RHEOLOGICAL CHANGES IN CRUDE OIL DILUTED WITH ALCOHOLS

BY

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Submitted in partial fulfillment of the requirements for the degree of Master of Engineering

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Faculty of Engineering,

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Signature of Author
DEDICATION

I dedicate this project wholeheartedly to the Almighty ALLAH for giving me strength and the courage to pursue this program. Furthermore, I dedicate it to my dear parents, brothers, sisters and my entire family for their unconditional support. Thank you.
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ABSTRACT

Growing oil demand is encouraging the development of the world’s huge energy resources of heavy oil and bitumen. But their high viscosity is a huge problem in their utilization as they cannot be transported without proper treatment. A number of methods have been developed for the transportation of heavy oil which includes use of diluents, heated pipelines, emulsions and crude oil upgrading.

Many kinds of diluents have been used to reduce the viscosity. Some of the most used diluents are gas condensates, light hydrocarbons and kerosene. Since the light crude oil and condensate reservoirs are depleting, there is a need to find more alternative diluents for the transport of these huge energy resources. Through many studies, it has been found that solvents having polar functional groups are more effective in reducing heavy oil viscosity.

Since alcohols have polar functional group in their molecule, so they could prove effective in heavy oil viscosity reduction. In this project, experiments were performed on heavy oil sample and a medium crude oil sample using different combinations of alcohols as solvents. Among the combinations used, a mixture of methanol and ethanol with toluene was found most efficient viscosity reducer of crude oils.
# LIST OF ABBREVIATIONS USED

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>API</td>
<td>American Petroleum Institute</td>
</tr>
<tr>
<td>CAF</td>
<td>Core Annular Flow</td>
</tr>
<tr>
<td>cP</td>
<td>Centipoises</td>
</tr>
<tr>
<td>DV</td>
<td>Digital Viscometer</td>
</tr>
<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
</tr>
<tr>
<td>MEK</td>
<td>Metylethylketone</td>
</tr>
<tr>
<td>mL</td>
<td>Milliliter</td>
</tr>
<tr>
<td>mPa.s</td>
<td>Milli Pascal second = centipoise</td>
</tr>
<tr>
<td>O/W</td>
<td>Oil/Water</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions per minute</td>
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</tbody>
</table>
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All the praises are for The Almighty, ALLAH, the most Beneficial and the most Merciful.

I would like to extend my gratitude to Dr. Michael J. Pegg who supervised my work and guided me throughout my degree program. I am also thankful to Dr. Stephan Kuzak who added his comments and corrected me where required.
CHAPTER 1
INTRODUCTION

1.1 Heavy Oil

Heavy oil is a type of crude oil that is very viscous. Because of its high viscosity, it does not flow easily. It is referred to as heavy oil because its density and viscosity are higher than the light crude oil. Crude oil with API gravity less than 20° is classified as heavy oil. And the crude oil with API gravity of less than 10° is termed extra heavy oil. API gravity is a specific gravity scale developed by the American Petroleum Institute to measure the relative density of various petroleum liquids, expressed in degrees. The lower the API number, the heavier the oil and the higher its specific gravity. The common characteristic properties of heavy oil are high viscosity, high specific gravity, high molecular composition, and low hydrogen to carbon ratio, high carbon residues and high contents of asphaltenes, heavy metal, sulphur and nitrogen.

Goodarzi et al., (2009) defined heavy oil in terms of viscosity for the class of crude oils ranging from 50cP to 5000cP. Heavy oil does not flow easily because of high viscosity. The relationship of viscosity and API gravity is shown in Fig. 1.1, which shows the heavy oil region in the high viscosity range.

Hydrocarbon resources of heavy oil and oil sands are nearly three times the conventional oil in place in the world. There are estimates that over two trillion barrels of oil is present in the oil sands of Alberta. In Canada, the contribution of heavy oil and oil sands resources is 20% of the total oil production. Herron (2000) in his article “Heavy Oil: A Solution to Dwindling Domestic Oil Supplies” wrote that the total estimate of worldwide deposits of heavy hydrocarbons is
around 5½ trillion barrels and the western hemisphere contains four-fifths of these deposits. From the crude oil distribution chart shown in Fig.1.2 it can be concluded that the outlook for domestic oil supplies can be much improved if the heavy oil hydrocarbon resources (both heavy crude oil and natural bitumen) are included in petroleum sources.

Figure 1.1 - General relationship between viscosity and API gravity of crude oil [Thomas, 2008]

Figure 1.2 - Distribution of conventional crude oil and heavy hydro carbons [Herron, 2000]

1.2 Viscosity of Heavy Oil

Meyer et al., (2007) explained the possible reason for high viscosity of heavy oil. According to them, the oil became heavy as a result of the eradication of light fractions through natural
processes after evolution from the natural source materials. A high proportion of asphaltic molecules with substitution of hetero-atoms in the carbon network of such as nitrogen, sulfur, and oxygen also play an important role in making the oil heavy. Therefore, heavy oil, regardless of its source, always contains the heavy fractions of asphaltenes, heavy metal, sulphur, and nitrogen. The large asphaltic molecules define the increase or decrease in the density and viscosity of the oil. Removal or reduction of asphaltene drastically affects the rheological properties of particular oil.

1.3 Asphaltenes

Petroleum asphaltenes represents a solubility class of petroleum fluids. They are defined formally as the crude oil fraction that is insoluble in n-alkane, usually n-pentane or n-heptane, but remains soluble in toluene or benzene. This operational definition of asphaltenes is used because asphaltenes contain about $10^5$ to $10^6$ molecules of different shapes and sizes and hence it is impossible to define any asphaltene purely by its chemical structure. Asphaltenes constitute the most refractory, polar and heaviest component in crude oil (Yen and Chilingarian, 1994). Because of these distinctive characteristics, asphaltene is considered a prime factor that causes difficulties in many petroleum operations such as production, transportation, refining, even wax crystallization, crude oil emulsification, and de-emulsification. It is natural to associate these negative impacts with particular molecular and thermodynamic properties of asphaltene. Such properties may include molecular weight, structures, and charge content as the molecular parameters, and unusual short-range interaction and strong propensity for self-association as thermodynamic related characteristics. It has taken researchers over a century trying to understand the molecular and colloidal properties of asphaltenes. Yet, many issues around asphaltene are still controversial and considered unsettled (Sheu, 2001).
1.3.1 Appearance

Asphaltenes extracted with n-heptane are usually shiny black solids (Fig.1.3). From their appearance, they are often assumed to be crystalline, but in fact they are amorphous. Solutions containing visible asphaltene aggregates do not transmit any light through crossed polarizing filters unless they also contain wax crystals. There is much less difference in appearance among asphaltene aggregates in crude oil before separation and drying. Describing asphaltene phase behavior as a liquid-liquid separation, as suggested by Hirschberg et al. (1984), has led to models that have been increasingly successful. The current evidence is consistent with the view that asphaltenes are liquids that may be in a glassy state, depending upon temperature.

Figure 1.3 - n-C₇Asphaltenes

1.3.2 Properties and characterization

Asphaltenes are the least soluble components of crude oil and have a tendency to aggregate together strongly. The asphaltenes are rich in ring groups; with a size of ring groups ranging from 1-7 rings in a single cluster. Bridges between these clusters give larger molecules and extreme diversity of composition. Because of the aggregation of the asphaltenes, total molecular analysis by methods such as mass spectrometry has not yet been achieved.
The results obtained while determining the molecular size or molecular weights were different, depending on the technique used. These measurements can produce results that are too high because of the tendency of asphaltene components to associate with each other. The maximum and minimum sizes are both controlled by solubility. The least soluble large aromatic clusters gives the smallest asphaltenes, with molar masses in the range of 400-500 Da (Dalton is defined as one twelfth of the mass of an atom of carbon-12 in its nuclear and electronic ground state, and has a value of $1.6605 \times 10^{-27}$ kg). The largest possible molar mass depends on the geological processes that form petroleum, and on solubility in the original petroleum liquid. There is no proper evidence available, but there is a consensus of most researchers that the upper limit of the molecular weight of asphaltenes is in the range of 2000-3000 Da. Due to molecular aggregation, all methods of measuring the average molar mass suffer from undefined biases and errors.

Leon et al, (1998) performed surface tension and stability measurements to examine the self-association behavior of two different asphaltene samples, one from a stable crude oil (non-precipitating) and the other from an unstable (precipitating) crude oil. Asphaltenes from unstable crude oils were characterized by high aromaticity, low hydrogen content, and high concentration of the aromatic rings. Asphaltenes from stable crude oils showed low aromaticity, high hydrogen content, and low condensation of their aromatic rings. Leon et al showed that these structural and compositional characteristics of the asphaltenes are strongly under the influence of their self-associating behavior. They found that asphaltenes from unstable oils begin to aggregate at lower concentrations than asphaltenes from stable oils.

Petersen (1967) used infrared spectrophotometry to study the presence of intermolecular and intramolecular hydrogen bonding in asphaltenes. He found that asphaltenes were more difficult to dissociate in carbon tetrachloride and exhibited more intramolecular bonding than maltenes.
He suspected that in addition to oxygen and nitrogen atoms, π-bases were important in hydrogen bonding. Since the association forces of hydrogen bonding are large, these forces probably play an important role in the properties and self-associating behavior of asphaltenes.

Maruska and Rao (1987) studied the role of dipoles in asphaltene association and concluded that interactions between hetero-atoms are responsible for asphaltene association. They quantified the dipole moment of asphaltenes by applying dielectric spectroscopy to several heavy oils with different asphaltene concentrations. The response of the permanent dipoles was measured as a function of concentration and temperature. They showed that as the concentration of asphaltenes exceeded 10%, the dielectric constant exhibited substantial negative deviation from linearity, signifying the onset of intermolecular interactions. They also noted that raising the temperature increased the dielectric constant, indicating dissociation of the aggregates.

Thus, it is seen that many researchers proposed different theories for the self-association property of asphaltenes, but up till now there has been no agreement on any proposal because of the complex nature of asphaltenes.

1.3.3 When do asphaltenes cause problems?

The problems caused by the presence of asphaltenes do not only depend upon the quantity of asphaltene in the oil. What matters is the stability of those asphaltenes and the stability depends on how good a solvent the rest of the oil is for its asphaltenes. De Boer et al. (1995) found that light oils containing small amounts of asphaltenes are more likely to cause problems during production than heavy oil with larger amounts of asphaltenes, because heavier oil also contains plenty of intermediate components that are good asphaltene solvents whereas the light oil may consist largely of paraffinic materials in which, by definition, asphaltenes have very limited
solubility. If heavier oils are mixed with another crude oil during transportation or by other steps in oil processing, the asphaltenes may become unstable and cause problems. This concludes unstable asphaltenes in crude oils as problematic.

The instability of asphaltenes in crude oil may occur due to compositional changes in the crude oil which can arise because of gas injection, phase separation, introduction of incompatible chemicals and mixing different crude oils. Also, temperature and pressure changes are major factors of asphaltene instability in crude oil.

Unstable asphaltenes can form a separate phase that might plug the oil-bearing rock formation near a well. They can also aggregate at oil/water interfaces where they stabilize water-in-oil emulsions, or at oil/solid interfaces where they can alter surface wetting properties or accumulate and plug well bores and flow lines. Asphaltene precipitation can cause major problems during the transportation of bitumen and heavy oil. The flow of paraffin diluted bitumen through transportation pipelines and processing equipment can result in deposition of precipitated asphaltenes. This deposition causes higher pumping rates and can lead to a buildup of internal pipeline pressure (Agrawala, 2001).

1.4 Objective

Having discussed the reasons for the high viscosity of heavy crude oil, it is established that self-association of asphaltenes needs to be inhibited in order to reduce the viscosity of crude oil so it can be easily transported via pipeline. Addition of diluents to heavy oil can break the aggregation or self-association of asphaltenes.
This study has two objectives. The first objective of this work was to study the effect of a mixture of alcohols as diluents on the viscosity of crude oils. The alcohols selected for this purpose were methanol, ethanol and propanol because of their higher polarities among alcohols. Different combinations and concentrations of these alcohols were used as diluents with toluene. It was expected that the high polarities of alcohols will cause a higher viscosity reduction of heavy oil.

The other objective was to achieve sufficient viscosity reduction of crude oils for pipeline transportation using minimum volume of diluents, reduced cost of diluents while avoiding flocculation of alcohols which could reduce the viscosity reduction. It should be stated here that theoretical derivation and calculation of combined solvent polarities is not part of this work.
CHAPTER 2

METHODS FOR PIPELINE TRANSPORTATION OF HEAVY OIL

Historically, demand for heavy and extra-heavy oil has been insignificant because of their high viscosity and composition complexity that make them difficult and expensive to produce, transport and refine. However, to replace the declining production of conventional middle and light oil, there is a growing interest in the use of non-conventional heavy and extra heavy oil resources to produce fuels and petrochemicals. But the transportation of heavy oil to energy markets presents vital challenges that require considerable technological developments in the production chain. The most convenient way of continuous and economical transportation of crude oils is through pipelines. However, because of the high viscosity, low mobility and flowability, and wax and asphaltene deposition on pipeline wall surfaces; transportation of heavy and extra heavy oils is complicated (Aburto et al., 2010).

Transportation of heavy crude oil and natural bitumen requires that the viscosity be low enough so that the size of the pipeline and the pumping requirements are optimum economically (Escojido et al., 1991). There are several methods of achieving these characteristics, some of which have been confirmed in the field and are currently being used, while others are in the process of being developed. These methods are:

- Heating
- Dilution
- Oil water emulsions
- Core annular flow
- Partial field upgrading
A brief description of each method follows (except for dilution which will be discussed in detail in next chapter).

### 2.1 Heating

Heating is a common method used to facilitate the transportation of heavy oil by pipeline (Hasan et al., 2010). This method has been in use since 1955 in Venezuela. The concept behind this method is that the viscosity will decrease as the temperature of the oil is increased, and lower viscosity is easier to pump. Therefore it is important to heat the oil to a point where the oil has a considerably reduced viscosity. Most pipelines are designed for viscosities of less than 500 centistokes at the pump outlet. Fig. 2.1 shows the relationship of viscosity and temperature for different Canadian crude oils from Alberta. It is clear from the figure that as the temperature of crude oil rises, the viscosity is reduced.

![Figure 2.1 - Response of viscosity to change in temperature in some Alberta oils (Raicar and Procter, 1984)](image-url)
The principle is to maintain the temperature at which the oil is produced at the well-head by insulating the pipelines (Aburto et al., 2010). However, external heating of the heavy oil is always required because of heat losses that result from low flow or unused pipeline capacity. Oil is then reheated in the pumping stations through direct-fired heaters. Insulation options include burying the pipeline to conserve heat. Traditional oil pipelines operate with a low vapor pressure restriction, close to ambient pressure, in order to maximize their capacity.

A direct-fired heater is generally used to raise the temperature of the oil. Heaters can be natural gas or fuel oil fired. Variations of temperature due to flow rate changes; cause a longitudinal expansion of the pipeline (Guevara et al., 1997). For above ground lines, expansion loops are used to absorb the expansion, and for buried lines, thicker steel is required in order to absorb longitudinal compression stresses. Plugging generally occurs when the lines are cooled down to ambient temperature; therefore displacement oil must be used during start-up (to heat the line) and shutdown operations (to secure future start-up without difficulty).

Ghannam and Esmail (2006) studied the thermal flow enhancement of a Canadian crude oil (density = 0.929, viscosity = 1375 cP at 393.15 K). The viscosity at 10 s⁻¹ shear rate was reduced from roughly 700 to 300 cP by heating the medium crude oil from 283 to 303 K. However, the authors concluded that the preheating of this kind of medium crude oil is unreasonable because subsequent heating is required to maintain flow.

Perry (2007) presented a theory that eliminates the need for direct heating along the pumping stations. This method is suitable for a pipeline that is at least 250 kilometers (km) long, (preferably 500 km long) with a high-pressure specification. The fluid to be transported should be diluted with a liquid hydrocarbon comprised of five or fewer carbon atoms and having a high
vapor pressure. The resulting expensive pipeline system may have a pressure drop of 1250 Pisa between stations, enough to cause a shear heating effect. The pump at the stations creates the turbulent flow of crude oil causing shear heating effect, thus increasing its temperature. Some pipeline designs can produce temperature increases of about a half degree Celsius for every 15–30 km of distance, with an equilibrium temperature at 338.7 K. Rather than wait for this effect to slowly heat the oil as it travels down the pipeline, a heater is proposed at the front end of the pipeline, so that the diluted heavy oil equilibrium temperature is maintained throughout the pipeline system. The higher the oil viscosity produces greater internal shear friction, which generates more heat, but since the system has to be designed considering shutdown conditions, diluted heavy oil is recommended. This shear heating effect is not seen with normal light and medium gravity oil, because the viscosity within the transport system is too low.

2.2 Oil in Water Emulsion

An effective way to reduce the viscosity of heavy oil is the formation of oil-in-water emulsions with the help of surfactant agents. An O/W emulsion is a mixture of two immiscible liquids in which the oil phase is dispersed into the continuous water phase. Some energy input is required to make the O/W emulsion, which can be done through shaking, stirring or some other kind of mixing process. Some surfactants (low molecular weight) are always added to the pipeline to ensure the stability of emulsions. In some cases, stabilizing agents are used to avoid phase separation. Generally, non-ionic surfactants represent a good choice because they are not affected by the salinity of the water, they are relatively cheap, and they do not produce any undesirable organic residues that affect oil properties (Rivas et al., 1998).
The cost of an O/W emulsion increases steeply by the use of surfactants, but if natural surfactants present in heavy oil are activated, then this is a reliable option. The ionization of acid groups present in fatty and naphthenic acids as well as asphaltenes with a strong alkali can make these surfactants more hydrophilic which helps reduce the interfacial tension (Langevin et al., 2004). Rivas et al. (1998) proposed the use of the natural molecules present in bitumen that which activated with amines can serve as natural surfactants to form a bitumen-in-water emulsion. Particles like silica, clay, iron oxides, etc. are good natural surfactants.

Economically, the main objective of the O/W emulsion method is to transport as much oil as possible with as little water as possible. Nevertheless, the required viscosity for transport, typically around 400 cP at ambient temperature, may be attained only with 25-30% w/w water content. A typical effect of the volume of water on viscosity of the emulsion is shown in Fig. 2.2. The viscosity decreases exponentially with water content. This curve is very important when selecting the optimum amount of water to be present in the emulsion.

While selecting the surfactants, it must be noted that surfactant should allow a simple break-up of the O/W emulsion before refining. Then, it is necessary to develop surfactants that may form a meta-stable and easy-to-break emulsion that should require the minimum quantity of surfactant and other additives.

Gregoli et al. (1990) developed a process to prepare a stable O/W emulsion using a static mixer consisting of baffle elements that cause the dispersion of the oil in water. Recently, an O/W emulsification technology was proposed to reduce crude oil viscosity using an eccentric cylinder mixer that produces a low energy laminar flow. The mixer's geometry allows the existence of
chaotic flows that are able to thoroughly mix well highly viscous fluids such as Zuata and Athabasca crude oils (Fournanty et al., 2008).

Figure 2.2 - Viscosity versus % continuous phase for emulsions (Escojido et al., 1991)

It is not easy to produce stable heavy O/W emulsions, but it is crucial to control and develop the process at every stage. In some cases, especially with extra-heavy oils, the formation of an oil-in water emulsion will not occur. Still, there have been a few scientific advances over the past years, allowing for a better understanding of these complex systems. However, there are still many unanswered questions associated to the unusual behavior of these emulsions. Its complexity comes from the molecular composition of oil, which covers a wide range of chemical structures and molecular weights.
2.3 Core Annular Flow

The core annular mode flow is another method used to enhance the transportation of viscous crude oil. This method is based on developing a core annular flow (CAF) to reduce the pressure drop in the pipeline caused by friction. In this method, a less viscous fluid such as water is introduced into the flow to act as a lubricating layer which absorbs the shear stress existing between the walls of the pipes and the fluid, thus reducing the resistance to flow and producing a total pressure drop equal to moving water (Guevara et al., 1997).

This method could be problematic because the crude oil has a tendency to adhere to the pipeline walls, thus leading to restriction and eventual blockage of the flow system. Such problems are exacerbated where flow must be stopped for a period of time, allowing stratification of the oil and water phases and increasing adhesion of the oil. Restarting the flow in such a stopped system may require a large pressure, possibly exceeding the pressure rating of some or all components of the flow system. In such a problem, washing of the flow system is also compulsory to remove adhered oil, causing additional expenses and down time for the flow system. Some investigations into how to avoid this problem have been undertaken, including some involving the use of coating materials on the pipeline’s inner surface which substantially prevent the adhesion of oil, which reduces the chance of crude oil coming into contact with the wall (Guevara et al., 1997).

Pressure drop for annular core flow as a function of the injected water fraction, for different superficial oil velocities, is presented in Fig.2.3. When the water fraction is increased, the pressure loss decreases to a minimum. The optimum water fraction to produce the minimum pressure drop is found to be 8-12%; however in actual field applications (longer pipelines) a 20% water fraction may be desired for operational reasons (Oliemans et al., 1987).
A basic process for restarting core flow with heavy oils after a long standstill period was proposed by Zagustin et al., 1988. First, a flow of a low viscosity fluid such as water is pumped into an inlet portion of the pipeline. Gradually this flow increases until the critical velocity is achieved, allowing annular flow in a steady state condition (Fig. 2.4). Next, the flow of heavy oil is pumped into the inlet portion of the pipeline, and is gradually increased either by adjusting a variable speed motor to the pump or by adjusting a control valve in a viscous oil bypass line. The increase of pressure due to the pumping of heavy oil is much smaller than the pressure peaks observed during the low viscosity fluid build-up stage.
2.4 Partial Field Upgrading

Another method for the transportation of heavy oil involves its alteration prior to its transportation. Partial upgrading is the process of modifying the composition of crude oil by making it less viscous, without significantly altering its refining characteristics. Full upgrading totally alters the crude composition, converting it into light synthetic crude oil which is much convenient to transport and is of more valuable (Urquhart, 1985).

The key advantage of this technique is that crude oil can be transported without making any changes to the pipeline system (Urquhart, 1985). Usually upgraders are placed at collection or gathering points. The upgraders process the heavy crude and recycle the diluents to send them back to the well heads. From that point, the upgraded crude is transported to the market via conventional pipeline.

Cabrera and Silverman (2012) presented a process to upgrade heavy oil in a cost efficient manner. An overview of this process is shown in Fig. 2.5. This process uses a circulating transport bed of hot sand to quickly heat the heavy feedstock and convert it to a lighter, more valuable product. The fundamental innovation of this method is that the asphaltenes present in heavy oil residue are dispersed and deposited on the sand in a thin film. This is achieved due to a high sand-to-oil ratio and efficient feed injection zone mixing. Less than two seconds are required for this process from feed in to product out. The very short residence time is at the heart of the process. The heaviest fractions of the liquid feed are converted to coke, which is directly deposited on the circulating sand particles. A small portion of residue feed converts to non-condensable product gas. The thin layer of coke on the sand bed is burnt off in the reheater; the sand bed is thereby regenerated and the coke burning also provides energy necessary to support
upgrading reactions. Product gas is collected and consumed as fuel gas in fired heaters and steam boilers.

Figure 2.5 - Process flow diagram of the Heavy oil Upgrading process (Cabrera and Silverman, 2012)

Another advantage of this process (Cabrera and Silverman, 2012) is that it does not accumulate large volumes of coke by-product that would have to be stored or transported offsite. The produced coke is consumed by the process itself and converted into onsite energy.

Figure 2.6 - Feedstock test facility at the Southwest Research Institute in San Antonio, Texas (Cabrera and Silverman, 2012)
CHAPTER 3
HEAVY OIL DILUTION

Dilution is one of the oldest methods for reducing the viscosity of heavy oils. This method has been used extensively in Canada, the USA and Venezuela. The classical diluents for this method are condensates, light hydrocarbons and naphtha (Guevara et al., 1997).

Dilution is an effective option to reduce oil viscosity and help its mobility in the pipeline since a ratio of 20–30% of solvent is often sufficient to avoid large pressure drops or the need for high temperatures. Diluting the crude may also facilitate certain operations such as dehydration and desalting. Where condensates or light crude oil is available to transport heavy and extra heavy oil by pipeline, dilution is the most widely used method. But it may require significant investments in pumping and pipelines due to the increase of the transport volume and the need to separate the solvent, process it and subsequently return it to the oil production site (Aburto et al., 2010).

3.1 Condensates as Diluents

Until the end of 1980s, condensates were used to facilitate the transportation of almost all Canadian crude. Fig. 3.1 shows the reduction in viscosity that can be obtained by blending condensate with heavy crude oils. There is an exponential relationship between the resulting viscosity of the mixture and the volume fraction of the diluents. This relationship shows that even small percentages of diluent have a noticeable effect on the viscosity of the mixture and therefore, it is apparent that there is an optimum percentage above which there is little further reduction (Guevara et al., 1997).
Using condensates as diluents is very effective but it also has some limitations. The first one is their availability which is related to natural gas demand. At the end of 1980’s, it was estimated that the production of condensates in the 2000s could not be sufficient to satisfy the whole demand for it as viscosity reducer, because of the anticipated increase of heavy oil production (Urquhart, 1985). Fig. 3.2 shows the projected production of heavy oil and the condensate requirement for its transportation. These estimates have been confirmed now.

Figure 3.1 - Effect of dilution with condensate on crude oil viscosity for different API gravities (Guevara et al., 1997)

Figure 3.2 - Production of heavy oil and bitumen and condensate requirement for their transportation (Urquhart, 1985)
3.2 Light Crude Oil as Diluent

Because of the high API gravity of light crude oils, their use as heavy oil diluent is a reasonable substitute for natural gas condensates. However, the mixture may affect asphaltene stability by initiating its flocculation and precipitation which may cause blockage of pipelines.

Light crude oils in the range of 35 to 42 API can be used; however, considerably more volume is required to do the same job compared with condensates. In general, about 80-100% more crude oil would be required to provide the same viscosity reduction. This means that the heavy crude gathering system needs to be modified. The diluents system would have to have twice the volume carrying-capacity as is required for condensates, and the blend pipeline system would have to be capable of moving correspondingly less heavy crude oil per unit of blend (Urquhart, 1985).

Yaghi and Bemani (2002) carried out the dilution of heavy oil using different fractions of light crude oil. The viscosity and specific gravity of the light crude oil used are 64mPa.s and 0.88 respectively at 30°C. Dilution of heavy oil with 15% light crude oil at 30°C reduces its viscosity to half of its original value, while dilution with 30% light crude reduces the viscosity to 1000mPa.s. This reduction is still not adequate for pipeline transportation. More light crude is needed to reduce the viscosity to a transportable value, and it also implies that expensive oil is needed for the transportation of a cheap one. Result of their work is shown in Fig. 3.3.
3.3 Kerosene as Diluent

Yaghi and Bemani (2002) also presented the viscosity behavior of heavy oil diluted with kerosene. Their result is shown in Fig. 3.4. It can clearly be seen that dilution with 10% kerosene caused a drastic viscosity reduction. With 20% addition, the viscosity was reduced to 250mPa.s. Heating the mixture of heavy oil and 15% kerosene to 50°C achieves the same viscosity reduction as the addition of 20% kerosene at room temperature. The problem with this choice of solvent is that kerosene is expensive and the use of 20% of it at 30°C is not economical.
3.4 Light Hydrocarbons/Naphtha as Diluent

Naphtha/light hydrocarbons have also been used as diluents for heavy oil in Canada and Venezuela. They are good viscosity reducers because of their high API and good compatibility with asphaltenes. Argillier et al. (2005) performed experiments on heavy oil dilution using naphtha as the solvent. The viscosity of the mixture of heavy oil and naphtha using different concentrations of naphtha is shown in Fig. 3.5. Naphtha is a petroleum fraction and it was analyzed using gas chromatography: it was composed of 24.9 weight percentage of n-paraffin, 29.4% of iso-paraffin, 30.9% of cyclic paraffin and 14.8% of aromatics.

![Figure 3.5 - Influence of naphtha weight fraction on heavy oil (Argillier et al., 2005)](image)

Argillier et al. extended their work using some polar components as co-solvents with naphtha. A polar co-solvent was added so the polarity of solvent might have an effect on the organization of asphaltenes in the diluted regime. The polarity of the solvent may break the self association of asphaltenes, thereby causing a reduction in viscosity. The co-solvents used were ethyl acetate, butyraldehyde, methyl ethyl ketone and butyronitrile. These solvents were mixed with naphtha at 10% and 50% volume fraction. The sample of heavy oil was then diluted with 15% by weight of above mentioned solvent mixtures. To compare the dilution efficiency of diluents, results were presented using relative viscosity defined as:
\[ \eta_{rel}(c, T) = \frac{\eta(c, T)}{\eta_{diluent}(T)} \]  

Where:

\[ \eta(c, T) = \text{viscosity of diluted heavy oil with concentration } c \text{ and temperature } T \]

\[ \eta_{diluent}(T) = \text{viscosity of solvent at temperature } T \]

Figure 3.6 - Influence of diluent polarity on the viscosity of diluted heavy oil (Argillier et al., 2005)

In Fig. 3.6, \( \delta \) is the Hansen’s solubility parameter which is the ratio of the cohesion energy \( (\Delta E_{LV}) \) and molar volume \( (V_m) \). Hansen’s solubility parameter is divided into three parts: the dispersion part \( \delta_d \), the polar part \( \delta_p \) and the hydrogen bonding part \( \delta_h \), called the cohesion energy parameters.

\[ \delta = \left( \frac{\Delta E_{LV}}{V_m} \right)^{1/2} \]  

\[ \delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \]
The results show that increasing the polarity of the solvent leads to a decrease in the relative viscosity. When the polar parameter becomes higher, the efficiency tends to increase. The highest degree of viscosity reduction was achieved using naphtha with methylethylketone (MEK). The change in viscosity with different concentrations of MEK is shown in Fig. 3.7.

![Figure 3.7 - Influence of diluted composition (naphtha/MEK) on viscosity of heavy oil (Argiller et al., 2005)](image)

3.5 Alcohols as Diluents

Alcohols are more polar than most common solvents. The higher polarity may have an enhanced effect on the structure of colloidal particles of asphaltenes. In order to further investigate the role of diluent polarity on heavy oil, alcohols have been tested as diluent. In another study, Argillier et al., (2001) performed dilution tests with alcohols of different chain lengths. They observed miscibility problems with alcohols lighter than butanol, so results were presented only for butanol up to octanol, for which no phase separation occurs. Their results are shown in Fig. 3.8, which shows the exponential decrease of heavy oil viscosity with the increasing weight percentage of alcohol.
Hasan et al. (2010) studied the viscosity behavior of heavy crude oil when it was blended with ethyl alcohol of 10% and 20% by volume. They found that the presence of 10% alcohol reduced viscosity by almost 80% at 25°C (i.e. from 10.0 to 2.0 Pa.s). Even more viscosity reduction was achieved by further addition of alcohol. The viscosity decreased from 10.0 to 0.95 Pa.s at 25°C in the presence of 20% alcohol by volume. It was concluded that the reduction of the measured viscosity is due to the interactions between the hydroxyl functions and some functionalities of the asphaltenes. As the oil–alcohol ratio decreases, the shear thinning behavior takes place, and the viscosity decreases as the temperature increases. From their study, it can be concluded that the blending of heavy crude oil with ethyl alcohol enhances the flowability of the heavy crude oil. Fig. 3.9 and 3.10 show the results of their study.
It is clear from Fig. 3.9 and 3.10 that viscosity decreases exponentially with the percentage of alcohols. This evolution is similar to the one observed with low viscosity hydrocarbon diluents, even though the alcohols are more viscous than low viscosity hydrocarbons.

Argillier et al., (2001) studied dilution with a blend of hydrocarbon cut and an alcohol, specifically hexanol in naphtha. Their results are presented in Fig. 3.11. The results show that addition of a small percentage of hexanol in the naphtha improved the viscosity reduction. The
addition of 10% hexanol in the naphtha improved the viscosity reduction by a factor of almost two. Increasing the percentage of alcohol could have been detrimental because it can be a compromise between the contribution of the alcohol viscosity (the alcohol is more viscous than the naphtha) and specific interactions between alcohols and asphaltenes.

Figure 3.11 - Influence of addition of hexanol in naphtha on the viscosity (Argillier et al., 2001)

Gateau et al., (2004) investigated the polarity effect of alcohols on asphaltenes. They prepared solutions of 3% by weight of I5 (asphaltenes precipitated from heavy oil using pentane) in hexanol/toluene mixtures. The volume fraction of hexanol has been varied from 0 to 50%. No flocculation of asphaltenes was observed using optical microscope even at 50% concentration of hexanol. Results are given in terms of relative viscosity. Result of their work is shown in Fig. 3.12.
Figure 3.12 - Influence of the volume fraction of hexyl alcohol of 3% I5 in hexyl alcohol/toluene mixture on the radius of gyration of the asphaltenes at 25°C (above line), the relative viscosity at 3°C (bottom line). (Gateau et al., 2004)

The graph shows that there is a minimum value for the radius of gyration and relative viscosity at 10% volume fraction of hexanol. This confirms the effect of hexanol on the organization of asphaltenes in the diluted regime. It can be assumed that hexanol might have established hydrogen bonds and polar interactions with the asphaltenes, and thereby replaced some of the asphaltenes/asphaltenes interactions. The minimum value of relative viscosity can be seen at the dilution of 10% hexanol by volume, this shows that the dissociation phenomenon is at its maximum and all linkages between the elementary particles are broken. Increase of relative viscosity with the hexanol fraction beyond 10% can be explained by assuming that hexanol acts as flocculent when all the possible sites able to establish associations between alcohol functions and asphaltenes are saturated, thus causing an increase in radius of gyration and relative viscosity.
CHAPTER 4

SOLVENT POLARITY AND DIELECTRIC CONSTANT

4.1 Molecular Polarity
Polarity can be defined as the capacity of a solvent for solvating dissolved charges or dipolar species (Katritzky, 2003). Reichardt (1988) defined polarity as “the overall solvation capability (or solvation power) for reactants and activated complexes as well as for molecules in the ground and excited states, which in turn depends on the action of all possible, specific and nonspecific, intermolecular forces between solvent and solute molecules, including Coulomb interactions between ions, directional interactions between dipoles, and inductive, dispersion, hydrogen-bonding, and charge transfer forces, as well as solvophobic interactions”. Molecules composed of very electronegative elements and very electropositive elements bonded together maximize the possibility of greatest polarity. However, if the molecule contains more than two different kinds of atoms, the molecular structure also influences the polarity.

4.2 Dielectric Constant of a Solvent
Generally, the dielectric constant of a solvent gives a rough measure of its polarity. It is a measure of a substance’s ability to insulate charges from each other. Taken as a measure of solvent polarity, a higher dielectric constant means higher polarity, and a greater ability to stabilize charges. The strong polarity of water is indicated, at 20°C, by a dielectric constant of 80. Generally, the non-polar solvents have a dielectric constant of less than 15. Technically, the dielectric constant measures the solvents ability to reduce the field strength of the electric field surrounding a charged particle immersed in it. This reduction is then compared to the field
strength of the charged particle in a vacuum. The dielectric constants of some of the common solvents are in Table 4.1. These values are obtained from an online source whose web link is provided in the references.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>80.1</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.7</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.6</td>
</tr>
<tr>
<td>Propanol</td>
<td>20.1</td>
</tr>
<tr>
<td>Hexanol</td>
<td>13.3</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>6.2</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.4</td>
</tr>
</tbody>
</table>

### 4.3 Dielectric Constant of a Mixture of Solvents

Several formulas are available for calculating the dielectric constant of a mixture of solvents if the dielectric constants of the individual components are known. One such formula called the Lichtenecker formula (Govinda, 1988) is mentioned below:

\[
\varepsilon_m = \exp\{V_1 \log \varepsilon_1 + V_2 \log \varepsilon_2\}
\]

Where

\(\varepsilon_m\) = Dielectric constant of the solvent mixture

\(V_1\) = Volume of solvent 1

\(V_2\) = Volume of solvent 2
\[ \varepsilon_1 = \text{Dielectric constant of solvent 1} \]

\[ \varepsilon_2 = \text{Dielectric constant of solvent 2} \]

This exponential equation indicates that when two solvents are mixed together, the dielectric constant of the mixture will add up and the resulting dielectric constant will be higher than the dielectric constant of the solvents mixed. Since the dielectric constant is increased, the polarity of the mixture will also be higher than the polarities of the solvents added.

According to the equation mentioned above, the mixture of methanol and ethanol will have a higher dielectric constant than the dielectric constant of either methanol or ethanol. Therefore, the polarity of a methanol-ethanol mixture will also be higher than the polarity of either methanol or ethanol.
CHAPTER 5

LABORATORY EXPERIMENT

5.1 Introduction

In the laboratory experiment, crude oil was diluted with toluene and alcohols. The viscosity of the diluted crude oil was measured using viscometer. The objective of this experiment was to study the effect of addition of alcohols as diluents on the viscosity of crude oil. The alcohols selected for this purpose were methanol, ethanol and propanol because of their high polarity among alcohols. Different combinations and concentrations of these alcohols were used as diluents with toluene.

5.2 Reagents

5.2.1 Heavy oil

Heavy oil from the western Canadian sedimentary basin was used. The crude oil density, API gravity and viscosity were measured and they are found to be 0.974 g/cm³, 13.8 API and 1300cP respectively. The asphaltene contents in heavy oil were found to be 12.2%. These measurements were carried out at 23°C.

5.2.2 Medium Crude Oil

A sample of Arab heavy crude oil was used to perform experiments. The density, API gravity and viscosity of the crude oil were 0.88 g/cm³, 27.7 API and 695 cP respectively. The asphaltene contents in this crude oil sample were 7.5%. These measurements were carried out at 23°C.
5.2.3 Alcohols

The alcohols used in this experiment were methanol, ethanol and propanol. All these alcohols were supplied by Sigma Aldrich Canada Ltd. The viscosities of these alcohols (methanol, ethanol and propanol) at 23°C were 0.58cp, 1.17cp and 2.26cp respectively.

5.3 Viscometers

Viscosity measurements were performed with Brookfield digital viscometer and Fann viscometer.

5.3.1 Brookfield Digital Viscometer

The Brookfield viscometer rotates a sensing element in a fluid and measures the torque needed to overcome the viscous resistance to the induced movement. This is accomplished by driving the immersed element, called spindle, through a beryllium copper spring. The degree to which the spring is wound, indicated on the digital display, is proportional to the viscosity of the fluid.

The viscometer is able to measure over a number of ranges but, for a given spring deflection, the actual viscosity is proportional to the spindle speed and is related to the spindle’s size and shape. For a material of given viscosity, the resistance will be greater as the spindle size and/or rotational speed increase. The minimum viscosity range can be obtained by using the largest spindle at the highest speed, while maximum range by using the smallest spindle at the slowest speeds.

A three digit LED display on the viscometer shows the torque required to overcome the viscous resistance to the induced movement. The viscosity of the sample can then obtained by multiplying the torque reading by the spindle/speed constant. The spindle/speed constant
depends on the spindle size and the operating speed of the motor. The readings obtained from Brookfield viscometer are accurate to within 1% of full scale when the spindle is centered in any container over 2.75" in diameter. A photo of the viscometer used for the experiment is shown in Fig. 5.1.

![Figure 5.16 - Brookfield RV-DV1 viscometer](image)

### 5.3.2 Fann Viscometer

The Fann model 35 viscometer are direct reading instruments. This is a rotational viscometer; the test fluid is contained in the annular space between an outer cylinder and the bob. Viscosity measurements are made when the outer cylinder, rotating at a known velocity, causes a viscous drag to be exerted by the fluid. This drag creates a torque on the bob, which is transmitted to a precision spring where its deflection is measured and then compared with the test conditions and the instrument's constants.
A stainless steel cup comes with the instrument that contains the test sample. The cup has a line at the proper 350 ml test fluid level. A scribed line on the rotor indicates appropriate immersion depth. If this immersion depth is exceeded, damage to bob shaft bearings may occur. After the bob is immersed in the test sample fluid, the motor is turned on and the dial reading is noted to get the viscosity reading.

This instrument gives the viscosity measurement over a wide range. The slowest rotor speed gives the highest range of the instrument and the fastest rotor speed gives the lowest range of the instrument. A photo of the Fann viscometer used is shown in Fig 5.2.

![Figure 5.2 - Fann model 35 viscometer](image)

5.4 Experimental Procedure

Crude oil sample was stirred thoroughly to make a homogenized sample. The viscosities of the pure samples were measured using the viscometers. Different combinations of alcohols were used as diluents in both the samples and viscosities were measured.
Viscosity measurements of heavy crude oil were made using Brookfield viscometer. The motor speed was selected at 50 RPM. LED display on the viscometer displays the torque reading. The torque reading was noted, only when it was stabilized. The torque reading was then multiplied by spindle/speed constant to get the viscosity of heavy oil sample, which in this case was 40, with spindle no.4 and at 50 RPM speed. After getting the viscosity of heavy oil sample, 1mL of methanol was added as a diluent in heavy oil sample and the same procedure was repeated to measure the viscosity of mixture. Viscosity of heavy oil was measured until the 5mL of methanol is mixed in heavy oil (only 1mL was added at a time). The same procedure was repeated with addition of ethanol in the same sample, followed by propanol.

Viscosity measurements of medium crude oil were made on Fann rotational viscometer. The motor speed selected for these measurements was 100 RPM. The dial reading gives the viscosity of the sample. Different combinations of alcohols and toluene were used as diluents for medium crude oil sample.
CHAPTER 6
Results and Discussion

6.1 Heavy Crude Oil Sample

The heavy oil sample used for the experiment was diluted with 10% toluene by volume. The toluene diluted heavy oil was further diluted with 5% alcohols (methanol, ethanol and propanol). The final volume of the sample after all the dilution was 305mL, which contains 85% heavy oil, 10% toluene and 5% alcohols. These values show concentration by volume. The results obtained during experiment are presented in the table 6.1.

Viscosity of the heavy oil sample = 1300 cP

Viscosity of the heavy oil sample with 10% toluene by volume = 872 cP

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Volume</th>
<th>Viscosity (centipoises)</th>
<th>Viscosity Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Methanol</strong></td>
<td>1 ml</td>
<td>848</td>
<td>34.8</td>
</tr>
<tr>
<td></td>
<td>2 ml</td>
<td>840</td>
<td>35.4</td>
</tr>
<tr>
<td></td>
<td>3 ml</td>
<td>824</td>
<td>36.6</td>
</tr>
<tr>
<td></td>
<td>4 ml</td>
<td>812</td>
<td>37.5</td>
</tr>
<tr>
<td></td>
<td>5 ml</td>
<td>784</td>
<td>39.7</td>
</tr>
<tr>
<td><strong>Ethanol</strong></td>
<td>1 ml</td>
<td>756</td>
<td>41.8</td>
</tr>
<tr>
<td></td>
<td>2 ml</td>
<td>736</td>
<td>43.4</td>
</tr>
<tr>
<td></td>
<td>3 ml</td>
<td>700</td>
<td>46.2</td>
</tr>
<tr>
<td></td>
<td>4 ml</td>
<td>672</td>
<td>48.3</td>
</tr>
<tr>
<td></td>
<td>5 ml</td>
<td>660</td>
<td>49.2</td>
</tr>
<tr>
<td><strong>Propanol</strong></td>
<td>1 ml</td>
<td>632</td>
<td>51.1</td>
</tr>
<tr>
<td></td>
<td>2 ml</td>
<td>600</td>
<td>52.9</td>
</tr>
<tr>
<td></td>
<td>3 ml</td>
<td>568</td>
<td>55.7</td>
</tr>
<tr>
<td></td>
<td>4 ml</td>
<td>536</td>
<td>58.5</td>
</tr>
<tr>
<td></td>
<td>5 ml</td>
<td>508</td>
<td>60.9</td>
</tr>
</tbody>
</table>
Methanol was the first diluent added in the toluene-diluted heavy crude oil sample. The addition of 5 ml of methanol to 290 ml of 10% toluene-diluted heavy oil reduced the viscosity by almost 7%. An increase in concentration of methanol leads to the higher viscosity reduction. The polarity of methanol induced the reduction of heavy oil viscosity. The polar group of methanol reacted with asphaltenes in the heavy oil making them stable and thus reduced the viscosity.

Ethanol was the second alcoholic solvent used as a diluent for heavy oil sample. The ethanol was added to the toluene-diluted heavy oil sample already having 5 ml methanol. Ethanol addition further reduced the viscosity by 9%, which is higher than the viscosity reduction due to methanol addition. The polarity of the diluent is the reason for higher viscosity reduction than methanol. The polarity of ethanol seems to have added up with the polarity of methanol, thus causing the higher viscosity reduction of heavy oil as compared to methanol.

Then same volumes of propanol were added to heavy oil sample having 5 ml each of methanol and ethanol plus 10% toluene. With the addition of propanol, the viscosity reduction was even
higher than ethanol and methanol. The viscosity reduced by 12% with 5 ml addition of propanol to the sample. The solvent polarity seems to have increased with the addition of propanol to the sample which already had methanol and ethanol. The higher polarity of diluents caused the higher reduction of viscosity.

The addition of a total of 15 ml of alcohols in heavy oil sample makes 5% volume concentration of alcohol and 10% volume concentration of toluene in the sample. The addition of 5% alcohols to toluene-diluted heavy oil sample reduced the viscosity by 28%. The overall viscosity reduction with total 15% volume concentration of solvent (10% toluene and 5% alcohols) was 61%. The higher reduction of viscosity of heavy oil with less volume of alcohols is because of the polar functional group in their molecules. Since asphaltenes are the most polar component of heavy oil, addition of solvent having polar functional group in its molecule caused the disassociation of asphaltenes. This has caused the smaller molecules of asphaltenes to dissolve in crude oil, thus making the asphaltenes stable. This reduces the concentration of unstable asphaltenes in heavy crude oil, thus making it less viscous. Fig 6.1 shows the graphical presentation of results of heavy oil viscosities of heavy crude oil sample.

The objective of this study counted on the high polarities of these alcohols by adding different volumes in order to achieve higher viscosity reduction of heavy oil as predicted by dielectric additivity formula (Lichtenecker formula, equation 4.1). The addition of 5 milliliters each of the alcohol to the heavy oil sample having 10% toluene caused a viscosity reduction of 61%. This reduction of viscosity of heavy oil is not enough for its transportation. However, considering the volume of solvents used, the viscosity reduction of 61% is quite substantial which ensures higher volume of heavy oil transportation at a time.
Actually, the higher polarities of alcohols used in this study did not succeed in reducing the viscosity of heavy oil as expected. In view of the cost involved, one would expect the viscosity reduction to be much higher. The viscosity reduction of about 70-75% using these combinations would justify their use in heavy oil transportation. However, despite the unfavorable economics of these alcohols, this study has scientifically established that it is possible to reduce heavy oil viscosity using these alcohols in view of their polarity. Therefore, depending on the circumstances, it is possible for an operator to use these combinations for heavy oil dilution.

### 6.2 Medium Crude Oil Sample

The alcohol combinations used for the dilution of heavy crude oil sample were also examined on the medium crude oil sample. Results of the experiment on the medium crude oil are shown in table 6.2.

Viscosity of medium crude oil sample = 695.4 cP

Viscosity of the heavy oil sample with 10% toluene by volume = 417.2 cP
Table 6.2-Results Showing Medium Crude Oil Viscosities for Different Combinations of Alcohols

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Volume (ml)</th>
<th>Viscosity (cP)</th>
<th>Viscosity Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>1</td>
<td>401.2</td>
<td>42.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>379.8</td>
<td>45.4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>369.1</td>
<td>46.9</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>353</td>
<td>49.2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>347.7</td>
<td>50.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1</td>
<td>339.6</td>
<td>51.2</td>
</tr>
<tr>
<td></td>
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<td>337</td>
<td>51.5</td>
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<td>3</td>
<td>339.6</td>
<td>51.2</td>
</tr>
<tr>
<td></td>
<td>4</td>
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<td>50.4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>361</td>
<td>48.1</td>
</tr>
</tbody>
</table>

Figure 6.2 - Viscosity changes of medium crude oil with different alcohol concentrations

The addition of methanol to toluene-diluted crude oil reduced the viscosity of the sample. The reduction was almost 8%, almost same as the viscosity reduction of heavy crude oil. The addition of methanol initiated the disassociation of asphaltenes, thus causing the viscosity reduction of crude oil sample. Addition of methanol was followed by the addition of ethanol. The viscosity of crude oil continued to decrease until the addition of 3 ml of ethanol. The polarity of methanol and ethanol added up and caused the further viscosity reduction. However,
more addition of ethanol resulted in the increase of viscosity rather than reduction. Since the asphaltene contents in the medium crude oil are less than the heavy crude oil sample, all the polar sites of asphaltenes would have been consumed with methanol and ethanol. This further addition of ethanol could not get dissolved in the sample and started the flocculation in the sample. More ethanol addition in the sample showed a sharp rise in the viscosity of crude oil sample, which confirms the flocculation in the sample. Fig 6.2 presents the graphical form of results for viscosity measurement of medium crude oil sample. The rise in the curve indicates the flocculation in the sample.

Comparing the results of two samples shows the effect of asphaltene concentration in the sample. No flocculation was observed in heavy crude oil sample, which has higher asphaltene contents, even with the addition of 15 ml of alcohols. But medium crude oil exhibited flocculation after the addition of 9 ml alcohols. This shows that the chances of flocculation are less when the asphaltene contents are higher and when the asphaltene contents in the crude oil are higher, the addition of alcohols could produce the higher viscosity reduction.

6.2.1 Mixture of Toluene and Methanol as Diluent

A mixture of 80% toluene and 20% methanol was used as diluent on the medium crude oil sample. The results are shown in table 6.3 and the graphical presentation of results is shown in Fig 6.3. The dilution of 10% by volume of the mixture produced the significant viscosity reduction of crude oil sample by almost 60%. The polarity of methanol induced its effect on the asphaltenes in the sample, reacting with them and breaking their self-association. The introduction of 20% methanol in toluene increased the viscosity reduction by almost 20%. The addition of 10% toluene to crude oil sample caused the viscosity reduction of 40%. The blending
of crude oil sample with the mixture of toluene and methanol reduced the viscosity and enhanced the flowability of the sample.

**Table 6.3 - Results Showing Viscosities Changes in Crude Oil Sample with the Mixture of Toluene and Methanol**

<table>
<thead>
<tr>
<th>Diluent volume (ml)</th>
<th>Viscosity (cP)</th>
<th>Viscosity Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>615.1</td>
<td>11.5</td>
</tr>
<tr>
<td>4</td>
<td>583.0</td>
<td>16.2</td>
</tr>
<tr>
<td>6</td>
<td>556.3</td>
<td>20.0</td>
</tr>
<tr>
<td>8</td>
<td>532.2</td>
<td>23.5</td>
</tr>
<tr>
<td>10</td>
<td>494.8</td>
<td>28.8</td>
</tr>
<tr>
<td>12</td>
<td>462.7</td>
<td>33.5</td>
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<tr>
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<td>36.2</td>
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<td>39.6</td>
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<td>18</td>
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<td>41.5</td>
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<tr>
<td>20</td>
<td>382.5</td>
<td>45.0</td>
</tr>
<tr>
<td>22</td>
<td>358.4</td>
<td>48.5</td>
</tr>
<tr>
<td>24</td>
<td>342.3</td>
<td>50.8</td>
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<tr>
<td>26</td>
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<td>28</td>
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<td>57.3</td>
</tr>
<tr>
<td>30</td>
<td>280.8</td>
<td>59.6</td>
</tr>
</tbody>
</table>

**Figure 6.3 - Viscosity behaviour of crude oil sample for mixture of toluene and methanol**
**6.2.2 Mixture of Toluene and Ethanol as Diluent**

Viscosity behaviour of the medium crude oil sample diluted with a mixture of 80% toluene and 20% ethanol is shown in Fig 6.4. Table 6.4 shows the results of the dilution of sample with the mixture. It can be seen that the addition of 5% mixture is capable of making drastic viscosity reduction. Dilution of crude oil sample with 5% mixture of toluene and ethanol reduced the viscosity by almost 43%. Further 5% addition of mixture into crude oil sample reduced the viscosity by 63%. This viscosity reduction is higher than the viscosity reduction caused by the mixture of toluene and methanol, even though methanol is more polar than ethanol. This shows ethanol is more efficient viscosity reducer of crude oil as compared to methanol.

**Table 6.4 - Results Showing Viscosities Changes in Crude Oil Sample with the Mixture of Toluene and Ethanol**

<table>
<thead>
<tr>
<th>Diluent Volume (ml)</th>
<th>Viscosity (cP)</th>
<th>Viscosity Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>628.5</td>
<td>9.6</td>
</tr>
<tr>
<td>4</td>
<td>572.3</td>
<td>17.7</td>
</tr>
<tr>
<td>6</td>
<td>529.6</td>
<td>23.8</td>
</tr>
<tr>
<td>8</td>
<td>494.8</td>
<td>28.8</td>
</tr>
<tr>
<td>10</td>
<td>470.7</td>
<td>32.3</td>
</tr>
<tr>
<td>12</td>
<td>438.6</td>
<td>36.9</td>
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<tr>
<td>14</td>
<td>422.6</td>
<td>39.2</td>
</tr>
<tr>
<td>16</td>
<td>398.5</td>
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<tr>
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<td>45.4</td>
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<td>369.1</td>
<td>46.9</td>
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<td>50.0</td>
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<tr>
<td>24</td>
<td>334.3</td>
<td>51.9</td>
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<td>304.9</td>
<td>56.2</td>
</tr>
<tr>
<td>28</td>
<td>283.5</td>
<td>59.2</td>
</tr>
<tr>
<td>30</td>
<td>262.1</td>
<td>62.3</td>
</tr>
</tbody>
</table>
6.2.3 Mixture of Toluene and Propanol as Diluent

A mixture of 20% propanol and 80% toluene was tested as diluent for medium crude oil sample. Results showing viscosity changes in crude oil sample with the mixture are shown in table 6.5. A viscosity reduction of almost 55% was observed with the dilution of 10% mixture of toluene and propanol in the sample. This viscosity reduction is less than what was observed with the dilution of methanol and ethanol. Since propanol is less polar than both methanol and ethanol, the mixture of toluene and propanol could not produce the results better than mixtures of toluene with methanol and ethanol. A graphical presentation of the results with the mixture of toluene and propanol is shown in Fig 6.5.
Table 2.5 - Results Showing Viscosities Changes in Crude Oil Sample with the Mixture of Toluene and Propanol

<table>
<thead>
<tr>
<th>Diluent Volume (ml)</th>
<th>Viscosity (cP)</th>
<th>Viscosity Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
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<tr>
<td>4</td>
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<td>548.3</td>
<td>21.2</td>
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<tr>
<td>8</td>
<td>521.5</td>
<td>25.0</td>
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<tr>
<td>10</td>
<td>489.4</td>
<td>29.6</td>
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<tr>
<td>12</td>
<td>473.4</td>
<td>31.9</td>
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<td>16</td>
<td>441.3</td>
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<td>52.7</td>
</tr>
<tr>
<td>30</td>
<td>315.6</td>
<td>54.6</td>
</tr>
</tbody>
</table>

Figure 6.5 - Viscosity behaviour of crude oil sample for mixture of toluene and propanol

6.2.4 Mixture of Toluene, Methanol and Ethanol as Diluent

Crude oil sample was also diluted with a mixture of 80% toluene, 10% methanol and 10% ethanol. The results are mentioned in table 6.6. The dilution of the 10% mixture reduced the viscosity of medium crude oil sample by almost 64%. The viscosity reduction observed with this
mixture is higher than all the mixtures used in this study. Methanol and ethanol are the most polar alcohols known. The polarity of methanol and ethanol seems to have added up and produced the superior results. The higher polarity of the mixture increased the viscosity reduction of the sample. Therefore, the addition of this mixture enhances the flowability of crude oil much better than other mixtures used in this study. Fig 6.6 shows the viscosity behaviour of crude oil sample with the dilution of mixture of toluene, methanol and ethanol.

Table 6.6 - Results Showing Viscosities Changes in Crude Oil Sample with the Mixture of Toluene, Methanol and Ethanol

<table>
<thead>
<tr>
<th>Solvent Volume (ml)</th>
<th>Viscosity (cP)</th>
<th>Viscosity Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>631.2</td>
<td>9.2</td>
</tr>
<tr>
<td>4</td>
<td>567.0</td>
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<td>6</td>
<td>548.3</td>
<td>21.2</td>
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<tr>
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<td>28</td>
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<tr>
<td>30</td>
<td>251.4</td>
<td>63.8</td>
</tr>
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</table>
6.2.5 Mixture of Toluene, Methanol and Propanol as Diluent

A mixture of 80% toluene, 10% methanol and 10% propanol was prepared to use as diluent of medium crude oil sample. Table 6.7 shows the results of the experiment. Almost 59% viscosity was reduced with the dilution of crude oil sample using this mixture. This reduction is almost the same as what was observed with the mixture of methanol and toluene. Since propanol is a polar solvent but its polarity is less than methanol. The polarity of the two solvents combined is almost the same as the polarity of methanol. Therefore, the mixture of toluene, methanol and propanol produced the same results as the mixture of toluene and methanol.
Table 6.7 - Results Showing Viscosities Changes in Crude Oil Sample with the Mixture of Toluene, Methanol and Propanol

<table>
<thead>
<tr>
<th>Diluent Volume (ml)</th>
<th>Viscosity (cP)</th>
<th>Viscosity Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>649.9</td>
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<td>604.4</td>
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<td>48.1</td>
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<tr>
<td>24</td>
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<td>52.7</td>
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<tr>
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</tbody>
</table>

Figure 6.7 - Viscosity behaviour of crude oil sample for mixture of toluene, methanol and propanol

6.2.6 Mixture of Toluene, Ethanol and Propanol as Diluent

Mixture of toluene, ethanol and propanol was also tested as the diluent of crude oil. The results are shown in table 6.8. Fig 6.8 shows the graphical presentation of viscosity changes in crude oil with the mixture. The addition of 10% mixture in crude oil sample caused the viscosity to reduce
by 53%. The polarity of the mixture induced the higher viscosity reduction as compared to the dilution of crude oil with toluene.

**Table 6.8 - Results Showing Viscosities Changes in Crude Oil Sample with the Mixture of Toluene, Ethanol and Propanol**

<table>
<thead>
<tr>
<th>Diluent Volume (ml)</th>
<th>Viscosity (cP)</th>
<th>Viscosity Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>666.0</td>
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<tr>
<td>4</td>
<td>620.5</td>
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</tr>
<tr>
<td>12</td>
<td>484.1</td>
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<td>50.4</td>
</tr>
<tr>
<td>30</td>
<td>329.0</td>
<td>52.7</td>
</tr>
</tbody>
</table>

**Figure 6.8 - Viscosity behaviour of crude oil sample for mixture of toluene, ethanol and propanol**
6.3 Economic Discussion

Economics is a vital part of any project. So it is also important to discuss the prices of solvents used in this project. The prices of the solvents used in the experiment are listed in table 6.9. These prices are obtained from the supplier’s website i.e. Sigma Aldrich Canada Ltd. The price of hexanol from the same supplier is $41.30/liter, which is cheaper than the solvents used in this experiment. But considering the polarities of all these solvents, hexanol is less polar than either of the alcohols used in the experiment.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Price (CAD per liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
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</tr>
<tr>
<td>Methanol</td>
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</tr>
<tr>
<td>Ethanol</td>
<td>36.00</td>
</tr>
<tr>
<td>Propanol</td>
<td>67.80</td>
</tr>
</tbody>
</table>
7.1 Conclusions

The following conclusions can be drawn from this study:

- Diluents having polar molecular groups are good viscosity reducers for heavy crude oils. Since asphaltenes are polar in nature, the polar groups of the diluents react with asphaltenes breaking its self-association and causing viscosity reduction of heavy oil.
- Alcohols are efficient diluents for heavy crude oil because of their higher polarities.
- The polarity of a mixture of methanol and ethanol is higher than the polarity of each of these alcohols. A mixture of methanol and ethanol caused the highest viscosity reduction of crude oil.
- Ethanol is more efficient viscosity reducer of crude oil as compared to methanol, even though ethanol is less polar than methanol.
- The viscosity reduction of crude oil using the alcohols will be higher if the asphaltene contents in the sample are higher.
- Less volume of alcohol is required to cause the same viscosity reduction as compared to condensates, kerosene, light hydrocarbons and other diluents.
- Higher volumes of heavy oil can be transported using alcohols as diluents, as they are efficient in viscosity reduction.
7.2 Recommendation

I recommend that extended work be done on the dilution of heavy oil with the combinations of alcohols that were used for medium crude oil in this study. In this way, a better combination of alcohols could be established for the maximum viscosity reduction of heavy oil using the minimum amount of solvent.
References


