APPLICATION AND EVALUATION OF A NEW TYPE OF SOLVENT TO REDUCE THE VISCOSITY OF HEAVY AND EXTRA-HEAVY OIL

A Thesis

by

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ABSTRACT

Increasing global demand for oil, coupled with high depletion rates of conventional oil resources, make the exploitation and production of unconventional oil resources necessary. Heavy and extra-heavy oil have been investigated for two decades as potentially productive unconventional resources. However, the production and transportation of highly viscous heavy and extra-heavy crude oils are two of the paramount concerns in the oil industry due to logistical difficulties and cost. Viscosity is highly sensitive to asphaltene content of heavy oils and bitumen. Asphaltene, the most polar and aromatic component of heavy oil, has a high propensity for self-association. These aggregation and self-association mechanisms affect the viscosity significantly. Chemical and thermal methods are traditional techniques for viscosity improvement of heavy crude oils.

The present work proposes a new type of plant-based solvent that contains functionalized molecules that are able to interact with asphaltene at the molecular level to modify viscosity. Various dosages of solvent, ranging from 5 to 20 wt%, were added to tested heavy-oil samples with high concentration of asphaltene, and viscosity measurements were conducted under a temperature range of 70 to 140°F and shear rates of 3 to 60 s^{-1}. Effects of solvent on the functional groups of asphaltene were evaluated both qualitatively and quantitatively by Fourier Transform Infrared (FTIR) analysis. Sensitivity of asphaltene aromaticity and stacking to solvent were evaluated by curve deconvolution and fitting routines of X-ray diffraction (XRD) patterns of solid asphaltenes.

The proposed solvent is a plant-based, non-hazardous substitute for the conventional hazardous solvents, e.g., toluene, that provides more efficient viscosity reduction compared to its conventional alternatives by interacting with asphaltene molecules and hindering self-association and aggregation processes. Asphaltene critical concentration in the heavy oil was delayed by adding the solvent, requiring more precipitating agent to separate asphaltene from oil. Furthermore, asphaltene aromaticity was decreased by addition of solvent. Its application also increases asphaltene solubility in the oil and decreases the probability of asphaltene precipitation and deposition.

DEDICATION

I dedicate this thesis to my parents for their continuous support and encouragement.

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Heavy Oil Definition

Increasing global demand for oil, coupled with high depletion rates of conventional oil resources, make the exploitation and production of unconventional oil resources necessary. Heavy and extra-heavy oil have been investigated for two decades as potentially productive unconventional resources. Generation of oil and gas are consequence of natural thermal development and transformation of sedimented organic matter embedded in source rocks. After generation process, oil and gas then start to leave the source rocks and migrate through pathways of porous permeable rocks called reservoir rocks. Wherever the migrating process is restricted by defaults of the draining system, accumulation of oil and gas results in generation of fields, from which they can eventually be extracted by industrial means. During this upward traveling process from source rocks to surface, hydrocarbons are exposed to continuous decline of temperature. If the temperature is low sufficiently and depth is shallow enough, such that bacterial life can be engendered, alteration in oil composition may occur. This alteration process, which is the consequence of bacterial activities, leads to increase in viscosity of the hydrocarbon. The aforementioned process is the main origin of heavy oils, extra-heavy oils, and bitumen. This type of crude oil is abundant in Canada (mainly Alberta), Venezuela (in the Orinoco Belt), and China (Henan oil field, Xinjiang oil field, Liaohe oil field, and Shengli oil field). The amount of heavy oil resources has been estimated to be around six trillion barrels, and one to two trillion barrels of that can be retrieved economically (IEA 2008).

Various definitions have been proposed to classified heavy oils and extra heavy oil. One of the prevalent definition is based on the API gravity:

1. Light crude: Oil with API gravity greater than 31.1° API, i.e. specific gravity less than 0.87.
2. Medium crude: oil with API gravity between 22.3 and 31.1° API, i.e. specific gravity between 0.87 and 0.92.
3. Heavy crude: which has an API gravity less than 22.3° API, i.e. specific gravity greater than 0.92.

Also, Canadian center for energy has classified heavy crude oil itself into more specified categories:

1. Heavy oil: defined as having API greater than 10, and viscosity less than 10,000 cp. It also flows at reservoir conditions.
2. Extra-heavy oil: oil with API gravity less than 10 and in-situ viscosity less than 10,000 cp. It has some mobility in reservoir conditions.
3. Bitumen: defined as having API less than 10 and in-situ viscosity greater than 10,000 cp. It does not flow at reservoir conditions.

Heavy Oil Characteristics

Bacterial activities lead to generation of various chemical and physical properties in heavy crude oil including high viscosity and high content of asphaltene, heavy metals, sulfur and nitrogen. All these specifications provoke challenges in extraction, upgrading, transport, and refining processes. Thus, to meet these challenges and design appropriate techniques, it is essential to investigate chemical and physical properties of heavy oils comprehensively and precisely.

Various studies conducted to understand chemical and colloidal classification of heavy and extra-heavy oils. The former one provides information on the elemental composition, chemical structure, and functional groups of macromolecules, while the latter one explains dispersion state of the asphaltene particles viewed as macromolecules in crude oils. Several techniques e.g. liquid chromatography, Nuclear magnetic resonance (NMR), X-ray and neutron scattering (SAXS and SANS), Infrared spectroscopy (IR), steric exclusion chromatography (SEC), and rheology methods have been used to achieve aforementioned goals.

Heavy part of the crude oil is defined as a portion with a boiling point greater than 350°C and an API gravity of less than 20. The structure of heavy compounds become more complex by increasing of boiling point, viscosity, density, molecular weight, and refractive index. These portions that have molecules with more than 25 carbon atoms mainly consist of polar compounds such as asphaltene and resin. In comparison with light fractions, heavy oils consist of compounds with a wide range of aromaticity, heteroatoms, and metals.

Naphthenic and aromatic compounds with more than six alkylated cycles are the main constituents of saturated and aromatic parts of heavy oils. Saturates consist of:

1. Normal alkanes (n-paraffins),
2. Branched alkanes (iso-paraffins),

3. Cyclo-alkanes (naphthenes).

Since n-paraffins are flexible hydrocarbons, they have propensity to cluster and precipitate from crude oil as wax solids. Iso-paraffins as branched molecules have tendency to delay the formation of wax nuclei and also initiate unstable wax solids. However, naphthenes tend to disturb the nucleation and growth processes of aforementioned proportions (Yen and Chilingarian 2000, Speight 1991).

As boiling point increases, the number of aromatic cycles as well as heteropolyaromatic structures would increase. The number of aromatic rings vary from one to three in vacuum gas oil and five to six in residues. Sulfur compounds of residues can be exist in following five categories:

1. Thiols
2. Sulfides
3. Disulfides
4. Sulfoxides
5. Thiophenes

The first four categories can be divided further into cyclic and acyclic structures or alkyl-, aryl-, and alkylaryl- derived species. Thiophenes, the major sulfur species in heavy oils, are condensed polyaromatic structures with benzo-, dibenzo-, and naphthobenzo-thiophenes derived structures. Nitrogen compounds in oil, that can be divided into basic and neutral, are less prevalent rather that other heteroatoms. However, they have substantial impact on hydro-treatment processes. Carboxylic functions and phenolic compounds are the main part of the oils that consist of oxygenated structures. Furthermore, based on the origin of the oil, porphyrin are present in the oil and contain nickel and vanadyl ions.

In order to draw a link between boiling point and physical properties such as density and viscosity, various distillation methods have been applied. However, this method suffers from the fact that boiling point is a function of chemical structures rather than average molecular weight. For instance, it has been observed that with the same molecular weight, non-polar components are more volatile rather than polar compounds due to the ability of former components to form aggregates. True boiling point method (TBP), potstill distillation, and stimulated distillation are prevalent distillation procedures.

Another class of fractionation is generated based on chemical types of crude oil. In these methods, different parts of the oil are classified based on their polarities. In the first step, the most polar component, asphaltene, is separated by addition of excessive amount of paraffinic solvents in various contact time and temperatures. Then saturates, aromatics, and resins are separated by means of analytical chromatography (HPLC), preparative liquid chromatography (flash chromatography), or Thin Layer Chromatography (TLC).

Functional groups of heavy oil constituents can be identified by several methods including High Performance Liquid Chromatography (HPLC), Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR), and spectroscopy techniques. The main purpose of HPLC method is to detect poly-aromatic hydrocarbons with up to eight poly-condensed aromatic structures. By applying NMR method, not only different types of proton can be distinguished but also aliphatic carbon can be differentiated from aromatic carbons. Furthermore, by using data from NMR, quantitative structural information such as C/H aliphatic and C/H aromatic ratios can be determined as well. Spectroscopy methods also can be utilized to determine the heteroatoms and the local atomic structures in close vicinity of them.

Heavy Oil Transportation

Presence of heavy ends compounds such as asphaltene, small amount of low molecular weight compounds, and high proportion of metals, sulfur and salts initiate severe difficulties during transportation of heavy crude oils including:

- Asphaltene precipitation that leads to pipeline clogging and initiation of multiphase flow.
- High viscosity that generates high pressure drop.

Several methods have been proposed and conducted to facilitate transportation of heavy and extra-heavy crudes through pipelines. All these methods can be classified into three main categories (Martinez-Palou et al. 2011):

- Viscosity improvement methods
- In-situ upgrading
- Drag reduction

Viscosity Improvement Methods

Improving viscosity of heavy and extra-heavy oil can be achieved by various techniques such as dilution, oil-in-water emulsions, increase of temperature, and modifying of oil’s pour point. These methods can be applied independently or simultaneously based on reservoir and crude oil characteristics.

Dilution

Light hydrocarbons, typically condensates from natural gas production, are employed at concentration of 20-30% to reduce viscosity and improve flowability of heavy crudes. Addition of diluents not only improves the viscosity of the oil but also facilitates dehydration and desalting processes. Although it has been used widely in industry, dilution has several drawbacks. First of all, the availability of condensates is a serious concern. Also due to increase in the volume of the oil that should be transported, significant cost is required to provide pumping equipment and pipelines. Furthermore, the separation processes and returning back the diluent to the production sites are other serious concerns. Last but not lease, the compatibility of diluent with oil is a crucial point. By addition of the diluent the composition of the oil may change and if the diluent is not compatible with asphaltene content, there would be a high chance of asphaltene precipitation and so pipeline clogging. So it is very important to design the method based on oil composition and other parameter such as transportation temperature and pressure. Application of dilution leads to promising results in term of reducing viscosity of the oil. It is shown by Yaghi and Al-Bemani 2002 that addition of 30% of light crude oil reduces viscosity from 15000 cp to 1000cp at ambient temperature. Also, Addition of 20 % kerosene decreased the viscosity to 250 cp. However high amount of diluent is needed to achieve this level of decrease in viscosity. Van Den and Schrijvers 2009 proposed a new method that consists of both dilution and upgrading processes. However, the upgrading part was minimized to make the method more economical. In this method, heavy crude oil is divided into two parts, then the first part is further separated into heavy portion and light portion. The heavy portion is thermally cracked and the residual fraction is used to the generation of power and heat. The lighter parts from different stages are then transported via pipelines. Since the upgrading process is minimized, the stability problems diminish as well. Same concept of limited upgrading has been employed by Myers et al. 2000 to improve oil viscosity. In this method, hydroconversion process is first applied to the heavy oil to reduce its viscosity to the range of 60 to 250 cp at 40°C and then by addition of naphtha or condensates the viscosity is further reduced to 40 cp. Iqbal and Floyd 2010 and Argillier et al. 2003 proposed methods based on the fact that deasphalting the oil may diminish its viscosity significantly. Knowing the fact that heavy oil is a colloidal suspension system, particles of asphaltene suspended in maltenes, it is possible to decrease its viscosity by breaking the colloid system.

It is also important to note that any improvement in solvents used to dilute the oils will enhance the effectiveness of dilution process. Henaut et al. 2011 employed dimethyl ether (DME) to modify rheology of several heavy crude oil samples. They showed that application of 23.4% (by mass) of mixture of DME/naphtha with the ration 1.4 diminishes oil viscosity from 940000 to 400 cp. Furthermore, it is easier to recover DME rather than other common solvents. Gateau et al. 2004 studied the effects of polarity on efficiency of solvents. They concluded that addition of limited amount of solvent with high polarity and hydrogen bonding parameter may lead to significant decrease in viscosity of the mixture of synthetic oil and asphaltenes.

Oil-in-Water Emulsions

Formation of oil in water emulsion is another method that has been used widely to transport heavy crude oil via pipelines. Water-in-oil (W/O) and oil-in-water-in-oil (O/W/O) emulsions generated naturally in petroleum production and transportation processes. These stable emulsions are not favorable since they have adverse effects on rheological properties of oil, and also they increase the risk of corrosion issues. However, oil-in-water emulsions have been extensively used in transportation of heavy oils. This process includes three steps: formation of oil-in-water emulsions, transportation of generated emulsions to destination, and demulsification process to separate oil from water (Poynter and Simon 1970).

Several methods have been conducted to generate emulsions including common homogenization, emulsification by membranes, and using ultrasonic waves. Also addition of surfactants to induce formation of emulsions and prevent phase separation is necessary (Rivas et al. 1998). Furthermore, it is possible to take advantage of natural surface active materials in the crude oil like asphaltene as an emulsifier agents. Particles such as silica, clay, and iron oxides are naturally hydrophilic, but can become oil-wet (hydrophobic) due to long term exposure to the crude in the absence of water (Langevin et al. 2004). To separate water from oil, different methods such as chemical demulsification, thermal demulsification, and electro-demulsification are utilized.

Ashrafizadeh and Kamran 2010 studied effects of various parameters such as pH, salt concentration, surfactant concentration, speed and time of mixing, temperature, and oil content on the rheological properties and quality of the oil-in-water emulsions. One of the most successful application of oil-in-water emulsion in transporting of heavy crude oil is Orimulsion® process developed by PDVSA. This process has become attractive since the dilution was not economical anymore at the end of eighties due to the issue with availability of condensates and light crude oils.

The efficiency of this method can be maximized by minimizing the required amount of water and surfactants. Also, surfactants should be capable of forming meta-stable and easy to break emulsions to avoid phase separation during the transportation while provide easy separation conditions at separation facilities. Another important issue is that the surfactants should be soluble in continues phase which is water in case of oil in water emulsions. So appropriate techniques must employ to assure migration of surfactants to oil water interface and so formation of oil droplets in water. Fournanty et al. 2008 and Gregoli et al. 1994 proposed novel mixing procedure to generate stable oil-in-water emulsions with low viscosities that consume lower amount of energy compared to Orimulsion process.

Application of anionic and non-ionic surfactants to produce oil-in-water emulsions studied by Zaki 1997 and Yaghi and Al-Bemani et al. 2002. They concluded that viscosity and stability of emulsions increase with increase of surfactants, however, the interfacial tensions and size of dispersed droplets drops by increasing the concentration of surfactants. It is also important to note that salinity of water can also affects the quality and characteristics of oil-in-water emulsions. Ahmed et al. 1999 showed that formation water can generate more stable emulsions since its interfacial tension with oil is smaller rather than water. Thus, a larger portion of oil can be transported. Hayes et al. 1988 proposed use of combination of surfactants, biological co-surfactants, and bio-emulsifier, surfactants of biological origins, to reduce and control effects of parameters such as composition of the oil, salinity and pH of water, temperature, and surfactant type.

Thermal Methods

Heating has been used extensively to facilitate production and transportation of heavy crude oils. The main idea is to keep the high temperature, at which the oil is produced, in the pipelines by providing insulation. Also, external heating is always necessary due to heat losses that can be done in reheating the oil in pumping stations. Insulation can be achieved by burying the pipelines to conserve heat. Furthermore, operation in low vapor pressure, near room temperature, can increase the capacity of pipelines as well.

Ghannam and Esmail 2006 investigated various methods for flowability enhancement of medium crude oil including heating and formation of emulsions. They showed that increase of temperature from 10°C to 50°C leads to viscosity reduction parameter of 96%. They also showed that sensitivity to temperature is more significant at higher viscosity. Another method proposed by Perry 2005 is to increase and maintain the temperature of crude oil in non-insulated pipelines by employing concept of shear heating. It is shown that by implementing proper design factors such as station spacing, line diameter, operating pressure range, and the viscosity specification of the transported oil it is possible to control the temperature and so eliminate external heating and insulation of pipelines. In this method the temperature is increased by friction in the pump due to pressure increments and the heat from internal shear friction of turbulent flow within the heavy oil as it flows at high velocities throughout the pipelines. So higher viscosity of the oil provides higher increase in temperature per distance of oil traveling. However, considering of shutdown conditions leads to limit the oil viscosity.

Transportation of heavy crudes produced from offshore is one the paramount issues in industry as the sever conditions of subsea environment. In small distances, these problems can be overcome by insulation of pipelines and minimizing moving duration to prevent temperature losses. However, in long distances providing booster pumps and/or external heating may lead to expensive costs and difficulties in implementation parts. A novel method proposed by Langner and Bass 2001 including application of electricity for heating up the pipelines. In this method the oil is transported via a single heated electrically insulated pipeline or a pipe-in-pipe subsea pipeline consists of an inner electrically insulted pipe that is surrounded concentrically by an electrically conductive outer pipe.

Chemical Methods

Chemical treatments are shown to be promising methods to modify heavy oil rheological properties by affecting asphaltene structural characteristics. The main concept was originated from the peptization effect of resin on asphaltene particles. Asphaltene micelles are stabilized by resin, the other polar constituent of oil that is soluble in aliphatic solvents, by the peptization process in which the aliphatic part of asphaltene is stretched by attachment of the resin polar part, resulting in the formation of a steric-stabilization layer around the asphaltene. However, the quantitative analysis of resin-asphaltene interactions cannot be done because of the existence of the same polar functional groups in both species, as well as their complex structures (Chang and Fogler 1994; Ortega-Rodríguez et al. 2003, Afra et al. 2016).

Effects of four aromatic polyisobutylene succinimides as asphaltene dispersant and viscosity reduction agent of heavy oil were evaluated by Chaavez-Miyauchi et al. (2013). The selection of these compounds were based on their capability of interacting with asphaltene particles via π−π stacking, hydrogen-bond formation, and acid−base interactions. They concluded that the viscosity improvement is mainly related to asphaltene disaggregation ability of added chemical rather that its dispersion−aggregate hindrance ability. Yang et al. (2014) evaluated the influence of dodecyl benzene sulfonic acid (DBSA) and lauric amine (LA) on the viscosity of heavy oil through differential scanning calorimetry (DSC) analysis and electrical conductivity measurement. They showed that viscosity of the oil system has reciprocal relationship with size of asphaltene particles. Also their results indicated that efficiency of amphiphiles is related to the ratio of resin to asphaltene as well. Application of ionic liquid in viscosity treatment of heavy oil was assessed by Subramanian et al. (2015). They observed ionic liquids with higher tail length have more efficient viscosity reduction ability. Based on this study, anion charge density and cation head groups are other important factors in effectiveness of viscosity modifiers.

Pour Points Modifiers

It is well known fact the wax crystallization affects properties of oil such as viscosity, pour point, and yield stress significantly. Hence, several chemical additives have been proposed to modify the nucleation, adsorption, and solubility of waxes in the oil called pour point depressants (PPD). Wax crystallites have propensity toward forming of gels that leads to increase both the cohesive and the adhesive forces and so result in dramatic increase of viscosity. The viscosity reduction conducive to high pressure losses that is detrimental to crude transportation. Major portion of microcrystalline waxes are branched-chain paraffins. Also the long, straight-chain naphthenic and aromatic paraffins also influence the formation of microcrystalline waxes and type of crystal growth of macrocrystalline waxes. However, it has been shown that n-paraffins are the main constituents of waxes deposited during production and transportation processes. This type of wax has molecules with straight-chain alkanes with more than 15 carbon atoms and very little branching (Sanjay et al. 1995). Different carbon numbers have been reported for precipitated waxes that are mainly in the range of 16 to 27. It has been also shown that with increase of temperature the number of carbon atoms are increased as well. To assess the problem of wax precipitation of a given crude oil the composition of crude oil in terms of concentration of n-paraffins, branched-praffins, naphthenes, aromatics, resins, and asphaltenes as well as the environment of production and transportation conditions should considered precisely.

Pour point depressants have ability to change growth and surface characteristics of wax crystals such that their propensity toward forming large crystals and adherence to metal surfaces may decrease significantly. Jafari Behbahani et al. 2008 studied the application of ethylene-vinyl acetate copolymer (EVA) with different molecular weights as flow improver on various crude oil samples. They concluded that with higher content of asphaltene it is more efficient to use low molecular weight flow improver, whereas in case of low asphaltene content, application of higher molecular weight flow improver leads to better performance. They also recommended use of diluents such as xylene to ensure better improvement in results.

Materials	Authors
branched poly-α-olefin	Morduchowitz and Bialy 1977
vinyl acetate-α-olefin styrene maleic anhydride copolymers	El-Naga et al. 1985
ethylene-vinyl fatty acid ester	Qian et al. 1994
Polybehenyl acrylate (PBA)	Chanda et al. 1998
long-chain fatty acid amides and poly-n-alkyl acrylates	Machado et al. 2001
methacrylate copolymers	Pedersen and Ronningsen 2003, Da Silva 2004, Song et al. 2005
ethylene-vinyl acetate	Jafari Behbahani et al. 2008

Table 1 - Various chemicals used as PPD

Chanda et al. 1998 utilized polybehenyl acrylate (PBA) with various molecular weights as pour point depressant and concluded that lower molecular weight polybehenyl acrylate combined with asphaltene soluble solvents has better efficiency in reducing the viscosity, pour point, and yield stress. Different chemicals that have been studied as PPD are listed in Table 1.

CHAPTER II

EXPERIMENTAL STUDY*

The objective of experimental work is to verify and evaluate the efficiency of proposed solvent. This will be done by experimentally identifying the viscosity reduction efficiency and alteration in asphaltene crystalline parameters though a series of viscosity measurements, X-ray diffraction, and Fourier Transform Infrared.

Materials

Two heavy oil samples from Mexican crude with the API of 9.1 and 9.6 were studied in the present work. The main constituents of proposed solvent, that is called ACC in the entire thesis, are anacardic acid, cardanol, and cardol that exist in cashew nut shell liquid (CNSL) (Figure 1). The weight percent of each compound vary based on the oil samples. In the present sturdy ACC consists of 73 wt% Anacardic acid, 15 wt% cardanol, and 12 wt % cardol. N-heptane and toluene with purity grades of 99 wt% and 99.3 wt% respectively, were used for conducting experiments.

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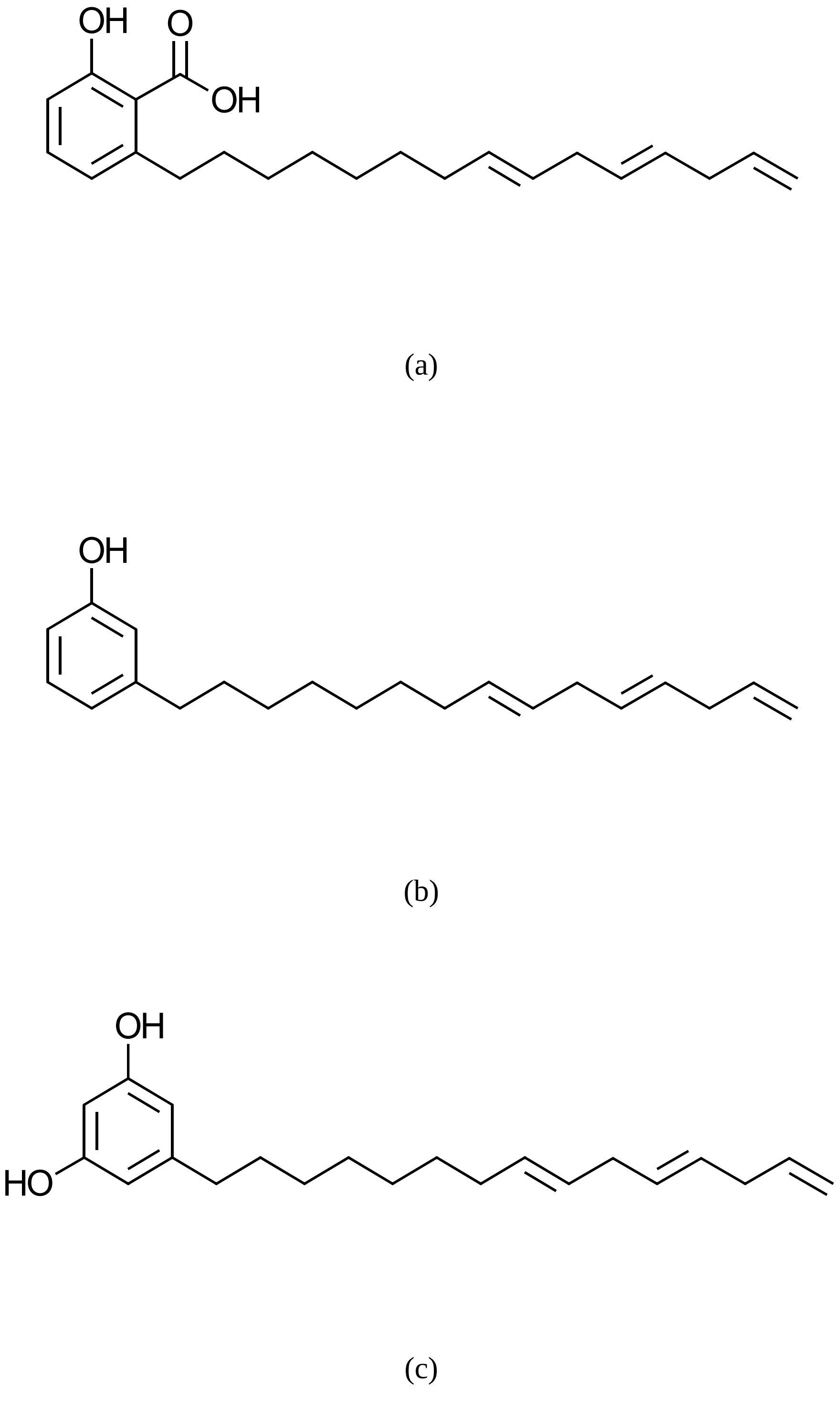

Figure 1 - Chemical structures of main constituents of ACC (a) Anacardic acid, (b) Cardanol, and (c) Cardol.

Viscosity

Viscosity, that is a fundamental feature of all liquids, can be defined as a measure of internal resistance of a liquid to flow. Viscosity also can be termed as a grad force and is a measure of the frictional properties of the fluid. Viscosity of both fluids and gases are function of temperature and pressure. Viscosity can be defined in two forms: dynamic viscosity and kinematic viscosity.

Dynamic viscosity is the tangential force per unit area required to slide one layer (A) against another layer (B) as shown in Figure 2, when the two layers are maintained at a unit distance, applying of force A leads to moving of layers with velocity of v_1 and v_2. The resistance of fluid to flow can be expressed in mathematical form as:

Shear stress = η (Strain or shear rate)

where η is the dynamic viscosity.

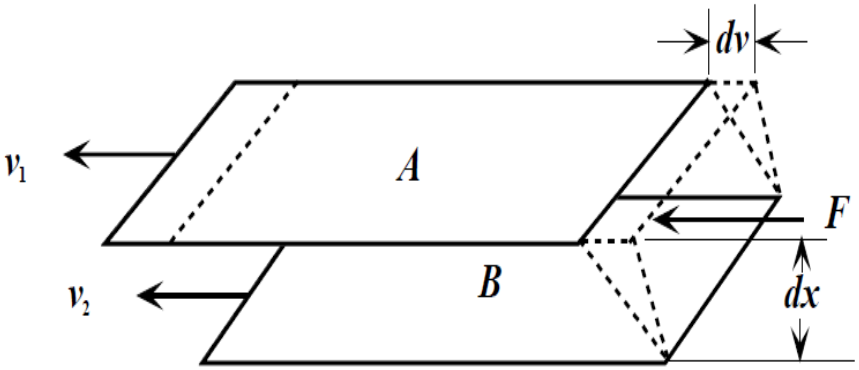

Figure 2 - Application of Force A to two parallel surfaces to define viscosity

If σ is shear stress and $\dot{e}$ is strain rate, then the expression becomes:

$$\sigma = \eta \dot{e}$$

The strain rate can be expressed as:

$$\dot{e} = \frac{1}{x}\frac{dx}{dt} = \frac{v}{x}$$

Where x is the length, t is the time, $\frac{dx}{dt}$ is the velocity v. Hence, the dynamic viscosity is expressed as:

$$\eta = \sigma \frac{x}{v}$$

Kinematic viscosity can be determined by knowing the density of the liquid (ρ) at desire temperature and pressure:

$$\nu = \frac{\eta}{\rho}$$

In the present work a coaxial-cylinder viscometer has been used to measure the viscosity of samples. In this apparatus, a known force or torque is applied to rotate a solid shape in the viscous fluid. Then its rate of rotation is measured and the viscosity of the fluid cab be calculated. Following advantages can be enumerated for Rotational viscometers (Viswanath et al. 2007):

- Steady state conditions
- Application of various shear rates to same sample
- Continuous measurement on materials with properties that may change with temperature

The viscometer consists of stationary frame from which a rotatable sleeve is suspended and includes a means for rotating the sleeve. Suspended within the sleeve is a bob capable of angular motion about the longitudinal axis of the sleeve. The device is constructed so that the bob and at least the portion of the sleeve near the bob may be immersed within the liquid, the viscosity of which is to be determined. The bob is suspended from the stationary frame by a low friction bearing which permits limited angular motion about its center of rotation. An arm is attached to the bob shaft or extended portion of the bob, and the arm is contacting an electronic force sensor. Given the known characteristics of the viscometer, the force applied on the force sensor is proportional to the viscosity of the liquid (Bi 2003).

FTIR

Fourier Transform InfraRed (FTIR), is a method to determine an infrared spectrum of absorption or emission of materials. In this technique, the absorbed and transmitted radiations from a sample are collected and used to generate a spectrum of a sample (Figure 3 and Figure 4).

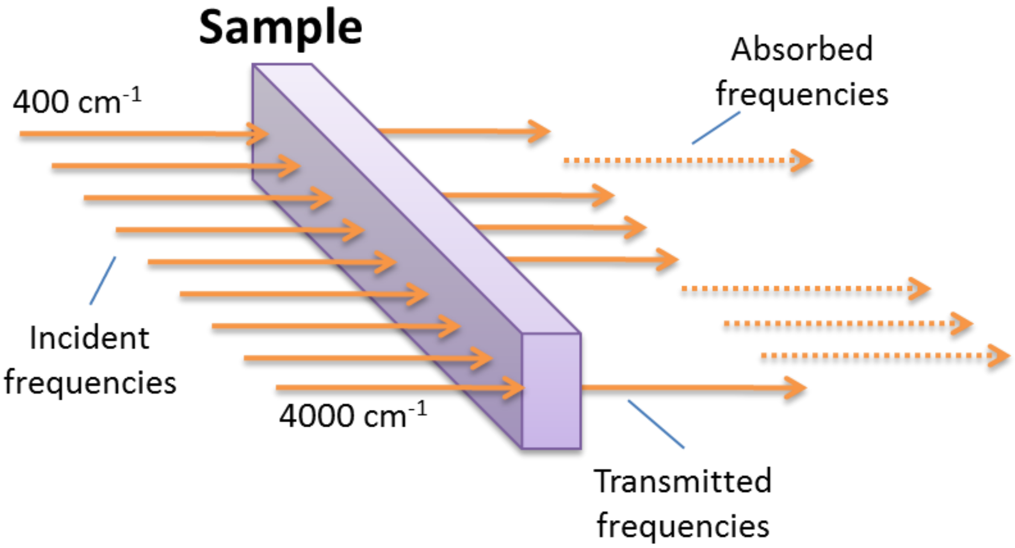

Figure 3 - FTIR thoery

Since a vibrational spectrum of a molecule is unique physical property, it can be utilized as fingerprint to identify it. It can be done by comparing the spectrum of the unknown molecule with reference spectrum.

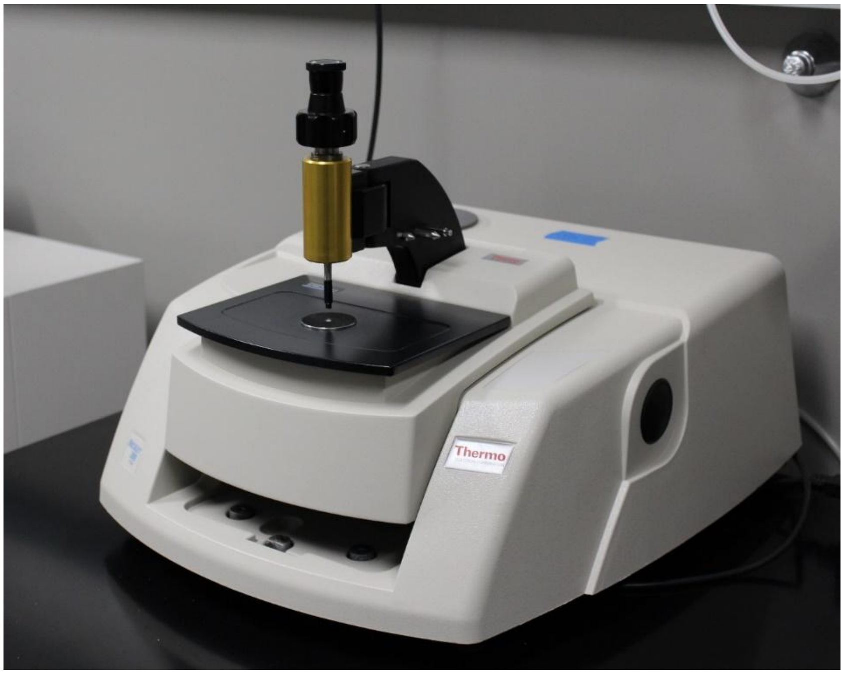

Figure 4 - FTIR equipment

Basically, the infrared spectrum is formed when electromagnetic radiations are absorbed at frequencies that related to the vibration of chemical bonds of a molecules. The energy of a molecule consists of different parts:

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational}$$

- $E_{translational}$: The translational energy relates to the displacement of molecules in space as a function of the normal thermal motions of matter.
- $E_{rotational}$: The rotational energy relates to the tumbling motion of a molecule, which is the result of the absorption of energy within the microwave region.
- $E_{vibrational}$: The vibrational energy relates to the absorption of energy by a molecule as the component atoms vibrate about the mean center of their chemical bonds.
- $E_{electronic}$: The electronic component is linked to the energy transitions of electrons as they are distributed throughout the molecule, either localized within specific bonds, or delocalized over structures, such as an aromatic ring (Coates 2000).

To observe electronic transitions, visible and ultraviolet radiation can be utilized to apply energy.

The net change in dipole moment during the vibration for the molecule or the functional group is necessary for infrared activity and so absorption of infrared radiation. One of the simple model that can be utilized to interpret the source of many of the distinctive frequencies of a particular combination of atoms within a molecule is the basic model of simple harmonic oscillator:

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{\kappa}{\mu}}$$

where

- ν is fundamental vibration frequency
- κ is force constant
- $\mu = \frac{m_1 m_2}{(m_1+m_2)}$ is reduced mass that m_1 and m_2 are the component masses for the chemical bond.

The above equation draws a link between frequency of vibration, molecular fragments, and strength of the covalent bond between two atoms. To simplify the vibration of a molecule, a threefold set of coordinate axes can be defined to determine minimum set of fundamental vibrations and then define a model based on these minimum set of vibrations.

For simplification of the vibration of a molecule, a model can be described in terms of minimum set of fundamental vibrations, based on a threefold set of coordinate axes. All possible vibrations can be projected on the threefold axes to be reduced to this minimum set. Following equations show the number of normal modes of vibration for given molecule:

$$\text{Non-linear} \qquad 3N-6$$

$$\text{Linear} \qquad 3N-5$$

where N is the number of component atoms in the molecules.

To detect an organic compound with aliphatic fragment or center, The C─H stretch vibrations for methyl and methylene can be used. Further information about basic structure can be obtained by investigation of bending vibrations. For instance, a combination of a strong methylene and a weak methyl band with a band at 720 cm^{-1} indicates a long chain of linear aliphatic structure.

It is mentioned before that all C─H stretching absorptions below the 3000 cm^{-1} are indicative of saturated hydrocarbon. Almost all absorption in the range of 3000 to 3150 cm^{-1} belong to unsaturated compounds or aromatic rings. The unsaturated hydrocarbons featuring C═C, with attached hydrogens, usually occur in between 1600 to 1680 cm^{-1}. The location of double bond and the spatial arrangement around it can be determined by the number of bands and their locations.

The presence of aromatic rings in a structure can be detected by the C─H and C═C─C ring-related vibrations. In comparison with

XRD

X-ray powder diffraction (XRD) is a rapid analytical technique utilized for phase identification of a crystalline material and can provide information on unit cell dimensions. A diffraction pattern of a material can be obtained by propelling an incident wave to it and recording the intensities and directions of the outgoing diffracted waves. There is a geometrical relationship between the crystal structure of material and the diffraction pattern. The diffraction pattern is a spectrum of real space periodicities in a material. Small angels are indicative of Atomic periodicities that have long repeat distances and high angels are the result of short repeat distances. Also, sharp and clear peaks belong to crystals with precise periodicities, whereas the diffraction peaks of crystals with defects are distorted, broadened, and weakened.

One of the most important application of x-ray powder diffraction is to recognize unknown crystals in a sample. It can be done by comparing the intensities and positions of peaks of the diffraction pattern with a known pattern belongs to standard sample or the pattern derived by calculation.

A powder X-ray diffractometer comprises an X-ray source, a sample stage, a detector and a way to vary angle θ (Figure 5). The detector, which is located opposite the source, gather the intensity of the x-ray it receives at 2θ away from the source path. The incident angle is than increased over time while the detector angle always remains 2θ above the source path (Grebenkemper 2014).

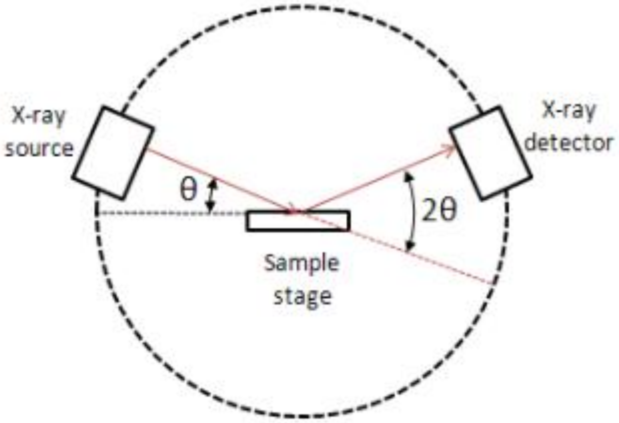

Figure 5 - XRD setup (Grebenkemper 2014)

SARA Analysis

To determine composition of heavy oil samples SARA analysis experiment was done based on ASTM D2007-11. In this method, the oil sample is classified into the hydrocarbon types of saturates, aromatics, resins and asphaltenes by separating each type based on its polarity and affinity for absorption to solid granular packing columns. In this method asphaltene is first precipitated by following procedure: 10 g of crude oil is mixed with 100 ml of n-pentane and the mixture is poured into a flask through a funnel with a filter paper. The asphaltene is left as a residue in the filter paper. The anti creep beaker with the solution is then kept on a hot plate at 105°C to evaporate the n-pentane. The remaining maltenes is weighed and the difference from the initial weight is the amount of asphaltenes.

Figure 6 shows the setup of the adsorption columns needed for the rest of the procedure. The top column consists of 50 g of attapulgus clay and the bottom column consists of attapulgus clay (50 g) and silica gel (200 g). The silica gel is at the bottom of the column. After extraction of asphaltene following procedure should be done to separate other portions of the oil: 25 ml of n-pentane is added to the top column until it completely fills the pores in the clay. The diluted sample (after asphaltene extraction step) is added to the clay and n-pentane is added to wash the walls of the tube and beaker. Air should not be allowed to enter the clay bed. N-pentane is then added to create a head level above the clay beds and 280 ml of effluent is collected in a conical flask.

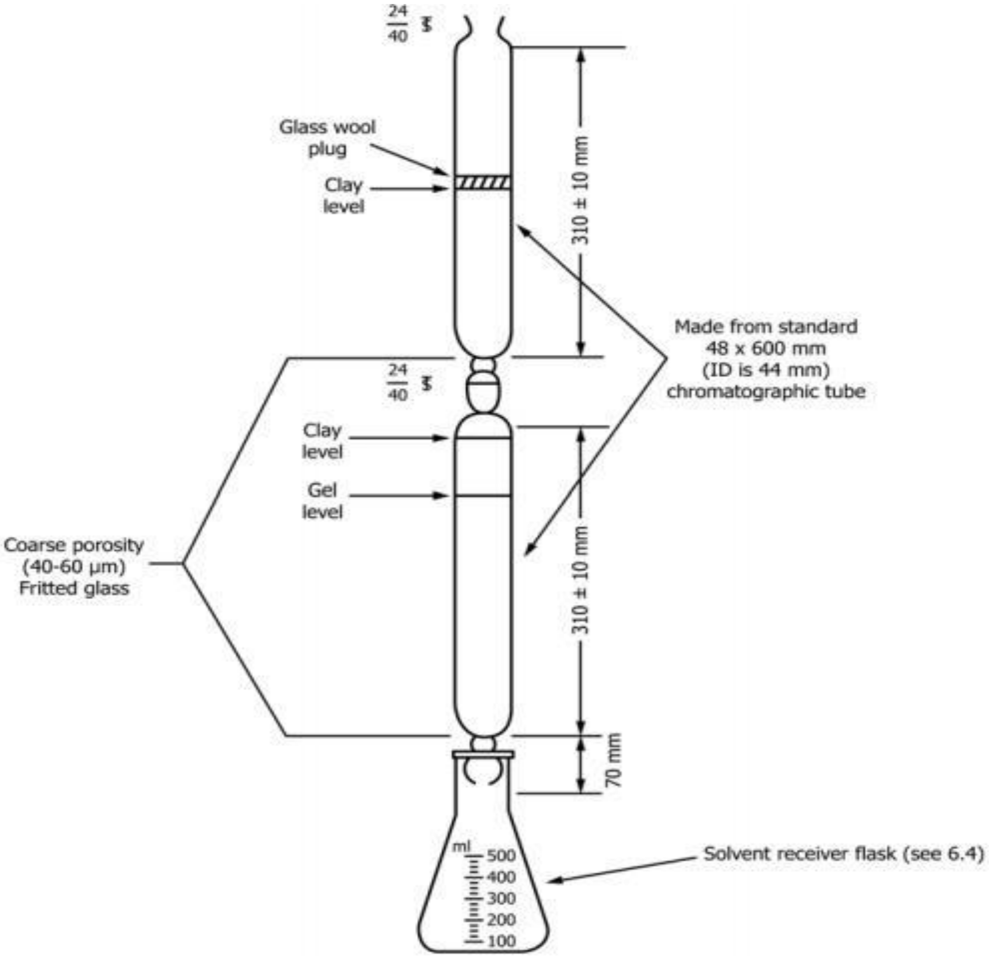

Figure 6 - Clay-gel percolating column

The two columns are disconnected and n-pentane is charged through the upper clay section until 200 ml has been collected. Only the solution from the lower column (saturates) is kept on a hot plate at 105°C using the anti creep beakers to evaporate the n-pentane. It is then weighed and the difference from the initial weight is the amount of saturates.

For resins determination, a 50-50 volume mixture of toluene-acetone is charged through the upper column. The effluent is collected in a separatory funnel until it is completely colorless. 10 g of anhydrous calcium chloride is added to the solution and is shaken and kept to rest for about 5 minutes. The solution is passed through a filter paper and collected in a conical flask. N-pentane is used to wash the separatory funnel and filter paper and remove traces of oil sample. The solution is evaporated at 105°C in a hotplate to remove the toluene-acetone and n-pentane. The remaining effluent is the resins and the amount is found by the weight difference from the initial weight. The amount of aromatics is the remaining percentage after adding the other components.

CHAPTER III

RESULTS*

SARA Analysis

The SARA composition of the heavy oil samples are shown in Table 2. It can be inferred from the results that both of the samples contain high amount of asphaltene and resin compound. High amount of asphaltene content is one the reason of high viscosity of the samples at ambient temperature.

	Saturates	Aromatics	Resins	Asphaltene
Sample A	20.6	34.5	19.1	25.8
Sample B	24.7	39.4	16.5	19.4

Table 2 - SARA analysis of heavy oil samples.

Viscosity Results

Viscosity is an important feature of liquids that has been widely used in various industries. Determining dimensionless groups like the Reynolds number, the optimum conditions for the chemical processes and operations, and calculation of the power requirements for the unit operations such as mixing, pipeline design, pump characteristics, atomization (liquid droplets), storage, injection, and transportation are all can be done by using the concept of viscosity (Viswanath et al. 2007). The flow features of liquids are mainly function of the viscosity and can be classified into three categories (Figure 7):

a) Newtonian

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b) Time independent Non-Newtonian, and

c) Time dependent Non-Newtonian.

A liquid is defined as Newtonian when its viscosity remains constant and is independent of the applied shear stress. However, the viscosity of a non-Newtonian liquid is a function of shear force and time. The viscosity of time dependent non-Newtonian fluids may alter with time under constant shear rate.

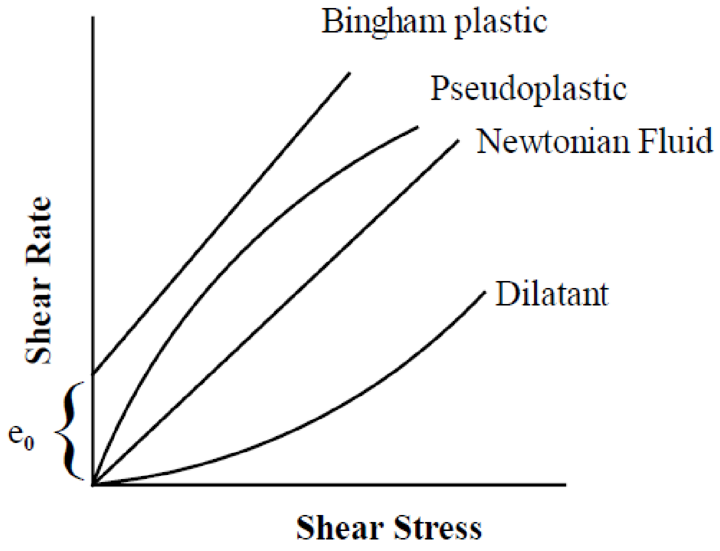


Figure 7 - Various types of fluids based on viscosity (Viswanath et al. 2007).

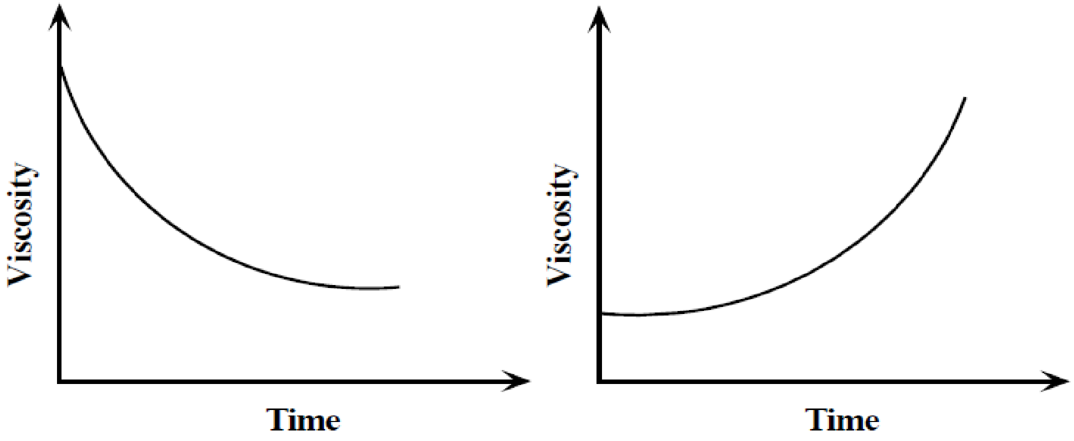
Change in Viscosity of time-dependent non-Newtonian fluids

In time independent non-Newtonian fluids, the shear rate and shear stress does not vary proportionally. There are three common types of time independent non-Newtonian fluids (Figure 8):

a) Shear-thinning or thixotropic: When the viscosity decreases with an increase in shear rate.

b) Shear-thickening or rheopectic: When the viscosity increases with an increase in shear rate.

c) Viscoplastic or Bingham plastic: which flow only if subjected to a shear stress bigger than a characteristic stress, the yield stress. Beyond this point, they may behave as Newtonian, shear thinning, or shear thickening liquids. Below their yield stress, these liquids behave like elastic solids.



a) Thixotropic fluid b) Rheopectic fluid

Figure 8 - Change in Viscosity of time-dependent non-Newtonian fluids (Viswanath et al. 2007).

Figure 9 and Figure 10 show the viscosity curves for heavy oil samples in the range of 1-60 s^{-1} of shear rate and at the temperature of 75, 100, 122, and 140 F. It can be inferred from these figures that heavy oil samples demonstrate shear thinning behavior at the low temperature range of 75 and 100 F over the observed range of shear rates and the viscosity reduces noticeably with temperature when temperature was increased from 75 to 140 F.

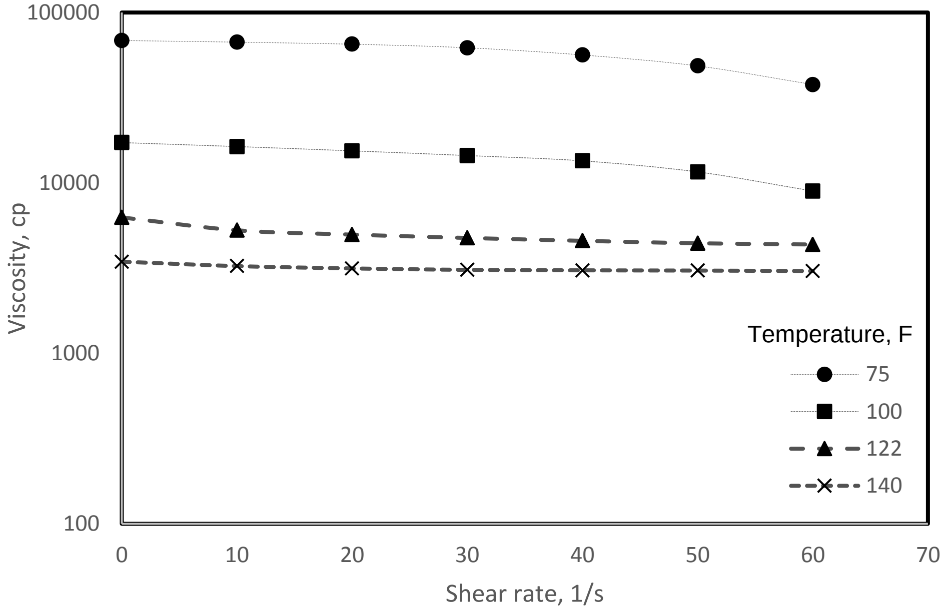


Figure 9 - Viscosity of sample A at various shear rates and temperatures.

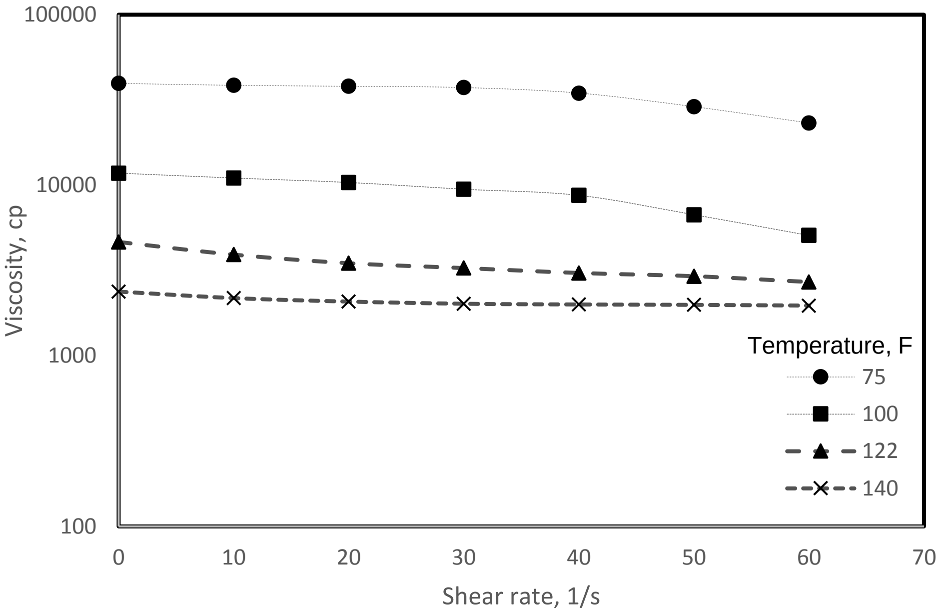


Figure 10 - Viscosity of sample B at various shear rates and temperatures.

In order to study the effects of asphaltene on the viscosity of the oils, viscosity measurements at the same temperatures and shear rates were done on their maltenes portions (deasphalted oil). The impact of the asphaltenes can note over the all range of shear rates and temperatures of 75 and 100 F in Figure 11 and Figure 12. It can be inferred from the results that the viscosity of the heavy oil samples decrease significantly as the asphaltene fraction were removed. Furthermore, the non-Newtonian behavior of oil samples at temperature of 75 and 100 F vanished and the samples become Newtonian after remove of asphaltene fractions.

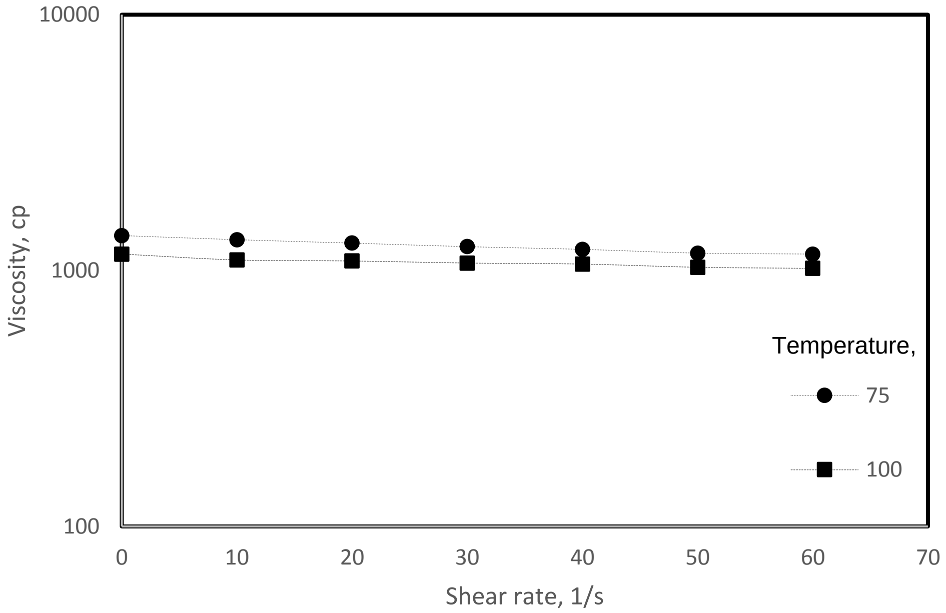


Figure 11 - Viscosity of maltenes A at various shear rates and temperatures.

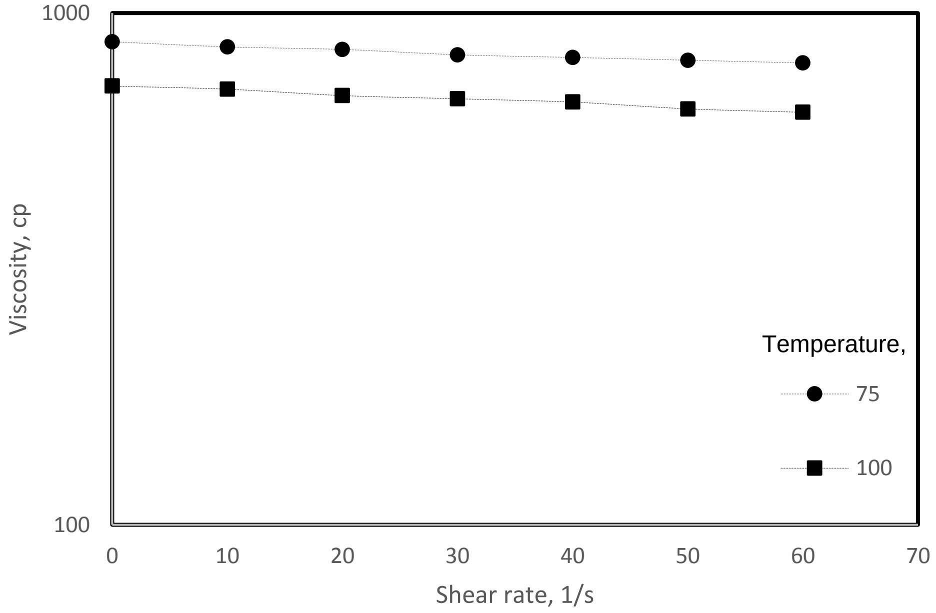


Figure 12 - Viscosity of maltenes B at various shear rates and temperatures.

The sensitivity of the viscosity of crude samples to the temperature are shown in Figure 13, that the viscosity of oil samples are plotted as a function of temperature. Reduction in viscosity of oil samples at higher temperatures can be ascribed to the higher kinetic energy of heavy molecules that leads to the generation of thermal expansion. Hence, the effect of the coherent forces between the heavy organic molecules may diminish at higher temperatures (Huc 2010).

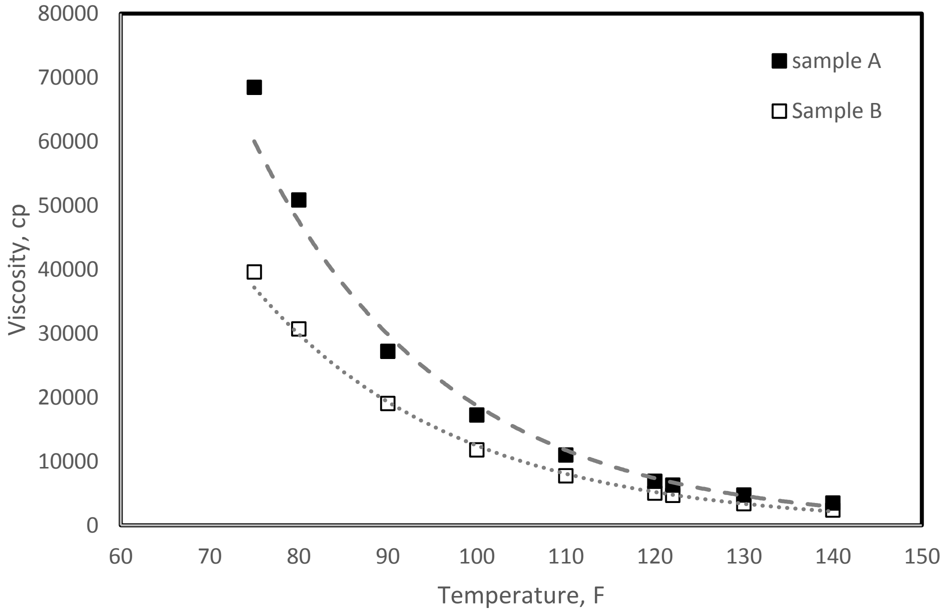


Figure 13 - Viscosity of heavy oil samples as function of temperature.

In other word, the viscosity of oil increases significantly at lower temperature due to entanglement of asphaltene aggregates in the maltenes that generate a concentrated system (Chávez-Miyauchi et al. 2013). At lower temperature, the rheological behavior is controlled by asphaltene and resin self-associations, while at higher temperature thermal effects are dominant as well as the resin peptizing effect.

Different concentrations of ACC were added to the heavy crude oil samples to study their effects on the viscosity. Figure 14 and Figure 15 show the results. The viscosity decreased exponentially as the solvent concentration increased. One reason for this decrease is that the solvent changed the state of the asphaltene particles in the heavy oil.

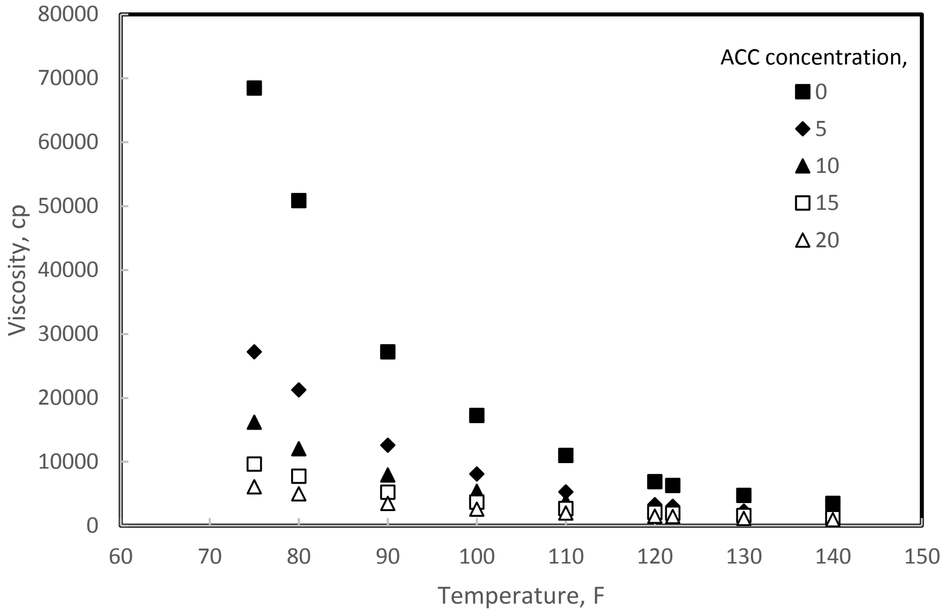


Figure 14 - Viscosity of heavy oil A at various ACC concentrations.

There are three states in which asphaltene particles exist in heavy crude oil: dissolved, steric-colloid, and micelles. The existence of these states depends on the temperature, pressure, oil composition, and polarity of the oil medium. Change in the pressure, temperature, or composition of the heavy oil leads to alteration of the solubility of the oil, such that the asphaltenes, as a surface-active material, starts to self-associate and form different geometric shapes suspended in the solution (Branco et al. 2001).

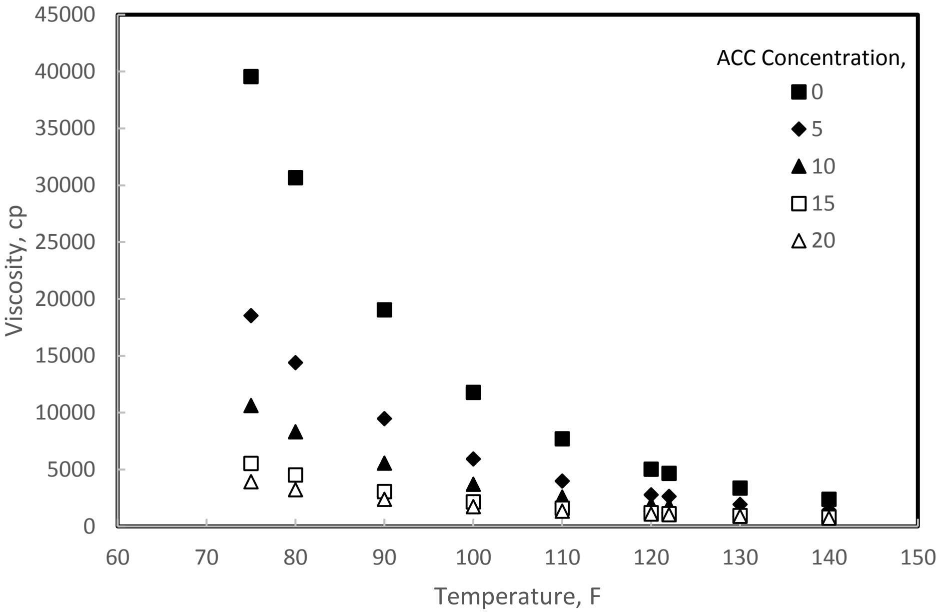


Figure 15 - Viscosity of heavy oil B at various ACC concentrations.

Adding solvent to the heavy oil altered its composition by breaking aggregates of asphaltenes and making them independent particles. This has been accomplished by the polar phenol groups of ACC that are able to interact with the functional groups of asphaltenes. The main reason for the instability of asphaltenes in an aliphatic environment is the existence of isolated polar groups along with the nonpolar hydrocarbon surface. By introducing ACC to the system, its molecules can adsorb on the asphaltene particles and obstruct their polar groups, thus increasing the ability of asphaltenes to interact with aliphatic by making their surfaces more nonpolar. This peptizing effect prevents asphaltenes from self-associating and so it is easier for the fluid to carry these particles and leads to a decrease in the heavy oil viscosity.

In order to draw a comparison between efficiency of ACC and other prevalent chemicals for reducing heavy oil viscosity, different concentrations of light crude oil were added to the crude samples and the same measurement were conducted. Results are shown in Figure 16 and Figure 17. It can be inferred from the results that addition of the same amount of light crude oil to heavy oil sample lead to lower viscosity reduction of the samples.

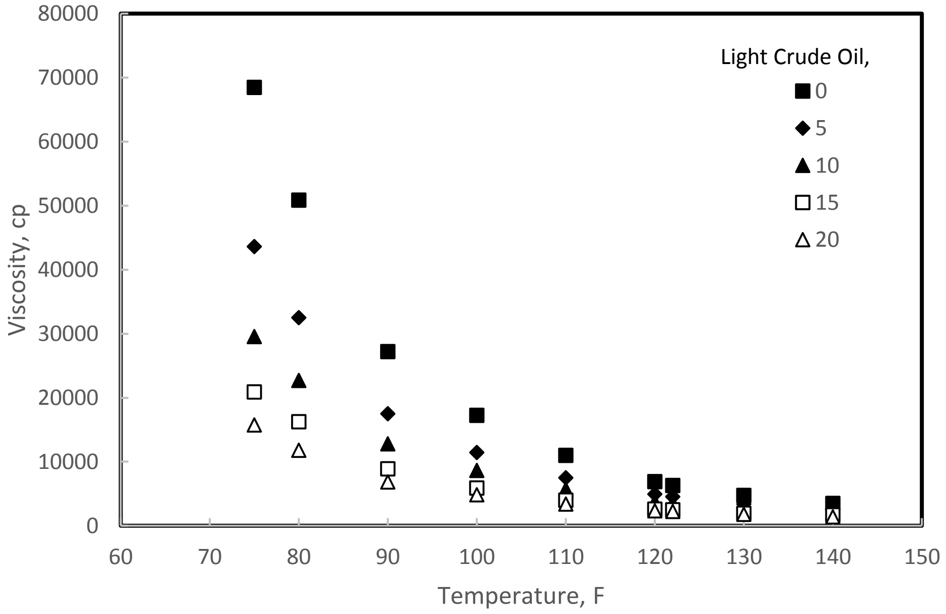


Figure 16 - Viscosity of heavy oil A at various light crude oil concentrations.

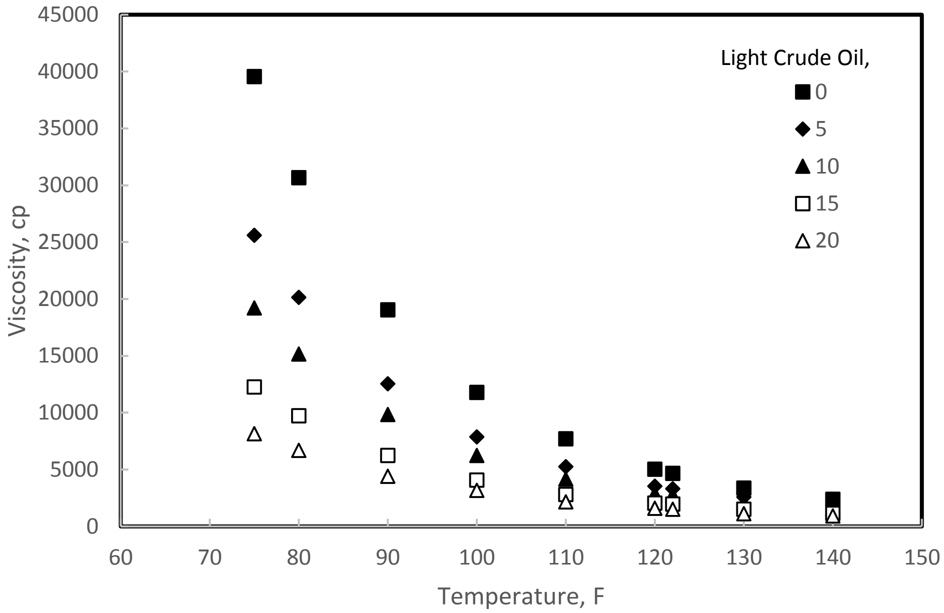


Figure 17 - Viscosity of heavy oil B at various light crude oil concentrations.

The viscosity reduction parameter proposed by Gonzalo-Rojas et al. (1977) was employed to assess the efficacy of ACC at various concentrations and temperatures. The parameter that shows the influence of additives at various temperatures independently of the variation of the viscosity of the original heavy crude oil with temperature is defined as follow:

$$\Psi(c, T) = 100 * (1 - \frac{\mu(c, T)}{\mu(0, T)})$$

where μ is the viscosity (cp), c is the concentration of additive (wt%), and T is the temperature (◦F). Figure 18 through Figure 21 show the values of Ψ at different temperatures, ACC concentrations, and light crude oil concentrations. It can be observed that ACC has the higher viscosity reduction parameter rather than light crude oil.

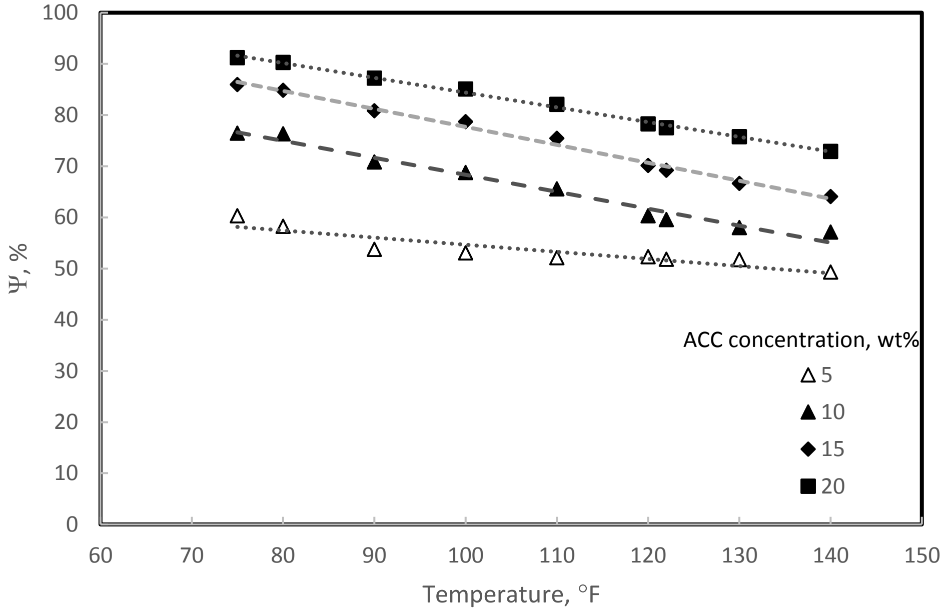


Figure 18 - Viscosity reduction parameter at various temperatures and ACC concentrations for sample A.

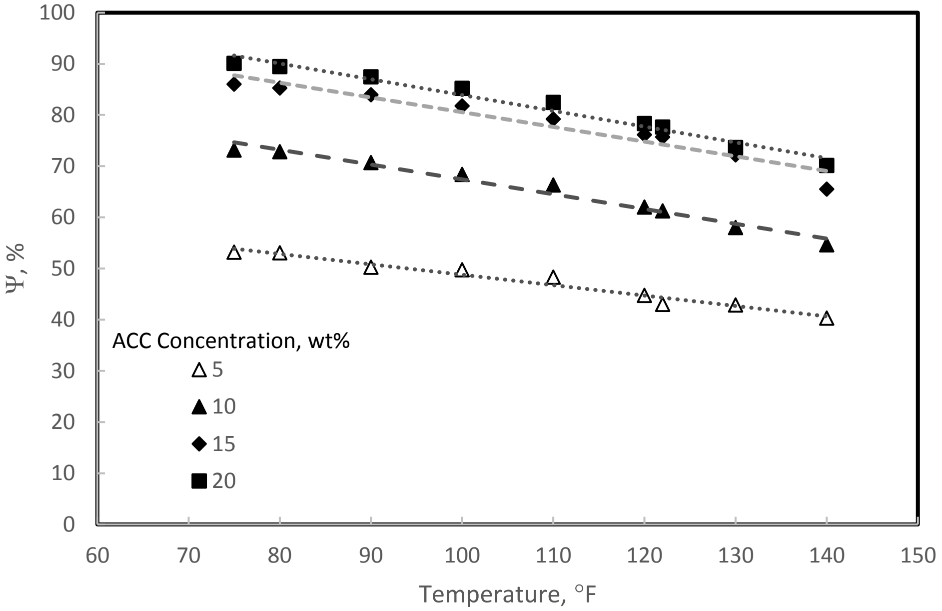


Figure 19 - Viscosity reduction parameter at various temperatures and ACC concentrations for sample B.

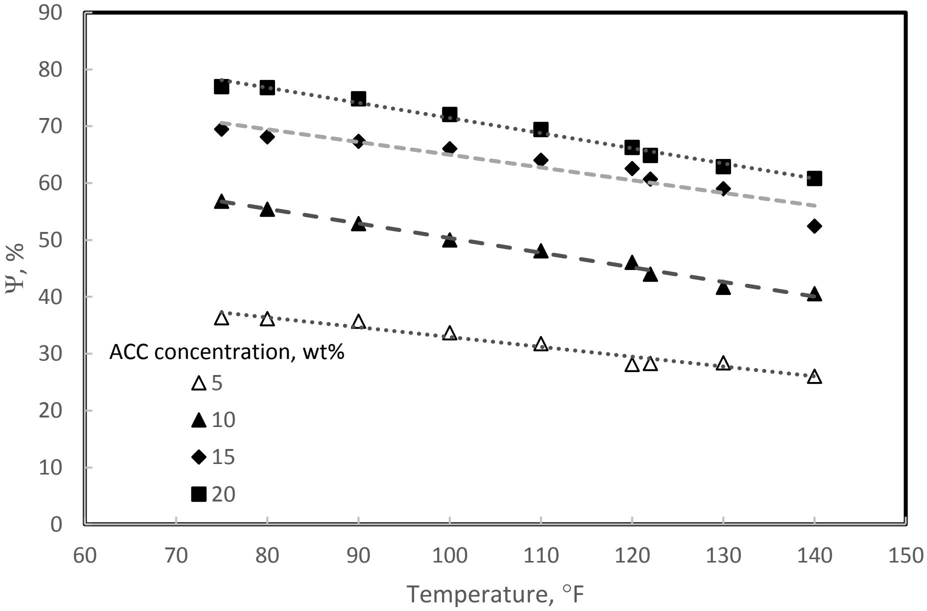


Figure 20 - Viscosity reduction parameter at various temperatures and light crude oil concentrations for sample A.

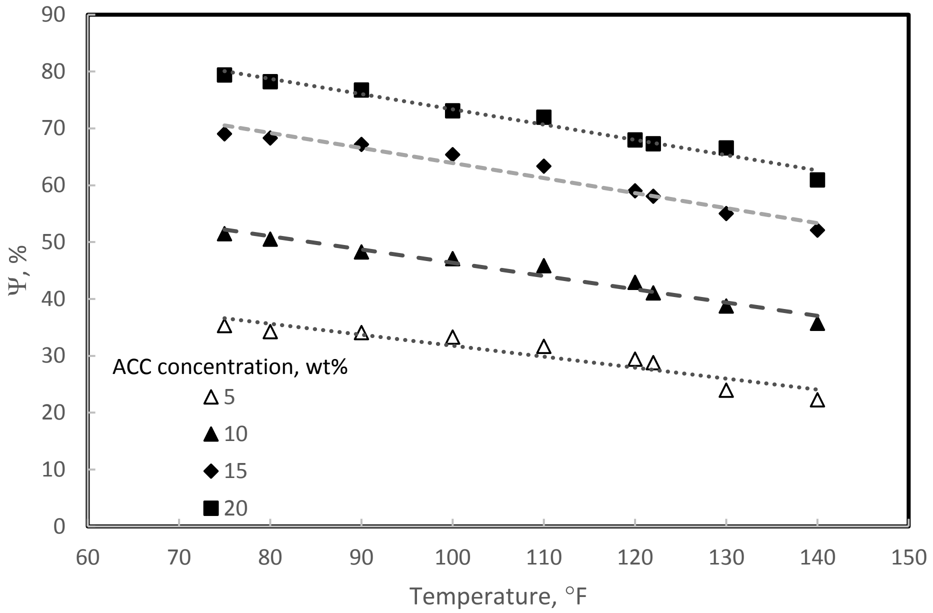


Figure 21 - Viscosity reduction parameter at various temperatures and light crude oil concentrations for sample B.

Due to the presence of aromatic and polar functional groups, asphaltenes tend to associate and form nanoaggregates. Several studies have been done to investigate this process, including defining the concentration at which nanoaggregation initiates and characterizing the nanoaggregates with various methods such as static light scattering, nuclear magnetic resonance, centrifugation measurements, and DC conductivity. Cluster formation can be observed following nanoaggregation if the concentration of asphaltene is increased in the crude oil. This concentration can be interpreted as the critical micelle concentration (CMC) of surfactants, the point at which viscosity elevation starts to occur. Perturbation of crude oil composition and environment can further aggravate the flocculation and precipitation of asphaltenes (Bouhadda et al. 2007; Lisitza et al. 2009; Storm and Sheu 1994).

In order to investigate the effects of addition of ACC to the asphaltene micellization, the crude samples were first deasphltenated by addition of excessive amount of n-pentane. Then the asphaltene were added to the maltenes at concentration range of 0 to 20 wt% with intervals of 2.5 wt% and the viscosity of reconstituted samples were measured. This results are further interpreted by analogy to colloidal suspension using the relative viscosity of the asphaltenes suspended in the maltenes (Argillier et al. 2001). The relative viscosity is expressed as $\mu_r = \frac{\mu_{rec}}{\mu_{mal}}$ where μ_{rec} is the viscosity of recombined sample and μ_{mal} is the viscosity of maltene. The curve of the relative viscosity versus asphaltene concentration is similar to a typical colloidal viscosity curve. These curves for tested oil samples are shown in Figure 22 and Figure 23. Two main region can be differentiated in these curves: the first region, named diluted, occurred when the relative viscosity increased linearly with the weight fraction of asphaltenes. In this part, the difference between viscosity of maltene and reconstituted oil is not significant; however, after the asphaltene content reached a critical concentration, the relative viscosity starts to increase exponentially with increasing asphaltene content. This part of the curve is highly sensitive to asphaltene incrementation such that a small increase in asphaltene results in substantial alteration of relative viscosity. The point in which the significant increase happens is considered as the critical concentration of asphaltene particles.

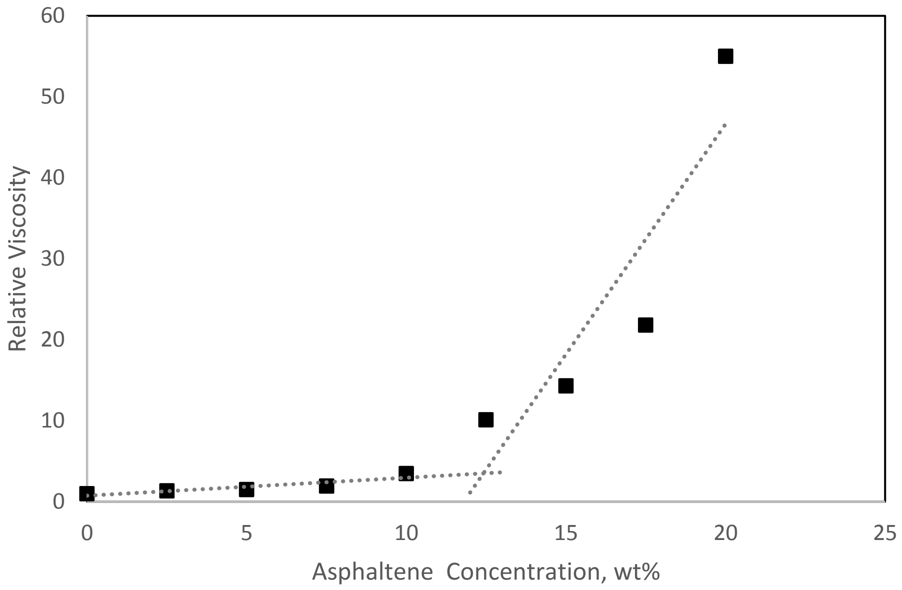


Figure 22 - Relative viscosity of recombined sample A as a function of asphaltene concentration.

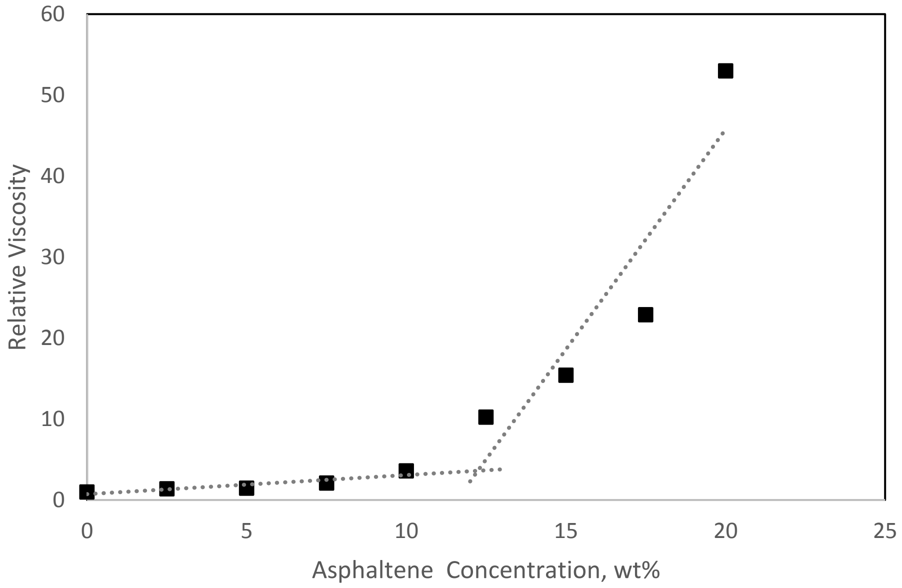


Figure 23 - Relative viscosity of recombined sample B as a function of asphaltene concentration.

This behavior can be explained by asphaltene aggregation propensity. In low concentrations, asphaltene molecules form some disk-like nanoaggregates due to the presence of their aromatic cores. These nanoaggregates consist of six to nine molecules with an average diameter of two nm. These nanoaggregates have no interaction because of the large distances between them. In the diluted regime, only long-range hydrodynamic interactions between asphaltene particles and maltenes exist, and cause the linear increase of the viscosity with respect to the asphaltene content. When the asphaltene concentration exceeds the critical concentration, nanoaggregates start to grow and further associate into micelles with an average diameter of 5 nm. Formation of these micelles initiate at the CMC value of the asphaltene and can be recognized by viscosity and surface tension measurements. In this region, short-range inter-particle interactions become dominant in the solution. In the current study, the critical concentration was determined by observing the sharp change in the relative viscosity curve of the reconstituted oil samples. The critical concentration are 12.41 and 11.96 for sample A and B respectively.

Of special interest in the present work is to study the effect of ACC on the critical concentration of asphaltenes. The critical concentrations of the treated oils in presence of 10 wt% ACC were measured at 75°F (Figure 24 and Figure 25) and were compared with that amount in untreated oil. It can be seen from the results that the critical concentrations of the oils are pushed forward in the presence of the ACC from 12.41 to 14.16 for sample A and from 11.96 to 14.08 for sample B. In other words, asphaltenes started to overlap and form aggregates at higher concentrations in the presence of ACC.

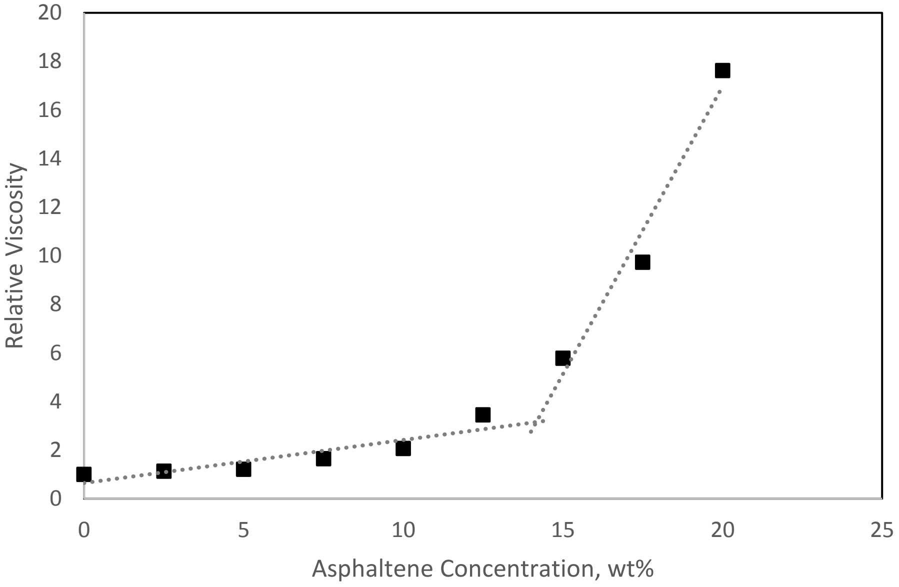


Figure 24 - Critical concentration of sample A after the addition of 10 wt% ACC.

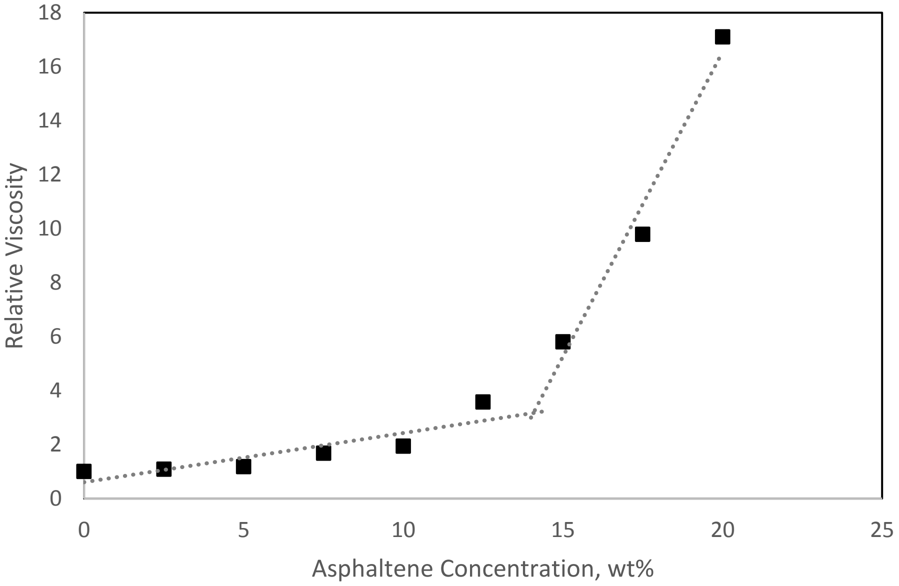


Figure 25 - Critical concentration of sample B after the addition of 10 wt% ACC.

Based on the literature, rheological properties of crude oil alter significantly at various concentrations of asphaltenes. To evaluate the effects of asphaltenes on the viscosity of the oil, models of colloidal dispersions were employed. The relative viscosity of the colloidal dispersion can be demonstrated as:

$$\mu_r = \frac{\mu}{\mu_0} = 1 + [\mu]\phi + K_1\phi^2 + K_2\phi^3 + \cdots$$

where μ is the viscosity of the colloidal dispersion (asphaltenes and maltenes), μ_0 is the viscosity of the continuous phase (maltene), $[\mu]$ is intrinsic viscosity, ϕ is volume fraction of asphaltene, and $K_1$and K_2 are coefficients. Intrinsic viscosity is defined to account for the effects of solvation and the shape of dispersed phase.

Investigation of the dependency of viscosity on temperature can be conducted by Arrhenius equation:

$$\mu_T = \mu_{T_0} \exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

where μ_T is the viscosity of fluid at absolute temperature, μ_{T_0} is viscosity of fluid at reference temperature, R is the universal gas constant, and E_a is the activation energy of viscous flow. To calculate E_a of an oil sample with different concentrations of asphaltene and ACC, values of $\ln(\frac{\mu_T}{\mu_{T_0}})$ versus $\frac{1}{R}(\frac{1}{T}-\frac{1}{T_0})$ were plotted so that the slope of the generated straight line was representative of E_a.

Figure 26 and Figure 27 show the activation energy of the oil samples in different concentrations of ACC that are in the range of 40.92 to 65.02 kJ/mol for sample A and 63.21 to 37.24 kJ/mol for sample B. The activation energy of both the oils and their mixtures with ACC decline as temperature increases. On the other hand, at a higher temperature, it is easier for the fluid to carry particles so that the flowability of the oil improves.

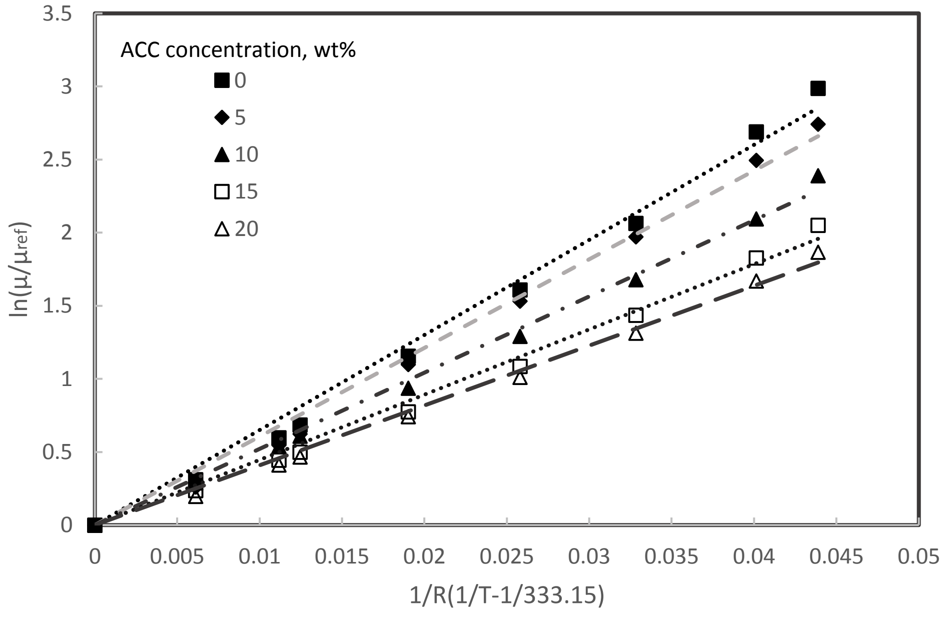


Figure 26 - Activation energy of sample A at different ACC concentrations.

It is also important to note that the activation energies of oils and ACC mixtures decline by addition of ACC. The reason is that due to the peptizing effect of ACC, asphaltene micelles break into smaller particles with lower inter-particle interactions. Hence, the required activation energy to overcome these inter-particle interactions is lower.

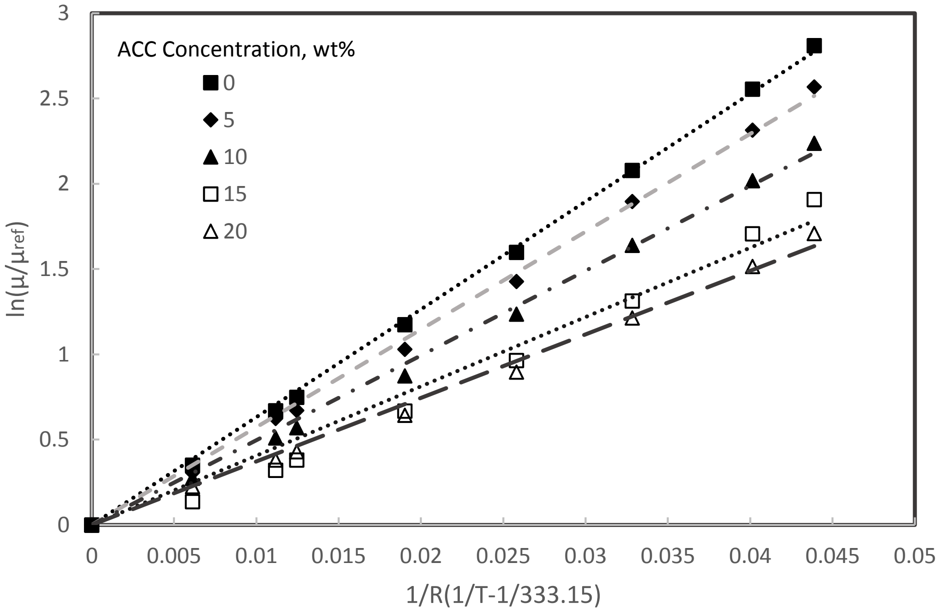


Figure 27 - Activation energy of sample B at different ACC concentrations.

Figure 28 and Figure 29 show the activation energy of heavy oil samples in various concentrations of light crude oil. it can be seen from the results that although addition of light crude oil leads to the reduction of activation energy of the oil sample, the amount of reductions are lower in comparison with addition of ACC.

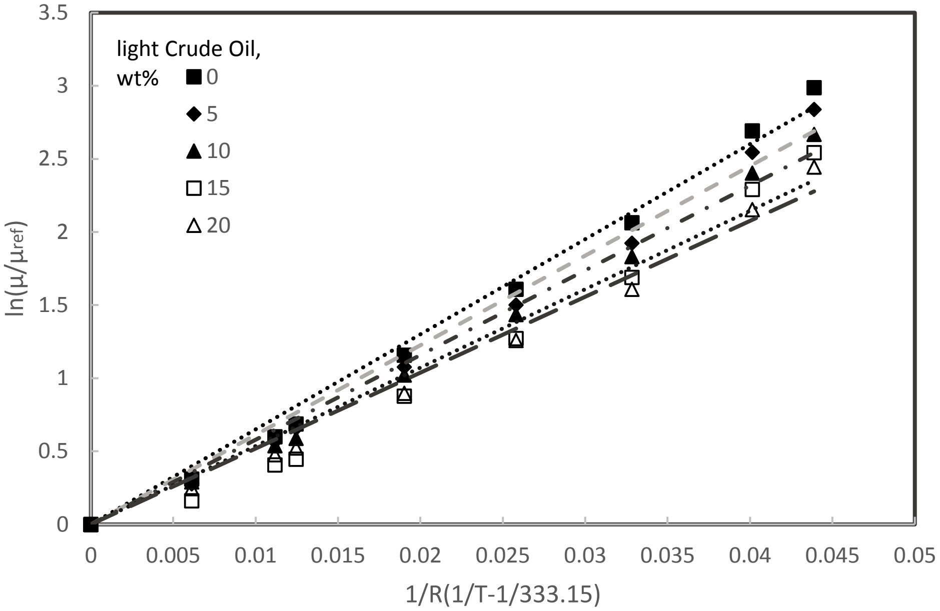


Figure 28 - Activation energy of sample A at different light crude oil concentrations.

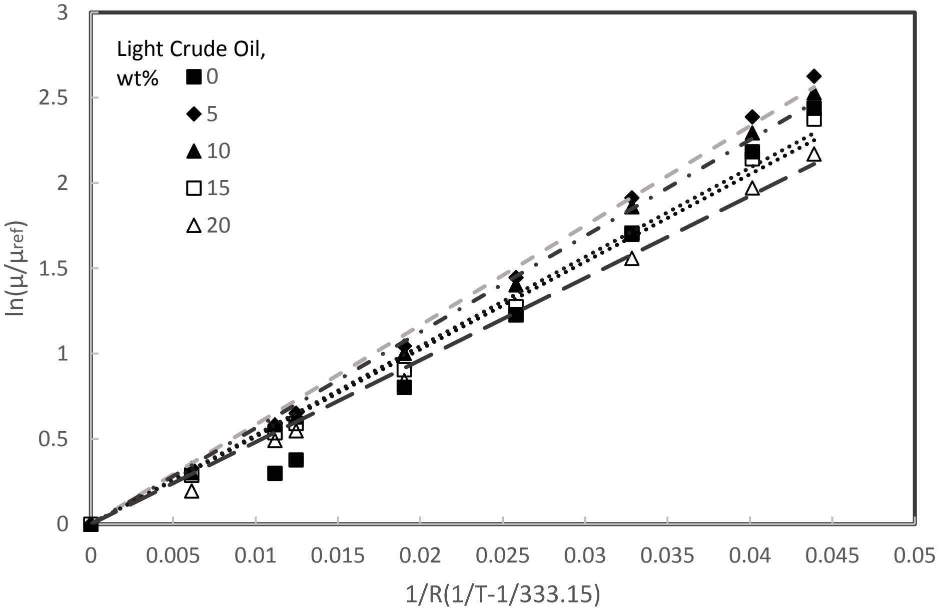


Figure 29 - Activation energy of sample B at different light crude oil concentrations.

XRD

X-ray diffraction is one the method that has been used widely to characterize the structural properties of asphaltene. Macrostructure analyses can provide sufficient information about discrete molecules with simple structure. For a much complicated and bulkier system such as asphaltene, it is necessary to have association and micelle formation information for better characterization. Short-range bonding distance between 0.5 and 2.5 Å are related to microstructure, whereas longer distances between 20 and 2000 Å are assumed as macrostructure. XRD provides microstructural information of asphaltene and dimension of unit cell (crystalline parameters) such as layer diameter, inter-lamellar distance, number of lamellar contributing to the micelle, height of the unit cell, and the aromaticity. These parameters can be related to other physical and chemical properties of asphaltene such as molecular weight.

Yen et al. 1961 studied the X-ray pattern of various asphaltene samples and determined the aromaticity of all these samples. They tried to produce asphaltene like X-ray pattern by combination of polyethylene and carbon black to investigate the origin of the peaks in the asphaltene X-ray pattern. They calculated aromaticity of different substances by using the number of saturated, aromatic, and total carbon atoms per structural unit and then compared these values to the results from X-ray patterns. Shirokoff et al. 1997 studied four asphaltene samples from various crude oils by evaluating the X-ray diffraction patterns. They concluded that the increase in the API gravity of the oil samples may lead to the decrease of aromaticity of asphaltene samples.

Generally, four peaks can be detected in the X-ray diffraction pattern of petroleum asphaltene. Their origin is due to the scattering of X-rays from the period molecular structure of asphaltene (Siddiqui et al. 2002):

1. γ peak: originates from aliphatic chains and condensed saturated rings and can be used to determine the packing distance of saturated structures.
2. Graphene peak: initiates by the stacks of aromatic molecules.
3. 10 peak: originates from the in-plane structure of the aromatics.
4. 11 peak: originates from the in-plane structure of the aromatics.

If the X-ray diffraction pattern of asphaltene consists of broad bands, it means that more short-range order exists in the structure and so the asphaltene is more amorphous. These features are showed in Figure 30.

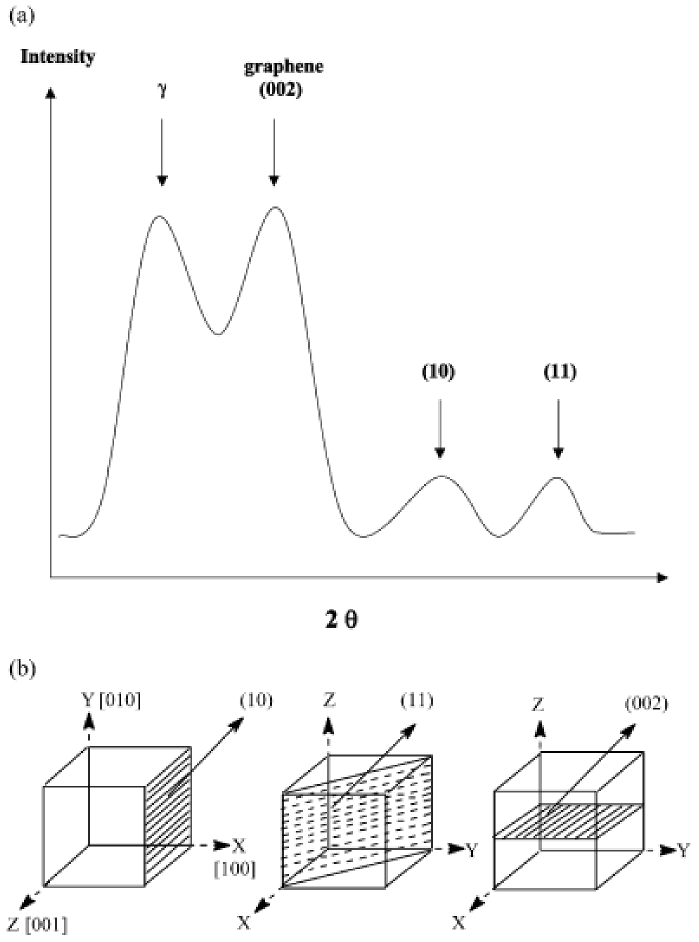


Figure 30 - The bands and planes of X-ray diffraction pattern of asphaltene (Siddiqui et al. 2002).

X-ray diffraction patterns of the (002) peak and the γ peak can be employed to characterize the aromatic sheet and saturated structure of asphaltene. Yen et al. (1961) proposed an approach to determine aromaticity of petroleum asphaltene with X-ray diffraction curves, in which the ratio of the integrated areas under the curves for γ and (002) bands ($A_\gamma$and A_{002}) would be representative of aromaticity:

$$f_a = \frac{A_{002}}{A_{002} + A_{\gamma}}$$

The equation used for calculation of f_a is based only on the stack cluster aromatic carbon to the graphene peak and not due to all the aromatic carbon of asphaltenes. Yen et al. 1961 showed that the calculated aromaticity values from XRD are in the good agreement with aromaticity values calculated by the number of saturated, aromatic, and total carbon atoms per structural units. Eilers 1949 observed that aromaticity and hydrogen to carbon ratio have inverse relation, so that an increase in hydrogen to carbon ratio lead to decrease in aromaticity. To evaluate the validity of this statement, the aromaticity and H/C of asphaltene samples were plotted by Yen et al. 1961. Although their results followed the conclusion made by Eilers 1949, it should be noted that due to presence of nitrogen, oxygen, and sulfur, this relationship would not be followed by all asphaltene samples.

Using X-ray diffraction curves and Bragg relation, additional crystalline parameters of asphaltene including the interlayer distance between aromatic sheets (d_M), the interchain distance between saturated parts (d_{γ}), the diameter of aromatic clusters perpendicular to the plane of the sheet (L_c), and the diameter of the aromatic planar sheet (L_a), can be approximated by the following equations.

Layer distance between aromatic sheets can be calculated using Bragg relation and the maximum of the graphene band:

$$d_M = \frac{\lambda}{2\sin\theta}$$

d_M, that is representative of the flatness and size of aromatic sheets, responds to the effects of impurities such as saturation, heteroatoms, and aliphatic and naphthenic edge groups that lead to bulges or bends in the aromatic sheets. The distance between the saturated portions of the molecules or inter-chain layer distance is calculated by following equation:

$$d_\gamma = \frac{5\lambda}{8\sin\theta}$$

It is shown in previous studies that interlayer spacing between aromatic sheets in fully ordered graphite structure is 3.354 Å, while it is 3.55 Å in amorphous carbon and it may decrease to 3.44 Å. Therefore, based on interlayer distance, asphaltene is categorized as the amorphous materials of little order. Results obtained by previous studies are summarized Table 3.

Asphaltenes	f_a	d_M	d_γ
Burgan	0.38	3.55	4.6
Wafra, No. A-1	0.37	3.57	4.6
Mara	0.35	3.57	4.7
Wafra, No.17	0.35	3.57	4.8
Ragusa	0.26	3.60	4.8
Baxteville (Resin)	0.22	3.70	4.7
Tabor vein	0.14	6.50	4.9
asph 1 F	0.16	3.51	4.28
asph 2 OA	0.29	3.48	4.87
asph 4 Alaska	0.23	3.50	4.31
Arab Heavy	0.19	3.6	4.4
Arab Medium	0.16	3.6	4.5
Arab Light	0.19	3.6	4.4
Arab Berri	0.20	3.6	4.4

Table 3 - Aromaticity and crystalline parameters for asphaltene from literature.

In the present work the repeatable structural features of asphaltenes were characterized by using X-ray diffraction method. Furthermore, aromaticity of asphaltene sample was calculated by X-ray pattern. Any alteration in these structural parameters and aromaticity due to addition of the solvent were also studied.

In order to obtain any quantitative information from X-ray diffraction patters of asphaltene it is necessary to fit a theoretical distribution to the pattern. In the present study Gaussian and Lorentzian fitting procedure were employed and applied by using Origin software. The fitting procedure starts with estimating initial values for the peaks of patterns that are γ band, graphene band, 10 band, and 11 band for asphaltene. In some cases 11 band cannot be recognized in the asphaltene pattern. Then the regression initiates with estimation of the peak width and intensity. Defining of the baseline is one of the major problem for asphaltene, since the baseline cannot be defined sufficiently at the high and low side of 2θ. Defining the baseline can introduce statistical inaccuracies that may influence the outcome, however, it was observed that the change in the baseline had very little influence on the relative results such as aromaticity. In all cases manual refinements were applied to enhance regression coefficients.

The final procedure includes following steps:

1. Determining a baseline at the lowest value in the high range of 2θ.
2. Fit the 10 band by initial estimations of other peaks.
3. Fit the γ and graphene bands by initial estimations of other peaks with the goal of producing the cumulative shape of patters.
4. Manually refine the position and parameters of the peaks.
5. Preform a regression analysis of each individual peaks.

Asphaltene crystalline parameters obtained by above procedure are reported in Table 4. Since aromaticity plays a key role in asphaltene stacking mechanism, its alteration due to the addition of ACC should be investigated to provide more information about the parameters that would change aromaticity. The main advantage of determining aromaticity using XRD is that it gives the aromaticity of the fraction of aromatic carbon that have ability of stacking (Andersen et al. 2005). The results of Table 4 shows that the primary aromaticity of the asphaltene sample was 0.23, however, after addition of ACC this value decreased to 0.19. It means that the introduction of ACC to the oil altered the structure of asphaltene cluster and made it less aromatic. Less aromaticity can be result of shortening of alkyl side chains or removal of aromatic rings. Results convey an increasing trend for d_M values after addition of ACC that is also in agreement with the decreasing trend of aromaticity. Reduction in aromaticity implies a decrease in the molecular moieties that initiate stacking and yields a less ordered structure.

Alteration of aromaticity and structural parameters of asphaltene due to various conditions such as aging and fractionation were reported in several previous studies (Andersen et al. 2005, Siddiqui et al. 2002). Results of current study, in agreement with those of previous works, show that various interactions including aging (hydrogenation) and hydrogen bonding affect the aromaticity and stacking behavior of the asphaltene. However, it should be noted that the structure of solid asphaltene might differs from its structure in dissolved state and thus requires further investigation on the structural properties, if any exist, in the dissolved state.

	f_a	d_M	d_γ
0 wt% ACC			
Lorentzian	0.23	3.42	4.39
Gaussian	0.23	3.46	4.48
20 wt% ACC			
Lorentzian	0.20	3.46	4.42
Gaussian	0.19	3.49	4.51

Table 4 - Crystalline parameters of asphaltene sample with 0 and 20 wt% of ACC

FTIR

Figure 31 shows FTIR spectrum of ACC. A broad peak at the wavenumber of 3310 cm^{-1} can be observed that is representative of axial stretching of O─H. Existence of the C─H bond in olefin can be proved due to a peak at 3,005 cm^{-1}. The peaks at 2,920 and 2,853 cm^{-1} can be assigned to C─H bond. The aromatic ring can be detected from the peak at 1,455 cm^{-1} which is representative of C═C. the peak at 1,260 cm^{-1} is related to Axial stretching of C─O. From the above information the existence of unsaturated phenolic compounds in the ACC can be proved.

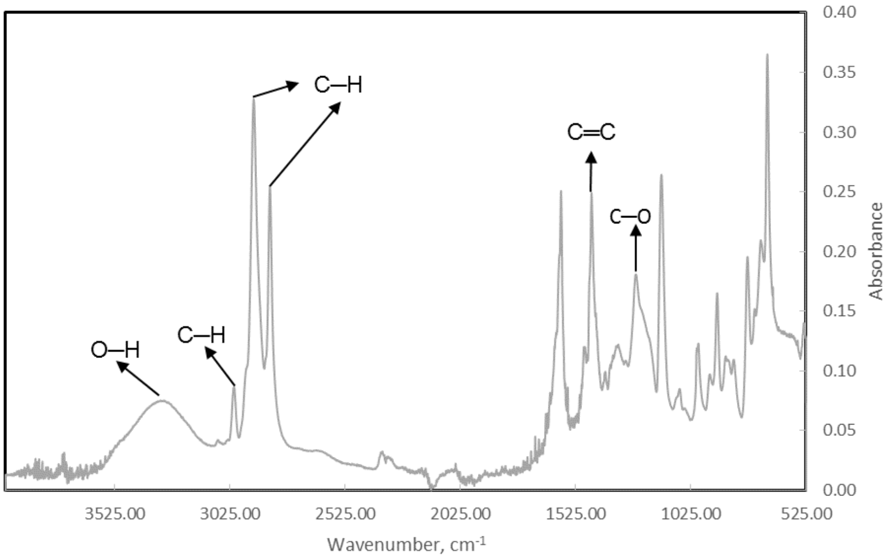


Figure 31 - FTIR spectrum of ACC.

The FTIR spectrum of asphaltene is shown in Figure 32. A broad peak at 3,360 cm^{-1} that can be assigned to O─H bonds. Presence of C─H bond can be proved by existence of two sharp peaks at 2,920 and 2,853 cm^{-1}. Also a peak at 1,590 cm^{-1} is representative of C═O bond. Finally, a peak at 1,450 cm^{-1} can be assigned to C═C bond. The spectrum and the functional groups in it are in agreement with previous studies (Perez-Hernandez et al. 2003).

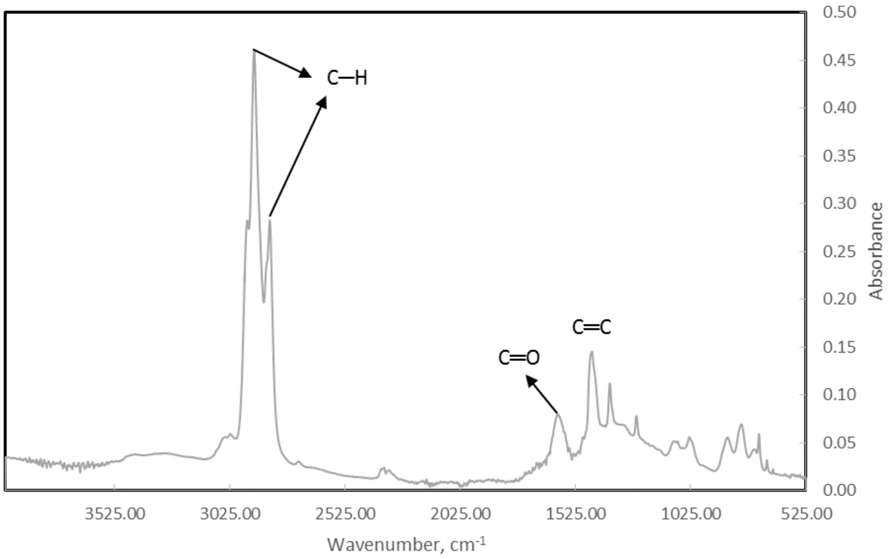


Figure 32 - FTIR spectrum of asphaltene.

The main mechanism that leads to improvement in the viscosity of the oil is the peptizing effect of ACC. Asphaltene molecules consist of polar and non-polar portions that are responsible for the formation of their particular solubility. The polar groups of ACC are able to interact with the polar functional groups of asphaltene particles and so decrease their polarity. Hence, due to decrease in the polarity, asphaltenes become able to interact with aliphatic portion of the oils. These interactions are also occurred between the π electrons of naphthalenic and aromatic parts of asphaltenes and OH functional groups of ACC.

In order to observe hydrogen bonding interactions between ACC and asphaltenes, the alteration of absorbance intensity of O─H peak of ACC after addition of asphaltene was investigated. This approach was done by Chang and Fogler 1994 to evaluate the effects of various amphiphiles on asphaltene stabilization. 5 wt% of asphaltene was added to the ACC and the change in the intensities of O─H peak both between 3100 to 3500 cm^{-1} and between 3640 to 3660 cm^{-1} were evaluated. It can be observed that intensity of O─H peak was decreased after addition of asphaltene (Figure 33).

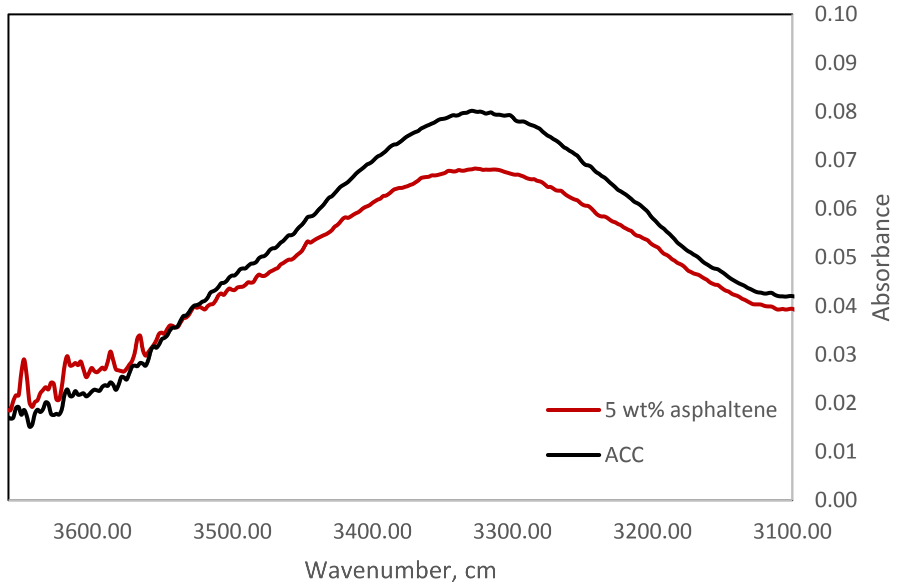


Figure 33 - FTIR spectrum of ACC (black) without asphaltene, and (red) with 5 wt% of asphaltene

To quantify the peptization effect of ACC the integrated absorbance of O─H peak was calculated using Origin software. It is observed that the integration of O─H peak absorbance decreases from 2.6 to 1.89 after addition of 5 wt% asphaltene. So addition of asphaltene leads to a decrease in free OH stretching bands of ACC.

CHAPTER IV

CONCLUSION

A new type of plant-based solvent was synthesized and evaluated in terms of reducing viscosity of heavy and extra heavy oil. Functionalized molecules of solvent are capable of interacting with asphaltene aggregate and lowering its size such that the viscosity of the oil is modified as well. Experimental evaluation was done by conducting compositional fractionation, viscosity measurements, FTIR, and XRD. Following result were observed from experimental studies:

- High viscosity reduction can be achieved in wide range of temperature by applying proposed solvent. These results were confirmed by the decreasing trend of activation energy after addition of solvent. The decrease of the viscosity was sufficient for transportation and production purposes.
- Efficiency of both proposed solvent and toluene were diminished at higher temperatures. This decreasing trend is due to the decreasing of solvent power and limiting hydrogen bonding formation at higher temperatures.
- Application of solvent leads to higher viscosity modification efficiency rather than toluene. Furthermore, as the solvent is a plant-based product, it does not have the toluene hazardous effects.
- Quantitative analysis of FTIR results indicates the formation of hydrogen bonding between molecules of solvent and asphaltene. This is the primary interaction that leads to breaking of asphaltene aggregations and lowering the viscosity.

- XRD results reveal the alteration of aromaticity and interlayer distance between aromatic sheets (d_M) after addition of solvent. The decrease of asphaltene aromaticity is indicative of the decrease in its propensity toward stacking. Also increasing of (d_M) value shows that the ordering of the asphaltene structure is reduced which is in agreement with aromaticity reduction.

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