

Natural Surfactants from Venezuelan Extra Heavy Crude Oil - Study of Interfacial and Structural Properties

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1. Introduction

Studies of the composition and physicochemical properties of heavy and extra heavy crude have been of great importance and interest to academia and the petroleum industry, due to the ability of these oils to form water in oil emulsions. Water in oil emulsions are known to form during crude oil production, oil sands extraction processes, and oil spills in aquatic environments. Often, these water-in-oil emulsions are undesirable since they can cause several problems including: production of an off-specifications crude oil (high solids and water content, >0.5%); corrosion and catalyst poisoning in pipes and equipment for water settling; and environmental issues when oil spills occur in rivers and oceans. Treatment of these emulsions is still a challenge in the petroleum industry due to their high stability versus coalescence. These emulsions are very stable, this stability is attributed largely to the adsorption of compounds with interfacial activity, such as asphaltenes, resins and carboxylic acids present in the oil, at the water - crude interface. Asphaltenes are a complex mixture of high-molecular weight compounds, where 90% or more of the mass is composed of carbon and hydrogen; the sulfur, oxygen, and nitrogen contents in asphaltenes are approximately 5%, 2%, and 1%, respectively, and trace quantities of other heteroatoms are present the high molecular weight components of crude oil. Reported data has shown that asphaltenes, are adsorbed at the crude oil-water interface. For instance, the high stability of the w/o emulsions could be due to strong interfacial films formed by asphaltenes. These films would be very resistant to coalescence (Yarranton et al, 2000; Ortiz et al, 2010; Spiecker, & Kilpatrick, 2004; Pauchard et al, 2009; Chaverot et al, 2010; Sjöblom et al 1992; McLean et al 1997)

The isolation of natural surfactants, using various methods such as separation by emulsification (Acevedo et al, 1992), chromatographic methods (Ramljak et al, 1977, Acevedo et al, 1999; Borges, 2009) has been reported. In this research, a modified chromatographic procedure, based on the proposed by Ramljak in 1977, has been used to isolate natural surfactants in crude oil and thus adapt to the properties of Venezuelan extraheavy crude oil from the Orinoco oil belt, followed by structural characterization of these surfactants, especially those derived from the acid. As mentioned above these natural surfactants play an important role in the stability of emulsions, there is great interest in

knowing how they are structurally. Also, the study of interfacial properties, specifically the interfacial tension is an essential tool for determining the ability of surfactants to reduce the tension to adsorb at water-oil interface. This thermodynamic property is used in this research to try to elucidate the action of natural surfactants, specifically the nature aliphatic carboxylic acids and asphaltenes in the formation of the interfacial film and consequently its close relationship with the stability of emulsions of w/o. This study consisted in measured interfacial tension versus concentration for the different natural surfactants. Interfacial tension measurements was doing by the hanging drop method, a bitumen droplet of known volume is formed at the tip of a hypodermic needle immersed in an aqueous solution.

Is important to know that the Orinoco Oil Belt is located along the southern margin of the Eastern Venezuela Basin, (south of the Guárico, Anzoátegui, Monagas, and Delta Amacuro states) parallel to the Orinoco River, covering a geographic area on the order of 55,000 sq km. Within it lies one of the largest oil deposits in the world, roughly 1.3 trillion barrels of "oil in place". Petróleos de Venezuela S.A. has estimated that the producible reserves of the Orinoco Belt are up to 235 billion barrels which would make it the largest petroleum reserve in the world, before Saudi Arabia. The area is divided, from West to East, into four distinct production zones: Boyaca, Junin, Ayacucho and Carabobo.

2. Experimental methods

2.1 Crude oil fractionation

2.1.1. Junín Asphaltenes (AJ) and Junín Maltenes (MJ): The crude oil studied was Junin, which is found at the Orinoco oil belt and has an API gravity of 8°. Asphaltenes were precipitated from the crude oil by the addition of 60 volumes of n-heptane. Previously, the crude oil was diluted in 1:1 toluene - crude oil. Said mixture was stirred mechanically for 6 hours and was then left standing for 24 hours. After this time, the solid was filtered, the solvent of the supernatant liquid was evaporated, leaving a resin - the maltenes - which was dried later and quantified. The solid was washed in a Soxhlet extractor with n-heptane until the solvent turned clear.

2.1.2. Chromatographic system with solvent recirculation: to extracted acid compounds, where the stationary phase was silica gel modified by potassium hydroxide (Ramljak *et al.*, 1977). The experimental procedure was as follows:

Stationary Phase: KOH was dissolved in isopropanol in a 1:25 w/v ratio at high temperature and it was mixed with a silica gel suspension (70-230 mesh) in chloroform (CHCl₃) in a 1:2 w/v ratio. It was stirred for 15 minutes. The KOH : silica gel ratio was 1:10. The mixture was transferred to a chromatographic column with solvent recirculation, the column was washed with 600 mL of moderately heated (50°C) CHCl₃ and it was refluxed for 15 minutes to remove excess KOH.

Sample: Junin crude oil was dissolved in the lowest amount of CHCl₃, keeping a 1:10 ratio of crude oil to silica gel. Once prepared, the sample was placed on the top of the column.

2.1.2.1. Extraction of the Basic - Neutral Fraction (FBN): 600 mL of CHCl₃ were placed in the flask and were moderately heated to start reflux until the solvent eluting from the column became colorless. The solvent in the flask was evaporated to dryness and was attached to a vacuum pump to be quantified later.

2.1.2.2. Extraction of the Acid Fraction (AcJ): The residue which was adsorbed on the column was treated with 600 mL of a 20% solution of formic acid (HCOOH) in CHCl_3 , repeating the previous procedure. Once the acid fraction was obtained, 90% of the solvent was evaporated; the organic residue was washed several times with water until the pH of the aqueous layer was close to 5 in order to remove excess HCOOH. Then, it was dried with magnesium sulfate (MgSO_4), filtered, and the rest of the solvent was evaporated. Finally, it was placed under high vacuum for 6 hours and it was quantified.

2.1.3. Acid-Free Asphaltenes (ASA): The basic - neutral fraction was passed another time through the chromatographic system using CHCl_3 as the elution solvent. Once the solvent was evaporated and the sample dried, the acid-free asphaltenes were precipitated using the previously described method.

2.2 Structural characterization

2.2.1. Molecular Weights by Vapor Pressure Osmometry (VPO): A Jupiter Instrument Co. model 833 vapor pressure osmometer was used to determine the molecular weights by VPO, using nitrobenzene as the solvent at a working temperature of 100 °C. The constant of the equipment was calculated using pyrene (202 g/mol) as the standard. The solutions analyzed were prepared in concentrations ranging from 1 to 6 g/L.

2.2.2. Elemental Analysis: A Herrman Moritz Macanal 10 micro analyzer was used to apply the high combustion method according to the AFNOR M03-032 standard, for C and H, and the AFNOR M03-08 and AFNOR M-025 standards for S.

2.2.3. Fourier Transform Spectroscopy Infrared (FTIR): Infrared spectra were obtained using a Bruker Optik GmbH Tensor 27 FT-IR, controlled by an Opus/IR software, which uses Fourier transform to process data. Samples were analyzed as liquid films in KBr cells and dry KBr pellets.

2.2.4. Nuclear Magnetic Resonance Spectroscopy (^1H NMR and ^{13}C NMR): Proton and carbon nuclear magnetic resonance spectra (^1H NMR and ^{13}C NMR, respectively) were obtained in a polynuclear JEOL Eclipse Plus 400 spectrometer (400 MHz), using tetramethylsilane as the reference and deuterated chloroform and carbon tetrachloride as the solvent for ^{13}C NMR and ^1H NMR, respectively. ^{13}C NMR spectrum were accumulated during 24 hours.

2.3 Interfacial characterization

Interfacial tension measurements by the Hanging Drop Method. A bitumen droplet of known volume is formed at the tip of a hypodermic needle immersed in an aqueous solution. The shape of a drop of liquid hanging from a syringe tip is determined from the balance of forces which include the surface tension of that liquid. The surface or interfacial tension at the liquid interface can be related to the drop shape through the Young-Laplace equation. (Hiemmenz, 1988)

This device consists of a visualization cell filled with double distilled water, where a drop of the solution is formed; a plastic syringe provided with a U-shaped needle was used to create the emerging drop; a lamp is used for illumination; a video system, to obtain the images; a computer, to obtain and digitalize the images for further treatment. The interfacial tension is

calculated using a computer program called DROP (Lopez de Ramos *et al.*, 1993). A battery of solutions of AJ, MJ, AcJ, and ASA samples in toluene was prepared with different concentrations ranging from 100 mg/L to 90000 mg/L. In order to test the tension values, a drop of solution and the double distilled water pre-saturated with toluene at neutral pH were put in contact in the visualization cell for 5 minutes until apparent equilibrium was reached. Then, the measurement was made. The method was validated by comparing the different values reported for pure substances and showed errors below 2%. Experiments were carried out at room temperature.

3. Results and discussion

The analysis presented in this work suggests that the chromatographic method used for separation of acids from extraveavy crude oil is efficient, effective and relatively fast. Table 1 shows the yields of the different isolated fractions. AcJ acids represent 1.6% of the crude oil, *i.e.* half of the acids present in the Carabobo crude oil (Acevedo *et al.*, 2005). However, these crude oil components showed a good interfacial activity, as will be shown later. Table 2 shows the H/C values. AcJ acids, which are amber colored resins, are a highly aliphatic fraction according to this ratio (H/C =1.6), contrasting with AJ and ASA, which are blackish brown and show an H/C value of about 1.12, which was expected for asphaltenes.

Samples	Yield (%p/p)
MJ	87
AJ	11
ASA	8.5
AcJ	1.6

Table 1. Yield of the different samples compared to the crude oil.

Samples	%C	%H	%S	H/C
MJ	85.32	11.8	3.43	1.671
AJ	84.33	8.43	5.30	1.199
ASA	84.72	8.39	4.83	1.118
AcJ	85.21	11.62	5.30	1.636

Table 2. Elementary analysis.

The molecular weights determined by VPO are reported in Table 3. The acid components (AcJ) showed a molecular weight of 474 g/mol, which is low and coincides with the values reported by Stanford *et al.*, who using other techniques reported values from 225 to 1000 for polar acid species which stabilize water in crude oil emulsions. Values reported for AJ and ASA are not significantly different as the error of this technique (VPO) is about 10% and they are within the expected range.

Samples	Molecular Mass (Da)
AJ	1010
ASA	950
AcJ	474

Table 3. Molecular weights obtained by Vapor Pressure Osmometry.

Figure 1 shows the FTIR spectra for the AcJ and AJ fractions. The spectra show a band at 3320 cm^{-1} attributed to $\nu_{\text{O-H}}$; the carbonyl signal, $\nu_{\text{C=O}}$, at 1709 cm^{-1} ; the $\nu_{\text{CH}_3+\text{CH}_2}$ signal at 2922 for the acids, as opposed to the spectrum of asphaltenes, where no carbonyl signal and no signal due to OH stretching can be seen; other signals typical for these kind of compounds can be observed (Khanna et al., 2006).

Figures 2 and 3 show the ^{13}C NMR and ^1H NMR spectra of the acid fraction. The signals corresponding to carboxylic groups (178 and 9.8 ppm, respectively) and the bands corresponding to the aromatic zone (about 126.6 and 7, respectively) and the aliphatic zone (from 14 to 52 ppm and from 0.5 to 3 ppm, respectively) can be clearly seen. The latter are the most intense signals. Figures 4 and 5 show the ^{13}C NMR and ^1H NMR spectra for the asphaltenes (AJ), which are similar to those previously reported by other researchers (Acevedo et al., 2005b).

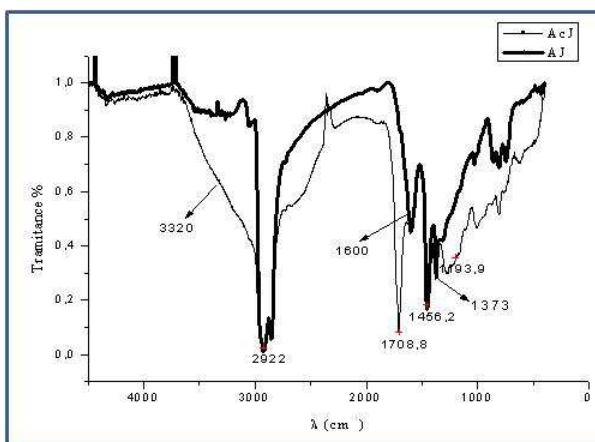


Fig. 1. Comparison of AcJ and AJ FTIR spectra.

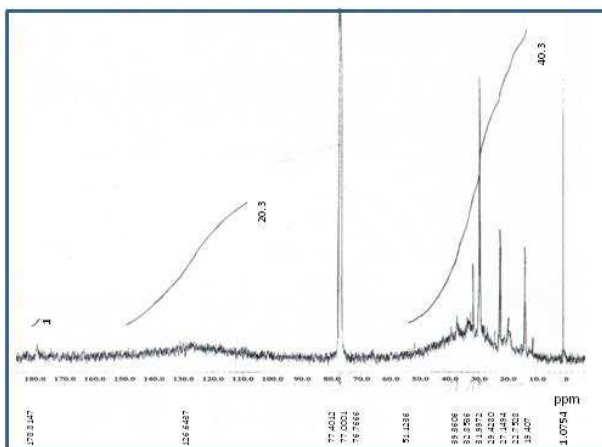


Fig. 2. ^{13}C NMR spectrum for AcJ.

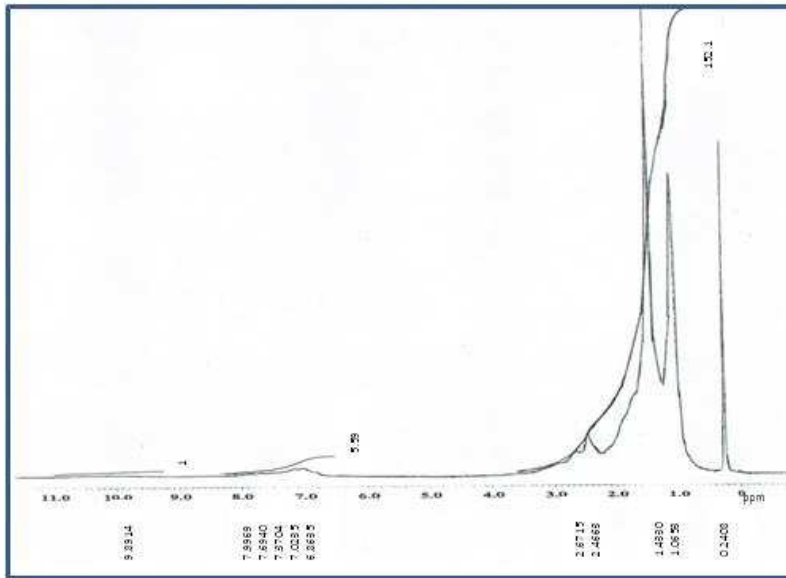


Fig. 3. ^1H NMR spectrum for AcJ.

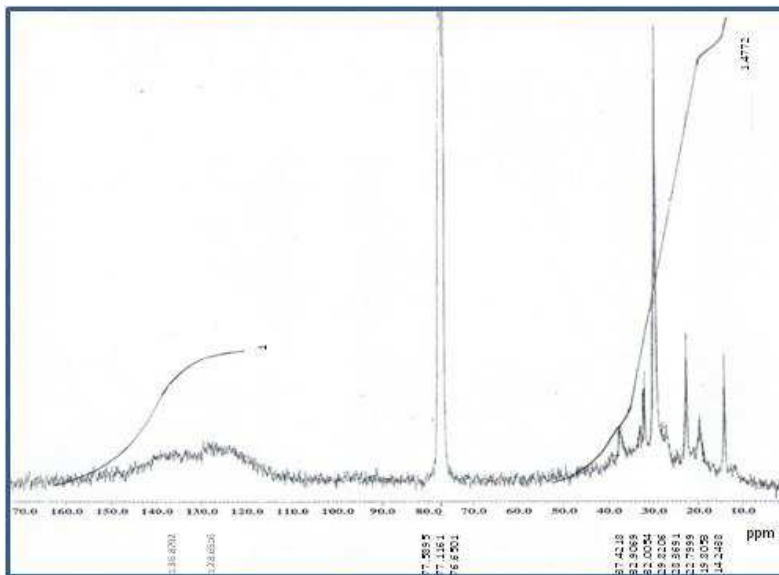


Fig. 4. ^{13}C NMR spectrum for AJ.

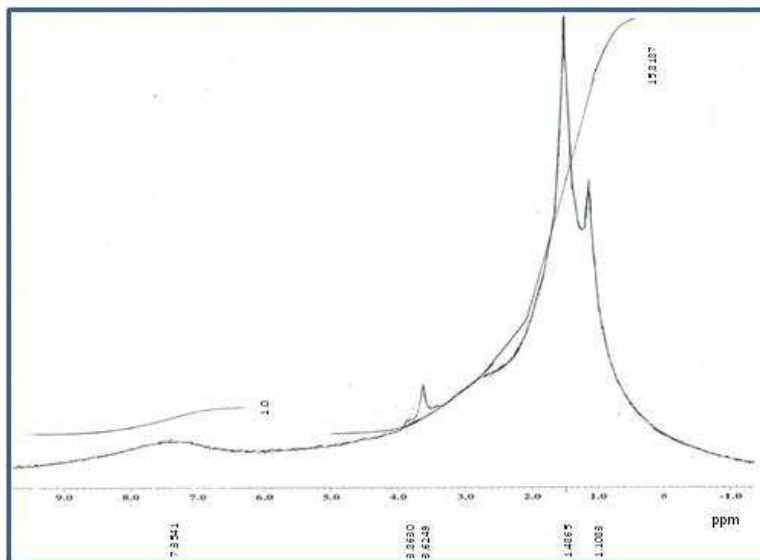


Fig. 5. ¹H NMR spectrum for AJ.

The adsorption of asphaltenes and other natural surfactants at the water/toluene interface has been studied here. The adsorption isotherms for the different systems studied (see Figure 5) show that there is a systematic decrease of the interfacial tension with the increase in the sample concentration until a concentration is reached after which the tension remains unchanged. This value corresponds to the saturation of the aggregates in the solution which coincides with the results reported by Acevedo et al. in 2005. The evidence presented in this work suggests that asphaltenes adsorb to the oil-water interface.

Maltenes show the highest tension values. The concentration of surface active species increases from MJ to AcJ, which was expected, because the polarity of the sample increases in the aforementioned direction. The acids fraction has low molecular weights, which favors the mobility of this species at the interface. As the tension curves are parallel, the concentration of each of the species to reach a specific interfacial tension was also calculated. The value of the AcJ concentration so obtained must correspond to the amount of acids present in each of the samples. Therefore, Table 5 shows the percentage of AcJ present in maltenes, asphaltenes, and acid-free asphaltenes. As can be seen, asphaltenes show the highest concentration of acids, suggesting that the AcJ are trapped by the asphaltene molecules which act as molecular traps, because these compounds are linked by hydrogen bonds, among other kind of interactions (π - π interactions) (Acevedo et al. 2007). On the other hand, acid-free asphaltenes (ASA) show a higher interfacial tension than AJ indicating that the acids were removed at least almost completely from the asphaltenes. It can also be seen that the saturation concentration for ASA is about 6000 mg/L, and it remains unchanged regardless of the concentration of asphaltenes in the solution, *i.e.* it shows $\delta\gamma/\delta(\ln C) \approx 0$ across a broad range of concentrations. This behavior may be related to the ability of asphaltenes to form aggregates and adsorb at the water - crude oil interface and the posterior flocculation of these aggregates to originate solid interfacial films.

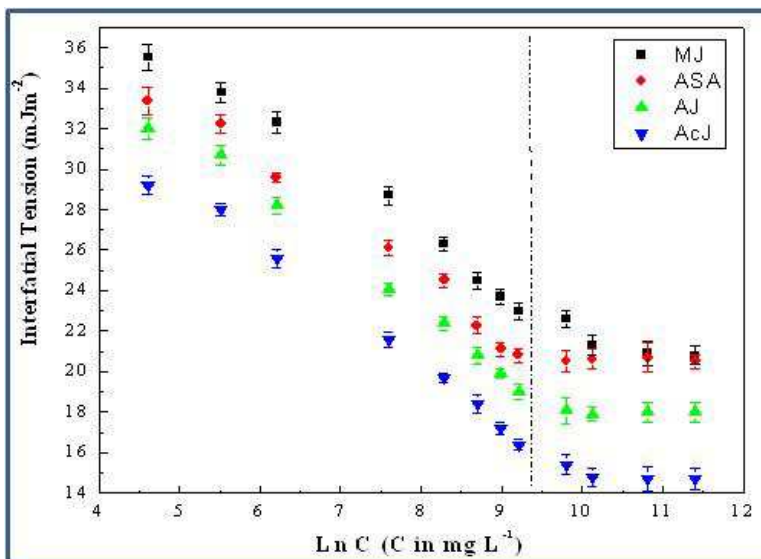


Fig. 6. Adsorption isotherm for maltenes (MJ), acid-free asphaltenes (ASA), asphaltenes (AJ) and acids (AcJ) at a water / toluene interface. The vertical line represents the maximum values used for the calculation of the slopes for each of the isotherms.

Sample	Slope (mJ/m ²)	Apparent Area per Molecule (Å ² /mol)	Molecular Weight (Da)	Percentage of Acids (AcJ)
MJ	-2.86±0.11	144±6	347±14	11±6
AJ	-2.91±0.09	141±4	340±10	41±4
ASA	-2.93±0.09	140±4	337±10	23±4
AcJ	-2.94±0.08	140±4	337±10	100±4

Table 4. Apparent area per molecule adsorbed at the interface and its respective molecular weight.

Another interesting aspect to discuss is the calculation of the apparent area of the species adsorbed at the interface and its relationship with the molecular weight of said species. As is well known, Gibbs adsorption equation allows us calculate the adsorption Γ (the concentration of the species that is adsorbed at the surface) from measurements of tension as a function of the concentration of the surfactant in the solution (Hiemmenz, 1998).

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln C} \quad (1)$$

If Γ is expressed in mol/cm², the average area per molecule at the interface in Å²/molecule is:

$$A = \frac{1}{\Gamma} = \frac{RT}{d\gamma / d \ln C} = \frac{411.6}{d\gamma / d \ln C} \quad (2)$$

where R is the gas constant, T is temperature and $\frac{d\gamma}{d\ln C}$ is the slope of the linear region of each of the adsorption isotherms. This equation allows us deduce some information regarding the orientation and conformation of the molecules at the interface.

On the other hand, we can establish a relationship between the average area per molecule of a species and its molecular weight by using an expression including both parameters:

$$M = \rho N_A A \epsilon \quad (3)$$

where: M: molecular weight (g/mol), ρ : density (1 g/cm³), N_A : Avogadro's number (6.023*10²³ molecules/mol), A: area (Å²/molecule) and ϵ : thickness (about. 4Å) (Acevedo et al., 1994).

This expression was used to carry out the respective calculations. The results for apparent area and molecular weights for the species adsorbed at the interface are shown in Table 4. It can be seen that the calculated values are the same since they are within the error range, obviously because the slopes are practically the same. This suggests that the species that is in direct contact with both phases is the same kind of compound, which has a molecular weight of about 350 Dalton. This leads us to suppose that these compounds are the acids present in the crude oil which had a VPO molecular weight of 470 Dalton. These values of molecular weights are similar to those reported when using other techniques such as ESI FTICR MS and FTICR MS for acid compounds adsorbed at the interfacial film of oil in water emulsions (Stanford et al., 2007).

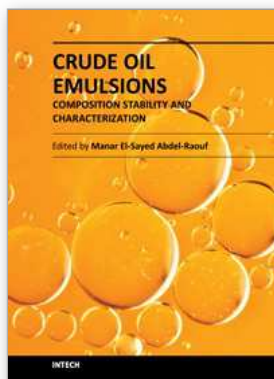
4. Conclusions

Acids present in the crude, which have molecular weights of about 400 Da, are present in higher concentrations in asphaltenes, and contribute significantly to the reduction of interfacial tension. In other words, asphaltenes act as molecular traps for acids. Also the results suggest the formation of a mixed interface composed of asphaltenes and carboxylic acids of low molecular weight. This film acts as a barrier separating the two phases and prevents coalescence process occurs. Furthermore, it was possible to confirm with simpler methods, that substances adsorbed at the water - crude oil interface have low molecular weights. This is using of Gibbs adsorption equation allows us calculate the adsorption Γ (the concentration of the species that is adsorbed at the surface) from measurements of tension as a function of the concentration of the surfactant in the solution. Once the parameter Γ is obtained, calculate the apparent area of the species adsorbed at the interface and its relationship with the molecular weight of said species.

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Crude Oil Emulsions- Composition Stability and Characterization

Edited by Prof. Manar El-Sayed Abdul-Raouf

ISBN 978-953-51-0220-5

Hard cover, 230 pages

Publisher InTech

Published online 02, March, 2012

Published in print edition March, 2012

Petroleum "black gold" is the most important nonrenewable source of energy. It is a complex mixture of different phases and components. Refining it provides a vast number of organic compounds, all of them of which are used to produce petroleum based products for numerous applications, from industry to medicine, from clothing to food industries. We can find petroleum based products all around us. This book deals with some important topics related to petroleum such as its chemical composition and stability. It is well-known that the chemical composition of crude oil differs according to the site of production, and its grade varies from waxy to asphaltenic crude. Both of them are refined to produce different products. The stability of crude oil on aging and transportation is governed by several factors and these factors are included within this book. Some new technologies for petroleum characterization are also introduced. This book is aimed at researchers, chemical engineers and people working within the petroleum industry.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

B. Borges (2012). Natural Surfactants from Venezuelan Extra Heavy Crude Oil - Study of Interfacial and Structural Properties, *Crude Oil Emulsions- Composition Stability and Characterization*, Prof. Manar El-Sayed Abdul-Raouf (Ed.), ISBN: 978-953-51-0220-5, InTech, Available from:

<http://www.intechopen.com/books/crude-oil-emulsions-composition-stability-and-characterization/natural-surfactants-from-venezuelan-extra-heavy-crude-oil-study-of-interfacial-and-structural-proper>

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