PIPE-LINE TRANSPORTATION OF HEAVY OIL-IN-WATER EMULSION

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ABSTRACT

The diverse factors affecting the viscosity of a viscous crude oil-in-water emulsion for pipeline transportation were studied. The factors that are taken into account is effect of oil content, type and concentration of the surfactant, and speed of mixing, Agent in water method is used in the preparation of oil in water emulsions. The oil content ratio used in this study is 50-50, 70-30, and 90-10 by volume. Different surfactants, namely Triton X-100, Span 80 and Tween 80 are used to determine the best surfactant to emulsify heavy oil. The speed of mixing used in this study is 1000rpm, 1500rpm and 2000rpm. This study is conducted in room temperature. Amine functional group demulsifier are used to study the destabilization of heavy oil in water emulsions. The demulsifier used in this study is hexylamine and dioctylamine. The viscosity of the oil in water emulsion was found to decrease as the oil content of the emulsion decreased, and the speed of mixing decreased. The stability of the crude oil-in-water emulsions increases as the oil content of the emulsions increases, the surfactant concentration increases, and the speed of mixing increases. Hexylamine remove more water over time in the destabilization process. Hence, hexylamine is a better demulsifier than dioctlamine. From this research it can be concluded that oil in water emulsion method can reduce the viscosity of heavy crude oil greatly.

Keywords: Oil in water emulsions; Stability; Transportation; Pipeline; Destabilization

ABSTRAK

Pelbagai faktor yang mempengaruhi kelikatan emulsi minyak dalam air dikaji untuk pengangkutan paip. Faktor-faktor yang diberi perhatian adalah nisbah isipadu minyak kepada air, jenis dan kepekatan pengemulsi (surfactant) dan kelajuan pengadukan. Kaedah agen dalam air digunakan untuk penyediaan emulsi minyak dalam air. Nisbah isipadu minyak kepada air yang digunakan dalam kajian ini ialah 50-50%, 70-30% dan 90-10%. Pengemulsi (surfactant) yang berbeza digunakan, iaitu Triton X-100, Span-80, dan Tween 80 untuk mengenalpasti pengemulsi yang terbaik dalam pengemulsian minyak pekat. Kelajuan pengadukan yang digunakan dalam kajian ini ialah 1000, 1500 and 2000 putaran per minit (rpm). Kajian ini dijalankan dalam suhu bilik. Penyahemulsi kumpulan berfungsi amino digunakan dalam penyahstabilan emulsi minyak dalam air. Penyahemulsi yang digunakan dalam kajian ini ialah hexylamine dan dioctylamine. Kelikatan emulsi minyak dalam air menurun apabila nisbah isipadu minyak kepada air menurun dan kelajuan pengadukan menurun. Kestabilan emulsi minyak dalam air meningkat apabila nisbah isipadu minyak kepada air meningkat, kepekatan pengemulsi (surfactant) meningkat dan kelajuan pengadukan meningkat. Hexylamine mengasingkan lebih banyak air dari masa ke semasa dalam proses penyahstabilan. Oleh itu, hexylamine adalah penyahemulsi yang lebih baik daripada dioctylamone. Daripada kajian ini dapat disimpulkan bahawa kaedah emulsi minyak dalam air dapat menurunkan kelikatan minyak pekat dengan berkesan.

Kata Kunci: Emulsi Minyak Dalam Air; Kestabilan; Pengangkutan: Saluran paip; Penyahstabilan.

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LIST OF ABBREVIATIONS

w/o	-	Water in oil
o/w	-	Oil in water
API	-	American Petroleum Institute
cP	-	Centi poise
U	-	velocity
F	-	Force
A	-	Area
γ	-	Surface tension
HLB	-	Hydrophilic Lipophilic Balance

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Most of the world's oil reserves are heavy and high pour point viscous hydrocarbons that are difficult and costly to produce and refine. In fact 70% of the total world's oil resources consist of heavy oil and bitumen. In Canada and Venezuela alone, the heavy crude oils and natural bitumen account for a large fraction of oil reserves, which together, account for about 55-65% of the known heavy crude oil deposits in the world**.** Heavy oil is defined by the United States Department of Energy as having API (American Petroleum Institute) gravities less that fall between 10.0^0 and 22.3^0. While extra heavy oils are defined as having API gravities less than 10.0° API. Heavy oils are classified as such using API gravity rather than viscosity values. (Amy H. and Batzle M., 2006).

As the reserves of conventional crude oil keep declining and high oil demands and prices, heavy crude oil and bitumen are becoming increasingly important source of hydrocarbon liquids. But the heavy crude oils and bitumen cannot be transported through conventional pipelines due to the high viscosity. Hence possible methods of transportation are needed to transport this viscous oil to the refinery.

Several transportation methods for heavy crude oil have been proposed and employed, including preheating of the crude oil with subsequent heating of the pipeline, dilution with lighter crude oils, partial upgrading and injection of a water sheath around the viscous crude. One of the latest pipeline techniques is to transport the viscous heavy crude oil as oil-in-water (O/W) emulsions. In this method, surfactants are used to prepare the oil in water emulsions. The oil phase becomes dispersed in the water phase and stable oil-in water emulsions are formed. This causes a significant reduction in the oil viscosity, and therefore in the transportation costs and problems. Besides that, some heavy crude oil has high sulfur content. Since water is the continuous phase, the crude oil has no contact with the pipeline wall. Therefore this reduces the pipe corrosion (S. N. Ashrafizadeh *et al.*, 2010)

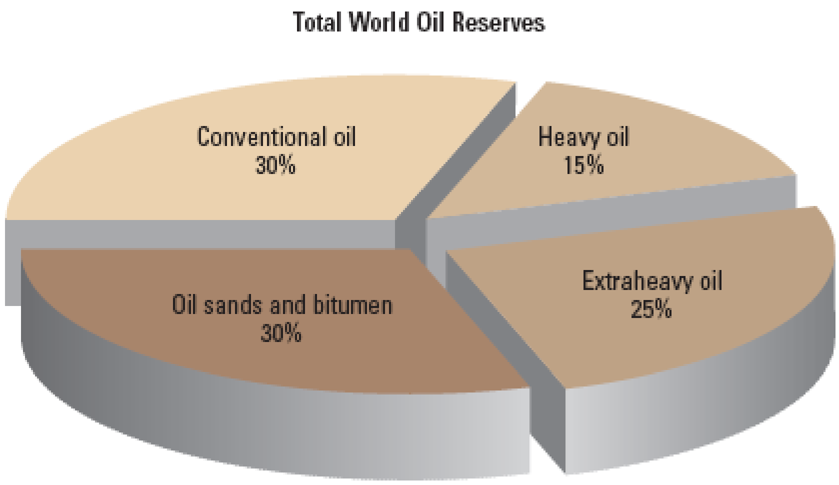

Figure 1.1: Total world oil reserves. Heavy oil, extra heavy oil and bitumen, make up about 70% of the world's total oil resources of 9 to 13 trillion bbl. (Source: (Amy H. and Batzle M., 2006).

1.2 RESEARCH BACKGROUND/PROBLEM STATEMENT

1.2.1 Problem Statement

Large fraction of world's potentially recoverable oil reserves contains heavy oil. The viscosities of these crudes at 25^0C vary from 1000 cP to more than 10000 cP. These viscous crudes account for 25% of the economically recoverable oil in United States. Hence the development of the vast amount of heavy crude oil will require an economical method. Conventional pipeline method is not suitable for transporting these heavy crudes from the reservoir to the refinery because of high viscosities involved. Normally, crude viscosities less than 300 cP are desired for pipelining. High viscosity causes flow problems. With increasing viscosity, the head loss due to friction increases and, therefore, greater pump horsepower is required. Thus, it is necessary to reduce the viscosity of the oil being transported.

1.2.2 Objective

The objectives in this present research are:

1. To investigate the various factors that is affecting the preparation of stable crude oil in water emulsion for pipeline transportation.
2. The influence of oil content in emulsion, type and concentration of the surfactant, speed of mixing are investigated for viscosity reduction.

1.2.3 Research Scope

The scope for this research is:

1. To comparatively study the effect of different surfactant in the formation of heavy oil in water emulsions.
2. To investigate the factors that reduce the viscosities of oil in water emulsion in pipeline transportation
3. To study the influence of amine functional group demulsifiers on the destabilization of heavy oil in water emulsions.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Crude Oil

Heavy crude oil or extra heavy crude oil is any type of crude oil which does not flow easily. It is referred to as heavy because it has the density or specific gravity that is approaching or even exceeding that of water. They 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 viscosity and high concentrations of sulfur and several metals, particularly nickel and vanadium. (Shadi Hassan, 2007)

Heavy oil is defined by the U.S. Department of Energy as having API (American Petroleum Institute) gravities that fall between 10.0° and 22.3°. Extra-heavy oils are defined as having API gravities less than 10.0° API. With a specific gravity of greater than 1, extra heavy crude is present as a dense non-aqueous phase liquid when spilled in the environment. Heavy oils are classified as such using API gravity rather than viscosity values. Two important distinctions must be made between API gravity and viscosity. First, viscosity determines how well oil will flow while API gravity typically determines the yield from distillation. Temperature and paraffin content can have a large effect on viscosity values while API gravity is not affected by these parameters. (Amy H. and Batzle M., 2006)

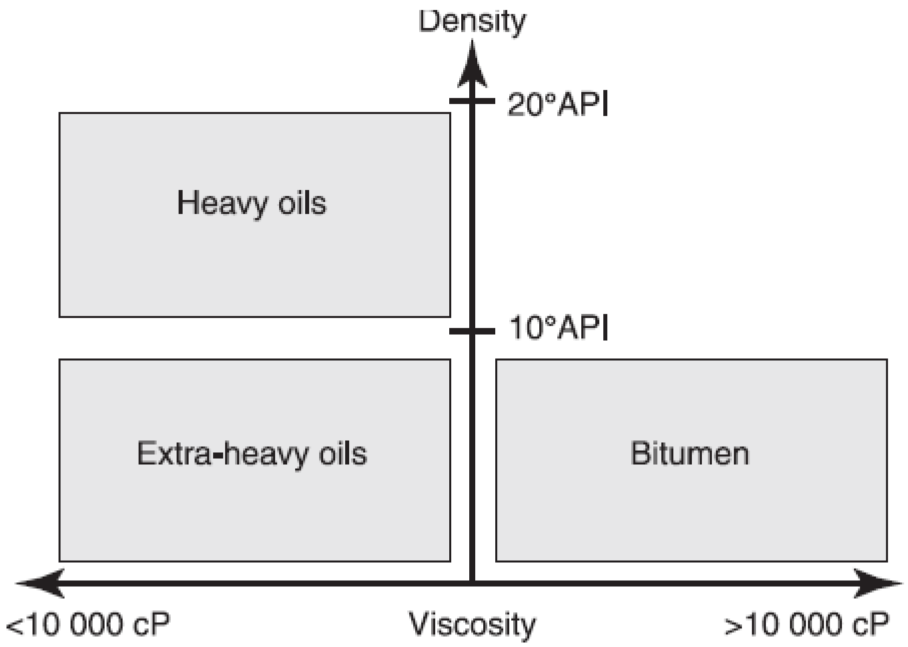

Figure 2.1: Viscosity and density of heavy, extra heavy oil and bitumen. (Source: Saniere A. *et al*,, 2004)

2.1.1 Heavy Crude Oil Formation

. Heavy oils usually begin as lighter oils (30–40° API) and are then altered, often by biodegradation. With aerobic biodegradation, meteoric water supplies nutrients, and oxygen and bacteria attack the lighter alkanes (straight chains) by oxidation, leaving the more complex compounds such as resins and asphaltenes behind. This is the most common mechanism for shallow heavy oils. In contrast, in deep reservoirs, anaerobic alteration can take place. In this case, the lighter alkanes are reduced to methane. This produces the seemingly contradictory result of producing heavy oils but the associated gases become lighter. A completely different potential mechanism involves the precipitation of asphaltenes. Heavy oil reservoirs have an advantage over their lighter counterparts, which is their longevity. Heavy oil field can produce for 100 years or more, as do the ones discovered in California in the late 1800s. (Amy and Batzle, 2006)

2.2 Heavy Crude Oil Composistions

Crude oil is a mixture of a large amount of hydrocarbons, varying amount of waxes and low content of asphaltenes. The carbon content normally is in the range of 83-87% and the hydrogen content ranges from 10-14%. In addition small amount of nitrogen, sulfur oxygen, nickel and vanadium may be found in the crude oils. Crude oils from different regions have different properties. Thousands of chemical compounds present in crude oil, herein it is impossible to achieve a complete definition of the structure and composition of each individual molecule. Therefore the most practical way to divide the crude oil is to do that with respect to their polarity and solubility, which is known as SARA separation. In the method, the crude oil system is isolated into four groups, which is

- Saturates,
- Aromatics,
- Resins
- 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 aromatics 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.

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. Asphaltenes are defined in terms of solubility class that is precipitated from the petroleum by the addition of an excess of a light alkanes like pentane, hexane or heptanes. The precipitate is soluble in 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 water in oil (W/O) emulsion. However the precipitation of asphaltene particles in oil systems might cause severe problems in the pipeline and oil well. (Shadi Hassan, 2007)

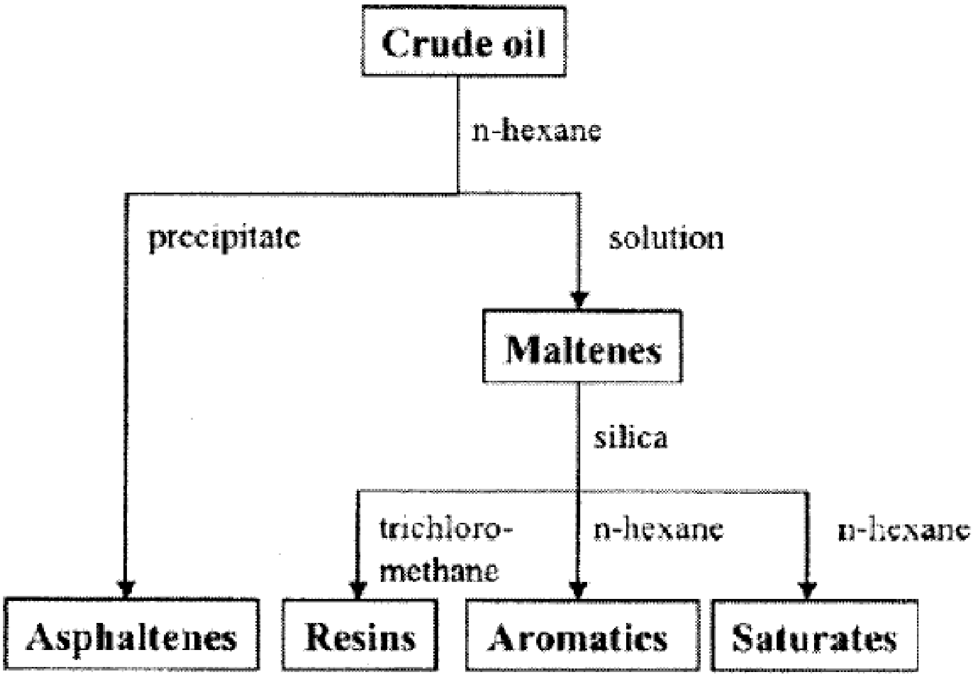

Figure 2.2: SARA separation scheme (Source: Shadi Hassan, 2007)

2.3 Emulsification

2.3.1 Emulsion Formation

An emulsion is a mixture of two or more immiscible or unblendable liquids. Emulsions are part of a general class of two-phase systems of matter called colloids. The terms colloid and emulsion are sometimes used interchangeably, but emulsion tends to imply that both the dispersed phase and the continuous phase are liquid. In an emulsion, one of the liquid (the dispersed phase) is dispersed in the other (the continuous phase). In crude oil in water emulsion (O/W), the oil is the dispersed phase while the water is the continuous phase. Other examples of emulsions in daily life include butter, margarine, espresso, mayonnaise, vinaigrettes, the photo-sensitive side of photographic film, milk and cutting fluid for metal working.

Emulsions are unstable and thus require certain energy input for the formation and stabilization. This can be done through shaking, stirring, homogenizers, or spray processes. The emulsions tend to break into the stable state of its primary constituent over time which is oil and water. For the emulsification of crude oil emulsion three criteria are necessary, that is.

- Two immiscible liquid must be brought in contact
- Surface active reagent must present as the emulsifier
- Sufficient mixing or agitating effect must be provided in order to disperse one liquid into another as droplets.

During the formation of emulsion, the deformation of droplet is opposed by the pressure gradient between the external (convex) and the internal (concave) side of an interface. The pressure gradient or velocity gradient required for emulsion formation is mostly supplied by agitation. The large excess of energy required to produce emulsion with small droplets can only be supplied by very intense agitation, which needs much energy. (Syauqi A. O, 2009)

2.3.2 Emulsion Stability

There are three types of emulsion instability: flocculation, creaming (sedimentation), and coalescence. Flocculation is a reversible formation of droplet clusters where two or more droplets clump together, only touching at certain points and 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 flocculation will increase the sedimentation-creaming rate. Sedimentation or creaming occurs due to the density difference between the two liquid phases. Creaming is promoted by large droplet sizes, high density differences and low viscosity of the continuous phase. Both flocculation and creaming processes are reversible. When agitated, the emulsion will revert to the original dispersion state. Coalescence is another form of instability, which is more severe phenomenon by the complete mergence of two bubbles into one. Coalescence is facilitated by film drainage and film rupture processes.

The properties of the interference between water and oil are vital in determining the stability of an emulsion system. The interface between the dispersed phase and the continuous phase increases the system free energy, therefore the emulsion are not thermodynamically stable, and tend to minimize the surface area by break up of emulsions. The stability of the emulsion will be poor if the interfacial film is weak. The dispersed droplets will collide and the collisions will lead to droplet fusion that is coalescence. (Shadi, 2007)

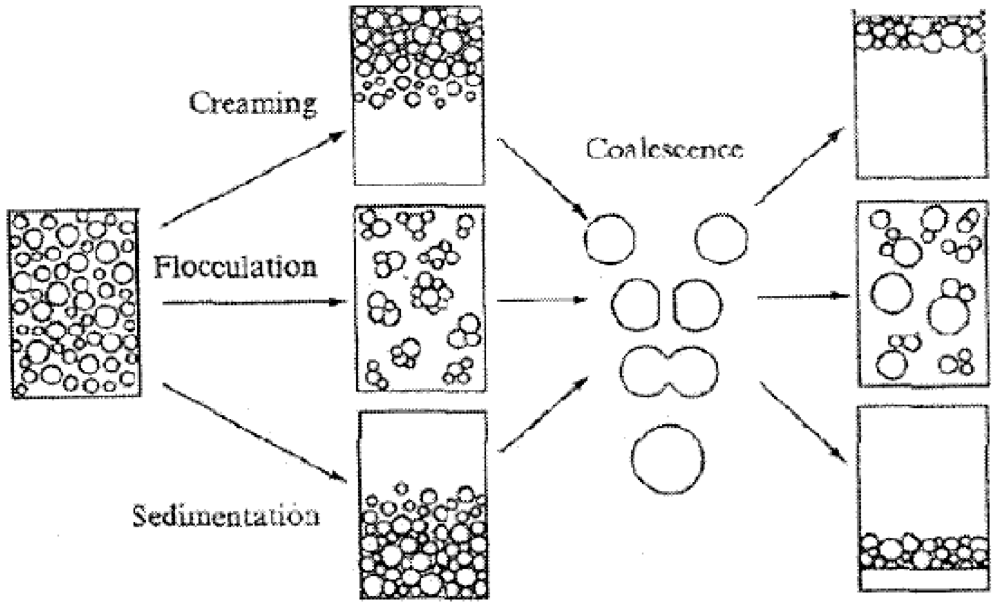

Figure 2.3: Emulsion breakdown and separation processes (Source: Shadi Hassan, 2007)

2.4 Rheology

2.4.1 Definition and Theory

Rheology is the study of the deformation and flow of matter under the influence of an applied stress. For example, shear stress or extension stress. The force can be applied in a various ways: a compression, a tension, a shearing process, or some combination of three. A simple type of deformation is shown in figure 2.4. The lower plate of two parallel plates 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*.

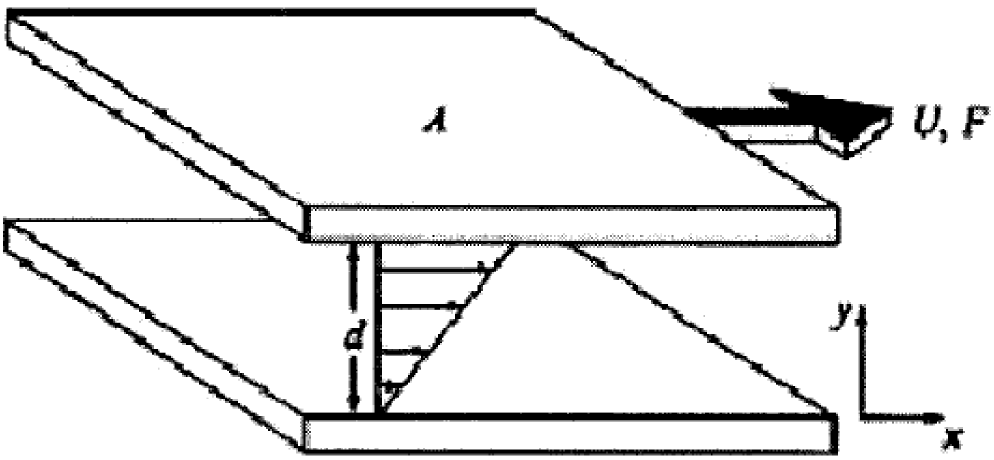

Figure 2.4: Deformation of a liquid under an applied shear force F (Source: Shukri, 2009)

With a simple laminar flow as consideration, the basic parameter can be defined as the following:

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

$\tau = \mathrm{d}F/\mathrm{d}A$ (2.1)

Stress 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.

$\mathrm{v} = \mathrm{d}x/\mathrm{d}y$ (2.2)

Shear rate is the speed of deformation.

$\gamma = \mathrm{d}v/\mathrm{d}h$ (2.3)

2.4.2 Newtonian Liquid and Non-Newtonian Liquids

Newtonian liquid exhibit constant viscosity independent of shear rate and type of flow, shear or extensional. Newtonian liquid also exhibit uniform resistance to flow independent or flow conditions.

Non-Newtonian liquids exhibit viscosity which changes with shear rate and with the type of deformation. In extensional flow, they exhibit elongational viscosities in no apparent relation to their shear viscosities. Non-Newtonian liquids also exhibit different resistance to flow, at different shear and extensional rates. In general, Non-Newtonian liquids can be

- 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 Newtonian, shear thinning or shear thickening liquids. Below their yield stress, these liquids behave like elastic solids.

Figure 2.5 shows the behavior of the viscosity of several rheologically different liquids and the resulting stress as a function of the shear rate.