 29 (1), pp. 91-105.

Collell, J., Ungerer, P., Galliero, G., Yiannourakou, M., Montel, F., Pujol, M., Molecular simulation of bulk organic matter in type ii shales in the middle of the oil formation window, (2014) Energy and Fuels, 28 (12), pp. 7457-7466.

Collell, J., Galliero, G., Gouth, F., Montel, F., Pujol, M., Ungerer, P., Yiannourakou, M.

---

*Speaker

sciencesconf.org:petrophase2017:145140

Molecular simulation and modelisation of methane/ethane mixtures adsorption onto a microporous molecular model of kerogen under typical reservoir conditions, (2014) Microporous and Mesoporous Materials, 197, pp. 194-203.

Collell, J., Galliero, G., Vermorel, R., Ungerer, P., Yiannourakou, M., Montel, F., Pujol, M. Transport of Multicomponent Hydrocarbon Mixtures in Shale Organic Matter by Molecular Simulations, (2015) Journal of Physical Chemistry C, 119 (39), pp. 22587-22595.

POSTERS
Shale Oil & Gas and Enhanced Oil Recovery

CO2 EOR is a promising technology, but not omnipotent from asphaltene flow assurance point of view

Takumi Watanabe*[1], Yoshihiro Miyagawa[2], and Hideharu Yonebayashi†[2]

[1]INPEX – 9-23-30 Kitakarasuyama, Setagaya-ku, Tokyo 157-0061 JAPAN, Japan
[2]INPEX – Japan

Abstract

Not only for enhancing oil recovery but also for storing greenhouse-effect gas in *in-situ* reservoir, CO2 EOR is recognized as the most promising technology, and widely applied in the world. The CO2 EOR daily production rate in U.S. had contributed more than 280 kilobarrels by 2012 (Godec. 2014). This contribution, except for a short period around 2002, has been a continuous upward trend during 1986-2012. According to the citation results of asphaltene-flow-assurance research during CO2 injection, many efforts have been taken into account from asphaltene risk evaluating point of view (Yonebayashi et al. 2016). In our notional CO2 EOR study in two oil fields A and B, asphaltene risk was similarly pre-analysed and discussed prior to implementation because CO2 addition to reservoir fluid is well known often to cause asphaltene precipitation, while CO2 injection is expected for more oil production. In addition to formation damage, this might result oil production decrease due to tubing plug, more operating-cost by frequent removal of asphaltene deposits, deterioration of separation efficiency due to asphaltene emulsion, facility shut-down for removing asphaltene sludge, etc.

This paper describes a case study that consists of experimental evaluation on the basis of isothermal depressurizing tests to measure asphaltene onset pressure (AOP). The field-A has three wells that have same source rock in the same geological area but fluid characteristics were slightly different each other. First, on the basis of natural depletion (i.e. no CO2 injection), AOPs were measured as baselines for each single fluid oil sample. Second, AOPs were measured on the CO2 mixing conditions; mixing ratio varied from 20, 40 to 60 mol%. Through those experimental evaluation, it was revealed how implementation of CO2 injection impacted on asphaltene precipitating risk. For accurate measurement, AOPs data were accumulated by using different techniques: high pressure microscopic (HPM) analysis, laser light scattering (LST) technique, and kinetic characteristic measurement (i.e. viscosity). The AOP interpretation was comprehensively performed to use all types of technique basis data. The same measuring exercise was performed for the field-B that had 10 times of asphaltene content (2.6wt%) compared with that of the field-A (0.2wt%). While lower asphaltene content, AOPs were higher in the field-A than B. This fact suggested that asphaltene was more easily precipitated in the field-A. Through equilibrating steps in isothermal depressurizing test repeatedly, however the precipitated asphaltene particles were found to re-dissolve in liquid more easily in the field-B than A.

---

*Speaker

†Corresponding author: hideharu.yonebayashi@inpex.co.jp

sciencesconf.org:petrophase2017:137146

Consequently, more careful assessment would be necessary for the field-A because of less remedial options in case of formation damaged by not-easy-dissolving asphaltene. Therefore, in the field-A, CO2 EOR might be considerable by selecting an area containing the least asphaltene content fluid (lightest API gravity in three fluids). Moreover, a core test was recommended to perform CO2-induced formation damage evaluation. In the field-B, pressure maintenance, by suspending producers and/or applying water injection as WAG, might be a remedial option just in case of formation damaged because of easy dissolution. Therefore, CO2 EOR should be considered with appropriate pressure control in the field-B.

Wetting Behavior and Phase Behavior in Binary Mixtures of the Type Water + Polyoxyethylene Alcohol

Li-Jen Chen*[1]

[1]National Taiwan University [Taiwan] (NTU) – No. 1, Sec. 4, Roosevelt Road, Taipei, 10617 Taiwan, Taiwan

Abstract

Consider a system of three phases in equilibrium. When a small amount of the middle phase is put onto the interface separating the upper and the lower phases, three different wetting behaviors of the middle phase are possible: nonwetting, partial wetting, and complete wetting behavior. A homemade pendent drop/bubble tensiometer was assembled and applied to perform the surface/interfacial tension measurements for the binary water + ethylene glycol monobutyl ether (C4E1) mixture over the temperature range from 50 to 128 oC at 100 bar. Note that this binary water + C4E1 system exhibits liquid-liquid equilibrium under the experimental temperature and pressure. The symbol CiEj is the abbreviation of a nonionic polyoxyethylene alcohol CiH2i+1(OCH2CH2)jOH. It was found that the C4E1-rich phase exhibits a sequence of wetting transitions, nonwetting → partial wetting → complete wetting, at the gas-water interface in the water + C4E1 system along with increasing the temperature. In addition, the effect of molecular structure on wetting behavior of the middle phase in binary water + polyoxyethylene alcohol mixtures was experimentally investigated by using different polyoxyethylene alcohols. Molecular structure of polyoxyethylene alcohols plays an essential role in the wetting behavior.

---

*Speaker

sciencesconf.org:petrophase2017:142346

Dynamics and wettability of petroleum fluids confined in shale oil rocks probed by multidimensional and multifrequency NMR relaxations

Jean-Pierre Korb*[1,2] and Benjamin Nicot

[1]Laboratoire de Physique de la Matière Condensée (LPMC) – Polytechnique - X – LPMC Ecole Polytechnique 91128 Palaiseau Cedex, France

[2]Sorbonne Université, UPMC Univ. Paris 06, Laboratoire Physicochimie des Electrolytes, Nanosystèmes Interfaciaux (Phenix) – CNRS : UMR8234 – 4 Place Jussieu, 75005 Paris, France

Abstract

It is of primary importance to probe *in situ* and non-invasively the dynamics and wettability of oil, water and gas trapped in the complex microstructure of shale-oil rocks. The main reason is because liquid and gas hydrocarbons can be produced from these organic and mineral sedimentary rocks. However, most of the usual techniques cannot separate these fluids in the complex microstructure of shale rocks. Here, we present the non-invasive nuclear magnetic relaxation dispersion of longitudinal relaxation rates 1/T1 (NMRD) and 2D spin-correlation T1-T2 at different frequencies for oil and brine in shale oil rocks as received. We describe the nuclear spin relaxation models used for obtaining important dynamical and structural parameters from these experiments. These models allow interpreting the very different T1/T2 ratio observed for these petroleum fluids on the 2D spin-correlation T1-T2 observed at two frequencies. They give also new informations on the dynamics and wettability of the embedded fluids as well as some structural measurement on the kerogen pore size.

---

*Speaker

How to monitor polymers in EOR samples - comparison of analytical techniques applied to polyacrylamide quantification

Perrine Wund*†[1], Aurélie Mouret[1], Cédric Robert[1], Yoann Lemonnier[1], Corinne Burnichon[1], Lauréline Seurre[1], and Jean-François Argillier[1]

[1]IFP Energies Nouvelles (IFPEN) – IFP Energies Nouvelles – France

Abstract

In the framework of chemically-based enhanced oil recovery (EOR), the impact of chemicals on the produced water cycle is rarely investigated. However, after their breakthrough, part of them will be recovered in the produced fluids and may strongly impair oil/water separation and water treatment processes.
Among classical chemical EOR approaches, polymer flooding involves injection of polyacrylamide (PAM)-based polymers into the reservoir to enhance recovery through a better sweep efficiency. Polymer breakthrough can easily be detected thanks to viscosity measurements, but this method suffers from several drawbacks: poor sensitivity, possible misinterpretation of results due to polymer degradation... There is thus a need for reliable, sensitive and quantitative analytical methods for polymer monitoring.

Our goal was to compare various techniques for measuring polymer concentration in brine. Samples were prepared with three different PAM-based industrial polymers (5 to 200 ppm polymer).
Five analytical methods were characterized: UV-visible spectrophotometry, bleach method (API method), carbon/nitrogen elementary analyzer, FTIR (with Attenuated Total Reflectance configuration) and N-bromination method. Their performances in terms of sensitivity, linearity and sample volume needed were assessed.

---

*Speaker

†Corresponding author: perrine.wund@ifpen.fr

Evaluation of Empirical Correlations, Cubic Equations of State and Neural Networks for Predicting the Minimum Miscibility Pressure for Pure and Impure CO2 Flooding

Verônica Pereira*[1], Victor Regueira[1], Gloria Costa[1], and Silvio Vieira De Melo†[1]

[1]Universidade Federal da Bahia - UFBA (BRAZIL) – Brazil

Abstract

Miscible gas injection is one of the most known enhanced oil recovery (EOR) techniques applied in the petroleum industry. In these processes, the Minimum Miscibility Pressure (MMP) is a key parameter to evaluate the miscibility of the gas with the crude oil and increase the recovery efficiency. Although CO2 flooding is one of the main methods used to improve oil production, a pure CO2 stream is not commonly available and impurities (CH4, N2, and H2S) are often present, strongly affecting the MMP. Experimental techniques, such as Slim Tube, Rising Bubble Apparatus or Vanishing Interfacial Tension tests, are commonly used to determine the MMP, but they are costly and time consuming. On the other hand, simulation of pure and impure CO2-oil MMP using mathematical models, such as equations of state, empirical correlations or artificial intelligence techniques, have been reported vastly in the literature. Empirical correlations are simple equations that require some physical properties of the system and can calculate the MMP quickly, but the prediction accuracy is associated to the characteristics of the oils used to develop them. The use of equations of state based on the key tie-line identification approach is more reliable than empirical correlations, but requires the oil composition and a proper heavy-end characterization. Finally, there are recent studies using neural networks to predict CO2-oil MMP and the results are promising. This work evaluates several empirical correlations with an extensive database of MMP for pure and impure CO2-oil systems available in literature and a new correlation is proposed with the bubble pressure and the reservoir temperature as input data. In addition, its accuracy is compared with different approaches using Cubic Equations of State and Neural Networks. The results confirmed the low performance of empirical correlations for predicting MMP with average deviation above 10 %, whereas cubic equation of state and Neural Networks approaches showed better results.

---

*Speaker

†Corresponding author: sabvm@ufba.br

The Critical Point of Complicated Mixture and the Development of Supercritical Miscible System

Zhentao Chen*[1], Zhongqiang Jiang , Xi Wu , Zhiming Xu , Suoqi Zhao , and Chunming Xu

[1]State Key Laboratory of Heavy Oil Processing, China University of Petroleum – China

Abstract

Multiple contact miscible floods with carbon dioxide or hydrocarbon solvents is considered to be one of the most effective EOR techniques applicable to light and medium oil reservoirs. Miscibility point is critical for solvents to achieve miscibility with the reservoir oil. For pure substance or mixture, supercritical miscible condition means that both temperature and pressure are higher than the critical point. This study performs phase behavior of complicated mixture containing binary solvents or diesel+solvent system by using the equipment HPVC250HT (Highest T & P: 400 & 25 Mpa). Obvious critical opalescent phenomenon of binary solvents and diesel+solvent "binary" system can be observed clearly through the window, thus the critical point can be tested accurately.
Firstly, the critical point of some pure solvents such as n-pentane and ethanol+ n-hexane mixture with different composition was measured. The results for binary solvents system are in good agreement with literature, therefore the reliability of the device and method was verified.

Then, the critical points of four binary mixture such as ethanol+ cyclohexane were determained. All critical curves belong to class I according to Scott and van Konynenburg's classification on the binary mixture's phase diagram, while the slope of the curves and the trend are different.
Finally, phase behavior of diesel mixed with two solvents (n-pentane and ethanol) was studied by changing the mass ratio of solvents from 1 to 4. The results show that both of the critical temperature and pressure increase while increasing the ratio of diesel, take n-pentane+FCC diesel for example, the critical temperature increases from 256 to 337.5 , critical pressure increases from 4.636 to 4.967 MPa. Thus the critical curves of binary solvents and solvent +diesel system are determined, thereby, the supercrical miscible system can be developed by the critical conditions determained herein.

---

*Speaker

Exploring Compositional Changes along InSitu Combustion Process of heavy oil by FT-ICR-MS

Fernando Rojas*[1], Hernando Bottia[1], and Jorge Orrego*†[1]

[1]Ecopetrol SA (ECP-ICP) – Colombia

Abstract

Air injection leading to in-situ combustion (ISC) processes have been achieving attention worldwide as EOR alternative and have been developing promptly in recent years. Unfortunately, emulsion formation during production is one of the common problems associated to this technology. Disclosing the chemical nature of the compounds involved in the emulsion stabilization process becomes a key point for ISC projects success. In the present work, the compositional changes after a laboratory scale low temperature regimen ISC procedure (200300○C, simulating LTO reaction conditions), performed over a Colombian heavy crude oil (under different oxidation exposition times) at several stages of oxidation were studied. The analyses were performed using both positive-ion atmospheric pressure photoionization (APPI) and negative-ion electrospray (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FTICR–MS). The general compositional changes observed for the whole crude oil subjected to ISC were confirmed through the isolation of acidic compounds, and the surface-active species comprising the original and oxidized crude oil. It was noticed that the oxidized crudes contain a wider variety of compounds available to build up the O/W interface and thus, these crude oils have a tendency to to form stable emulsions.

---

*Speaker

†Corresponding author: jorge.orrego@ecopetrol.com.co

APLICATION OF GLYCERIN INFLUENCE IN SURFACTANTS SOLUTION FOR ENHACED OIL RECOVERY

Fabiola Curbelo*†[1], Clauber Lucian Maia‡[2], Danilo Leite[2], Rafael Fernando Ungarato*§[3], Julio Cézar Freitas*¶[4], and Alfredo Ismael Curbelo Garnica*‖[2]

[1]Federal University of Paraiba, Departament of Chemical Engineering (UFPB) – Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil

[2]Federal University of Paraiba, Department of Chemical Engineering (UFPB) – Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil

[3]Oxiteno S. A. Indústria e Comércio – Av. Airton Senna da Silva, 3001, Sonia Maria, Mauá, São Paulo, SP, 09380-440, Brazil

[4]Federal University of Rio Grande do Norte (UFRN) – Av Senr Salgado Filho, S/N Caixa Postal 1524 - Campus Universitario - Lagoa Nova CEP 59072-970 / Natal - RN, Brazil

Abstract

Over years the oil production in a reservoir tends to decrease, not only by the oil volume reduction and pressure drop, but also by the gradual changes in the physical and chemical properties of the oil, causing running the oil from the reservoir out to the well, meaning an increasingly difficult and costly production. Many researches on Enhanced Oil Recovery [EOR] in mature fields have been carried out, since conventional recovery methods are able to extract only a portion of the oil from the reservoir. The challenge to tertiary methods lies in the interaction of injected agents and reservoir fluid. Surfactants can interact by forming solution micelles or hemimicles at the interfaces, and these aggregates can have remarkable effects in many industrial processes. Due to their physical properties, surfactants have been used in enhanced oil recovery, however their adsorption in the reservoir is so undesirable as unavoidable, once the reduction of their concentration may imply in a lower efficiency of the method. Thus, in the last years it is being developed strategies to mitigate the adsorption of surfactant in several configurations, in order to make the project economically successful and to improve the EOR. Glycerin, a byproduct produced by the transesterification of vegetable oils, has been massively made after a government incentive to produce biodiesel in Brazil. Because of its high viscosity, glycerin was incorporated in several industrial processes as in the manufacture of cosmetics, paints and lubricants. Nevertheless, its production is greater than demand, potentially representing one considerable environmental problem. Thus, the injection of glycerin/surfactant is a technological alternative to improve the adsorption and oil recovery. Due to the facilitation in the oil mobility through the increase of the solution's

---

*Speaker

†Corresponding author: fabioladias@yahoo.com

‡Corresponding author: clauberlucian@gmail.com

§Corresponding author: rafael.ungarato@oxiteno.com

¶Corresponding author: juliofreitasj@hotmail.com

‖Corresponding author: alfredocurbelo@yahoo.com

sciencesconf.org:petrophase2017:148594

viscosity, glycerin contributes in the sweep efficiency, as well as making an added value compound in an environment-friendly way. This work aims to evaluate the influence of glycerin on adsorption and oil recovery using two types of surfactants, one ionic from vegetable source (coconut oil saponified – OCS) and the other nonionic (tween 20 – T20). For the adsorption experiments, surfactant solutions were prepared in salt concentrations of 2 wt% of KCl, with 20 wt% of glycerin and without the last one. The adsorbent was sandstone (10- 14 Mesh - Tyler series sieves), the most common rock type found in Brazilian reservoirs. Dynamic adsorption experiments were led in 250 mL carried out at ambient temperature in continuous stirred Dubnoff shaking bath to achieve equilibrium. Both surfactants were effective in the oil recovery, reaching oil recovery factors of up to 75%. Oil mobility was improved when in presence of glycerin, raising viscosity, therefore sweep efficiency. The greatest recovery factors were obtained for the OCS surfactant, which is the most suitable for use in EOR due to its biodegradability, vegetable origin, easy obtainment and low cost.

STUDY OF BATCH AND FIXED BED PROCESSES IN OIL REMOVAL FROM PRODUCED WATER USING COMMERCIAL ACTIVATED CARBON AS ADSORBENT – SCALE-UP PROPOSE FOR CONTINUOUS PROCESS

Alfredo Ismael Garnica*†[1], Dimitri Araujo[1], Renata Braga[2], Rennio Sena[1], and Fabiola Curbelo*‡[3]

[1]Federal University of Paraiba, Department of Chemical Engineering (UFPB) – Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil

[2]Federal Universityof Rio Grande do Norte, Agricultural School of Jundiaí (UFRN) – Campus Universitário, Macaíba, Rio Grande do Norte, 59280-000, Brazil

[3]Federal University of Paraiba, Departament of Chemical Engineering (UFPB) – Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil

Abstract

Nowadays, growing environmental awareness and current legislation rigor has contributed to implementation of effluent treatment station as a critical step in the industrial production cycle, regardless of operation field. Many residues were generated, from oil and gas production and exploration activities, like produced water, that to be discarded or injected (EOR), it is necessary a prior treatment so that concentration values of oil and greases of this effluent is according limits established by Brazilian environmental layers. In this work, adsorptive capacity of commercial activated carbon in emulsified oil removal in produced water, evaluating batch operation and continuous contact in fixed bed column was investigated. The adsorbent porous structure from the N2 adsorption at 77 K was obtained. Microporous area, external surface area, pore diameter and micropores volume were obtained from BET and Langmuir methodology. Freundlich and Langmuir isotherms models fit to experimental data was investigated. The initial oil concentration in produced water was 228 mg/L. Commercial activated carbon isotherm at 25 $\circ$C obtained from bath (Dubnoff Shake) was statistically significant for the Freundlich model, with confidence level of 95%. Freundlich constant values obtained indicated a favorable adsorption process for activated carbon-oil system. For Langmuir model, constant values were not statistically significant, without physically sense. Breakthrough curve was obtained through experiments carried out in a glass column of 3.2 cm internal diameter and activated carbon mass of 8.0 g, reaching a fast adsorbent saturation. The results showed a continuous oil removal capacity of 90%, with a final oil concentration

---

*Speaker

†Corresponding author: alfredocurbelo@yahoo.com

‡Corresponding author: fabioladias@yahoo.com

in effluent of 22.8 mg/L, until reaching the breakthrough point, fixed at C/C0 = 0.30. For the same organic load, batch process in one stirred tank (completely mixed flow reactor – CMFR) needed 9 times more activated carbon than the continuous process. For two tanks in series, batch process needed 2.5 times more adsorbent and, for three tanks in series, 1.4 times more adsorbent. Therefore, column operation presented greater operational advantages, besides having a significant saving of materials in its construction, when compared with continuous stirred tank reactor (CSTR). From breakthrough volume, VRUP = 13.5 L, and column exhaustion volume, VEXA = 15.5 L, fraction of capacity left unused bed (LUB) was calculated, which was 12.9 %; the adsorptive capacity demonstrated by column, qCOL = 442.34 mg/g, and total amount of effluent that can be per day in laboratory scale, VLAB = 209.1 L/day. Thus, scale-up of process was proposed, to filtration rate constant, to treat 1000 L/day of effluent, it was of a column of 7 cm diameter, 129 cm of bed height, breakthrough time of 4.3 days and a commercial activated carbon mass of 2.56 kg.

ORALS
Petroleum Properties

Strange Brew – Mixtures of Heavy Oil and Solvent

Harvey Yarranton*[1]

[1]University of Calgary – Canada

Abstract

Heavy oil is the black sheep of petroleum resources due to its high viscosity and lower quality for refining. Thermal methods are usually required to produce heavy oil but they are energy intensive, environmentally challenging, and marginally economic at today's prices. Solvent addition is an attractive alternative to produce heavy oils but faces many challenges, one of which is a lack of data and models for the wide range of phase behavior, compositions, and properties encountered in mixtures of heavy oil and solvents.

In this presentation, the current state of mapping out the phase behavior of mixtures of heavy oil and *n*-alkanes is reviewed including vapour-liquid boundaries, liquid-liquid boundaries, and asphaltene-rich phase yields. The transition from particulate to liquid heavy phases is examined and the heavy phase composition is presented in terms of the solvent, maltene, and C5-asphaltene (*n*-pentane insoluble) content. Trends that emerge from the data are discussed and still unresolved issues are identified.

A methodology to characterize heavy oils for phase behavior modeling is presented. The methodology partially accounts for the difference between non-associating species (approximated as maltenes) and associating species (approximated as C5-asphaltenes). The ability of equations of state to model the phase behavior for mixtures of heavy oil and solvent is assessed with a focus on the Peng-Robinson cubic equation of state, cubic plus association, and PC-SAFT. The strengths and limitations for modeling these processes are discussed including the prediction of: the onset of a second liquid phase for flow assurance; the amount of the heavy phase for froth treatment, and; the phase amounts, compositions, and properties for solvent deasphalting and *in situ* recovery processes.

---

*Speaker

sciencesconf.org:petrophase2017:153394

Atomic force microscope as a tool to detect asphaltene particles in crude oil

Lia Balestrin[1], Mateus Cardoso[2], and Watson Loh*†[1]

[1]University of Campinas (UNICAMP) – Brazil
[2]Brazilian Nanotechnology National Laboratory (LNNano) – Brazil

Abstract

The precipitation of asphaltene is a main problem in the process of extraction and oil production and it has been the focus of many studies on their characterization and on the effects of additives to inhibit their formation and/or deposition. However, most of these studies were accomplished in model systems such as asphaltene solutions in organic solvents, which turn the comparison with crude oil more difficult. Herein we describe the use of atomic force microscopy to identify colloidal particles of asphaltene aggregates present in crude oils. The methodology involved the addition of oil, its subsequent washing in toluene to remove oil excess, followed by drying and the image recording. Following this protocol, we were able to monitor asphaltene aggregates and how they were affected by aggregation inhibitor, good and bad solvent.

As a result, nanoparticles with dimensions ranging from a few of nanometers to few micrometers were observed. The particles observed in crude oil and asphaltene solutions in organic solvents are similar. However, the structures in model system are, on average, larger than those observed in the parent crude oil. This may be a consequence of the influence of the maltene fraction, which was not present in the model organic solutions. AFM images of maltene samples, on the other hand, presented significantly fewer nanoparticles.

In addition, more particles are observed when heptane is added, whereas their size decreases with toluene addition. The addition of inhibitor such as DBSA (4-Dodecylbenzenesulfonic acid) led to observation of more and smaller nanoparticles. Finally, the use of HOPG (Highly Ordered Pyrolytic Graphite) as a low energy substrate producing images that contain particles in the same size range as the ones detected on mica.

The main observations derived from this methodology agree with those reported from earlier studies on asphaltene colloidal particles obtained from scattering experiments and other microscopy analyses, validating the proposed methodology.

Therefore, this present experimental approach not only confirms this methodology as a valid one for the investigation of colloidal asphaltene particles in crude oils and model systems. Moreover, this is an accessible protocol to obtain information on how asphaltene particles are affected by changes in oil composition or inhibitors.

---

*Speaker

†Corresponding author: wloh@iqm.unicamp.br

sciencesconf.org:petrophase2017:145279

Contribution of molecular simulation to systematic thermophysical property prediction for upstream and downstream applications

Philippe Ungerer*[1], Marianna Yiannourakou† , Xavier Rozanska , Alexander Mavromaras , Julien Collell[2], François Montel[3], Sophie Loehle[4], Maxime Durot , Ahmed Alfarra , Philippe Ricoux , and Meriam Chebre

[1]Materials Design SARL – - – 18 rue de Saisset 92120 Montrouge, France
[2]Fluid and Organic Geochemistry Department (Total EP) – CNRS : UMR5150, LFC-R : UMR5150 – France
[3]TOTAL S.A. – TOTAL FINA ELF – CSTJF Avenue Larribau 64018 Pau, France
[4]TOTAL S.A. – TOTAL Marketing Services – Centre de Recherche de Solaize, BP22 – 69360, Solaize Cedex, France

Abstract

The purpose of the talk is to outline recent results obtained during a cooperative project of Total and Materials Design, using molecular simulation techniques including computational quantum chemistry (QM), molecular dynamics (MD), and Monte Carlo (MC), to predict properties for molecular systems of interest to Total. The program was focused on reasonable targets in the scope of the MedeA® software environment. Comparison with reviewed available experimental data was made, thus enabling us to estimate uncertainties. In the field of fuels and lubricants, thermodynamic and transport properties have been determined for a set of gasoline-range light hydrocarbons and oxygen-bearing compounds. A significant set of heavier esters and glycerides considered in new formulations for lubricants has been also investigated.

For Exploration and Production, thermodynamic properties of heavy hydrocarbons (branched and linear alkanes up to C80), organic sulfur compounds, and light hydrocarbons used as tracers have been computed using a combination of QM, MD and MC methods. Valuable results, among others, are the thermodynamic properties of heavy linear, branched alkane conformers by QM, the prediction of critical properties and acentric factor for C16-C35 hydrocarbons (n-and iso-alkanes, naphthenes, aromatics) and sulfur compounds.

For Refining and Chemistry, the phase diagrams of binary systems involving light oxygen-bearing polar compounds and light hydrocarbons have been predicted using MedeA®-GIBBS. For instance, the effect of pressure on T,x binary diagrams is predicted.

The main conclusion is that the atomistic simulation techniques are sufficiently mature to predict accurately and store systematically simulation results of many fluids and materials.

---

*Speaker

†Corresponding author: myiannourakou@materialsdesign.com

sciencesconf.org:petrophase2017:143908

In a few instances, simulation results helped to identify minor errors in experimental data reports.

Simulation methods can still be improved. Currently, the main limitations seem to be the availability of well-tested forcefield for multifunctional molecules or ionic systems, the conceptual and practical difficulties in predicting the melting properties of molecular crystals of unknown crystal structure, the computing time for heavy compounds and complex systems, and multicomponent reactive systems. More generally, there is a need of expertise to select methods for difficult predictions. Future use of simulation to propose molecular descriptors with physical or chemical insight is also a very interesting perspective to cover more needs with molecular simulation methods through Quantitative Structure-Activity Relationships (QSPR).

PP-O3

Quartz Crystal Microbalance Enables Selection of the Right Asphaltene Inhibitor for Application in a Real Field Condition

Edris Joonaki*[1], Rod Burgass[1], Aliakbar Hassanpouryouzband[1], and Bahman Tohidi[1]

[1]Centre for Flow Assurance Research Studies (CFAR), Institute of Petroleum Engineering, School of Energy, Geoscience, Infrastructure and Society, Heriot-Watt University – Riccarton, Edinburgh, EH14 4AS, UK, United Kingdom

Abstract

Gas injection is one of the most common EOR approaches. However, it is well known that gas injection into the reservoir fluid can cause asphaltene precipitation and deposition. This results in formation damage, oil production reduction due to pipeline plugging, increased operating costs due to removal of asphaltene deposits and other problems. Therefore, the potential for asphaltene deposition should be evaluated. Despite several decades of R&D projects, gas induced asphaltene deposition is still a major flow assurance challenge. Use of chemical additives is probably the most effective option for preventing or reducing asphaltene problems. However, several challenges associated with the use of aforementioned chemicals remain unresolved. Selection of inhibitors for asphaltene deposition is commonly based upon simple tests conducted on stabilised crude oil samples at ambient conditions. The results obtained from the current testing techniques in the labs are sometimes in disagreement with the outcome at field conditions. In some cases the chemical additives appear to aggravate the asphaltene deposition problems in the field. Hence, the commercial techniques which are employed to select the most appropriate asphaltene inhibitor based on their efficiency should be revisited to provide a better methodology for choosing the most suitable strategy for inhibitor/solvent injection. This research study addresses this asphaltene challenge using Quartz Crystal Microbalance (QCM) technique, with emphasis on selection of chemical additives for remediation/prevention strategies to handle gas induced asphaltene deposition problems. The proposed technique can work at high pressure conditions, simulating effect of pressure and dissolved gas on asphaltene phase behaviour and deposition tendencies with and without inhibitors. It can also measure deposited mass or mass changes due to asphaltene deposition in the nanogram range under real reservoir conditions. In this study, the ability of different asphaltene inhibitors to shift asphaltene onset pressures (AOPs) and reduce the amount of deposited asphaltenes in live crude oils is investigated. A comparison between the results of the QCM technique at high pressure and dead crude oil testing is presented. The results of this work indicate that the new technique can provide a robust, reliable method for evaluation of asphaltene inhibitors and deposition risks which has some advantages over other conventional techniques including; applying more realistic pressure and temperature conditions, small size of the sample, being non-destructive, real time deposition rate, using live oil samples (in addition to dead/stabilised samples).

---

*Speaker

Extraction and molecular-level characterization of soluble organics in produced water from a Gulf of Mexico platform

Andrew Yen*[1], Priyanka Juyal†[1], Amy Mckenna‡[2], and Ryan Rodgers[2,3,4]

[1]Nalco Champion – An Ecolab Company, Sugar Land, TX 77478, United States
[2]National High Magnetic Field Laboratory (MagLab) – 1800 East Paul Dirac Drive, Tallahassee, FL 32310, United States
[3]Future Fuels Institute (FFI) – 1800 East Paul Dirac Drive, Tallahassee, FL 32310, United States
[4]Department of Chemistry, Florida State University, (FSU) – 95 Chieftain Way, Tallahassee, FL 32306, United States

Abstract

Abstract:
Produced water is the primary waste stream generated by oil and gas industry resulting from the separation of oil, gas, and water at production facilities. The physical and chemical properties of produced water vary considerably from one field to another, and may even alter significantly over time for the same reservoir. It is typically a mixture of formation / injection process water and contains organics, salts, production chemicals, solids, and trace metals. Understanding produced water characteristics is necessary for regulatory compliance of federal laws pertaining to disposal. Oil, grease, and the dissolved hydrocarbon constituents of produced water receive the most attention in both onshore and offshore operations primarily due to their environmental toxicity. Soluble organics are not easily removed from produced water and therefore are typically discharged to the ocean or re-injected at onshore locations. With the stringent EPA discharge regulations of 29 ppm for total oil and grease content in overboard water and the expected new regulations of 10 ppm for offshore oil production; the industry is challenged to develop most accurate analytical methods to determine water soluble organics in the discharge water. A greater understanding is needed of the chemistry of soluble compounds, for effective management and improved filtration/ removal techniques. Here, we identify dissolved organic hydrocarbons in overboard water and interfacial material collected at oil/water interface from a platform in the Gulf of Mexico. Organic materials were extracted with an acid digestion method. Extraction from approximately 100 mL of produced water yielded less than 1 mg of dissolved neutral and basic hydrocarbons, and 7 mg of acidic hydrocarbons. All of the acidic heteroatom compound classes were determined by high resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). Carboxylic acids, naphthenic acid, and sulfur containing acids were identified. The implication of these surface active organic compounds to real-world field problems will be discussed.

---

*Speaker
†Corresponding author: pjuyal@nalco.com
‡Corresponding author: mckenna@magnet.fsu.edu

DIRECT OBSERVATION OF ASPHALTENE NANOPARTICLES ON MODEL MINERAL SUBSTRATES

Gijo Raj*[1], Alain Lesimple[1], Jamie Whelan[1], and Pance Naumov†[1]

[1]New York University Abu Dhabi (NYUAD) – P.O. Box 129188 Saadiyat Island, United Arab Emirates

Abstract

The propensity for adherence to solid surfaces of asphaltenes, a complex solubility class of heteropolycyclic aromatic compounds from the heavy fraction of crude oil, has long been the root-cause of scale deposition and remains an intractable problem in petroleum industry. Despite that the adhesion is essential to understand the process of asphaltene deposition, the relation between the conformation of asphaltene molecules on mineral substrates and its impact on adhesion and mechanical property of the deposits is not completely understood. To rationalize the primary processes in the process of organic scale deposition, here we use atomic force microscopy (AFM) to visualize the morphology of petroleum asphaltenes deposited on model mineral substrates. High imaging contrast was achieved by differential adhesion of the tip between asphaltenes and the mineral substrate. While asphaltenes form smooth continuous films on all substrates at higher concentrations, they deposit as individual nanoparticles at lower concentrations. The size, shape and spatial distribution of the nanoaggregates are strongly affected by the nature of the substrate; while uniformly distributed spherical particles are formed on highly polar and hydrophilic substrates (mica), irregular islands and thicker patches are observed with substrates of lower polarity (silica and calcite). Asphaltene nanoparticles flatten when adsorbed on highly oriented pyrolytic graphite due to π-π interactions with the polycyclic core. Force-distance profiles provide direct evidence of the conformational changes of asphaltene molecules on hydrophilic/hydrophobic substrates that result in dramatic changes in adhesion and mechanical properties of asphaltene deposits. Unlike flat surfaces, the AFM phase contrast images of defected calcite surfaces show that asphaltenes form continuous deposits to fill the recesses, and this process could trigger the onset for asphaltene deposition. Finally, we demonstrate the application of correlative microscopy techniques combining Digital Pulsed Force Microscopy and confocal Raman 2D imaging for probing the adhesion, stiffness and average sheet size of polycyclic aromatic cores present in asphaltene nanoparticles.

---

*Speaker

†Corresponding author: pance.naumov@nyu.edu

sciencesconf.org:petrophase2017:146552

PP-O6

Ultra-Small-Angle Scattering Investigation of the Structure and Precipitation Mechanism of Asphaltenes in Solvent Mixtures

Yuan Yang*[1], Chaisoontornyotin Wattana[1], and Michael Hoepfner†[1]

[1]Department of Chemical Engineering, University of Utah (ChE, UTAH) – 50 S. Central Campus Dr.,
Room 3290 MEB, Salt Lake City, UT 84112-9203, United States

Abstract

In this talk, we will present first of their kind experimental results demonstrating the application of ultra small-angle X-ray scattering (USAXS) to characterize precipitating asphaltenes. USAXS was found to be capable of monitoring time-resolved changes in size and morphology of asphaltenes as they transition from the nano to the micrometer length scale. It is accepted that asphaltene molecules self-assemble in crude oil and solvents into fractal clusters with Rg (radii of gyration) less than 40 nm and fractal dimensions ranging between 1.6 and 2.1 [1]. With the addition of an antisolvent (e.g., heptane), the stable clusters of asphaltenes can be destabilized and further aggregate into insoluble clusters with sizes in the micrometer length scale and a more compact internal structure (i.e., higher fractal dimension) [1]. Insoluble and precipitating asphaltene clusters can travel to interfaces and result in fouling of production lines and process equipment or stabilization of water-in-oil emulsions. Despite decades of extensive study, it is unclear what structural changes occur at the nano and micrometer length scales for both soluble and insoluble asphaltenes during the destabilization and precipitation process. In this study, USAXS results generated on beamline 9-ID-C at the Advanced Photon Source at Argonne National Lab will be presented to explore the mechanism of asphaltene destabilization and precipitation. Because USAXS is able to detect a wider range of scattering vectors (q), both soluble and precipitating asphaltenes with larger length scales can be observed simultaneously. The precipitation process was monitored as a function of time after adding an antisolvent by measuring the structural changes of both soluble and insoluble/precipitating clusters for long mixing times (greater than 24 hours) and large length scales (greater than 1000 nm). It was observed that the compactness and size of insoluble asphaltenes increase as a function of time, while the structural properties of soluble asphaltenes remain the same. Moreover, it is revealed that the precipitated asphaltenes have surface fractal geometry (i.e., rough surfaces with a compact core). Trace quantities of inorganic solids (R=0.1 nm-1 micron) were detected in the samples investigated and likely contributed to the observed precipitation mechanism by acting as nucleation sites for asphaltenes. Inorganic solids are present in real-world oil production and processing environments, and this result is of direct scientific and industrial importance. Overall, this study provided an improved mechanistic understanding of asphaltene assembly during precipitation and showed the powerful ability of USAXS for the investigations of asphaltene-related problems. [1] Hoepfner, M. P.; Vilas Boas Favero, C.; Haji-Akbari, N.; Fogler, H. S. The Fractal Aggregation of Asphaltenes. Langmuir 2013, 29, 8799–8808.

---

*Speaker

†Corresponding author: hoepfner@chemeng.utah.edu

POSTERS
Petroleum Properties

Characterizing Asphaltene Concentrations with UV-vis-NIR Spectroscopy

Theodore Garver*[1], Nancy Luo[1], and Paul Pastushak[1]

[1]Innotech Alberta – 250 Karl Clark Road Edmonton, AB T6N1E4, Canada

Abstract

The amount of asphaltene in a bitumen or crude oil sample is a key characteristic influencing the color and viscosity of the sample. Direct methods of measurement of asphaltene by precipitation by pentane (C5 asphaltenes) and heptane (C7 asphaltenes) may be calibrated against more rapid but indirect methods of asphaltene quantification using UV-visible-NIR absorbance analysis. There exists a theoretical basis for characterizing a solubility defined substance using absorbance spectra. The electronic polarizability of asphaltene, characterized by the complex refractive index, is related to the solubility of the asphaltenes. Asphaltene was fractionally precipitated from Long Lake bitumen using toluene-pentane and toluene-heptane mixtures. The resulting asphaltenes and the residual asphaltenes in bitumen were characterized with NIR and UV-visible spectroscopy. The electronic absorbance observed in the NIR region was fit to exponential functions that were used to calibrate against percent asphaltene. Soluble aromatic substances with absorbance in the UV-visible region contribute to NIR spectra with a vibrational combination peak at around 2100 nm but not in the signal from the electronic transitions. We describe a method incorporating the use of the sum of the area of the electronic signal for the calibration against gravimetric methods.

---

*Speaker

sciencesconf.org:petrophase2017:130064

Modeling Electrophoretic Mobility and Charge Inversion of Asphaltene Dispersions

Jose Manuel Del Rio[1], Felipe Jimenez-Angeles[1], and Carlos Lira-Galeana*†[1]

[1]Mexican Inst. of Petroleum (IMP) – Eje Central Lazaro Cardenas 152, San Bartolo Atepehuacan,
Gustavo A. Madero, Mexico 07730, Mexico, Mexico

Abstract

Abstract:
We model the electrophoretic mobility and charge inversion of a colloidal dispersion of asphaltenes in aqueous and non-aqueous media using the Ornstein-Zernike integral equation in the Hypernetted-Chain / Mean Spherical Approximation (HNC / MSA). Our model consists of a solution of spherical colloidal particles suspended in a uniform medium of dielectric constant er; the particles' diameter is aM, the solute concentration is rM, and the charge zMe; e is the elementary positive charge and zM is the number valence. The asphaltenes' charge is compensated by counterions of charge ze and diameter a. The equations are solved using a form of the Galerkin method. As a result, we obtain the concentration profiles ri(r) of the species around a central colloidal particle as a function of aM, zM, and rM. The cumulative charge density s(r) and mean electrostatic profiles y(r) are obtained by integration of Poisson's equation. The Z-potential is the mean electrostatic potential at the closest approach distance between the counterions and the colloidal particles, Z = y(aM/2+a/2). The electrophoretic mobility (me) of the colloidal particles as a function of the Z-potential is calculated using the Smoulochowski equation, me=ere0 z/h. Electrophoretic mobility and charge inversion of asphaltene dispersions are analyzed in the concentrated regime. A comparison of our model with Z- potential data shows that our approach is a rigorous and accurate method to predict the electrophoretic mobility of asphaltene dispersions in the entire concentration range. These results find application in higher-order models of flow assurance, as required in the design of petroleum production operations.
Corresponding author: e-Mails: clira@imp.mx; cliragaleana@gmail.com

---

*Speaker

†Corresponding author: cliragaleana@gmail.com

High-Pressure Hight-Temperature Phase Equilibria of Crude Oil + CO2

E. Chidi Efika*†[1], Carolina Contreras Quintanilla[1], Geraldine Torín Ollarves[1], Chris Tighe[2], and J. P. Martin Trusler[1]

[1]Qatar Carbonates and Carbon Storage Research Centre (QCCSRC) – Department of Chemical Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ., United Kingdom
[2]Imperial College London – Department of Chemical Engineering, Imperial College London, South Kensington campus, London, SW7 2AZ, United Kingdom

Abstract

For the purpose of more accurate development and operation of carbon capture and storage (CCS) and enhanced oil recovery (EOR) processes, an overall understanding of the phase behavior of mixtures of CO2 and crude oil system is essential. However, the complex nature of crude oil presents a challenge, especially in relation to the phase behavior of these systems at high pressures and temperatures under CO2 addition. Since the purity of injected CO2 has an impact on the overall economics of CCS process, it is also important to know the effects of impurities such as diluent gases (e.g. N2 and O2) and acid gases (e.g. H2S and SO2) among others.
Experimental data on the phase equilibria of crude oils with CO2 are scarce and limited with respect to the temperature and pressure of study [1-3]. In this work, we report experimental measurements of the phase behavior of crude oil under CO2 addition. The experiments were performed in a synthetic apparatus designed to measure the phase behavior of CO2 and hydrocarbon systems at high temperatures and pressures. The apparatus consisted of a thermostated variable-volume view cell driven by a computer-controlled servo motor system, equipped with a sapphire viewing window and two calibrated syringe pumps for quantitative fluid injection. The experimental equipment has been described in detail in a previous publication [4]. The crude oil (API gravity of 31) was supplied as 'dead' oil without solution gas. Prior to use, it was vacuum filtered and centrifuged to remove particulates and water. Phase behavior measurements were made for both the dead oil and also a reconstituted 'live' oil (prepared by the addition of solution gas comprising methane, ethane and propane) under addition of CO2. Temperatures up to 423.15 K, pressures up to 40 MPa and varying CO2 mass fractions in the crude oil were investigated. Preliminary measurements of the effects of diluent gases have also been conducted. Finally, we report density measurements for the dead crude oil.

The experimental data were compared with predictions based on the Peng-Robinson 78 (PR78) and Soave-Redlich-Kwong (SRK) equations of state with group contribution formulae for the binary interaction parameters [5]. The predictive capability of SAFT-g-Mie [6, 7] was also tested in order to model the phase equilibria of this mixture.

---

*Speaker

†Corresponding author: e.efika@imperial.ac.uk

sciencesconf.org:petrophase2017:140200

References

F.M. Orr Jr, A.D. Yu, C.L. Lien, Soc. Petrol Eng. J. 21, 480-492, 1981.

E.A. Turek, R.S. Metcalfe, R.E. Fishback, SPE Reserv. Eng. 3, 505-516, 1988.

M.A. Lucas, G.R. Borges, I.C.C. da Rocha, A.F. Santos, E. Franceschi, C. Dariva, J. Supercritical Fluids. 118, 140-147, 2016.

S.Z. Al Ghafri, G.C. Maitland, J.P.M. Trusler, Fluid Phase Equilib. 57, 1-33, 2014.

J.N. Jaubert, J. Qian, R. Privat, C.F. Leibovici, Fluid Phase Equilib. 338, 23-29, 2013.

V. Papaioannou, T. Lafitte, C. Avendano, C.S. Adjiman, G. Jackson, E.A. Muller, A. Galindo, J. Chem. Phys. 140, 054107, 2014.
M.S. Wertheim, J. Stat. Phys. 35, 35-47, 1984.

Robust Solution of an eCPA EoS for Complex Multiphase Mixtures involving Multiple Associating Compounds and Salts

Wenlong Jia*[1] and Ryosuke Okuno[2]

[1]Southwest Petroleum University – China
[2]University of Texas at Austin – 200 E. Dean Keeton Street, Stop C0300, Austin, Texas, 78712, United States

Abstract

Objectives/scope

Many hydrocarbon and chemical processes involve complex mixtures with multiple associating compounds and salts, such as bitumen, alcohols, ethers, amines, and brines. The electrolyte cubic-plus-association equation of state (eCPA EoS) is capable of predicting phase equilibria of these mixtures, because it accounts for interactions between associating compounds and ions. The eCPA EoS is formulated as a nonlinear function of compressibility factor (Z), and mole fractions of unbounded association sites (i) of all associating components. However, the eCPA EoS has no analytical solutions in terms of Z because it is implicit in Z that is related to i defined by a set of nonlinear coupled associating terms. Previous publications either do not present details of solution for i, or do not robustly find the correct Z. The purpose of this paper is to present a robust solution method for an eCPA EoS as well as its application for multiphase flash.

Methods procedures

The eCPA EoS has been implemented in an in-house multiphase flash code. Nested loops are used to solve for variables i and Z. The inner loop uses a damped Newton-Raphson method to robustly solve the coupled associating terms for i for a given Z. The damping factor is calculated based on an exponential function so that the factor gradually increases with increasing iteration step. Based on the resulting i, an interval Newton method is employed to solve the eCPA EoS for Z in the outer loop. The key to ensuring the robustness is that the algorithm finds monotonic intervals that include all real roots; therefore, the eCPA EoS can be efficiently solved within each interval using the Newton method. Finally, the one that yields the minimum Gibbs free energy is selected as the correct root. With the new method, multiphase equilibria of complex mixtures are simulated robustly.

Results

The new method is applied to mixtures containing up to 10 associating components (e.g., CO2, water, resins, asphaltene, alcohols, and amines) and three salts. Results show that, for vast majority of conditions, the inner-loop and outer-loop algorithms rapidly converge

---

[*] Speaker

within twelve and five iterations, respectively. Also, this method can always find the desired Z with the minimum Gibbs free energy. Conversely, previous methods that use the roots for the cubic EoS as initial guesses for the Newton method are shown to not converge to the correct solution because the association part becomes more dominant with increasing number of associating compounds. In comparison with the alternative robust bisection method, the proposed method is shown to be computationally more efficient.

Novelty

The new method can always find the correct root with a minimum Gibbs free energy no matter how many associating compounds are present in the mixture of interest. Case studies show that the enhanced robustness contributes to reliable multiphase equilibrium simulation for complex mixtures in many practical cases, e.g., mixtures involving alcohols, glycols, water, brine, bitumen and asphaltene. The eCPA EoS is shown to capture the effect of different salt species on asphaltene precipitation from bitumen/solvent/brine mixtures.

PP-P5

Investigation of blending phenomenon between hydrocarbon binders for road materials incorporating reclaimed asphalt pavement

Sabine Vassaux*[1], Vincent Gaudefroy†[1], Audrey Pévère , Virginie Mouillet , Laurence Boulangé , and Véronique Montero

[1]Matériaux pour Infrastructure de Transport (IFSTTAR/MAST/MIT) – IFSTTAR – Centre de Nantes
Route de Bouaye - BP 4129 44341 Bouguenais Cedex, France

Abstract

One issue of asphalt pavement mixtures improvement is linked to the addition of reclaimed asphalt pavement (RAP) at low manufacturing temperature. Recycling practices lead to the question of the blending quality between old and fresh binder. A low blending state of the virgin bitumen with the RAP aged one, could led to a double coating phenomenon and decrease mechanical properties and durability of asphalt mixtures. Therefore, the aim of the study is to better understand blending mechanisms occurring between hydrocarbon binders. More precisely, the study will investigate, from a physical and chemical point of view, how binders wet and diffuse together. Some hydrocarbon binders were tested: virgin bitumens and other ones which were aged thanks to standardized laboratory procedures. Different chemical additives (polymer, rejuvenator) were added to the virgin binder, in order to modify its formulation. Both virgin and aged binders were put into contact according to various temperature conditions. Contact angle experiments were employed to assess firstly contact at the "binder/binder" interface. Then, FTIR imaging technique has been used to visualize chemically the final diffusion state between binders. This visualization was performed by monitoring specific infrared oxidative functions at the interphase of double-layered samples. In addition, binders surface tension and viscosity were also characterized and correlated with blending imaging. Results show that bitumen surface tension and viscosity are function of asphaltene content and blending temperature. The temperature difference between binders plays a crucial role on the blending quality, both on the wetting and diffusion stages.

---

*Speaker

†Corresponding author: vincent.gaudefroy@ifsttar.fr

sciencesconf.org:petrophase2017:142297

Evaluation of the Expanded Fluid Model for Predicting the Viscosity of Oils with Equations of State: Effect of Characterization Methods

Victor Regueira[1], Verônica Pereira[1], Silvio Vieira De Melo*[1], and Gloria Costa†[1]

[1]Universidade Federal da Bahia - UFBA (BRAZIL) – Brazil

Abstract

Design and assessment of oil extraction, pipeline transportation and process simulation require a good knowledge of oil viscosity at different conditions. There are many methods regarding viscosity modeling in the literature: some are empirical, such as LBC, Standing and Andrade correlations; others are theoretical, most used for hydrocarbon gases; and also semi-empirical approaches, such as corresponding states and the friction theory models. However, few models are enough accurate for light and heavy oils over a wide range of temperature, pressure and composition. Further, models are not suitable to calculate the viscosity of oils characterized using pseudocomponents. The recently developed expanded fluid (EF) model is known for its capacity to properly calculate the viscosity of heavy oils and its mixtures with solvents at high pressures and temperatures with a minimum amount of experimental data. However, one of the EF model drawbacks is the requirement of accurate density data at the evaluated conditions. To overcome this difficulty, the density could be predicted with a Cubic Equations of State (CEOS) with a temperature-dependent volume translation. A proper oil heavy-end characterization is also essential if accurate density predictions are needed. Besides its strong dependency on density predictions, the EF model also needs to be compared with other relevant viscosity models to a better evaluation of its performance. The main objective of this work is to evaluate the EF model using experimental and CEOS predicted density data to calculate viscosity of oils for a large database of reservoir fluids from different regions. The EF model was compared with other models available in literature. In addition, a sensitivity analysis was carried out to study the effect of the characterization methods on density predictions and consequently their effects on the viscosity. Results confirmed the hypothesis of strong dependence of density predictions and a proper characterization to accurately calculate oil viscosity. Results are also noteworthy due to the simplicity of the model with a need of few parameters to be estimated. Therefore, the EF model can be considered as a powerful tool for oil viscosity predictions for characterized oils.

---

*Corresponding author: sabvm@ufba.br

†Speaker

Compositional grading under the influence of thermal diffusion and molecular association

Rogerio Esposito*[1], Pedro Henrique Alijo[2], José Antonio Scilipoti[3], and Frederico Tavares[3]

[1]Petrobras S.A. – Brazil
[2]UERJ - University of the State of Rio de Janeiro – Brazil
[3]UFRJ - Federal University of Rio de Janeiro – Brazil

Abstract

The influence of both thermal diffusion and molecular association on compositional grading is evaluated based on Irreversible Thermodynamics concepts, using also the CPA-EoS. The Heat-of-Transport (HoT) model parameters for hydrocarbons are re-estimated for a new critical-transition case study and kept to be used in a second example that deals with three-phase equilibrium at *in situ* conditions due to asphaltene segregation and high CO2 content. The HoT parameter of CO2 was fitted to match a huge saturation-pressure variation along depth, reproducing also the GOC location with reasonable accuracy. As for the liquid-liquid interface, CPA-EoS fitting was crucial to detect it starting from association-energy parameters recently published in the literature. Once the model is set, one can infer important properties like viscosity in the asphaltic zone, increasing the reliability of the production forecasts regarding, for example, aquifer acting and both condensate and heavy-oil rates.

---

*Speaker

sciencesconf.org:petrophase2017:142377

Predicting the risk of asphaltene precipitation by the modified ASIST method

Luisa L. O. Setaro[1], Verônica J. Pereira*[1], Silvio A. B. Vieira De Melo†[1], and Gloria M. N. Costa[1]

[1]Universidade Federal da Bahia - UFBA (BRAZIL) – Brazil

Abstract

One of the main reasons of well productivity decreasing is asphaltene precipitation in oil reservoirs and production facilities. Precipitation is caused by changes on temperature, pressure and composition. Therefore, evaluation of the risk of asphaltene precipitation is always necessary along the oil production well lifespan. In literature, there are many methods to predict the risk of asphaltene precipitation, but none of them is broadly accepted. Most of these methods require a large amount of experimental data, which often cannot be easily measured due to the need of high-cost specific equipment and quite time-consuming experimental runs.

Wang *et al.* (2006) proposed a method to predict the onset of asphaltene precipitation by depletion based on the Asphaltene Instability Trend (ASIST) technique. This method is well grounded although it needs several experimental data: the formation volume factor at the bubble point and at 1 atm, the gas-oil ratio at the bubble point, the onset solubility parameter (measured from n-C7 titration) and the temperature at n-C7 titration. However, these data are not easily determined. To overcome this hurdle, this study proposes two new approaches to evaluate the risk of asphaltene precipitation using a modified ASIST method when experimental data are not fully available. One of these approaches considers that the onset solubility parameter and the temperature at n-C7 titration are average constants, calculated following Wang's method. The other approach assumes that both the formation volume factors and the gas-oil ratio can be calculated by Pedersen's characterization (using the software SPECS) or Standing's correlation. The results of both approaches were compared to evaluate their effects on the solubility parameter used to predict the risk of asphaltene precipitation in live oil. Furthermore, the performance of Wang's method was evaluated for the case where CO2 displacement is used as a special recovery technique.

When employing either the Standing's correlation or Pedersen's characterization to calculate the gas-oil ratio and both the formation volume factors, as well as the mean values of the onset solubility parameter and the temperature at n-C7 titration, the modified ASIST method is completely predictive and much easier to use because less input data are required (just the reservoir temperature, composition and API). This proposed modified ASIST method was applied to several oils with experimental data on asphaltene precipitation available in literature. Differently from Wang *et al.* (2006), who compared three methods to predict the risk of asphaltene precipitation without knowing whether the oils were unstable or stable, in our study only oils previously known as unstable were considered to validate the proposed modified method.

---

*Speaker

†Corresponding author: sabvm@ufba.br

sciencesconf.org:petrophase2017:144074

Stability analysis of asphaletenes in heavy fuel oil by Turbiscan Technology (ASTM D7061)

Christelle Tisserand[1], Yoann Lefeuvre , Jérémy Cohen* , Pascal Bru , and Meunier Gérard

[1]Formulaction – Formulaction – 10 impasse Borde Basse, 31240 L'Union, France

Abstract

Reduction in the quality of crude oil throughout the world, due to diminishing resources and increasing refinery efficiency, has led to the production of worsening quality heavy fuel oils. Asphaltenes, a mixture of heavy hydrocarbons, tend to precipitate when the solubility changes due to temperature variation, blending..., thus blocking pipework, clogging filters or plugging burners... Therefore, extractions sites, refineries and heavy oil users (marine companies, electrical power plants...) have to systematically test the intrinsic stability of heavy fuel oils as well as the efficiency of additives. We will present one technology that can answer all these needs and monitor all destabilisation phenomena. It is based on Multiple Light Scattering (MLS) and is associated to a vertical scanning of the sample. It is like a high resolution electronic eye, enabling to identify and quantify instability phenomena before they are visible to the operator (5 to 50 times earlier than the naked eye). Physical parameters and kinetics can be computed in order to facilitate and improve comparisons between formulations. For asphaltenes stability in heavy fuel is has even been granted ASTM (D7061). The ASTM D 7061 method is well known to monitor additives efficiency in order to stabilize fuel oils.

---

*Speaker

Rheological Study of Water in Oil Emulsions of Heavy Oils

Dorval Neto[1], Cristina Sad[1], Paulo Filgueiras[1], Mayara Silva[1], Francine Santos[1], Laine Pereira[1], Rayane Corona[1], João Bassane[1], Eustaquio Castro[1], and Valdemar Lacerda Jr[*][†][1]

[1]Federal University of Espirito Santo, Chemistry Department – Av. Fernando Ferrari 514, Goiabeiras, CEP: 29.075-910, Brazil

Abstract

Heavy oils are characterized by the high amount of resins and asphaltenes, natural emulsifiers that combined with the presence of water and shear, in the stages of production and transportation of oil, provide the formation of emulsions1, usually water in oil emulsions (W/O). The present study evaluated the rheological behavior of W/O emulsions of five heavy oils from the sedimentary basin of the Brazilian coast, with API gravity between 10.8 and 19.9. Factors related to stability (temperature, amount of emulsified water, salt concentration) and rheological behavior of the W/O emulsions (dynamic viscosity, stress and shear rate) were evaluated. These factors were related to the chemical composition of petroleum in terms of saturates, aromatics, resins and asphaltenes (SARA). The emulsions were prepared with deionized water, formation water (55·103 mg·L-1 of NaCl) and water saturated with sodium chloride (270·103 mg·L-1 of NaCl) under mechanical stirring at 5000 rotations per minute (rpm). Rheological tests of the emulsions were performed from 30 to 80 °C and the data obtained was analyzed using the Oswald-de-Waele equation. The results of the rheological evaluation showed that in the stable emulsions, those in which no emulsified water after shearing was identified, there was up to 1212% increase in the dynamic viscosity caused by the increase of the aqueous phase and the influence of the salt concentration. The increase in temperature minimized this effect, and at 60 °C a reduction of more than 80% was observed in the dynamic viscosity of these emulsions. In the stable emulsions, the flow index was positive, showing reduction as a function of the increase of the amount of emulsified water, but inversely related to temperature. For the unstable emulsions, characterized by the presence of non-emulsified water, the dynamic viscosity was lower than the dehydrated oils, and most of them with a negative flow index. In most unstable emulsions, the elevation of salt concentration and temperature aided in the stabilization of the emulsions. It was observed that oils with total acid number less than 1.3 mgKOH·g-1 and asphaltene/resin, aromatic/saturated and asphaltene/aromatic ratios higher than 0.2 formed unstable emulsions, resulting in the appearance of non-emulsified water during the rheological tests.

---

[*] Speaker

[†] Corresponding author: vljuniorqui@gmail.com

Expanded Fluid Based Thermal Conductivity Model for Hydrocarbons and Crude Oils

Francisco Ramos-Pallares*[1], Florian Schoeggl[2], Shawn Taylor[3], and Harvey Yarraton†[2]

[1]Department of Chemical and Petroleum Engineering, Univeristy of Calgary – Canada
[2]Department of Chemical and Petroleum Engineering, University of Calgary – Canada
[3]Schlumberger-Doll Research Center – United States

Abstract

A full phase thermal conductivity model for pure hydrocarbons, crude oils, and their mixtures was developed based on the concept that the fluid properties that depend on the spacing between molecules, such as viscosity and thermal conductivity, decrease monotonically as the fluid expands from the liquid-solid phase transition to the dilute gas state. Hence, the thermal conductivity of the fluid at any condition can be correlated to the fluid density as follows:
where λ and λG are the fluid and the dilute gas thermal conductivity, respectively; $\lambda{*}s$ and $\beta\lambda$ are defined as:

where ρ and P are the density and pressure, respectively, $c2\lambda$ and $c3\lambda$ are fluid-specific parameters and λso and ρso are the thermal conductivity and density at the liquid-solid phase transition, respectively. A method for the prediction of ρso has been reported elsewhere [1].

The correlation was developed based on a dataset collected from the literature for *n*-alkanes, branched alkanes, aromatics and cyclics at temperatures and pressures up to 500∘C and 100 MPa, respectively. The correlation was tested on the thermal conductivity data for 7 crude oils each modeled as a single component fluid. Crude oil data were measured in this study using a hot wire apparatus at temperatures and pressures up to 150∘C and 10 MPa, respectively. The correlation fit the data for over 50 different hydrocarbons to within 1% and the data for 7 crude oils to within 0.8%.

Mass-based mixing rules including binary interaction parameters were developed for the correlation parameters to model mixtures. The model with tuned interaction parameters fit the data of 20 pure hydrocarbon binaries and 5 oil/solvent pseudo-binaries with average deviations of 1 and 1.2%, respectively. A correlation was developed for the interaction parameters as function of specific gravity.

Correlations for the three fluid-specific parameters were also developed to make the model predictive for oils characterized based on a distillation assay. This method relies on a separate characterization for maltenes and asphaltenes. The maltene fraction is represented as pseudo-components with model parameters calculated as a function of molecular weight

---

*Speaker

†Corresponding author: hyarrant@ucalgary.ca

sciencesconf.org:petrophase2017:144669

and boiling point. The asphaltene fraction is represented as a single component with fixed model parameters. The parameters of the whole fluid are calculated by combining those of the maltene pseudo-components and asphaltenes using the mixing rules with correlated interaction parameters. The method predicted the thermal conductivity of 7 crude oils to within 4%.

Ramos-Pallares, F. *et al. Energy and Fuels*, 2016, **30**, 7134-7157.

PP-P12

On Diffusion Mechanism Discrimination In Heavy oil + Light Hydrocarbon Pseudo Binary Mixtures

Mohammad Pourmohammadbagher*[1], Hemant Bansal[1], Petr Nikrityuk[1], and John Shaw†[1]

[1]Department of Chemical and Material Engineering, University of Alberta, Canada – Edmonton, Alberta Canada T6G 2H1, Canada

Abstract

Heavy oils comprise two nominal phases – a continuous maltene-rich liquid phase and a nano-dispersed asphaltene-rich phase separable by filtration [1]. The impact of this phase behavior on dominant or active diffusion mechanisms in these hydrocarbon resources and on the ongoing development of processes for their production, transport and refining is poorly understood. This contribution builds on our prior work [2]. The potential roles played by Fickian diffusion, Single-File diffusion arising from constrictions among nano-dispersed domains, and sorption of penetrants by dispersed phase domains are explored. Detailed models including these behaviors were prepared and applied to previously published composition profile data for light hydrocarbons diffusing into heavy oils and heavy oil fractions. The dominant diffusion mechanism is shown to shift from Fickian diffusion to some combination of Single-File diffusion + sorption as light hydrocarbon penetrant mass fraction decreases. Impacts of sorption and Single-File diffusion cannot be discriminated based on mathematics alone. Analysis of diffusion processes for toluene in carbon nanotube + polybutene mixtures [3], where all three mechanisms arise, provides insights. Analysis of diffusion experiments with well-defined nanostructured fluids where sorption does not occur comprises planned and much needed future work.

Key Words: Diffusion, Mechanism, Single-file, Fickian, Sorption,

References:

(1) Zhao, B.; Shaw, J. . Composition and Size Distribution of Coherent Nanostructures in Athabasca Bitumen and Maya Crude Oil. *Energy & Fuels* **2007**, *21* (5), 2795–2804.

(2) Alizadehgiashi, M.; Shaw, J. M. Fickian and Non-Fickian Diffusion in Heavy Oil + Light Hydrocarbon Mixtures. *Energy and Fuels* **2015**, *29* (4), 2177–2189.
(3) Pourmohammadbagher, M; M.Sc; Thesis in progress

---

*Speaker

†Corresponding author: jmshaw@ualberta.ca

FORMULATION OF DISPERSANTS OF ASPHALTENES IN VENEZUELAN CRUDE OIL BY ADDITION OF CASHEW NUT SHELL LIQUIDS

Ivan Villanueva*†[1], Jennifer Villamizar[1], Maria Losada[1], Victor Perez[1], Henry Labrador[1], and Juan Pereira[1]

[1]Laboratory of Petroleum, Hydrocarbon and Derivates (PHD), University of Carabobo, Valencia, Venezuela – Venezuela

Abstract

National oil industry seeks to optimize the production processes of crude oil, supported by technological development. Within these stages, chemical treatment, is widely used in order to give to the crude oil flow adequate conditions for efficient processing. Dispersants are used here to increase the stability of asphaltenes, among other reasons. The precipitation of asphaltenes in crude oil is a complex process and its inhibition involves the use of various preventive methods. Actually, in Venezuela, the additives for the formulation of dispersants are high interest. So it opens the opportunity to evaluate alternative sources of raw materials with orientations to this type of applications. In this sense, it was proposed the extraction of the cashew (Anacardium occidentale L.) nut shell liquids (CNSL) as an alternative of raw material for the formulation of dispersants of asphaltenes. CNSL is an important agricultural byproduct of cashew nut national production. In the present work, it was proposed to evaluate the stabilizing activity of CNSL in the Furrial crude oil. CNSL was obtained by a solid-liquid extraction with hexane. The yield of the extraction was found that vary with the method employed and the duration of the treatment. At full reflux for 3 h, 20.5g / 100g cashed nut shell, was obtained. The oil characterization was determinated by infrared spectroscopy, acid number, refractive index, density and viscosity. Solutions of CNSL in xylene and diesel, were prepared at different concentrations and added to the crude oil. The stability of the asphaltenes was evaluated through the dispersion test and the flocculation threshold. The dispersion test and flocculation threshold showed that by the addition of CNSL / solvent solution, the formation of precipitated was reduced. It was possible to stabilize 77% of the asphaltenes with respect to whithout dispersant sample. This evaluation was made comparatively with two synthetic polymer dispersant solutions based on alkylphenol resins, which achieved 100% stability. Also, through the flocculation threshold, it was found that there was an increase in the tolerance to the addition of heptane in 34%, showing its stabilizing activity. The results of the presents study suggest that CNLS can be used as economically source for formulations of dispersants and also to incorporate it as a potential source of monomers in the synthesis of polymeric dispersants.

---

*Speaker

†Corresponding author: ivillanu@uc.edu.ve

Flocculant-induced asphaltene precipitation from crude oil: structure and kinetics

Lia Balestrin*†[1], Celso Bertran[1], Mateus Cardoso[2], and Watson Loh[1]

[1]University of Campinas (UNICAMP) – Brazil
[2]Brazilian Nanotechnology National Laboratory (LNNano) – Brazil

Abstract

Studies related to asphaltene aggregation are of great relevance owing to asphaltene precipitation during the process of extraction and oil producting. However, most of these studies were conducted using model systems such as asphaltene solutions in organic solvents, making the direct comparison with real systems more difficult. Following earlier studies on colloidal aspects of asphaltenes,2 this work aims to employ SAXS measurements to identify the effect of n-heptane on the microstructure of asphaltene in crude oil. Moreover, we present kinetic studies on asphaltene deposition on gold using a quartz-crystal microbalance (QCM).
The SAXS results of crude oils confirmed the presence of asphaltene aggregates as fractal-like particles of colloidal dimensions. The data fitting revealed structures composed of at least two levels of organization, the first one with few nanometers, and the second one larger than 100 nm, but whose precise size could not be determined with the setup used. The measurements on oil samples containing heptane indicated a growth of the asphaltene nanoaggregates (smaller size population) by a factor of 2 - 3 until addition of 60 wt.% of the flocculant. On the other hand, the addition of toluene (a good solvent) does not significantly change the asphaltene nanostructure in the same concentration range.

QCM measurements were done using heptane in the range of 0 to 115 % of the onset determined by optical microscopy. These data can be analyzed in two regimes, the faster one within the first minutes and the slower one lasting up to days. A possible interpretation for this is the initial formation of a monolayer followed by aggregate growth and deposition and surface rearrangement. In agreement with what was expected, the mass deposited is higher in heptane concentrations closer or above the onset. Even for compositions well below the precipitation onset, a measurable mass increase is observed. The amount of precipitated asphaltene was also determined in batch experiments as a function of time, confirming that the measured mass increases with time.

1- Loh, W.; Mohamed, R. S.; dos Santos, R. G. Crude Oil Asphaltenes: Colloidal Aspects. Encycl. Surf. Colloid Sci. 2007, 1 (1), 1–18.
2- Padula, L.; Balestrin, L. B. S.; Rocha, N. D. O.; de Carvalho, C. H. M.; Westfahl, H.; Cardoso, M. B.; Sabadini, E.; Loh, W. Role of Asphaltenes and Additives on the Viscosity and Microscopic Structure of Heavy Crude Oils. Energy & Fuels 2016, 30 (5), 3644–3651.

---

*Speaker
†Corresponding author: lia.bsb@gmail.com

Equilibrium partitioning of naphthenic acids and bases and their interactions

Are Bertheussen*†[1], Sébastien Simon[1], and Johan Sjöblom[1]

[1]Ugelstad Laboratory, Department of Chemical Engineering, the Norwegian University of Science and Technology (NTNU) – N-7491 Trondheim, Norway

Abstract

Produced water is generated during the production of oil and gas and it contains both dissolved and dispersed oil components. In order to be able to discharge or reinject produced water, it is important to know and understand what factors could influence its composition. The equilibrium partitioning of two acids and two bases of different molecular weight were analyzed over a pH interval using heptane as the oil phase and 3.5wt.% NaCl as the water phase. Phenylacetic acid would represent the low molecular weight acid while 4-heptylbenzoic acid was chosen to represent the high molecular weight one. Likewise, 4-ethylaniline and 4-decylaniline were chosen as corresponding bases. The partitioning of the two acids and the low molecular weight base was successfully modelled by considering the acid dissociation constant pKa in aqueous phase and the partition ratio Pwo of the unionized species between oil and aqueous phase. The high molecular weight base did not significantly partition into the aqueous phase at the pH range studied. The results show that acid species are more water soluble than basic species of similar molecular weight. In presence of calcium the partitioning of acids is successfully modelled by accounting for the precipitation of naphthenate soap with a solubility constant Ks. The kinetic interfacial tension between heptane and 3.5% NaCl aqueous buffer was also analyzed with oils that contained single compounds, two bases, two acids and all four components over a pH interval to identify any interfacial acid-base interactions. No significant interfacial interaction could be identified, mostly due to similar pKa values.

Acknowledgement
This work was carried out as a part of SUBPRO, a Research-based Innovation Centre within Subsea Production and Processing. The authors gratefully acknowledge the financial support from SUBPRO, which is financed by the Research Council of Norway, major industry partners and NTNU.

---

[*] Speaker

[†] Corresponding author: are.bertheussen@ntnu.no

Phase Behavior of Asphaltene-Rich Heavy oil + Polystyrene + Toluene Mixtures

Sourav Chowdhury*[1] and John Shaw†[1]

[1]Department of Chemical and Materials Engineering, University of Alberta, Canada – Edmonton,
Alberta Canada T6G 2H1, Canada

Abstract

Heavy oils comprise two nominal phases – a continuous maltene-rich liquid phase and a nano-dispersed asphaltene-rich phase separable by filtration [1]. The asphaltene-rich phase can aggregate, and deposit, causing technological risk assessment and process operation challenges for the hydrocarbon production, transport and refining industries. When non-adsorbing polymers are added to nano-colloids in good solvents two stable fluid phases arise due to depletion flocculation. One phase is rich in polymer –polystyrene in this case. The other phase is rich in nano-colloid – asphaltenes in this case. In our prior work, we explored the phase behavior of mixtures comprising chemically separated asphaltenes + toluene + polystyrene experimentally, and modeled their phase behavior [2-6]. In this contribution, we investigate the phase behavior of asphaltene-rich, naturally-occurring hydrocarbons + toluene + polystyrene using a combination of X-ray and acoustic transmission measurements. Depletion flocculation driven phase separation is shown to arise for the pseudo ternary (Athabasca Bitumen, comprising 18.6 wt % pentane asphaltenes, plus atactic polystyrene, with a mean molar mass of 400,000 AMU, plus toluene) at ambient conditions. The experimental methods, phase boundaries, tie lines and a fluid-fluid critical point are presented and discussed, and the phase behavior is modeled using a Fleer-Tuinier framework. The outcomes of this work are expected to improve the understanding of current production, transport, and refining processes, and may lead to the development of new low environmental impact de-asphalting processes for heavy oils.

Keywords: Asphaltene, Polymer, Phase behavior, Depletion

References

Zhao, B.; Shaw, J. M., *Energy & Fuels* **2007**, *21* (5), 2795–2804.

Khammar, M., Shaw, J.M., *Energy & Fuels* **2012**, 26 (2), 1075-1088.

Khammar, M., Shaw, J.M., *Fluid Phase Equilibria* **2012**, 332(0), 105-119.

Pouralhosseini, S., Eslami, F., Elliot, J., Shaw, J.M., *Energy & Fuels* **2016**, 30(2), 904-914.

Pouralhosseini, S., Shaw, J.M., *Energy & Fuel* **2015**, 29(8), 4864-4873.

Pouralhosseini, S., Alizadehgiashi, M., Shaw, J.M., *Energy Fuels* **2015,** 29 (8), 4855–4863.

---

*Speaker

†Corresponding author: jmshaw@ualberta.ca

PP-P17

EFFECT OF FLUOROCARBON SURFACTANTS CHAIN STRUCTURE ON THE WETTABILITY ALTERATION OF SANDSTONES

Ivan Moncayo-Riascos*†[1] and Bibian Hoyos*[1]

[1]Universidad nacional de Colombia – Colombia

Abstract

Enhanced oil recovery (EOR) by chemical flooding improves oil recovery efficiency significantly by improvement in microscopic displacement of oil trapped in the reservoir rock. In this field, the surfactant play a key role because it can significantly reduce the interfacial tensions and alter wetting properties of reservoir rocks.
In this work the wettability alteration of sandstones surfaces caused by the presence of partially fluorocarbonated organosilane surfactants, with linear and branched chain (perfluorodecyl and fluorocarbamate, respectively) was evaluated. To this end, we built a phenomenological model to evaluate the wettability alteration, using molecular dynamics. We represent the experimental set-up based on a previous work1, obtaining simulation results for the coating configuration with each surfactant and the contact angle of liquid droplets on each of them. The calculations were made using the contact angle of n-decane and water droplets as evaluation parameter of the wettability alteration. Additionally, the effect of heteroatom content in the surfactant structure was also evaluated.

The results show that, since the linear chain generates smaller lateral interactions between molecules of surfactant, the adsorption configuration obtained with perfluorodecyl is more compact than the coating with fluorocarbamate. The linear chain of perfluorodecyl allows to obtain an orientation of the fluorocarbon chain towards the outside of the solid (in contact with the liquid phase). The branched chain of fluorocarbamate has instead a configuration with one chain oriented towards the solid and the other orientated towards the contact with the liquid phase.

In the case of the multilayer coating with the fluorocarbamate, we obtained that the external layers, which are in contact with the liquid phase, do not have an orderly configuration since the thickness of the coating reduces the interaction between the outer surfactant molecules and the solid. Therefore, the obtained surfactant-liquid density profiles show a behavior similar to a liquid-liquid interface and not to a solid-liquid, as in the monolayer coating case.

The contact angle evaluation of the n-decane and water droplets shows that the fluorocarbonated organosilanes structures promote the gas-wet preferential state with both surfactants generating lipophobic and hydrophobic surfaces (with contact angles larger than 50○). The results obtained show a good approximation with the contact angles measured experimentally, therefore the models and methodology used were appropriates to represent

---

[*] Speaker

[†] Corresponding author: idmoncay@unal.edu.co

the phenomena of wettability alteration.

From the evaluation of the interaction energies between the chain of the surfactants and the liquid phase, we determined the main molecular features to promote lipophobic and hydrophobic surfaces. The results show that the heteroatoms content in the branched chains of the fluorocarbamate (N, SO2, C=O) generate attractive interactions with the liquid phase, while with the perfluorodecyl the interactions obtained were mostly repulsive, generated by the lineal fluorocarbonated chain. Additionally, we found that the surfactants evaluated favor the liquid molecules remaining in the bulk of the droplet, since the surfactant-liquid attractive interactions are substantially smaller than the interaction energies between the molecules of the liquid.

(1) Moncayo-Riascos, I.; de León, J.; Hoyos, B. A. *Energy & Fuels* **2016**, *30* (5), 3605–3614.

Low Frequency Dielectric Relaxation of Supramolecular Petroleum Fluids

Tinu Abraham*†[1,2], Harshita Wadhawan[2], Ankur Goswami[2], and Thomas Thundat[2]

[1]Department of Chemical and Materials Engineering (Alberta, Canada) – Canada
[2]University of Alberta, Canada – Edmonton, Alberta Canada T6G 2H1, Canada

Abstract

Dielectric monitoring of cooperative long range segmental molecular motion and secondary localized molecular motions provides a link connecting molecular motion mechanisms to bulk properties such as viscosity and rheological behaviour. Determining these dielectric relaxation behaviors in supramolecular petroleum fluids such as heavy and extra heavy oil having asphaltenes and resins could be useful in characterizing their complex molecular structure. Additionally, a knowledge of the electrical frequency corresponding to the dominant dielectric relaxation mechanism can aid in implementing accurate electrical heating strategies in oil sands and other unconventional heavy oil reservoirs. In this work, dielectric spectroscopy was conducted to determine the dielectric relaxation mechanisms in bitumen and its subcomponents such as maltenes and asphaltenes extracted from Athabasca oil sands. The spectroscopy was conducted by sweeping frequency between 1 Hz and 1 MHz at temperatures varying between 20 to 250○C. Data was analyzed both isothermally and isochronically. While two types of dielectric relaxations were observed in bitumen, asphaltenes showed only one type of relaxation while maltenes did not show any relaxations in the observed frequency and temperature ranges. The manner of variation of these relaxations indicated by the dispersion of dielectric constant and loss peaks with respect to temperature are indicative of the molecular motion mechanisms. Greater molecular motions arising from segmental or chain motion occur at higher temperatures and lower relaxation times as compared to local side chain molecular motions. While, α relaxations arising due to molecular segmental motion resulting in glass transition was observed at 180○C for bitumen, it was observed at 100○C for asphaltenes and was not at all observed for maltenes. β relaxation arising due to local side chain motion of molecules was seen to occur at 80○C for bitumen only. Maltenes which can be thought to be devoid of polar groups did not show any β relaxation behaviour as well. On an isothermal plot, β relaxations were seen to occur after 100 kHz for bitumen and α relaxations occurring due to long chain segmental motion were seen to occur at lower frequencies less than 1 kHz. On plotting the conductivity spectrum, it was observed bitumen showed ionic conductivity after 70○C, whereas maltenes showed conductivity after 50○C possibly due to the absence of asphaltenes. Asphaltenes being in a solid powder like state, showed ionic conductivity only after 180○C. These insights about dielectric relaxation and conductivity patterns in supramolecular petroleum fluids at different frequencies and temperatures would aid in the development of studies modelling molecular motion mechanisms governing rheological properties.

---

*Speaker

†Corresponding author: tinu@ualberta.ca

Investigation of Adhesion Properties between Asphalt and Silica using a Digital Oil Model

Kazuya Ishitsuka*[1], Yunfeng Liang[2], Yoshihiro Masuda[2], and Toshifumi Matsuoka[3]

[1]Sustainable Resources Engineering, Hokkaido University – Japan
[2]Center for Engineering, Research into Artifacts (RACE), the University of Tokyo – Japan
[3]Fukada Geological Institute – Japan

Abstract

In this study, we investigated adhesion properties between asphalt and silica using molecular dynamics (MD) simulations, and quantified the adhesion loss in the presence of water molecules. The aim is to show how the adhesion properties (and their water-resistance) can be tuned by changing the surface chemistry of minerals.
We used digital oil, which is a full molecular model of crude oil (i.e. digital oil model) constructed on the basis of various analytical experiments. By "distillation" of light oil components away from the digital oil model, the asphalt model was obtained. In addition, we determined the optimal combination of molecules from the "distilled" crude oil by fitting experimental data of asphalt (such as element analysis). Fully hydroxylated (hydrophilic) and siloxane bridged (hydrophobic) silica surfaces were employed. First, we calculated the density, viscosity, and heat capacity of asphalt system. Second, we studied the adhesion energies (with two different silica surfaces). Third, tensile strains were applied to examine stress-strain relationship and the failure type of the interfacial systems. The temperature considered in this study is from 260 K to 360 K.

Based on the calculated heat capacity, we categorize the asphalt systems into the low-temperature solid ($<$ 320 K) and high-temperature viscous liquid-like regimes ($>$ 320 K). Under all temperature condition examined in this study, the magnitude of adhesion energy increased with increasing temperature. The hydrophobic surface showed higher adhesion energy than that of hydrophilic surface. This energy pattern reflects failure types applying tensile strain. We observed a typical cohesive failure for both the asphalt–solid interface systems over 320 K, when the asphalt is liquid-like. Under 320 K, we observed cohesive failure for the asphalt – hydrophobic silica system (i.e. the failure occurs within the asphalt material), whereas, in asphalt–hydrophilic silica systems, we observed interfacial failure (i.e. the failure occurs at the interface region).

In the presence of water molecules to the interfacial system, interfacial failure was observed under all temperatures examined in this study. This observation indicates that water molecules decreased adhesion strength. In addition, adhesion loss due to water molecules was quantified using the energy ratio, which calculates how water decreases the adhesive energy. The larger the energy ratio, the higher resistance to water damage. Under low-temperature condition ($<$ 320 K), the energy ratio of hydrophobic surface is greater than that of hydrophilic silica. This indicates that the hydrophobic surface is a way to improve the water

---

*Speaker

resistance to the adhesion loss. At elevated temperatures, the energy ratios of both surfaces increase. This is presumably because asphalt can uptake some interfacial water, and reduce the overall tension between asphalt and silica surface.

Our results demonstrate the effectiveness of digital oil model and MD simulations to study the interface adhesion mechanisms of asphalt and aggregate minerals.

PP-P20

Development of Digital Oil for an Extra Heavy Oil for Investigation of Enhanced Oil Recovery

Yunfeng Liang*[1]

[1]Center for Engineering, Research into Artifacts (RACE), the University of Tokyo – Japan

Abstract

The operational development of an extra heavy oil is more complicated than that of light oil due to its high viscosity. Characterization of heavy oil fluid compositions is by no means a trivial task. In this paper, we will show our newly developed algorithm on construction of a digital oil model for an extra heavy crude oil.

In an earlier work, a digital oil model has been constructed for a light oil based on analytical experiments: the gas and light fraction components were analyzed by gas chromatography, and hundreds of molecule species, including n-alkanes, iso-alkanes, naphthenes, alkylbenzenes, and polyaromatics (with a maximum of 3 aromatic rings), were modeled. On the other hand, the heavy fraction and asphaltene components were represented by molecular mixtures using an improved quantitative molecular representation (QMR) method, which were consistent with analytical experiments, such as elemental composition, molecular weight from gel permeation chromatography (GPC), 1H-NMR and 13C-NMR spectroscopy data. When we apply this digital oil method to heavy oil, the major difficulty is that we could not characterize the light fraction components by gas chromatography methods. This is true even when we separate the light fractions into saturates and aromatics with the help of SARA analysis. In addition, the saturate fractions always contain a few percent of aromatics. Because a "true" saturates model could not be constructed due to the restriction of the software implementation of the current QMR method, a new QMR method was developed in this study. The new algorithm enabled us to construct non-aromatic molecules with branched alkyl chains or naphthenic rings, and also alkylbenzene molecules with mono-aromatic rings. Furthermore, an optimization process for imitating molecular weight distributions by some QMRs was developed. Finally, the saturate and aromatic models were represented by 2-5 QMRs (12-20 types of molecules), which successfully reproduce molecular weight distribution of the Gas Chromatography Distillation (GCD) experiments (**Fig.1**). Due to the low concentration of the asphaltenes (_˜ 0.4 wt%), we have constructed the digital oil for the crude oil by combining all saturates, aromatics, and resin molecules. The calculated density at ambient conditions is 0.943 g/cm3, which is in good agreement with our measured data of 0.954 g/cm3. With the generated digital oil model, we are planning to explore improved recovery methods for extra heavy oil.

---

*Speaker

Coarse-graining polycyclic aromatic hydrocarbons using SAFT-gamma force fields: application to molecular simulations of asphaltenes

Guadalupe Jiménez-Serratos*[1], George Jackson[1], Tim Totton[2], and Erich Müller†[1]

[1]Imperial College London (ICL) – Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom
[2]British Petroleum (BP) – United Kingdom

Abstract

Fully atomistic simulations of asphaltenes have allowed the study of trends in aggregation phenomena and the understanding of the role that molecular structure plays therein. However, the detail included at this scale of molecular modelling is at odds with the required spatial and temporal resolution needed to fully understand the aggregation process [1]. The computational cost required to explore larger systems can be reduced by using coarse-grained (CG) models, which lump a few atoms into a single segment with effective interactions. A key challenge in CG modelling is obtaining reliable force fields that exhibit good representability, robustness, and transferability.

In this work, we use a top-down approach to estimate CG parameters by correlating experimental thermophysical fluid data of well defined molecules through a molecular-based equation of state, the statistical associating fluid theory, SAFT-gamma [2]. To specifically develop force fields for asphaltenes, we explore trends in the behaviour of small polynuclear aromatic hydrocarbons and propose simple fittings of the parameters as a function of the ratio between the number of carbons not linked to hydrogen and the total number of carbons. The new parameters obtained, alongside others published for small organic molecules [3] allow the construction of asphaltene models by joining different chemical moieties, in a group-contribution fashion [2] (Fig 1.)

We apply the procedure to two model asphaltene molecules from the literature and simulate CG systems of 27 asphaltenes with explicit solvent (toluene and heptane). We find an excellent match of cluster size, radii of gyration, and shape-factor distributions with those from equivalent atomistic simulations [1]. Finally, we exploit the advantages of the CG representation by simulating a system containing 500 molecules of asphaltene in toluene and heptane identifying the bulk aggregation behaviour. The procedure is general and predictive, hence can be employed to other asphaltene molecular structures and mixtures.

References

Headen, T. F. et al. (2017) *Energy and Fuels*, (31), 1108–1125.

---

*Speaker

†Corresponding author: e.muller@imperial.ac.uk

M´uller, E.A., and Jackson, G. (2014). *Annual Rev. Chem. Biomolec. Eng.*, (5), 405-427.

Herdes, C., Totton, T. S., and M´uller, E. A. (2015). *Fluid Phase Equilibria*, (406), 91–100.

Constant Mass Study based Black Oil Tables Improve the Accuracy of Black Oil Reservoir Simulation

Vassilis Gaganis*[1], Giorgos Kampolis[1], and Nikos Varotsis†[1]

[1]Technical University of Crete [Chania] – Plateia Agiou Titou 73132 Chania - Crete, Greece

Abstract

As the hydrocarbon phases flow through the porous medium during production they are subjected to pressure variations which continuously disturb the previously established equilibria and alter the values of their thermodynamic properties. Although such processes can be adequately predicted using a fully compositional reservoir simulation model, the increased number of primary variables and the need to solve the phase behavior for each block and at each time step require a very considerable CPU time thus rendering history matching and production optimization as extremely time consuming tasks. As a result, most operators prefer to deal with the compositional phenomena by utilizing the black oil approach according to which the continuity equations need only to be solved for each phase rather than for each component. This way, equilibrium calculations are skipped online through the use of volumetric factors (Bo, Rs, Bg) under the assumption that the reservoir fluid phases' compositions at any pressure can be approximated by mixing the produced stock tank oil and surface gas at different ratios. By tabulating those properties against pressure in Black Oil Tables (BOTs), black oil simulation can provide reliable predictions for all types of depletion and waterflooding projects and combined with the very low CPU requirements makes the method very popular to the oil industry.

For guaranteeing adequate accuracy for the black oil approach of vital importance is that the volumetric factors required to compute volumes at surface conditions during simulation are calculated along the actual compositional path that is followed by the fluid in the reservoir during depletion. Currently, engineers generate BOTs based on the Differential Liberation (DV) or the Constant Volume Depletion (CVD) paths since those are the major depletion PVT studies performed in the lab. Nevertheless, recent studies showed that the phase compositions which prevail in the grid blocks follow closely the compositional path of the Constant Composition Expansion (CCE) study and this finding is even more profound for the simulation of very volatile and near critical oils.

In this work, the improvement of reservoir simulation predictions accuracy by using CCE based BOTs is investigated. For a large variety of fluids of varying volatility, BOTs were generated following the composite DV and CCE paths and further introduced to a commercial reservoir simulator to run depletion and waterflooding scenaria. The resulting pressures and rates from each black oil simulation run were compared against the predictions obtained by running fully compositional models. It is shown that depending on the fluid volatility, the rates predicted using DV-based black oil simulation may deviate up to more than 10% from the respective compositional one. On the other hand, black oil simulation utilizing tables generated following the composite CCE path minimizes those errors thus enhancing the advantages of this popular type of reservoir modeling.

---

*Corresponding author: gaganis@mred.tuc.gr

†Speaker

Heat capacity and Joule-Thomson coefficient of the binary system methane + n-decane

Teresa Regueira*[1], Christos P. Chatziagapiou[1], Farhad Varzandeh[1], Erling H. Stenby[1], and Wei Yan†[1]

[1]Center for Energy Resources Engineering (CERE) Technical University of Denmark, DTU (DENMARK) – DK-2800 Kgs. Lyngby, Denmark

Abstract

The accurate knowledge of heat capacity as a function of temperature and pressure is important to many industrial applications. This property is used in energy balances, in entropy and enthalpy calculations or in the study of phase transitions. As one of the second order derivative properties of Gibbs energy, heat capacity is difficult to describe accurately and modelling of this property is a demanding test for equations of state. Heat capacity values of hydrocarbon mixtures are important for the oil and gas industry to build models for reservoir fluids in broad temperature and pressure ranges. Particularly, data on asymmetric binary systems have a special relevance to test model capabilities.

The Joule-Thomson coefficient (μJT) indicates the rate of temperature change with pressure during an isenthalpic expansion. This coefficient is important for high pressure reservoirs where the reverse Joule-Thomson effect is commonly observed. The effect results in an increase in temperature after depressurization, which can potentially damage the surface production facilities and affect well integrity and safety. High pressure Joule-Thomson coefficients for hydrocarbon mixtures are scarce due to the difficulty and uncertainty associated with their direct experimental determination. Joule-Thomson coefficients can also be determined indirectly by combining heat capacity and volumetric data.

We have chosen methane + n-decane as a model reservoir fluid system to measure its heat capacities and Joule-Thomson coefficients, which can be used to test any thermodynamic model intended for describing these properties. The isobaric heat capacity of the mixture was measured in the methane mole fraction range from 0.2 to 0.8. The μJT was also obtained by combining the measured heat capacity values with density values from the literature at pressures up to 60 MPa. Heat capacities were measured by using a Calvet type differential heat-flux calorimeter C80 from Setaram. Self-designed high pressure cells allowing circulation of fluid were used for the high pressure heat capacity measurement. The heat capacity was determined in three measurement steps according the method previously described by Bessières et al. [1]. Initially, the specific isobaric heat capacity for six n-alkanes, i.e. n-hexane, n-octane, n-decane, n-dodecane, n-tetradecane and n-hexadecane up to 10 MPa was also measured in order to validate the experimental procedure. The Joule-Thomson coefficients of these n-alkanes are also reported.

Finally, four different cubic and non-cubic models, i.e. Soave-Redlich-Kwong, Peng-Robinson,

---

*Speaker

†Corresponding author: weya@kemi.dtu.dk

Perturbed Chain Statistical Associating Fluid Theory [2], and Soave-Benedict-Webb-Rubin [3], were used to predict the reported properties of the pure n-alkanes and the binary mixtures.

D. Bessières, H. Saint-Guirons, J.-L. Daridon, J. Therm. Anal. Calorim. 62 (2000) 621-632.

J. Gross, G. Sadowski, Ind. Eng. Chem. Res. 40 (2001) 1244-1260.

G.S. Soave, Fluid Phase Equilib. 164 (1999) 157-172.

Density and compressibility of multicomponent n-alkane mixtures up to 463 K and 140 MPa

Teresa Regueira*[1], Erling H. Stenby[1], and Wei Yan†[1]

[1]Center for Energy Resources Engineering (CERE) Technical University of Denmark, DTU (DENMARK) – DK-2800 Kgs. Lyngby, Denmark

Abstract

The increasing worldwide energy demand together with the declining conventional oil and gas reservoirs has moved the oil and gas industry towards the exploration of deeper formations with extreme temperature and pressure conditions. Production under these conditions is risky and knowledge of the thermophysical properties of the reservoir fluids under these conditions is essential for the planning and prediction of the reservoir production. Density is a key property for the understanding of the volumetric behaviour of the reservoir fluids; it is used for fluid characterization and also in the estimation of oil and gas resources. Specifically, the compressibility of the reservoir fluids is one of the driving factors in the primary reservoir production [1].

Reservoir fluid samples are not easy available and the use of well-defined hydrocarbon mixtures as model fluids allows the understanding of the contribution of the different compounds to the final reservoir properties. Thus, in this work we have determined the density values of two multicomponent mixtures composed of methane, n-butane, n-octane, n-dodecane, n-hexadecane, n-eicosane, one of them is a model volatile oil whereas the other represents a gas condensate. The density was measured in the temperature range up to 463.15 K and pressures up to 140 MPa. Excess volume and isothermal compressibility were determined from the experimental density values. The predictive capability of different equations of state (SRK [2], PR [3], PC-SAFT [4]) was also tested for the studied systems.

F. Jahn, M. Cook, M. Graham, Hydrocarbon exploration and production, 2nd ed., Elsevier., 2008.

G. Soave, Chemical Engineering Science 27 (1972) 1197-1203.

D.-Y. Peng, D.B. Robinson, Industrial & Engineering Chemistry Fundamentals 15 (1976) 59-64.

J. Gross, G. Sadowski, Industrial & Engineering Chemistry Research 40 (2001) 1244-1260.

---

[*] Speaker

[†] Corresponding author: weya@kemi.dtu.dk

Atomic force microscope as a tool to detect asphaltene particles in crude oil

Lia Balestrin[1], Mateus Cardoso[2], and Watson Loh*†[1]

[1]University of Campinas (UNICAMP) – Brazil
[2]Brazilian Nanotechnology National Laboratory (LNNano) – Brazil

Abstract

The precipitation of asphaltene is a main problem in the process of extraction and oil production and it has been the focus of many studies on their characterization and on the effects of additives to inhibit their formation and/or deposition. However, most of these studies were accomplished in model systems such as asphaltene solutions in organic solvents, which turn the comparison with crude oil more difficult. Herein we describe the use of atomic force microscopy to identify colloidal particles of asphaltene aggregates present in crude oils. The methodology involved the addition of oil, its subsequent washing in toluene to remove oil excess, followed by drying and the image recording. Following this protocol, we were able to monitor asphaltene aggregates and how they were affected by aggregation inhibitor, good and bad solvent.
As a result, nanoparticles with dimensions ranging from a few of nanometers to few micrometers were observed. The particles observed in crude oil and asphaltene solutions in organic solvents are similar. However, the structures in model system are, on average, larger than those observed in the parent crude oil. This may be a consequence of the influence of the maltene fraction, which was not present in the model organic solutions. AFM images of maltene samples, on the other hand, presented significantly fewer nanoparticles.

In addition, more particles are observed when heptane is added, whereas their size decreases with toluene addition. The addition of inhibitor such as DBSA (4-Dodecylbenzenesulfonic acid) led to observation of more and smaller nanoparticles. Finally, the use of HOPG (Highly Ordered Pyrolytic Graphite) as a low energy substrate producing images that contain particles in the same size range as the ones detected on mica.

The main observations derived from this methodology agree with those reported from earlier studies on asphaltene colloidal particles obtained from scattering experiments and other microscopy analyses, validating the proposed methodology.
Therefore, this present experimental approach not only confirms this methodology as a valid one for the investigation of colloidal asphaltene particles in crude oils and model systems. Moreover, this is an accessible protocol to obtain information on how asphaltene particles are affected by changes in oil composition or inhibitors.

---

*Speaker

†Corresponding author: wloh@iqm.unicamp.br

PVT Properties of Live Crude Oils from Primary High Pressure Separators in Production Platforms

Krishnaswamy Rajagopal*†[1] and Luciana Andrade

[1]Federal University of Rio de Janeiro (LATCA-UFRJ) – Av. Horácio Macedo, 2030 - Centro de Tecnologia Bloco I Sala I-122 - Cidade Universitária - Ilha de Fundão, Rio de Janeiro, RJ, Brasil cep 21941-909, Brazil

Abstract

The physical and compositional properties of reservoir fluids at different conditions of temperature and pressure determine the phase behavior of fluids and affect the production. The properties of live crude oil produced during the primary oil and gas separation of reservoir fluids are important in planning transportation, storage and secondary separation processes of production. In this study, we have obtained experimental data of solution gas-oil ratio and oil formation volume factor from the PVT analyses of several live naphthenic –aromatic crude oils from Brazilian off-shore wells. The experimental data were correlated with the available literature correlations. The literature correlations ,mainly derived from properties of oils of different origins, were inadequate to represent the measured data. A new correlation is proposed to effectively represent our experimental data with in experimental error. The proposed correlation has been successfully used for estimating properties of naphthenic – aromatic live crude oils .

---

*Speaker

†Corresponding author: raja@eq.ufrj.br

Prediction of Asphaltenes Destabilization Onset by ASIST: A Comparison with Experimental Data Obtained by Acoustic Resonator Method

Mohamed Saidoun*† , Jean-Luc Daridon[1], Hervé Carrier[1], Nicolas Passade-Boupat , and Jean-Philippe Gingras

[1]Laboratoire des Fluides Complexes et leurs Réservoirs (LFC-R) – Université de Pau et des Pays de l'Adour [UPPA], CNRS : UMR5150, TOTAL – BP 1155 - 64013 Pau, France

Abstract

Anticipation of asphaltene deposition in upstream production systems is a key step in early project phase. Overpassing the limits of infinitely diluted systems: [Wang and Buckley] (i) developed the Asphaltene Instability Trend (ASIST). This method enables extrapolating the destabilization onset up to reservoir conditions from limited number of ambient Refractive Index (RI) measures on stock-tank oils (STO) and series of precipitants. Presented as sensitive to temperature, pressure, time and composition, the model allows a qualitative prediction of where and when asphaltene may precipitate. Although [Creek et al.] (ii) experimentally verified the ASIST technique by NIR light scattering and microscopic observations on one STO recombined with gas mixtures; more validations are needed to confirm its universal applicability as asphaltene destabilization is an oil-specific phenomenon.
Sensitive quartz crystal resonator (QCR) measures at ambient conditions and in pressurized systems are compared to predictions from ASIST on a problematic crude. Results of various conditions are discussed and perspectives indicate the remaining uncertainties to be investigated in future applied research.

(i) Wang JX and Buckley JS. An Experimental Approach to Prediction of Asphaltene Flocculation. 2001; SPE-64994.

(ii) Creek JL, Wang JX, Buckley JS. Verification of Asphaltene-Instability-Trend (ASIST) Predictions for Low-Molecular-Weight Alkanes. 2009; SPE-125203.

---

*Speaker

†Corresponding author: mohamed.saidoun@gmail.com

Development of a Desalting and Dehydration Process of Heavy and Extra Heavy Oils

Cristina Sad*[1], Paulo Filgueiras , Mayara Silva , Laíne Pereira , Rayane Corona , João Bassane , Francine Santos Dalapícola , Dorval Neto , Valdemar Júnior , and Eustáquio Castro*

[1]Federal University of Espirito Santo, Chemistry Department (LabPetro - UFES) – Av. Fernando Ferrari 514, Goiabeiras, CEP: 29.075-910, Brazil

Abstract

The water separation step and consequently the salts separation in heavy and extra heavy crude oils is certainly the most complex and important part of the process, since its presence contributes to the occurrence of corrosion, formation of hydrates and increase of the viscosity, which can hinder the flow, amongst others.1 In this sense, the development of new technologies and the improvement of the existing techniques are of great relevance to guarantee the processing of these oils with a view to productivity gains. The salts present in petroleum interfere in the characterization of its physicochemical properties, and from the measurements of these properties is established the price of crude oil. Therefore the water and salt need to be removed before these analyses. In this work, a new desalting and dehydration apparatus was developed for heavy and extra heavy crude oils. In the first step the desalination process is accomplished in several washing steps and the extracted oil salts are monitored by ionic conductivity.2 In the second step the dehydration processes by gradient of reduction of the oil vapor pressure was performed. Operational conditions were studied before and after the desalting and dehydration process and the following parameters were evaluated: density, kinematic viscosity, total salinity index, total sulfur, total acid number and ionic conductivity. The efficiency of the desalting and dehydration process was above 99.7 (less than 10 mg.kg-1) and 99.5% (less than 0.1% v/v) respectively, evaluated in situ in the prototype by the measurement of the conductivity and salt content in the "wash" water. The monitoring of the oils profile was done by the technique of spectroscopy in the medium infrared region in the dehydrated oil and indicated no loss of organic compounds after the dehydration process.

---

*Speaker

Study of Stability and Homogeneity of Water-in-Oil Emulsions of a Heavy Oil

Mayara Silva*†[1], Cristina Sad‡ , Dorval Neto , Francine Santos , João Bassane , Rayane Corona , Laíne Pereira , Paulo Filgueiras , Valdemar Júnior , and Eustáquio Castro

[1]Universidade Federal do Espírito Santo (PPGQUI - UFES) – Av. Fernando Ferrari n515, Vitória -ES, Brazil

Abstract

In this work a stability and homogeneity study of water-in-oil (W/O) emulsions of a heavy oil (°API 13.7) with asphaltenes content of 7.10% w/w and 32.0% w/w of resins. The W/O emulsions were prepared by adding increasing volumes of 10, 20, 30 and 40% w/v of two different types of water (deionized water and formation water) and a saturated sodium chloride solution under mechanic stirring of 2500, 5000, 10000 and 15000 rpm. The factors which influence the stability of an W/O emulsion were studied: aging, temperature, shear, water content and salt concentration. The results showed that the three types of emulsions studied presented average droplet diameter ranging from 1 to 10 μm, and the emulsions kept stable even after aging of 30 days. After this time, the emulsions were subjected to temperatures from 30 to 80○C at 10○C intervals and the same remained stable. This stability may be related to the high content of asphaltenes and resins of the studied oil. In terms of the effect of salinity, emulsions prepared with formation water (salt content of 55.000 mg.L-1) presented an average droplet diameter higher than those prepared with saturated sodium chloride solution (270.000 mg.L-1) and deionized water, respectively. This may be related to the amount of ions of different charges present in the formation water. The work proved to be important because it is necessary to prepare, on a laboratory scale, stable W/O emulsions to study and understand their behavior in order to support the de-emulsification actions of these.

---

*Speaker

†Corresponding author: sna.mayara@gmail.com

‡Corresponding author: cristinasad@gmail.com

Complex two and three-phase envelopes of reservoir fluids with asphaltenes: Understanding different behaviors and a new integral strategy for their calculation.

Martin Cismondi*[1]

[1]Instituto de Investigación y Desarrollo en Ingeniería de Procesos y Química Aplicada (IPQA-UNC-CONICET) – Argentina

Abstract

Regardless their cubic or SAFT nature, equations of state (EoS) have been used to model asphaltenes phase behaviour in reservoir fluids for at least two decades already. The importance of the upper and lower asphaltene onset pressures (AOP's) is widely recognized in the literature, where many studies of either experimental or modelling character are available, with different approaches. In terms of algorithms or calculation methods, most studies normally resort to a series of two-phase and multiphase flashes. New flash algorithms were even proposed focused on asphaltenic systems. But, surprisingly, no explicit method for tracing different phase boundaries like AOP lines and the intermediate bubble line are found in the literature. No attention has been paid either to study the different possible behaviours, i.e. how these and other related segments can arrange in the complete phase envelope of a specific asphaltenic reservoir fluid, as predicted by a model.

In this work, a new integral algorithmic strategy for the construction of complete phase envelopes based on an EoS, including AOP lines and other related segments, has been proposed and implemented. Every segment is treated as the boundary of either a two-phase or three-phase region in the pressure-temperature diagram for a specific fluid. In other words, every point along these lines determines the T-P conditions where an incipient phase appears or disappears. In the first case, the method of Michelsen for tracing two-phase boundaries is used, while for three-phase saturation lines an equivalent method was designed, including a second set of K factors and a phase fraction as extra independent variables.

Several fluids from the literature are taken as case studies to illustrate the application of the proposed strategy and discuss different types of behaviour. Specific issues as recognition of unstable segments like false bubble curves, are also discussed. In sum, computer codes based on the proposed strategy can become a useful tool for researchers or professionals dealing with asphaltene phase behaviour in reservoir fluids.

---

*Speaker

sciencesconf.org:petrophase2017:145335

PP-P31

Selective ionization of petroporphyrins in crude-oils by electron transfer MALDI-MS

Deisy Giraldo-Dávila[1], Juan Ramirez-Pradilla*[1], Cristian Blanco-Tirado[1], and Marianny Combariza†[1]

[1]Universidad Industrial de Santander [Bucaramanga] (UIS) – Cra 27 Calle 9 Ciudad Universitaria Bucaramanga-Santander-Colombia, Colombia

Abstract

Nowadays matrix assisted laser desorption ionization (MALDI) is a solid, reliable and fast ionization technique in mass spectrometry routinely used for the analysis of peptides, biomolecules, organic compounds and macromolecules. The most common ionization mechanisms in MALDI are related to secondary reactions involving proton transfer/abstraction or adduct formation (Na+/K+/Ag+); however, not every molecule is able to acquire charge through these processes. Thus, alternative ionization pathways such as electron transfer/capture become relevant for the analysis of compounds unsuitable to charge acquisition by any other means. For a successful electron transfer (ET) reaction in MALDI, the ionization potential of the matrix (IPM) must be higher than the ionization potential of the analyte (IPA). This means that a "universal" ET matrix should, to begin with, have a high IP. We have previously reported the use of oligo-*p*-cyano-phenylenevinylene derivatives (CNPV-CH3 and CNPV-OCH3) as high-performance ET MALDI matrices, for the analysis of porphyrin derivatives, because these compounds not only exhibit high IPs but also excellent optoelectronic properties when compared to a standard ET matrix such as DCTB.

Petroporphyrins are important biomarkers with relatively complex structures that are preserved despite the maturation processes of petroleum. Detection of these compound families is currently an analytical challenge due to their presence in low concentrations (10-40 ppm) in complex mixtures of hydrocarbons. Petroporphyrins extraction and concentration workouts involve convolute multiple steps, as illustrated by a previous work were we reported the MS analysis of porphyrins from a Colombian crude-oil using soxhlet and column chromatography purification. Aiming towards a simpler method for petroporphyrins analysis, we report the selective ionization of these compounds directly from crude-oils using an ET-MALDI-TOF approach based on oligo-*p*-cyano-phenylenevinylene derivatives (CNPV-CH3 and CNPV-OCH3) as matrices. To test the performance of the new ET MALDI matrices we extracted the petroporphyrin fraction from two crude oils following well stablished protocols such as adsorption in mineral surfaces, soxhlet extraction, flash column chromatography and asphaltene precipitation and compared the analysis of these fractions with an approach in which the whole crude oil was subjected directly to ET MALDI using oligo-*p*-cyano-phenylenevinylene derivatives as matrices.

Our preliminary results show that CNPV-CH3 is a suitable matrix for the analysis of petroporphyrins fractions extracted from mineral surfaces, precipitated asphaltenes and by soxhlet

---

*Speaker

†Corresponding author: marianny@uis.edu.co

followed by column chromatography. We also observed selective ionization of petroporphyrins when analyzing the whole crude oil directly by ET MALDI using CNPV-CH3 as matrix. Interestingly, similar mass spectra were recorded by either direct analysis of the whole crude samples or by petroporphyrins fraction analysis. In addition, we assigned molecular formulas belonging to different homologous series such as Ethio, DPEP, Di-DPEP for both petroporphyrins detected in the fractions and in whole crude oils.

Finally, with this work we demonstrate the use of ET-MALDI, using oligo-*p*-cyano-phenylenevinylene derivatives as matrices, as an effective tool for direct petroporphyrin analysis in complex hydrocarbon mixtures.

Coarse-Grained Molecular Simulations to Investigate Asphaltenes and Sodium Naphthenates at the Oil–Water Interface, and their Participation in the Mechanism of Enhanced-Oil Recovery by Low Salinity Water Injection

Yosadara Ruiz-Morales*[1]

[1]Instituto Mexicano del Petróleo (IMP) – Eje Central Lazaro Cardenas Norte 152, Mexico City 07730, Mexico

Abstract

Injection of low salinity water has been proposed as an enhanced-oil recovery method. Underlying the enhanced-oil-recovery mechanisms remains controversial and not well understood. The majority of the proposed mechanisms rely on rock-fluid interactions. In the present work we study an alternative fluid-fluid mechanism, recently proposed in the literature, that is the increase in oil-water interfacial visco-elasticity upon injection of low salinity water, as a suppressor of oil trapping by snap-off. The effect of oil asphaltenes and sodium naphthenates at the oil-water interface is investigated and the reduction of the oil-water interfacial tension is evaluated. Instead of atomistic models, the coarse-grained model molecules at the mesoscale level, using dissipative particle dynamics (DPD), are adopted. DPD is a relatively new method proposed to study the hydrodynamics behavior of complex fluids. The method is based on the dynamics of soft particles interacting by conservative, dissipative, and random forces. Bead-spring-type particle models, where particles represent a group of atoms or a liquid volume, are used in the DPD calculations. DPD can process a much larger spatial and temporal scale system than molecular dynamics (MD) can. We conclude that the mechanism of low salinity water injection involves a synergy between wettability alteration (rock-fluid interaction), and snap-off suppression by fluid-fluid interactions, which increases the elasticity of the oil-water interface. We find that asphaltenes have affinity for the oil water interface and they tend to align their PAH region horizontally to the oil-water interface or perpendicularly, reducing the interfacial tension, and increasing the elastic moduli. The elasticity of the film depends on the surface coverage by asphaltenes, which in turn depends on the type of asphaltene (interface active or less interface active), and on their interaction with sodium naphthenates, which also have affinity for the oil-water interface. The surface active asphaltenes reduce the interfacial tension more effectively. These coarse-grained molecular simulations findings are in accordance with experimental reports in the literature.

---

*Speaker

Asphaltene precipitation in paraffinic froth treatment – effect of non-traditional solvent and temperature

Yuming Xu*[1]

[1]CanmetENERGY, Natural Resources Canada – 1 Oil Patch Drive, Devon, Alberta, Canada

Abstract

In surface mining oil sand operations bitumen is extracted from oil sand ore using a warm water extraction process. This produces bitumen froth which typically contains 60 wt% bitumen, 30 wt% water, and 10 wt% mineral solids. The bitumen froth is then cleaned in a froth treatment process in which the froth is diluted with solvent to enhance the separation of bitumen from the water and solids. There are two froth treatment processes depending on the solvent used: naphthenic and paraffinic. In the traditional naphthenic process naphtha is the solvent. Emulsified water in the froth is difficult to remove completely in this process, so the final diluted bitumen product still contains a small amount of water (1 to 2 wt%) and mineral solids such as clay (In the newer paraffinic froth treatment (PFT) process light alkanes such as pentane and hexane are used as solvent which precipitates some of the asphaltenes in the bitumen. The precipitated asphaltenes form agglomerates with the mineral solids and water droplets. These agglomerates quickly settle out from the diluted bitumen phase leaving a very clean diluted bitumen product.

In order to precipitate the required amount of asphaltenes the solvent-to-bitumen ratio used is typically high. In this work we investigated asphaltene precipitation using solvents that are not typically used to precipitate asphaltenes such as butane, neopentane as well as carbon dioxide, at different temperatures. It was found that the solvent-to-bitumen ratio can be decreased significantly by using these solvents or by combining them with a traditional solvent. The effect of the solvent on asphaltene precipitation can be explained in terms of the solubility parameters of the solvent. A general correlation was obtained between the asphaltene content in the bitumen product and the solubility parameters of the solvent.

---

*Speaker

Interaction of low salinity water (LSW) with crude oils

Ana Cosultchi*[1]

[1]Instituto Mexicano del Petróleo - IMP (MEXICO) (IMP) – 152, Eje Central Lazaro Cardenas, Mexico City, Mexico

Abstract

Recovery of hydrocarbons using low salinity water (LSW) is a recent EOR technique explained within an extensive body of literature containing experimental work and a series of explanation of the physicochemical mechanisms, which are supposed to lay behind the additional hydrocarbon recovery. The most cited aspects are: a) variation of wettability of calcite surface from oil wet to water wet; b) dissolution of the calcite surface as a consequence of pH reduction; c) the presence of the so call potential determining ions (SO4-, Ca++, Mg++) within the low salinity water, which contribute to displace the organic compounds out of the surface.
Usually water-flooding tests, the most assisted Laboratory experiments provide useful information on the applicability of this technology. However, other kind of systematic experiments is required to understand what happens between LSW and crude oil and LSW and minerals. The brine composition and its pH play an important role within calcite and dolomite dissolution. At pH$<$ 6, calcite dissolution occurs through proton-promotion, while at pH$>$ 7 dissolution is inhibited as the surface metals are highly hydrated.

The results are summarized below.

> The pH of LSW after contact with crude oil of water shows a decrement. The pH can drop until 4.00 following an inverse relationship to TBN/TAN ratio (total basic/total acidic numbers).
>
> The pH of LSW after contact with minerals (calcite, quartz, clays) shows an increment. The pH can rise above 9.00 depending on the cations and salinity of water; and the minerals contacted.
>
> When in contact with LSW minerals experience dissolution or adsorption of cations from brine. Such ionic interchange depends on mineral type, with clays at the head of the list; and the cation type and concentration of water.
>
> Dissolution of light aromatic species in LSW depends on water salinity reduction and the time of contact. The effect is known as salting-in.
>
> Lowering of the interfacial tension between LWS and crude oils associates to the salinity of water; temperature; and the aromatic content of the crude oil.

---

*Speaker

Waxy crude oil fractions separation by liquid propane

Marcia Oliveira*[1], Carmem Lucia Teixeira[1], Humberto Lopes[1], Francis Meireles[1], and Gaspar Gonzalez

[1]Petrobras Research Center (PETROBRAS) – Brazil

Abstract

Crude oil fractionation have been used to develop characterization and classification procedures for petroleum samples and, in a more limited extent, to investigate the composition and phase behavior of crude oil fractions. In a previous studies the solution behavior of the solid and liquid phases separated from a heavy crude oil by propane were examined and compared with the asphaltenes and other crude oil components.

In this contribution, an improved experimental setup to fractionate the oil samples by precipitation with liquefied gases at high pressure and high temperature is described. The system permitted the injection of predefined volumes of oil and gas pressurized above its saturation pressure to get a homogeneous mixture and subsequent fractionation of the oil sample. The solid and liquid fractions separated for waxy crude oil samples were characterized by physical chemical methods and the results compared with a data for the corresponding (original) crude oil.

The crude oil fractions characterizations shows that parameter like SARA analyses, elemental composition (C, H, N and O), FTIR spectra and thermo-gravimetric analysis display compositional continuity across the liquid extract and the most complex solid residue. Petroleum stability characterized by the solubility parameter at the phase separation in conjunction with the concepts described in the Boduszynski continuity model may be useful to assess petroleum stability in relation to flow assurance and solids formation and deposition.

---

*Speaker

sciencesconf.org:petrophase2017:146467

Liquid viscosity of undefined petroleum fractions using thermodynamic characterization with functional groups

Bernardo Carreón-Calderón*[1], Verónica Uribe-Vargas[1], and Humberto Aguilar-Cisneros[1]

[1]Mexican Institute of Petroleum (IMP) – Eje Central Lázaro Cárdenas Norte 152, Col. San Bartolo Atepehuacan, Deleg. Gustavo A. Madero, C.P. 07730 México., Mexico

Abstract

Undefined petroleum fractions are hydrocarbon mixtures where forming pure compounds are unknown. Hence, estimation of their properties is usually performed by empirical o semi-empirical methods, in which chemical structure of some forming identified pure compound does not play any role in such estimation. Recently, a new method to estimate the so-called chemical pseudo-structures of undefined petroleum fractions has been proposed[1–4] . In the current work, liquid viscosity of undefined petroleum fractions at 313.15, 323.15, 373.17, and 408.15 are estimated by using methods developed for hydrocarbon mixtures where forming pure compounds are known. That is, pseudo-structures of these undefined petroleum fractions are calculated in order to estimate liquid viscosity by using methods requiring chemical structures of forming pure compounds. The results are in agreement with experimental data showing 20% errors.

B. Carreón-Calderón, V. Uribe-Vargas, E. Ramírez-Jaramillo, M. Ramírez-de-Santiago, Thermodynamic Characterization of Undefined Petroleum Fractions using Group Contribution Methods, Ind. Eng. Chem. Res. 51 (2012) 14188–14198.

B. Carreón-Calderón, V. Uribe-Vargas, M. Ramírez-de-Santiago, E. Ramírez-Jaramillo, Thermodynamic Characterization of Heavy Petroleum Fluids Using Group Contribution Methods, Ind. Eng. Chem. Res. 53 (2014) 5598–5607.

V. Uribe-vargas, B. Carreón-calderón, E. Ramírez-jaramillo, M. Ramírez-de-Santiago, Thermodynamic Characterization of Undefined Petroleum Fractions of Gas Condensate using Group Contribution, Oil Gas Sicience Technol. 71 (2016) 1–12.

H. Aguilar-cisneros, V. Uribe-vargas, B. Carreón-Calderón, J.M. Domínguez-esquivel, M. Ramirez-de-Santiago, Hydrogen Solubility in Heavy Undefined Petroleum Fractions Using Group Contributions Methods, Oil Gas Sicience Technol. 72 (2017) 1–11.

---

*Speaker

Rheology of Reconstituted Safaniya Vacuum Residue Based on Physical and Chemical Separation

Mildred Becerra*[1], Nicolas Linden[1], Nympha Escobar[1], and John Shaw†[1]

[1]University of Alberta (U of A) – 116 St. and 85 Ave. Edmonton, Alberta T6G 2R3, Canada

Abstract

The rheology of hydrocarbon resources, resource fractions and blends is a key property for production, transport and refining operations, and particularly for bitumens and heavy oils that are well known for their high complex viscosities. While direct measurement is essential for detailed design, fluid characterization and "viscosity" prediction are frequently used in engineering calculations.1, 2 "Viscosity" prediction and correlation for high boiling point fractions and asphaltene-rich resources is particularly challenging because these fluids comprise two or more phases and exhibit non-Newtonian behaviors at temperatures, where constituents in maltenes solidify.3-7 We rarely reflect on the appropriateness or generalizability of fluid characterizations that underlie calculations and the limits they impose on the certainty of computed outcomes. For example, in a prior work, we investigated the rheology of reconstituted mixtures of chemically separated pentane asphaltene and maltene fractions from two crude oils along with replacing asphaltenes from one crude oil with asphaltenes from the other crude oil during the reconstitution process.8 We demonstrated systematic underestimation of viscosity of reconstituted crudes (attributed to the presence of residual solvent), and showed that asphaltenes are not interchangeable. In this contribution, we compare the rheological behavior of mixtures of chemically separated and physically separated (nanofiltered) asphaltene/asphaltene-rich and maltene/maltene rich fractions used to reconstitute Safaniya vacuum residue. Reconstituted samples of chemically separated pentane asphaltene and maltene fractions have lower complex viscosities than Safaniya vacuum residue, even when care is taken to minimize residual solvent (an expected outcome), while reconstituted samples based on nanofiltered permeates and retentates have two to ten times greater complex viscosities at the same temperature and shear conditions. For base oils with low minimum boiling ranges, solvent elimination also removes light ends and viscosities arising on recombination of chemically separated oils may be less than or greater than the viscosity of the base oil. These and related results underscore the intrinsic uncertainty of viscosity prediction and the need for benchmark measurements to support computations, particularly for heavy oils, bitumens and related fluids.

References

1. Satyro, M. A.; Yarranton, H. W.,. *Fluid Phase Equilibria* **2010,** *298* (1), 1-11.

2. Yarranton, H.; van Dorp, J.; Verlaan, M.; Lastovka, V.,. *Journal of Canadian Petroleum Technology* **2013**, 176-191.

---

*Speaker

†Corresponding author: jmshaw@ualberta.ca

3. Bazyleva, A.; Becerra, M.; Stratiychuk-Dear, D.; Shaw, J. M., *Fluid Phase Equilibria* **2014,** *380* (0), 28-38.

4. Bazyleva, A.; Fulem, M.; Becerra, M.; Zhao, B.; Shaw, J. M.,. *Journal of Chemical and Engineering Data* **2011,** *56* (7), 3242-3253.

5. Bazyleva, A. B.; Hasan, A.; Fulem, M.; Becerra, M.; Shaw, J. M.,. *Journal of Chemical and Engineering Data* **2010,** *55* (3), 1389-1397.

6. Fulem, M.; Becerra, M.; Hasan, M. D. A.; Zhao, B.; Shaw, J. M.,. *Fluid Phase Equilibria* **2008,** *272* (1-2), 32-41.

7. Hasan, M. D. A.; Fulem, M.; Bazyleva, A.; Shaw, J. M., Rheological Properties of Nanofiltered Athabasca Bitumen and Maya Crude Oil. *Energy & Fuels* **2009,** *23* (10), 5012-5021.

8. Hasan, M. D. A.; Shaw, J. M., *Energy & Fuels* **2010,** *24* (12), 6417-6427.

Asphaltene 2017

Characterization of Petrophase asphaltene using Ultrahigh-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry.

Matthias Witt*[1]

[1]Bruker Daltonik GmbH – Fahrenheitstrasse 4, 28359 Bremen, Germany

Abstract

The asphaltene sample was analyzed by ultrahigh resolution mass spectrometry using a solarix 2XT 7T FTICR mass spectrometer (Bruker, Bremen, Germany) and laser desorption ionization (LDI) as well as atmospheric pressure photoionization (APPI). High hetero atom content of the detected compounds was observed with both ionization methods with up to nine hetero atoms. Average hetero atom number of 2.7 using LDI was slightly lower than APPI with 3.3. Vanadyl porphyrins could be directly detected in the asphaltene sample with both ionization methods with similar relative abundance. DBE of the detected vanadyl porphyrins was higher using LDI than APPI. The H/C ratio decreased constantly in the Sx and N1Sx class with number of sulfur atoms, but in the O1Sx class the H/C ratio was mainly constant with number of sulfur atoms using APPI and even slightly increased using LDI. An increase in DBE was observed with number of sulfur atoms in Sx and N1Sx. Increase in DBE as rather low for class O1Sx with hetero atom number. High aromaticity (low average H/C and DBE values) was confirmed with a 1600 cm–1/2900 cm–1 ratio (aromatic/aliphatic signal ratio) of 0.22 obtained by FT-IR.

---

*Speaker

Characterization of common asphaltene sample using Fourier transform ion cyclotron resonance mass spectrometry

Keita Katano*[1], Teruo Suzuki[1], and Ryuzo Tanaka[1]

[1]Japan petroleum energy center (JPEC) – 4-10, Ohnodai 1-Chome, Midori-ku, Chiba-shi, Chiba 267-0056, Japan, Japan

Abstract

To characterize the common asphaltene sample of the inter laboratory study for PetroPhase 2017 at the molecular level, Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) equipped with 12 Tesla super conductive magnet was used. Because of the ultra-high resolution power, molecular formulas of petroleum molecules are almost uniquely assigned. Two ionization methods were used in the measurements. One is atmospheric pressure photoionization (APPI) method. This method effectively ionizes aromatic molecules in petroleum material. The other is laser desorption ionization (LDI) method. LDI method is sensitive for polyaromatic and N containing species. In the case of APPI method, the sensitivity of obtained mass spectrum was very low, and it seemed that the vaporization by heating in ionization process is not so effective for desorption of asphaltene. In contrast, the mass spectrum for LDI method was observed with enough sensitivity. Mean molecular weights calculated from these spectra were 506 (APPI) and 558 Da (LDI), respectively. We did not observe high molecular weight species over 1000 Da using FT-ICR MS. For estimation of structural building block of the asphaltene, we have also applied a technique of collision induced dissociation (CID) in a collision cell of FT-ICR MS. For APPI method, CID measurements were not performed because the amount of ions was not enough. For that reason, the mass spectra obtained before/after CID were compared for LDI method. At low collision energy, alkyl side chains and bridges were mainly cleaved, and aromatic cores were observed as fragment ions. The degree of unsaturation before CID ranged from DBE 11 to 35. Where, DBE (Double bond equivalence) represents the number of rings plus the number of double bonds to carbon in a given molecular formula. After CID, the range of DBE was shifted to lower region (5 to 27). It means that the asphaltene contains not only single core structure but also multi ones. From the analysis of observed fragment ions, it is clearly shown that 3 to 5 rings aromatics are most abundant as structure building blocks. As a further analysis, we are now trying fractionation based on polarity of asphaltene molecules. In this separation, asphaltene will be separated into 5 fractions (nonpolar, weak base, weak acid, strong base, and strong acid).

---

*Speaker

Study of the special sample "Asphaltene 2017" by dynamic and static light scattering

Vladimir Kuryakov*[1] and Pier Giorgio De Sanctis Lucentini[2]

[1]Oil and Gas Research Institute of the Russian Academy of Sciences (OGRI RAS) – Russia, 119333, Moscow, Gubkina Str. 3, IPNG (OGRI RAS), Russia

[2]Gubkin Russian State University of Oil and Gas (National Research University) – 119991, Moscow, Leninskii prospect 65, Russia

Abstract

Operationally defined as the fraction of petroleum insoluble in an alkane but soluble in toluene, the asphaltenes appear as mixture of molecules and not as a pure substance. Samples prepared with oil coming from different reservoirs may present, in principle, differences in their characteristics that will be reflected in an increased uncertainty for the observed physico-chemical quantities. Indeed the investigation of the same asphaltenes sample in different laboratories and with different experimental techniques may lead to a more deep knowledge of the underlying physico-chemical characteristics and to a more accurate predictions about its behavior. Here we present a detailed study of the "Asphaltene 2017" solutions in toluene by means of *Dynamic* (DLS) and *Static* (SLS) *Light Scattering.* The DLS method allows to measure the sizes of particles in a liquid environments for the range from half nanometers up to several micrometers. In the present work the aggregation kinetics of the asphaltene aggregates is measured at various concentration of the precipitant (heptane). After that the heptane was added above the threshold concentration, the aggregates size measured by the DLS varied in range from 70-100 nm to 0.8-1.0 μm, in about one hour. The measurements of the scattering intensity after the addition of the precipitant allowed us to observe not only the aggregation process, but even the sedimentation one. With regard to the sedimentation process there were observed typical times of more than 10 hours. The present research made possible to estimate a threshold for the stability of the asphaltenes. We studied the effect of the ultrasonic dispersion on the supramolecular asphaltene complexes formed after lowering the mixture dissolving power by adding heptane. Our results indicate a process of a secondary aggregation, which occurs after the mechanical destruction (via ultrasonic dispersion) of the asphaltene aggregates that have previously fallen out. The study was supported by the Russian Foundation for Basic Research, Grant no. 17-08-00362-a.

---

*Speaker

sciencesconf.org:petrophase2017:145007

Fluorescence, UV-vis and FTir Spectra of the Petrophase 2017 Asphaltene and Crude Oil Samples

Sharath Chandra Mahavadi*[1] and Simon Andersen*[2]

[1]Schlumberger-Doll Research (SLB) – United States
[2]Asphalteam – Denmark

Abstract

As part of the Petrophase 2017 conference a new public database is developed with contributions from various research organization. This is the first attempt to combine efforts and resources to provide an overall picture of the same samples of both asphaltene and parent crude oil.

Spectra of the database samples of n-heptane asphaltenes and crude oil were analyzed using various optical spectroscopic techniques including ultraviolet–visible spectroscopy (UV-vis), fluorescence, and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The Fluorescence and UV-vis spectra were recorded as a function of concentration between 0.2 and 1000 ppm. Fluorescence spectra were obtained in both transmission mode and front face mode and the UV-vis absorbance was used to compensate for inner-filter effects. This correction is seen to restore a linear relation between fluorescence and concentration and also leads to overlay of spectra. Fluorescence spectral information mainly relates to the aromatic structures of the sample. The FTIR spectra measured by ATR were analyzed in detail to provide a quantitative description of the functional group distribution and the hydrocarbon structure of the samples. This information will be useful not only in comparison with other analytical chemical techniques but will also provide information about the effect of concentration on the state of both asphaltenes and crude oil in dilute solutions.

---

*Speaker

A-5

Asphaltene aggregation in PetroPhase 2017 samples.

Paul Hazendonk*[1], Andrew Pomerantz[2], Lamia Goual[3], and Sudipa Mitra-Kirtley[4]

[1]Department of Chemistry and Biochemistry, University of Lethbridge – 4401 University Dr,
Lethbridge, Alberta, T1K 3M4, Canada
[2]Schlumberger-Doll Research – United States
[3]Department of Petroleum Engineering, University of Wyoming – 1000 E. University Avenue, Laramie,
WY 82071, United States
[4]Rose-Hulman Institute of Technology – United States

Abstract

Asphaltene aggregation was studied in the sonicated and untreated PetroPhase 2017 samples using various physiochemical methodologies. Initially the physical properties (density, surface area, *etc.*) of the samples were compared against those of asphaltenes extracted from petroleum, coal, and immature source rock.
The critical nanoaggregate and cluster concentrations of these asphaltenes were determined from the variations of direct current (DC) conductivity with asphaltene concentration in anhydrous toluene. In the diffusion-dominated regime, the molecular and aggregate size of asphaltenes were estimated from their effective diffusion coefficient.

Characterization at the molecular level was undertaken by: *i)* elemental analysis where C, H, N and S abundances were obtained by combustion, and that for O was afforded by pyrolysis; *ii)* speciation of the various S environments was achieved using X-ray absorption near edge structure (XANES) spectroscopy, resolving the sulfide, thiophene and sulfoxide functions; *iii)* infrared spectroscopy (IR) allowed for the speciation of the various C and O environments, such as aliphatic, aromatic and carbonyl; and *iv*) the distribution rings sizes of the fused aromatic cores was probed by visible and near-infrared (VIS-NIR) spectroscopy. High-field H-1 Nuclear magnetic resonance (NMR) spectroscopy and relaxation measurements were employed to corroborate the speciation results and identify signals associated with the predominant aggregation states. Deconvolution analysis made it possible to obtain separate relaxation times for several chemical environments for each discernible aggregate phase. The corresponding T1/T2 ratios allowed for estimates of correlation times (tc) associated with their reorientational dynamics, which in turn gave thier hydrodynamic radii (rH). The relaxation results were compared with self-diffusion constants obtained by pulsed field gradient Hahn-echo (PFGHE) and DC conductivity measurements. The aggregate size distribution will be compared between the sonicated and untreated samples as well with asphaltenes samples from a variety of sources.

---

*Speaker

sciencesconf.org:petrophase2017:145369

What are the molecules responsible for the generation of fullerene type peaks in (+) LDI FT-ICR MS spectra of crude oils?

Sunghwan Kim*[1], Eunji Cho , Moonhee Park , and Young Hwan Kim

[1]Department of Chemistry, Kyungpook National University – South Korea

Abstract

Sunghwan Kim1,2, Eunji Cho1, Moonhee Park3, Young Hwan Kim3,4
1 Kyungpook National University, Department of Chemistry, Daegu 702-701, Republic of Korea

2 Green-Nano Materials Research Center, Daegu 702-701, Republic of Korea

3 Biomedical Omics Group, Korea Basic Science Institute, Yeongudanji-ro, Cheongju, 28119, Republic of Korea

4 University of Science and Technology, Department of Bio-Analytical Science, Daejeon 305-333, Republic of Korea

In the previous study, it has been shown that fullerene can be generated from the LDI FT-ICR MS analysis of asphaltene. Strong peaks spaced by 24 were observed in the (+) LDI FT-ICR MS spectra. In this study, it is investigated to find out the specific components that are responsible for the generation of fullerene type peaks. First, asphaltene samples prepared by Petrophse2017 was studied by use of 2D high resolution GC-MS (2D HR GC-MS) coupled to pyrolysis. Pyrolyzed asphaltene sample was analyzed by 2D HR GC-MS to find out structural motif comprising asphaltene. Second, fractionated crude oil was analyzed by LDI FT-MS to find out the fractions from that fullerene type peaks could be observed. The obtained spectra are provided in Figure 1.

Figure 1. (+) LDI FT-ICR MS spectra of fractionated oil. Sample experimental conditions including laser power (70%) were used to obtain all four spectra.
It is clear that the more aromatic the fractions are the more fullerene type peaks are observed. In addition, the fractions were studied with various laser power to find compounds that negatively correlate with fullerene type peaks. We expect that combining the data obtained from pyrolysis 2D-GC HR MS and (+) LDI FT-ICR MS can help us to identify structural motif comprising asphaltene.

---

*Speaker

Study of asphaltene desorption at the oil-water interface

Alain Cagna* , Anne-Sophie Quinquis , and Dominique Langevin†[1]

[1]Laboratoire de Physique des Solides (LPS) – CNRS : UMR8502, Université Paris XI - Paris Sud – Bat. 510 91405 Orsay cedex, France

Abstract

Asphaltene adsorption at oil-water interfaces is considered to be irreversible by some authors, reversible by others. Since asphaltene layers' composition is still a matter of debate, working with the highly purified sample provided by Total helped to reduce problems linked to the competition of different species for the interface. We used a Tracker instrument (Teclis) in which rinsing procedures were applied. We measured the time variation of tensions and elasticities of the interfaces between water and asphaltene solutions in toluene. We will present dynamic tension and elasticity data to characterize both adsorption and desorption kinetics, for different asphaltene concentrations in toluene. The adsorption reversibility was cheched at different adsorption times (i.e. for different consolidation times of the initial asphaltene layer).

---

*Speaker

†Corresponding author: dominique.langevin@u-psud.fr

sciencesconf.org:petrophase2017:151048

A-8

Solubility Characteristics of Petrophase Asphaltenes

Estrella Rogel*[1], Cesar Ovalles[1], David Lavenson[2], and Andrew Pomerantz[3]

[1]Chevron ETC – 100 Chevron Way Richmond, CA 94801, United States
[2]Chevron ETC – 1400 Smith St Houston TX 77002, United States
[3]Schlumberger-Doll Research – 1 Hampshire St. ambridge, MA 02139, United States

Abstract

The solubility distribution of the Petrophase asphaltenes was determined by using the Solubility Profile technique. The result of this test indicates a solubility distribution similar to others determined previously for heptane asphaltenes extracted using the conventional gravimetric method ASTM D6560. Based on this result, an average solubility parameter of 20.0 MPa0.5 was determined for these asphaltenes. In contrast, asphaltenes precipitated from the same crude oil using the in-line filtration method have a solubility parameter of 19.2 MPa0.5. Typical solubility parameter values range between 19.0 MPa0.5 to 22.0 MPa0.5. The solubility of the Petrophase asphaltenes in heptane as a function of the temperature was also evaluated. The results show that around 45 wt. % of the Petrophase asphaltenes are dissolved in heptane when the temperature increases from 35○C to 195oC. This indicates a behavior within the range observed for heptane extracted asphaltenes previously studied in our group.

---

*Speaker

ASCI: A tool for asphaltene risk assessment in oilfield production

Jean-Philippe Gingras*†[1] and Nicolas Passade-Boupat*[1]

[1]PERL – TOTAL – Pôle Économique 2 - B.P. 47 64170 LACQ, France

Abstract

The prediction of the risk related to asphaltenes in flow assurance for oil production requires a robust and straightforward workflow. In this context, Total has developed the Asphaltene Solubility Class Index (ASCI) method to characterize the solubility of asphaltene. ASCI measurements on PetroPhase native crude, whole extracted asphaltenes and different asphaltene fractions from this native crude oil will be carried out to determine the asphaltene stability and their polydispersity in terms of solubility. The fractionation will be done by adding different heptol to the native crude oil at large volume ratio. The effect of asphaltene solubility and polydispersity measured with ASCI method will then be investigated using emulsions and deposition lab-scale tests to illustrate the relevance of ASCI as a key method for risk prediction and understanding asphaltenes/crude oil behavior in oilfield production.

---

*Speaker

†Corresponding author: jean-philippe.gingras@total.com

sciencesconf.org:petrophase2017:151819

Interrelation of Physico-Chemical Properties and Precipitation/Deposition Tendency of Asphaltenes

Mohammad Tavakkoli[1], Sara Rezaee[1], Jun Kuang[1], Mohammed Abutaqiya[1], and Francisco Vargas*†[1]

[1]Chemical and Biomolecular Engineering Department, Rice University – 6100 Main St., MS-362, Houston, Texas, 77005., United States

Abstract

In this talk we will present the results of extraction and quantification of the saturates, aromatics, resins and asphaltenes from the parent crude oil and comparison of the properties of the asphaltenes obtained and the asphaltene sample provided. These properties include the elemental analysis, aromaticity factor, and molecular weight distribution using size exclusion chromatography. Furthermore, we also investigated the polydisperse nature of the asphaltene fraction collected from the parent crude oil as well as the precipitation and deposition tendency. The experimental data of asphaltene precipitation collected at ambient conditions were modeled using the Perturbed Chain form of the Statistical Associating Fluid Theory. It was found that the inclusion of the asphaltene polydispersity concept is necessary to reasonably match the asphaltene precipitation experimental data. The model was then used to predict asphaltene phase behavior at reservoir conditions at various values of gas-oil ratio. With this study we aim to relate the physico-chemical properties determined by other research groups to the behavior of the asphaltene to better understand the mechanisms and underlying phenomena that govern asphaltene precipitation, aggregation, and deposition.

---

*Speaker

†Corresponding author: fvargas@rice.edu

A-11

Crude Oil and Asphaltene Analysis Using an Orbitrap

Christianne Wicking*[1], Mike Hodges[2], and Huang Zeng[3]

[1]BP – Pangbourne Technology Centre, United Kingdom
[2]BP – Sunbury, United Kingdom
[3]BP – Houston, United States

Abstract

Crude oil is a complex mixture of thousands of different compounds. To understand the composition of crude oil, analysis is required that can characterise the different components. High resolution mass spectrometry (HRMS) using Orbitrap technology has been applied to analyse an asphaltene and its parent oil. With a resolution of over 200,000 FWHH at 400 m/z, electrospray ionisation mass spectrometry (ESI-MS) and atmospheric pressure photoionisation (APPI-MS) has been applied to target the heteroatom containing components and aromatic compounds present in crude oil and asphaltene samples. Through the use of this technique, different classes present in each sample can be identified and compared and the nature of the crude oil and asphaltenes can be understood.

---

*Speaker

A-12

Thermal analysis coupled to multiple mass spectrometric techniques for the analysis of asphaltenes and originating crude oils

Christopher Rüger*†[1], Christoph Grimmer[1], Martin Sklorz[1], Anika Neumann[1], and Ralf Zimmermann[1,2]

[1]University of Rostock – Dr.-Lorenz-Weg 1 18059 Rostock, Germany
[2]Helmholtz Zentrum München German Research Center for Environmental Health (HMGU) – Germany

Abstract

Introduction:
Low quality petroleum can contain high amounts of asphaltenes, which cause serious flow assurance challenges. Thermal analysis (TA) coupled to mass spectrometry is a powerful technique to characterize desorption and pyrolysis processes. In the desorption phase, volatile species are desorbed, whereas in the pyrolysis phase non-volatile high molecular structures decompose. In this study, TA was coupled to several mass spectrometric techniques. Single photon ionization (SPI) was deployed as universal soft ionization technique, whereas resonance enhanced multi photon ionization (REMPI) (set-up 2) [Geißler et al., 2009] and atmospheric pressure chemical ionization (APCI) (set-up 3) [R´uger et al., 2015] are sensitive towards aromatic and polar compounds. TA APCI was realized on an ultra-high resolution mass spectrometer (FT-ICR MS) to decipher the evolved pattern on the molecular level. Gas chromatography electron impact (GC-EI) was applied for an unbiased pattern and structural information (set-up 1) [Otto et al., 2015].

Method:

For the set-up 1) 0.5 mg of the asphaltene was used directly. The parent crude oil was diluted by a factor of 100 in dichloromethane. The sample is placed in a μ-vial and inserted into the desorption/pyrolysis unit. Two GC runs are acquired subsequently for 300 $\circ$C (desorption) and 500 $\circ$C (pyrolysis). For set-up 2) and 3) 2-5 mg of the asphaltene and parent oil were analyzed directly. The sample is heated from 20 to 600 $\circ$C with 10 K/min under inert-gas. Mass spectra are recorded on-line. For set-up 3) alternating collision induced dissociation (CID) spectra are acquired.

Results:

For the parent oil, set-up 1) revealed dominant signals for linear, cyclic and branched alkanes from C8 to C37 in the thermodesorption step, whereas in the pyrolysis step a dominant pattern of alkenes occur. For the asphaltene, no signal was revealed in the thermodesorption step. The pyrolysis step is comparable to the parent oil pattern (figure 1). A higher

---

*Speaker

†Corresponding author: Christopher.Rueger@uni-rostock.de

relative contribution of heterocyclic aromatics was found for the asphaltene pyrolysis. Alkylated phenanthrenes/anthracenes, naphthalenes and benzenes were found for the asphaltene pyrolysis with the REMPI-MS (set-up 2) (figure 2). As for the set-up 1) almost the total intensity was recorded for temperatures above 330 ◦C. SPI confirmed the alkene pattern from the GC-EI and additionally revealed dienes as well as H2S. In the set-up 3 species with m/z up to 650 are visible for the asphaltene and m/z 750 for the parent oil (figure 3). The molecular pattern of the asphaltene pyrolysis is dominated by aromatic CHS-, CH-class and CHS2 compounds. In the CID spectra the CHS and CHS2-class species remain with a high abundance and can be therefore attributed to heterocyclic aromatic core structures.

Conclusion:

Evolved gas analysis, by means of thermal analysis, coupled to mass spectrometry is a powerful tool for the characterization of high complex petroleum samples, such as asphaltenes. Liquid and solid samples can be used directly. Detailed molecular information on the volatile compounds and species evolved in the pyrolysis was revealed combining the different approaches. Especially, pyrolysis allow insights into the molecular architecture of asphaltenes.

A-13

Thermal Maturity Assessment of the Petrophase Asphaltene

Andrew Pomerantz*[1] and Kyle Bake[1]

[1]Schlumberger-Doll Research – United States

Abstract

Thermal maturation is the process by which petroleum (including asphaltenes) are generated by thermal cracking of kerogen. The composition of the generated petroleum varies greatly with the level of maturity under which the petroleum was generated. For example, petroleum generated at low maturity is rich in asphaltenes and lean in gas, while petroleum generated at high maturity is lean in asphaltenes and rich in gas. Recently it has been shown that the composition of the asphaltenes also varies greatly with the level of maturity-increasing maturity results in the removal of heteroatomic species (particularly sulfur and oxygen) in the low maturity range followed by an increase in aromaticity and in the size of fused ring systems in the high maturity range. Here, the composition of the Petrophase asphaltene was measured using three techniques that are sensitive to the level of maturity of asphaltenes: 1) elemental analysis, which quantifies the abundance of heteroatomic species; 2) infrared spectroscopy, which measure the distribution of carbon-carbon, carbon-hydrogen, and carbon-oxygen containing functional groups; and 3) optical spectroscopy, which measures the relative abundance of fused ring systems of different size. The results of these measurements are used to estimate the maturity at which the asphaltene was generated.

---

*Speaker

Asphaltene Characterization Methods for Interlaboratory Study

Paula Fiorio[1], Fernanda Barbosa[2], Peter Seidl*†[1], Maria José Guimarães[1], Lina Quintero[3], érika Chrisman[1], and Sônia Menezes[4]

[1]Federal University of Rio de Janeiro (UFRJ) – Brazil
[2]Fernanda Barbosa (Fernanda Barbosa) – Ilha do Fundao. CETEM, Rio de Janeiro, Brazil
[3]Ecopetrol – Colombia
[4]Petrobras (CENPES) – Brazil

Abstract

Solid deposition is a serious technical problem in the oil industry. The precipitation of heavy organic solids especially asphaltenes in wells and pipelines has a significant effect on the economics of oil production because of reduction in well productivity and clogging up of the production facilities. The precipitation of asphaltenes has been attributed to a number of factors including changes in pressure, temperature, chemical composition of a crude oil or mixing crudes with other oils or diluents. To avoid the costly consequences on crude oil production, it has become very important to understand asphaltene aggregation and its causes.

The adoption of fast and reliable asphaltene extraction procedures provides a more comprehensive understanding of asphaltene molecular structure and the mechanisms that lead to their precipitation. Depending on the origin of the crude oil from which they are precipitated, asphaltenes can exhibit wide differences in composition and structure. The amount and length of the alkyl side chains as well as the number of aromatic rings may change in such a way that the variations of molecular weight and aromaticity factor of asphaltenes are notorious.

The precipitation of asphaltenes was carried out by an alternative method based on the selective extraction of the constituents using a mixture of a naphthenic and a paraffinic solvent. In a typical experiment, a mixture of crude oil and solvents was stirred in a reactor in a solvent-to-oil ratio of 8:1 (v/w) at ambient pressure and temperature. The mixture was settled for 2 hours and after that period a vacuum system and a Whatman filter paper were employed in order to separate the solvent mixture soluble fraction from the asphaltene fraction.

This method was applied to the sample that was provided for the asphaltene session in order to provide reliable data of asphaltene structural properties. The asphaltenes obtained were characterized by elemental analysis and NMR. Elemental analysis reveals the C/H ratio and reflects the degree of condensation of the aromatic rings. The NMR analysis gives the functionalities of the chemical species of the hydrocarbons that are extracted.

---

*Speaker

†Corresponding author: pseidl@eq.ufrj.br

sciencesconf.org:petrophase2017:152073

A Study in the Aggregation Behaviors of Asphaltenes: Gel Permeation Chromatography with Online Detection by Inductively Coupled Plasma Mass Spectrometry and Characterization of Fractions by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Jonathan Putman*†[1,2,3,4], Sara Gutiérrez Sama[3,4,5], Caroline Barrère-Mangote[3,4], Ryan Rodgers[1,2,6], Ryszard Lobinski[3,7], Alan Marshall[1,2], Brice Bouyssière‡[3,4,5], and Pierre Giusti[3,4]

[1]National High Magnetic Field Laboratory, Florida State University – 1800 East Paul Dirac Drive, Tallahassee, FL 32310, United States
[2]Department of Chemistry and Biochemistry, Florida State University – 95 Chieftain Way, Tallahassee, FL 32306, United States
[3]TOTAL RC – CNRS Joint Laboratory C2MC, Complex Matrices Molecular Characterization – Centre national de la recherche scientifique - CNRS (France) – BP 27, 76700 Harfleur, France
[4]TOTAL Raffinage Chimie, TRTG – TRTG – BP 27, 76700 Harfleur, France
[5]Laboratoire de Chimie Analytique Bio-Inorganique et Environnement (LCABIE) – CNRS : UMR5254, Université de Pau et des Pays de l'Adour – HELIOPARC - 2 Avenue du Président Angot 64000 PAU, France
[6]Future Fuels Institute, Florida State University (FFI) – 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, United States, United States
[7]Laboratoire de Chimie Analytique Bio-Inorganique et Environnement (LCABIE) – CNRS : UMR5254, Université de Pau et des Pays de l'Adour [UPPA] – HELIOPARC - 2 Avenue du Président Angot 64000 PAU, France

Abstract

Asphaltenes are commonly considered the most problematic components of heavy oil. Asphaltenes can cause complications across the entire production chain, from oil recovery and transportation all the way through to the upgrading and refining processes.1 It is well known that metal containing petroporphyrins are involved in macromolecular aggregation with asphaltenes, but the forces driving the process are not well understood. Are metalloporphyrins contributing to aggregation, and if so, how? Or do other functional groups and the chemical environment dictate asphaltene precipitation and the porphyrins indiscriminately trapped in the process? Is there a structural dependence of the porphyrinic species

---

*Speaker
†Corresponding author: jputman@magnet.fsu.edu
‡Corresponding author: brice.bouyssiere@univ-pau.fr

that report to the asphaltenes? To answer these questions, the molecular composition and porphyrin distribution must be understood as a function of aggregation potential. Here, we studied the aggregation behaviors of purified asphaltenes and their corresponding whole crude oil by gel permeation chromatography (GPC). The size profiles for Vanadium and Nickel, two of the most abundant heavy-metals present in petroleum, were determined on-line with elemental detection by inductively coupled plasma (ICP) mass spectrometry. Four fractions of varying aggregation state were analyzed by Fourier Transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Previous results from an atmospheric residual sample revealed that aggregation dependence was not correlated with an increase in polar or aromatic species abundance. Somewhat surprisingly, aggregation was more correlated with an increased relative abundance of larger and more aliphatic compounds, suggesting that aggregation is more dependent on weaker intermolecular forces between long-chain alkyl substitutions. To determine the significance of these results and to expand our present knowledge of asphaltene behavior, the current study seeks to ascertain the relationship between aggregation that occurs during GPC separations and asphaltene precipitation. Work supported by NSF Division of Materials Research through DMR-11-57490, Conseil Régional d'Aquitaine (20071303002PFM), and FEDER (31486/08011464).
(1) Adams, J. J. *Energy Fuels* 2014, *28*, 2831.

A-16

Analysis of Petrophase Asphaltene Sample by Extrography Coupled with Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Steven Rowland*[1,2], Martha Chacon[2], and Ryan Rodgers[1,2]

[1]Future Fuels Institute (FFI) – 1800 E. Paul Dirac Drive, Tallahassee, FL, 32310, United States
[2]National High Magnetic Field Laboratory (NHMFL) – 1800 E. Paul Dirac Drive, Tallahassee, FL, 32310, United States

Abstract

The work presented here focuses on the analysis of the whole Petrophase asphaltene sample as well as extrography fractions isolated by a novel separation technique. Positive-ion atmospheric pressure photoionization (+ APPI) was utilized to ionize asphaltene compounds prior to mass spectral analysis. Extrography fractions were also analyzed and revealed a separation based on complex structural motifs. Early-eluting fractions resemble the composition observed by analysis of the whole asphaltene; whereas later-eluting fractions revealed new elemental compositions not observed in the mass spectrum of the whole asphaltene. Aggregation tendencies were also evaluated for each fraction and revealed increased aggregation in late-eluting fractions. These results demonstrate that the compounds most responsible for asphaltene aggregation are not usually observed by direct infusion mass spectrometry and that the extractive pre-fractionation developed in this work separates asphaltenes based on aggregation tendency. Thus, the developed extraction method allows for more complete analysis of the asphaltene species that disproportionately contribute to aggregation related problems.

---

*Speaker

A-17

Micro x-ray fluorescence and micro x-ray absorption near-edge structure studies on Petrophase asphaltene

Sudipa Mitra-Kirtley*[1,2,3]

[1]Rose-Hulman Institute of Technology (RHIT) – 5500 Wabash Avenue Terre Haute IN 47803, United States
[2]Sirine Fakra (LBL) – Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States
[3]Andrew Pomerantz (SLB) – Schlumberger-Doll Research, Cambridge, MA 02139, United States

Abstract

Heteroatom chemistry is of great importance to fossil fuel industry as this reveals chemical composition, environmental deposition, and other important information. Micro-focused X-ray fluorescence (μXRF) elemental and chemical mapping, sulfur K-edge X-ray absorption near-edge structure (μXANES) spectroscopy and X-ray diffraction (μXRD) have been performed on an asphaltene sample to localize and determine the speciation of sulfur, an important heteroatom. XRF mapping targeted the distribution of the main elements present, Si, S, Ca and Fe. Multiple regions of the samples were chosen for XANES analysis to determine sulfur chemical speciation. The thiophene forms were dominant in the sample. A previous study* on a set of asphaltenes, even with large gradient of asphaltene content, showed similar abundance of thiophenic forms. *Pomerantz, Seifert, Bake, Craddock, Mullins, Kodalen, Mitra-Kirtley, and Bolin; Energy Fuels, **2013**, *27* (8), pp 4604–4608

---

*Speaker

Structural features of asphaltenes from an Arabian heavy crude oil

Cristian Blanco-Tirado*[1], Martha Chacón-Patiño[2], Marianny Combariza-Montañez[1], and Cristian Blanco-Combariza[3]

[1]Universidad Industrial de Santander [Bucaramanga] (UIS) – Cra 27 Calle 9 Ciudad Universitaria Bucaramanga-Santander-Colombia, Colombia
[2]National High Magnetic Field Laboratory – United States
[3]Universidad Industrial de Santander (UIS) – Colombia

Abstract

Theoretical periodic tables of aromatic families were converted to graphs detailing the relationship between the DBE value of the molecule vs the number of carbon atoms contained. These graphs were overlaid with the FT-ICR MS data obtained following the analysis of Arabian heavy crude asphaltenes. The resulting graphs showed that the DBE vs C values observed in the periodic tables of aromatic compounds match the results of the FT-ICR analysis. Fractionation of samples by TLC prior to FT-ICR MS analysis enhanced data correlation at the planar limits of compound families. IRMPD FT-ICR MS experiments mostly remove side chains, leaving condensed aromatic core structures which are further compared to the theoretical planar limits of the aromatic periodic tables. Our results show that, by plotting the information obtained from the periodic tables of aromatic compounds, lines of tendency are formed, corresponding to the theoretical planar limits of a given compound family. This information can be used to accurately predict the nature of the molecules' growth along the same DBE value. When compared to FT-ICR data of whole asphaltenes, the resulting HC signals show an overlap with the theoretical planar limits. Upon TLC fractionation of asphaltenes, previously unseen signals appear, coinciding more closely with the established planar limits, indicating that fractionation improves the signal-to-noise ratio of molecules in the asphaltene. Further fragmentation, by IRMPD FT-ICR MS, exposes the aromatic cores of the molecules, populating the planar limit. This translates to a robust way of identifying the structural features of the molecules corresponding to the ions from the sample. The analytical pipeline proposed here gives credence to our hypothesis that it is possible to elucidate the core structural information of asphaltenes from FT-ICR MS data.

---

*Speaker

Asphaltene aggregation in PetroPhase 2017 samples

Paul Hazendonk*†[1], Andrew Pomerantz[2], Lamia Goual[3], and Sudipa Mitra-Kirtley[4]

[1]Department of Chemistry and Biochemistry, University of Lethbridge – 4401 University Dr, Lethbridge, Alberta, T1K 3M4, Canada
[2]Schlumberger-Doll Research – United States
[3]Department of Petroleum Engineering, University of Wyoming – 1000 E. University Avenue, Laramie, WY 82071, United States
[4]Rose-Hulman Institute of Technology – United States

Abstract

The Asphaltene 2017 sample was initially studied by elemental analysis to obtain its: carbon, hydrogen, nitrogen, and sulfur abundances via combustion, and oxygen abundance by pyrolysis. Subsequently, the various bonding environments were investigated on an element-specific basis. X-ray absorption near edge structure (XANES) spectroscopy was used to speciate the sulfur environments, resolving forms such as sulfide, thiophene, and sulfoxide. Infrared (IR) spectroscopy was employed to resolve carbon functionalities such as aliphatic, aromatic, and carbonyl. The distribution and sizes of fused aromatic cores were probed by visible and near-infrared (VIS-NIR) spectroscopy. Additionally, physical properties including density and surface area were measured. The measured properties of the Asphaltene 2017 sample are then compared against properties of asphaltenes extracted from petroleum, coal, and immature source rock. In addition, the critical nanoaggregate and cluster concentrations of these asphaltenes were determined from the variations of direct current (DC) conductivity with asphaltene concentration in anhydrous toluene. In the diffusion-dominated regime, the molecular and aggregate size of asphaltenes were estimated from their effective diffusion coefficient and further compared with values obtained using Diffusion Ordered Spectroscopy (DOSY) experiments. Spin-spin and spin-lattice 1H relaxation times at 700 MHz were obtained in toluene and chloroform for the aromatic, aliphatic and alicyclic environments, to probe changes in the size distribution of the nano-aggregates near the critical concentrations. These results will be compared to those obtained from other petroleum asphaltenes.

---

*Speaker

†Corresponding author: paul.hazendonk@uleth.ca

Microstructure of Solvated Asphaltenes Investigated by Small-Angle Neutron Scattering

Michael Hoepfner*†[1] and Thomas Headen[2]

[1]University of Utah, Department of Chemical Engineering – Salt Lake City, UT 84112, United States
[2]ISIS Neutron and Muon Source, Science and Technology Facilities Council, Rutherford Appleton Laboratory – Rutherford Appleton Laboratory, Harwell Campus, Didcot OX11 0QS, UK, United Kingdom

Abstract

Small-angle neutron scattering (SANS) was performed on the Asphaltene 2017 sample dispersed in deuterated heptane-toluene blends to measure their solvated microstructure. Experiments were performed on the NIMROD instrument at the ISIS Pulsed Neutron and Muon Source in May 2017. Quantitative values of the radius of gyration, cluster molecular weight, and fractal dimension were obtained and compared to previous measurements on other asphaltene samples. Previous work has demonstrated that the size and molecular weight of asphaltene clusters will increase as the heptane content of the solvent is increased and that the fractal dimension remains constant. The increase in size of asphaltene clusters indicates that the mixture is approaching the phase transition point for asphaltene stability. The investigation of the microstructural changes of solvated asphaltenes induced by decreasing solvent quality provides valuable insight into the destabilization mechanism of asphaltenes.

---

*Speaker

†Corresponding author: michael.hoepfner@utah.edu

A Comprehensive Study on Asphaltene Characterisation Using NMR, FTIR, ESEM, EDX, QCM Techniques: from Reservoir to Ambient Conditions

Edris Joonaki*[1]

[1]Centre for Flow Assurance Research Studies (CFAR), Institute of Petroleum Engineering, School of Energy, Geoscience, Infrastructure and Society, Heriot-Watt University – Riccarton, Edinburgh, EH14 4AS, UK, United Kingdom

Abstract

Asphaltenes are giant molecules including a few percent of heteroatoms (e.g. Oxygen (O), Sulphur (S)) linked to small amount of metal atoms (e.g. Vanadium (V), Nickel (Ni), Iron (Fe), etc.) with peripheral aliphatic substitutes. Asphaltenes are recognised to be precipitated and aggregated due to injection of gas or gas & liquids (e.g. for EOR purposes) which cause asphaltene deposition and a restricted flow accordingly. Cross fertilization of compositional data obtained by various analytical techniques elucidate many problems which have been strongly debated for many years. Molecular level information of asphaltenes has become crucial but has not completely found a home. The capability to achieve new information has increase our ability to utilise it to make the right decisions.

In this work, Nuclear magnetic resonance (NMR), High Pressure-High Temperature Quartz Crystal Microbalance (HPHT-QCM), Fourier Transform Infrared (FTIR) spectroscopy, Environmental Scanning Electron Microscopy (ESEM), Energy dispersive X-ray (EDX) analysis, and generally hybrid analytical platforms have led to an explosion in the attainable detailed (molecular level) compositional information of provided asphaltenes.

The HPHT-QCM experiments were conducted to determine the Asphaltene Onset Pressure (AOP) of parent crude oil used in this study due to injection of natural gas and CO2 at reservoir condition. Additionally, the effect of injected gas on molecular composition changes of asphaltene deposits has been investigated. EDX and FTIR techniques were also utilised to conduct the elemental and functional group analysis of the asphaltenes.

H and C NMR are appropriate techniques for studying of asphaltene structure despite its complexity. 1H & 13C NMR experiments were carried out to investigate the structural parameters of asphaltenes. The results from each technique are in consistent with other different techniques used in this research study.

---

*Speaker

A-22

Stability analysis of asphaletenes by Turbiscan Technology

Christelle Tisserand*[1]

[1]Formulaction – Formulaction – 3-5 Rue Paule Raymondis, 31200 Toulouse, France

Abstract

Reduction in the quality of crude oil throughout the world, due to diminishing resources and increasing refinery efficiency, has led to the production of worsening quality heavy fuel oils. Asphaltenes, a mixture of heavy hydrocarbons, tend to precipitate when the solubility changes due to temperature variation, blending..., thus blocking pipework, clogging filters or plugging burners... Therefore, extractions sites, refineries and heavy oil users (marine companies, electrical power plants...) have to systematically test the intrinsic stability of heavy fuel oils as well as the efficiency of additives. We will present one technology that can answer all these needs and monitor all destabilisation phenomena. It is based on Multiple Light Scattering (MLS) and is associated to a vertical scanning of the sample. It is like a high resolution electronic eye, enabling to identify and quantify instability phenomena before they are visible to the operator (5 to 50 times earlier than the naked eye). Physical parameters and kinetics can be computed in order to facilitate and improve comparisons between formulations. For asphaltenes stability in heavy fuel is has even been granted ASTM (D7061). The ASTM D 7061 method is well known to monitor additives efficiency in order to stabilize fuel oils.

---

*Speaker

A-23

Electron paramagnetic resonance study of the PetroPhase 2017 asphaltene sample

Vincent Dappe*†[1], Karima Ben Tayeb[1], Sandra Mariette[2], Olivier Serve[2], Vincent Livadaris[3], and Hervé Vezin[4]

[1]LAboratoire de Spectrochimie Infrarouge et Raman (LASIR) – CNRS : UMR8516, Université Lille I - Sciences et technologies – Bâtiment C5 59655 Villeneuve d'Ascq Cedex, France
[2]Total RC RD (Total RC RD) – Total Raffinage Chimie – TRTG - TOTAL Research Technology Gonfreville, France
[3]Total RC RD (Total RC RD) – TRTG - TOTAL Research Technology Feluy, Belgium
[4]Université Lille Nord de France – Université Lille Nord de France – F-59655 Villeneuve d'Ascq, France

Abstract

Currently, the conversion of heavy crude oils causes numerous problems due to their inherently poor qualities [1]. They are characterized by their high viscosity and contain large molecular weight fractions such as asphaltenes which are particularly refractory to conversion processes. More especially, the self-association behavior of asphaltenes (i.e. coke precursors) during conversion processes holds them responsible for drastic catalyst deactivation and rapid fouling of treatment unities [2]. Despite the numerous studies made in petroleum field research these last decades, mechanisms of asphaltenes aggregation still remain unresolved. Physicochemical characteristics of asphaltenes can vary greatly depending on the oil origin, the phase from which they have been extracted (atmospheric or vacuum residues) and the conditions of extraction used themselves (precipitant, sample-to-precipitant ratio, temperature ...) [3]. So, it remains difficult to precisely characterize these molecules.
The electron paramagnetic resonance (EPR) technique lays on the interaction between a magnetic field (B0) and a magnetic moment of an unpaired electron (electron spin S≠0). In this way, EPR spectroscopy is a powerful tool to investigate *in situ* such complex materials since asphaltenes contain high levels of paramagnetic centers. In continuous wave, EPR spectrum of asphaltenes displays two distinct signals, i.e. free organic radicals (intense single line) and V4+ corresponding to tetrahedral vanadyl complexes VO2+ (16 lines), i.e. with atoms arranged practically in a plane.

The development of the HYperfine Sublevel CORrElation spectroscopy (HYSCORE) sequence (Pulsed EPR) allows the investigation of the molecular structure of a selected paramagnetic center and its local environment [4] through the interactions between unpaired electrons and surrounding atoms with nuclear spin I≠0 (1H, 13C, 14N, 31P...). Results showed that free organic radicals contain preferentially aliphatic carbons and hydrogens. When targeting the specific environment of V4+, two different nitrogen signals (N1 and N2) are observed pointing out that the asphaltene sample was constituted of two types of vanadium complexes. The first one is engaged in a porphyrinic structure (N1) and the second

---

*Speaker
†Corresponding author: vincent.dappe@ed.univ-lille1.fr

one in a non-porphyrinic structure (N2). The signal intensity of 2D HYSCORE spectra highlights that N2 is preferentially located in the plane perpendicular to the vanadyl group VO2+. However, it can also be concluded that, in the parallel plane, the signal of N1 is so intense that its contribution outweighs that of N2, which could explain the lower signal intensity of N2 in the parallel plane.

References

Leyva, C., Ancheyta, J., Berrueco, C., Millán, M., 2013. *Fuel Processing Technology*, 106, 734-738.

Trukhan, S.N., Kazarian, S.G., Martyanov, O.N., 2017. *Energy&Fuels*, 31, 387-394.

Pantoja, P.A., Mendes, M.A., Nascimento, C.A.O., 2013. *Journal of Petroleum Science and Engineering*, 109, 198-205.

Ben Tayeb, K., Delpoux, O., Barbier, J., Marques, J., Verstraete, J., Vezin, H., 2015. *Energy&Fuels*, 29, 4608-4615.

Supramolecular assembly and paramagnetic impurities in asphaltene by ultra-fast MAS NMR spectroscopy

Kevin Sanders[1], David Gajan[1], and Guido Pintacuda*[1]

[1]Institut des Sciences Analytiques (ISA) – CNRS : UMR5280, Université de Lyon, École Normale Supérieure - Lyon, Université Claude Bernard - Lyon I – 5 rue de la Doua, 69100 Villeurbanne, France

Abstract

Nuclear magnetic resonance (NMR) with magic-angle spinning (MAS) is a powerful tool for the structural characterization of solids. Development in probe and magnet technology has recently enabled breakthroughs in this area, notably allowing the sensitive detection of resolved 1H signals by sample rotation at ultrafast (> 60 kHz) rates.

We investigate the potential of this technology to unveil macroscopic structures and local environments in an asphaltene sample. Notably (i) we acquire 1H-1H SQ-DQ correlation experiments, which report on short-range 1H-1H contacts, revealing intermolecular interactions present in the aggregate domain structures, and (ii) we exploit paramagnetic relaxation enhancements to amplify the signals of 1H nuclei surrounding trace metal impurities.

Together these preliminary results represent a promising future for NMR studies of asphaltene samples.

---

*Speaker

NIR Absorbance of Asphaltene

Theodore Garver*[1]

[1]Innotech Alberta – 250 Karl Clark Road Edmonton, AB T6N1E4, Canada

Abstract

The near infrared spectra (NIR) of asphaltenes contains contributions both electronic and vibrational absorbance. The electronic absorbance is due to the conjugation of multiple aromatic moieties. At NIR wavelengths between 1000 and 1600 nm the electronic spectrum of asphaltene may be fit with functions with one exponential that may be used to characterize the concentration of the asphaltene. Each source bitumen or oil must be calibrated independently because the asphaltene from different sources has different mass extinction coefficients (absorptivity).

---

*Speaker

A-26

DIRECT OBSERVATION OF ASPHALTENE NANOPARTICLES ON MODEL MINERAL SUBSTRATES

Gijo Raj*[1], Alain Lesimple[2], Jamie Whelan[2], and Panče Naumov†[2]

[1]New York University Abu Dhabi (NYUAD) – P.O. Box 129188 Saadiyat Island, United Arab Emirates
[2]New York University Abu Dhabi – P.O. Box 129188 Saadiyat Island, United Arab Emirates

Abstract

The propensity for adherence to solid surfaces of asphaltenes, a complex solubility class of heteropolycyclic aromatic compounds from the heavy fraction of crude oil, has long been the root-cause of scale deposition and remains an intractable problem in petroleum industry. Despite that the adhesion is essential to understand the process of asphaltene deposition, the relation between the conformation of asphaltene molecules on mineral substrates and its impact on adhesion and mechanical property of the deposits is not completely understood. To rationalize the primary processes in the process of organic scale deposition, herein we use atomic force microscopy (AFM) to visualize the morphology of Petrophase2017 asphaltenes deposited on mica and highly oriented pyrolytic graphite (HOPG) substrates. When deposited from dilute toluene solutions (W = 0.001 %), asphaltenes form isolated spherical objects of c.a. 6-7 nm high on hydrophilic and polar substrate (mica). However the height of asphaltene nanoaggregates are significantly reduced (c.a. 3.5 nm) on hydrophobic and non-polar substrate (HOPG). The reduction in the height of asphaltene nanoaggregates on HOPG is attributed to a flattening effect due to hydrophobic and π π interactions between the electron cloud systems of polycyclic aromatic rings in the asphaltene molecule and the hexagonally arranged C atoms on the HOPG substrate. Force-distance profiles provide direct evidence to of the conformational changes of asphaltene molecules on hydrophilic/hydrophobic substrates that result in dramatic changes in adhesion and mechanical properties of asphaltene deposits. Finally, we demonstrate the application of correlative microscopy techniques combining Digital Pulsed Force Microscopy and confocal Raman 2D imaging for probing the adhesion, stiffness and average sheet size of polycyclic aromatic cores present in asphaltene nanoparticles.

---

*Speaker

†Corresponding author: pance.naumov@nyu.edu

Delta 13C values for heteroatom classes of Asphaltene 2017 derived from LDI(+)-FTICRMS data

Peter Arisz*[1,2,3]

[1]Maastricht University (M4I) – Universiteitssingel 50;6229 ER Maastricht, Netherlands
[2]Jos Pureveen (Shell Global Solutions International BV the Netherlands) – Netherlands
[3]Ron Heeren (M4I - Maastricht University) – Universiteitssingel 50;6229 ER Maastricht, Netherlands

Abstract

A drop of asphaltene 2017 solution was dried on a stainless steel MALDI target plate. The sample was measured on a 9.4T Bruker Solarix with laser desorption ionization (LDI). In order to measure high resolution spectra only ions in the mass range m/z 475 to 525 were transferred with the quadrupole to the FT-cell. The data of 3812 transients were summed. An absorption mode Fourier Transform (aFT) spectrum was calculated with AutoVectis and the spectrum was recalibrated with Peak-to-Peak software, both from Spectroswiss. The mass peaks in the peaklist were assigned to various heteroatom and 13C-isotope classes with PetroOrg software. Peak-pairs of the monoisotopic and the first 13C-isotope peaks were selected in Excel and the delta 13C values of individual peak pairs were calculated.
Two assumptions are made for the analysis. First, it is assumed that both the monoisotopic and the 13C-isotope peaks are completely separated from other isobaric mass peaks. Second, it is assumed that the intensities of the monoisotopic and the 13C-isotope peaks are measured with equal probability.

Peak-pairs of the eight most abundant classes were processed. Sorted by decreasing abundance these are N1S1, N1, S1, N2, S2, N1S2, N2S1, and HC (hydrocarbons). All of these classes show up both as radical-cations and as protonated ion species. The number of peak-pairs per class ranges from 56 to 108. There is a strong 1:1-correlation (R2 0.91) between the relative intensities of these two types of ions.

Due to the inherent nature of FTMS, the variance in the peak ratio of individual peak-pairs is large. However, the error in mean value (± tn-1*σ/) is reduced significantly by the large number of peak-pairs (n). Plotting the average delta 13C values of the most abundant classes shows that NS-classes are most depleted, followed by S-classes. HC class has 'normal' values whereas N-classes are (relatively) enriched. There turns out to be a high correlation (R2 0.91) between the delta 13C values of radical-cations and protonated ions.
It is concluded that in the mass range m/z 475 to 525 mainly N- and S-containing classes are measured by LDI(+)-FTMS of Asphaltene 2017. There is a high correlation between the abundance of radical-cation and protonated ion species. Also there is a high correlation between the delta 13C values derived from radical-cations and protonated ions. Exceptional low and high delta 13C values in the range of about -400 to +100 are found for individual heteroatom classes, however, no violation of our assumptions is discovered so far.

---

[*]Speaker

A-28

CHARACTERIZATION OF PRECIPITATED ASPHALTENES (ROUND ROBIN TEST SPONSORED BY 2017 PETROPHASE)

Marcia Oliveira*†[1], Sonia Maria Menezes , Luiz Chinelatto , Luiz Carlos Marques , and Hercílio Honorato

[1]Petrobras Research Center (PETROBRAS) – Brazil

Abstract

The asphaltene sample prepared by the group of Marianny Y. Combariza at the Industrial University of Santander (Colombia) was characterized by TGA, NMR, FTIR and elemental analysis techniques. Although extremely important for determination of molecular weight and other relevant molecular structures, mass spectrometry analysis was not performed due to unavailability of the FT-ICR MS equipment at the moment.

This study had the purpose to collaborate and participate using our expertise in this unique interlaboratorial program initiative. Sharing the results with other labs, will give the participants a chance to unify concepts and methodologies for the analysis of such complex class of compounds. Based in those results, we intend to use the best methodologies and techniques for the characterization of Brazilian crude oils and asphaltenes.

The NMR analysis suggests a highly condensed aromatic asphalthene with some alkyl substitution and TGA shows a mass loss of 51% after introducing air which is in agreement with the highly condensed aromatic system observed by NMR. Elemental analysis shows a high sulfur content that was confirmed by the observation of the 1028.7cm-1 absorption band at the FTIR spectrum. DOSY showed apparently only the presence of nanoaggregates by the diffusion coefficient. A higher gradient power DOSY experiment will be run in the near future to try to discriminate aggregate sizes.

---

[*] Speaker

[†] Corresponding author: marcia.khalil@petrobras.com.br

sciencesconf.org:petrophase2017:157928

Analysis PetroPhase 2017 asphaltene by laser desorption ionization Fourier transform mass spectrometry

Johann Le Maître[1], Marie Hubert-Roux[1], Benoit Paupy[2], Sabrina Marceau[2], Carlos Afonso*[3], and Pierre Giusti[2]

[1]Normandie Univ, FR 3038; IRCOF, (COBRA) - Université de Rouen, CNRS : UMR6014, INSA Rouen – Université de Rouen, CNRS : UMR6014 – 1 rue tesnière 76821 Mont Saint Aignan CEDEX, France
[2]TOTAL RAFFINAGE CHIMIE (TRTG) – Total Raffinage Chimie – Département Analyse BP 27 - 76700 Harfleur, France
[3]Normandie Univ, FR 3038; IRCOF, (COBRA) - Université de Rouen, CNRS : UMR6014, INSA Rouen – Université de Rouen, CNRS : UMR6014 – 1 rue Tesnière, 76821 Mont St Aignan CEDEX, France

Abstract

* carlos.afonso@univ-rouen.fr

Asphaltenes are defined based on their solubility. Within a petroleum product, they constitute the fraction insoluble in non-polar n-heptane solvents but soluble in aromatic solvents such as toluene. Structurally, asphaltenes are considered to be complex mixtures of polycyclic hydrocarbons rich in heteroatoms.1 For this joint effort concerning the analysis of a common asphaltene sample, we used a FTICR instrument equipped with a 12T superconducting magnet2 and fitted with MALDI and APPI ionization sources.3 The results obtained from the asphaltene sample were compared to the crude oil and VGO samples. The data were internally calibrated yielding a typical *m/z* error below 200 ppb, and were further processed with PetroOrg and OriginPro softwares.

We were not able to obtain an efficient ionization of the asphaltene by APPI. However, the LDI-FTICR analysis afforded the ionization of the asphaltene sample with a very good yield. As observed previously, a series of fullerenes ions were detected separated by 24u.4,5 Compared to the VGO and the crude oil samples, the asphaltene yielded lower amount of N1 species, but higher amount of sulfur containing species. We observed also that the number of radical species are obtained in a lower extent with the asphaltene sample. As expected, the asphaltene sample presents an ion distribution that is always shifted towards the high DBE values.

1. Gaspar A, Zellermann E, Lababidi S, Reece J, Schrader W. *Energy & Fuels.* 2012;26:3481-3487. doi:dx.doi.org/10.1021/ef201312m.

2. Marshall AG, Hendrickson CL. *Int J Mass Spectrom.* 2002;215(1-3):59-75. doi:10.1016/S1387-3806(01)00588-7.

3. Purcell JM, Merdrignac I, Rodgers RP, Marshall AG, Gauthier T, Guibard I. *Energy*

---

[*] Speaker

and Fuels. 2010;24(4):2257-2265. doi:10.1021/ef900897a.

4. Pereira TMC, Vanini G, Tose L V., et al. *Fuel*. 2014;131(April):49-58. doi:10.1016/j.fuel.2014.04.049.

5. Santos VG, Fasciotti M, Pudenzi MA, et al. *Analyst*. 2016;141(9):2767-2773. doi:10.1039/C5AN02333E.

Authors index

AUTHOR	PAGES
Abraham Tinu	p259 (PP-P18)
Abutaqiya Mohammed	p295 (A-10)
Adams Jeramie	p165 (FA-P20) – p189 (UF-O05) - p193 (UF-P3)
Afonso Carlos	p317 (A-29)
Ageorges Valentin	p156 (FA-P11)
Agger Christian	p147 (FA-P03)
Aguilar-Cisneros Humberto	p281 (PP-P36)
Ahmed Arif	p48 (PC-P04)
Akhmetkhanova Nelya	p126 (E-P10) - p111 (E-O3)
Al-Awadi Hameed	p179 (FA-P31)
Alfarra Ahmad	p28 (PC-O02) - p230 (PP-O02)
Alijo Pedro Henrique	p246 (PP-P07)
Alvarenga Suyane	p83 (PC-P26)
Alvarez Fernando	p150 (FA-P05) - p151 (FA-P06) - p153 (FA-P08)
Amaral Monique	p59 (PC-P10)
Andersen Simon	p289 (A-04) - p36 (PC-O07)
Andrade Luciana	p270 (PP-P26)
Andrade Rafhael	p144 (FA-P01)
Arangalage Mélanie	p155 (FA-P10)
Araujo Dimitri	p224 (SO-P9)
Araujo Edson	p46 (PC-P03)
Araujo Elayne	p46 (PC-P03) - p85 (PC-P28)
Argillier Jean-François	p218 (SO-P4) - p106 (E-K)
Arias John	p197 (UF-P6)
Arif Ahmed	p30 (PC-O03)
Arisz Peter	p315 (A-27) - p66 (PC-P16)
Azevedo Luis	p170 (FA-P24)
Bajic Steve	p82 (PC-P25)
Bake Kyle	p299 (A-13)
Balestrin Lia	p229 (PP-O01) - p254 (PP-P14) - p269 (PP-P25)
Bansal Hemant	p252 (PP-P12)
Baraille Isabelle	p28 (PC-O02)
Barbier Jérémie	p95 (PC-P34)
Barbosa Fernanda	p300 (A-14) - p75 (PC-P21)
Barrère-Mangote Caroline	p301 (A-15) - p93 (PC-P33) - p95 (PC-P34)
Bassane Joao	p249 (PP-P10) – p272 (PP-P28) - p273 (PP-P29)
Bazzano Francesca	p182 (UF-K)
Becerra Mildred	p282 (PP-P37)
Bégué Didier	p28 (PC-O02)
Belati Allan	p169 (FA-P23)
Bello Forero Josué	p83 (PC-P26)
Ben Tayeb Karima	p310 (A-23)
Bernadas Manuel	p100 (PC-P38)
Bertheussen Are	p255 (PP-P15)

Bertran Celso	p254 (PP-P14)
Birdwell Justin	p84 (PC-P27)
Blakney Greg	p26 (PC-K)
Blanco-Combariza Cristian	p305 (A-18)
Blanco-Tirado Cristian	p102 (PC-P40) - p305 (A-18) - p275 (PP-P31) - p41 (PC-O11)
Bluck David	p145 (FA-P02)
Boak Lorraine	p177 (FA-P30)
Boek Edo	p69 (PC-P18)
Bonoldi Lucia	p182 (UF-K)
Borges Gustavo	p59 (PC-P10)
Bottia Hernando	p221 (SO-P7)
Boulangé Laurence	p244 (PP-P05)
Bouriat Patrick	p130 (E-P12) - p131 (E-P13) - p132 (E-P14)
Bourrel Maurice	p204 (SO-K)
Bouyssière Brice	p301 (A-15) - p132 (E-P14) - p95 (PC-P34) - p28 (PC-O02) – p93 (PC-P33)
Bozorgmehry Boozarjomehry Ramin	p167 (FA-P22)
Braga Glauco	p116 (E-P02) - p128 (E-P11)
Braga Renata	p116 (E-P02) - p224 (SO-P9)
Brana-Mulero Francisco	p145 (FA-P02)
Bru Pascal	p248 (PP-P09)
Burgass Rod	p232 (PP-O03)
Burnichon Corinne	p218 (SO-P4)
Cabral Anna	p85 (PC-P28)
Cagna Alain	p292 (A-07)
Cajaiba Joao	p169 (FA-P23)
Campbell Darin	p190 (UF-O06)
Campos Flavio	p144 (FA-P01)
Carati Claudio	p182 (UF-K)
Cardoso Giuseppe	p196 (UF-P5)
Cardoso Marcus	p164 (FA-P19)
Cardoso Mateus	p229 (PP-O01) - p254 (PP-P14) - p269 (PP-P25)
Carreon-Calderon Bernardo	p281 (PP-P36)
Carrier Hervé	p174 (FA-P27) - p271 (PP-P27) - p138 (FA-O3) - p28 (PC-O02)
Carrillo Carlos	p120 (E-P04)
Carvalho Alexandre	p162 (FA-P17)
Carvalho Suzanny	p177 (FA-P30)
Castillo Jimmy	p100 (PC-P38)
Castro Eustaquio	p272 (PP-P28) - p273 (PP-P29) - p249 (PP-P10)
Cevada Enrique	p152 (FA-P07)
Chacon Martha	p303 (A-16) - p53 (PC-P07) - p26 (PC-K)
Chacon Martha L.	p91 (PC-P32)
Chacon-Patino Martha	p305 (A-18) - p199 (UF-P8) - p41 (PC-O11)
Chapoy Antonin	p167 (FA-P22)
Chatziagapiou Christos P.	p266 (PP-P23)
Chebre Meriam	p230 (PP-O02)

Chen Li-Jen	p216 (SO-P2)
Chen Zhentao	p220 (SO-P6) - p40 (PC-O10)
Chinelatto Luiz	p316 (A-28)
Cho Eunji	p291 (A-06)
Chowdhury Sourav	p256 (PP-P16)
Chrisman Erika	p77 (PC-P22) – p300 (A-14)
Christensen Anders	p208 (SO-O03)
Christensen Jan	p61 (PC-P12) - p62 (PC-P13) - p187 (UF-O03)
Christensen Jan H.	p97 (PC-P35)
Christensen Peter	p97 (PC-P35)
Cismondi Martin	p274 (PP-P30)
Clingenpeel Amy	p26 (PC-K)
Cohen Jérémy	p248 (PP-P09)
Collell Julien	p230 (PP-O02) - p210 (SO-O04)
Combariza Marianny	p275 (PP-P31)
Combariza Montanez Marianny	p102 (PC-P40) - p41 (PC-O11) - p305 (A-18)
Contreras Quintanilla Carolina	p240 (PP-P03)
Corilo Yuri	p53 (PC-P07) - p26 (PC-K)
Corona Rayane	p249 (PP-P10) - p272 (PP-P28)
Correa Rodrigo	p83 (PC-P26)
Correra Sebastiano	p159 (FA-P14) - p158 (FA-P15)
Costa Gloria	p245 (PP-P06) - p219 (SO-P5)
Costa Gloria M. N.	p247 (PP-P08)
Cosultchi Ana	p279 (PP-P34)
Coutinho Joao	p59 (PC-P10)
Couto Bruno	p50 (PC-P05)
Cui Chen	p65 (PC-P15)
Curbelo Fabiola	p116 (E-P02) - p128 (E-P11) - p46 (PC-P03) - p85 (PC-P28) - p89 (PC-P31) - p222 (SO-P8) - p224 (SO-P9)
Curbelo Garnica Alfredo Ismael	p46 (PC-P03) – p116 (E-P02)
Dalmazzone Christine	p109 (E-O2)
Dappe Vincent	p310 (A-23)
Daridon Jean-Luc	p174 (FA-P27) - p271 (PP-P27) - p138 (FA-O3) - p161 (FA-P16)
Dariva Claudio	p59 (PC-P10)
Darjani Shaghayegh	p111 (E-O3)
Davies Craig	p107 (E-O1) – p140 (FA-05)
Davletbaev Alfred	p206 (SO-O02)
Dayton David	p201 (UF-P9) - p187 (UF-O03) – p62 (PC-P13)
De Leon Jennifer	p55 (PC-P08) - p57 (PC-P09)
De Sanctis Lucentini Pier Giorgio	p288 (A-03) - p122 (E-P06)
Dechabo Victor	p52 (PC-P06)
Del Rio Jose Manuel	p239 (PP-P02)
Desprez Alain	p95 (PC-P34)
Diaz Zavala Nancy	p123 (E-P07)
Dicharry Christophe	p130 (E-P12) - p131 (E-P13) - p132 (E-P14)

Dominguez Jose	p123 (E-P07)
Dominguez Jose Manuel	p157 (FA-P12) - p158 (FA-P13)
Dongwan Lim	p30 (PC-O03)
Dörk Stephan	p67 (PC-P17)
Duchemin Benoît	p156 (FA-P11)
Durot Maxime	p230 (PP-O02)
Dutta Richard	p153 (FA-P09)
Eastoe Julian	p107 (E-O1)
Eaton Paul	p189 (UF-O05) - p194 (UF-P3)
Edwards Kathleen	p31 (PC-O04)
Efika E. Chidi	p240 (PP-P03)
Eno Nathan	p101 (PC-P39)
Eschner Markus	p73 (PC-P20)
Escobar Nympha	p282 (PP-P37)
Esposito Rogerio	p246 (PP-P07)
Eunji Cho	p30 (PC-O03)
Fakra Sirine	p84 (PC-P27)
Fan Zhaoyang	p60 (PC-P11)
Filgueiras Paulo	p249 (PP-P10) - p272 (PP-P28) - p273 (PP-P29)
Filho Paulo	p121 (E-P05)
Fiorio Paula	p300 (A-14) - p77 (PC-P22)
Flego Cristina	p182 (UF-K)
Fleming Felipe	p170 (FA-P24)
Flores César	p150 (FA-P05) - p151 (FA-P06) - p152 (FA-P07) – p153 (FA-P08)
Fonseca Guilherme	p121 (E-P05)
Franceschi Elton	p59 (PC-P10)
Freitas Julio Cézar	p116 (E-P02) - p46 (PC-P03) - p89 (PC-P31) - p222 (SO-P8) - p128 (E-P11) – p85 (PC-P28)
Fumoto Eri	p195 (UF-P4)
Furuichi Naoto	p114 (E-P01)
Gabrielsen Jostein	p187 (UF-O03)
Gaganis Vassilis	p265 (PP-P22)
Gajan David	p312 (A-24)
Gallardo Rivas Nohra	p123 (E-P07)
Galliero Guillaume	p210 (SO-O04)
Garden Simon	p83 (PC-P26)
Garnica Alfredo Ismael	p85 (PC-P28) - p89 (PC-P31) – p128 (E-P11) - p222 (SO-P8) - p224 (SO-P9)
Garver Theodore	p313 (A-25) - p238 (PP-P01)
Gaudefroy Vincent	p244 (PP-P05)
Gérard Meunier	p248 (PP-P09)
Gerek Ince Nevin	p145 (FA-P02)
Gingras Jean-Philippe	p37 (PC-O08) - p294 (A-09) - p271 (PP-P27)
Giraldo Deisy	p41 (PC-O11)
Giraldo-Davila Deisy	p275 (PP-P31)
Giusti Pierre	p301 (A-15) - p93 (PC-P33) - p95 (PC-P34) - p317 (A-29) - p101 (PC-P39)

Golchha Abhishek	p175 (FA-P28)
Goldstein Allen	p34 (PC-O06)
Gonçalves Ronaldo	p172 (FA-P25)
Gonzalez Gaspar	p280 (PP-P35)
Goswami Ankur	p259 (PP-P18)
Goual Lamia	p290 (A-05) - p306 (A-19)
Gozzo Fabio	p164 (FA-P19)
Grasseschi Daniel	p192 (UF-P1)
Grimes R.	p189 (UF-O05) - p194 (UF-P3)
Grimmer Christoph	p297 (A-12) - p63 (PC-P14)
Groeger Thomas	p71 (PC-P19) - p73 (PC-P20)
Guidetti Stefania	p182 (UF-K)
Guimaraes Maria José	p300 (A-14) - p77 (PC-P22)
Gumaste Koushik	p186 (UF-O02)
Gutierrez Sama Sara	p301 (A-15) - p93 (PC-P33) - p95 (PC-P34)
Halim Amalia	p208 (SO-O03)
Han Yehua	p60 (PC-P11) - p39 (PC-O10)
Hancock Peter	p95 (PC-P34)
Hansen Asger	p62 (PC-P13) - p97 (PC-P35) - p187 (UF-O03)
Harper Michael	P38 (PC-O9)
Hartman Ryan	p135 (FA-O1)
Hase Alfred	p137 (FA-O2)
Hassanpouryouzband Aliakbar	p167 (FA-P22) - p232 (PP-O03)
Hazendonk Paul	p290 (A-05) - p306 (A-19)
Headen Thomas	p307 (A-20) - p69 (PC-P18)
Heeren Ron	p66 (PC-P16)
Hench Kyle	p153 (FA-P09)
Hendrickson Christopher	p26 (PC-K)
Hernandez Edgar	p150 (FA-P05) - p152 (FA-P07) - p153 (FA-P08)
Hernandez Neidy	p100 (PC-P38)
Hernandez-Bravo Raiza	p157 (FA-P12) - p158 (FA-P13)
Hirohama Seiya	p145 (FA-P02)
Hodges Mike	p296 (A-11)
Hodgson Natalie	p140 (FA-O5)
Hoepfner Michael	p307 (A-20) - p163 (FA-P18) - p235 (PP-O06)
Honorato Hercilio	p316 (A-28)
Hosseini Seyedahmad	p88 (PC-P30)
Hou Shuxin	p141 (FA-O6)
Hou Zhen	p190 (UF-O06)
Hoyos Bibian	p55 (PC-P08) - p57 (PC-P09) - p257 (PP-P17)
Hubert-Roux Marie	p317 (A-29)
Ishitsuka Kazuya	p260 (PP-P19)
Iulmukhametova Regina	p125 (E-P09)
Izza Hidaya	p44 (PC-P01)
Jackson George	p263 (PP-P21)

Jakobsen Simon	p61 (PC-P12)
Jalan Amrit	p31 (PC-O04)
Jennerwein Maximilian	p73 (PC-P20)
Jia Wenlong	p242 (PP-P04)
Jiang Zhongqiang	p220 (SO-P6)
Jihyun Ha	p30 (PC-O03)
Jimenez-Angeles Felipe	p239 (PP-P02)
Jimenez-Serratos Guadalupe	p263 (PP-P21)
Joonaki Edris	p308 (A-21) - p167 (FA-P22) - p232 (PP-O03)
Joshi Nikhil	p135 (FA-O1)
Julia Creasey	p140 (FA-O5)
Junior Valdemar	p272 (PP-P28) - p273 (PP-P29)
Juyal Priyanka	p233 (PP-O04)
Kabbach Clara	p172 (FA-P25)
Käfer Uwe	p71 (PC-P19)
Kampolis Giorgos	p265 (PP-P22)
Katano Keita	p287 (A-02)
Kilpatrick Peter	p38 (PC-O09)
Kim Nilo	p176 (FA-P29)
Kim Sunghwan	p291 (A-06) - p48 (PC-P04) - p29 (PC-O03)
Kim Young Hwan	p291 (A-06) - p48 (PC-P04)
Kiminami Narihito	p114 (E-P01)
Kireev Victor	p206 (SO-O02)
Korb Jean-Pierre	p217 (SO-P3) - p28 (PC-O02)
Koroishi Erika	p176 (FA-P29)
Korpela Jyrki	p118 (E-P03)
Kosov Victor	p52 (PC-P06)
Kovaleva Liana	p125 (E-P09) - p206 (SO-O02)
Krier Gabriel	p95 (PC-P34)
Kristensen Mette	p97 (PC-P35) – p187 (UF-O03)
Kuang Jun	p295 (A-10) - p173 (FA-P26)
Kuryakov Vladimir	p288 (A-03) - p122 (E-P06) - p52 (PC-P06)
Kushnerick Doug	p31 (PC-O04)
Labrador Henry	p253 (PP-P13) - p193 (UF-P2)
Lacerda Jr Valdemar	p249 (PP-P10)
Lalli Priscila	p53 (PC-P07) - p26 (PC-K)
Landoni Alberto	p182 (UF-K)
Langevin Dominique	p292 (A-07) - p106 (E-K)
Lauren Susanna	p118 (E-P03)
Lavenson David	p293 (A-08)
Law Jason	p69 (PC-P18)
Le Maitre Johann	p317 (A-29)
Lefeuvre Yoann	p248 (PP-P09)
Leite Danilo	p222 (SO-P8)
Lemonnier Yoann	p218 (SO-P4)

Lequeux François	p155 (FA-P10)
Lescoulie Sandrine	p37 (PC-O08)
Lesimple Alain	p314 (A-26) - p234 (PP-O05)
Liang Yunfeng	p260 (PP-P19) - p262 (PP-P20)
Lienemann Charles-Philippe	p95 (PC-P34)
Ligiero Leticia	p132 (E-P14)
Lim Dongwan	p48 (PC-P04)
Lima Guilherme	p170 (FA-P24)
Linden Nicolas	p282 (PP-P37)
Lira-Galeana Carlos	p239 (PP-P02)
Liu Fang	p126 (E-P10)
Livadaris Vincent	p310 (A-23)
Lizcano Carlos	p75 (PC-P21) - p197 (UF-P6)
Llovera Ligia	p193 (UF-P2)
Lobinski Ryszard	p301 (A-15) - p93 (PC-P33) - p95 (PC-P34)
Loehle Sophie	p230 (PP-O02)
Loh Watson	p164 (FA-P19) - p229 (PP-O01) - p254 (PP-P14) - p269 (PP-P25)
Lopes Gustavo	p85 (PC-P28)
Lopes Humberto	p280 (PP-P35)
Lopez Alfonso	p150 (FA-P05) - p151 (FA-P06) - p152 (FA-P07) - p153 (FA-P08)
Lopez Marure Arturo	p124 (E-P08)
Loriau Matthieu	p37 (PC-O08)
Losada Maria	p253 (PP-P13)
Lu Jie	p26 (PC-K)
Lübeck Josephine	p62 (PC-P13) - p187 (UF-O03)
Lucas Elizabete	p177 (FA-P30)
Luis Miguel	p193 (UF-P2)
Luiz Carlos Palermo	p177 (FA-P30)
Luo Nancy	p238 (PP-P01)
Mahavadi Sharath Chandra	p289 (A-04)
Maia Clauber Lucian	p222 (SO-P8)
Malmquist Linus	p62 (PC-P13)
Mante Ofei	p62 (PC-P13) - p201 (UF-P9) - p187 (UF-O03)
Marceau Sabrina	p101 (PC-P39) - p317 (A-29)
Marcus Heydrich	p139 (FA-O4)
Mariath Rubia	p87 (PC-P29)
Mariette Sandra	p310 (A-23)
Marques Luiz Carlos	p316 (A-28)
Marshall Alan	p26 (PC-K) – p301 (A-14)
Marsis Emanuel	p175 (FA-P28)
Martin Beatrice	p37 (PC-O08)
Martinez Ortega Fernando	p184 (UF-O01)
Martinez-Mora Omar	p157 (FA-P12)
Masuda Yoshihiro	p260 (PP-P19)
Matsuoka Toshifumi	p260 (PP-P19)

Mavromaras Alexander	p230 (PP-O02)
Mccartney Thomas	p198 (UF-P7)
Mckenna Amy	p26 (PC-K) - p233 (PP-O04)
Medine Gavin	p188 (UF-O04)
Meireles Francis	p280 (PP-P35)
Melo Banda Jose	p123 (E-P07)
Menezes Sonia	p300 (A-14) - p77 (PC-P22) - p316 (A-28)
Mennito Anthony	p31 (PC-O04) - p37 (PC-O09)
Merino-Garcia Daniel	p164 (FA-P19) - p134 (FA-K) – p176 (FA-P29)
Meunier Gérard	p109 (E-O2)
Michelsen Michael	p205 (SO-O01)
Middleton Joshua	p140 (FA-O5)
Miranda Alma Delia	p157 (FA-P12) - p158 (FA-P13)
Miranda Daniele	p50 (PC-P05)
Miranda Luise	p162 (FA-P17)
Mitra-Kirtley Sudipa	p290 (A-05) - p304 (A-17) - p306 (A-19) - p84 (PC-P27)
Miyagawa Yoshihiro	p214 (SO-P1)
Molina Daniel	p98 (PC-P36)
Molinas Bernardo	p160 (FA-P15)
Moncayo-Riascos Ivan	p257 (PP-P17)
Montanari Erica	p182 (UF-K)
Montanari Luciano	p182 (UF-K)
Montel François	p230 (PP-O02)
Montero Véronique	P244 (PP-P05)
Morantes Lina	p79 (PC-P23) - p98 (PC-P36)
Moreno Carmelo	p69 (PC-P18)
Morrison Damian	p95 (PC-P34)
Mouillet Virginie	p244 (PP-P05)
Moura Lyzette	p81 (PC-P24)
Mouret A	p109 (E-O2) - p218 (SO-P4)
Müller Erich	p263 (PP-P21) – p69 (PC-P18)
Musin Airat	p125 (E-P09)
Naderi Hassan	p88 (PC-P30)
Narasimhan Prasad	p145 (FA-P02)
Nardi Andrea	p193 (UF-P2)
Naumov Pance	p314 (A-26) - p234 (PP-O05)
Navarro Lina	p75 (PC-P21) - p197 (UF-P6)
Nesello Caio	p128 (E-P11)
Neto Dorval	p249 (PP-P10) - p272 (PP-P28) - p273 (PP-P29)
Neumann Anika	p297 (A-12) - p67 (PC-P17)
Newberry Michael	p175 (FA-P28)
Ng Samson	p163 (FA-P18)
Nicot Benjamin	p217 (SO-P3)
Nielsen Nikoline	p61 (PC-P12)
Nielsen Sidsel	p208 (SO-O03)

Nieto Sofia	p101 (PC-P39)
Nikrityuk Petr	p252 (PP-P12)
Nino Gomez Martha	p184 (UF-O01)
Noïk C	p109 (E-O2)
Nowak Jeremy	p34 (PC-O06)
Okuno Ryosuke	p242 (PP-P04)
Oliveira Marcia	p316 (A-28) - p162 (FA-P17) - p50 (PC-P05) - p280 (PP-P35)
Orlandi Ezequiel	p138 (FA-O3)
Orrego Jorge	p221 (SO-P7)
Ortiz Keyla	p99 (PC-P37)
Ovalles Cesar	p293 (A-08)
Padula Lilian	p170 (FA-P24)
Paiva Evanice	p46 (PC-P03)
Panariti Nicoletta	p182 (UF-K)
Panuganti Sai	p173 (FA-P26)
Park Moonhee	p291 (A-06)
Pascaud Laurent	p101 (PC-P39)
Passade-Boupat Nicolas	p37 (PC-O08) - p294 (A-09) - p132 (E-P14) - p271 (PP-P27)
Pastushak Paul	p238 (PP-P01)
Pauchard Vincent	p126 (E-P10) - p111 (E-O3)
Paupy Benoit	p101 (PC-P39) - p317 (A-29)
Pavoni Silvia	p159 (FA-P14)
Pedrosa Nuno	p149 (FA-P04) - p161 (FA-P16)
Peixinho Jorge	p156 (FA-P11)
Penaloza Jhon	p75 (PC-P21) - p197 (UF-P6)
Pereira Juan	p130 (E-P12) - p131 (E-P13) – p253 (PP-P13)
Pereira Laine	P249 (PP-P10) - p272 (PP-P28) - p273 (PP-P29)
Pereira Maria Luiza	p192 (UF-P1)
Pereira Veronica	p245 (PP-P06) - p219 (SO-P5) - p247 (PP-P08)
Perez Victor	p130 (E-P12) - p131 (E-P13) - p253 (PP-P13)
Pévère Audrey	p244 (PP-P05)
Pfeiffer Jens	p137 (FA-O2)
Picon Hernandez Hector	p184 (UF-O01)
Pimentel Lucas	p169 (FA-P23)
Pinappu Sai Reddy	p186 (UF-O02)
Pinho Bruno	p135 (FA-O1)
Pintacuda Guido	p312 (A-24)
Pita Luz	p120 (E-P04)
Planche Jean-Pascal	p165 (FA-P20)
Podgorski David	p26 (PC-K)
Pomerantz Andrew	p290 (A-05) - p293 (A-08) - p299 (A-13) - p0 (A-19) - p84 (PC-P27)
Pontarollo Alberto	p160 (FA-P15)
Poulsen Kristoffer	p187 (UF-O03)
Pourmohammadbagher Mohammad	p252 (PP-P12)
Poveda-Jaramillo Juan Carlos	p98 (PC-P36) - p99 (PC-P37) - p79 (PC-P23)

Pureveen Jos	p66 (PC-P16)
Putman Jonathan	p301 (A-15) - p93 (PC-P33) – p26 (PC-K)
Qian Kuangnan	p31 (PC-O04)
Queiroz Alex	p169 (FA-P23)
Quinquis Anne-Sophie	p292 (A-07)
Quintero Lina	p300 (A-14) - p77 (PC-P22)
Raj Gijo	p314 (A-26) - p234 (PP-O05)
Rajagopal Krishnaswamy	p270 (PP-P26)
Ramirez-Pradilla Juan	p275 (PP-P31)
Ramos-Pallares Francisco	p250 (PP-P11)
Redmond Mark	p139 (FA-O4)
Regueira Teresa	p266 (PP-P23) - p268 (PP-P24)
Regueira Victor	p245 (PP-P06) - p219 (SO-P5)
Respini Marco	p188 (UF-O04)
Rezaee Sara	p295 (A-10) - p173 (FA-P26)
Rezende Fabiola	p121 (E-P05)
Ribeiro Vinicius	p83 (PC-P26)
Riches Eleanor	p82 (PC-P25)
Ricoux Philippe	p230 (PP-O02)
Robert Cédric	p218 (SO-P4)
Rodgers Ryan	p301 (A-15) - p303 (A-16) - p53 (PC-P07) - p91 (PC-P32) - p93 (PC-P33) - p199 (UF-P8) - p201 (UF-P9) - p26 (PC-K) - p233 (PP-O04)
Rodriguez Maria	p120 (E-P04)
Rogel Estrella	p293 (A-08) - p154 (FA-P09) - p45 (PC-P02)
Rojas Fernando	p221 (SO-P7)
Ronningsen Hans Petter	p141 (FA-O6)
Rosa Paulo	p164 (FA-P19)
Rosario Francisca	p196 (UF-P5)
Rowland Steven	p303 (A-16) - p91 (PC-P32) - p199 (UF-P8) - p201 (UF-P9) - p26 (PC-K)
Rozanska Xavier	p230 (PP-O02)
Rucker Steven	p38 (PC-O09)
Rüger Christopher	p297 (A-12) - p63 (PC-P14) - p67 (PC-P17) - p71 (PC-P19)
Ruidiaz Eddy	p176 (FA-P29)
Ruiz-Morales Yosadara	p277 (PP-P32)
Rytting Mckay	p38 (PC-O09)
Ryuzo Tanaka	p27 (PC-O01)
Sad Cristina	p249 (PP-P10) - p272 (PP-P28) - p273 (PP-P29)
Saidoun Mohamed	p271 (PP-P27)
Samdoval Gustavo	p144 (FA-P01)
Sanders Kevin	p312 (A-24)
Sandoval Diego	p205 (SO-O01)
Santos Dalapicola Francine	p272 (PP-P28) - p249 (PP-P10) - p273 (PP-P29)
Santos Silva Hugo	p28 (PC-O02)
Sarginson Helen	p140 (FA-O5)
Sasaya Kazuyo	p114 (E-P01)

Sato Shinya	p195 (UF-P4)
Sawczuk Marcin	p102 (PC-P40)
Schabron John	p189 (UF-O05) - p194 (UF-P3)
Scheer Agnes	p87 (PC-P29)
Schoeggl Florian	p250 (PP-P11)
Scilipoti José Antonio	p246 (PP-P07)
Seidl Peter	p309 (A-14) - p166 (FA-P21) - p75 (PC-P21) - p77 (PC-P22)
Sena Rennio	p224 (SO-P9)
Serratos Guadalupe	p69 (PC-P18)
Serve Olivier	p310 (A-23)
Setaro Luisa L. O.	p247 (PP-P08)
Seurre Lauréline	p218 (SO-P4)
Shank Roxanne	p198 (UF-P7)
Shaw John	p252 (PP-P12) - p256 (PP-P16) - p282 (PP-P37)
Shekarifard Ali	p88 (PC-P30)
Shi Quan	p65 (PC-P15) - p39 (PC-O10)
Shibuya Takehiro	p114 (E-P1)
Silva Fernanda	p77 (PC-P22)
Silva Joao	p196 (UF-P5)
Silva Mayara	p249 (PP-P10) - p272 (PP-P28) - p273 (PP-P29)
Simon Sébastien	p255 (PP-P15) - p32 (PC-O05) - p87 (PC-P29)
Siqueira Renato	p144 (FA-P01)
Sjoblom Johan	p255 (PP-P15) - p32 (PC-O05)
Sklorz Martin	p297 (A-12) - p67 (PC-P17)
Smith Donald	p26 (PC-K)
Soares Edson	p144 (FA-P01)
Soares-Bassani Gabriel	p176 (FA-P29)
Sodero Ana Carolina	p28 (PC-O02)
Sorbie Ken	p177 (FA-P30)
Sorensen Henrik	p147 (FA-P03)
Sorrentino José	p120 (E-P04)
Sousa Roxana	p116 (E-P02)
Souza Rodrigo	p83 (PC-P26)
Stead Paul	p175 (FA-P28)
Stenby Erling H.	p266 (PP-P23) - p268 (PP-P24) - p205 (SO-O01) - p208 (SO-O03)
Streibel Thorsten	p63 (PC-P14)
Subramanian Sreedhar	p32 (PC-O05)
Sultanguzhin Ruslan	p206 (SO-O02)
Suzuki Teruo	p287 (A-02)
Sykora Juan	p130 (E-P12) - p131 (E-P13)
Szczepanski Richard	p149 (FA-P04) - p161 (FA-P16
Taghikhani Vahid	p167 (FA-P22)
Taheri-Shakib Jaber	p88 (PC-P30)
Takanohashi Toshimasa	p195 (UF-P4)
Talini Laurence	p155 (FA-P10)

Tanaka Auro	p81 (PC-P24)
Tanaka Ryuzo	p287 (A-02)
Tavakkoli Mohammad	p295 (A-10) - p173 (FA-P26)
Tavares Frederico	p246 (PP-P07)
Taylor Shawn	p250 (PP-P11)
Teixeira Adriana	p144 (FA-P01)
Teixeira Carmem Lucia	p280 (PP-P35)
Teixeira Raquel	p83 (PC-P26)
Thompson Roney	p144 (FA-P01)
Thundat Thomas	p259 (PP-P18)
Tighe Chris	p240 (PP-P03)
Tisserand Christelle	p309 (A-22) - p248 (PP-P09) - p109 (E-O2)
Tohidi Bahman	p232 (PP-O03) – p167 (FA-P22)
Toma Henrique	p192 (UF-P1)
Tomasi Giorgio	p62 (PC-P13) - p187 (UF-O03)
Torin Ollarves Geraldine	p240 (PP-P03)
Torres Mary	p98 (PC-P36)
Tort Frederic	p165 (FA-P20)
Totton Tim	p263 (PP-P21)
Trevisan Osvair	p176 (FA-P29)
Trusler J. P. Martin	p240 (PP-P03)
Tsutomu Nakamura	p27 (PC-O01)
Tukhbatova Elmira	p125 (E-P09)
Uetani Takaaki	p114 (E-P01)
Ulbrich Anne	p63 (PC-P14)
Ungarato Rafael	p121 (E-P05) - p85 (PC-P28) - p89 (PC-P31) - p128 (E-P11) - p222 (SO-P8)
Ungerer Philippe	p230 (PP-O02)
Uribe-Vargas Veronica	p281 (PP-P36)
Ursini Cleber	p50 (PC-P05)
Vale Mariana	p89 (PC-P31)
Vallverdu Germain	p28 (PC-O02)
Varela Junior Jaldyr	p81 (PC-P24)
Vargas Francisco	p295 (A-10) – p173 (FA-P26)
Vargas Vicmary	p100 (PC-P38)
Varotsis Nikos	p265 (PP-P22)
Varzandeh Farhad	p266 (PP-P23)
Vassaux Sabine	p244 (PP-P05)
Vaz Alexandre	p196 (UF-P5)
Vazquez Almaguer Ariana Margarita	p123 (E-P07) - p124 (E-P08)
Vazquez Flavio	p150 (FA-P05) - p151 (FA-P06) - p152 (FA-P07) - p153 (FA-P08)
Velasquez Ana	p57 (PC-P09)
Velasquez Ingrid	p130 (E-P12) - p131 (E-P13)
Verdier Sylvain	p61 (PC-P12) - p62 (PC-P13) - p97 (PC-P35) - p187 (UF-O03) – p201 (UF-P9)
Vermorel Romain	p210 (SO-O04)
Vezin Hervé	p310 (A-23)

Vieira De Melo Silvio	p245 (PP-P06) - p219 (SO-P5) - p247 (PP-P08)
Vieira Lenise	p50 (PC-P05)
Villamizar Jennifer	p253 (PP-P13)
Villanueva Ivan	p253 (PP-P13)
Wadhawan Harshita	p259 (PP-P18)
Wang Fei	p173 (FA-P26)
Wang Shu	p190 (UF-O06)
Ward Claire	p140 (FA-O5)
Ware Rebecca	p201 (UF-P9)
Watanabe Takumi	p214 (SO-P1)
Watanasiri Suphat	p190 (UF-O06)
Wattana Chaisoontornyotin	p163 (FA-P18) - p235 (PP-O06)
Wei Duo	p32 (PC-O05)
Wei Yan	p179 (FA-P31)
Wellons Helen	P31 (PC-O4)
Wendt Jürgen	p71 (PC-P19) - p73 (PC-P20)
Whelan Jamie	p314 (A-26) - p234 (PP-O05)
Wicking Christianne	p296 (A-11)
Wilharm Thomas	p71 (PC-P19) - p73 (PC-P20)
Witt Matthias	p286 (A-01) - p45 (PC-P02)
Wu Xi	p220 (SO-P6)
Wund Perrine	p218 (SO-P4)
Xiaohong Zhang	p149 (FA-P04) – p161 (FA-P16)
Xu Bo	p139 (FA-O4)
Xu Chunming	p220 (SO-P6)
Xu Gang	p145 (FA-P02)
Xu Yuming	p278 (PP-P33)
Xu Zhiming	p220 (SO-P6)
Yamamoto Carlos	p87 (PC-P29)
Yan Wei	p266 (PP-P23) - p268 (PP-P24) - p205 (SO-O01)
Yang Yuan	p235 (PP-O06)
Yarranton Harvey	p228 (PP-K) - p250 (PP-P11)
Yen Andrew	p135 (FA-O1) - p233 (PP-O04)
Yeung Hoi	p179 (FA-P31)
Yiannourakou Marianna	p230 (PP-O02)
Yonebayashi Hideharu	p114 (E-P01) - p214 (SO-P1)
Yorozu Hirokazu	p114 (E-P01)
Yudin Dmitrii	p52 (PC-P06)
Yudin Igor	p52 (PC-P06)
Zambrano Urrutia Naydu	p184 (UF-O01)
Zamora Edgar	p150 (FA-P05) - p153 (FA-P08)
Zeng Huang	p296 (A-11)
Zhang Jingzhou	p163 (FA-P18)
Zhang Linzhou	p65 (PC-P15) - p39 (PC-O10)
Zhang Yanfen	p60 (PC-P11)

Zhang Yunlong	p38 (PC-O09)
Zhao Suoqi	p65 (PC-P15) - p220 (SO-P6)
Zimmermann Ralf	p297 (A-12) - p63 (PC-P14) - p67 (PC-P17) – p71 (PC-P19) – p73 (PC-P20)
Zinnatullin Rasul	p206 (SO-O02)
Zonta Pier	p160 (FA-P15)
Zorgani Ezzidene	p179 (FA-P31)

© Crédits photos : OTAH / Fotolia