Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 70 (2015), No. 6, pp. 909-1132

ENHANCED OIL RECOVERY (EOR)

ASPHALTENES

HYDRATES

Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 70 (2015), No. 6, pp. 1035-1049
© L. Davarpanah et al., published by IFP Energies nouvelles, 2013
DOI: 10.2516/ogst/2012066

Structural Study of Asphaltenes from Iranian Heavy Crude Oil

L. Davarpanah, F. Vahabzadeh* and A. Dermanaki

Department of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), 424 Hafez Ave, Tehran - Iran
e-mail: leiladavarpanah@gmail.com - far@aut.ac.ir - alidermanaki@gmail.com

* Corresponding author

Résumé — Étude structurale d'asphaltènes de pétrole brut lourd iranien — Dans la présente étude, la précipitation d'asphaltènes du pétrole brut lourd iranien (au large du golfe Persique) a été effectuée au moyen de *n*-pentane (n-C_5) et de *n*-heptane (n-C_7) comme alcanes légers précipitants. Plusieurs techniques analytiques, chacune utilisant différents principes, ont ensuite été utilisées pour caractériser la structure des asphaltènes précipités. Le rendement en asphaltènes obtenu par l'utilisation du précipitant *n*-pentane était plus élevé que pour les asphaltènes précipités à l'aide du *n*-heptane. L'extraction des asphaltènes a affecté les fractions de maltènes n-C_5 et n-C_7 à des températures inférieures à 204 °C, comme l'indiquent les données obtenues par la technique de distillation simulée. La viscosité du pétrole lourd est influencée par la teneur et le comportement des asphaltènes. La dépendance de la viscosité du pétrole lourd testé avec le taux de cisaillement appliqué a été déterminée et l'écoulement était faible à γ. supérieur à 25 s^{-1}. Les échantillons de pétrole lourd reconstitués ont été préparés en ajoutant différentes quantités d'asphaltènes aux maltènes (pétrole lourd désasphalté) et les effets des asphaltènes ont été plus prononcés à la basse température de 25 °C, comparés à ceux obtenus à des températures plus élevées. Selon le modèle de loi de puissance utilisé dans cette étude, la fluidité du pétrole lourd testé a révélé un caractère pseudoplastique. Les résultats structuraux obtenus à partir de la spectroscopie InfraRouge à Transformée de Fourier (IRTF) ont montré la présence de différents groupes fonctionnels dans les asphaltènes précipités. Par exemple, la présence de différents hydrocarbures (aliphatique, aromatique et alicyclique), basée sur leurs caractéristiques dans le spectre IRTF, a été confirmée. Les résines sont des dispersants efficaces et le retrait de cette fraction du pétrole brut perturbe la nature colloïdale du pétrole lourd, la floculation et la précipitation des asphaltènes finissant par se produire. L'apparition de pores sur les images SEM *(Scanning Electron Microscopy)* a été utilisée comme indicateur du détachement de la résine. A l'aide de la spectroscopie de Résonance Magnétique Nucléaire (RMN) ^1H et ^{13}C, deux paramètres structuraux importants des asphaltènes ont été déterminés. A savoir, l'aromaticité (f_a) et le nombre moyen d'atomes de carbone par chaîne alkyle latérale ($n_{carbone}$), où f_a pour les asphaltènes n-C_5 était plus faible (0,39) que celui obtenu avec le solvant n-C_7 (0,49). En outre, les valeurs du paramètre $n_{carbone}$ étaient respectivement de 7,7 et 5,7 pour les asphaltènes n-C_5 et n-C_7. L'identification structurale des composés du pétrole représente un prérequis pour les différentes techniques utilisables pour la transformation du pétrole lourd.

Abstract* — *Structural Study of Asphaltenes from Iranian Heavy Crude Oil — *In the present study, asphaltene precipitation from Iranian heavy crude oil (Persian Gulf off-shore) was performed using* n*-pentane (*n-C_5*) and* n*-heptane (*n-C_7*) as light alkane precipitants. Several analytical techniques, each following different principles, were then used to structurally characterize the precipitated asphaltenes. The yield of asphaltene obtained using* n*-pentane precipitant was higher than asphaltene precipitated with the use of* n*-heptane. The asphaltene removal affected the* n-C_5 *and* n-C_7 *maltene fractions at temperatures below 204°C, as shown by the data obtained through the simulated distillation technique.*

Viscosity of heavy oil is influenced by the asphaltene content and behavior. The viscosity dependence of the test heavy oil on the shear rate applied was determined and the flow was low at γ. *above 25* s^{-1}. *The reconstituted heavy oil samples were prepared by adding different amounts of asphaltenes to the maltenes (deasphalted heavy oil) and asphaltene effects were more pronounced at the low temperature of 25°C as compared with those at the higher temperatures. According to the power law model used in this study the flowability of the test heavy oil exhibited a pseudoplastic character. Structural results obtained from Fourier Transform InfraRed (FTIR) spectroscopy showed the presence of the different functional groups in the precipitated asphaltenes. For instance, the presence of different hydrocarbons (aliphatic, aromatic and alicyclic) based on their characteristics in the FTIR spectra was confirmed. Resins are effective dispersants, and removal of this fraction from the crude oil is disturbing to the colloidal nature of heavy oil; asphaltene flocculation and precipitation eventually occur. Appearance of pores in the Scanning Electron Microscopy (SEM) images was used as an indicator of the resin detachment. With the use of* ^{1}H *and* ^{13}C *Nuclear Magnetic Resonance (NMR) spectroscopy, two important structural parameters of the asphaltenes were determined. Namely, the aromaticity* (f_a) *and the average number of carbon atoms per alkyl side chain* (n_{carbon}), *where* f_a *for* n-C_5 *asphaltenes was lower (0.39) than that obtained with* n-C_7 *solvent (0.49). Additionally, the* n_{carbon} *parameter values were 7.7 and 5.7 for* n-C_5 *and* n-C_7 *asphaltenes, respectively. Structural recognition of the oil constituents is the prerequisite of different techniques usable for heavy oil upgrading.*

INTRODUCTION

With the depletion of conventional crude oil resources, increased attention has been paid to the exploration of abundant heavy oil reserves. A major problem in this matter, however, is the high viscosity of the heavy crude oils, and asphaltenes play a central role in this issue (increased viscosity of the heavy oils is associated with an increased asphaltene content) [1, 2]. Asphaltenes as the multi-component petroleum fraction are soluble in aromatic solvents and insoluble in low-boiling-point *n*-alkane solvents, such as *n*-pentane and *n*-heptane [3, 4]. According to the solubility results obtained through asphaltene precipitation with the use of mixtures of heptane and toluene solvents (heptol), a lower toluene volume fraction was needed for precipitation of asphaltenes in the presence of resins (1:1 asphaltenes to resins mass ratio) than in the absence of resins. Apparently, asphaltenes in the mixture of solvents possessing less aromaticity form larger aggregates because of the lower compatibility of solvent-solutes (asphaltenes and resins) as compared with the interactions between aromatic solvents and the solutes [5]. By increasing the aliphatic nature of solvent mixtures the π bond and polarity character of the solvent decrease and this affects the asphaltene aggregation positively, while by increasing the aromaticity of the solvent mixture, the aggregation size of asphaltenes decreases [5]. The tendency of the colloidal particles to aggregate or separate, as a character of colloidal solution stability/instability, is determined by the overall interactions between these particles, and different types of attractive and repulsive interactions are actually involved in stabilization mechanisms in colloidal dispersions [6, 7]. Van der Waals, steric, depletion, hydrophobic and hydration interactions may all play a role in describing the colloidal solution behavior [6]. In the case of aromatic solvents the hydrophobic interactions between the aromatic core of the asphaltene and the solvent increase compatibility between them, which ultimately facilitate asphaltene aggregation. The role(s) of these colloidal interactions in increased/decreased aggregation of asphaltenes should be quantified and these would definitely be more informative in handling asphaltene studies than just using high-technology equipment. Asphaltenes and resins are both polydisperse and constitute the crude oil's colloidal nature [8]. The following section, theory, summarizes some high-technology techniques regarding asphaltene structural characterization.

Oil production in the Persian Gulf began in the 1950s, and, to administer the oil and gas fields, the Iranian Offshore Oil Company (IOOC) has re-organized its activities since 1979. The focal points at the present time are on four areas especially; Bahregan, Khark, Sirri and Lavan [9]. One of the goals of the IOOC during the last few years was to acquire more knowledge of the characterization of the heavy crude oil components by providing a friendly environment for conducting research, especially at the national level. Figure 1 shows the details of geographical location.

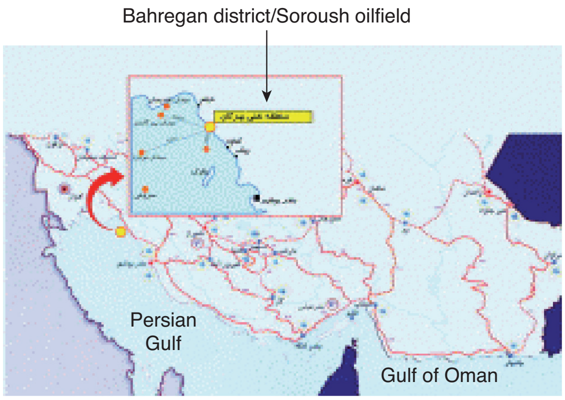

Figure 1

Geographical location of the heavy crude oil sample used in the present study provided by the IOOC as the authority for exploring crude oil resources in the area shown.

As has been mentioned above, recognition of the significant contributions of asphaltenes and resins to the colloidal nature of heavy oils helps in developing and exploring applications of emulsification technology in treating heavy oil in different sectors of the petroleum industry. Resins in crude oil consist mainly of naphthenic aromatic hydrocarbons with alicyclic chains and resins as interfacially active components are effective as dispersants of asphaltenes [10]. The subject of emulsification has also generated research interest in the Iranian petroleum industry and structural characterization of asphaltenes from Soroush oilfield (Bahregan district) is targeted at the present time, so formation of the oil-in-water (O/W) and water-in-oil (W/O) types of emulsions could be studied in some depth. The structurally complex nature of heavy oil components exhibits different rheological behaviors and the viscosity of these oils varies from a few thousand to millions of centipoises at the reservoir temperature, while 400 cP is considered to be the desirable viscosity for pipeline transportation of heavy oil-in-water emulsions [1, 11].

With all this in mind, the objectives of the present work were defined: structural characterization of asphaltenes of the Soroush heavy oil sample and along with this the flow behavior of the crude oil sample was studied and the asphaltene content dependency of viscosity in terms of reconstituted heavy oil was evaluated. The oil sample was provided by the IOOC, and Nuclear Magnetic Resonance (NMR), Scanning Electron Microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy were used in this structural characterization study.

1 THEORY

Developing high-technology techniques is a continuous effort by which the strength of uncontrollable factors or noises in a particular experiment decreases, thus giving good knowledge to researchers for obtaining responses with acceptable variation when the experiment is faced with maximum noise. This is accomplished by improving the signal-to-noise ratio. In conducting experiments to thoroughly study the complex colloidal behavior of asphaltenes, several factors play a role: use of high-technology equipment in well-developed facilities with researchers skilled in solving specific problems with the assistance/cooperation of universities and other research centers. The principles of some high-technology techniques used in asphaltene studies are briefly described below.

Although X-Ray Diffraction (XRD) is used primarily to examine the crystalline structure of materials, and to determine bond lengths and angles, expansion coefficients, and atomic and molecular weights, XRD is also used to investigate the existence of short-range order atoms in noncrystalline systems such as liquids and gases [12]. On the other hand, hydrogen atoms with their small number of electrons are very weak in scattering X-rays and electrons and there are thus some difficulties in locating hydrogen atoms in X-ray studies [13]. Protons, on the other hand, scatter neutrons very efficiently and neutron diffraction studies can preferably be used to locate the hydrogen atoms and the related short-range order of these atoms in liquids. Structural information from a fraction of a nanometer to the micrometer level can be obtained with the use of the Small-Angle Neutron Scattering technique (SANS) (physical chemistry). A SANS study on the asphaltene fractions obtained from B6 oil (19.8°API) using mixtures of deuterated heptane-toluene solvents showed that polar and π bonding interactions were involved in the less soluble fraction of the asphaltenes and chemical species in this fraction significantly contributed to the asphaltene aggregation [13, 14]. Results obtained from SANS curves (neutron intensity *versus* scattering vector) of B6 whole asphaltene in mixtures of *d*-heptol were indicative of correlation length, which increased with decreasing toluene content within the soluble regime, and the authors suggested that interaggregate associations between asphaltenes increased as the solvating power of *d*-heptol decreased [13].

Vapor Pressure Osmometry (VPO), which is used for determination of molar mass of polymers (asphaltenes as the test solute) operates on the basis of the Membrane Osmometry (MO) principle. In this technique two chambers, each with some specifications, are separated by a semi-permeable membrane tightly held between the chambers. One chamber, which is closed to the atmosphere, contains a reservoir of the solvent (saturated solvent atmosphere) and the other chamber is left open to the atmosphere and contains the test solution. As the chemical potential of the solvent is higher than that of the test solution, there is a tendency for the solvent to flow to the chamber containing the test solution through the membrane (diffusion pressure of the solvent molecules from the pure solvent reservoir through the membrane is greater than the diffusion pressure of the solvent molecules from the test solution through the membrane). The pressure of the solvent decreases and the solvent vapor pressure of the test solution changes, and upon the condensation of solvent into the test solution from the saturated solvent atmosphere heat is released so the thermistor, placed in the chamber, will be warmed (the thermistor measures voltage changes by change in temperature). The chemical potential across the membrane can be determined accordingly [14]. As pointed out in the literature, use of a single solvent in the VPO technique limits the application of this method in studying whole asphaltenes, the soluble and the least soluble fractions. For instance, in an asphaltene precipitation study on B6 crude oil using a mixture of heptane-toluene, about 30-40% of the whole asphaltenes, by mass, were the least soluble fractions (precipitated fractions), having apparent molar masses of 12 000-17 000 g/mol [14]. The molar mass of this fraction was considerably higher than that of the "whole" and "soluble" asphaltenes (2 500-3 500 g/mol) and the polar and hydrogen bonding interactions among the least soluble fraction of asphaltenes (precipitate) were assumed to play a significant role in the absence of the soluble fraction with the solvating character [14].

Vibrational Spectroscopy (VS) is the result of molecular motion because of electromagnetic radiation absorption and its interactions with the dipole moment character of the molecule. For molecules whose permanent dipole moments are zero or the dipole moment is inactive and does not change during molecular vibration, then other molecule properties such as polarizability instead of the dipole moment character are used for the VS. Raman Spectroscopy (RS) requires a fluctuating polarizability of the molecule rather than a fluctuating dipole moment [15]. In the study on asphaltenes precipitated from the Algerian Hassi-Messaoud oilfield (API = 43), a combination of XRD and Raman Spectroscopy was used to characterize the poly-condensed aromatic core which was attached to the hydrocarbon side chains. Aggregation, flocculation and precipitation of asphaltenes are under the influence of the core and heteroatoms such as oxygen, nitrogen, sulfur and metals. According to the results of that study, eight asphaltene molecules were estimated to be present in each asphaltene aggregate [16].

Solid-state NMR spectra present very broad transitions in contrast to the solution NMR spectra, which show sharp peaks. The effects of anisotropic NMR interactions are averaged in the solution NMR, while the full effects of the anisotropic interactions are observed in the solid-state NMR. Magic-angle spinning, cross-polarization and special two-dimensional experiments are among the techniques used to suppress anisotropic NMR interactions, thus providing high-resolution spectra for the solid-state NMR. A high signal-to-noise ratio improves the technique and in addition to this, Pulsed Field Gradient Spin Echo Nuclear Magnetic Resonance (PFG-SE NMR) has been used for asphaltene studies. Results obtained from Venezuelan asphaltenes using PFG-SE NMR showed the diffusion coefficient of the asphaltenes in deuterated toluene was in the order of 1×10^{-10} m^2/s, which decreased with increasing asphaltene concentration, indicating an increase in the aggregate size [14]. Intermolecular π and hydrogen bonds are involved in asphaltene aggregate formation and resins with the capacity to disrupt the electron exchange between the donor and acceptor molecules reduce the tendency for asphaltenes to aggregate [5]. In fact, determination of the diffusion coefficient for protein as the self-associated molecules (protein's folded structure) has long been practiced [17]. However, self-association of the asphaltenes or asphaltene aggregates is under the influence of various operational factors when a precipitation protocol is followed [18].

2 MATERIALS AND METHODS

2.1 Materials

A heavy crude oil sample was supplied from the Research and Development Center of the IOOC. The crude oil was taken from Soroush oilfield and separation was performed in two steps at the specified pressure and temperature. The crude oil was then forwarded to a desalter followed by dehydrator units: at this stage nearly all water present in the system was removed. The specifications of the Soroush heavy oil used in this study are given in Table 1a. The solvents used for the asphaltene extractions were light alkanes, namely *n*-pentane and *n*-heptane. The reagents were all analytical grade *(Merck)* and were purchased from the local market.

TABLE 1

a) Crude oil properties (Soroush oilfield)

Specification	
Gravity (°API)	19
Molar density (kgmol/m^3)	2.54
Surface tension (mN/m)	27.3
Reid vapor pressure (MPa)	0.0426
Sulfur content (wt%)	3.5-4.5
Refractive index	1.49
Flash point (°C)	74.3

b) SARA analysis

Precipitant	Content (wt%)			
	Saturates	Aromatics	Resins	Asphaltenes
n-pentane	32.8	38	7.7	21.5
n-heptane	35.7	36.6	12.2	15.5

2.2 SARA Analysis

According to the experimental details given in the standard ASTM D2007-03 method [19], the main constituents of the crude oil sample, namely, Saturates, Aromatics, Resins and Asphaltenes (SARA), were determined. SARA analysis was accomplished using the clay and silica gel adsorption chromatographic method, where differences in the adsorbents' behavior in response to each of the four fractions were used in the separation process. The eluent solvents used were n-C_5 and n-C_7.

SARA analysis was repeated twice and the data were accurate ± 2.5%.

2.3 Precipitation of Asphaltene

Asphaltene extraction was performed following the details given in the standard ASTM D2007-03 method [19]. Briefly, one volume of the crude oil was agitated with 40 volumes of the *n*-alkane solvent (either *n*-pentane or *n*-heptane) using a magnetic stirrer for 12 h. With the use of a laboratory heater a moderate temperature (about 30-40°C) was applied to warm the mixture with intermittent swirling to hasten the dissolution. The mixture was then filtered using 2.5-μm Whatman filter paper, and the resulting filter cake, composed mainly of the asphaltenes, was washed thoroughly with the solvent until the solvent wash was colorless. The precipitated asphaltenes were dried at about 100°C using a magnetic stirrer until a constant weight was obtained. With the use of a rotary evaporator (*Buchi* Rotovapor R-205) the solvent was evaporated and the remainder as the deasphalted heavy oil (maltenes) was used for further analysis.

Asphaltene precipitation experiments were repeated twice and the data were accurate ± 2.5%.

2.4 Simulated Distillation Method

Simulated distillation by gas chromatography has long been used by the petroleum industry for obtaining the boiling point distribution of petroleum products [20-22]. The gas chromatograph designed by the manufacturer is equipped with a Programmable Temperature Vaporizer (PTV) and with the use of the PTV, the hydrocarbon components of the sample are eluted in order of increasing boiling point. Boiling points are assigned to the time axis using a calibration curve which is constructed by analyzing a mixture of hydrocarbons treated under the same chromatographic conditions and according to the specifications given in the relevant ASTM test method; no cracking of the sample components will occur (Agilent Technologies Simulated Distillation – SIMDIS analyzer, *Agilent Technologies*, USA). In the present study with the use of this method the simulated distillation curves (*i.e.*, the boiling point *versus* retention time) were obtained for the samples of the crude oil and maltenes and the carbon number distributions of the test hydrocarbons were grouped according to the relevant distillation temperature.

The simulated distillation analysis was carried out in the Research Institute of the Petroleum Industry (RIPI) laboratory. The test samples (the heavy crude oil and the maltenes) were diluted with carbon disulfide (CS_2) (0.2 g per 10 mL CS_2) as received by that laboratory.

The following sections briefly describe the different analytical techniques that were used to structurally characterize the asphaltenes obtained.

2.5 FTIR Spectroscopy

FTIR spectra were recorded on a *Bruker* IFS 88 spectrometer in transmittance mode over the wavenumber region of 400-4 000 cm^{-1}. The KBr pellet technique was used in this analysis.

2.6 NMR Spectroscopy

The history of ^1H and ^{13}C NMR spectroscopy shows that application of these techniques for compositional characterization of petroleum fractions was a breakthrough and was considered a novel development in this area [23-25]. According to the specifications given in the literature, there are two problems in obtaining quantitatively reliable data using ^{13}C NMR spectroscopy to study asphaltenes: differences in relaxation times for different molecules present in asphaltenes and the extensive variations in the Nuclear Overhauser Enhancement (NOE) parameter [24]. The solutions to these problems have been developed on the basis of instrumental advancement in NMR spectroscopy (*i.e.*, suppressing NOE effects and use of alternative relaxation mechanisms).

Liquid-state ^1H and ^{13}C NMR were conducted in the present work, and some structural estimations were obtained, using an Avance DRX-500 *Bruker* spectrometer operating at a ^1H resonance frequency of 500 MHz and a ^{13}C resonance frequency of 125 MHz, with deuteriochloroform ($CDCl_3$) as the solvent. It was necessary to accumulate the ^{13}C spectra overnight to obtain an acceptable signal-to-noise ratio. A total of 10 240 scans were obtained in the present work for n-C_5 and n-C_7 asphaltenes using a pulse flip angle of 90°. To ensure the complete relaxation of slowly relaxing carbons a delay time of 4 s between scans was used. According to the literature the relaxation time of petroleum asphaltene is less than 1 s, even in the absence of any relaxation agent [24]. In the present study no relaxation agent was used and to eliminate the NOE effect an inversely-gated ^1H decoupling technique was applied. Considering this relaxation time and using the inversely-gated ^1H decoupling technique and according to the ^{13}C NMR a signal of high quality was obtained, and according to the literature this approach provides quantitative results [26]. All samples were approximately 50-80 mg diluted with 0.4-0.5 mL of deuteriochloroform in 5-mm sample tubes.

According to the definition given in the literature for the chemical shift parameter as a quantitative measurement used in NMR spectrometry, the integration can be performed using the specified regions in ^1H and ^{13}C NMR spectra. For instance and according to the literature, there are different integration domains for ^1H NMR spectra [27]. In the present study, the three integration domains were used for quantification of ^1H NMR spectra, while ^{13}C NMR spectra were studied using two different regions for integration. The details of these divisions, along with typical spectra for ^1H and ^{13}C of the asphaltenes, are given in the results and discussion section. Several studies have shown the relevance of NMR for assaying the aromaticity and n_{carbon} of asphaltene fractions of crude oil.

2.7 SEM Images

Samples of n-C_5 and n-C_7 asphaltenes were coated with a thin layer of gold under vacuum and examined by Scanning Electron Microscopy (*Philips* XL-30).

2.8 Rheological Measurements

Rheological measurements of the crude oil sample were carried out using a *Paar Physica* controlled-stress rotational rheometer (model MCR 301, *Paar Physica*, Stuttgart, Baden-Wuttenberg, Germany) in an oscillatory mode. A 25-mm diameter stainless steel parallel plate assembly with a gap of 0.5 mm was used in the time-oscillation mode. The rheological data were fitted to appropriate rheological models using the MATLAB software.

Viscosity measurements were repeated twice and the data were accurate ± 2.5%.

3 RESULTS AND DISCUSSION

3.1 Flow Behavior of the Crude Oil

The viscosity determination is the focal point in predicting the flow behavior and in providing an estimation of the energy requirements for the processes involved in the fluid treatments. These are the main considerations in any process improvement(s). Figure 2a shows the viscosity dependence of the test heavy oil on the shear rate applied; the resistance of the test heavy oil to flow was low at the shear rates above 25 s^{-1}. Temperature affects the fluid viscosity strongly and in the present study, the flowability character of the test heavy oil at 45°C and 60°C reached a plateau at a shear rate of about 10 s^{-1}. The aggregation tendency of complex molecules such as asphaltenes, resins and the other high-molecular-weight components of the heavy oil, decreases with increasing temperature, and the result of less agglomerated species of the heavy oil constituents, at high temperatures, is the reduction of the viscosity. By finding the resistance to flow character of the fluid (shear stress "τ") as the function of the velocity gradient that exists between adjacent fluid molecules (shear rate "$\gamma\cdot$") one can describe the fluid behavior. According to the results presented in Table 2, the flowability of the test heavy oil exhibited a pseudoplastic character ($n < 1$) and the experimental data was fitted well to the power law model describing non-Newtonian fluids *(Fig. 2b, Tab. 2)*:

$$\tau = k\,\gamma^{\cdot n} \tag{1}$$

where n and k are the flow behavior index (dimensionless) and the consistency index (Pa s^n), respectively. The logarithm of Equation (1) is as follows:

$$\log\tau = \log k + n\log\gamma\cdot$$

With use of a log-log plot of τ against $\gamma\cdot$, the values of k and n can be determined (shear stress *versus* shear rate is shown for the experiment at 25°C – *Fig. 2b*). The results in Table 2 also show that with increasing temperature from 25°C to 60°C, the flow behavior index increased and the

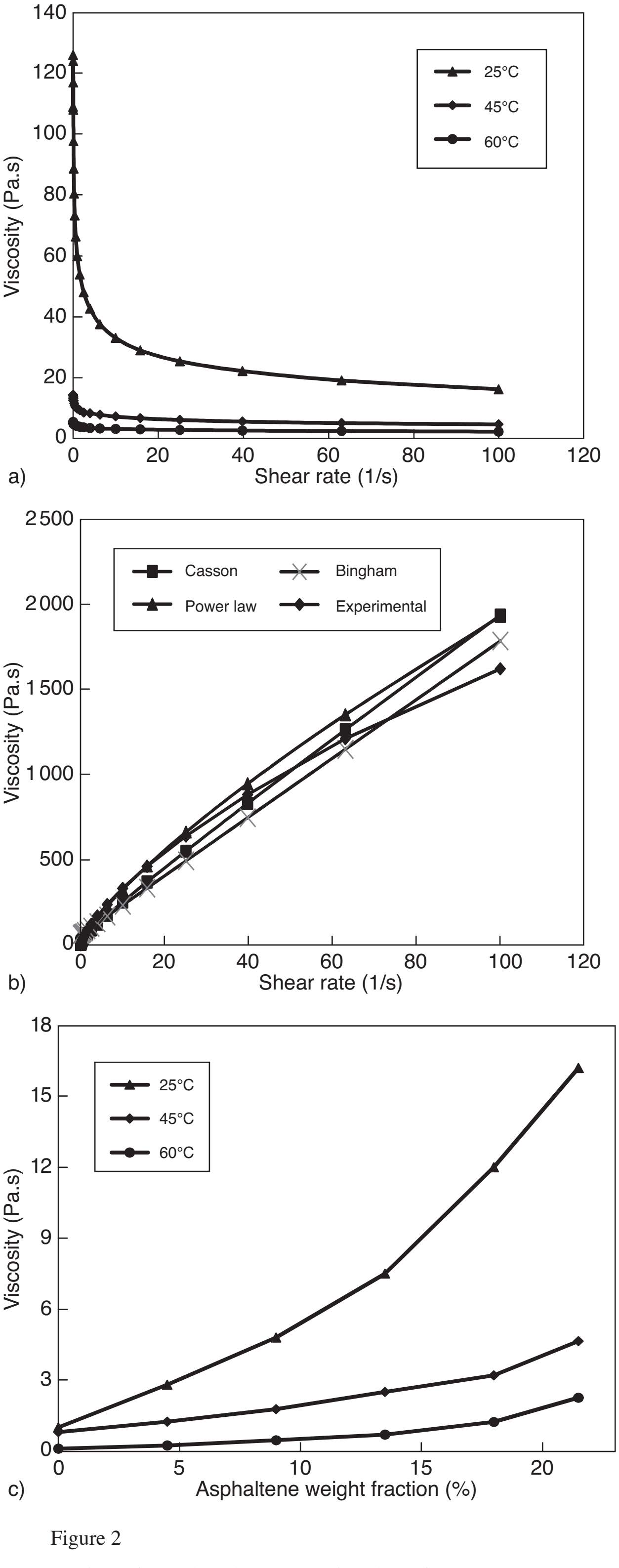

Figure 2

a) Plots of the viscosities as the function of the shear rate at three test temperatures; b) relationship between shear stress and shear rate for the heavy crude oil sample according to the suggested rheological models; c) and a plot of the viscosity for five reconstituted heavy crude oil samples with five different asphaltenes contents.

TABLE 2

Use of rheological models and the corresponded model parameters in describing flow behavior of crude oil sample

	Temperature											
	25°C				45°C				60°C			
Model	τ_0 (Pa)	k (Pa s^n)	n	R^2	τ_0 (Pa)	k (Pa s^n)	n	R^2	τ_0 (Pa)	k (Pa s^n)	n	R^2
Casson	8.13	4.11	—-	0.98	0.57	2.2	—-	0.99	0.15	1.53	—-	0.99
Power law	—-	54.65	0.77	0.99	—-	9.26	0.88	0.99	—-	3.86	0.9	0.99
Bingham	61	17.23	—-	0.97	8.66	4.81	—-	0.99	3.13	2.33	—-	0.99

approach of the rheology of the test sample was more Newtonian. The characterization of the rheological behavior of the test sample fluid was also performed using two other models; namely, Bingham *(Eq. 2)* and Casson *(Eq. 3)*, which have been previously applied for predicting heavy crude oil flowability [28]:

$$\tau = \tau_0 + k\gamma^{\cdot} \tag{2}$$

$$\tau = (\tau_0^{0.5} + k\gamma^{\cdot 0.5})^2 \tag{3}$$

where τ_0 is yield stress. The experimental data were fitted using each of these two models and Table 2 shows the model parameters n, k and τ_0. The models gave excellent fit to the data ($R^2 > 0.97$). The amount of asphaltenes clearly affects the viscosity of heavy oil and in the present study further experiments were directed towards reconstituted heavy oil samples, which were prepared by adding the different amounts of the precipitated asphaltenes to the maltene (deasphalted heavy oil). Figure 2c shows the measured viscosity of the reconstituted heavy oil sample *versus* its asphaltene weight fraction at three test temperatures. Viscosity is influenced by the aphaltene content and Figure 2c shows this effect was more pronounced at the low temperatures; for instance, increasing the asphaltene weight fraction from 10% to 20% resulted in a noticeable increase in the viscosity value as compared with between these values at 45°C and 60°C *(Fig. 2c)*.

3.2 Use of *n*-Alkane Solvents (*n*-Pentane and *n*-Heptane) for Asphaltene Precipitation

First, through the use of the most generally accepted approach, the crude oil sample was separated into groups, or solubility classes, of aliphatic hydrocarbons, aromatic hydrocarbons, resins and asphaltene compounds with the SARA technique. The results of this separation are given in Table 1b and a relatively simple description of the technique is presented in Figure 3. The saturates consisted of naphthenes and paraffins, while the aromatics, resins and asphaltenes formed a continuum of polynuclear aromatic units of increasing molar mass, polarity and heteroatom content [18]. Figure 4 shows the asphaltene yield as a function of the *n*-alkane solvent-to-crude oil volume ratio. The yield increased as more solvent was added to the oil sample but this trend reached a plateau at precipitant to oil volume ratios above 20. The higher capacity of *n*-pentane for the precipitation of asphaltenes compared with the yield obtained with *n*-heptane is a common finding reported in the literature [26]. Apparently, the use of higher carbon-number alkane solvents results in lower asphaltene yields and increased levels of resinous materials [26, 32]. Similar behavior is observed for oils from different sources that have different API gravities using n-C$_5$ and n-C$_7$ for asphaltene precipitation [33], and the results of the present work showed the same behavior: 21.5% *versus* 15.5% for n-C$_5$ and n-C$_7$ asphaltenes, respectively *(Fig. 4)*. This dependency of asphaltene yield on the type and amount of solvent used for precipitation shows that differences exist between asphaltene molecules, and it appears that some components of this crude oil fraction are soluble in one but not in the other solvent.

TABLE 3

Carbon number distributions of the original crude oil sample used in the present work along with the maltenes obtained through the simulated distillation method.

Carbon no.	Amount distilled (wt%)		
	Crude oil sample	n-C$_5$ maltene	n-C$_7$ maltene
$C_1 - C_{10}$	9.25	3.5	2.75
$C_{11} - C_{20}$	21.75	21	21.25
$C_{21} - C_{30}$	20.5	24.25	22.75
$C_{31} - C_{40}$	14.25	18	16.25
$C_{41} - C_{50}$	10.25	11.75	11.25
C_{50}+	23	20.5	24.75

Besides the importance of the solvent in obtaining consistent asphaltene fractions, attempts were made to standardize the separation method in terms of solvent-to-crude oil ratio, time of contact and temperature. Upon filtration of the solvent-oil mixture, the washing of the precipitated asphaltenes was also found to considerably affect the yield and properties of the asphaltene fraction [18]. Some maltene components, such as resins, were found trapped within the structure of the precipitated asphaltenes but increased washing of the filter cake with solvent aided in removing these types of impurities [18].

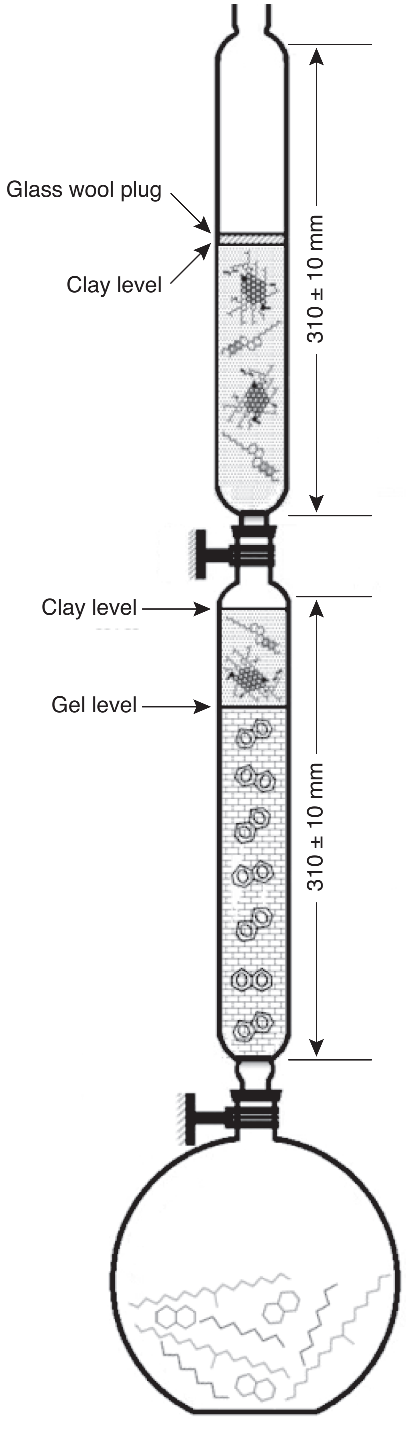

Figure 3

The clay (░) – silica gel (▦) – absorption chromatographic method used for the separation of crude oil constituents (the standard ASTM D2007-03 method). The symbols used are representatives of the molecular structures of different hydrocarbon types present in crude oil: asphaltenes (▩), resins (⌬⌬⌬〰), aromatics (⌬⌬), and saturates (〰) [19, 29-31].

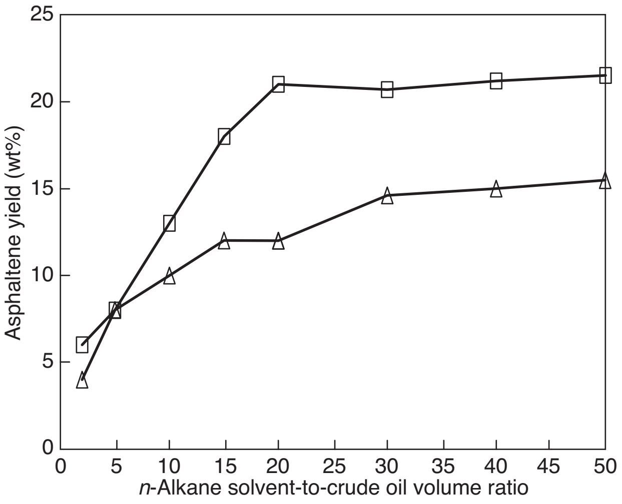

Figure 4

Asphaltene yield as a function of test solvent used for the precipitation. The symbols (□) and (Δ) are used for *n*-pentane and *n*-heptane solvents, respectively.

The washing was continued until the wash solvent was colorless, which could be used as an indication of obtaining asphaltenes that are less soluble in toluene. In other words, removing the resinous materials increased the probability of encountering the self-association behavior of the asphaltenes [18].

3.3 Simulated Distillation Analysis

Simulated distillation is a method that is routinely used for petroleum fractionation. Its operation is based on the relationship that exists between the distillation temperatures used in the process and the amount of distillates obtained, which is proportional to the distribution of the carbon numbers of the distillates [22]. The specifications just described are presented in Table 4. Figure 5 shows the simulated distillation curves, and it clearly shows that the weight percentages of n-C$_5$ and n-C$_7$ maltene fractions at temperatures below 204°C were very similar (6.25 and 6 wt%). These amounts were considerably lower compared with those obtained from the oil sample (12.5 wt%). Figure 4 also shows that the amount of distillates from the n-C$_5$ maltene fraction at temperatures above 649°C was lower compared with the other two (6.25 *versus* 10.5 wt% for the n-C$_7$ maltene and 10 wt% for the heavy crude oil), and the n-C$_7$ maltene fraction was heavier at these test temperatures.

Upon precipitation of the asphaltenes, different analytical techniques were used to characterize its structure, as described below.

TABLE 4

Infrared absorption frequencies assigned to a typical FTIR spectrum [27, 30, 31, 34][a]

Bond	Frequency range (cm^{-1})	Attributed to
C – H	3 000-2 850 1 450 and 1 375 1 465 2 900-2 700	Alkanes (stretch) – CH_3 (bend) – CH_2 (bend) Aldehyde
= C – H	3 100-3 000 1 700-1 000 3 150-3 050 1 000-700	Alkenes (stretch) Alkenes (bend) Aromatics (stretch) (out-of-plane bend)
C = C	1 680-1 600 1 600-1 400	Alkenes Aromatics
C = O	1 740-1 720 1 725-1 700 1 750-1 730 1 700-1 640	Aldehyde Carboxylic acid Ester Amide
C – O O – H	1 300-1 000 3 650-3 200 3 300-2 500	Alcohols, esters, carboxylic acids Alcohols, phenols Carboxylic acids

[a] The characteristics that were most often seen in the asphaltene spectrum are presented.

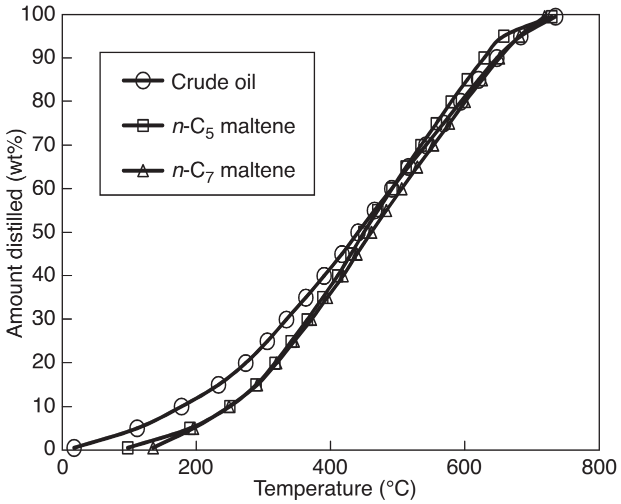

Figure 5

Quantification of the maltenes that were distilled using the simulated distillation method when *n*-pentane (□) and *n*-heptane (Δ) were used for the asphaltene precipitation. The (○) symbol is used for the crude oil sample.

3.4 NMR Analysis

Among the compositional characterization techniques used for petroleum fractions, ^{13}C and ^1H NMR spectroscopy have gained popularity [23]. By determining the number, type and relative positions of hydrogen and carbon atoms through ^1H and ^{13}C NMR spectra, several parameters are calculable, which provide information to predict the structure of the average molecule in a given fraction, such as asphaltene [23, 34]. The various types of protons that are present in the asphaltene fraction express different intensities. Through the use of integration measured over three distinct regions in the ^1H NMR spectrum, the average number of carbon atoms per alkyl substituent, or the n_{carbon} parameter, was determined. This parameter is defined as $n_{carbon} = [H_\alpha + (H_\beta + H_\gamma)]/H_\alpha$, where the α-hydrogen band refers to the α-hydrogen-to-aromatic ring (2-5 ppm region), the β + γ.-hydrogen band refers to the β + γ.–hydrogen-to-aromatic ring (– 0.5-2 ppm region), and the aromatic hydrogen band refers to the aromatic hydrogens (5-10 ppm region) [26]. Figure 6 shows the ^1H NMR spectra of the *n*-C_5 and *n*-C_7 asphaltenes obtained in this work, while the '*n*' parameter reported here was 7.7 and 5.7 for asphaltenes precipitated with *n*-C_5 and *n*-C_7, respectively *(Fig. 7)*. These "*n*" values are in agreement with those reported elsewhere for the Maya in a heavy crude oil sample (20.9°API) [25]. During asphaltene extraction, it was discovered that the level of associated impurities (*i.e.*, oils and resins) could affect the values of the '*n*' parameter. This was explained in terms of the impurities that remained with the unfractionated asphaltenes, *i.e.*, a lower '*n*' value correlated to fractionated asphaltenes [25]. Furthermore, the aromaticity parameter, f_a, which is the ratio between the number of aromatic carbons and the total number of carbons, aliphatic carbons (C_{al}) + aromatic carbons (C_{ar}), present in an average molecule of asphaltene ($f_a = C_{ar}/(C_{ar} + C_{al})$), can be calculated from the ^{13}C NMR spectrum [24]. According to the two different integration domains present in that spectrum, the aromatic band (100-170 ppm region) and the aliphatic band (– 10 to 70 ppm region), the aromaticity factor was calculated [26]. The above detailed information is presented in Figure 8 as an example of the ^{13}C NMR spectra we obtained. The f_a values are shown in Figure 7, where the aromaticity parameter was found to be lower for the *n*-C_5 asphaltenes than that of the *n*-C_7 asphaltenes (0.39 *versus* 0.49). The stability of crude oils, in terms of the structural characterization of asphaltenes, has previously been studied, and the researchers concluded that higher values of f_a indicate a higher degree of aromatic condensation and higher levels of hydrogen deficiency in the asphaltene structure [35]. In a separate study, higher values of f_a for *n*-C_7 asphaltenes corresponded to a higher extraction capacity of aromatics from a crude oil sample using *n*-heptane through the sample's asphaltene fraction, and similar findings are reported in the present work [26]. The f_a values may not be a good structural parameter to differentiate the structures of asphaltenes, however, because a study by Trejo *et al.* [25] showed that higher numbers of aromatic carbons were found in the asphaltene fraction that had a lower f_a value.

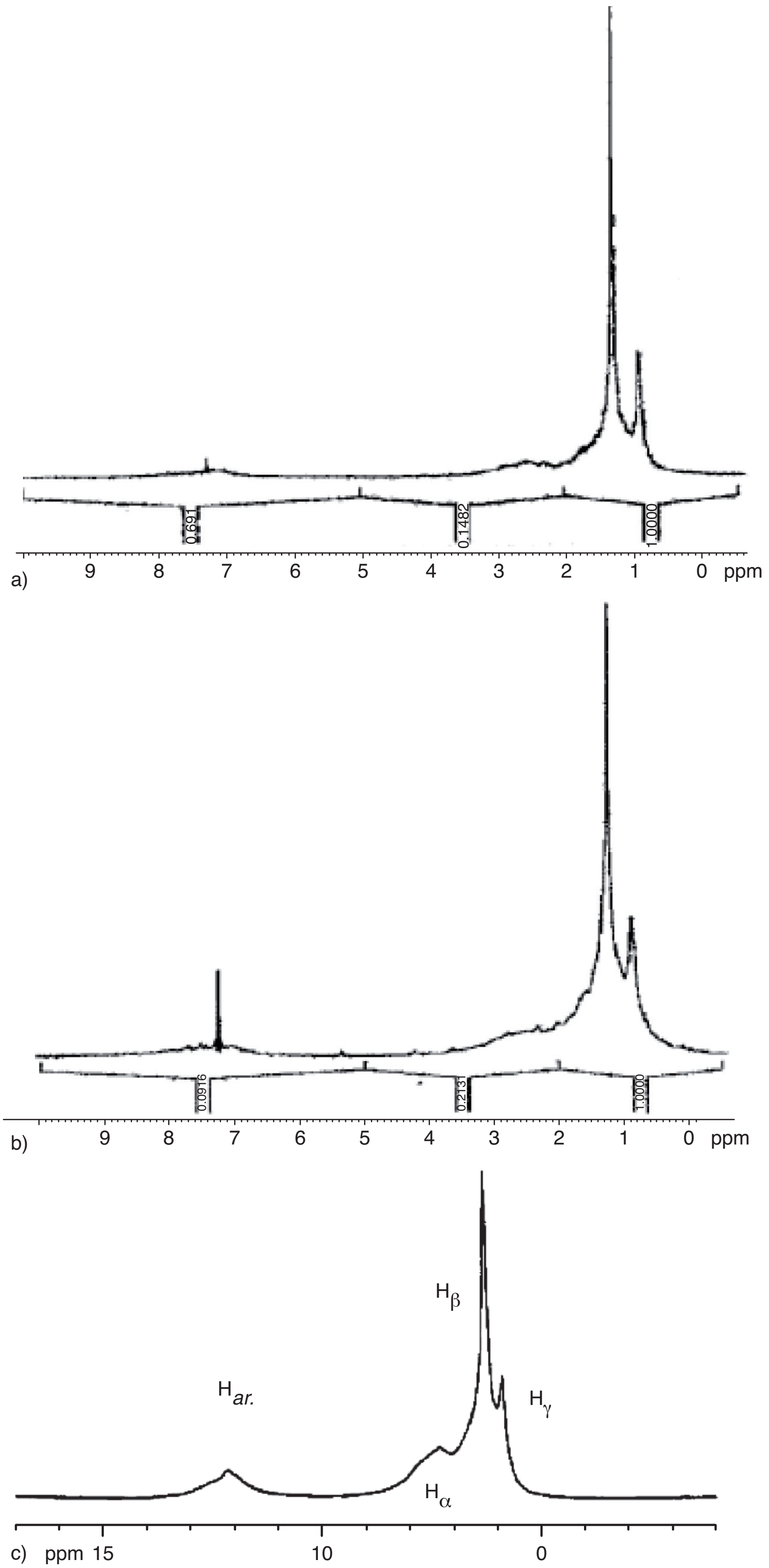

Figure 6

^{1}H NMR spectra of a) C5-asphaltene; b) C7-asphaltene. c) Typical ^{1}H spectrum of asphaltene is also given [27].

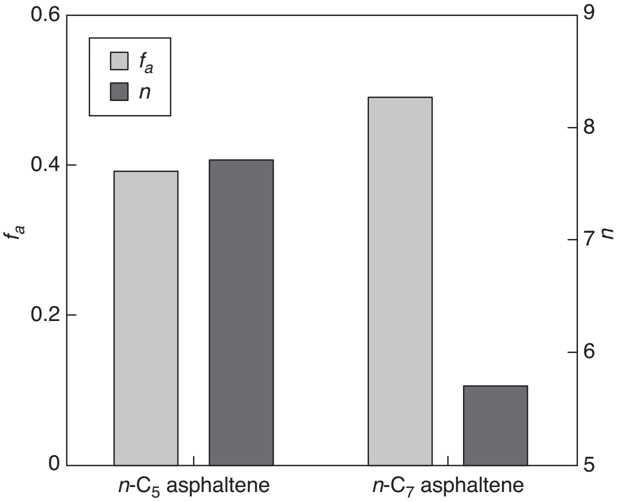

Figure 7

Structural parameters of the precipitated asphaltenes that were calculable from the ^{13}C and ^{1}H NMR spectra.

3.5 FTIR Analysis

Mixtures of decalin, tetralin and naphthalene chemicals have been used in the literature as representative of typical heavy oil constituents to study the correlation between FTIR spectra and molecular structural parameters; obtaining information in this regard is important in molecular changes which may occur in heavy oils under mild thermal processing [31]. No attempts were made in this regard in the present study and the FTIR spectra results of *n*-pentane and *n*-heptane precipitated asphaltenes given in Figure 9 both show similar absorption bands (*i.e.*, the intensities of the absorbance bands do not vary considerably). Stretching and bending are two types of vibrational motions in a molecule upon absorption of IR frequencies of electromagnetic radiation. As seen in Figure 9, a peak to the left of 3 000 cm^{-1} (*i.e.*, 3 421 and 3 398 cm^{-1} for heptane-, and pentane- precipitated asphaltenes, respectively) was related to the $=C-H$ stretching of the aromatic rings. The peaks at frequencies of 3 400-3 200 cm^{-1} represented the stretching of the carboxylic $-OH$ and $N-H$ groups, while peaks at frequencies of 1 640-1 550 cm^{-1} corresponded to $N-H$ bending in amide groups [27, 34, 36]. Also, absorption peaks at 2 920 and 2 865 cm^{-1} corresponded to methyl and methylene groups (*i.e.*, the stretching in aliphatic groups) [27, 37, 38]. Methylene and methyl groups have characteristic absorptions of approximately 1 450 and 1 375 cm^{-1}, respectively *(Fig. 9)*. The presence of some weakly resolved peaks to the right of 1 000 cm^{-1} and to the left of 500 cm^{-1} corresponded to carbon-hydrogen out-of-plane bending in aromatic rings (*i.e.*, rings with alkyl substituents) [34]. Absorption peaks at 1 115 and 1 112 cm^{-1} (*i.e.*, 1 300-1 000 cm^{-1}) may correspond to the $C-O$ stretch in the oxyester structure [34].

Specifications of the different bands typically assigned to the FTIR spectrum of asphaltenes are presented in Table 4. The results of FTIR spectra obtained in the present study were in agreement with the relevant findings reported in the literature; apparently distributions of these functional groups in the precipitated asphaltenes were not under the influence of the *n*-alkane solvents used here *(Fig. 9)*. Combinations of FTIR and NMR can be used to correlate and derive specific structural parameters [31]. Considering the heavy crude oil sample used in this study, more work is needed to make a correlation between FTIR and NMR results as has been frequently reported in the literature [24].

3.6 Developed SEM Images

SEM micrographs taken with a *Philips* XL-30 Scanning Electron Microscope were used to analyze the asphaltene surface morphology *(Fig. 10)*. Figure 10 shows a smooth surface that possesses small pores distributed irregularly over this continuous phase. The formation of these pores or cavities may be due to the previous presence of resinous materials that supported the dispersion of asphaltenes in crude oil, and the cavities are a result of their removal [4, 24, 39]. In this figure, agglomerated asphaltenes are also seen. This agglomeration has been described in terms of the ability of resins to solubilize asphaltenes in crude oil (*i.e.*, the interactions between the components present either in asphaltenes or resins that have polar functional groups). For instance, a phenolic hydroxyl group, a hydrogen ion donor, in resins can be hydrogen-bonded to an oxygen or nitrogen atom in asphaltenes [24]. The state of agglomeration was more uniform and more homogeneous in n-C_5 asphaltenes compared with the n-C_7 asphaltenes *(Fig. 10)*. These microscopic structures of asphaltenes show that the precipitation process (*i.e.*, the degree of purity of asphaltenes with regard to resins) and the solvent used affected the morphologies obtained. It has been found elsewhere that the co-precipitation of resins with asphaltenes using *n*-propane as a precipitant provided smooth and amorphous surfaces, while the use of *n*-pentane as an extracting solvent gave porous surfaces with pores of different sizes that were observed with SEM analysis [26].

CONCLUSION

In this study, the structural characterization of asphaltenes from Iranian heavy crude oil (Persian Gulf offshore) with relatively low API gravity (19°API) was determined using different analytical techniques. The yield of asphaltenes that was precipitated with *n*-pentane was higher compared with that obtained with *n*-heptane (21.5 *versus* 15.5 wt%). According to the simulated distillation data, the asphaltene removal

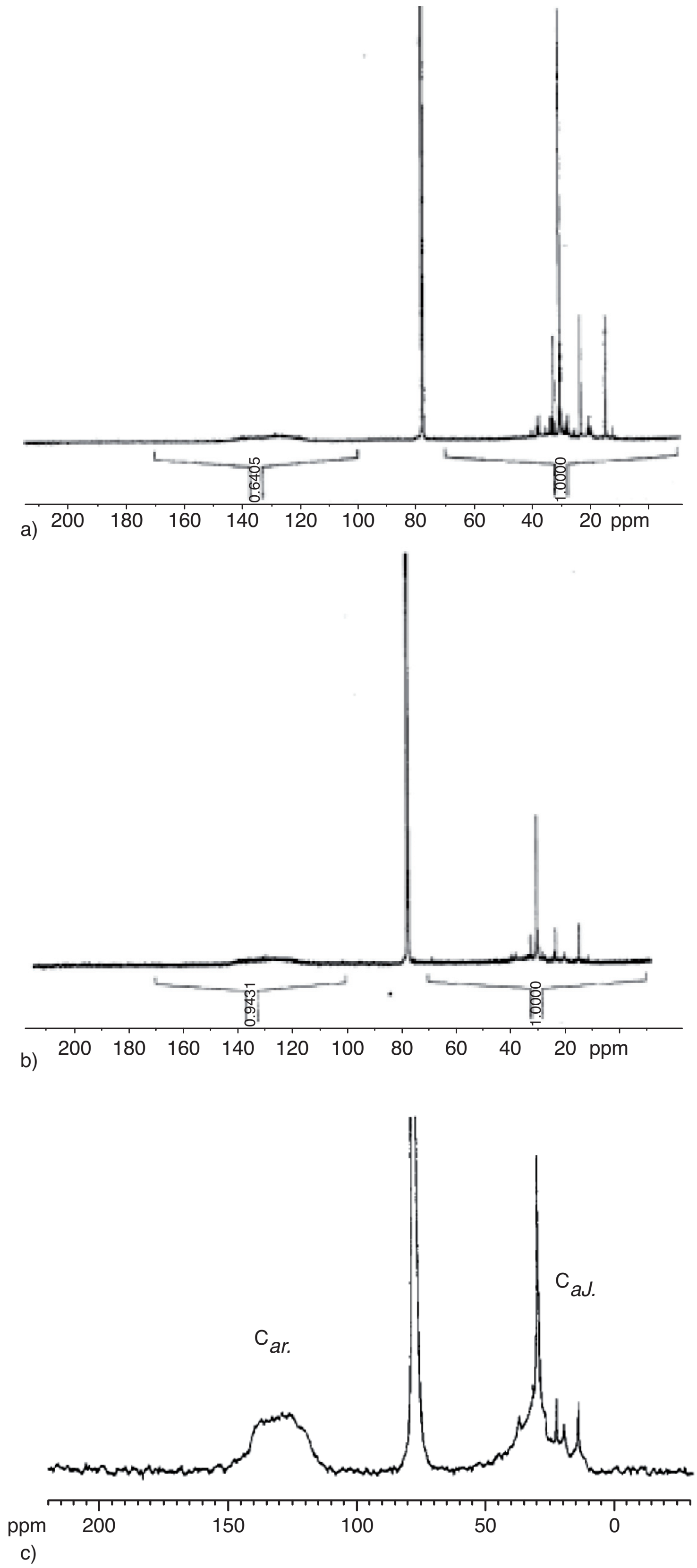

Figure 8

a) ^{13}C NMR spectra of C_5-asphaltene; b) C_7-asphaltene. c) Typical ^{13}C NMR spectrum of asphaltenes is also given [27].

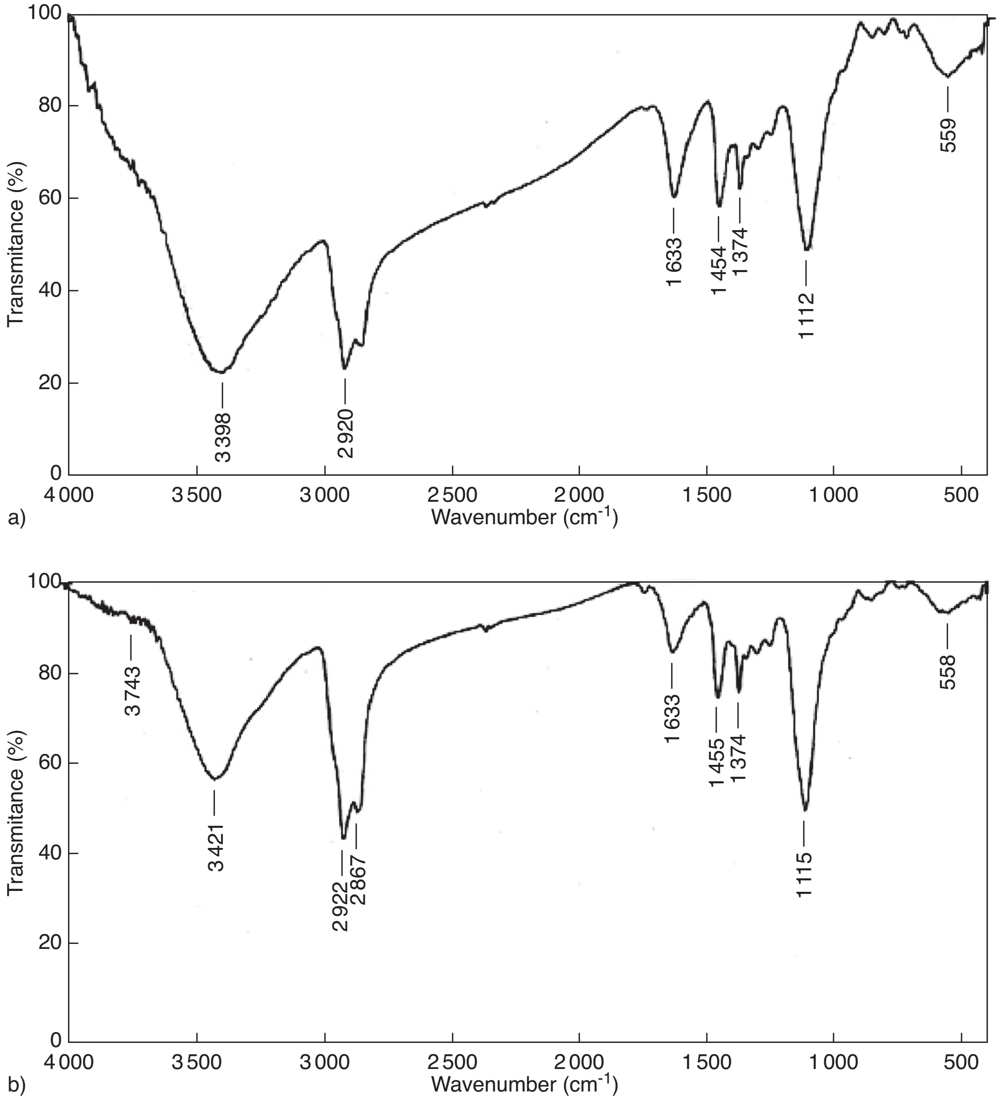

Figure 9

Infrared spectra of the extracted asphaltenes using a) *n*-pentane; b) *n*-heptane.

affected n-C_5 and n-C_7 maltene fractions at temperatures below 204°C and amounts of these fractions were similar to each other and were found to be lower than that of the original crude oil sample. The reconstituted heavy oil samples were prepared in this study through addition of different amounts of asphaltenes to the deasphalted heavy oil (maltenes) and the effects of asphaltenes on the viscosity were more pronounced at 25°C compared with those at the higher temperatures (45°C and 60°C). According to the power law model used in this study, the flowability of the test heavy oil exhibited a pseudoplastic character. Two structural parameters, namely the aromaticity and average number of carbon atoms per alkyl substituent, were determined from ^{1}H and ^{13}C NMR spectra. Infrared spectra confirmed the presence of different functional groups in the precipitated asphaltenes, and the results showed relevancy to other heavy crude oils as reported in the literature. Resins are effective dispersants, and disturbance of the heavy oil colloidal nature is the result of the resin removal from its origin; asphaltene flocculation and precipitation eventually occur. The interpretation given of the morphological characteristics of the precipitated asphaltenes was on the basis of SEM images, indicating the necessity of resins for keeping the asphaltene colloidal nature of the heavy oil intact.

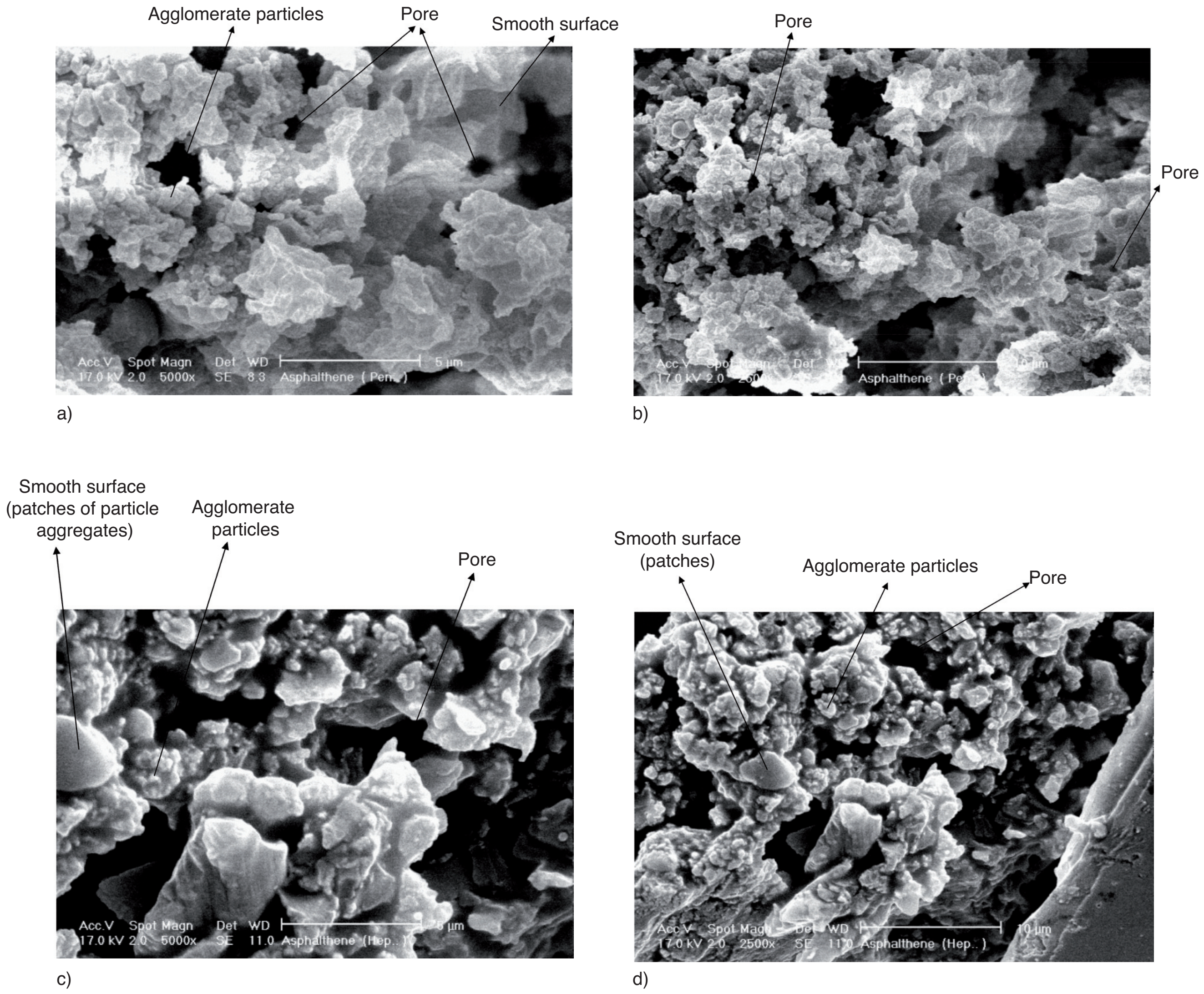

Figure 10

SEM images of asphaltene surfaces, extracted using *n*-pentane (a and b) and *n*-heptane (c and d). The pores and agglomerate particles (either covered in patches with smooth outer bounds or not covered in patches) could be observed in the figure, as indicated by the arrows.

In fact, studying the fundamental mechanisms driving asphaltene colloidal behavior is the key element in keeping the dispersive nature of the heavy oil, and Gawrys and Kilpatrick [14] with the use of several widely recognized methods such as Near-Infrared Spectroscopy (NIP), VPO, PFG-SE NMR and SANS studied asphaltene aggregation behavior. With regard to the colloidal nature of the heavy oil, interest in the petroleum industry has long been developed to study and explore applications of the emulsification technology in treating heavy oil in different sectors of this industry. Structural recognition of the oil constituents, of course, is the prerequisite of these studies.

ACKNOWLEDGMENTS

The work was supported by the IOOC and the authors gratefully acknowledge their help. The Research Institute of the Petroleum Industry (RIPI) provided some technical assistance upon our request.

REFERENCES

1 Gateau, P., Hénaut I., Barré L., Argillier J.F. (2004) Heavy oil dilution, *Oil Gas Sci. Technol.* **59**, 503-509.

2 Saniere A., Hénaut I., Argillier J.F. (2004) Pipeline transportation of heavy oils, a strategic, economic and technological challenge, *Oil Gas Sci. Technol.* **59**, 455-466.

3 Jeribi M., Almir-Assad B., Langevin D., Hénaut I., Argillier J.F. (2002) Adsorption kinetics of asphaltenes at liquid interfaces, *J. Colloid Interface Sci.* **256**, 268-272.

4 Trejo F., Ancheyta J., Rana M.S. (2009) Structural characterization of asphaltenes obtained from hydroprocessed crude oils by SEM and TEM, *Energy Fuels* **23**, 429-439.

5 Spiecker P., Gawrys K., Trail C.H., Kilpatrick P. (2003) Effects of petroleum resins on asphaltene aggregation and water-in-oil emulsion formation, *Colloids Surf. A: Physicochem. Eng. Aspects* **220**, 9-27.

6 McClements D.J. (2005) *Food Emulsions, Principles, Practices and Techniques*, 2nd ed., CRC Press, Boca Raon, FL.

7 Davarpanah L., Vahabzadeh F. (2012) Formation of oil-in-water (O/W) *Pickering emulsions via complexation between* β*-cyclodextrin and selected organic solvents*, Starch-Starke, accepted for publication.

8 Xia L., Lu S.H., Cao G. (2004) Stability and demulsification of emulsions stabilizes by asphaltenes or resins, *J. Colloid Interface Sci.* **271**, 504-506.

9 www.iooc.co.ir

10 Schorling P., Kessel D.G., Rahimian I. (1999) Influence of the crude oil resin/asphaltene ratio on the stability of oil/water emulsions, *Colloids Surf. A: Physicochem. Eng. Aspects* **152**, 95-102.

11 Ahmad N., Nassar A., Zaki N., Gharieb H. (1999) Formation of fluid heavy oil-in-water for pipeline transportation, *Fuel* **78**, 593-600.

12 Pomeranz Y., Meloan C. (1977) *Food Analysis: Theory and Practice*, Avi Publishing Company Inc., Westport, CT, USA.

13 Spiecker P., Gawrys K., Kilpatrick P. (2003) Aggregation and solubility behavior of asphaltenes and their subfractions, *J. Colloid Interface Sci.* **267**, 178-193.

14 Gawrys K., Kilpatrick P. (2004) Asphaltene aggregation: techniques for analysis, *Instrum. Sci. Technol.* **32**, 247-253.

15 Bromberg J. (1984) *Physical Chemistry*, Allyn and Bacon Inc., New York.

16 Bouhadda Y., Bormann D., Sheu E., Bendedouch D., Krallafa A., Daaou M. (2007) Characterization of Algerian Hassi-Messaoud asphaltene structure using Raman spectrometry and X-ray diffraction, *Fuel* **86**, 1855-1864.

17 West E.S., Todd W.R. (1961) *Textbook of Biochemistry*, 3rd ed., The Macmillan Company, New York.

18 Alboudwarej H., Beck J., Svrcek W.Y., Yarranton H.W., Akbarzadeh K. (2002) Sensitivity of asphaltene properties to separation techniques, *Energy Fuels* **16**, 462-469.

19 ASTM D2007-03, Standard test method for characteristic groups in rubber extender and processing oils and other petroleum-derived oils by clay-gel absorption chromatographic method (2003).

20 ASTM D7169-05, Standard test method for boiling point distribution of samples with residues such as crude oils and atmospheric and vacuum residues by high temperature gas chromatography (2005).

21 ASTM D2887-08, Standard test method for boiling range distribution of petroleum fractions by gas chromatography, (2008).

22 Green L.E, Schmauch L.J., Worman J.C. (1964) Simulated distillation by gas chromatography, *Anal. Chem.* **36**, 1512-1516.

23 Clutter D.R., Petrakis L., Stenger R.L., Jensen R.K. (1972) Nuclear magnetic resonance spectrometry of petroleum fractions: Carbon-13 and proton nuclear magnetic resonance characterizations in terms of average molecular parameters, *Anal. Chem.* **44**, 1395-1405.

24 McLean J.D., Kilpatrick P.K. (1997) Comparison of precipitation and extrography in the fractionation of crude oil residua, *Energy Fuels* **11**, 570-585.

25 Trejo F., Centeno G., Ancheyta J. (2004) Precipitation, fractionation and characterization of asphaltenes from heavy and light crude oils, *Fuel* **83**, 2169-2175.

26 Luo P., Wang X., Gu Y. (2010) Characterization of asphaltenes precipitated with three light alkanes under different experimental conditions, *Fluid Phase Equilib.* **291**, 103-110.

27 Calemma V., Iwanski P., Nali M., Scotti R., Montanari L. (1995) Structural characterization of asphaltenes of different origins, *Energy Fuels* **9**, 225-230.

28 Hasan Sh., Ghannam M., Esmail N. (2010) Heavy crude oil viscosity reduction and rheology for pipeline transportation, *Fuel* **89**, 1095-1100.

29 Langevin D., Poteau S., Henaut I., Argillier J.F. (2004) Crude oil emulsion properties and their application to heavy oil transportation, *Oil Gas Sci. Technol.* **59**, 511-521.

30 Morrison R., Boyd R.N. (1977) *Organic Chemistry*, Allyn and Bacon Inc., New York.

31 Guo A.J., Ren Z.H., Tian L.Y., Wang Z.X., Li K.Q. (2007) Characterization of molecular change of heavy oil under mild thermal processing using FT-IR spectroscopy, *J. Fuel. Chem. Technol.* **35**, 169-175.

32 Miller J.T., Fisher R.B., Thiyagarajan P., Winans R.E., Hunt J.E. (1998) Subfractionation and characterization of Mayan asphaltene, *Energy Fuels* **12**, 1290-1298.

33 Ancheyta J., Centeno G., Trejo F., Marroquin G., Garcia J.A., Tenorio E., Torres A. (2002) Extraction and characterization of asphaltenes from different crude oils and solvents, *Energy Fuels* **16**, 1121-1127.

34 Pavia D., Lampman G., Kriz G. (1976) *Introduction to Organic Laboratory Techniques, a Contemporary Approach*, W. B. Saunders Company, Philadelphia.

35 Leon O., Rogel E., Espidel J., Torres G. (2000) Asphaltene: tructural characterization, self-association and stability behavior, *Energy Fuels* **14**, 6-10.

36 Bayramoglu G., Arica M.Y. (2008) Removal of heavy mercury (II), cadmium (II) and zinc (II) metal ions by live and heat inactivated Lentinus edodes pellets, *Chem. Eng. J.* **143**, 133-140.

37 Perez-Hernandez R., Mendoza-Anaya D., Mondragon-Galicia G., Espinosa M.E., Rodriguez-Lugo V., Lozada M., Arenas-Alatorre J. (2003) Microstructural study of asphaltene precipitated with methylene chloride and *n*-hexane, *Fuel* **82**, 977-982.

38 Coelho R.R., Hovell I., Monte M.B., Middea A., Soruza A.L. (2006) Characterisation of aliphatic chains in vacuum residues (VRs) of asphaltenes and resins using molecular modeling and FTIR techniques, *Fuel Process. Technol.* **87**, 325-333.

39 Friberg S.E., Huafang Y., Midttun O., Sjoblom J., Aikens P.A. (1998) Location of crude oil resin molecules at an interface- model oil, *Colloids Surf. A: Physicochem. Eng. Aspects* **136**, 43-49.

Final manuscript received in May 2012
Published online in April 2013

Cite this article as: L. Davarpanah, F. Vahabzadeh and A. Dermanaki (2013). Structural Study of Asphaltenes from Iranian Heavy Crude Oil, *Oil Gas Sci. Technol* **70**, 6, 1035-1049.