Rheology of Heavy Crude Oil and Viscosity Reduction for Pipeline Transportation

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ABSTRACT

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The rheological properties of heavy crude oil have been investigated using RheoStress RS100 from Haake. The effects of shear rate, temperature and oil concentration on the viscosity have been determined. From the rheological data, it was observed that blending the heavy crude oil with a limited amount of lighter crude oil worked better than using the other alternatives and was considered as the proposed method of reducing the viscosity. Therefore, the rheological behavior of heavy crude oil and heavy crude oil-light crude oil (O-light) mixtures has been studied and a series of experiments was conducted. The experiments were performed in terms of studying the effect of shear stress τ, shear rate γ, yield stress τ_0, thixotropic behavior, the storage modulus G', the loss modulus G'', the complex modulus G^*, and the complex viscosity η^*. The results showed a significant viscosity reduction of 0.375 Pa.s at room temperature 298 K through which it complies with the desired value required for pumping the heavy crude oil through the pipelines. Moreover, the heavy crude oil showed a thixotropic behavior with heysteresis area of 321.65 KPa.s^{-1} which decreases with temperature. It was clear that the heavy crude oil required a yield stress of 0.7 Pa, whereas it did not require any yield stress to pump the heavy crude oil-light crude oil mixture. In addition, it was noted that the complex modulus, the storage modulus and the loss modulus showed a direct proportional with frequency and inverse proportional with temperature. The complex viscosity of the heavy crude oil decreased with temperature and fraction of water added, and it reached 225 Pa.s at 338 K.

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Finally, I am sincerely grateful to *my parents* who deserve big thanks for their great support and constant encouragement.

DEDICATION

To my parents

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CHAPTER I

INTRODUCTION

1.1 Problem Statement

Oil transportation has become a complex and highly technical operation. One of the major difficulties in the pipeline transportation is the high viscous fluids that require efficient and economical way to transfer the heavy crude. Herein, studying the rheological properties of the heavy crude oil helps determining the best method of reducing its viscosity.

1.2 Research Objectives

The proposed work will focus on many significant points in order to come up with a good understanding of the flow properties of the heavy crude oil and how to enhance it. The main theme of this investigation is to examine the rheological properties and the characterization of the heavy crude oil as well as to study the rheological properties of the viscosity reduction suggested method.

For better understanding, the research objective is divided into four steps as given below:

- Investigating different methods of reducing the viscosity of the heavy crude oil such as forming oil-aqueous solution of surfactant emulsions (O/W), blending the heavy crude oil with alcohol, and blending the heavy crude oil with lighter crude oil. The experiments are conducted at room temperature as well as at different temperatures.
- Verifying different rheological models such as Bingham, Power law and Casson.

- Investigating the rheological properties of the heavy crude oil by studying the effect of shear stress τ, shear rate γ, yield stress τ_0, thixotropic behavior, the storage modulus G', the loss modulus G'', the complex modulus G^*, and the complex viscosity η^*.
- Studying the rheological properties of the proposed method of reducing the viscosity.
- Summary of the proposed methodology is shown in Fig. 1 in the following section.

1.3 Organization Of The Thesis

Chapter II discusses the literature review. Chapter III discusses the experimental setup and the results of the work. Chapter IV summarizes the conclusions drawn from this project.

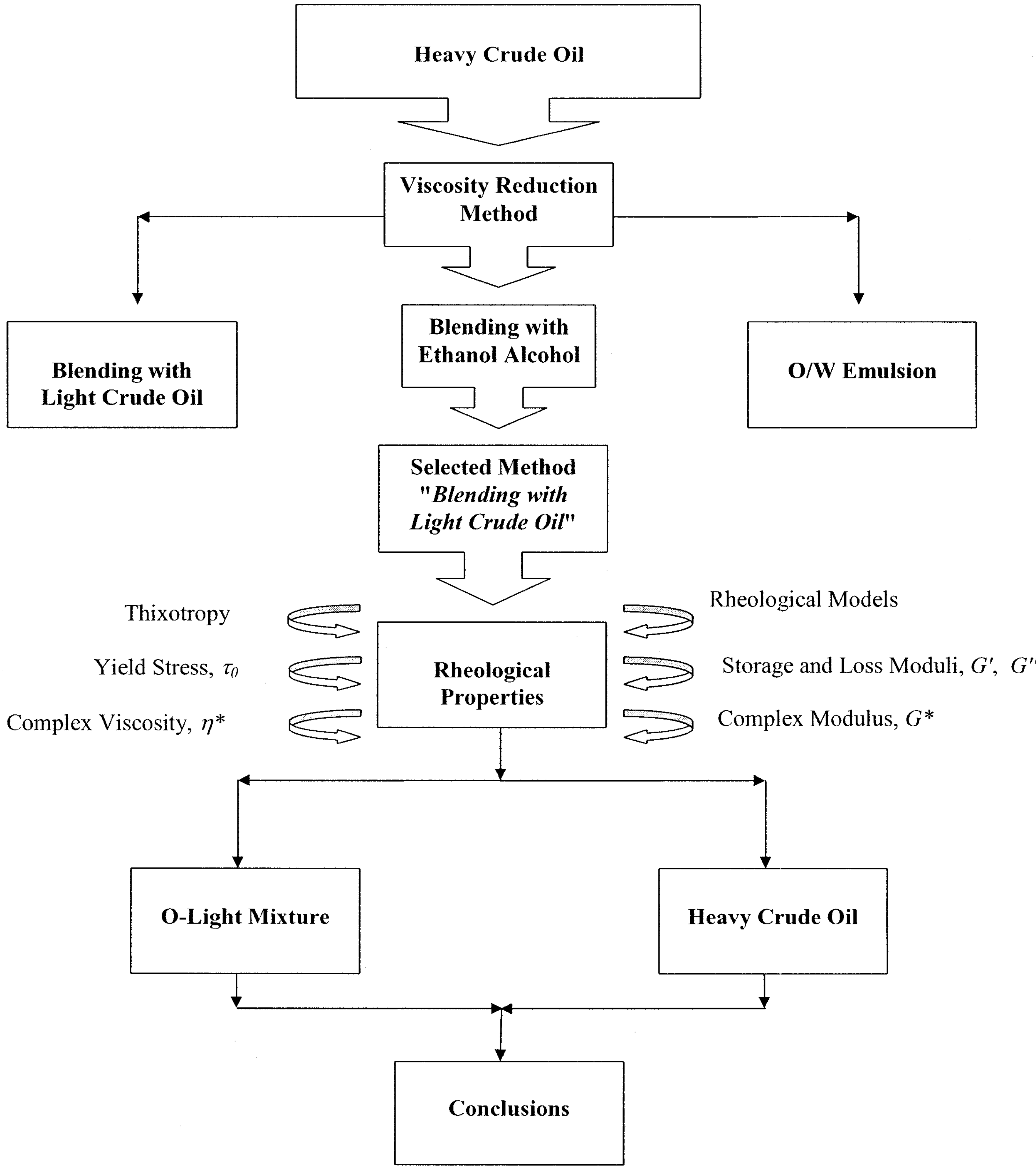


Fig. 1. Methodology of the study.

CHAPTER II

LITERATURE REVIEW

2.1 Crude Oil in Canada

Canada is considered as one of the greatest oil producers in the world. It produces over 2.5 million barrels of oil per day. Crude oil is one of the most actively traded commodities in the world. Oil prices change daily in response to fluctuating conditions that affect supply and demand. Global demand for crude oil has been intensifying steadily over the past 20 years, as world demand for crude has grown from 60 million barrels per day to 84 million barrels per day. Canada produces crude oil and almost 50 percent of the produced crude oil is classified as heavy oil, which is denser, thicker and more costly to produce and refine into other products. The market price for heavy oil is only about one-half that of light crude oil, which is the price generally quoted by the media. Total Canadian production is projected to increase from the current 2.5 million barrels per day to reach 4.9 million barrels per day by 2020. Canada has huge, undeveloped oil deposits. Some related facts are shown in Table 1:

Table 1. 2005 Statistics [1].

Reserves at 2005 Year End	Conventional oil	5,210 millions barrels
Production	Conventional oil	1.36 million barrels per day
Prices	Crude oil: WTI at cushing on Nymex	$56.56 (US$/bbl)
Exports	Crude oil	1.58 million barrels per day
Imports	Crude oil	927,000 barrels per day

Canada has many crude oil pipelines which are distributed over the whole country. For instance, Enbridge, Inter Pipeline, Pacific Energy Partners, Pembina, Plains All American Inc, Portland Pipeline Corporation, Rainbow Pipeline Company Limited, Terasen, and Trans-Northern Pipeline Inc. Those pipelines are shown on the map in appendix A.

In addition to the pipelines, Canada also has a variety of well equipped refineries which receive the crude oil for further processing. Examples are:

From West to East: Chevron (North Burnaby, British Columbia), Husky (Prince George, British Columbia), Petro-Canada (Edmonton, Alberta), Shell Canada (Scotford, Alberta), Imperial Oil (Strathcona, Alberta), Consumer's Co-op (Regina, Saskatchewan), Imperial Oil (Sarnia, Ontario), Sunoco (Sarnia, Ontario), Shell Canada (Corumna, Ontario), Imperial Oil (Nanticoke, Ontario), Petro-Canada (Montreal, Quebec), Shell Canada (Montreal, Quebec), Ultramar Canada (St. Romuald, Quebec), Irving Oil (Saint John, New Brunswick), Imperial Oil (Dartmouth, Nova Scotia), North Atlantic Refining (Come by Chance, Newfoundland) [2].

The refineries shown on the map in appendix A are full-product petroleum refineries. This map does not include bitumen and heavy oil up-graders or petrochemicals plants. Arrows indicate direction of flow.

2.2 Environmental Challenges of Heavy Crude Oils

Heavy crude oils have a density (specific gravity) approaching or even exceeding that of water. They usually are extremely viscous, with a consistency ranging from that of heavy molasses to a solid at room temperature. Heavy crude oils are not easy to be pumped through the pipelines because of the high concentrations of sulfur and several metals, particularly nickel and vanadium.

However, there is a growing interest in developing the vast resources of these crude oils. Thus, the oil industry and government energy agencies are developing new, cost-effective methods for extracting the heavy oils from the reservoir, upgrading them either in situ or at the wellhead, transporting the heavy crude oils or synthetic crude (syncrudes) produced at the well to the refinery, and refining the heavy oils and syncrudes to obtain high yields of valuable light and middle distillate fuels.

Environmental concerns about heavy crude oils are of two types:

- Chemical wastes and by-products of heavy crude oil production, upgrading, and refining may cause serious ecological injury if released to the environment.
- Spills of heavy crude oils and syncrudes are difficult to clean up and may cause long-term injury to the affected environment.

Many of the in situ and wellhead upgrading and refining technologies produce waste gases and solids which might cause sever ecological injury. Besides, those problems caused by heavy oils are difficult to be cleaned up. Moreover, the oil, may be extremely persistent and may cause chronic injury to the affected environment [3].

2.3 Crude Oil Characteristics and Compositions

Crude oil contains different amounts of hydrocarbons. The quality of crude oil is determined by a number of characteristics that affect the proportions of transportation fuels and petroleum products produced when the oil is refined. Some of the physical properties that mainly affect the behavior and persistence of crude oil are:

Specific Gravity

The American Petroleum Institute has developed the API gravity scale which expresses the ratio of weights of equal volumes of oil and pure water at a temperature of 16 °C and one atmosphere pressure [4].

$$API \text{ gravity} = \frac{141.5}{SG} \text{ at } 60\ ^{\circ}\text{F} - 131.5 \quad (1)$$

Crude oil is characterized as heavy, intermediate, or light with respect to its API gravity.

- *Heavy crude*: crude oils with API gravity of 18 degrees or less is characterized as heavy. The oil is viscous and resistant to flow, and tends to have a lower proportion of volatile components [5].
- *Intermediate crude*: crude oils with an API greater than 18 and less than 36 degrees are referred to as intermediate.
- *Light crude*: crude oils with an API gravity of 36 degrees or greater.

Viscosity

Viscosity is the measure of the flow properties of the oil-material [6]. Some factors affect the viscosity of an emulsion. Examples of those factrs are: [7].

- Viscosity of the continuous phase
- Viscosity of the dispersed phase
- Volume fraction of the dispersed phase
- Temperature
- Average droplet size and size distribution
- Presence of solids in addition to the dispersed phase liquid
- Shear rate

• Nature and concentration of the emulsifying agent

Crude oils are complex fluids that can cause a variety of difficulties during the production, separation; transportation and refining of oil [8, 9]. Wax formation and deposition are some of the problems that can be encountered [10, 11]. In fact, wax crystals precipitate below a critical temperature as the solubility of high molecular weight paraffins decreases, and the flow properties of the oil change.

The formation of emulsion is another problem that occurs in the petroleum industry. Indeed, crude oil is often mixed with water when it comes out from a well. As the oil-water mixture passes over chokes and valves mechanical input leads to the formation of water-in-oil (W/O) emulsions [12, 13, 14]. Such emulsions are considered as a ruthless problem within the petroleum industry due to their various costly problems in terms of production loss, transport difficulties and chemical expenses.

Heavy crudes account for a large fraction of the world's potentially recoverable oil reserves. The viscosities of those crudes at room temperature vary from 0.10 Pa.s to more than 100 Pa.s. Generally, crude viscosities less than 0.40 Pa.s is the classical maximum desired pipeline viscosity [15, 16, 17].

Therefore, different methods are used in order to reduce the viscosity of the heavy crude for the pipeline transportation. For instance, dilution with lighter crudes or alcohols, heating and the use of surfactants to stabilize emulsions are some of those common methods.

Heating is a common method utilized to overcome the above noted problems of transporting heavy oil by pipeline [8]. The basis for this method lies in the fact that as heavy oil is heated, the viscosity of the heavy oil is reduced and thus made easier to pump. Thus it is important to heat the oil to a point where the oil has a substantially reduced viscosity. A principle draw back to the use of heated pipelines is the high capital and operational cost of such a heated pipeline over long distances [18]. In addition, underwater pipeline transportation of heavy oil through a heated pipeline is very difficult due to the cooling effect of the surrounding water and the practical difficulty of maintaining pumping stations and heating stations [19, 20].

Another method utilized in the transportation of heavy oil is the formation of the emulsions [21, 22]. In such a method the heavy oil is suspended as micro-spheres of oil stabilized in a water continuous phase by the use of surfactants and detergents forming an oil-in-water (O/W) emulsion, and thus achieving a reduction in the apparent viscosity [23, 24]. The principle difficulty with the use of this technology is the selection and cost of the surfactant component of the emulsion. Not only must the surfactant be capable of stabilizing the emulsion during transportation, but it also must be capable of separation once the destination point of the pipeline is reached [19, 25].

Blending of heavy oils with lighter oils, hydrocarbon gases or alcohols are other alternatives in order to reduce the viscosity of the heavy oils [26].

A clear image of the phenomena of crude oils, waxes, surfactants and emulsions is mainly given and illustrated in the following sections.

2.4 Crude Oil Classifications

Crude oil is a mixture of a large amount of hydrocarbons, varying amount of waxes and low content of asphaltenes [7]. The carbon content normally is in the range of 83-87%, and the hydrogen content ranges from 10-14% [27]. In addition, small amounts of nitrogen, sulfur, oxygen, nickel and vanadium may be found in the crude oils [27]. Crude oils from different regions have different properties [28, 15]. Thousands of chemical compounds present in crude oil, herein it is somehow impossible to achieve a complete definition of the structure and composition of each individual molecule. Therefore, the most practical way to divide the crude oils is to do that with respect to their polarity and solubility [19, 29], which is known as SARA separation. In this method, the SARA separation scheme is displayed in Fig. 2. The crude oil system is isolated into four groups of Saturates, Aromatics, Resins and Asphaltenes. Saturates are defined as non-polar hydrocarbons including straight and branched alkanes, and cycloparaffins compounds (naphtenes). Wax which mainly consists of the long chain paraffins is believed to be a sub-class of saturates. In addition, Aromatics refer to all compounds with one or more aromatic nuclei which may be linked up with naphtene rings and/or aliphatic side chains. Saturates and aromatics generally are the lightest fractions of the crude oil [27, 9].

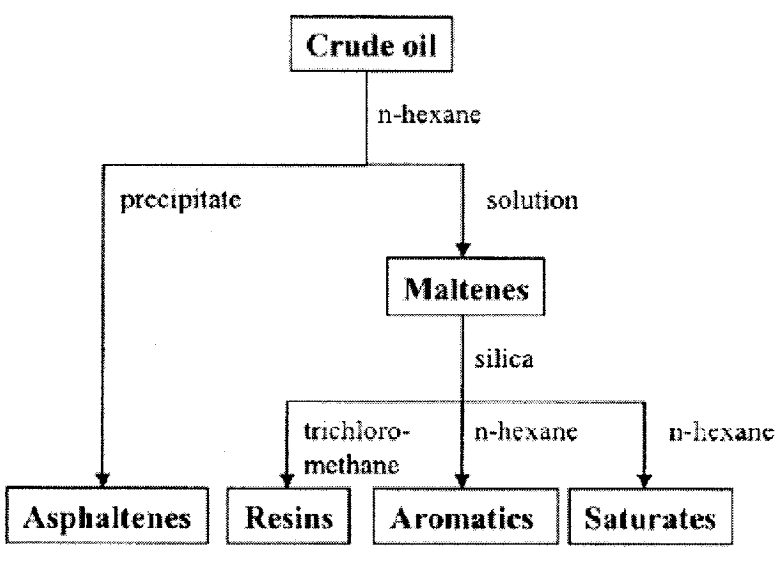


Fig. 2. SARA separation scheme [30].

Resins are another classification of crude oil and are defined as polar molecules often containing heteroatom such as nitrogen, oxygen or sulfur. This fraction tends to dissolve in light alkanes such as n-heptane or n-pentane but do not have the tendency to dissolve in liquid propane [9]. Asphaltenes are defined in terms of a solubility class that is precipitated from petroleum by the addition of an excess of a light alkanes like pentane, hexane or heptane. The precipitate is soluble in aromatic solvents like toluene and benzene [30]. Asphaltenes are the heaviest, most aromatic components of crude oil with the largest percentage of heteroatom (O, S, and N). Those components have a great impact on oil production and transportation by increasing the stability of the W/O emulsion. However, the precipitation of asphaltene particles in oil systems might cause sever problems in the pipeline and oil well. Efficient processing of asphaltic oils has been and remains a big challenge in petroleum refining industry [30, 9].

2.5 Emulsion

An emulsion is a mixture of two immiscible liquids in which fine droplets of one liquid (the dispersed phase) is dispersed in another (the continuous phase), as droplets of colloidal sizes (~ 0.1-10 μm) or larger [31, 32]. Emulsions are of great concern due to their widespread occurrence in everyday life and industry. Examples of emulsions include butter and margarine, espresso, mayonnaise, the photo-sensitive side of photographic film, and cutting fluid for metalworking. Emulsions are unstable and therefore they require certain energy acquired through shaking, stirring, homogenizers, or spray processes to be formed. Over time, emulsions tend to revert to the stable state of oil separated from water [33, 34].

Emulsions are also of great importance in the petroleum industry, through which they are typically undesirable regarding their remarkable influences on the production loss and the pipeline transportation difficulties [16].

Regarding emulsion stability, the break-up mechanism involves three different processes: flocculation, sedimentation (creaming) and coalescence [35, 36]. Sedimentation and creaming result from a density difference between the two liquid phases and is promoted by large droplet sizes, high differences in density and low viscosity of the continuous phase [37, 38, 39]. Flocculation is a reversible formation of droplet clusters where two or more droplets clump together, touching only at certain points and with virtually no change in total surface area. In flocculation the individual droplets retain their size and shape, but lose their kinetic independence because the aggregate moves as a single unit. Formation of flocculates will increase the sedimentation-creaming rate. Processes of creaming, sedimentation and flocculation are all reversible. Application of agitation will promote the recovery of original dispersion state. A much more severe phenomenon is coalescence, the complete mergence of two bubbles into one. Processes that facilitate the coalescence are film drainage and film rupture. The mechanisms are illustrated in Fig. 3 [40].

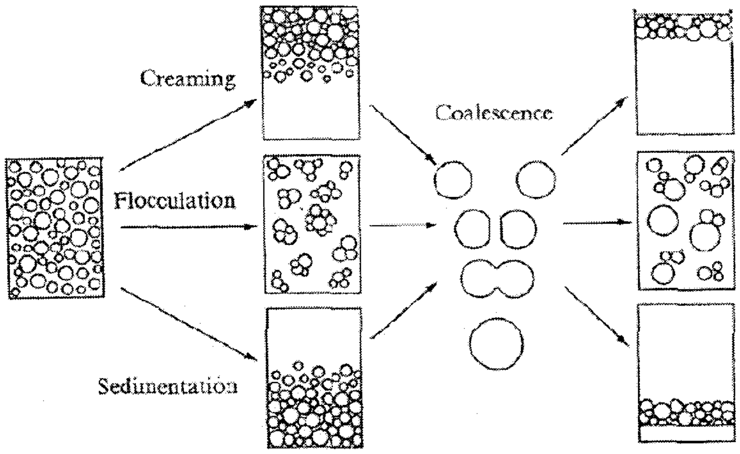


Fig. 3. Illustration of emulsion breakdown and separation processes [40].

The properties of the interface between water and oil are vital in determining the stability of an emulsion system. The formation of interface between the dispersed phase and the continuous phase increases the system free energy, therefore the emulsions are not thermodynamically stable, and tend to minimize the surface area by break-up of emulsions. If the interfacial film is weak, the emulsions stability will be poor. The dispersed droplets will collide and the collisions will lead to droplet fusion, i.e. coalescence. Many studies have been carried out to improve the understanding of the stabilisation-destabilisation mechanisms of crude oil emulsions [41, 42]. Indigenous amphiphilic substances in the crude oil, i.e., asphaltenes and resins, are traditionally considered as natural emulsifiers responsible for the stabilization of W/O emulsions. Formation of rigid, three-dimensional films of asphaltene aggregates at the oil-water interface is believed to protect water droplets from coalescence. In addition waxes, fine solids (e.g. scale, sand and clay) and naphthenates may contribute to the film strength at the oil-water interface. Furthermore, the stability of emulsions also depends on the aggregation state of asphaltenes [30, 43, 44].

2.6 Wax

Many crude oils throughout the world contain significant quantities of wax, which can crystallize during production, transportation and storage of the oil, which may lead to flow restriction and plug the pipelines as shown in Fig. 4. The presence of long-chain saturated alkanes in crude oil can lead to relentless problems associated with wax precipitation and deposition in petroleum transport pipelines and processing equipments [11, 45]. Furthermore, the presence of solid waxes in oil systems may affect the prediction and evaluation of the flow properties [46].

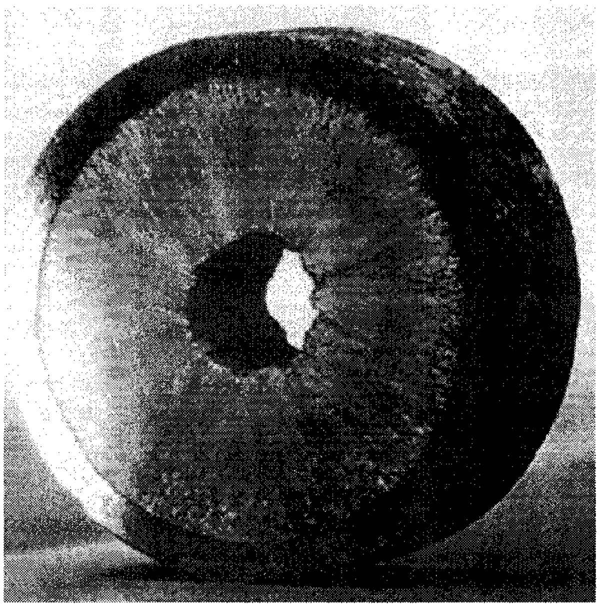


Fig. 4. Cross-sectional view of a plugged pipeline [30].

Waxes distribute differently from oil fields to oil fields, and they have a broad molecular weight distribution ranging approximately from 10 to 100 carbons or even higher. Waxes are classified as straight-chain n-alkanes/paraffin (C20-C40), and microcrystalline consisting of high molecular weight isoparaffins and cycloparaffin as shown in Fig. 5.

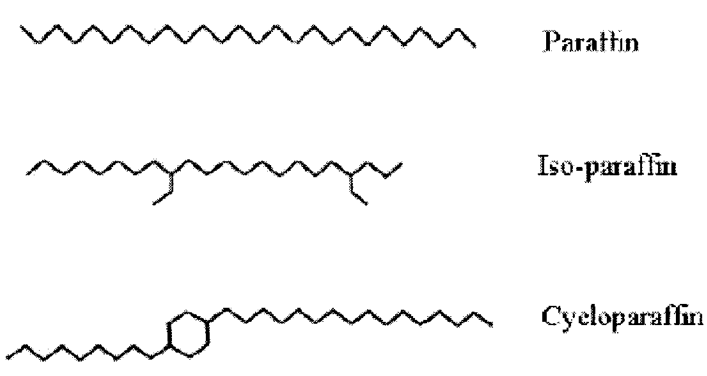


Fig. 5. Molecular structures schematics of three kinds of waxes [30].

Some types of waxes crystallize as large needles and plates such as paraffins whereas other types like microcrystalline is termed amorphous wax, which consist of branched and cyclic hydrocarbons. In general, Crude oils contain not only nparaffins but also considerable amounts of isoparaffins and cyclic compounds [10]. It is found that n-paraffin dissolved in organic solvents display a sharp transition in gel strength at the pour point, whereas by addition of isoparaffins, the build up in gel strength as a function of temperature is much more gradual, because increasing isoparaffin fraction facilitates the formation of amorphous wax solids [45].

At high temperatures, waxes are in the molten state, and crude oils normally behave like Newtonian liquids [45, 47]. If waxy crude is allowed to cool to the temperatures below the wax appearance temperature (WAT), wax will precipitate, agglomerate and entrap the liquid oil into its structure, and the crude will become a two-phase dispersion with wax solid particles dispersed in the liquid hydrocarbons. Precipitation of wax significantly increases crude viscosity and will gradually change the flow properties of the crude from Newtonian to non-Newtonian behaviour. The crude begins to show non-Newtonian flow behaviour at a temperature called the abnormal point [46, 48], which is generally a few degree Celsius below the WAT. Further cooling of the crude enhances the gel formation.

2.7 Surfactants

2.7.1 Definition

Surfactants are chemical agents that lower the interfacial tension between two liquids and hence cause an easier spreading. They are usually organic compounds which contain both hydrophobic groups (their tails) and hydrophilic groups (their heads) as shown in Fig. 6. Thus, they are soluble in water and organic solvents [32, 49].

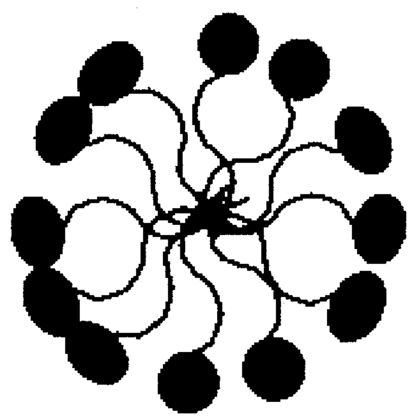


Fig. 6. Hydrophobic and hydrophilic groups in surfactants [3].

2.7.2 Operation and Effect

Surfactants lower the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Surfactants can form aggregates called micelles. The critical micelle concentration (CMC) is the concentration at which surfactants start forming micelles. Afterwards, their tails form a core that encapsulates an oil droplet, and their heads form an outer shell that maintains favorable contact with water.

Surfactant systems represent systems between ordered and disordered states of matter. That is why their thermodynamics are of great concern.

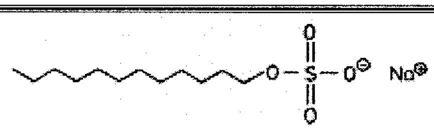
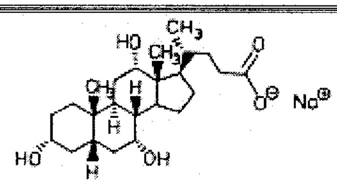
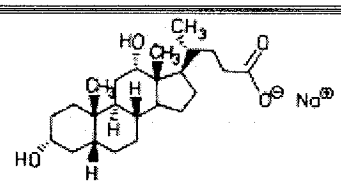
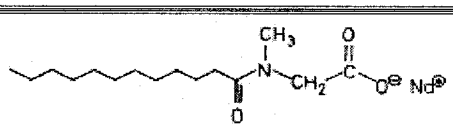
2.7.3 Classifications

Surfactants can be categorized according to the charge present in the hydrophilic portion of the molecule (after dissociation in aqueous solution):

- Anionic surfactants which have negative charge.
- Nonionic surfactants which have no charge groups.
- Cationic surfactants which have positive charge.
- Zwitterionic surfactants which have two oppositely charged groups.

Some examples of surfactants are shown in Table 2.

Table 2. Surfactant classifications [3].

	Sodium Dodecylsulfate (SDS)
	Sodium Cholate
	Sodium Deoxycholate (DOC)
	N-Lauroylsarcosine Sodium Salt

2.7.4 Applications

The surfactants are of great importance in the detergent industry, in emulsification, lubrication, catalysis, tertiary oil recovery, and in drug delivery.

- In biochemistry surfactants have allowed the investigation of molecular properties of membrane proteins and lipoproteins, acting as solubilizing agents and as probes for hydrophobic binding sites. The properties of surfactants, as well as further facts relevant to the particular experiments, must be carefully considered [3, 36].
- Surfactants have been used in the investigation of the denaturation of bacteriorhodopsin and in thermal stability experiments of rhodopsin.
- In electrophoresis, many techniques require the use of surfactants. For instance, the popular techniques of SDS-PAGE is based on a specific type of surfactant-protein interaction through which 2D-PAGE uses SDS in one direction and Triton X-100 in the other. This technique has been used to identify proteins containing long hydrophobic regions and relies on the different binding ability of non-ionic surfactants to water-soluble and intrinsic membrane proteins [50].
- Common techniques use surfactants in high performance liquid chromatography. For example, ion-exchange HPLC, reversed-phase HPLC and sizeexclusion-HPLC may require surfactants to solubilize membrane proteins.
- Crystallization of membrane proteins was achieved using short chain surfactants, which are believed to shield the hydrophobic intermembrane part of the molecule. Thus the polar interactions between individual molecules come into play, providing the stabilizing force in crystallization [3, 49].

- Further applications of surfactants in biochemistry are the solubilization of enzymes in apolar solvents via reversed micelles and the isolation of hydrophobic proteins.

2.7.5 Triton X-100 Surfactant

Triton X-100 surfactant was used during the experiments. A breif summary of this type of surfactants is given as follows.

2.7.5-1 Product Description

Triton X-100 is a high-purity, water-soluble, liquid, nonionic surfactant that has come to be recognized as the performance standard among similar products. It is an octylphenol ethoxylate consisting of 9 to 10 moles of ethylene oxide and is supplied as a 100% active product. The purity of Triton X-100 makes it desirable for uses where a refined grade of surfactant is required.

2.7.5-2 Special Features

- Excellent compatibility with anionic surfactants
- Excellent wetting ability
- Excellent detergency and oil removal properties

The physical properties are shown below in Table 3.

Table 3. Typical physical properties [51].

Actives Content, wt% Appearance	100 Clear liquid
Color, APHA Viscosity at 25□, cP	100 240
Pour Point, □ (°F) Specific Gravity at 25/25□	7 (45) 1.07
pH, 5% aqueous solution Cloud Point, 1% aqueous solution,□	6 65
Density at 25□, lb/gal Flash Point, Tag Open Cup, °F HLB Value	8.9 > 300 13.5

2.7.5-3 Performance Properties

Triton X-100 has performance properties which are described below as follows:

- **Solubility and Compatibility**

Triton X-100 is soluble at 25 ^{0}C in all proportions in water, toluene, xylene, trichloro-ethlene, ethylene glycol, ethyl ether, ethyl alcohol, isopropyl alcohol, ethylene dichloride, and many other solvents. Triton X-100 is insoluble in kerosene, mineral spirits, and VM&P naphtha, unless a coupling agent is used. Oleic acid is an effective coupling agent in systems based on aliphatic solvents. Solutions containing up to 5% Triton X-100 in 40% phosphoric acid or 30% hydrochloric acid are stable for at least 48 hours at room temperature.

Triton X-100 is compatible with anionic, cationic, and nonionic surfactants. Like other alkylaryl polyether alcohol, this surfactant will discolor on dry caustic and anhydrous metasilicate. However, Triton X-100 can be used in formulations containing moderate quantities of these alkalis with sufficient stability. It is completely stable in liquid formulations containing sodium hydroxide, showing no change in color or physical properties, and in the presence of mild, alkaline builders normally used in the preparation on metal cleaners and cleaning compounds [40].

2.8 Rheology

2.8.1 Theory

Rheology is the study of the deformation and flow of matter under the influence of an applied stress. The force can be applied in various ways: as a tension, a compression, a shearing process, or some combination of three. One simple type of deformation, shear, is illustrated in Fig. 7 [50]. The lower plate of two parallel ones is held constant. The upper plate is pulled with a velocity U with respect to the lower one. The applied shearing force is F, acting in the x direction over area A. With consideration of simple laminar flow, we can define the basic parameters as the following:

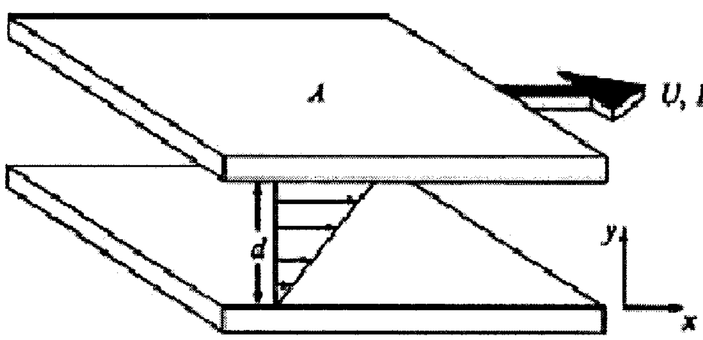


Fig. 7. Deformation of a liquid under an applied shear force "*F*"[50].

Shear stress is a stress state where the stress is parallel or tangential to a face of the material, as opposed to normal stress when the stress is perpendicular to the face. It is defined as the forced divided by the area over which it is applied [30]:

$$\tau = \mathrm{d}F / \mathrm{d}A \qquad (2)$$

Shear strain is the displacement of any plane relative to a second plane, divided by the perpendicular distance between planes. It is the force causing such deformation [30].

$$v = dx / dy \tag{3}$$

Shear rate is the speed of deformation [30]:

$$\gamma = dv / dt \tag{4}$$

2.8.2 Newtonian Vs. Non-Newtonian Liquids

Newtonian liquids exhibit constant viscosity independent of shear rate and of type of flow, shear or extensional. Equivalently, Newtonian liquids exhibit uniform resistance to flow independent of flow conditions. Non-Newtonian liquids exhibit viscosity which changes with the shear rate and with the type of deformation. In extensional flows, they exhibit elongational viscosities in no-apparent relation to their (shear) viscosities. Equivalently, non-Newtonian liquids exhibit different resistance to flow, at different shear and extensional rates. Non-Newtonian liquids, in general, can be [52]:

- *Shear thinning*, or thixotropic when their viscosity decreases (thins) with increasing shear rate.
- *Shear thickening*, or rheopectic when their viscosity increases (thickens) with increasing shear rate.
- *Viscoplastic* or Bingham plastics, 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. Fig. 8 illustrates the behaviour

of the viscosity of several rheologically different liquids and the resulting stress as a function of the shear rate.

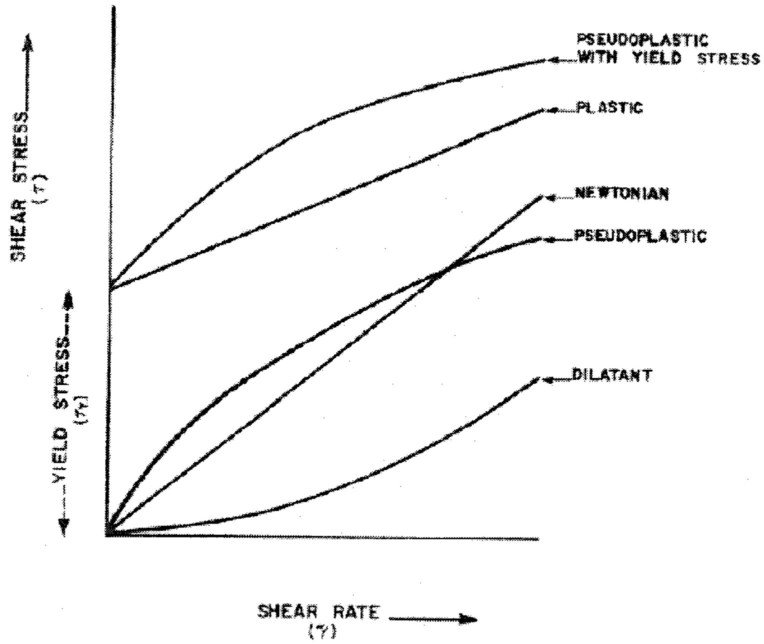


Fig. 8. The evaluation of shear stress with the shear rate for different materials [50].

Important fundamental differences between Newtonian and non-Newtonian liquids include:

- *Viscosity*: the viscosity of Newtonian liquids is constant. The viscosity of non-Newtonian liquids depends on the shear rate and may increase or decrease with shear rate. Some non-Newtonian liquids exhibit yield stress in addition. Thus, shear thinning liquids reduce friction and wear while shear thickening liquids increase them. Furthermore, viscoelastic liquids exhibit large elongational viscosity, independent of (shear) viscosity.
- *Normal stress*: the normal stress difference of Newtonian and viscous inelastic liquids in viscometric flows where there is only shear deformation is zero. Non-

Newtonian, viscoelastic liquids exhibit nonzero normal stresses in viscometric flows.

- *Elasticity and time-dependent stress*: due to elastic macromolecules, the stress grows and relaxes exponentially at a rate inversely proportional to their relaxation time. In Newtonian liquids, the stress grows and relaxes in phase with shear rate, or with zero relaxation time.

2.8.3 Rheometry

It is the experimental part of rheology. It deals with finding appropriate ways to measure deformation under imposed stress, and vice versa, in order to formulate a working constitutive equation. Investigations in this area have produced several commercially available rheometers to measure viscosity, normal stresses, relaxation times, and elongational viscosity. Some widely used rheological instruments are the *cone and plate*, *concentric cylinder*, *capillary* and *parallel plate* rheometers [53].

- *Concentric cylinder*: The sample is placed in the gap between two concentric cylinders. The inner cylinder is then driven at a constant torque (angular force) and the strain (angular deflection) or rate of strain (speed at which the inner cylinder rotates) is measured. The viscosity of the fluid between the plates governs the speed at which the inner cylinder rotates: the faster it spins at a given torque the lower the viscosity of the liquid being analyzed. The torque can be varied in a controlled manner so that the (apparent) elastic modulus or viscosity can be measured as a function of shear stress. This instrument can be used for measuring the viscosity of non-Newtonian liquids, the viscoelasticy of semi-solids and the elasticity of solids.

- *Parallel plate*: In this instrument the sample is placed between two plates: the bottom one is stationary and the top one rotates. A constant torque is applied to the upper plate, and the angular deflection or rate of strain is measured, depending on whether one is analyzing a predominantly solid or liquid sample. The main problem with this type of experimental arrangement is that the shear strain varies across the sample. The shear strain in the middle of the sample is less than that at the edges. Thus parallel plate arrangements are only suitable for samples where the rheological properties are independent of shear rate, and are therefore not suitable for non-Newtonian liquids or solids.
- *Cone and plate*: This is essentially the same design as the parallel plate instrument, except that a cone replaces the upper plate. The cone is specially designed to have a slight angle so that there is a constant shear strain across the sample. Thus it can be used to analyze non-Newtonian materials [54].

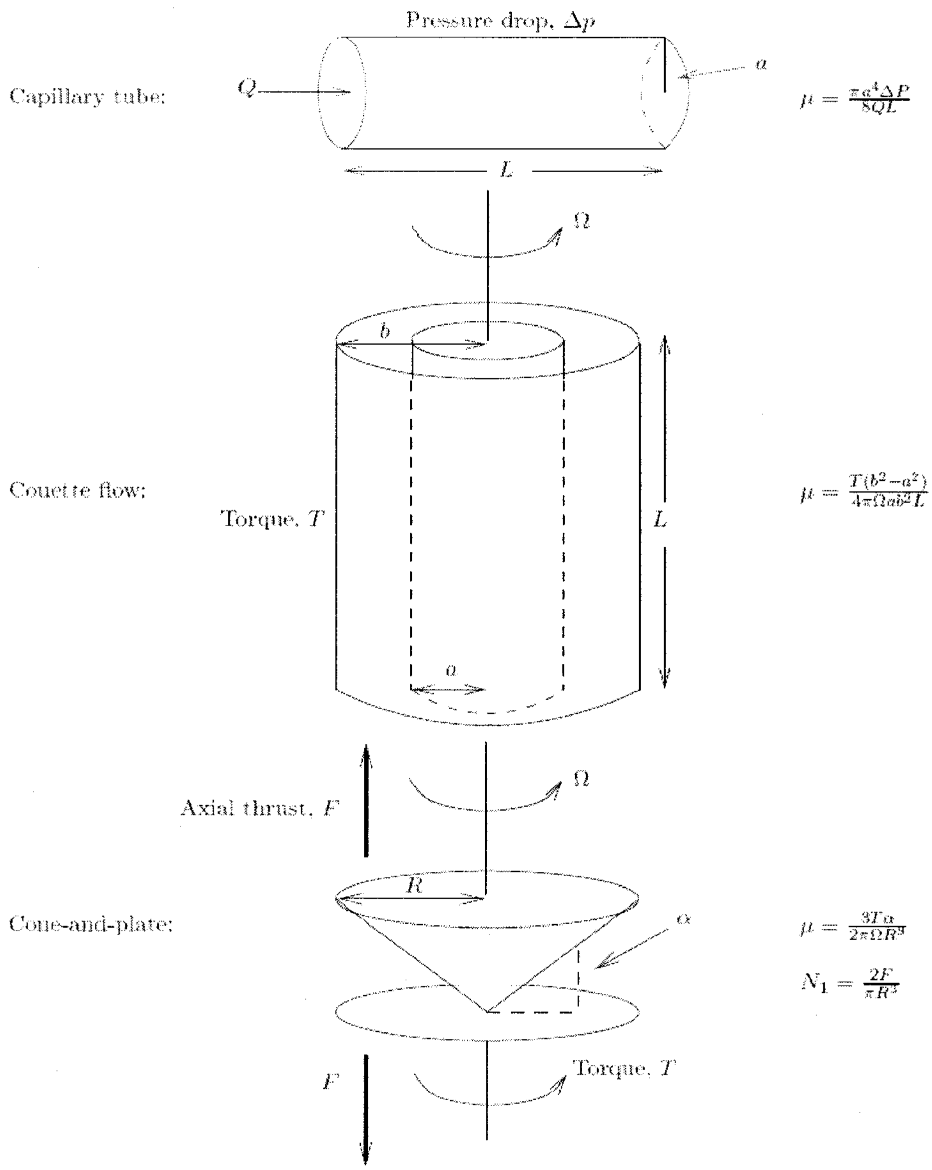


Fig. 9. Different types of rheometers [53].

Any of these arrangements can be used to carry out simple viscosity measurements on fluids, by measuring the variation of shear stress with shear rate. However, some of them can also be used for more expensive applications such as the transient and dynamic rheological tests.

2.8.4 Applications

Rheology has important applications in many fields. For instance, it is implemented in the fields of engineering, geophysics and physiology. Particularly, hemorheology, the study of blood flow, has an enormous medical significance. In geology, solid earth materials that exhibit viscous flow over long time scales are known as rheids. In engineering, rheology has had its predominant application in the development and use of polymeric materials (plasticity theory has been similarly important for the design of metal forming processes, but in the engineering community is often not considered a part of rheology). Rheology modifiers are also a key element in the development of paints in achieving paints that will level but not sag on vertical surfaces [55, 56].

2.8.5 Rheological Models

Different rheological models are described by some equations; a short description of them is as follows [50]:

- *Power Law Equation* for pseudoplastic or dilatant fluids:

$$\tau = K\gamma^n \qquad (5)$$

Where K is the consistency coefficient (also called viscosity), and n is the power law index.

- *Bingham Model* [30, 50]:

$$\tau = \tau_B + \eta_P \, \gamma \qquad (6)$$

It can be used to describe the plastic behaviors with a linear equation where η_p is the plastic viscosity and τ_B is the yield stress. Yield stress is an important property for the restart of transport. It is the upper limit of shear stress before flow occurs, at which point that the range of reversible elastic deformation ends and range of irreversible deformation or viscoelastic-viscous flow begins [57].

- *Casson Model*:

$$(\tau)^{0.5} = (\tau_0)^{0.5} + K(\gamma)^{0.5} \quad (7)$$

2.8.6 Rheological Tests

It is very essential in the field of fluid mechanics to perform the rheological tests to study the properties of the investigated material which help the fluid scientists to have analytical techniques to measure these properties. Most rheological tests involve applying a force to a material and measuring its flow or change in shape. Rheology is important in a number of different areas of fluid science. The flow of fluids through pipes or the ease at which they can be packed into containers is largely determined by their rheology. Instruments are needed for routine analysis in quality assurance laboratories, and for fundamental studies in research and development laboratories.

2.8.6.1 Shear-Rate Dependent Non-Newtonian Behavior

The viscosity is independent of the shear rate in a Newtonian liquid. The viscosity of many liquid fluids varies with the shear rate, yet is independent of the length of time that the fluid is subjected to the shear [58]. For example, the viscosity of a fluid may increase or decrease as the shear rate is increased, whereas it is constant for a Newtonian liquid. In these fluids the viscosity is referred to as an apparent viscosity, because it is no longer a constant. The choice of shear rate to use when measuring the apparent viscosity of a non-Newtonian liquid is a particularly important consideration when carrying out rheological measurements in a laboratory. The two most common types of shear-rate dependent non-Newtonian liquids are [59]:

- *Pseudoplastic fluids:* they are the most common types of non-Newtonian behavior exhibited by liquid fluids through which the apparent viscosity of a fluid decreases as the shear rate is increased, and is therefore referred to as *shear thinning*. Pseudoplasticity may occur for a number of different reasons, *e.g.*, polymers may align themselves with the flow field, solvent molecules bound to a particle may be removed, or aggregated particles may break down.
- *Dilatant fluid:* dilatant behavior is much less common than pseudoplastic behavior. It takes place when the apparent viscosity increases when the shear rate is increased, and is therefore sometimes referred to as *shear thickening* [52].

2.8.6.2 Time-Dependent Non-Newtonian Behavior

There are many fluids whose rheological properties depend on the duration of the applied shear. In some cases this change is reversible and the fluid will recover its original apparent viscosity if it is allowed to stand at rest for a sufficiently long period. In other cases the change brought about by shearing the sample is irreversible. Time dependent non-Newtonian behavior is classified in two different ways [60, 61]:

- *Thixotropic fluids*: thixotropy is the property of some non-Newtonian pseudoplastic fluids to show a time-dependent change in viscosity; the longer the fluid undergoes shear, the lower its viscosity. A thixotropic fluid is a shear-thinning fluid which takes a finite amount of time to reach an equilibrium viscosity when introduced to a step change in shear rate. Thixotropy is a relative measure of the extent and speed of recovery of the internal structure of a material during and after shear. It is useful because it allows an estimate of the effects of agitation and pumping for prolonged periods, and also the effects of ceasing the agitation (i.e. how quickly the structure will rebuild, and how difficult it will be to restart the process as a result). Many gels and colloids are thixotropic materials. In addition, some clays is also thixotropic, with their behavior of great importance to structural and geotechnical engineers. In earthquake zones, clay-like ground can exhibit characteristics of liquefaction under the shaking of a tremor, greatly affecting earth structures and buildings. Thixotropic fluids have many applications such as the thickening of food stuffs and medical products. For example, toothpaste is a thixotropic fluid that allows it to be squeezed out of the tube, but retain a solid shape on the brush.

- *Rheopectic fluids:* In some fluids, the apparent viscosity of the fluid increases with time when it is subjected to a constant shear rate. This is because of different reasons for this. When the shear rate increases, it results in increasing the frequency of collisions between droplets or particles in fluids that can lead to enhanced aggregation and consequently an increase in apparent viscosity [62].

In some fluids the time dependent rheological properties are irreversible, *i.e.,* once the shear force is removed the system does not regain its initial rheological properties. Liquids fluids that experience permanent change are called *rheodestructive.* This type of behavior might occur when aggregated particles are permanently disrupted and do not reform with time.

2.8.6.3 PLASTICS

Many fluids exhibit a kind of rheological behavior known as *plasticity*. A plastic material has elastic properties below a certain applied stress, the yield stress, τ_0 [58].

2.8.6.3-1 Newtonian Plastic Behavior

The Newtonian plastic material is referred to as a *Bingham plastic*. Two equations are needed to describe the rheological behavior of a Bingham plastic, one is below the yield stress and one is above it [63, 64]:

$$\tau = E\gamma \qquad \text{(for } \tau < \tau_0\text{)} \qquad (8)$$

$$\tau - \tau_0 = \eta d\gamma/dt \qquad \text{(for } \tau \geq \tau_0\text{)} \qquad (9)$$

where E is the shear modulus, η is the viscosity and τ_0 is the yield stress. Fluids that exhibit plastic behavior usually consist of a network of aggregated molecules or particles dispersed in a liquid matrix [65].

2.8.6.3-2 Non-Newtonian Plastic Behavior

Fluids may exhibit non-Newtonian behavior similar to that described earlier for liquids, *e.g.* psuedoplastic, dilatant, thixotropic, rheopectic above the yield point. On the other hand, the material may also exhibit non-Newtonian elastic behavior below the yield stress, *e.g.*, the yield point may not be sharply defined, and instead, the stress may increase dramatically, but non-instantaneously, as the shear rate is increased.

2.8.6.4 VISCOELASTICITY

Some materials are not pure viscous or pure elastic, but have rheological properties that are partly viscous and partly elastic. Viscoelastic materials exhibit both viscous and elastic behavior simultaneously, while plastic materials exhibit elastic behavior below the yield stress, and viscous behavior above the yield stress. When a force is applied to a viscoelastic material, it takes some finite time to take-up its new dimensions. In addition, when the force is removed the material does not return instantaneously back to its non-deformed state, and it may even remain permanently deformed [64].

Transient and dynamic measurements are the two types of experimental tests used by fluid scientists to characterize the viscoelastic properties of fluids. Both types of tests can be carried out using simple shear, simple compression or bulk compression of fluids, depending on how the instruments are designed [66].

2.8.6.4-1 Transient Experiment

In a transient experiment a constant force is applied to a material and the resulting strain is measured as a function of time, or vice versa.

- *Creep*: in this test, a constant stress is applied to a sample and the corresponding strain is followed as a function of time. When the results are measured, they are expressed in terms of a parameter called the compliance J = strain /stress, because the stress remains constant. The change in strain of a material can also be measured when the stress is removed, (i.e. creep recovery).

- *Stress relaxation:* in this test, a constant strain is applied and the change in the stress is measured with time. These types of experiments are referred to as stress relaxation. The same types of information can be obtained from either creep or stress relaxation experiments, and the method used usually depends on the instrument available [50].

2.8.6.4-2 Dynamic Experiments [30, 50, 67]

In a dynamic experiment a sinusoidal stress is applied to a material and the resulting sinusoidal strain is measured, or vice versa. In this test, for linear viscoelastic materials, if an oscillating strain is applied at a given pulsation, ω, with deformation amplitude, γ_0:

$$\gamma(t) = \gamma_0 * \sin(\omega t) \tag{10}$$

An important term, complex modulus G^*, is defined as the ratio of the maximum stress τ_0 and the maximum strain γ_0:

$$G^*(\omega) = \tau_0 / \gamma_0 \tag{11}$$

Complex modulus, G^*, is constant for a given radial frequency, ω. The storage and loss moduli are derived from the phase angle and complex modulus:

$$G'(\omega) = G^*(\omega) \cos(\delta) \tag{12}$$

$$G''(\omega) = G^*(\omega) \sin(\delta) \tag{13}$$

Where G' is the measure of the energy stored in the material per cycle, whereas G'' is a measure of the energy dissipated as heat (and therefore lost) per cycle. For a perfectly elastic material the stress and strain are completely in phase and for a perfectly viscous material all the energy is lost as heat. The substance complex modulus can be also defined as:

$$G^* = G' + iG'' \tag{14}$$

The complex viscosity, η^*, can be defined as the total resistance against the applied dynamic shear rate as:

$$\eta^* = G^* / \omega \tag{15}$$

CHAPTER III

EXPERIMENTATIONS

3.1 Materials

A crude oil sample was collected from Husky Energy from the Lloydminster area, Canada. The characteristics of the crude oil sample are presented in Table 4. Initially, the crude oil was homogenized by shaking it for an hour to ensure that the heavy crude oil's physical properties are the same anywhere the sample is taken for the measurements. After homogenization, the crude oil was used for this investigation. The commercial non-ionic surfactant Triton X-100 from Sigma-Aldrich Canada Ltd. was used as an emulsifying agent to form oil-water emulsion. A surfactant material is usually added into the oil-aqueous solution emulsion system as an emulsifying agent to accomplish two functions. The first function is to lower the oil/aqueous solution interfacial tension, therefore, assists in the formation of the emulsion system. The second function of the surfactant material is to stabilize the presence of the oil droplets phase within the aqueous continuous phase to avoid the oil droplets coalescence mechanism [68, 69]. An alcohol (Ethanol 99%), provided from the chemicals store at Concordia university in Montreal, as well as the light crude oil with viscosity of 0.300 Pa.s, provided from Shell Canada in Montreal, were used as alternative blending materials.

Table 4. Characteristics of the heavy oil in Lloydminster at 288 K.

Property	
Formation types	Sparky, Waseca, McLaren, GP, Colony, Lloyd etc.
Oil Density, kg/m^3	995
API^0 Gravity	10.71

3.2 Preparation of Emulsion

Aqueous solution of surfactant was made initially for preparing oil-in-water (O/W) emulsion. The aqueous solution of surfactant, having concentration of 1000 ppm, was prepared with distilled water. The measured volume of aqueous solution of surfactant was transferred into a conical flask provided with a stirrer, and the required amount of the crude oil was added according to the desired emulsion concentration. The mixing was then provided to form stable and homogeneous emulsion by breaking large liquid drops into smaller drops. All surfactant solutions were prepared before mixing with the crude oil. Afterwards, the emulsion was taken for the measurements.

3.3 Experimental Set-up

The measurements were carried out using RheoStress RS100 from Haake [69]. This rheometer has several operating test modes. It has a universal controlled rate (CR) mode, a controlled stress (CS) mode, and an oscillation (OSC) test mode. In the CS mode, shear stress is applied to a test sample by means of extremely low inertia. The drive shaft of the RS100 is centered by an air bearing to ensure an almost frictionless transmission of the applied stress to the test fluid. The resulting deformation of the sample is detected with a digital encoder that processes 10^6 impulses per revolution. This resolution makes it possible to measure small yield values, strains, or shear rates. The computer controlled rheometer can be easily switched between both CS and CR modes, and it can provide oscillating stress inputs and autostrain. A controlled variable lift speed is used to position the cone on the plate. A thermal gap size is controlled to compensate for any of the sensor generated heat. The software package "Haake Windows" controls both test routines and data evaluation. The rheometer is equipped with a cone and plate sensor. This cone-plate sensor was used with a cone angle of °4, cone diameter of 35 mm, and 0.137-mm gap at the cone tip. The experimental set-up is shown in Fig. 10.

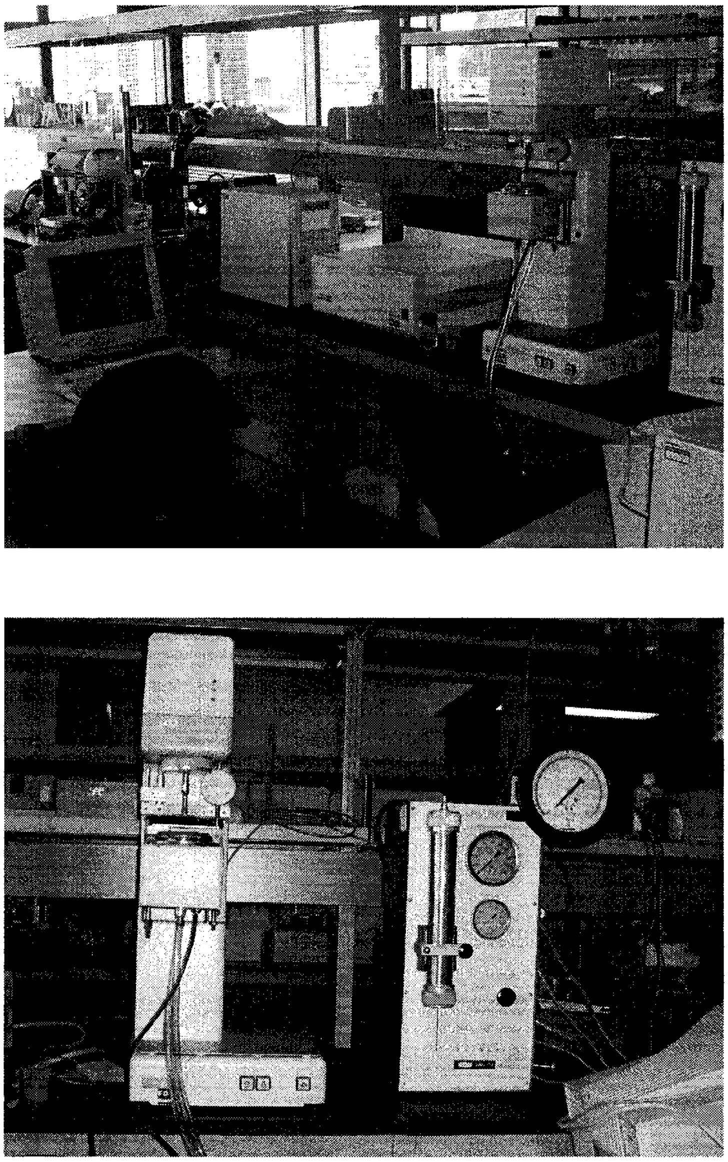


Fig.10. Experimental set-up.

3.4 Results and Discussion

3.4.1 Rheological Models

Different rheological models are verified so that the best model that fits the measurements is selected. The test is conducted under the CR mode at room temperature 298 K, and the values of shear stress and shear rate are obtained. These data are plotted in in order to accomplish the best fit model. Power law, Bingham, and Casson models are investigated in this study, and their equations, which are explained earlier in chapter 2, are used to calculate the measured values of shear stress and shear rate as well. As shown in Figs. 11 to 13, the heavy crude oil fits the power law model over a wide range of shear rates of 0.6 to 740 s^{-1} since it has the highest regression correlation coefficient, R^2, of 0.994. This conclusion agrees with other works [51].

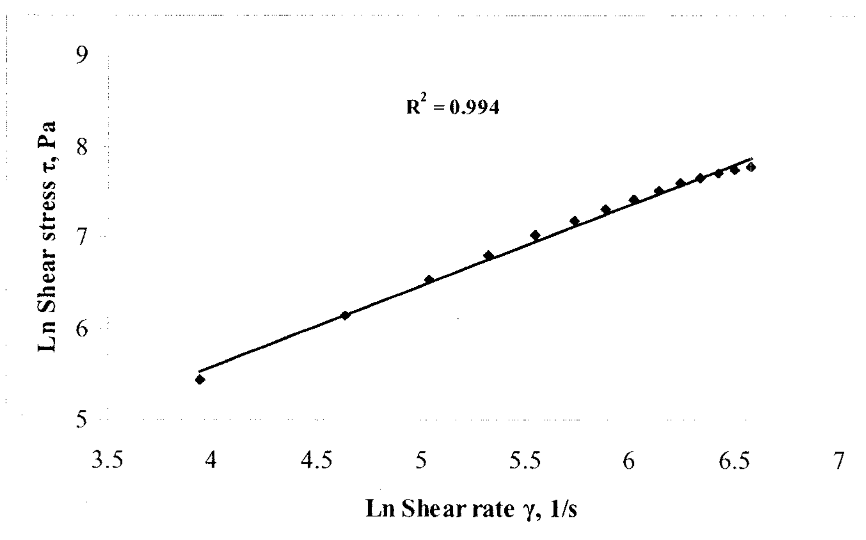


Fig. 11. Power law model.

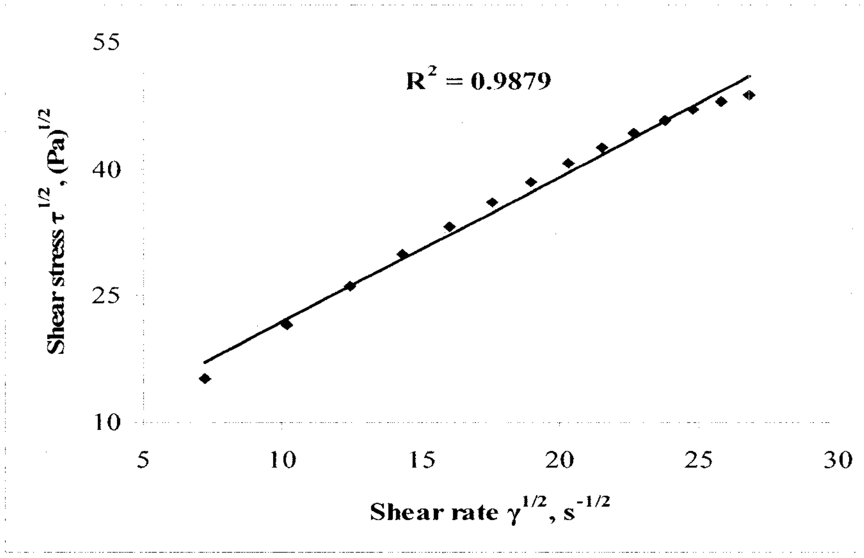


Fig. 12. Casson model.

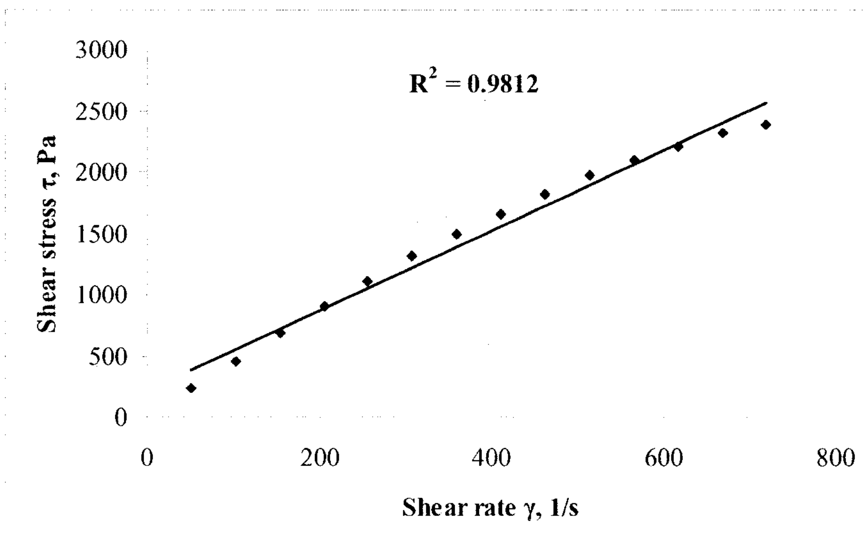


Fig. 13. Bingham model.

3.4.2 Steady Flow Test (viscosity measurements)

3.4.2-1 Effect of Temperature and Shear Rate

This test provides the flow behavior curve in terms of the viscosity-shear rate or shear stress-shear rate relationships. Fig. 14 shows the effect of temperature on viscosity-shear rate for pure crude oil over the range of 298 to 348 K (25 to 75 ^{0}C) in 10 degrees increment. The test is done using the CR mode. It is observed that the crude oil shows non-Newtonian shear thinning behavior over the range of shear rates from 0.6 to 740 s^{-1} in which the apparent viscosity decreases considerably with temperature and is reduced by one half when it is heated from 298 to 348 K. It is also demonstrated that the viscosity differences are larger at low shear rates than at high shear rates. As the temperature increases, the compositions of the heavy crude oil (i.e. asphaltenes, resins, waxes etc.) with high molecular weight will not have the chance to agglomerate and form aggregates, and thereby breaking the bonds between the solid particles, and hence reducing the oil viscosity. To access the extent of the viscosity reduction, the degree of viscosity reduction (DVR) is introduced and it can be calculated using Eq. (16) [5].

$$\text{DVR}\ \% = (\eta_r - \eta_c) * 100 / \eta_r \tag{16}$$

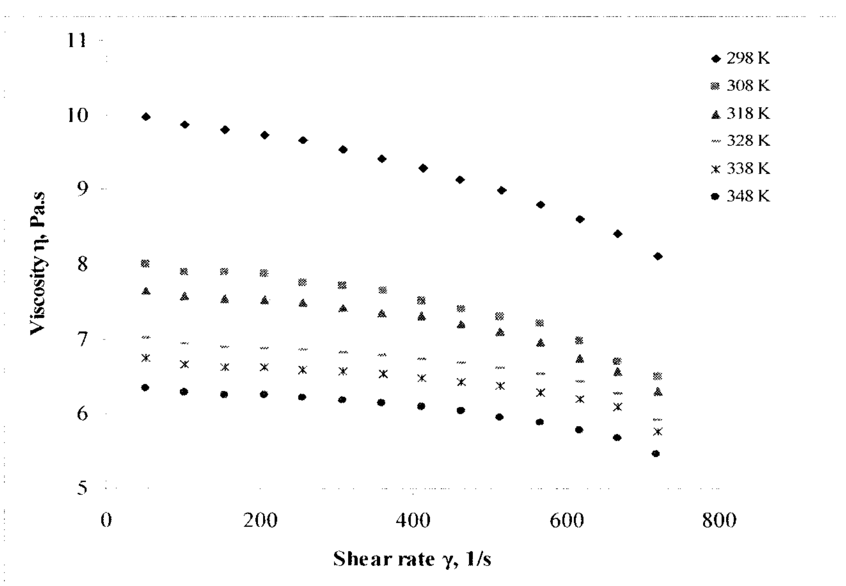


Fig. 14. Viscosity of heavy crude oil versus shear rate at different temperatures.

Where η_r is the reference viscosity at 50 s^{-1} shear rate and 298 K, Pa.s, and η_c is the corresponding viscosity at 50 s^{-1} shear rate and corresponding temperature, Pa.s.

Table 5 reports the DVR % over the temperature range of 298 to 348 K. It is noted that there is a significant increase in DVR % from 0% to 36% when the temperature increases from 298 to 348 K. This can be attributed to certain reasons. The first reason is due to the strong effect of temperature on the viscosity of heavy components in the crude oil (i.e. wax and asphaltene). The second reason is due to the effect of high temperatures on the chemical structure of heavy components which results in destroying the ordered structures of heavy components in the crude oil phase, and hence reducing the oil viscosity [70].

Table 5. DVR % of pure oil versus temperature.

Temperature, K	**DVR %**
298	0
308	20
318	23
328	30
338	32
348	36

Moreover, it is found that the viscosity of the heavy crude oil depends on the shear rate. The viscosity reaches low values at high shear rates. This means that the flow encounters less resistance at higher shear rates. This is due to the molecular chains found in the heavy crude oil. As the shear rate increases, the chain type molecules disentangled, stretched, and reoriented parallel to the driving force, and hence reducing the heavy crude oil viscosity [5, 69].

3.4.2-2 Oil/Water Emulsion

Generally, emulsions are of great interest in many industrial applications. The formation of O/W emulsion is one of the alternatives to enhance the flowability of crude oil through the pipelines. That is why, it is very important to study the mechanical behavior of the O/W emulsion. It is established that the rheological properties of emulsions and their stability are affected by the volume fraction of the dispersed phase and chemical composition of each phase [5]. Surfactants are chemical materials used as emulsifying agents in order to obtain O/W stable emulsions by lowering the interfacial tension between the crude oil-water system, and by stabilizing the presence of the droplets phase within the continuous phase to prevent the coalescence action of the droplets phase [68, 69]. It is reported that the viscosity of heavy crude oil decreases as the concentration of the aqueous solution of surfactant increases [65]. Figs. 15 and 16 show the viscosity behavior of O/W emulsion versus shear rate which ranges from 0.6 to 740 s^{-1}. The experiments are carried out at different aqueous solution of surfactant concentration (10% and 20% by volume, respectively), and over the temperature range of 298 to 348 K. The viscosity is found to be less than that obtained for the crude oil, and is reduced from 10.0 Pa.s to 8.0 Pa.s at 298 K for the 90% O/W emulsion. Similarly, the viscosity is found to be less than that obtained for the crude oil, and is reduced from 10.0 Pa.s to 6.5 Pa.s at 298 K for the 80% O/W emulsion. The results show a significant non-Newtonian shear thinning behavior with shear rate up to 410 s^{-1}. It is well known that the surface tension of most liquids decreases with increasing temperature. The increased kinetic energy imparted to the surface molecules at higher temperature will tend to overcome the net attractive force of the bulk liquid. Usually, both viscosity and interfacial tension decrease with increasing temperature; any increase in temperature usually makes emulsification easier. However, an abnormal increase of temperature is to be avoided because it tends to coagulate the particles, thereby causing a deterioration of the emulsions [67]. The viscosity reduction of the O/W emulsion can be attributed to the efficiency of the surfactant in reducing the interfacial tension of the adsorption film in emulsion, resulting in deformation of the dispersed phase easier and leading to reducing the oil droplet sizes [51]. At higher shear rates > 410 s^{-1}, it is noted that the crude oil exhibits Newtonian flow behavior for all temperatures. This means that the viscosity becomes independent with increasing temperature. This can be simply explained by the smaller influence of temperature on the viscosity of water when compared with that of oil. In general, it is found that the higher the viscosity, the stronger the temperature dependence.

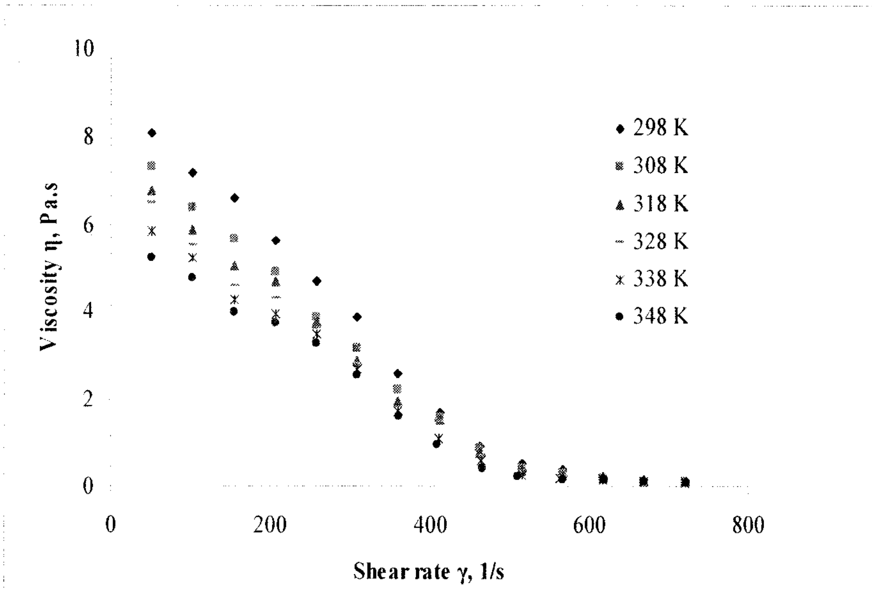


Fig.15. Viscosity-shear rate behavior of 90% O/W emulsion at different temperatures.

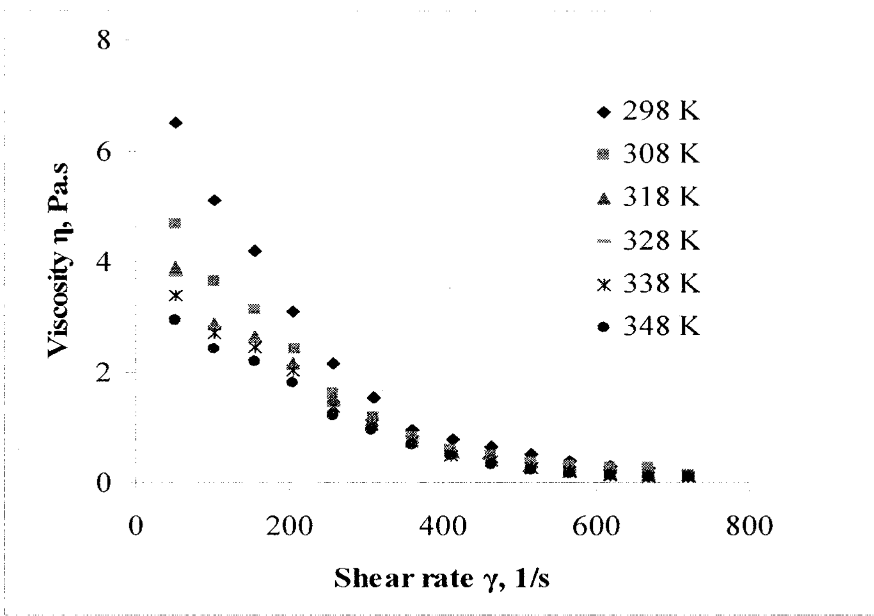


Fig.16. Viscosity-shear rate behavior of 80% O/W emulsion at different temperatures.

3.4.2-3 Effect of Ethanol Alcohol

Figs. 17 and 18 illustrate the viscosity behavior when the heavy crude oil is blended with ethanol alcohol in the same volume ratios (90% and 80%, respectively). As shown in the figures, the non-Newtonian behavior is the same as that for the heavy crude oil shown in Fig. 14. For 90% heavy crude oil-10% alcohol mixture, the viscosity is found to be five times less than that obtained for the crude oil, and is reduced from 10.0 Pa.s to 2.0 Pa.s at 298 K. On the other hand, for 80% heavy crude oil-20% alcohol mixture, the viscosity is found to be ten times less than that obtained for the crude oil, and is reduced from 10.0 Pa.s to 0.95 Pa.s at 298 K. This suggests that the supplementary reduction of the measured viscosity is due to the interactions between the hydroxyl functions and some functionalities of the asphaltenes through which it comes from the ability of a polar solvent to the structure of the colloidal particles of asphaltenes [26]. As the oil-alcohol ratio decreases, the shear thinning behavior takes place, and the viscosity decreases as the temperature increases. From the foregoing results, it can be concluded that blending the heavy crude oil with ethanol alcohol enhances the flowability of the heavy crude oil and it is much better than the results obtained from the O/W emulsion technique.

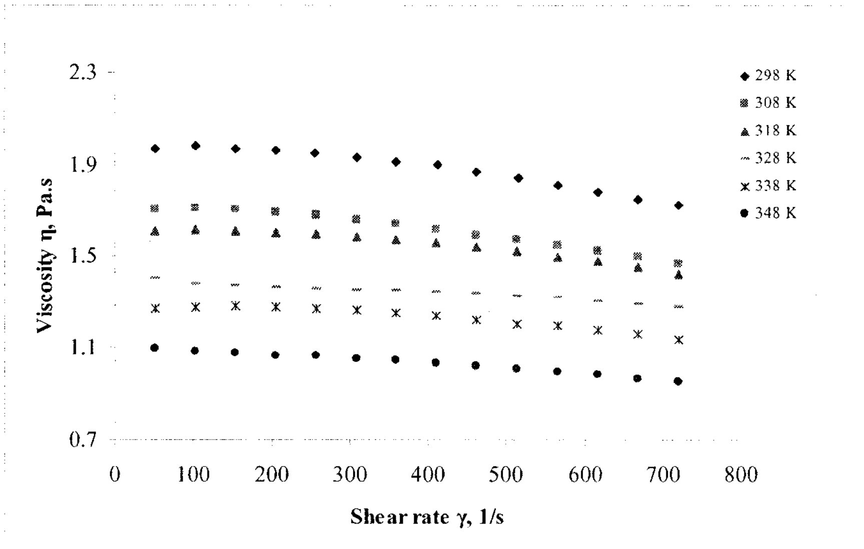


Fig. 17. Viscosity-shear rate behavior of 90% O-ethanol alcohol.

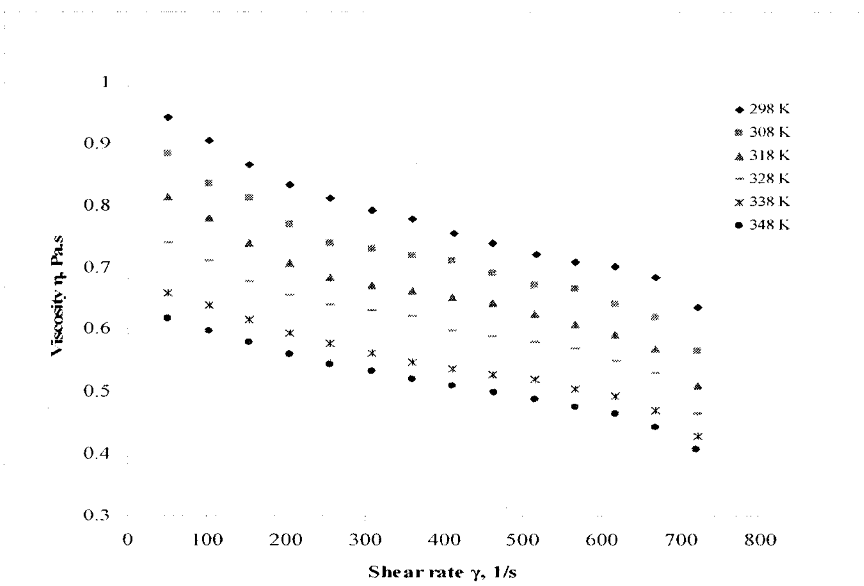


Fig. 18. Viscosity-shear rate behavior of 80% O-ethanol alcohol.

3.4.2-4 Effect of Light Crude Oil

Another alternative for viscosity reduction is tested by blending the heavy crude oil with lighter crude oil (around 0.300 Pa.s). The objective from the blending process is to form a less viscous and less dense crude oil which will be more desirable and more suitable for the pipeline transportation. As Figs. 19 and 20 illustrate the viscosity behavior when the heavy crude oil is blended with a lighter crude oil in the same volume ratios (90% and 80%, respectively). The blending mixture behaves similarly as that for the heavy crude oil shown in Fig. 14. For 90% heavy crude oil-10% light crude oil mixture, the viscosity is found to be eight times less than that obtained for the crude oil, and it is reduced from 10.0 Pa.s to 1.2 Pa.s at 298 K. On the other hand, for 80% heavy crude oil-20% light crude oil mixture, the viscosity is found to be twenty six times less than that obtained for the heavy crude oil, and it is reduced from 10.0 Pa.s to 0.375 Pa.s at 298 K. As a conclusion, this technique is more recommended than the other viscosity reduction alternatives, since the viscosity is reduced to 0.375 Pa.s at 298 K when the heavy crude oil is blended with 20% of lighter crude oil. Table 6 shows a comparison between the all techniques tested in this work. The results were carried out at room temperature 298 K.

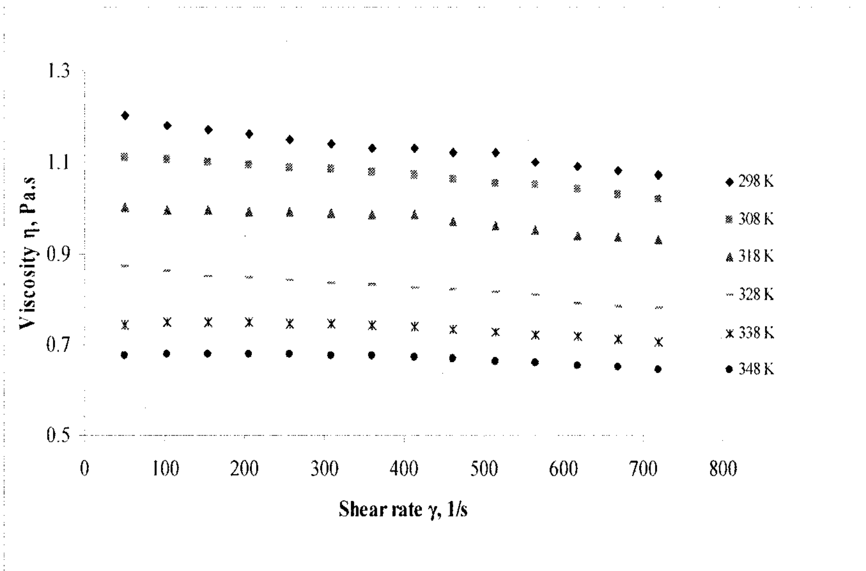


Fig. 19. Viscosity-shear rate behaviour of 90% O-light mixture.

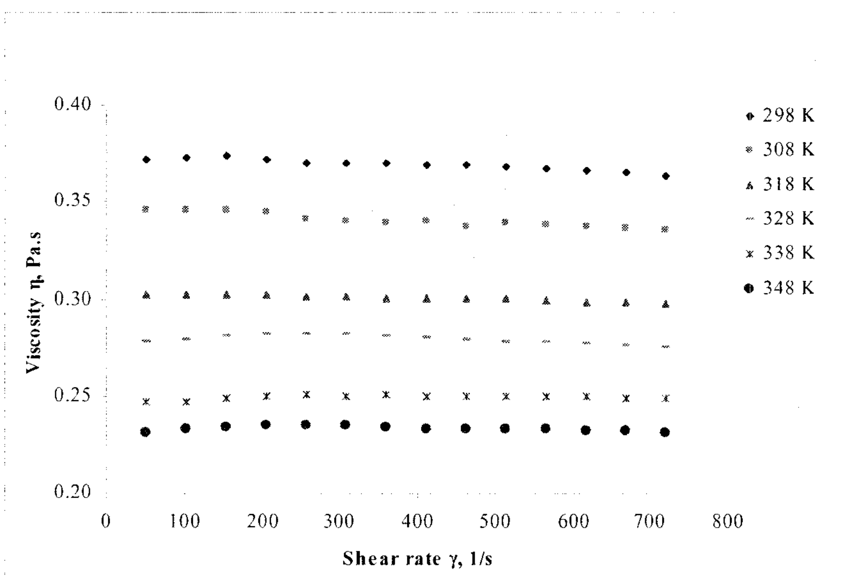


Fig. 20. Viscosity-shear rate behaviour of 80% O-light mixture.

Table 6. Measured viscosities at room temperature 298 K and shear rate 51.74 s^{-1}.

Sample	**Viscosity η, Pa.s**
Heavy Crude Oil	10.0
90% O/W Emulsion	8.0
80% O/W Emulsion	6.5
90% O/Alcohol	2.0
80% O/Alcohol	0.95
90% O/Light Crude Oil	1.2
80% O/Light Crude Oil	0.375

3.4.3. Rheological Properties Measurements

From the preceding results, it can be concluded that blending the heavy crude oil with a limited amount of lighter crude oil is the best method to reduce the viscosity. Herein, the rheological properties of the heavy crude oil as well as the heavy crude oil/light crude oil mixtures are studied in terms of the yield stress, τ_o, thixotropic behavior, loss and storage moduli, G'', G', the complex moddulus G^*, the complex viscosity η^*, transient behavior and viscosity measurements. These properties are studied at different temperatures.

3.4.3-1 Yield Stress Measurements

The yield stress is defined as a limiting stress below which a sample behaves as a solid. At low stress, the elastic deformation takes place, which disappears when the applied stress is released. The relationship between the elastic deformation and the applied stress is linear. However, above the yield stress point, the applied stress leads to unlimited deformation which causes the sample to start flow [69]. Figs. 21 to 23 illustrate the relation between the shear stress and the shear rate through which the yield measurements are conducted for the heavy crude oil as well as for the heavy crude oil-light crude oil mixtures at different concentrations and different temperatures as well. The heavy crude oil is subjected to constant values of shear stress range from 0.09 to 4.0 Pa under certain period of time 150 seconds. The test is conducted under the CS mode. The variation of the yield stress with oil content and temperature as well are deduced from the obtained figures. It can be observed that the yield point which is required to start the flow decreases as both the temperature and the fraction of water added increase. The yield point of the heavy crude oil reached a value of 0.7 Pa at room temperature 298 K and decreased to 0.4 Pa when the temperature was changed from 298 to 338 K. On the other hand, it was observed that the 90% O-light crude oil mixture and 80% O-light crude oil mixture required no yield stress value, that means the addition of the light crude oil to the heavy crude oil eliminated any further stresses to be applied. Table 7 shows a summary of the measured values of the yield stress.

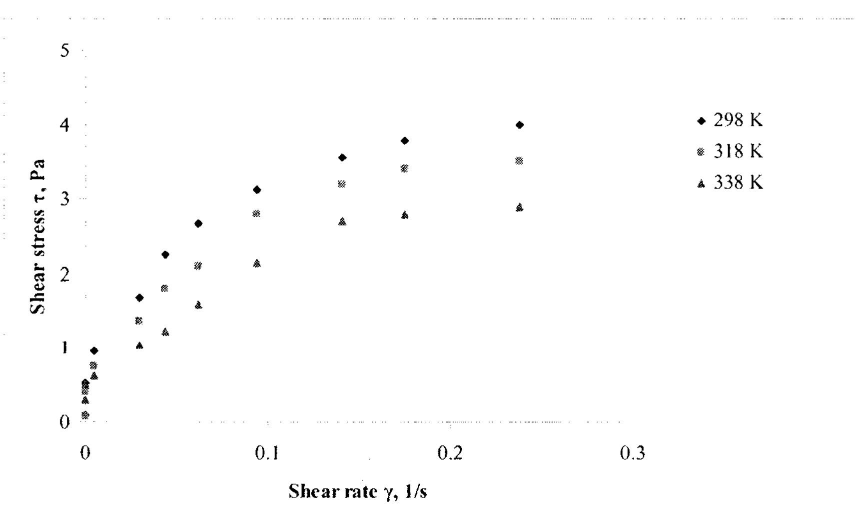


Fig. 21. Yield stress measurements of heavy crude oil at different temperatures.

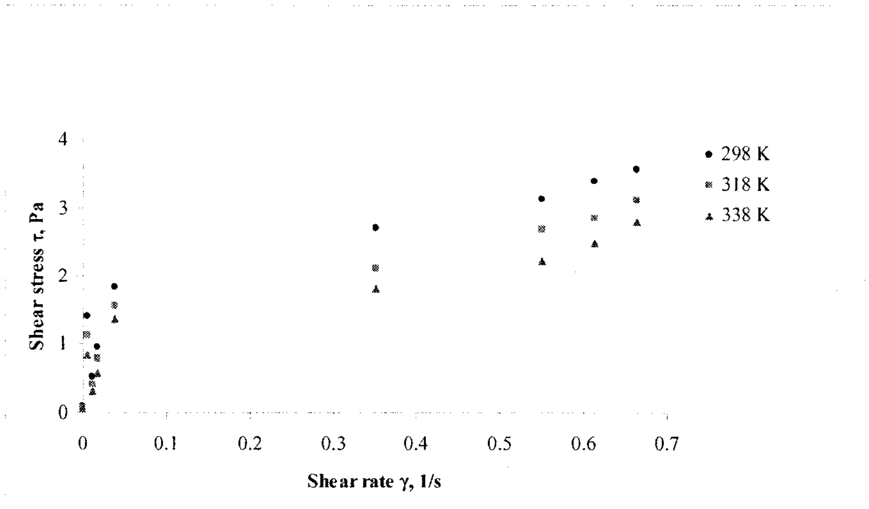


Fig. 22. Yield stress measurements of 90% O-light mixture.

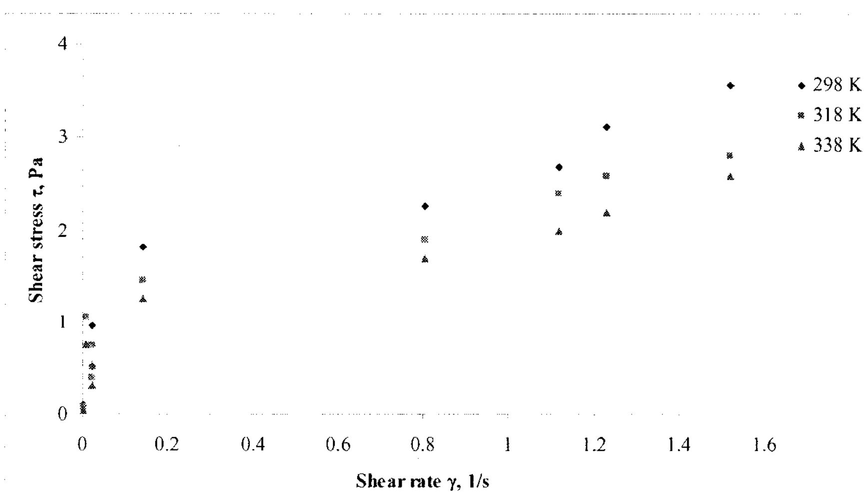


Fig. 23. Yield stress measurements of 80% O-light mixture.

Table 7. Yield stress measurements at different temperatures.

Sample	Yield stress τ_o, Pa
Heavy Crude Oil (298 K)	0.7
Heavy Crude Oil (318 K)	0.5
Heavy Crude Oil (338 K)	0.4
90% O-Light Crude Oil (298 K)	0.0
80% O-Light Crude Oil (298 K)	0.0

3.4.3-2 Thixotropy Measurements

In this test, the heavy crude oil is subjected to a constant range of shear rate under the CR mode so that the loop experiment can be performed. The values range from 0.6 to 740 s^{-1} under certain period of time 300 seconds. The apparatus was programmed to gradually increase the assigned shear rate from a given initial value of 0.6 s^{-1} to terminal value of 740 s^{-1}. The stresses and the shear rates of flow were recorded. The resulting up curve was obtained in the process of gradually increasing the shear rate. After reaching the assigned maximum rate, a gradual decrease gives the down curve, which should be identical to the up curve for time-independent rheological behavior. The curves form a hysteresis process that encloses an area. The test is done for the heavy crude oil as well as for the heavy crude oil-light crude oil mixtures at different vol.% ratios.

Fig. 24 shows the thixotropic behavior for the heavy crude oil through which the hysteresis phenomenon is clear. The area between the up and down curve (hysteresis area) is the measure of thixotropy, and is calculated and found to be 321.65 KPa.s^{-1}.

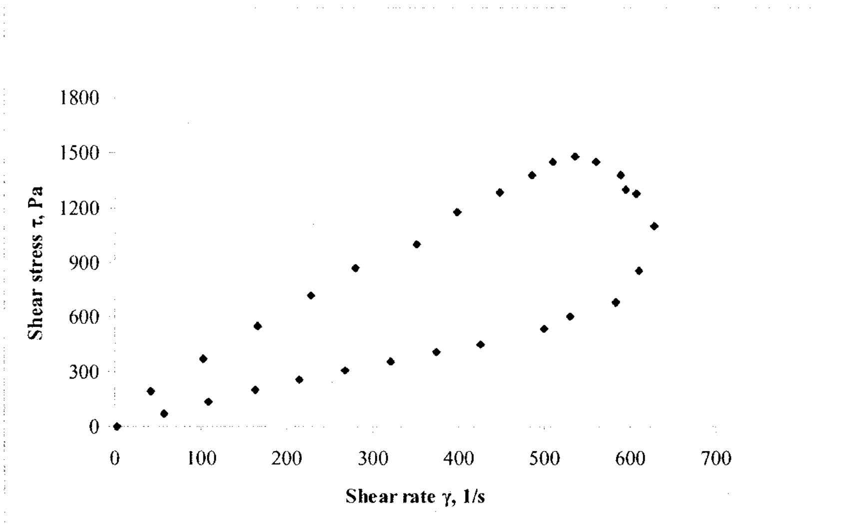


Fig. 24. Thixotropic behavior of heavy crude oil at room temperature.

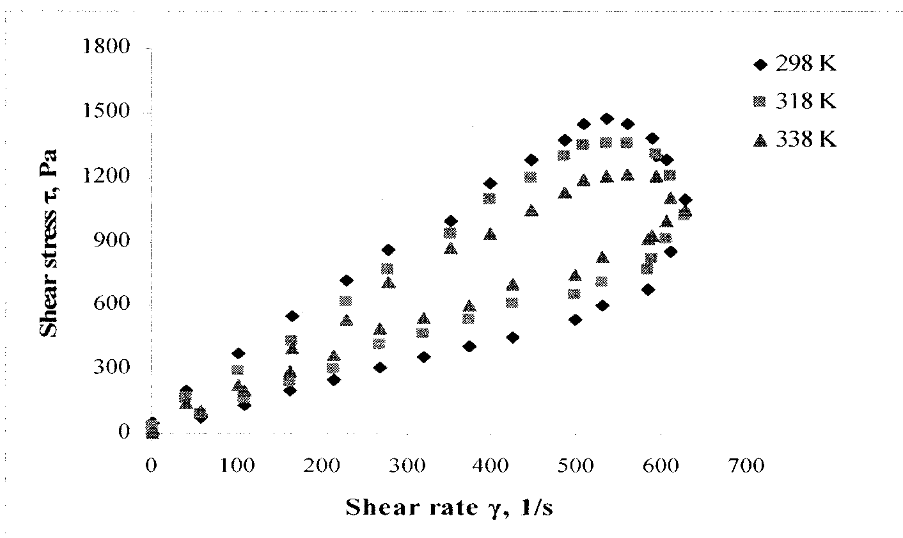


Fig. 25. Thixotropic behavior of heavy crude oil at different temperatures.

Fig. 25 shows that the resulting hysteresis decreases with temperature, and therefore the energy required to breakdown the thixotropy is less at 338 K compared to the energy required at 298 K. This can be observed clearly since the area decreases from 321.65 KPa.s^{-1} at 298 K to 118.62 KPa.s^{-1} at 338 K. The addition of the light crude oil eliminates the thixotropic behavior and leads to reversible processes through which the up curve area is almost identical to the down area curve. The results show an approximate identical up and down curve areas which results in an unnoticeable thixotropic behavior. This can be shown in Figs. 26 and 27. Table 8 shows the hysteresis area at different temperatures.

Table 8. Hysteresis area at different temperatures.

Temperature, K	**Hysteresis area, KPa.s^{-1}**
Heavy Crude Oil (298)	321.65
Heavy Crude Oil (318)	207.83
Heavy Crude Oil (338)	118.62
90% O-Light Crude Oil (298)	3.78
80% O-Light Crude Oil (298)	1.07

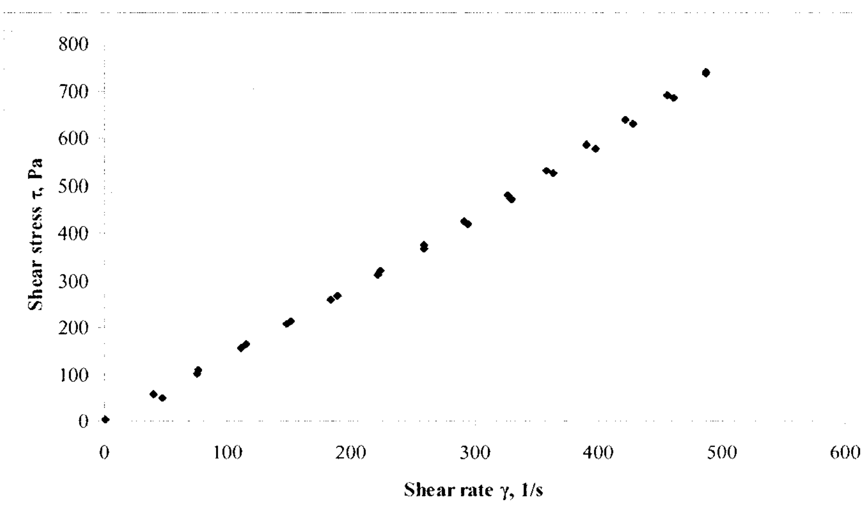


Fig. 26. Thixotropic behavior of 90% O-light crude mixture.

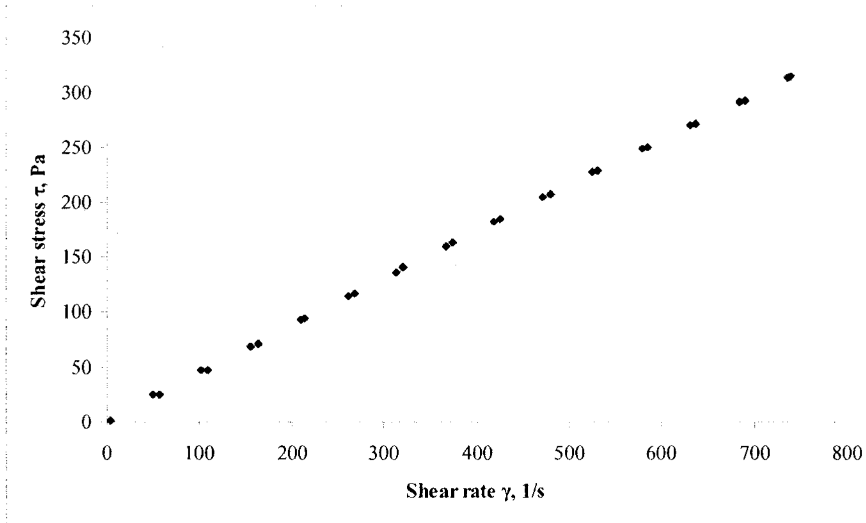


Fig. 27. Thixotropic behavior of 80% O-light crude mixture.

3.4.3-3 Transient Measurements

Heavy crude oil has complex rheological behavior. Transient characteristics are of great concern of heavy crude oil. Therefore, transient test is conducted to study the transient behavior of the heavy crude oil as well as to study the time dependence effect. The heavy crude oil is subjected to constant values of shear rate from 0.6 to 740 s^{-1} over the temperature range of 298 to 348 K under the CR mode, and the resulting stress is measured as a function of time as shown in Fig. 28. The test is done for the heavy crude oil and for the heavy crude oil-light crude oil mixtures at different vol.% ratios. It is noted that the heavy crude oil has no transient behavior since the shear stress shows time independent behavior.

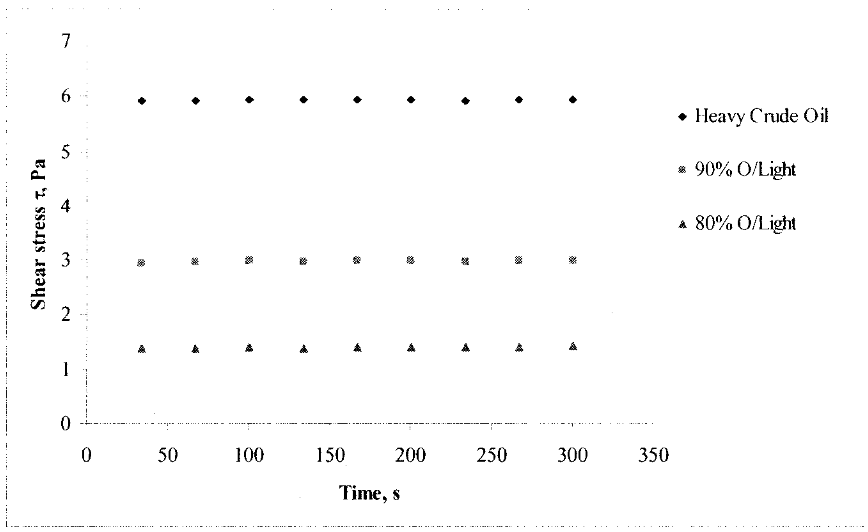


Fig. 28. Transient behavior of heavy crude oil and O-light mixtures.

3.4.3-4 Dynamic Measurements

A dynamic test is important to investigate the linear viscolelastic properties of crude oil samples under different conditions. It investigates the effect of oscillating stresses or strains on the flow behavior of crude oil samples.

It is necessary to determine the linear viscoelastic range. It is the range where the complex modulus, $G*$, is constant with stress where the internal temporary bonds of the sample structure will not be destroyed [5, 67]. The linear viscoelastic range was found to be from 0.01 to 0.7 Hz.

This test is performed under the OSC mode through which a certain stress is applied at different values of frequencies. The measurements are taken at room temperature as well as at different temperatures. The results are shown in the following figures where the storage modulus, G', the loss modulus, G'', the complex modulus, G^*, and the complex viscosity, $\eta*$, are plotted versus frequency at room temperature and at different temperatures as well.

Fig. 29 shows that the loss modulus, G'', and the storage modulus, G', of the heavy crude oil show similar linear relationship response over the entire range of frequency. The results show that the loss modulus, G'', reaches values that are higher than the values of the storage modulus, G', and this happens as well for the heavy crude oil-light crude oil mixtures as shown in Figs. 30 and 31. This means that the energy stored in the heavy crude oil per cycle is less than the energy dissipated as heat and therefore lost per cycle. Therefore, the heavy crude oil tends to behave in a viscous behavior more than it behaves in a solid-like material. Moreover, it is noted that the loss modulus, G'', and the storage modulus, G', decrease with the volume fraction of water added.

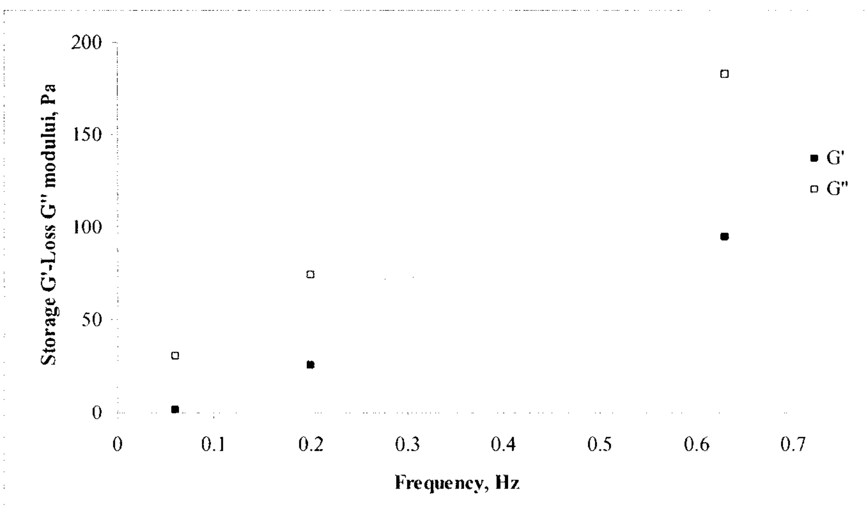


Fig. 29. Storage and loss moduli of heavy crude oil at room temperature.

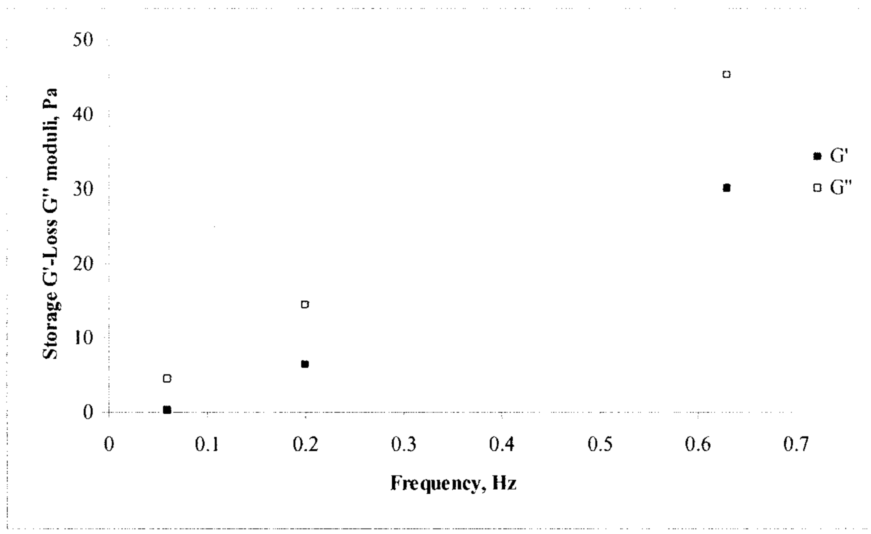


Fig. 30. Storage and loss moduli of 90% O-light crude mixture at room temperature.

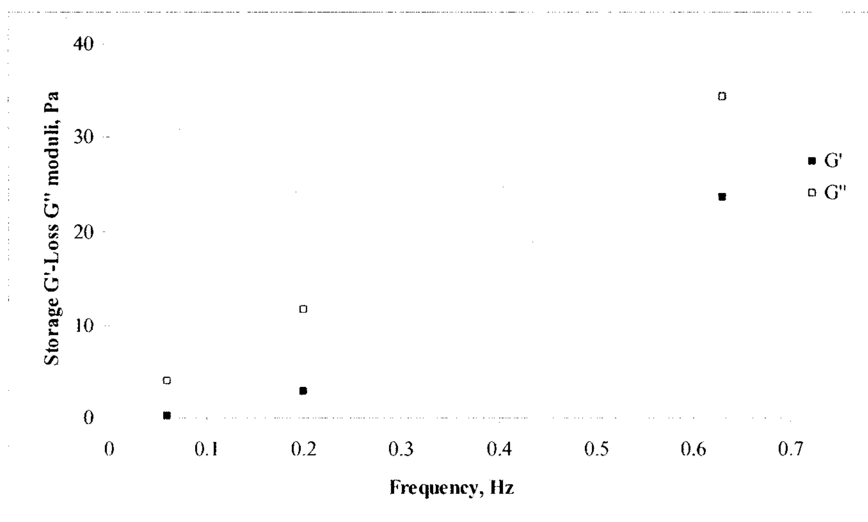


Fig. 31. Storage and loss moduli of 80% O-light crude mixture at room temperature.

The frequency spectrum of the pure heavy crude oil and of the heavy crude oil-light crude oil mixtures are illustrated in Figs. 32 to 39. It is remarkably noted that the moduli of the heavy crude oil decrease with the temperature, since the storage modulus, G', dropped from 93.7 to 43.6 Pa, and the loss modulus, G'', from 182.5 to 98.0 Pa when the temperature was changed from 298 K to 338 K. Similarly, for the heavy crude oil-light crude oil mixtures, the storage modulus, G', dropped from 30.0 to 8.0 Pa, and the loss modulus, G'', from 45.39 to 26.1 Pa for 10% addition of light crude oil when the temperature was changed from 298 to 338 K. Besides, the storage modulus, G', dropped from 23.6 to 7.1 Pa, and the loss modulus, G'', from 34.27 to 13.0 Pa for 20% addition of light crude oil when the temperature was changed from 298 to 338 K. From the foregoing results, it is obvious that both the loss and the storage moduli are strong temperature and frequency dependent [5, 69].

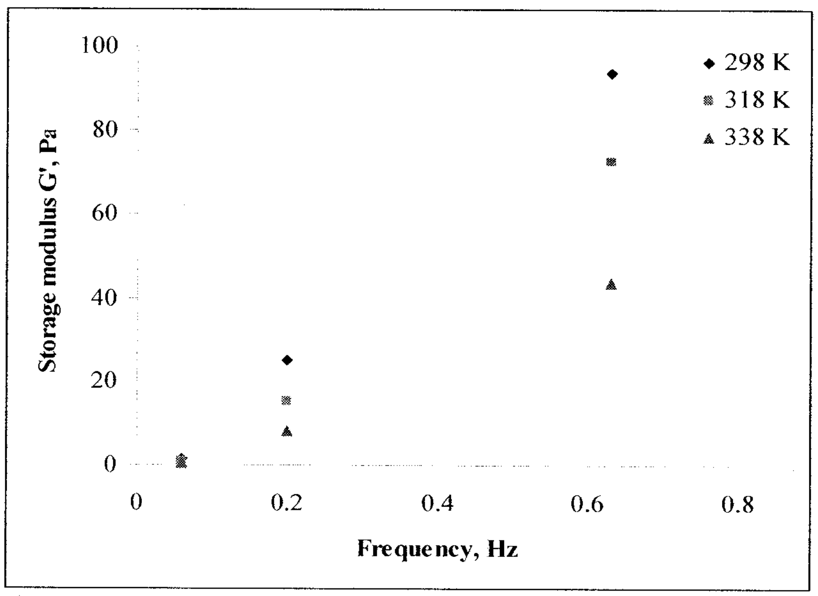


Fig. 32. Storage modulus of heavy crude oil at different temperatures.

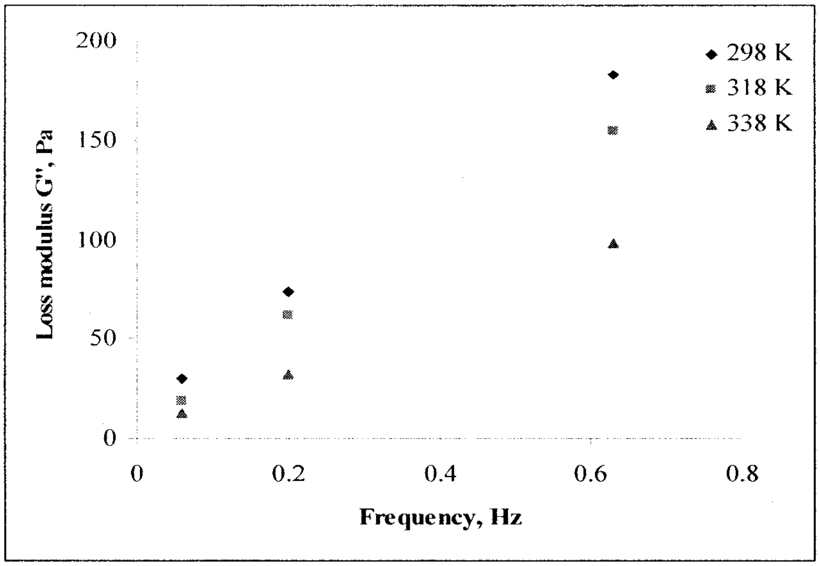


Fig. 33. Loss modulus of heavy crude oil at different temperatures.

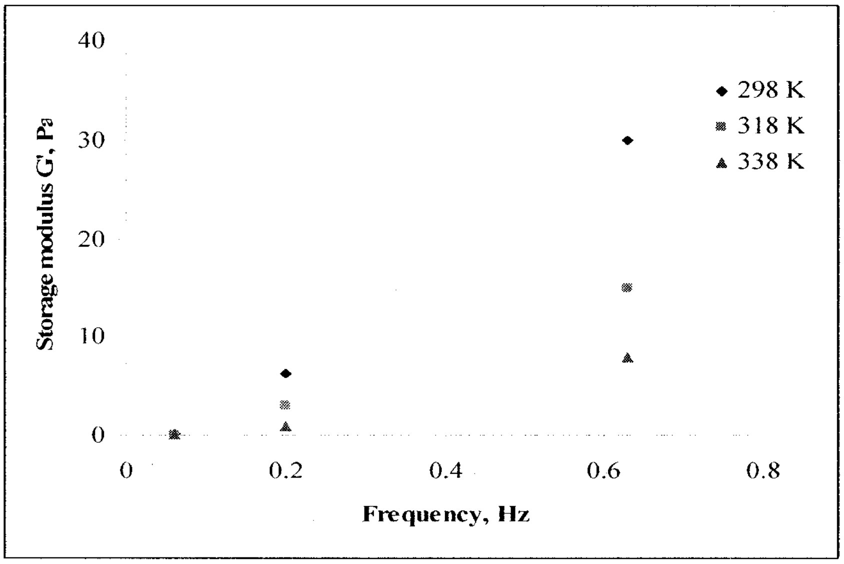


Fig. 34. Storage modulus of 90% O-light crude mixture at different temperatures.

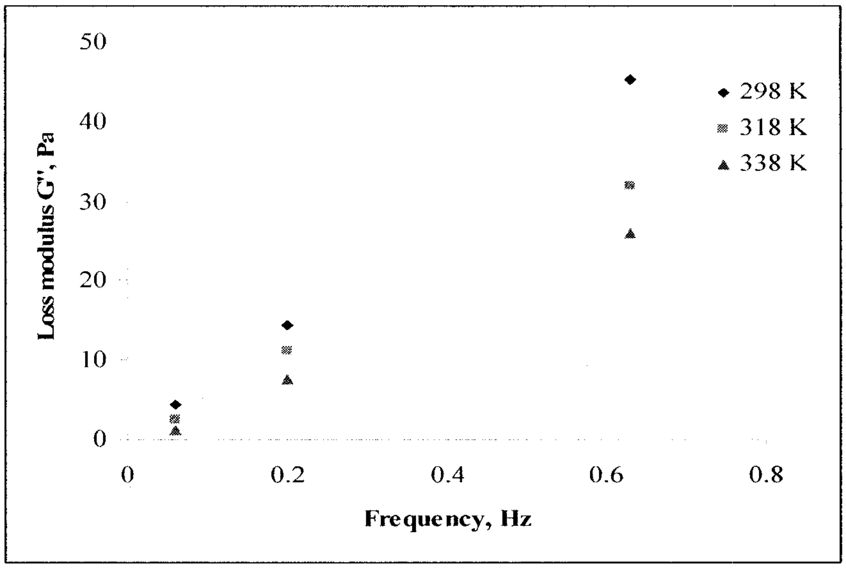


Fig. 35. Loss modulus of 90% O-light crude mixture at different temperatures.

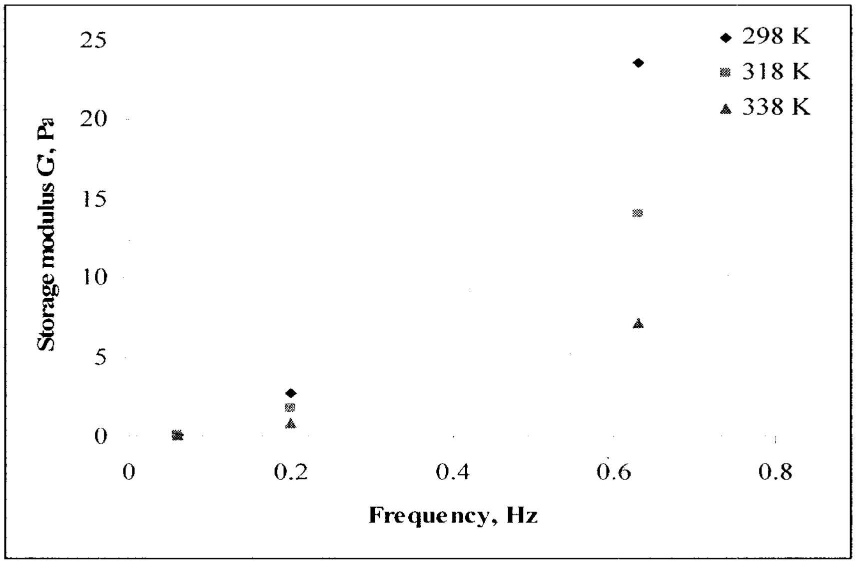


Fig. 36. Storage modulus of 80% O-light crude mixture at different temperatures.

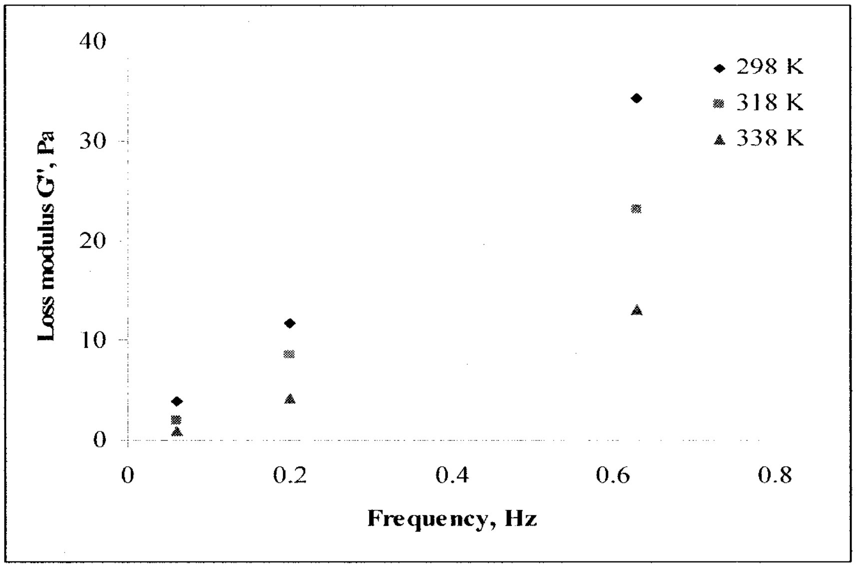


Fig. 37. Loss modulus of 80% O-light crude mixture at different temperatures.

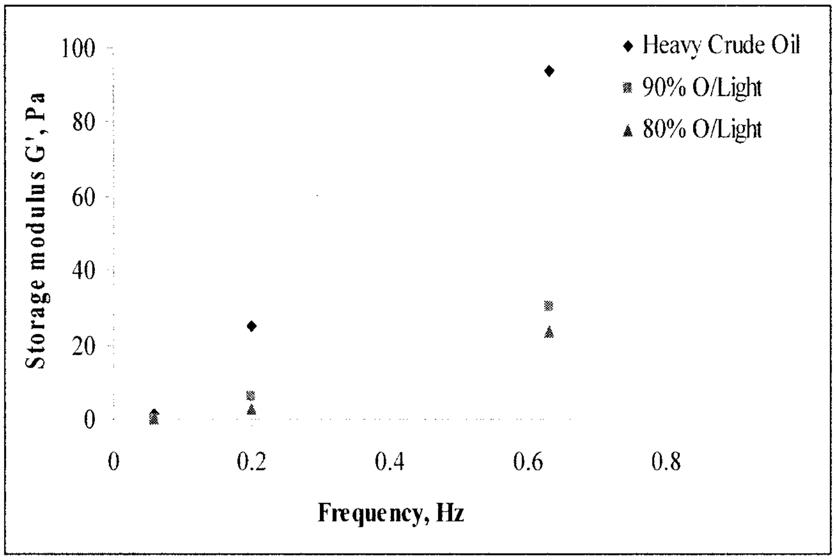


Fig. 38. Storage modulus of heavy crude oil and O-light mixtures.

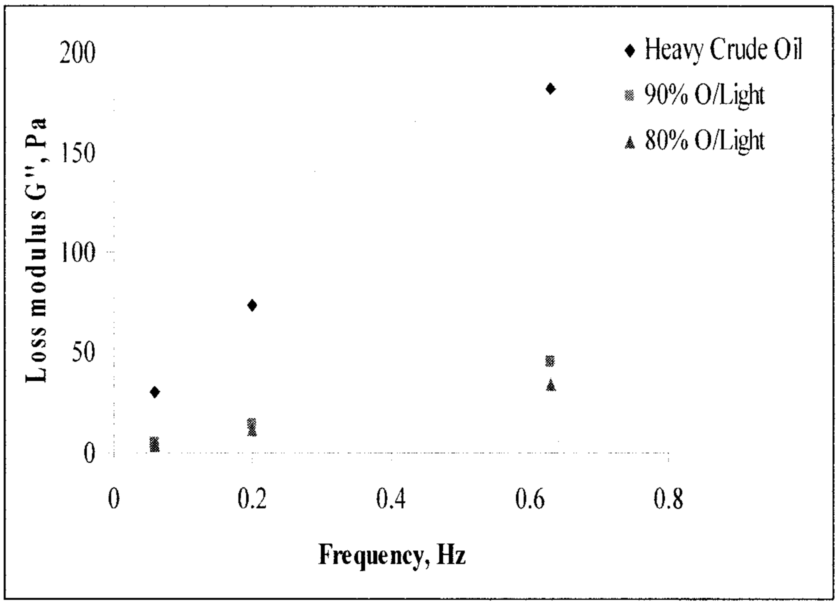


Fig. 39. Loss modulus of heavy crude oil and O-light mixtures.

The behavior of a complex modulus, G^*, for the heavy crude oil and for the heavy crude oil-light crude oil mixtures at different temperatures and different water concentration is plotted versus frequency as shown in Figs. 40 to 43. The complex modulus, G^*, increases gradually with frequency over the entire range of 0.01 to 0.7 Hz. As can be observed, the complex modulus, G^*, decreases significantly with the temperature as well as decreases with the volume fraction of water added [5, 67].

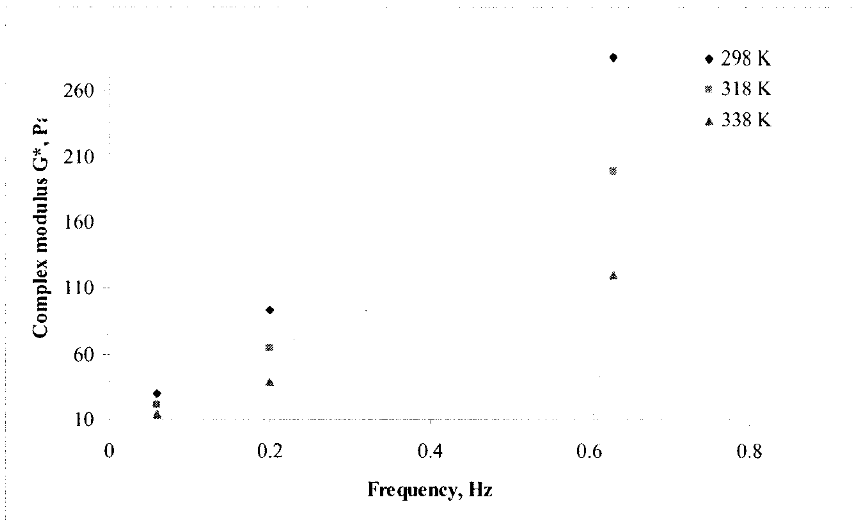


Fig. 40. Complex modulus of heavy crude oil at different temperatures.

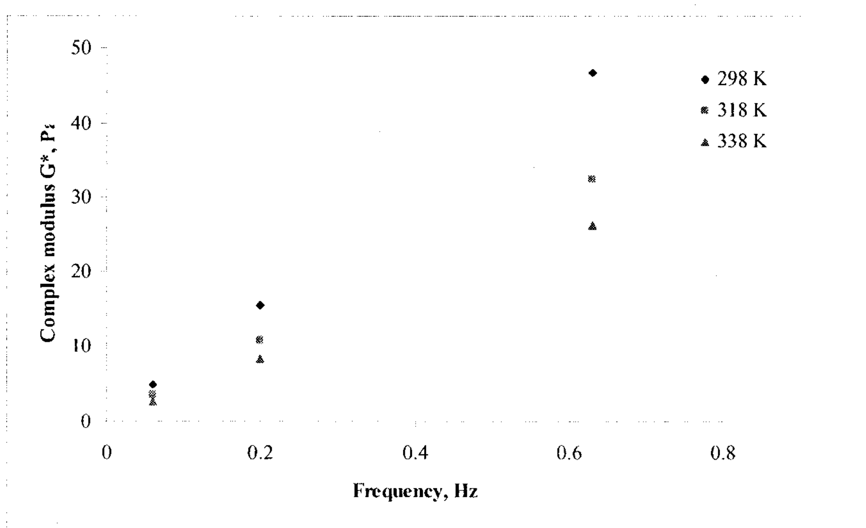


Fig. 41. Complex modulus of 90% O-light crude at different temperatures.

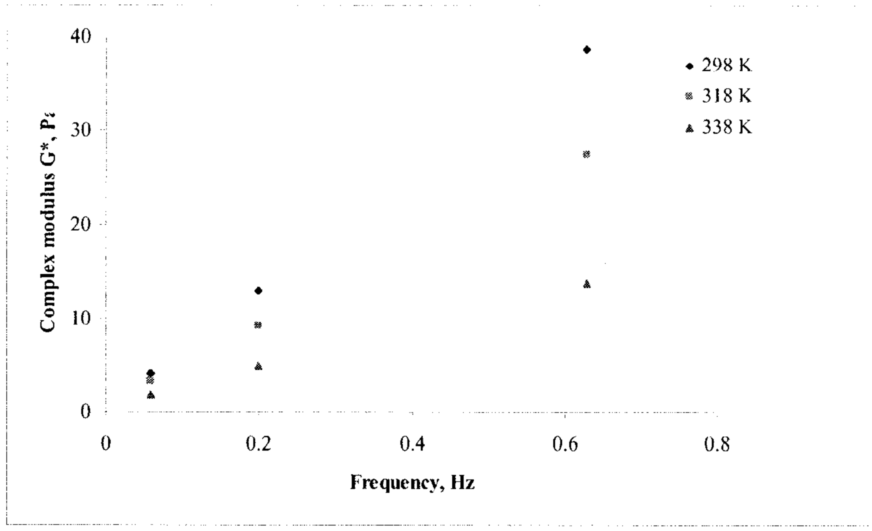


Fig. 42. Complex modulus of 80% O-light crude at different temperatures.

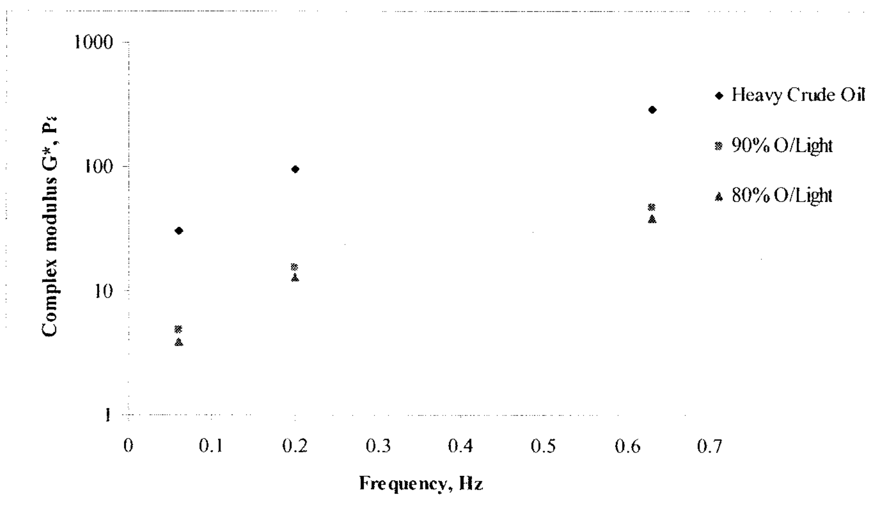


Fig. 43. Complex modulus of heavy crude oil and O-light mixtures at room temperature.

Figs. 44 to 47 illustrate the variation of the complex viscosity, η^*, with the frequency, and it is clear that the complex viscosity has a slight decrease with the frequency. This means that the complex viscosity, η^*, has an inverse proportional with the frequency. In addition, the results show that the complex viscosity, η^*, of the heavy crude oil depends strongly on the temperature, since it decreased from 481 to 225 Pa.s when the temperature was changed from 298 K to 338 K. In addition, the results show that the complex viscosity, η^*, decreases as the oil content decreases as well and reaches 66 Pa.s for 80% oil-light crude oil mixture. Table 9 shows the measured complex viscosity, η^*, at room temperature 298 K.

Table 9. Complex viscosity at 298 K.

Sample	Complex Viscosity, η^*, Pa.s
Heavy Crude Oil	481
90% O-Light Crude Oil	82
80% O-Light Crude Oil	66

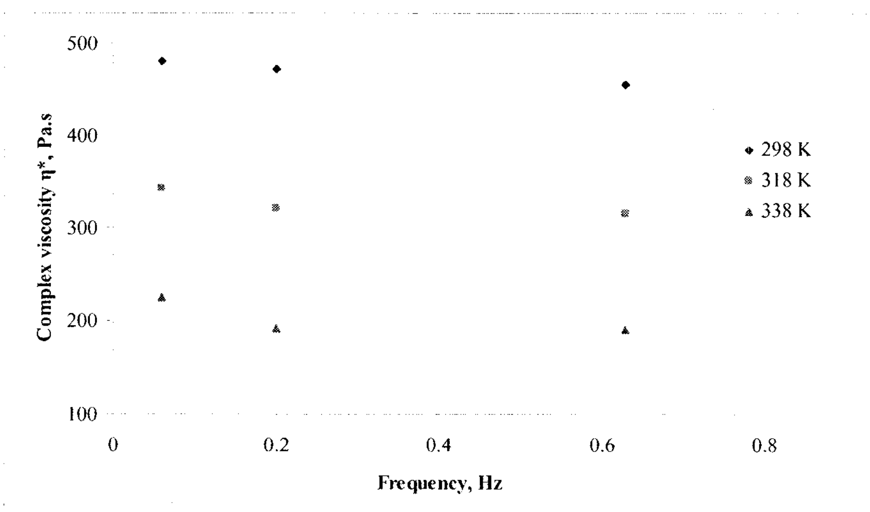


Fig. 44.Complex viscosity of heavy crude oil at different temperatures.

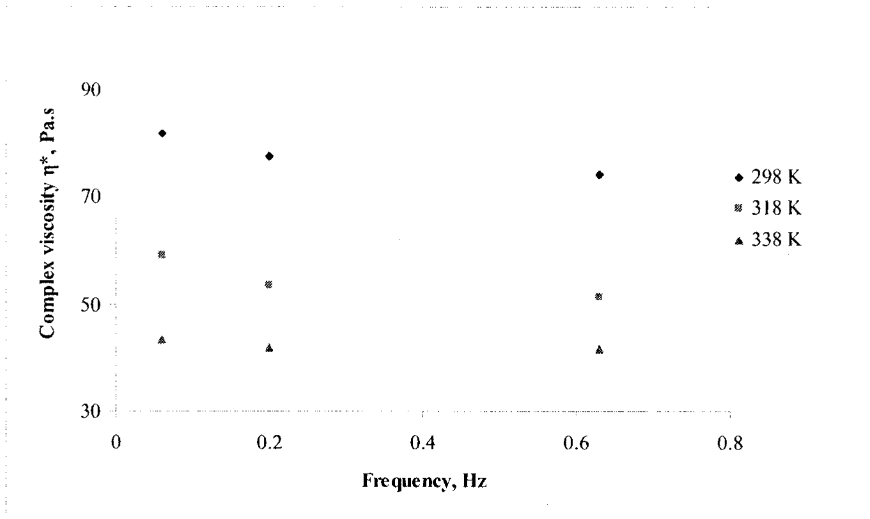


Fig. 45.Complex viscosity of 90% O-light crude mixture oil at different temperatures.

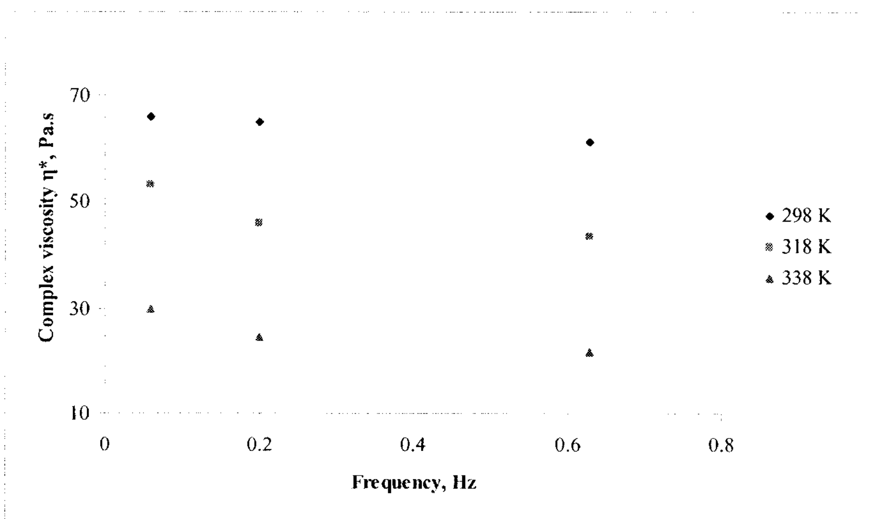


Fig. 46.Complex viscosity of 80% O-light crude mixture oil at different temperatures.

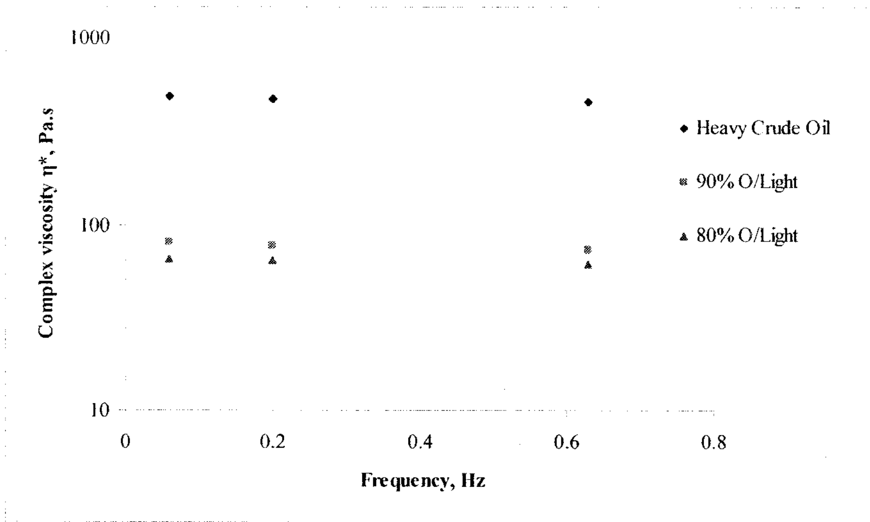


Fig. 47. Complex viscosity of heavy crude oil and O-light mixtures at room temperature.

CHAPTER IV

SUMMARY AND CONCOLUSIONS

4.1 CONCLUDING REMARKS

The rheological properties of the heavy crude oil were studied. The results showed a shear thinning behavior that follows the power law model over a wide range of shear rates of 0.6 to 740 s^{-1}. It was observed that the viscosity decreased with temperature at different values of shear rates. The viscosity of the heavy crude oil decreased from 10.0 Pa.s to 2.5 Pa.s when the temperature increased from 298 to 348 K.

Different methods of reducing the viscosity of the heavy crude oil were investigated in this work. It was observed that blending the heavy crude oil with a limited amount of lighter crude oil is the most appropriate and favourable method. The viscosity of heavy crude oil decreased from 10.0 Pa.s to 0.375 Pa.s at 298 K when the heavy crude was mixed with 20 volume % of light crude oil. On the other hand, the viscosity decreased from 0.950 Pa.s at 298 K to 0.620 Pa.s at 348 K when the heavy crude oil was blended with ethanol alcohol, and decreased from 6.50 Pa.s at 298 K to 0.3 Pa.s at 348 K when the 80% heavy crude oil and 20% aqueous solution of surfactant was used.

The rheological properties of the heavy crude oil and light crude oil at different volume % ratios for different temperatures were studied. From the results, it was shown that the heavy crude oil required yield stress of 0.7 Pa whereas it required no further stress to start the flow of the heavy oil-light oil mixture with the addition of 10 and 20 volume % of light crude oil.

Moreover, the heavy crude oil showed a significant thixotropic behavior with 321.65 $KPa.s^{-1}$ hysteresis area which decreases with temperature. The addition of the light crude oil by 10 and 20 volume % resulted in the disappearance of the hysteresis area.

Neither the heavy crude oil nor the heavy oil-light oil mixture showed any transient behavior, hence there is no time dependency (i.e shear stress is not a function of time). In addition, it was clear that both the storage and the loss moduli depend strongly on the temperature and the frequency as well. The results showed that the storage modulus was less than the shear modulus, and thus the energy stored in the material is less than the heat dissipated within the material.

Furthermore, the complex modulus and the complex viscosity of the heavy crude oil and the heavy oil-light oil mixture were investigated and the results showed that the complex viscosity decreased from 481 to 455 Pa.s at room temperature 298 K over 0.01 to 0.7 Hz range of frequencies, and it is decreased from 481 Pa.s at 298 K to 225 Pa.s at 338 K for the heavy crude oil. The complex modulus showed a significant dependence on the frequency, and it decreased as the volume % of the heavy crude oil decreased and as the temperature increased.

4.2 RECOMMENDATIONS AND FUTURE WORK

- To develop a new empirical model in order to predict the viscosity of the heavy crude oil-light crude oil mixture as a function of oil content, temperature and shear rate.

- To perform a complete and efficient pipeline design and calculate the power required and the cost needed to pump the heavy crude oil with low viscosity and compare it to the case where the heavy crude oil is pumped normally.

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APPENDICES

APPENDIX A

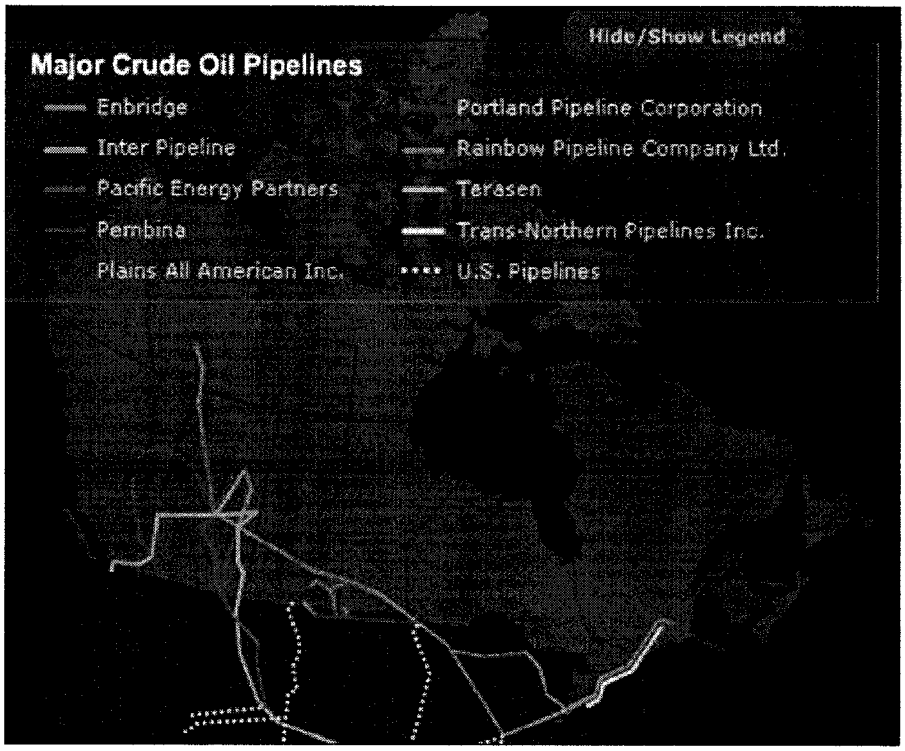

Fig. 55. Canada's crude oil pipelines.

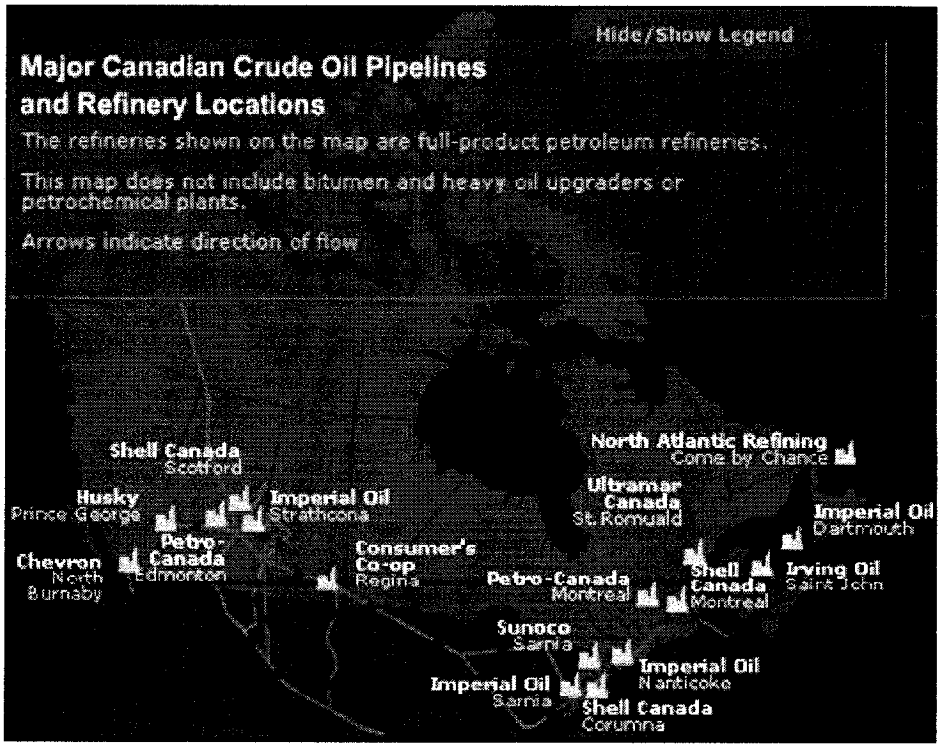

Fig. 56. Refinery locations in Canada [73].

APPENDIX B

Table 10. Dynamic measurements of heavy crude oil at different temperatures.

w, s^{-1}	**G', Pa**	**G'', Pa**	**G*, Pa**	**η*, Pa.s**
T=298 K				
0.06	1.46	30.17	30.21	480.74
0.20	25	73.5	93.86	472.72
0.63	93.73	182.5	285.87	454.97
T=318 K				
0.06	0.9	19	20.56	34.2667
0.20	15	61.4	64.26	32.13
0.63	72.6	154	198.46	31.5016
T=338 K				
0.06	0.4	13	13.5	225
0.20	8	32	38.4	192
0.63	43.6	98	120.3	190.952

Table 11. Dynamic measurements of 90% O-Light crude mixture at different temperatures.

w, s^{-1}	**G', Pa**	**G'', Pa**	**G*, Pa**	**η*, Pa.s**
T=298 K				
0.06	0.13	4.39	4.9	81.6667
0.20	6.35	14.31	15.51	77.55
0.63	30	45.29	46.7	74.127
T=318 K				
0.06	0.07	2.4	3.55	59.1667
0.20	3	11	10.7	53.5
0.63	15	32	32.42	51.4603
T=338 K				
0.06	0.02	1.2	2.6	43.3333
0.20	0.92	7.4	8.4	42
0.63	8	26.1	26.3	41.746

Table 12. Dynamic measurements of 80% O-Light crude mixture at different temperatures.

w, s^{-1}	G', Pa	G", Pa	G*, Pa	η*, Pa.s
T=298 K				
0.06	0.11	3.95	3.96	66
0.20	2.75	11.66	12.98	64.9
0.63	23.6	34.27	38.61	61.2857
T=318 K				
0.06	0.05	2	3.2	53.3333
0.20	1.8	8.5	9.2	46
0.63	14	23	27.36	43.4286
T=338 K				
0.06	0.01	0.9	1.8	30
0.20	0.85	4.2	4.9	24.5
0.63	7.1	13	13.7	21.746

Table 13. Transient measurements at room temperature.

Heavy crdue oil		*80% O-Light crude mixture*		*90% O-Light crude mixture*	
τ, Pa	t, s	τ, Pa	t, s	τ, Pa	t, s
5.92	33.85	1.37	33.85	2.93	33.85
5.92	67.18	1.37	67.18	2.96	67.18
5.94	100.5	1.39	100.5	2.98	100.5
5.94	133.9	1.38	133.9	2.96	133.9
5.94	167.2	1.39	167.2	2.98	167.2
5.94	200.5	1.40	200.5	2.98	200.5
5.92	233.9	1.39	233.9	2.96	233.9
5.94	267.2	1.40	267.2	2.99	267.2
5.94	300.5	1.41	300.5	2.99	300.5

Table 14. Thixotropic measurements of heavy crude-light crude mixtures at room temperature.

90% O-Light crude mixture		*80% O-Light crude mixture*	
τ, Pa	**γ, s^{-1}**	**τ, Pa**	**γ, s^{-1}**
47	50	25.1	50
76	103	47.9	103
111	155	69.6	155
148	210	92.4	210
184	261	114.2	261
222	313	136.2	313
259	367	160	367
295	419	182	419
330	472	205	472
363	526	227	526
398	579	249	579
429	632	270	632
461	685	292	685
487	737	313	737
488	740	314	740
456	691	293	691
423	638	271	638
391	585	250	585
358	532	228	532
327	480	207	480
293	426	184	426
259	374	163	374
224	321	140	321
189	269	117	269
152	215	93.9	215
116	164	71.4	164
77	109	47.4	109
40	58	24.5	58
1	4	0.642	4

Table 15. Thixotrpoic behavior of heavy crude oil at different temperatures.

γ, s^{-1}	**τ (298 K), Pa**	**τ (318 K), Pa**	**τ (338 K), Pa**
3.6	51	32	18
42	197	170	140
102.6	374	290	230
166	554	432	400
229	717.4	618	540
280	866	774	710
352	997.5	938	870
399	1175	1100	938
449	1282	1200	1049
486	1374	1300	1131
510	1447	1347	1191
536	1476	1360	1206
560	1450	1354	1213
589	1380	819	930
595	1300	1302	1206
607	1280	915	1000
629	1100	1020	1050
611	850	1206	1109
584	680	767	915
530	600	714	833
500	536	655	744
425.7	448.8	610	700
374.4	409.1	536	600
320.8	361.8	469	543
268.6	311.4	417	491
214.9	255.1	305	365
163.6	198.3	246	290
109	134	171	200
57.88	71.2	89	112
3.599	2.666	1.7	1.7

Table 16. Yield measurements of heavy crude oil at different temperatures.

γ, s^{-1}	**τ (298 K), Pa**	**τ (318 K), Pa**	**τ (338 K), Pa**
0.0001636	0.09	0.07	0.5
0.00008459	0.524	0.4	0.3
0.005026	0.955	0.75	0.62
0.03005	1.68	1.38	1.04
0.094	3.13	2.8	2.16
0.04386	2.25	1.8	1.23
0.06248	2.68	2.1	1.6
0.175	3.75	3.4	2.8
0.1409	3.56	3.2	2.7
0.2381	3.99	3.5	2.9

Table 17. Yield measurements of 90% O-Light crude mixture at different temperatures.

γ, s^{-1}	**τ (298 K), Pa**	**τ (318 K), Pa**	**τ (338 K), Pa**
0.00064	0.09	0.07	0.05
0.012	0.5124	0.416	0.325
0.018	0.949	0.79	0.57
0.00664	1.39	1.12	0.84
0.039	1.83	1.54	1.36
0.613	3.38	2.84	2.47
0.351	2.69	2.1	1.8
0.55	3.12	2.67	2.21
0.664	3.56	3.1	2.8

Table 18. Yield measurements of 80% O-Light crude mixture at different temperatures.

γ, s^{-1}	**τ (298 K), Pa**	**τ (318 K), Pa**	**τ (338 K), Pa**
0.00363	0.09	0.065	0.046
0.023	0.514	0.395	0.305
0.023	0.95	0.74	0.52
0.00785	1.39	1.05	0.75
0.144	1.82	1.46	1.25
0.807	2.26	1.9	1.7
1.12	2.68	2.4	2
1.23	3.11	2.58	2.19
1.52	3.55	2.8	2.58

Table 19. Viscosity measurements of heavy crude oil at different temperatures.

25 °C		35 °C		45 °C	
η, Pas	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**
9.97E+00	5.17E+01	8.00E+00	5.17E+01	7.65E+00	5.17E+01
9.87E+00	1.03E+02	7.90E+00	1.03E+02	7.57E+00	1.03E+02
9.80E+00	1.55E+02	7.89E+00	1.55E+02	7.55E+00	1.55E+02
9.73E+00	2.06E+02	7.87E+00	2.06E+02	7.53E+00	2.06E+02
9.66E+00	2.57E+02	7.76E+00	2.57E+02	7.49E+00	2.57E+02
9.54E+00	3.09E+02	7.72E+00	3.09E+02	7.43E+00	3.09E+02
9.42E+00	3.60E+02	7.65E+00	3.60E+02	7.34E+00	3.60E+02
9.28E+00	4.12E+02	7.50E+00	4.12E+02	7.31E+00	4.12E+02
9.13E+00	4.63E+02	7.40E+00	4.63E+02	7.21E+00	4.63E+02
8.98E+00	5.15E+02	7.30E+00	5.15E+02	7.10E+00	5.15E+02
8.80E+00	5.66E+02	7.20E+00	5.66E+02	6.97E+00	5.66E+02
8.60E+00	6.18E+02	6.98E+00	6.18E+02	6.74E+00	6.18E+02
8.40E+00	6.70E+02	6.70E+00	6.69E+02	6.57E+00	6.69E+02
8.10E+00	7.21E+02	6.50E+00	7.21E+02	6.30E+00	7.21E+02
55 °C		**65 °C**		**75 °C**	
η, Pas	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**
7.01E+00	5.18E+01	6.75E+00	5.17E+01	6.33E+00	5.17E+01
6.94E+00	1.03E+02	6.66E+00	1.03E+02	6.28E+00	1.03E+02
6.90E+00	1.55E+02	6.63E+00	1.55E+02	6.25E+00	1.55E+02
6.87E+00	2.06E+02	6.63E+00	2.06E+02	6.25E+00	2.06E+02
6.85E+00	2.57E+02	6.60E+00	2.57E+02	6.22E+00	2.57E+02
6.83E+00	3.09E+02	6.58E+00	3.09E+02	6.19E+00	3.09E+02
6.79E+00	3.60E+02	6.53E+00	3.60E+02	6.14E+00	3.60E+02
6.73E+00	4.12E+02	6.49E+00	4.12E+02	6.10E+00	4.12E+02
6.68E+00	4.63E+02	6.43E+00	4.63E+02	6.04E+00	4.63E+02
6.61E+00	5.15E+02	6.37E+00	5.15E+02	5.95E+00	5.15E+02
6.53E+00	5.66E+02	6.30E+00	5.66E+02	5.89E+00	5.66E+02
6.43E+00	6.18E+02	6.21E+00	6.18E+02	5.78E+00	6.18E+02
6.28E+00	6.69E+02	6.09E+00	6.69E+02	5.67E+00	6.69E+02
5.93E+00	7.21E+02	5.76E+00	7.21E+02	5.45E+00	7.20E+02

Table 20. Viscosity measurements of 90% O/W emulsion at different temperatures.

25 ^{0}C		35 ^{0}C		45 ^{0}C	
η, Pas	γ, s^{-1}	η, Pas	γ, s^{-1}	η, Pas	γ, s^{-1}
8.09E+00	5.17E+01	7.33E+00	5.17E+01	6.77E+00	5.18E+01
7.20E+00	1.03E+02	6.38E+00	1.03E+02	5.87E+00	1.03E+02
6.59E+00	1.55E+02	5.68E+00	1.55E+02	5.07E+00	1.55E+02
5.63E+00	2.06E+02	4.90E+00	2.06E+02	4.69E+00	2.06E+02
4.71E+00	2.57E+02	3.86E+00	2.58E+02	3.76E+00	2.57E+02
3.86E+00	3.09E+02	3.14E+00	3.10E+02	2.87E+00	3.09E+02
2.58E+00	3.60E+02	2.21E+00	3.60E+02	1.94E+00	3.62E+02
1.67E+00	4.13E+02	1.56E+00	4.12E+02	1.51E+00	4.10E+02
9.01E-01	4.62E+02	8.76E-01	4.66E+02	7.75E-01	4.65E+02
5.02E-01	5.16E+02	3.90E-01	5.16E+02	3.74E-01	5.15E+02
3.51E-01	5.66E+02	2.98E-01	5.66E+02	2.52E-01	5.66E+02
2.15E-01	6.18E+02	1.85E-01	6.18E+02	1.72E-01	6.18E+02
1.28E-01	6.69E+02	1.26E-01	6.69E+02	1.24E-01	6.69E+02
1.01E-01	7.20E+02	9.40E-02	7.20E+02	9.10E-02	7.20E+02
55 ^{0}C		**65 ^{0}C**		**75 ^{0}C**	
η, Pas	γ, s^{-1}	η, Pas	γ, s^{-1}	η, Pas	γ, s^{-1}
6.49E+00	5.17E+01	5.86E+00	5.17E+01	5.25E+00	5.17E+01
5.53E+00	1.03E+02	5.25E+00	1.03E+02	4.75E+00	1.03E+02
4.60E+00	1.55E+02	4.25E+00	1.55E+02	3.98E+00	1.55E+02
4.29E+00	2.06E+02	3.92E+00	2.06E+02	3.70E+00	2.06E+02
3.62E+00	2.58E+02	3.46E+00	2.58E+02	3.27E+00	2.57E+02
2.79E+00	3.08E+02	2.67E+00	3.09E+02	2.51E+00	3.09E+02
1.82E+00	3.59E+02	1.71E+00	3.61E+02	1.61E+00	3.62E+02
1.49E+00	4.12E+02	1.09E+00	4.12E+02	9.35E-01	4.09E+02
6.84E-01	4.64E+02	5.72E-01	4.64E+02	4.12E-01	4.67E+02
3.17E-01	5.15E+02	2.68E-01	5.16E+02	1.99E-01	5.10E+02
2.27E-01	5.66E+02	1.83E-01	5.64E+02	1.49E-01	5.66E+02
1.65E-01	6.18E+02	1.50E-01	6.18E+02	1.37E-01	6.19E+02
1.18E-01	6.69E+02	1.15E-01	6.69E+02	1.12E-01	6.69E+02
8.43E-02	7.20E+02	8.36E-02	7.20E+02	7.82E-02	7.23E+02

Table 21. Viscosity measurements of 80% O/W emulsion at different temperatures.

25 ^{0}C		**35 ^{0}C**		**45 ^{0}C**	
η, Pas	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**
6.49E+00	5.19E+01	4.67E+00	5.19E+01	3.90E+00	5.17E+01
5.11E+00	1.03E+02	3.66E+00	1.03E+02	2.88E+00	1.03E+02
4.21E+00	1.55E+02	3.13E+00	1.55E+02	2.62E+00	1.54E+02
3.10E+00	2.06E+02	2.40E+00	2.07E+02	2.13E+00	2.06E+02
2.14E+00	2.58E+02	1.60E+00	2.57E+02	1.53E+00	2.58E+02
1.53E+00	3.09E+02	1.16E+00	3.10E+02	1.12E+00	3.09E+02
9.36E-01	3.60E+02	8.25E-01	3.60E+02	8.06E-01	3.61E+02
7.76E-01	4.12E+02	5.82E-01	4.12E+02	5.52E-01	4.12E+02
6.42E-01	4.66E+02	4.77E-01	4.64E+02	4.51E-01	4.63E+02
5.06E-01	5.15E+02	3.50E-01	5.15E+02	2.87E-01	5.14E+02
3.85E-01	5.66E+02	2.89E-01	5.66E+02	2.12E-01	5.67E+02
2.95E-01	6.18E+02	2.58E-01	6.18E+02	1.69E-01	6.18E+02
2.61E-01	6.69E+02	2.56E-01	6.69E+02	1.30E-01	6.69E+02
1.30E-01	7.21E+02	1.28E-01	7.20E+02	1.24E-01	7.20E+02
55 ^{0}C		**65 ^{0}C**		**75 ^{0}C**	
η, Pas	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**
3.73E+00	5.17E+01	3.39E+00	5.17E+01	2.94E+00	5.19E+01
2.79E+00	1.03E+02	2.69E+00	1.03E+02	2.42E+00	1.03E+02
2.53E+00	1.54E+02	2.44E+00	1.55E+02	2.18E+00	1.55E+02
2.09E+00	2.06E+02	2.02E+00	2.06E+02	1.80E+00	2.06E+02
1.37E+00	2.58E+02	1.37E+00	2.57E+02	1.20E+00	2.58E+02
1.11E+00	3.09E+02	1.05E+00	3.09E+02	9.29E-01	3.09E+02
7.80E-01	3.60E+02	7.63E-01	3.60E+02	6.90E-01	3.61E+02
5.39E-01	4.11E+02	4.96E-01	4.12E+02	4.79E-01	4.12E+02
4.34E-01	4.62E+02	3.87E-01	4.63E+02	3.14E-01	4.63E+02
2.75E-01	5.15E+02	2.60E-01	5.15E+02	2.38E-01	5.15E+02
2.11E-01	5.66E+02	1.85E-01	5.66E+02	1.61E-01	5.66E+02
1.57E-01	6.17E+02	1.36E-01	6.18E+02	1.25E-01	6.18E+02
1.11E-01	6.69E+02	1.11E-01	6.69E+02	1.08E-01	6.69E+02
1.18E-01	7.20E+02	1.12E-01	7.20E+02	1.07E-01	7.20E+02

Table 22. Viscosity measurements of 90% O-Light crude mixture at different temperatures.

25 °C		35 °C		45 °C	
η, Pas	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**
1.20E+00	5.17E+01	1.11E+00	5.17E+01	1.00E+00	5.17E+01
1.18E+00	1.03E+02	1.10E+00	1.03E+02	9.95E-01	1.03E+02
1.17E+00	1.55E+02	1.10E+00	1.55E+02	9.94E-01	1.55E+02
1.16E+00	2.06E+02	1.09E+00	2.06E+02	9.93E-01	2.06E+02
1.15E+00	2.57E+02	1.09E+00	2.57E+02	9.90E-01	2.57E+02
1.14E+00	3.09E+02	1.08E+00	3.09E+02	9.88E-01	3.09E+02
1.13E+00	3.60E+02	1.08E+00	3.60E+02	9.86E-01	3.60E+02
1.13E+00	4.12E+02	1.07E+00	4.12E+02	9.84E-01	4.12E+02
1.12E+00	4.63E+02	1.06E+00	4.63E+02	9.70E-01	4.63E+02
1.12E+00	5.15E+02	1.05E+00	5.15E+02	9.60E-01	5.15E+02
1.10E+00	5.66E+02	1.05E+00	5.66E+02	9.50E-01	5.66E+02
1.09E+00	6.17E+02	1.04E+00	6.17E+02	9.40E-01	6.17E+02
1.08E+00	6.69E+02	1.03E+00	6.69E+02	9.35E-01	6.69E+02
1.07E+00	7.20E+02	1.02E+00	7.20E+02	9.30E-01	7.20E+02
55 °C		**65 °C**		**75 °C**	
η, Pas	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**
8.70E-01	5.17E+01	7.44E-01	5.17E+01	6.78E-01	5.17E+01
8.60E-01	1.03E+02	7.50E-01	1.03E+02	6.80E-01	1.03E+02
8.50E-01	1.55E+02	7.50E-01	1.55E+02	6.78E-01	1.55E+02
8.45E-01	2.06E+02	7.50E-01	2.06E+02	6.79E-01	2.06E+02
8.40E-01	2.57E+02	7.48E-01	2.57E+02	6.79E-01	2.57E+02
8.35E-01	3.09E+02	7.47E-01	3.09E+02	6.77E-01	3.09E+02
8.30E-01	3.60E+02	7.44E-01	3.60E+02	6.75E-01	3.60E+02
8.25E-01	4.12E+02	7.41E-01	4.12E+02	6.73E-01	4.12E+02
8.20E-01	4.63E+02	7.35E-01	4.63E+02	6.70E-01	4.63E+02
8.15E-01	5.15E+02	7.29E-01	5.15E+02	6.64E-01	5.15E+02
8.10E-01	5.66E+02	7.23E-01	5.66E+02	6.60E-01	5.66E+02
7.90E-01	6.18E+02	7.18E-01	6.17E+02	6.55E-01	6.18E+02
7.85E-01	6.69E+02	7.13E-01	6.69E+02	6.51E-01	6.69E+02
7.80E-01	7.20E+02	7.07E-01	7.20E+02	6.45E-01	7.20E+02

Table 23. Viscosity measurements of 80% O-Light crude mixture at different temperatures.

25 °C		35 °C		45 °C	
η, Pas	γ, s^{-1}	η, Pas	γ, s^{-1}	η, Pas	γ, s^{-1}
3.72E-01	5.17E+01	3.45E-01	5.17E+01	3.02E-01	5.17E+01
3.73E-01	1.03E+02	3.45E-01	1.03E+02	3.02E-01	1.03E+02
3.74E-01	1.55E+02	3.46E-01	1.55E+02	3.02E-01	1.55E+02
3.72E-01	2.06E+02	3.44E-01	2.06E+02	3.02E-01	2.06E+02
3.70E-01	2.57E+02	3.41E-01	2.57E+02	3.01E-01	2.57E+02
3.70E-01	3.09E+02	3.40E-01	3.09E+02	3.01E-01	3.09E+02
3.70E-01	3.60E+02	3.39E-01	3.60E+02	3.00E-01	3.60E+02
3.69E-01	4.12E+02	3.40E-01	4.12E+02	3.00E-01	4.12E+02
3.69E-01	4.63E+02	3.37E-01	4.63E+02	3.00E-01	4.63E+02
3.68E-01	5.15E+02	3.39E-01	5.15E+02	3.00E-01	5.15E+02
3.67E-01	5.66E+02	3.38E-01	5.66E+02	2.99E-01	5.66E+02
3.66E-01	6.17E+02	3.37E-01	6.17E+02	2.99E-01	6.17E+02
3.65E-01	6.69E+02	3.36E-01	6.69E+02	2.99E-01	6.69E+02
3.63E-01	7.20E+02	3.35E-01	7.20E+02	2.98E-01	7.20E+02
55 °C		65 °C		75 °C	
η, Pas	γ, s^{-1}	η, Pas	γ, s^{-1}	η, Pas	γ, s^{-1}
2.78E-01	5.17E+01	2.47E-01	5.17E+01	2.31E-01	5.17E+01
2.79E-01	1.03E+02	2.47E-01	1.03E+02	2.33E-01	1.03E+02
2.81E-01	1.55E+02	2.49E-01	1.55E+02	2.34E-01	1.55E+02
2.81E-01	2.06E+02	2.50E-01	2.06E+02	2.35E-01	2.06E+02
2.82E-01	2.57E+02	2.51E-01	2.57E+02	2.35E-01	2.57E+02
2.81E-01	3.09E+02	2.50E-01	3.09E+02	2.34E-01	3.09E+02
2.81E-01	3.60E+02	2.50E-01	3.60E+02	2.34E-01	3.60E+02
2.80E-01	4.12E+02	2.50E-01	4.12E+02	2.33E-01	4.12E+02
2.79E-01	4.63E+02	2.50E-01	4.63E+02	2.33E-01	4.63E+02
2.78E-01	5.15E+02	2.50E-01	5.15E+02	2.33E-01	5.15E+02
2.78E-01	5.66E+02	2.50E-01	5.66E+02	2.33E-01	5.66E+02
2.77E-01	6.17E+02	2.50E-01	6.18E+02	2.32E-01	6.17E+02
2.76E-01	6.69E+02	2.49E-01	6.69E+02	2.32E-01	6.69E+02
2.75E-01	7.20E+02	2.49E-01	7.20E+02	2.31E-01	7.20E+02

Table 24. Viscosity measurements of 90% O-Ethanol alcohol mixture at different temperatures.

25 ^{0}C		35 ^{0}C		45 ^{0}C	
η, Pas	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**
1.97E+00	5.17E+01	1.71E+00	5.17E+01	1.61E+00	5.17E+01
1.98E+00	1.03E+02	1.71E+00	1.03E+02	1.61E+00	1.03E+02
1.97E+00	1.55E+02	1.70E+00	1.55E+02	1.61E+00	1.55E+02
1.96E+00	2.06E+02	1.69E+00	2.06E+02	1.60E+00	2.06E+02
1.95E+00	2.57E+02	1.68E+00	2.57E+02	1.60E+00	2.57E+02
1.93E+00	3.09E+02	1.66E+00	3.09E+02	1.59E+00	3.09E+02
1.91E+00	3.60E+02	1.64E+00	3.60E+02	1.57E+00	3.60E+02
1.90E+00	4.12E+02	1.62E+00	4.12E+02	1.56E+00	4.12E+02
1.87E+00	4.63E+02	1.59E+00	4.63E+02	1.54E+00	4.63E+02
1.84E+00	5.15E+02	1.57E+00	5.15E+02	1.52E+00	5.15E+02
1.81E+00	5.66E+02	1.55E+00	5.66E+02	1.50E+00	5.66E+02
1.78E+00	6.17E+02	1.52E+00	6.17E+02	1.48E+00	6.17E+02
1.75E+00	6.69E+02	1.49E+00	6.69E+02	1.45E+00	6.69E+02
1.72E+00	7.20E+02	1.47E+00	7.20E+02	1.42E+00	7.20E+02
55 ^{0}C		**65 ^{0}C**		**75 ^{0}C**	
η, Pas	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**	**η, Pas**	**γ, s^{-1}**
1.40E+00	5.17E+01	1.27E+00	5.17E+01	1.10E+00	5.17E+01
1.38E+00	1.03E+02	1.28E+00	1.03E+02	1.09E+00	1.03E+02
1.37E+00	1.55E+02	1.28E+00	1.55E+02	1.08E+00	1.55E+02
1.37E+00	2.06E+02	1.28E+00	2.06E+02	1.07E+00	2.06E+02
1.36E+00	2.57E+02	1.27E+00	2.57E+02	1.06E+00	2.57E+02
1.36E+00	3.09E+02	1.26E+00	3.09E+02	1.05E+00	3.09E+02
1.35E+00	3.60E+02	1.25E+00	3.60E+02	1.04E+00	3.60E+02
1.35E+00	4.12E+02	1.24E+00	4.12E+02	1.03E+00	4.12E+02
1.34E+00	4.63E+02	1.22E+00	4.63E+02	1.02E+00	4.63E+02
1.33E+00	5.15E+02	1.21E+00	5.15E+02	1.01E+00	5.15E+02
1.32E+00	5.66E+02	1.19E+00	5.66E+02	9.94E-01	5.66E+02
1.30E+00	6.17E+02	1.18E+00	6.17E+02	9.80E-01	6.17E+02
1.29E+00	6.69E+02	1.16E+00	6.69E+02	9.67E-01	6.69E+02
1.28E+00	7.20E+02	1.14E+00	7.20E+02	9.53E-01	7.20E+02

Table 25. Viscosity measurements of 80% O-Ethanol alcohol mixture at different temperatures.

25 °C		35 °C		45 °C	
η, Pas	γ, s^{-1}	η, Pas	γ, s^{-1}	η, Pas	γ, s^{-1}
9.43E-01	5.18E+01	8.84E-01	5.17E+01	8.13E-01	5.17E+01
9.06E-01	1.03E+02	8.35E-01	1.03E+02	7.79E-01	1.03E+02
8.66E-01	1.55E+02	8.13E-01	1.55E+02	7.39E-01	1.55E+02
8.33E-01	2.06E+02	7.70E-01	2.06E+02	7.06E-01	2.06E+02
8.12E-01	2.57E+02	7.38E-01	2.58E+02	6.84E-01	2.57E+02
7.92E-01	3.09E+02	7.29E-01	3.09E+02	6.71E-01	3.09E+02
7.78E-01	3.60E+02	7.19E-01	3.60E+02	6.61E-01	3.60E+02
7.55E-01	4.12E+02	7.09E-01	4.12E+02	6.51E-01	4.12E+02
7.38E-01	4.63E+02	6.90E-01	4.63E+02	6.41E-01	4.63E+02
7.21E-01	5.15E+02	6.71E-01	5.15E+02	6.25E-01	5.15E+02
7.09E-01	5.66E+02	6.65E-01	5.66E+02	6.07E-01	5.66E+02
7.01E-01	6.18E+02	6.40E-01	6.17E+02	5.91E-01	6.18E+02
6.84E-01	6.69E+02	6.19E-01	6.69E+02	5.68E-01	6.69E+02
6.35E-01	7.21E+02	5.64E-01	7.20E+02	5.10E-01	7.20E+02
55 °C		**65 °C**		**75 °C**	
η, Pas	γ, s^{-1}	η, Pas	γ, s^{-1}	η, Pas	γ, s^{-1}
7.39E-01	5.17E+01	6.57E-01	5.17E+01	6.17E-01	5.17E+01
7.10E-01	1.03E+02	6.38E-01	1.03E+02	5.98E-01	1.03E+02
6.76E-01	1.55E+02	6.14E-01	1.55E+02	5.80E-01	1.55E+02
6.54E-01	2.06E+02	5.94E-01	2.06E+02	5.60E-01	2.06E+02
6.39E-01	2.57E+02	5.77E-01	2.57E+02	5.44E-01	2.57E+02
6.30E-01	3.09E+02	5.62E-01	3.09E+02	5.32E-01	3.09E+02
6.20E-01	3.60E+02	5.47E-01	3.60E+02	5.20E-01	3.60E+02
5.98E-01	4.12E+02	5.36E-01	4.12E+02	5.10E-01	4.12E+02
5.89E-01	4.63E+02	5.27E-01	4.63E+02	4.99E-01	4.63E+02
5.79E-01	5.15E+02	5.21E-01	5.15E+02	4.88E-01	5.15E+02
5.68E-01	5.66E+02	5.03E-01	5.66E+02	4.75E-01	5.66E+02
5.49E-01	6.18E+02	4.94E-01	6.17E+02	4.64E-01	6.17E+02
5.28E-01	6.69E+02	4.69E-01	6.69E+02	4.43E-01	6.69E+02
4.65E-01	7.20E+02	4.28E-01	7.20E+02	4.07E-01	7.20E+02

Table 26. Power law model calculations

Ln τ	Ln γ
6.13	4.64
6.53	5.04
6.80	5.33
7.01	5.55
7.17	5.73
7.31	5.89
7.42	6.02
7.51	6.14
7.59	6.24
7.65	6.34
7.70	6.43
7.74	6.51
7.77	6.58
5.44	3.95

Table 27. Bingham model calculations

τ, Pa	γ, s^{-1}
2.3E+02	5.2E+01
4.6E+02	1.0E+02
6.8E+02	1.5E+02
9.0E+02	2.1E+02
1.1E+03	2.6E+02
1.3E+03	3.1E+02
1.5E+03	3.6E+02
1.7E+03	4.1E+02
1.8E+03	4.6E+02
2.0E+03	5.1E+02
2.1E+03	5.7E+02
2.2E+03	6.2E+02
2.3E+03	6.7E+02
2.4E+03	7.2E+02
2.3E+02	5.2E+01

Table 28. Casson mode calculations

$\gamma^{1/2}$, $s^{-1/2}$	$\tau^{1/2}$ (298 K), $Pa^{1/2}$
15.17	7.19
21.40	10.16
26.12	12.43
30.00	14.36
33.29	16.04
36.12	17.58
38.63	18.98
40.79	20.29
42.71	21.52
44.37	22.68
45.81	23.79
47.03	24.85
48.02	25.86
48.74	26.84