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Flow Improvers for Heavy Crude Oil Transport in Pipe

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Submission date: June 2014
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Preface

This master thesis was given by Norwegian University of Science and Technology (NTNU), Faculty of Natural Science and Technology (NT), Department of Chemical Engineering, Steady field Polymer and Colloid Chemistry. The thesis was conducted in collaboration with Statoil ASA in the period 14th of January to 10th of June 2014. All work was performed at Statoil ASA, Rotvoll, Trondheim.

I would like to thank my supervisor at Statoil ASA, Einar Eng Johnsen for all guidance and help trough the master thesis. I am thankful for all counselling and support from Robert Orr, Harald Kallevik, Anne Rossbach Hammer and Hege Christin Widerøe at Statoil ASA during my practical work and evaluation of results in this thesis. In addition I would like to thank my supervisor at NTNU, Johan Sjøblom, for support throughout the process.

Declaration of compliance

I, Stine Fagerdal, declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU).

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Abstract

The transportation of heavy oil is challenging as the oil has high viscosity and heavy components like asphaltenes. By finding an effective flow improver the transporting could be less demanding and more cost effective.

Asphaltene aggregation is suspected to have an effect on the viscosity of the crude oil as asphaltenes act as colloids in the crude oil, and aggregate together. Traditionally it is accepted that asphaltenes are stabilized by other polar components, resins. Resin has a polar and a non-polar part that disperses the asphaltenes in the crude oil, and the structure of resins seems to be important. The polarity of the asphaltenes is believed to be an important parameter for finding a solvent that could have a stabilizing effect as resins. Solvents with active molecules as alcohol and ketone might have the potential to reduce the viscosity of a heavy oil by interacting with the asphaltenes.

To find a solvent to be used as a flow improver the solubility parameters of Hildebrand and Hansen has been looked into. Different solvents already tested by other have been looked into, and the solubility parameters between these have been compared. Hildebrand solubility parameters around 22 $MPa^{0.5}$ seem to be a good start point for finding a chemical that can be used as a flow improver.

In the experimental work three different crude oils have been tested by adding thirteen different types of solvents in various amounts. The solvents were added in small amounts (≤ 3 wt %) to study the solvent's effect to reduce the viscosity by dispersing the asphaltenes in the oil. The analyses used to detect the effect from the studied solvents are Karl Fischer titration, viscometer, rheometer, near infrared spectroscopy and nuclear magnetic resonance spectroscopy.

The three different crude oils that have been tested can be characterized as relatively viscous, with viscosity values ranging from 345 to 4152 mPa·s at the actual test temperatures.

The glycols have an opposite effect, they increased the viscosity in all tested crude oils. Some of the added solvents, as 1-hexanol and 2-butanone, have reduced the viscosity of the crude oil. However, this seems to be rather a diluting effect than a clear effect of dispersing the asphaltenes and thereby reducing the viscosity. The commercial products used in the experimental work, one viscosity reduction chemical and three asphaltene dispersant chemicals, reduced the viscosity mainly because of dilution.

Using a glycol, 1-hexanol or 2-butanone in small amounts (≤ 3 wt %) as flow improver are not preferred instead of additive a lighter petroleum product, as naphtha, to reduce the viscosity of the oil.

Sammendrag

Det er utfordrende å transportere tung olje da oljen har høy viskositet og inneholder tunge komponenter som asfaltener. Ved å benytte en effektiv flytforbedrer vil transporten være mindre krevende og mer kosteffektiv.

Det mistenkes at asfaltenenes aggregering påvirker viskositeten av råoljen ettersom asfaltener opptrer som kolloider i råolje hvor de aggregerer sammen. Tradisjonelt sett er det akseptert at andre polare komponenter i råoljen, resiner, stabilisere asfaltenene. Resiner har en polar og en upolar del som hjelper til å dispergere asfaltener i råoljen, og strukturen til resiner ser ut til å være avgjørende. Polariteten til asfaltener er antatt å være en viktig parameter for å finne et løsemiddel som kan ha en stabiliserende effekt. Løsemidler med aktive molekyler som alkohol og keton kan ha potensialet til å redusere viskositeten av en tung olje ved å stabilisere asfaltener.

I prosessen for å finne et løsemiddel har Hildebrand og Hansens løselighetsparameter blitt benyttet. Tidligere har ulike løsemidler blitt testet av andre. Disse har blitt studert og løselighetsparameterne mellom de ulike løsemidlene har litt sammenlignet. Hildebrands løselighetsparameter rundt 22 MPa$^{0.5}$ ser ut til å være et godt utgangspunkt for å finne et kjemisk stoff som kan brukes som en flytforbedrer.

I det eksperimentelle arbeidet er det benyttet tre ulike råoljer hvor tretten løsemidler har blitt tilsatt i ulike mengder. Løsemidlene ble tilsatt i små mengder (≤ 3 vekt %) for å studere evnen til å redusere viskositeten ved å dispergere asfaltener i råoljen. Analysemetodene som ble benyttet for å påvise virkninger av de ulike tilsatte løsemidlene var Karl Fischer titrering, viskosimeter, reometer, nær infrarød spektroskopi og kjernemagnetisk resonansspektroskopi.

De testede råoljene kan karakteriseres som relativt viskøse med viskositet mellom 345-4152 mPa·s på de aktuelle temperaturene.

Glykoler viste seg å ha motsatt virkning en antatt da de økte viskositeten i alle råoljene. Noen av løsemidlene, som 1-heksanol og 2-butanon, har redusert viskositeten til råoljen. Den reduserte viskositeten viser å være en fortynningseffekt og ikke en effekt av dispergerte asfaltener. De kommersielle produktene anvendt i det eksperimentelle arbeidet, et viskositetsreduserende kjemikalie og tre asfalten dispergeringsmidler, reduserte også viskositeten, men i hovedsak på grunn av en fortynningseffekt. Kjemikalier som glykoler, 1-heksanol eller 2-butanone i små mengder (≤ 3 vekt %) som flytforbedrer er ikke å foretrekke fremfor tilsatts av et lettere petroleumsprodukt, nafta, for å redusere viskositeten av oljen.

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Abbreviations

API	American Petroleum Institute
DEG	Diethylene Glycol
IR	Infrared
MEG	Monoethylene Glycol
NIR	Near Infrared
NMR	Nuclear Magnetic Resonance
OD	Optical Density
R/A	Resin to Asphaltene Ratio
SARA	Saturates, Aromatics, Resins and Asphaltenes
TEG	Triethylene Glycol
UTV	Variable Temperature Unit
UV	Ultraviolet

List of Symbols

μ_r	Relative Viscosity	
V	Dispersed Phase	
ΔH_{vap}	Enthalpy of Vaporisation	KJ/mol
V_m	Molar Volume	m^3/mol
δ	Solubility Parameter	$MPa^{0,5}$
δ_d	Dispersion Forces	$MPa^{0,5}$
δ_p	Polar Forces	$MPa^{0,5}$
δ_h	Hydrogen Forces	$MPa^{0,5}$
vol %	Volume Percent	
wt %	Weight Percent	
T	Temperature	°C
μ	Dynamic Viscosity	mPa·s
ν	Kinematic Viscosity	mm^2/s
ρ	Density	g/cm^3

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1 Introduction

Production of heavy crude oils causes different challenges in the process equipment and pipelines than conventional oils. Heavy crude oil has physicochemical properties like high viscosity and density as well as a relatively high amount of heavy components as asphaltenes and resins. Usually the crude oil is transported from the production field to the refineries in pipelines. By reducing the viscosity the transportation of the crude oil will be much less demanding. (1) (2)

There are different ways to reduce the viscosity of heavy oils. Two well-known methods are to add a diluent with a lighter crude oil, and warming the pipeline to reduce the viscosity. The diluent added will represent 20-30 % of the volume which is a high ratio of the transported medium. Three other possible ways to reduce frictional pressure loss in transportation of oils are adding a drag reducing polymer, transport the oil as an oil-in-water emulsion and adding chemicals.

The focus of this thesis is how added chemicals could affect the asphaltene aggregation size and thereby reduce the viscosity of the oil. By adding chemicals with active molecule groups the idea is to stabilize the asphaltene as small aggregates. (3)

The idea of the experimental work is to test if small amounts (≤ 3 wt %) with alcohol and ketone as active groups could be used as a viscosity reduction chemical in transport of the oil. By adding a minor amount of a chemical to transport the oil the operational cost will drop as well as the total volume of the transported oil.

The chemicals used in the experimental work are based on reported effects in literature as well as the solubility parameters of Hansen and Hildebrand.

Three different solvent groups have been tested; a reference group, chemicals with active molecules and commercial products. The reference group of solvents consists of a light crude oil, toluene, n-alkane and water. The solvents with active molecule groups consist of four alcohols and one ketone. One of the commercial products is marked as viscosity reduction chemical and three of the products as asphaltene dispersion chemicals.

2 Asphaltenes in Heavy Crude Oil

The world has an increased oil demand which leads the petroleum industry to exploit unconventional crude oil reservoirs. Reservoirs with heavy oils represent a source of hydrocarbons of the same order of magnitude as the ones of conventional oils. However, production and transportation is challenging as these oils have a very high viscosity. (2)

2.1 Challenges with Asphaltenes in Crude Oil

Petroleum is a complex mixture of hydrocarbons where asphaltenes are one of the components. Asphaltene molecules vary in size depending on pressure, temperature and composition of the crude oil. Asphaltenes in crude oil can cause large challenges in the petroleum processing system. During petroleum production or recovery the asphaltenes may precipitate which leads to high viscosity and solid residues.

Temperature and pressure affect the asphaltene depositions in the petroleum production. Many reservoirs have high temperature and pressure which will decrease over production time, upstream in the production equipment and risers. The same effect will be found when transporting the oil in pipelines from the production field to the refinery. In order to prevent large chemical and physical changes of the crude oil it is important to find the right asphaltene stabilizing chemical. (1) (2)

2.2 Categorization of the Crude Oil and Asphaltenes

Petroleum is a mixture of different compounds consisting of hydrocarbons, heteroatoms and metals. The various compounds can differ widely in molecular structure, volatility, density and viscosity. The light crude oil has low density where several of the molecules are volatile, while the heavy oil has high density and high viscosity. (4)

Petroleum is usually divided into fractions; saturates, aromatics, resins and asphaltenes (SARA). The saturate fraction is non-polar and includes linear, branched and cyclic alkanes. Long-chain linear alkanes ($>C_{20}$) are known as waxes, or paraffinic waxes, and can make oil recovery challenging as the wax becomes solid at low temperatures. Aromatics are slightly more polar and consist of one or more aromatic rings connected by double bonds. Saturates and aromatics constitute the majority of the crude oil. Resins and asphaltenes are the most polar and complex components in crude oil. The majority of heteroatoms and metals are found in these fractions. Most of the heavy molecules in crude oil are represented by resin and asphaltene, and are found in a higher amount in heavy oil than in light crude oil. (5) (6)

The definition of heavy oil is usually based on density, API gravity [1] (American Petroleum Institute), or viscosity, but the generic term of heavy oil is usually applied to crude oils with gravity less than 20˚ API. (4)

2.2.1 Chemistry and Physical Properties of Asphaltenes

In general asphaltenes are soluble in aromatic solvents and not in n-alkanes. Asphaltenes are defined as the solubility class of petroleum that is insoluble in light alkanes as n-heptane but soluble in toluene and benzene. (4) (6)

Pure asphaltene looks like black dry powder. The structures of asphaltenes are known as the heaviest and most polar molecules in the crude oil. They are consisting of aromatic polycyclic cluster containing heteroatoms such as sulphur, oxygen and nitrogen, and trace metals like nickel, vanadium and iron. (5) (7)

The molecular structures of asphaltenes vary, and the asphaltenes are therefore defined as a solubility group and not a chemical group. Asphaltenes may consist of several sheets of condensed ring systems interconnected with alkyl side-chains, which gives a highly active surface. (8) (9) Examples of some suggested molecular asphaltene structures are shown in Figure 2-1.

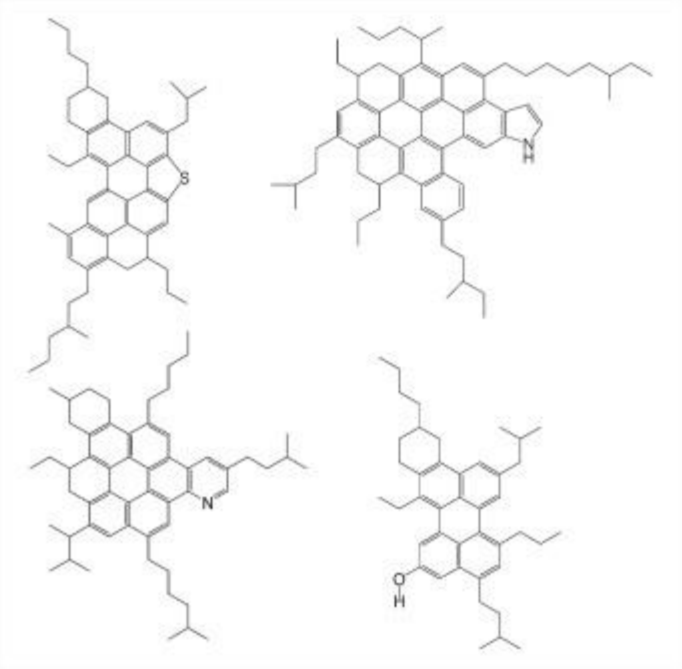

Figure 2-1: Some molecular structures of asphaltenes. (8)

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[1] API gravity is a measure of how heavy or light a petroleum liquid is compared to water

The molecular weight of asphaltenes is commonly mentioned to be around 750 g/mole. (8) This molecular weight is an approximation as the asphaltene has a strong tendency to self-aggregate, making it difficult to determine the exact molecular weight. Asphaltenes vary in structure which will also affect the weight. (7)

Traditionally it is accepted that asphaltenes are stabilized by another group of polar component, resins. Resins have a less molecular weight and act like an amphiphilic molecule. (10)

As resins stabilize the asphaltenes they have a strong tendency to connect to asphaltenes. Resins reduce the asphaltene aggregate size by breaking the π- π and hydrogen bonding between the asphaltene monomers. Asphaltenes with more polar components, such as heteroatoms, is claimed to need a significant higher resins concentration to prevent asphaltene aggregation. The aggregation is assumed to be driven by the polar heteroatoms interactions such as hydrogen bonding. (1) (11)

2.2.2 Asphaltene Behaviour in the Crude Oil

It is assumed that the asphaltenes are dispersed in the petroleum fluid as colloids, where colloid particles consist of different amount of asphaltene molecules aggregated together, from one molecule to many. As the asphaltenes aggregate together some colloids are bigger and heavier and may have an influence on the viscosity of the crude oil. (5) (9)

Asphaltenes can interact with themselves or other molecules by different driving forces. Some of the forces are hydrogen bonding between functional groups, π- π overlap between aromatic sheets and acid-base interactions. (10) (11)

Other chemical molecules than resins can also be used to prevent asphaltene aggregation, but the molecular structure seem to play an important role on the stabilizing effect. A long alkyl chain length will increase the lipophilic character of the final aggregate (stabilizing molecule-asphaltene molecule). The lipophilic character will help disperse the molecule in a non-polar media. A bigger alkyl chain will also prevent the asphaltene molecules or asphaltene aggregates to interact with each other as the distance between the compounds will increase with the alkyl chain. It can be assumed that the lipophobic–lipophilic balance of the molecule is crucial to the size of the asphaltene aggregate.

The molecular volume seems to also have a stabilizing effect. A higher volume of the stabilizing molecule would keep the asphaltenes separated as the interactions strength among them will be reduced with the distance and aggregation would be avoided. (10)

As mentioned above the asphaltene aggregates are affected by the temperature. The aggregate can be found in smaller sizes at higher temperature and larger forms at lower temperature. (11) As the temperature increases further the asphaltenes will not aggregate together. The bonds between solid particles will break hence reducing the viscosity of the oil. An opposite effect will be observed if the temperature decreases. (12)

Asphaltenes are believed to organize themselves in different structures in the crude oil depending on the amount of asphaltenes in the crude oil. A theory is that with low content the asphaltenes are bigger molecules that have enough space to move around. At a given content the asphaltenes begin to reorganize them self into smaller molecules, most likely to make it easier to move around each other. For a very high asphaltene content the asphaltenes could create a gel-structure. (13) (14)

The resins are believed to stabilize the asphaltenes by interaction between the polar components between resins and asphaltenes. The more non-polar part of the resin molecules are interacting with the oil phase and dispersing the asphaltene-resin molecule in the oil. (10) There is a theory that asphaltenes and resins together forms micelles in the crude oil. This is a theory that is discussed and has not been proved. However, resins are regarded to have “solvency power” with respect to asphaltenes; the solubility of asphaltenes is claimed to be dependent on the amount of resins in the oil. The resins amount seems to influence the aggregate size as the smallest aggregate size is found at high resin to asphaltene ratios (R/A). There are some disagreements around this statement, that more resins increase the solubility of asphaltenes, while others means the resin is an important factor of the asphaltene aggregation. (8) (11) (15)

There are also some discussions around the reversibility of the asphaltene aggregation. Different references claims that asphaltene aggregation is reversible but they are affected by time, pressure and temperature. (5)

3 Addition of Chemicals to Reduce the Viscosity

It is believed that the asphaltene aggregation has an influence on the viscosity of the crude oil. Different chemicals can be added to prevent asphaltene aggregation in the crude oil to make the transportation easier from the production field to the refinery.

As mention, it is traditionally accepted that asphaltenes are stabilized by another aromatic hydrocarbon component, resin. Different chemicals could be used as resin-like molecules that stabilize asphaltenes by inhibiting self-aggregation between asphaltene-asphaltene molecules. (10)

3.1 Chemicals as Reference Solvents

Various solvents will behave differently in crude oil depending on their solubility, chemical composition and polarity (more of solubility is discussed in Chapter 4). In the experimental work some chemicals with known behaviour are used as a reference for the added solvents with active groups and the commercial products.

Naphtha, Toluene, N-alkane and Water

Today a lighter crude oil, naphtha, is used to reduce the viscosity of a heavy oil. The amount of naphtha is significant and represents 20-30 % of the volume of the transported medium. The naphtha consists mainly of small light hydrocarbons and is used as a diluent. The naphtha could give a slight asphaltene aggregation effect of the crude oil but not in any significant way.

Toluene is known to disperse asphaltenes in the crude oil while n-alkane has the opposite effect. N-hexane is a light component which has the ability to cause asphaltene aggregation and at the same time has almost the same molecular size as 1-hexanol.

Water is always present in the crude oil, but treated crude oil has minor amounts. Water is present as droplets in the oil, water-in-oil emulsion. An emulsion of water-in-oil has a higher viscosity than the plane oil. (16)

These chemicals, naphtha, toluene, n-hexane and water were used as reference solvents in the experimental work.

3.2 Chemicals with Active Groups

From different experiments it is claimed that a polar component can have an effect on asphaltene aggregation. The active group is thought to stabilize the asphaltenes by forming colloids in the same way an inhibitor or resins do. (17)

3.2.1 Chemistry of Alcohol and Ketone

The hydroxyl group is the defining functional group in alcohols and is a polar group that forms hydrogen bonds to other structures. The structure of an alcohol are found as linear, short- or long-chain, or branched. Each alcohol molecule can have more than one hydroxyl group, and include other functional groups. Molecules with more than one hydroxyl group are called diol, triol etc. diol is also known as glycol.

The functional group of ketone is a polar carbonyl group. The oxygen has a greater electronegativity than carbon which makes carbonyl group able to interact with other polar components by hydrogen bonding. (18)

3.2.2 Chemicals with Active Groups as Flow Improver

Different studies have shown a positive effect by use of chemicals with active groups as a flow improver. Alcohols, as glycol, are readily available and could be useful to reduce the viscosity in heavy crude oils. Various alcohols and one ketone have been studied and tested in the experimental work. (3) (17) Other polar components, as butyronitrile, ethanol and different N-aryl amino alcohols, with interesting results have been reported in the literature. More information about other polar components is found in former literature study. (19)

1-Hexanol

Gateau et al. (17) have tested 1-hexanol as a solvent to reduce the viscosity of heavy oil. Figure 3-1 shows the structure of 1-hexanol.

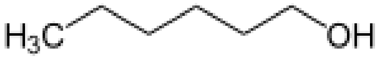

Figure 3-1: Molecule structure of 1-hexanol. (20)

Gateau et al. studied the asphaltene behaviour in a pentane/1-hexanol/toluene mix as the asphaltenes are known to be solved in toluene and found in colloidal form. The solvent solution was prepared with 3 wt % pentane in 1-hexanol/toluene mixture where 1-hexanol varied from 0 to 50 vol %. The study showed that the smallest particles and the lowest relative viscosity were observed for a 1-hexanol content of 10 vol % in toluene both at the temperature 3˚C and 25˚C.

Further Gateau et al. looked into the influence of hydrogen bonding. The best effect on viscosity reduction was found in a mixture of solvent in naphtha. A mixture of solvent nonane was also tested with less effect. The tested crude oil was diluted with 15 wt % of mixtures 90 vol % solvent/10 vol % naphtha or nonane. Several solvents were tested were 1-hexanol was the best reducing viscosity chemical. However, there was no typical relationship between the hydrogen bonding parameter and the viscosity reduction. This could probably be explained that the polarity from the solvate had an impact as well as the hydrogen bonding.

Gateau et al. explained this behaviour as 1-hexanol is able to build hydrogen bonds and polar interactions with the asphaltenes to prevent asphaltene-asphaltene interactions. The asphaltenes are saturated when all the possible sites have interacted with the alcohol function. By adding more 1-hexanol after this point the alcohol acts like a flocculent. An increase of the 1-hexanol fraction leads thereby to an increase of particle size and relative viscosity. (17)

Dihydric Alcohols

The use of dihydric alcohols such as monoethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG) have shown a reduced viscosity in crude oils with high viscosity. (21) The dihydric alcohols could be used in a mix or separately. Structures of dihydric alcohols are illustrated in Figure 3-2.

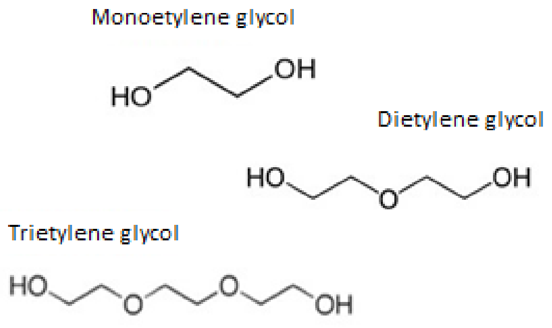

Figure 3-2: Structure of monoethylene glycol, diethylene glycol and triehtylene glycol. (20)

The tested crude oil was petroleum pitch. The amount of dihydric alcohols that was added was 0.5-2 wt % which gave a reduced viscosity of the tested crude oil. Addition of 2 wt % dihydric alcohol to a petroleum pitch reduced the viscosity around 43 % at temperature 150° C. The significant viscosity reduction has been observed on samples where the viscosity is above 100 mPa·s. (21)

Butanone

The influence of polarity on the asphaltenes behaviour was studied by Gateau et al. (17) by using a polar solvent as butanone in heavy oil. The experiment tested different polar solvents mixed with naphtha and nonane. The molecule structure of butanone is illustrated in Figure 3-3.

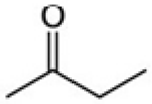

Figure 3-3: Molecule structure of 2-butanone. (20)

The experiment concluded that the best reduction of viscosity was reached in naphtha with butanone, not in nonane. According to Gateau et al. this result could be explained by naphtha being a better solvent for asphaltenes than nonane. The asphaltenes swell up in a more aromatic solvent such as naphtha, while in the nonane they will be more compact. This contributes to make the polar sites more available for the polar solvent. Gateau et al. suggested that this could be thought as the maximum efficiency is reached when all the polar sites on the asphaltenes are bonded with the polar solvent. (17)

3.3 Commercial Products

In the industry the use of inhibitors to prevent asphaltene aggregation is a well-known method, and many resin-shaped products have been analysed with good results in the viscosity of the crude oil. It seems that there are different stabilizing forces that play an important roll depending on the composition and structure of the inhibitor. (10)

Asphaltene Dispersant

Armohib Ai-1000, Duomeen T and Ethoduomeen T/13 are commercial products from AkzoNobel. These products are known to be asphaltene dispersants consisting of active components as diaminopropane. The recommended amount of added asphaltene dispersant chemical is 250-1000 ppm. (22)

Figure 3-4 illustrates the active component diaminopropane.

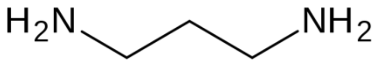

Figure 3-4: 1.3-Diaminopropane (20)

Armohib Ai-1000, Duomeen T and Ethoduomeen T/13 have been tested in the experimental work.

Solvtreat EFI-201

Clariant Oil Services has tested a solvent with positive result on the viscosity reduction of the crude oil. The crude oil is from Alberta, Canada, and the crude sample characteristics as high viscosity and high asphaltene content. The physical properties of the crude oil sample are given in Table 3-1.

Table 3-1: Physical properties of the crude oil.

Crude Oil Properties	
Geographic Area	Alberta, Canada
Asphaltene [wt %]	11.44
Wax [wt %]	1.10

Solvtreat EFI-201 was tested with a concentration of 10 000 ppm and gave a result with an average viscosity reduction at 54 %.The Solvtreat EFI-201 specific composition is not known, but the information that is given is that “the Solvtreat formulations contain specific base solvents with various dissolving/dispersing agents”. (23) Solvtreat EFI-201 is a commercial product from Clariant which has been tested in the experimental work.

3.4 Crude Oil Specifications

3.4.1 Effects of Solvents in Crude Oil

Even if a particular chemical shows to reduce the viscosity there are different factors to look into before the solvent can be used in the production process. (4) (24)

Emulsion

There are large differences in polarity between water and crude oil. The presence of water in crude oil can make a large effect on the added chemical as a solvent. An added substance as a chemical solvent could be soluble in one of the phases or in both, but the concentration of the solvent in these two phases could vary in amount. The equilibrium ratio of solvent concentration in the two phases is known as the partition coefficient or distribution coefficient. A solvent of alcohol could be soluble in water depending on the molecular structure. If the hydrocarbon group is large enough compared to the hydroxyl group the molecule would be hydrophobic and prefer the crude oil phase. (25) To detect the full effect of the added chemical the crude oil should contain as little water as possible. (3)

If water is present or if a chemical not soluble in oil has been added, drops dispersed in the oil, an emulsion, exists. Einstein developed a thermodynamic model for colloids. The model described how the relative viscosity (μ_r) of an emulsion increases linearly with the volume fraction of the dispersed phase (V) as given in Equation 3-1.

$$\mu_r = 1 + 2.5\,V$$

Equation 3-1

Equation 3-1 shows that the viscosity will increase if the added chemical is not fully soluble in the oil. (16)

Polarity

The asphaltenes are claimed to be a “highly polar” component in crude oil as they are insoluble in non-polar solvents, but soluble in solvents like toluene. Asphaltenes are still insoluble in polar solvents like water and comparing toluene to water the toluene is relatively non-polar. As the asphaltenes are insoluble in water the same are claimed for glycerol and methanol. The more correct state is that asphaltenes are not polar in chemical sense, but considered as more polar than other hydrocarbons components in crude oils.

The asphaltene could still have some polarity as nitrogen and oxygen atoms will contribute significantly to a permanent polarity, but the total amount of nitrogen and oxygen in asphaltenes is usually lower than 4 %. The content as polyaromatic compounds can contribute to an increased polarity as these may act as polar molecules in contact with other polar molecules. (26)

Even if the asphaltenes consist mostly of hydrocarbons the polarity of the solvent has shown an effect on the size of the aggregates. (11)

Viscosity

Viscosity is defined as “the ration of shearing stress to velocity gradient” by Newton`s law. The units for viscosity are Pa·s, while in this report the unit mPa·s is used.

A fluid can be characterized as a Newtonian or Non-Newtonian fluid. A fluid that is Newtonian is independent of strain or shear rate which means if the force used is doubled the share rate will be doubled. This means that the viscosity will change with temperature but not change with strain rate. Non-Newtonian fluids have not the same respond and the share rate will more or less double when doubling the force depending on shear thinning or shear thickening tendencies. A shear thinning fluid will be easier to deform at higher shear rates, meaning an increase in relatively velocity cause a reduction in viscosity. A shear thickening fluid will show the opposite behaviour and have more resistance the higher shear rate.

Newtonian fluids such as water are purely viscous and metals are purely elastic materials. Many materials have both elastic and viscous characteristics, and such materials are called viscoelastic. (27)

4 Solubility Parameter

In the search for the right solvent to prevent asphaltene aggregation one can perhaps use the solubility parameter concept. The solubility parameter is based on the assumption that "like dissolve like". Asphaltene molecules will not be soluble in certain liquids (alkanes). This can be due to the large differences in the interaction energy between asphaltene molecules and the solvents molecules as the interaction energy between asphaltene-asphaltene molecules and solvent-solvent molecules will be stronger. To achieve some solubility the interaction energy between the asphaltene-solvent molecules should be as close to the asphaltene-asphaltene molecules and solvent-solvent molecules as possible. There are different ways to calculate the solubility parameter. Hildebrand and Hansen are known approaches, in addition the solubility parameter can be split into van der Waal and acid-base contributions. (28) (29) In this report the Hildebrand and Hansen will be considered as solubility parameters. More information about the solubility parameter is found in former literature study. (19)

4.1 Hildebrand Solubility Parameter

Hildebrand was one of the first to use the term solubility parameter. The enthalpy of vaporisation (ΔH_{vap}) is the reflection of the cohesive forces in a liquid, therefore the enthalpy can be used as a measurement for these interaction energies. The enthalpy of vaporisation is depending of the molar volume (V_m), which gives the solubility parameter as the square root of the cohesive energy density as given in Equation 4-1.

$$\delta^2 = \frac{\Delta H_{vap}}{V_m}$$

Equation 4-1

where δ is the solubility parameter given in [$MPa^{0.5}$]. (28) (29)

Table 4-1 is presenting relevant solvents with molecular structure, function group and the solubility parameter given by Hildebrand.

Table 4-1: The Hildebrand solubility parameter. (30) (31) (32)

Molecule	Molecule structure	Function group	Solubility parameter [$MPa^{0.5}$]
Toluene	C_6H_5-CH_3	Aromatic	18.2
n-Hexane	C_6H_{14}	Alkane	14.9
Water	H_2O	Non-organic	47.9
1-Hexanol	C_6H_{13}-OH	Alcohol	21.9
Monoethylene glycol	C_2H_4-$(OH)_2$	Alcohol	29.9
Diethylene glycol	C_4H_8O-$(OH)_2$	Alcohol	24.8
Triethylene glycol	$C_6H_{12}O_2$-$(OH)_2$	Alcohol	21.9
2-Butanone	C_4H_8O	Ketone	19.3

4.2 Hansen Solubility Parameter

Hansen solubility parameter is a bit more expanded than Hildebrand and splits up the solubility parameter into three different contribution forces, dispersion, polar and hydrogen binding. The total solubility parameter can be written as in Equation 4-2.

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad \textbf{Equation 4-2}$$

where the subscript d, p and h represent the dispersion, polar and hydrogen bonding forces. (28)

From Hansen solubility parameter every solvent and solute has three parameters, thus for non-polar solvents δ_p=δ_h=0 and δ_d=δ. (33) Table 4-2 is presenting relevant solvents given by the Hansen solubility parameter.

Table 4-2: Hansen solubility parameter. (30) (34) (35) (36)

Molecule	Dispersion forces δ_d	Polar forces δ_p	Hydrogen forces δ_h	Solubility parameter [$MPa^{0.5}$]
Toluene	18.0	1.4	2.0	18.2
n-Hexane	14.9	0.0	0.0	14.9
Water	15.5	16.0	42.4	47.9
1-Hexanol	15.9	5.8	12.5	-
Monoethylene glycol	17.0	11.0	26.0	32.9
Diethylene glycol	16.6	12.0	20.7	29.1
Triethylene glycol	16.0	12.5	18.6	-
2-Butanone	16.0	9.0	5.1	19.1

4.3 Solubility of Asphaltene and Crude Oil

The solubility parameters of pure components are usually estimated based on chemical and physical parameters. The asphaltenes can be composed of different heteroatom functional groups that will vary in amount from asphaltene to asphaltene. The composition of these functional groups as well as location of these groups will affect the solubility parameter of asphaltene molecules.

In the literature there are reported different Hildebrand solubility parameter values for asphaltenes. From different experiments a solubility parameter for asphaltenes is ranging from 17.7 to 21.4 $MPa^{0.5}$. (37)

In the same way that asphaltenes can vary in the molecular structure and contents of functional groups the crude oil will vary in composition of hydrocarbons and content of asphaltenes. This makes it difficult to estimate an exact solubility parameter of crude oils. However, bitumen has been tested and values for solvents from the Hildebrand solubility parameter are found. All good solvents for bitumen have values between 17.8 and 25.8 $MPa^{0.5}$, however, not all solvents in this range are good solvents. This shows that the Hildebrand solubility parameter is not a good enough approximation, probably because not all interactions between the molecules are taken into consideration.

The Hildebrand solubility of the hydrocarbons are mainly determined by the dispersive interactions, but to make a more correct estimate the polar and hydrogen bonding interaction should also be taken into consideration. This could contribute to a more correct picture of their stability. The Hansen solubility parameter takes all this interactions in consideration and will therefor probably give a better estimate. Hansen solubility parameters have been used to estimate values for an Venezuelan bitumen oil with the result $\delta_d = 18.6\ MPa^{0.5}$, $\delta_p = 3.0\ MPa^{0.5}$, $\delta_h = 3.4\ MPa^{0.5}$. (17)

A good approach to find a good solvent could be to make solubility tests in a large number of solvents with known solubility parameters. From these test results an average solubility value from the best solvents could be concluded as the solubility parameter of the crude oil. (26)

5 Experimental Methods

Different kind of experimental methods can be used to determine the chemical and physical properties of a crude oil as viscosity, density and chemical compositions. (4) (38) This chapter presents the analyses that were used in the experimental work.

5.1 Karl Fischer Titration

The water amount can affect the quality, stability and reactivity of petroleum products. Karl Fischer titration is a classic titration method in analytic chemistry used to determine the amount of water in a sample. The method uses chemicals which react in an equal amount as the water in a sample. The titration method can use volumetric or coulometric titration, both methods use iodine as the measured chemical to detect the water amount. (39)

In the volumetric method the iodine is included with the reagents while in the coulometric method the iodine is generated at an electrode. Both methods are based on the same two reactions. The first reaction uses an alcohol, usually methanol or ethanol, sulphur dioxide (SO_2) and a base (RN) to form an alkylsulfite intermediate as in Equation 5-1.

$$CH_3OH + SO_2 + RN \leftrightarrow [RNH]SO_3CH_3$$

Equation 5-1

In the second reaction the alkylsulfite product reacts with iodine (I_2) and water as in Equation 5-2.

$$[RNH]SO_3CH_3 + I_2 + H_2O + 2RN \leftrightarrow [RNH]SO_4CH_3 + 2[RNH]I$$

Equation 5-2

Water and iodine are consumed in equimolar amounts and the water amount in a sample can be calculated. (40)

Volumetric titration method was used in the experimental work to measure the water amount. The analysis was performed on a Sigma-Aldrich instrument and the purpose of the measurement was to ensure that the used crude oils did not contain more water than is normal in oil production (< 0.5 wt %).

5.2 Viscometer

Anton Paar SVM 3000 viscometer is a rotational viscometer with cylinder geometry and a u-tube (often called Stabinger). The viscometer determines the dynamic viscosity [mPa·s] and the density [g/cm^3] of a sample, while the kinetic viscosity [mm^2/s] is calculated from these two measured values.

An outer tube is filled with the sample liquid that rotates at a constant speed and temperature. Inside the outer tube a lightweight measuring rotor with a built-in magnet floats in the sample. The low density of the rotor allows it to be centred by the centrifugal forces. The rotating magnet creates an eddy current field with an exact speed dependent brake torque. As the rotor floats and the measuring sensor is contactless there is no undesirable influence of external friction. The viscosity of the sample fluid drives the rotor and leads to a steady speed of the rotor. This is determined by the equilibrium between the effect of the eddy current brake and the shear forces that work in the sample. The speed of the rotor is used to calculate an unambiguous value of the fluid's viscosity. Figure 5-1 illustrates the basic of the viscometer. (41) (42)

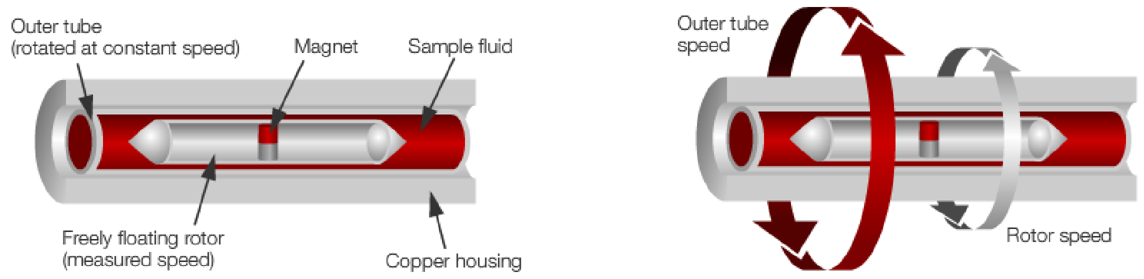

Figure 5-1: Basics of Anton Paar Viscometer SVN 3000. (41)

The density is measured in a built-in density cell that uses the oscillating U-tube principle. Both cells, outer tube and U-tube, are filled in one cycle. This makes the viscometer able to measure the dynamic viscosity and density simultaneously.

A fully automatic sampler changer, Xsample 460H, can be used to measure a large number of samples. The changer pre-heats the samples and can handle up to 44 samples. (41) (42)

Measuring range for the SVM 3000 is presented in Table 5-1.

Table 5-1: Detection limits with repeatability of the Anton Paar SVM 3000. (41)

Measuring	Range	Repeatability
Dynamic viscosity [mPa·s]	0.2 to 20 000	0.1 %
Density [g/cm^3]	0.65 to 3.0	0.0002 g/cm^3
Temperature [°C]	-56 to 105	0.005 °C

The Anton Paar SVM 3000 with the auto sampler Xsample 460H was used in the experimental work to measure the dynamic viscosity and density of all the samples.

5.3 Rheometer

The Anton Paar Physica MCR rheometer uses an air bearing-supported synchronous motor. Permanent magnets with high energy are placed on a small rotor disc to produce a constant magnetic field which provides fast and delay-free response. The stator field is produced by a series of coils and the rotor is moving synchronous at the same speed.

Different measurement geometrics can be used to perform analyses. A rotating bob in a pressure cell is one geometric. A pressure cell is completely sealed agent the environment to counter for any evaporation and can measure up to a pressure of 150-400 bar. In viscous fluids a bob cup system with reduced gap can reduce the friction heat when measuring. A pressure cell with and a bob is illustrated in Figure 5-2.

Figure 5-2: High-pressure cell with measuring system. (43)

The rotating bob in a fluid sample creates a torque value which can be measured and used to calculate the viscosity at a given temperature, share rate and pressure. A Peltier system is used to control the temperature of the sample during the analysis. (44) (43)

The Anton Paar Physica MCR 501 rheometer was used in the experimental work to check the shear dependence of the viscosity. In the analyses a pressure cell, without pressure, and a rotating bob with reduced gap were used to measure the clean crude oils and a selection of the blended samples.

5.4 Near Infrared Spectroscopy

The near infrared light is electromagnetic radiation in the infrared (IR) region which is close to the visual spectrum. The wavelengths of near infrared spectrum are in the range of 760 to 2500 nm which are not harmful like wavelengths in the X-ray or UV range (Ultraviolet).

The principle of near infrared spectroscopy is that the infrared radiation is absorbed by a molecule and causes individual bonds to vibrate. Photons in the NIR region has enough energy to create molecular vibrations, where the main bonds are N-H , C-H and O-H bonds. The analysis is a quick measurement technique that takes less than one second, is easy to use and needs little or no sample preparation. (45)

The NIR light is partially adsorbed by the sample. In addition will particles present in the sample cause the NIR light to scatter which will be detected as absorbance. By changing the amount or size of the particles in a sample the detected absorbance will change. This changed absorbance will be reflected in the NIR spectra as a shift in the baseline where the baseline will lower as the particles decrease.

A typical baseline shift caused by changes in the absorbance is shown in Figure 5-3.

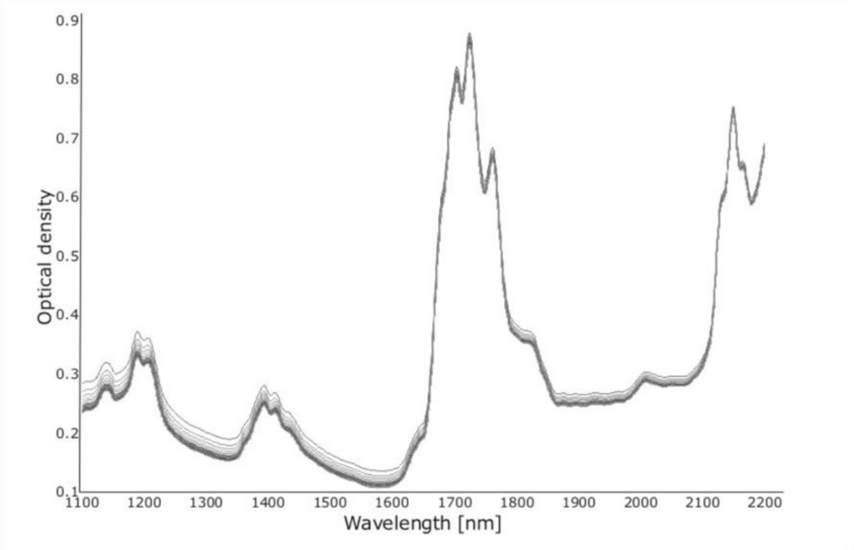

Figure 5-3: Optical density, a sum of scattering and absorption of transmitted light, plotted against wavelength [nm] for several NIR spectra. The baseline is lowering at 1600 nm as the particles are decreasing in size. (46)

The particles are assumed to be small relative to the wavelength which makes it possible to use the Rayleigh limit ($r/\lambda \leq 0.05$). The Rayleigh scattering is based on the theory that the particle is so small that the electromagnetic field is uniform over the particle. The light extinction within the Rayleigh limit can be considered as a sum of the absorbance and scattering contribution, represented by the particle cross-section in Equation 5-3.

$$\sigma_{tot} = \sigma_{sc} + \sigma_{abs}$$ **Equation 5-3**

where σ_{tot}, σ_{sc} and σ_{abs} are the total, scattering and absorbance cross-section, respectively. The particle size is an important contributor to the total light extinction as the ratio of scattering to absorption scales with r^3. The optical density (OD) is defined in Equation 5-4.

$$OD = \log\left(\frac{I_0}{I}\right) = 0.434\, N\sigma_{tot}$$ **Equation 5-4**

where I_0 and I are the intensities of incident and transmitted light while N is the particle diameter.

Crude oils as well as asphaltene solutions have little or no absorbance of light at 1600 nm, but the light will still scatter when particles are present. This makes it possible to use NIR to detect any changes in the asphaltene aggregation size when adding solvents into the crude oil. (46) (47)

Near infrared spectroscopy was used in the experimental work to identify the asphaltene behaviour when adding different solvents into the crude oils. The used instrument was a Lunar NIR AOTF Spectrometer from producer Brimrose Corporation of America.

5.5 Nuclear Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy is a technique that measures the absorption of electromagnetic radiation of materials in a magnetic field. The life-time of the signal, T_2 relaxation time, can be used to determine how a sample is composed. Different compounds in a sample will undergo relaxation at different times, and the intensity of the signal represents the amount of the compound that undergoes the relaxation at that specific time. (48) (49)

As the composition of a sample can be determined by NMR spectroscopy it is also possible to say something about the homogeneity of the sample. If the curve only shows one peak, it suggests that the sample is blended properly. If the curve shows two or more peaks however, the sample is not homogeneous. The shape of the curve also contributes to interpretation of the homogeneity of the sample.

A principle for measuring T_2 relaxation of two mixable fluids is presented in Figure 5-4. A viscous oil (Marcol 82) and a less viscous oil (Isopar L) is mixed and the mixture of these fluids will give a T_2 relaxation time between the individual T_2 relaxation times of the oils. The fluids are properly blended as the curve representing the mixture (green) shows only one peak. The viscosity of the mixture will also lie between the original oils. (50)

T_2 relaxation measured of two mixable oils is presented in Figure 5-4.

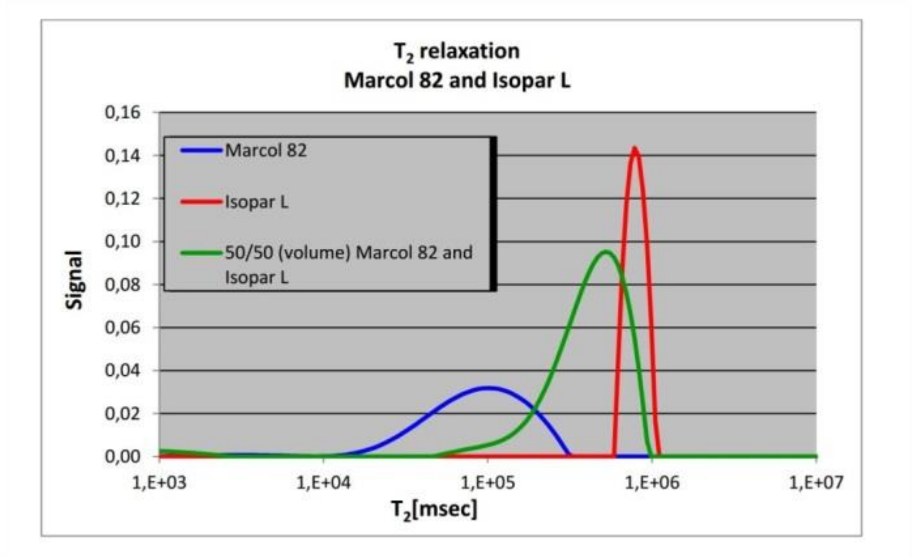

Figure 5-4: T_2 relaxation measured with NMR spectroscopy of two mixable fluids with relaxation time [ms] versus signal. The results of the total signals are normalised. (50)

5.5.1 Low-Field NMR on Asphaltenes

The detection and identification of asphaltene molecules with low-field NMR spectroscopy is difficult. (51) Substances with high viscosity will go through relaxation faster than those with low viscosity. (52) Asphaltenes have usually higher contents of free radicals compared to other components in the crude oil. This results in a faster spin relaxation of asphaltene protons and contributes to a faster T_2 relaxation, and a shorter relaxation time. (53)

Droplets bigger than 0.5 µm in diameter can be detected at the Low-Field NMR spectroscopy. This makes it possible to detect an emulsion phase in a sample. (50)

5.5.2 T_2 Relaxation

For measuring T_2 relaxation the CPMG-sequence is the most common technique. This sequence is called a spin echo sequence and starts with a so-called 90° pulse, and then continues with multiple 180° pulses. Between the 90° pulse and the first 180° pulse a time of τ will transpire, and between every 180° pulse a time of 2τ will transpire as shown in Figure 5-5. This sequence is used to re-phase protons that rotate with different speed due to in homogeneities in the magnetic field. This is repeated several times, and the echo signal decreases for each pulse only due to T_2 relaxation. (50) (54) (46)

Figure 5-5 illustrating CPMG-sequence with pulse and τ.

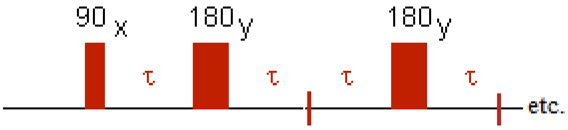

Figure 5-5: CPMG-sequence timeline. (55)

The CPMG-sequence was used to measure the homogeneity of the samples in the experimental work, and the analysis time was set so that all components did undergo relaxation with good margin.

The instrument used in the experimental work is delivered from AnTek AS. The instrument is a bench top instrument with permanent magnets with a magnetic field at approximately 0.5 Tesla. At 0.5 Tesla the proton has a frequency at 22 MHz. The instrument is equipped with a UTV (variable temperature unit) which regulates the temperature around the test tubs when measuring. (50)

6 Material and Method

In the experimental work there have been tested three crude oils and thirteen chemicals. It was expected that some of the chemicals had an effect on the dynamic viscosity by affecting the asphaltenes in the crude oil. An activity and risk assessment was performed before the experimental work started. The overview of the activity and risk assessment are found in Appendix A.

6.1 Material and Chemicals

Analyses instruments used in the experimental work are presented in Table 6-1.

Table 6-1: Overview of the analyses instruments.

Method	Instrument	Purpose
Karl Fischer Titration	Sigma-Aldrich	Water amount in crude oils
Viscometer	Anton-Peer SVM 3000	Dynamic viscosity and density
Rheometer	Anton Paar Physica MCR 501	Shear dependence of the viscosity
NMR spectroscopy	AnTek AS, 22 MHz	Relaxation time
NIR spectroscopy	Lunar NIR AOTF Spectrometer	Size of asphaltene particles

The specifications of the crude oil used in the experimental work are presented in Table 6-2.

Table 6-2: Specifications of the crude oils. Density and dynamic viscosity is measured at the viscometer. (14) (56)

Crude oils	Density (20°C) [g/cm^3]	Viscosity (20°C) [mPa·s]	Asphaltenes [wt %]	Wax [wt %]	TAN
Crude oil A	0.9377	345.27	2.8	0.9	2.2
Crude oil B	0.9748	3480.0 (50°C)	20.6	3.2	0.99
Crude oil C	0.9673	4152.4	17	-	2.2

Chemicals used as reference solvents in the experimental work are presented in Table 6-3 with specifications and purpose.

Table 6-3: Chemicals used as a reference solvent in the experimental work.

Chemicals	Specifications	Purpose
Naphtha	Lighter crude oil	Dilution effect
Toluene	Aromatic	Dilution effect and asphaltene dispersing effect
n-Hexane	Alkane	Dilution effect and asphaltene aggregation effect
Water	Tap water	Emulsification

Solvents with active molecule groups used in the experimental work are presented in Table 6-4.

Table 6-4: Chemicals used with active molecule groups. (32)

Chemicals	Specifications
MEG	Alcohol
DEG	Alcohol
TEG	Alcohol
1-Hexanol	Alcohol
2-Butanone	Ketone

Commercial products form Clariant and AkzoNobel used in the experimental work are presented in Table 6-5.

Table 6-5: Commercial products.

Chemicals	Specifications
Solvtreat EFI-201	Viscosity reduction chemical from Clariant
Armohib Ai-1000	Asphaltene dispersant chemical from AkzoNobel
Duomeen T	Asphaltene dispersant chemical from AkzoNobel
Ethoduomeen T/13	Asphaltene dispersant chemical from AkzoNobel

Additional specifications of the solvents are found in Appendix B, B.1 Chemical Properties.

6.1.1 Karl Fischer Titration

The Karl Fischer volumetric titration was used to detect the water amount (wt %) in the clean crude oils. Samples of crude oil (0.3 ml) were injected and analysed at a temperature of 50°C using chemical Hydranal-Solvent CM that consisted of 30 % chloroform.

6.2 Pretest

A pretest was performed to get an overview of how the samples should be treated before analysed to make sure a good blending and a homogeneous sample. The analyses used in the pretest were viscometer and NMR spectroscopy.

6.2.1 Making the Pretest Samples

Crude oil A was tested by adding 2 wt % of 1-hexanol, “Prestest A” samples. The temperature heating was at 40°C and the shaking was performed at 175 rpm. A specified overview of the treatment is given in Table 6-6.

Table 6-6: Overview of the series “Pretest A” samples.

Sample name	Crude oil fraction [wt %]	1-Hexanol fraction [wt %]	Temperature [°C]	Shaking time [h]	Storage time [h]
1 H Crude oil A	100	0	40	1	-
A-1 H	98	2	40	1	-
A-2 H	98	2	40	2	-
A-4 H	98	2	40	4	-
A-2 H*	98	2	40	2	24
1-Hexanol	0	100	-	-	-

A-2 H* = A-2 H sample stored 24 hours

Also crude oil B was tested by adding 2 wt % of 1-hexanol, “Pretest B” samples. The temperature heating was at 50°C and the shaking was performed at 175 rpm. A specified overview of the treatment is given in Table 6-7.

Table 6-7: Overview of the series “Pretest B” samples.

Sample name	Crude oil fraction [wt %]	1-Hexanol fraction [wt %]	Temperature [°C]	Shaking time [h]	Storage time [h]
1 H Crude oil B	100	0	50	1	-
B-2 H	98	2	50	2	-
B-4 H	98	2	50	4	-
B-24 H	98	2	50	24	-
1-Hexanol	0	100	-	-	-

6.2.2 Viscometer

Viscometer Anton-Peer SVM 3000 was used to measure the dynamic viscosity and density. Three parallels were measured from each sample. The temperature program for “Pretest A” was 20, 30, 40, 30, 20°C while the fill temperature was 30°C. The temperature program was used to make sure that the sample did not change after being heated. For “Pretest B” the auto sampler was pre-heated to 50°C and the temperature program for the measurements was 50, 40, 30, 20, 50°C. The last measuring point was just for practical reason, to have a less viscous oil in the cleaning procedure of the instrument.

6.2.3 Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy was used to measure the T_2 relaxation time of the samples to decide the homogeneity of the samples. Three parallels were measured from each sample at the temperature of 30°C.

6.3 Main Experiment

Crude oils were added solvents in small amounts (≤ 3 wt %) to study the solvent`s effect to reduce the viscosity by dispersing the asphaltenes in the oil. The analyses used in the main experimental work were viscometer, rheometer and NIR spectroscopy. A selection were in addition analysed with NMR spectroscopy.

All the blended samples made in the experimental work are named from their crude oil and added solvent.

A test matrix of all the samples are given in Table 6-8, Table 6-9 and Table 6-10 to make an overview of the samples in the experimental work.

Table 6-8: Samples made from crude oil A shaken for 2 hours at 40°C.

Sample name	Series (added amount of solvent)				
	0 wt %	0.5 wt %	1 wt %	2 wt %	3 wt %
Crude oil A	X				
A-Naphtha		X	X	X	X
A-Toluene		X	X	X	X
A-n-Hexane		X	X	X	X
A-Water				X	
A-MEG				X	
A-MEG*				X	
A-DEG				X	
A-DEG*				X	
A-TEG				X	
A-TEG*				X	
A-1-Hexanol		X	X	X	X
A-2-Butanone		X	X	X	X
A-Solvtreat		X	X	X	X
A-Chem A				X	
A-Chem D				X	
A-Chem E				X	

A-MEG*= A-MEG shaken for 66 hours at 40°C
A-DEG*= A-DEG shaken for 66 hours at 40°C
A-TEG*= A-TEG shaken for 66 hours at 40°C

Table 6-9: Samples made from crude oil B shaken for 4 hours at 50°C.

Sample name	Series (added amount of solvent)				
	0 wt %	0.5 wt %	1 wt %	2 wt %	3 wt %
Crude oil B	X				
B-Naphtha		X	X	X	
B-Toluene		X	X	X	
B-n-Hexane		X	X	X	
B-Water				X	
B-MEG				X	
B-DEG				X	
B-TEG				X	
B-1-Hexanol		X	X	X	
B-2-Butanone		X	X	X	
B-Solvtreat		X	X	X	
B-Chem A				X	
B-Chem D				X	
B-Chem E				X	

Table 6-10: Samples made from crude oil C shaken for 4 hours at 40°C.

Sample name	Series (added amount of solvent)				
	0 wt %	0.5 wt %	1 wt %	2 wt %	3 wt %
Crude oil C	X				
C-Naphtha				X	
C-Toluene				X	
C-n-Hexane				X	
C-Water				X	
C-MEG				X	
C-DEG				X	
C-TEG				X	
C-1-Hexanol				X	
C-2-Butanone				X	
C-Solvtreat				X	
C-Chem A				X	
C-Chem D				X	
C-Chem E				X	

The clean crude oils were shaken and/or heated before any sampling was made to make sure that the crude oil was homogeneous. All the samples have been treated as similarly as possible in the blending, analyses and storage to prevent sources of error.

6.3.1 Making the Samples

The clean crude oil A and crude oil C were shaken (175 rpm) at room temperature (30 minutes) before the samples of crude oil and solvent were made to make as homogeneous crude oil as possible. Crude oil B was preheated to 50°C to reduce the viscosity of the crude oil before transferred into smaller samples bottles.

A set of samples were made by adding different solvents (2 wt %) into the crude oil A. All the samples of crude oil A, including the sample with clean crude oil, were shaken (175 rpm) at 40°C for 2 hours. After analyses of the 2 wt % samples new sets of blends were made of the most interesting solvents. Sets of 0.5, 1 and 3 wt % added solvents were made and analysed.

Sample series of 2 wt % solvents in crude oil B was blended. The crude oil was cooled down to room temperature before any solvents were added to prevent evaporation of the solvents. After the solvents was added the samples were first heated (50°C, 30 minutes) and further shaken for 4 hours (50°C, 175 rpm). After analyses of the 2 wt % samples there were also made new blends of the most interesting solvents added in crude oil B. Blends of 0.5 and 1 wt % solvents were made and analysed.

Crude oil C samples with 2 wt % solvents were blended by shaken (175 rpm) at 40°C for 4 hours.

Samples made form crude oil A with 2 wt % glycol (MEG, DEG and TEG) was extra treated by shaken (175 rpm) at 40°C for 66 hours. This was done at the end of the experimental work.

To make sure that there was no loss of samples at the blending all the samples were weighed before and after heating and shaking. The first analysis began after the samples were cooled down to room temperature (22°C, about 30 minutes).

Between the analyses the samples were stored in a refrigerator (+5°C).

6.3.2 Viscometer

Three parallels were measured from each sample of crude oil A at the temperatures 20, 30 and 40°C. As the parallels of crude oil A have little or no deviation there was measured two parallels of each blends of crude oil B and C. The temperature program of crude oil A and C was 20, 30, 40, 30, 20°C while the fill temperature was 30°C. For crude oil B the auto sampler was pre heated to 50°C and the temperature program for the measurements was 50, 40, 30, 20, 50°C.

6.3.3 Rheometer

The clean crude oils and selection of three samples (crude oil A, B and C with 2 wt % 1-hexanol) were measured with the rheometer to check the shear dependence, in addition to the dynamic viscosity. Crude oil samples of oil A and C were measured at 20°C while crude oil B was measured at 50°C.

6.3.4 Near Infrared Spectroscopy

The NIR analyses were done to detect any changes in the asphaltene aggregation size between the various blends and the clean crude oils. The samples were preheated to 30°C and each sample was measured three times. Because of the oil's viscosity, the analysis was preformed directly in the sample bottle. The probe that was used, had a gap of 0.5 mm.

6.3.5 Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy was used to measure the T_2 relaxation time of the samples made of crude oil A with 2 wt % solvent (except the samples made from the commercial products). Three parallels were measured from each sample at the temperature of 30°C.

The extra treated samples of crude oil A and glycol was analysed a second time. Three parallels were measured from each sample at the temperature of 30°C.

6.3.6 Asphaltene Dispersant Chemical

The asphaltene dispersant chemicals (1000 ppm) were blended with toluene and the blends were named Chem A, Chem D and Chem E. The Chem A consisted of toluene and Armohib Ai-1000, Chem D consisted of toluene and Duomeen T and Chem E consisted of toluene and Ethoduomeen T/13.

The chemicals had to be heated before blending as they were more or less in a waxy and at solid phase at room temperature. The crude oils were added 2 wt % of the blend asphaltene dispersant chemicals and toluene.

7 Results

Results from the analyses of crude oil A, crude oil B and crude oil C are presented in this chapter. All results of the crude oils are presented of the samples with 2 wt % solvent. The average values from the measured parallels are used to present the results.

The samples are presented with a unique colour throughout the report. The blue colours are presenting the reference chemicals, the red and yellow colour presents the solvents with active group (red presents alcohols, yellow presents ketone) and green presents the commercial products.

All background information of the samples is found in Appendix D.

7.1 Viscometer

The viscometer was used to detect the changes in the dynamic viscosity between the various samples of the crude oils. Crude oil A and crude oil C are presented at 20°C while crude oil B is presented at 50°C. Figure 7-1 presents the viscosity reduction in percent of the samples with 2 wt % solvent.

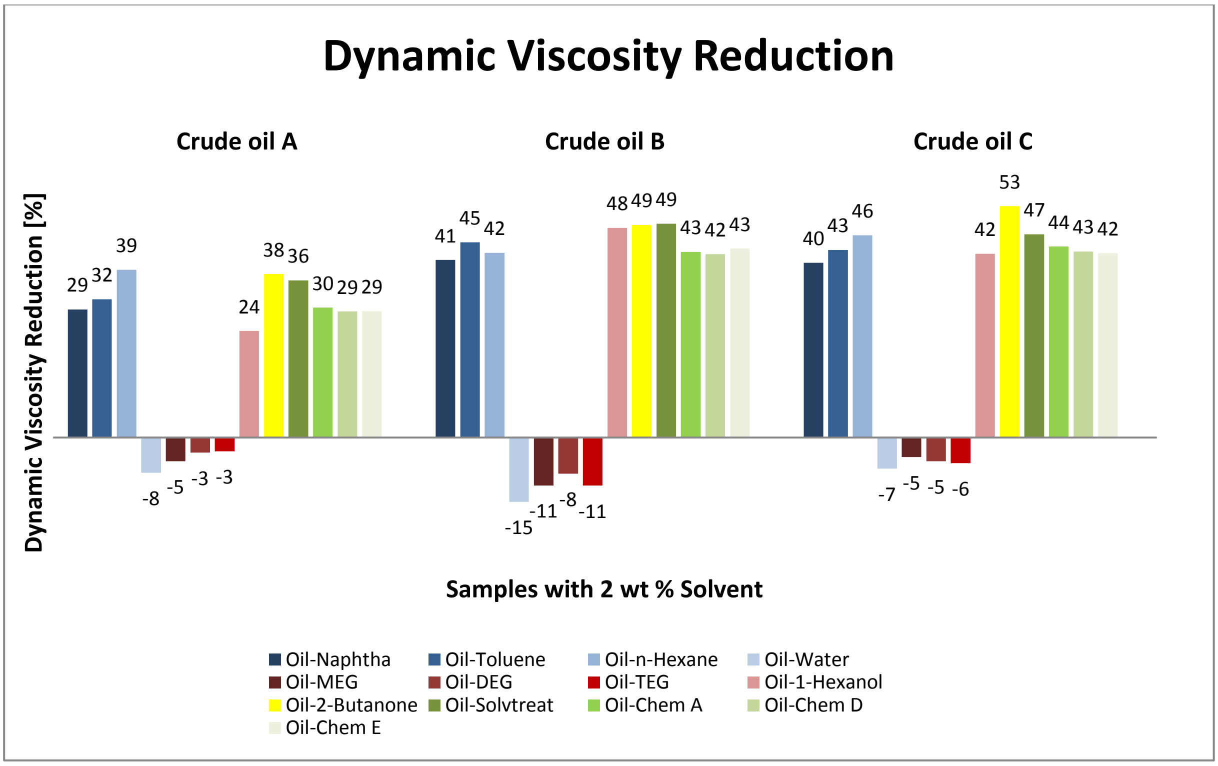

Figure 7-1: Percent reduction of the dynamic viscosity by adding 2 wt % of solvents in crude oils.

The alcohols MEG, DEG and TEG had a negative effect and increased the viscosity of the crude oils. The viscosity reduction is found between -3 to -11 %. The same effect is found for water which represents a lower value than the glycols with viscosity reduction between -7 to -15 %.

For crude oil A the remaining solvents give a viscosity reduction in the range of 24-39 % where the “A-1-hexanol” sample presents the lowest value and “ A-N-hexane” presents the highest value.

For crude oil B the remaining solvents give a viscosity reduction in the range of 41-49 % where the “B-Naphtha” sample presents the lowest value and “B-Solvtreat” and “B-2-butanone” presents the highest value.

The remaining solvents of crude oil C give a viscosity reduction in the range of 40-53 % where the “C-Naphtha” sample presents the lowest value and “C-2-butanone” presents the highest value.

The measured dynamic viscosity and density is found in Appendix E.

Dynamic viscosity contribution per added molecule is presented in Figure 7-2. The samples added commercial products are not presented in this Figure.

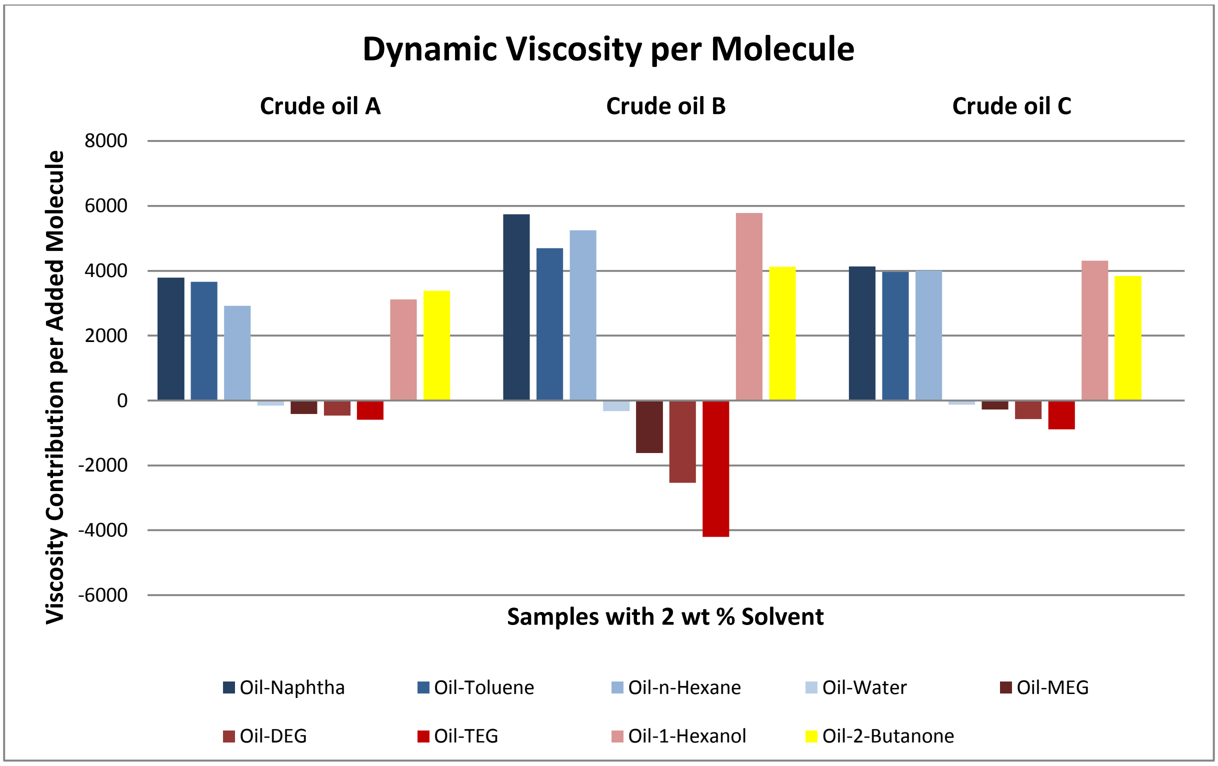

Figure 7-2: Dynamic viscosity contribution per added molecule of crude oil samples with 2 wt % solvent.

The water and glycols have a negative contribution to the dynamic viscosity per added molecule. The highest contribution per molecule for crude oil A is naphtha while crude oil B and C has the highest contribution per molecule from 1-hexanol.

7.2 Rheometer

The crude oils are not shear dependent of the viscosity. The result from the rheometer is presented in Appendix F.

7.3 Near Infrared Spectroscopy

The result of the NIR spectroscopy presents first the whole spectrums of the crude oils with 2 wt % solvents, then an excerpt of the optical density at 1600 nm.

The NIR spectrum of crude oil A with 2 wt % solvent is presented in Figure 7-3.

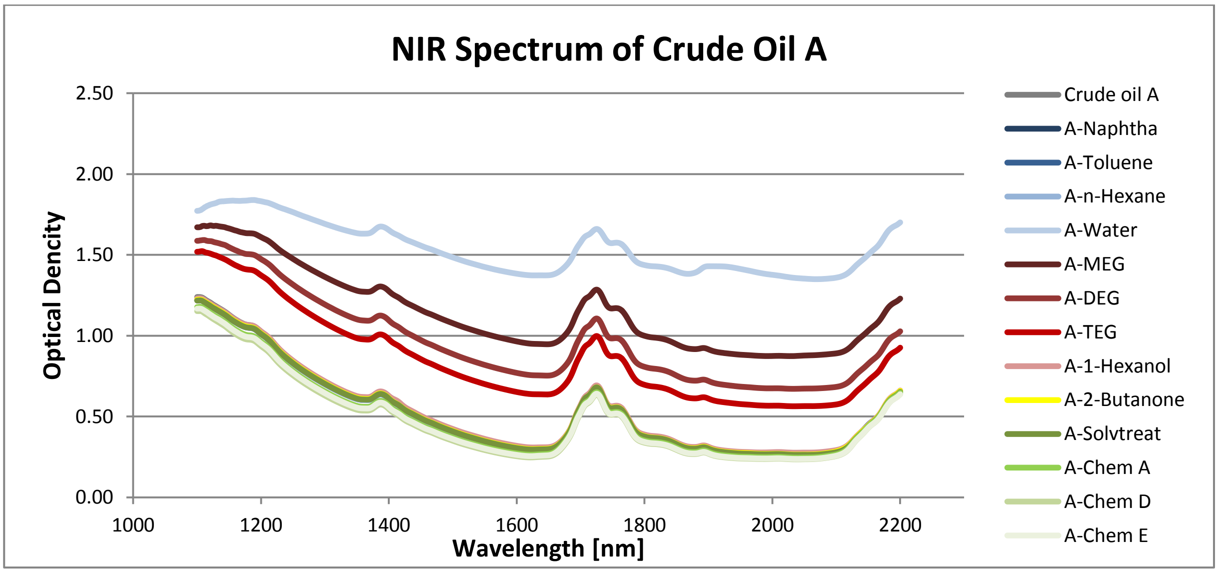

Figure 7-3: NIR spectrum of crude oil A with 2 wt % solvent given by optical density in range 0.00-2.50 and wavelength 1100-2200 nm.

The samples “A-Water”, “A-MEG”, “A-DEG” “A-TEG” have a distinctly higher optical density than the clean crude oil and the other blends. The remaining samples have little or no difference in the optical density compared to the crude oil. The excerpt of the NIR spectrum at 1600 nm gives a better overview of the samples and is presented in Figure 7-6.

The NIR spectrum of crude oil B with 2 wt % solvent is presented in Figure 7-4.

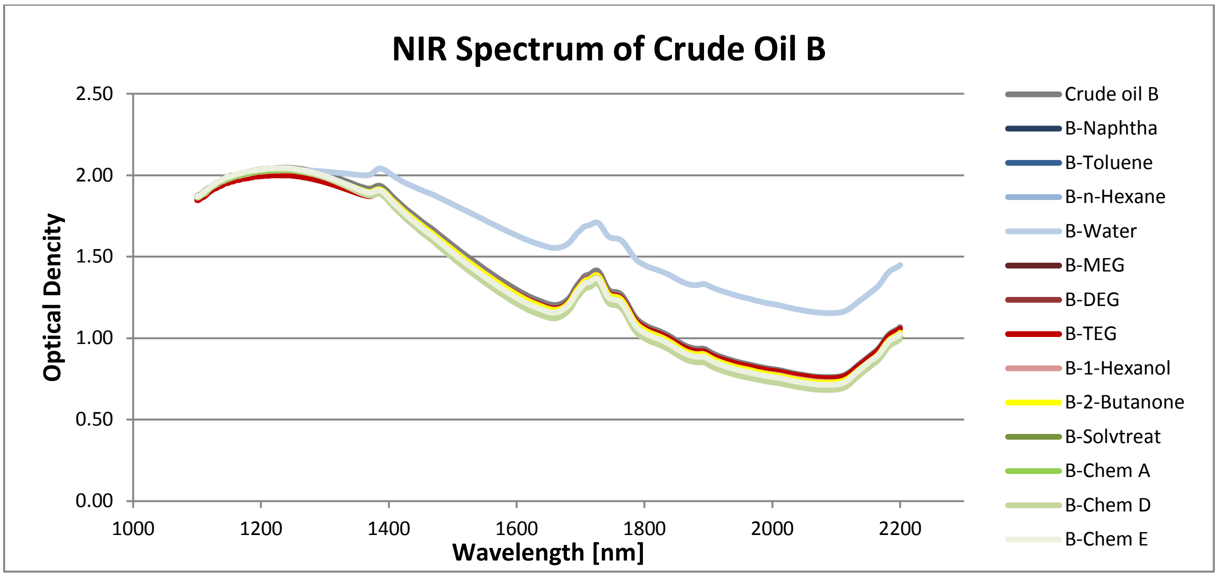

Figure 7-4: NIR spectrum of crude oil B with 2 wt % solvent given by optical density in range 0.00-2.50 and wavelength 1100-2200 nm.

The sample “B-Water” has a distinctly higher optical density than the clean crude oil and the other blends. The remaining samples have little or no difference in the optical density compared to the crude oil. The excerpt of the NIR spectrum at 1600 nm gives a better overview of the samples and is presented in Figure 7-6.

The NIR spectrum of crude oil C with 2 wt % solvent is presented in Figure 7-5.

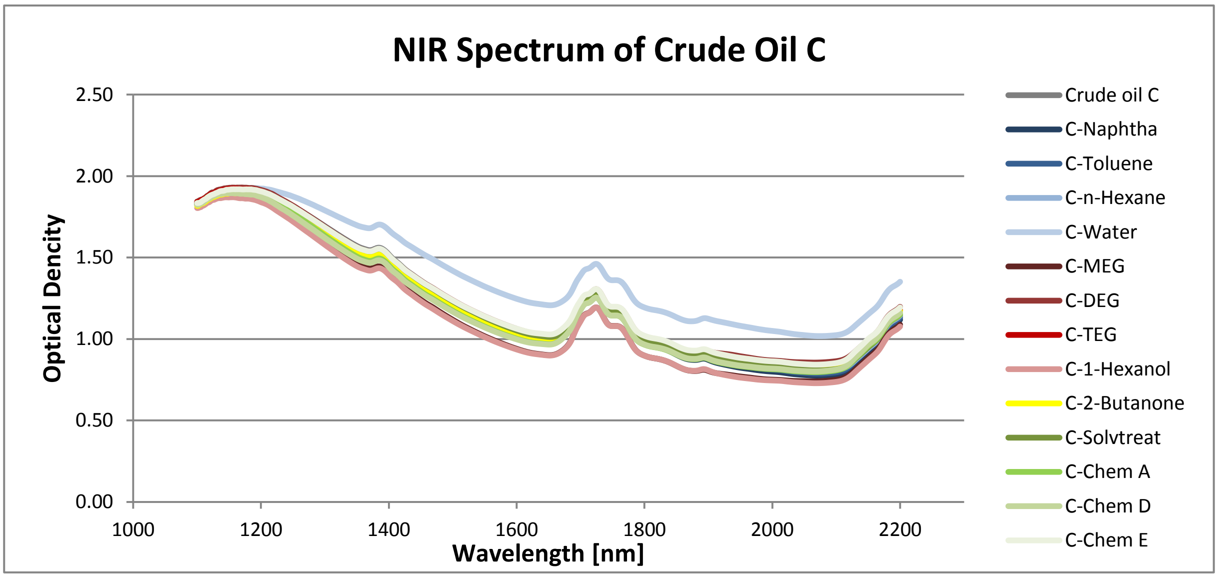

Figure 7-5: NIR spectrum of crude oil C with 2 wt % solvent given by optical density in range 0.00-2.50 and wavelength 1100-2200 nm.

The sample “C-Water” has a higher optical density than the rest of the samples. The remaining samples have little or no difference in the optical density compared to the crude oil. The excerpt of the NIR spectrum at 1600 nm gives a better overview of the samples and is presented in Figure 7-6.

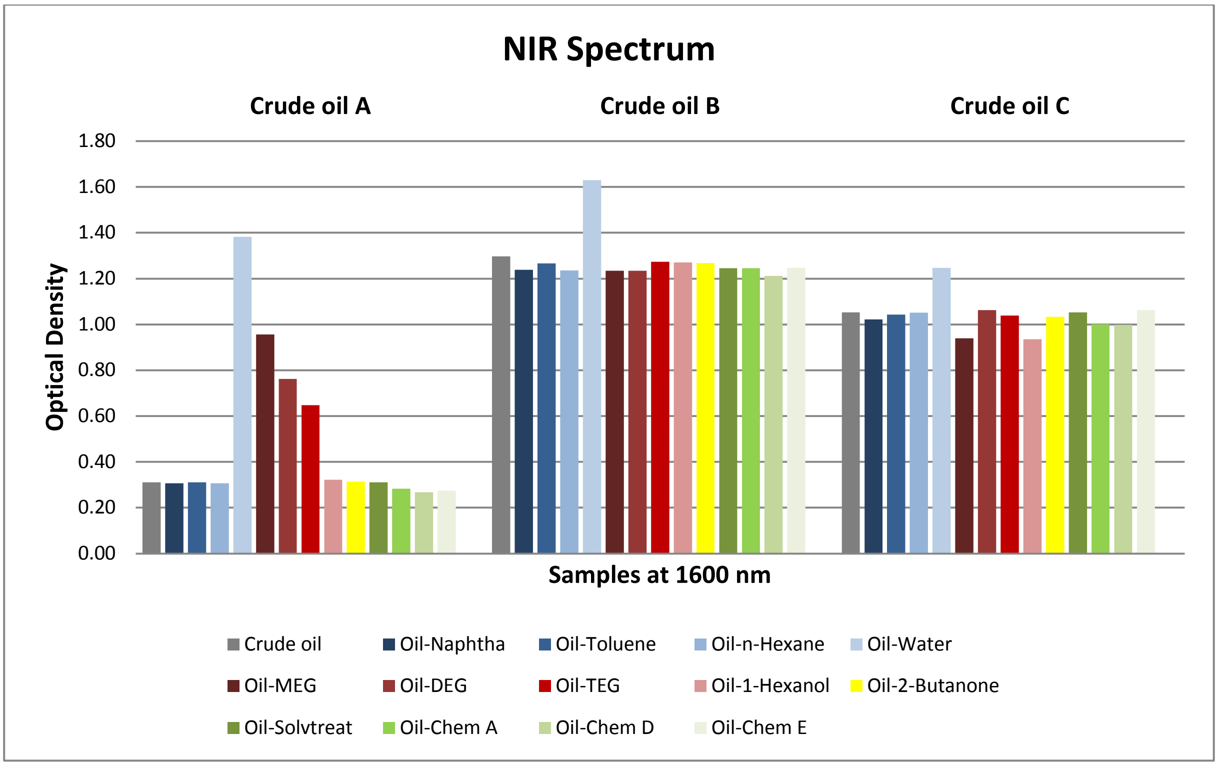

Figure 7-6: An excerpt of the optical density at 1600 nm presents the clean crude oils and crude oil samples with 2 wt % solvent.

The excerpt shows that it is overall relatively small changes in the optical density except from the few samples mentioned above. From crude oil A the samples “A-Chem A”, “A-Chem D” and “A-Chem E” have a lower optical density compared to the rest of the samples and the pure crude oil. From crude oil B the sample “B-Chem D” has the lowest optical density compared to crude oil B and the blended samples. The last crude oil, crude oil C, the samples “C-MEG” and “C-1-Hexanol” has the lowest optical density while the samples “C-Chem A” and “C-Chem D” have a relatively low optical density compared to the clean crude oil.

A full overview of the average values and deviation from the NIR spectroscopy measurement are presented in Appendix G.

7.4 Nuclear Magnetic Resonance Spectroscopy

A selection of the crude oil A samples have been analysed with NMR spectroscopy to control the homogeneity of the blended samples of different solvents. The samples added glycols and water have a tendency of inhomogeneity. The result is presented in Appendix H.

8 Discussion

All samples are made by adding a given weight percent (wt %) solvent into a crude oil in addition the clean crude oils are analysed. The results are presented with an average value from two or three measured parallels. The first samples are analysed with three parallels. As the deviation was insignificant between the parallels some further samples were analysed with two parallels.

The analysis methods used in the experimental work were considered based on properties of the chemicals, expected and wanted results, and the total amount of samples. Different methods to blend samples were considered. A mechanical blender was discussed but decided not to use as the volatile components could get lost. A more reliable method to be sure none of the light components in the crude oils, or from the solvents, got lost, was a closed bottle shaken and heated for a given time. The NMR spectroscopy was used to analyse the homogeneity of the samples in the pretest as well as the homogeneity of one sample series where most of the chemicals were used, crude oil A with 2 wt % solvent (except the commercial products). The viscometer with an auto sampler was used to analyse the dynamic viscosity and density of all samples. The rheometer was considered instead of the viscometer. Based on the time and amount of samples the viscometer was used while an excerpt of samples was analysed on the rheometer. All samples were tested with NIR spectroscopy to detect any change in the asphaltene particle size.

Before any samples were made the Karl Fischer titration was performed on all three crude oils. All crude oils contained some water but not more water than is normal in oil production. Crude oil A had the smallest amount with 0.027 wt % of water, crude oil B had 0.15 wt % and crude oil C 0.51 wt %. Any amount of water in a crude oil could affect the result of adding a solvent in small amounts. An overview of the analysis is given in Appendix B, B.2 Karl Fischer Titration.

8.1 Solvents Used in the Experimental Work

Chemicals that were used as solvents were decided from Hildebrand and Hansen solubility parameter or reported in the literature with interesting results. In addition four different solvents were used as a reference. These chemicals have a known behaviour in crude oils and asphaltenes.

The solvents naphtha, toluene and n-hexane were used as a reference for the dilution effect of added chemicals. In addition, toluene and n-alkane were used to compare the different behaviour of asphaltene aggregation as these are chemicals known to affect the asphaltenes in crude oils. The n-alkane used was n-hexane and could also be a reference to the effect of the molecule size compared to 1-hexanol. By compering 1-hexanol to n-hexane the effect of the alcohol group could be detected.

The last reference solvent is water. A water-in-oil emulsion presents the effect of an emulsion which gives a known negative effect on the viscosity. Water was tested in the end of the experimental work after a suspicion that some of the solvents could have created an emulsion in the crude oil.

Further were some commercial products tested. The Solvtreat EFI-201 was tested from the beginning with the other solvents. The asphaltene dispersion products Armohib Ai-1000, Duomeen T and Ethoduomeen T/13 were tested in the end of the experimental work.

8.2 Pretest

The pretest was done to make sure the samples were made homogeneous before analysed. Depending on the properties of the different crude oils, and the treatment of the crude oil in the process equipment, the temperature was decided and various shaking times were tested. The pretest studied different shaking times of two crude oils, crude oil A and B with 1-hexanol.

The tested crude oil samples were added 2 wt % of 1-hexanol, in addition were the clean crude oils analysed for comparison. The blended samples are added an amount of 1-hexanol in the range 1.998-2.023 wt %. All samples were weighted before and after heating /shaking and the weight loss is found between 0.000 to 0.007 wt %. The differences between the samples are negligible and are found in Appendix C, C.1 Properties of Pretest Samples.

The viscometer and NMR spectroscopy were used as analysis methods to study any change in the samples given different shaking times. The results from the viscometer and NMR spectroscopy of the pretest samples are found in Appendix C, C.2 Analyses. None of the samples showed any remarkable deviations.

The results from the viscometer of “Pretest A” show no changes in the dynamic viscosity with increasing shaking and heating time. Further the series of “Pretest A” samples showed no inhomogeneous tendency from the NMR spectroscopy where all the samples had similar and uniform curves. A storage time of 24 hours has no impact on the samples homogeneity.

The results from the “Pretest B” have a change in the dynamic viscosity between 2 hours to 4 hours where the dynamic viscosity increases. This was seen at the lowest temperatures, 20°C and 30°C. This small increased viscosity could be caused by a minor change in the homogeneity of the blend where the sample “B-4H” has been better blended than the sample “B-2H”. The results from the NMR spectroscopy showed no inhomogeneous tendency of “Pretest B” samples.

Some of the solvents used in the experimental work are a bit more viscous than 1-hexanol, but it is assumed that all the solvents will need more or less the same time to blend in as the crude oil is the most viscous component. Thereby the shake and heating time was decided to 2 hours at 40°C for the crude oil blends of oil A. The shake and heating time was decided to 4 hours at 50°C for the crude oil blends of oil B. Crude oil C was not pretested but the shake and heating time were decided from the results of “Pretest A” and “Pretest B” as well as from the crude oils properties and earlier experience from handling crude oil C. (57) The blends of crude oil C was decided to be shaken for 4 hours at 40°C.

8.3 Main Experiment

Crude oil A was the first crude oil that was studied. Samples with 2 wt % solvent were made and thereby a selection of the most interesting solvents was made with 0.5, 1 and 3 wt %. Just adding small amounts of solvents, preferably less than 2 wt %, to reduce the viscosity is interesting for the production. (3) Anyway, adding 3 wt % solvent was important to detect the trend in viscosity change versus different amounts of solvent. Further crude oil B was tested in the same way (0.5, 1 and 2 wt %). At last crude oil C was tested but only in the 2 wt % series. This was done as the various amounts of added solvents did not give any more information than the 2 wt % series. All results presented in Chapter 7 are based on the crude oils with 2 wt % solvent.

The commercial products from AkzoNobel are diluted in toluene. The chemical amount of 1000 ppm was recommended from the producer and thereby used in the experimental work. To study the effect from these products they are not only compared to the clean crude oil but also to the sample where crude oil is added toluene.

To make sure that the samples were as stable as possible all the samples were stored in a refrigerator (+ 5°C) between the different analyses. This made sure that the volatile chemicals did not evaporate and by that change the samples.

8.4 Uncertainty in the Measurements

All blended samples have been added a specified amount of solvent. The samples with 0.5 wt % solvent have been added solvents in the amount range of 0.499-0.507 wt %. The samples with 1 wt % solvent are found in the range 0.998-1.003 wt % while the 2 wt % samples are found between

1.998-2.076 wt %. The samples with 3 wt % are found in the area 2.998-3.014 wt %. The differences between the samples are negligible and have no detectable impact on the results.

All samples have been weighted before and after heating/shaking to make sure that none of the volatile components have got lost. The weight loss is found between 0.000 to 0.010 wt % which corresponds to maximum 0.5 % of the added material (if one assumes that in worst case all of the weight loss is due to the added material flashing off). This gives little or no impact on the results.

An overview of the added amount solvent and weight loss are given in Appendix D.

8.4.1 Viscometer

All samples have been analysed on the viscometer. The measured values are found in Appendix E as an average value with deviation based on three or two parallels to ensure a reliable result.

In the results in Chapter 7.1 Viscometer and Appendix E, E.1 Dynamic Viscosity and E.2 Density the crude oil A and C are presented at 20°C while crude oil B is presented at 50°C. By presenting crude oil B at a higher temperature the dynamic viscosity is closer to crude oil A and C and will thereby give a better comparative basis.

Analyses on the viscometer were performed with an auto sampler. Crude oil samples in sample glasses with tight rubber tops were placed into the auto sampler. The auto sampler preheated crude oil A and C to 30°C and crude oil B to 50°C to make sure the viscometer was able to inject the viscous oils. As some of the added chemicals were volatile the samples were never placed in the auto sampler for more than 6 hours before the analyses started to make sure the samples did not change.

Dynamic Viscosity

All samples made of crude oil B measured at 20°C are outside the detection limit of the instrument. In addition are samples of crude oil B with 0.5 wt % solvents measured at 30°C outside the detection limit (Appendix E, E.3 Row Data Viscometer).

The highest deviation between parallels measurement on one sample is found for samples made of crude oil B. Considered the samples used to present the result, the highest deviation is found in sample “B-DEG” with viscosity and deviation of 3770.5 ± 67.9 mPa·s. The viscosity and deviation for the pure crude is 3480.0 ± 43.3 mPa·s. The differences in dynamic viscosity between the different samples are remarkable larger than the deviation between the parallels of the sample.

The deviation between the parallels of samples used to present the result made from crude oil A and C is minor and negligible. The highest deviation of samples made of crude oil A is sample “A-Water”, 373.41 ± 1.47 mPa·s while the pure crude oil A has a viscosity of 345.27 ± 0.10 mPa·s. The pure crude oil C has a viscosity and deviation of 4152.4 ± 21.7 mPa·s, while the sample with highest deviation is presented from the “C-Chem E” sample with 2393.1 ± 20.3 mPa·s.

The viscosity reduction is lower for crude oil A, 24-39 %, compared to crude oil B and C, where the viscosity reduction was up to 53 % (Figure 7-1). A crude oil with low dynamic viscosity will get a minor reduction of adding a viscosity reduction chemical than a crude oil with high viscosity. The percentage reduction will be higher as higher viscosity of the oil because of the viscosity differences between the clean crude oil and the added chemical.

The dynamic viscosity is presented as percent reduction when 2 wt % solvent were added, Chapter 7.1 Viscometer. A more correct way could be to present it as viscosity contribution per added molecule. The challenge is that none of the commercial products has any information of the molecule weight and could thereby not be compared on this basis. However, the viscosity contribution per added molecule of the reference solvents and the active molecule solvents has been presented in Figure 7-2. This did not give any other conclusive information then the plot based on wt %.

Density

All density results have small and insignificant deviations (Appendix E, E.3 Row Data Viscometer). Considered the samples used to present the result, the highest deviation is found in sample “B-Chem E” with 0.9546 ± 0.0007 g/cm^3 while the clean crude oil B has 0.9565 ± 0.0005 g/cm^3.

8.4.2 Rheometer

Measurements can be unstable at low shear. At a high shear the friction heat can affect the result and make the sample look shear dependence. This will easier impact the result of an viscous oil then a lighter oil. The stabile values of the measured samples are presented in Appendix F which show that none of the tested samples are shear dependence. The rheometer gives a bit different viscosity values then the viscometer as the instrument measures the samples with another technic. The differences in the viscosity are found in the range -5.6 to 11.26 %.

8.4.3 Near Infrared Spectroscopy

All samples were analysed with NIR spectroscopy. All results are presented from an average value from three measurements where every parallel has been evaluated before use. The average value with deviation is presented in Appendix G.

The highest deviation is found in the sample of clean crude oil B with optical density and deviation of 1.298 ± 0.014. The samples with closest optical density are “B-TEG” with 1.274 ± 0.002 and “B-1-Hexanol” with 1.271 ± 0.008. The small change in optical density makes it difficult to distinguish these samples even though the deviation is relatively small. Other samples have minor deviations or/and clearer change in the optical density and are discussed later in this chapter.

8.4.4 Nuclear Magnetic Resonance Spectroscopy

The NMR spectroscopy were performed on an excerpt of the crude oil A samples with 2 wt % solvent, (except the samples made from the commercial products) to study the homogeneity of the different added solvents, Appendix H. There were measured three parallels of each sample where all the parallels were considered before an average value was used as a result. None of the parallels showed any noticeable deviations with the highest deviation presented of sample “A-n-Hexane”, 18.1 ± 0.3 ms, while the clean crude oil A has 14.3 ± 0.2 ms.

8.5 Important Observations

8.5.1 Increase in Viscosity by Adding Glycols and Water

The water increases the dynamic viscosity as expected, where the viscosity reduction is -7 to -15 % (Figure 7-1). Water in crude oil will create a water-in-oil emulsion which is known to increase the viscosity. A similar result has the crude oil samples added glycols with a viscosity reduction of -3 to -11 %.

The same trend is found when dynamic viscosity is presented as the viscosity contribution per molecule (Figure 7-2), but here the water has a smaller contribution while TEG has the highest negative contribution followed by DEG and then MEG. The glycols have two hydroxyl groups per molecule. By presenting the viscosity contribution per hydroxyl group added into the crude oil the contribution will be halved. The DEG and TEG would still have a higher negative contribution to the viscosity compared to MEG. These solvents, DEG and TEG, have a bigger molecule structure then MEG with one and two oxygen atoms. The size of the molecule and the oxygen atoms could contribute somehow to the increased viscosity.

If the glycols have the ability to solve in crude oil the viscosity of the samples should have decreased compared to the clean crude oil as the glycols has a lower viscosity than the crude oil itself (Appendix B).

The extra treated samples, “A-MEG*”, “A-DEG*” and “A-TEG*”, had still an increased viscosity after 66 hours of shaking (Appendix E, E.3.1 Row Data Viscometer). The viscosity increased even a bit more but the change is small, the crude oil A sample with 2 wt % of MEG increased from 364.09 ± 0.12 to 382.73 ± 0.10 mPa·s at 20°C (about 5 %).

An increased optical density of the samples added water is probably caused by a water-in-oil emulsion (Figure 7-6). Water droplets scatter the light and increase the optical density at 1600 nm. The crude oil A samples with glycols also increases the optical density. The clean crude oil A has an optical density of 0.3057 ± 0.0001 while adding glycols increases the optical density between 0.6521 ± 0.0003 to 0.9648 ± 0.0007 (Appendix G). The glycols in crude oil A could have created some type of emulsion or affected the asphaltenes to aggregate which would be an unfortunate situation and unwanted. Any aggregation of asphaltenes would increase the optical density.

The glycols have not the same effect in crude oil B and C. In crude oil B the samples added MEG and DEG have a relatively low optical density, 1.234 ± 0.002 and 1.234 ± 0.004, while the clean crude oil B has 1.298 ± 0.014. In crude oil C the sample added MEG has a lower optical density 0.9396 ± 0.0046 compared to the clean crude oil C 1.053 ± 0.007 while the DEG has a higher optical density then the clean crude oil 1.062 ± 0.006. These results show no pattern comparing between the different crude oils, or the dynamic viscosity results, and makes the result difficult to explain.

The NMR spectroscopy showed that the added solvents with negative effect on the dynamic viscosity seemed to consist of a second phase with longer T_2 relaxation time. This was seen at the samples “A-Water”, “A-MEG”, “A-DEG” and “A-TEG” (Appendix H).

The sample “A-Water” was expected to have a second phase that could be caused by a water-in-oil emulsion. The second phase is shown as a peak between the blended sample and the pure water which indicates a phase combined of the two elements, water and oil that are not totally mixed. This second phase consist of 1.1 vol % of the total sample. Some droplets in the emulsion could be too small to be detected at the NMR spectroscopy (<0.5 µm in diameter) given the added amount of water was 2 wt % (≈1.9 vol %).

The samples blended with glycols have their second phase at the same relaxation time as the pure glycols indicating that the samples are not totally blended. “A-MEG” is found with 1.1 vol %

(2 wt % ≈1.7 vol %) while “A-DEG” and “A-TEG” are found with 0.3 and 0.2 vol % (2 wt % ≈1.7 vol %). It seems like the glycols is not totally solved in crude oil A, but these last chemicals, DEG and TEG, seem to have a tendency to be easier solved then MEG. This could also be the case in crude oil B and C.

The same samples were treated for 66 hours before a second analysis. The “A-MEG*” sample did still have a second phase consisting of 0.7 vol %. The “A-DEG*” and “A-TEG*” sample had lost their second phase signal which indicate that the solvent have been blended in the crude oil. DEG and TEG seems to be totally solved after sufficient treatment with shaking at the given temperature, while MEG is more difficult to solve.

There is some uncertainty about the exact size of the second phase signal and the deviation of this (Even there were measured three parallels of each sample). Still it is clear that the “A-MEG” sample has a bigger peak than the “A-DEG” and “A-TEG” sample, and that the treated sample “A-MEG*” still has a peak while the “A-DEG*” and “A-TEG*” sample loses their second phase signal more or less.

Even though it seems like the samples are better blended after 66 hours the dynamic viscosity has still increased compared to the clean crude oil. This is the opposite effect than expected form the literature. It seems like two hydroxyl groups has a different effect in the crude oil, or on the asphaltenes, than one hydroxyl group. Overall the results from the measured viscosity show negative effect of adding a glycol in a crude oil.

Looking closer at the Hildebrand solubility parameters the DEG and TEG are more likely to get solved in a heavy crude oil and connect with asphaltenes than MEG. The MEG could be partly dissolved and partly dispersed, and create an emulsion. This could explain the NMR spectroscopy result. However, this seem not to be the explaining of the increased viscosity as the extra treated samples of DEG and TEG still give an increased viscosity.

The increased viscosity is the opposite of what is expected from the solubility parameters where the TEG has the closest Hildebrand solubility parameter to crude oil and asphaltenes with 21.9 MPa$^{0.5}$ while MEG has a solubility parameter of 29.9 MPa$^{0.5}$. Locking at the viscosity reduction, Figure 7-1, MEG and TEG are increasing the viscosity relatively in the same range. From the molecular contribution, Figure 7-2, TEG is contributing to the highest increased viscosity per added molecule in all three crude oils.

The solvents 1-hexanol and TEG has the same Hildebrand solubility parameter, 21.9 MPa$^{0.5}$, and the solvents should have had the same ability to solve into the crude oil and affect the asphaltenes from this parameter. Looking at Hansen solubility parameter 1-hexanol has lower polar and hydrogen forces (5.8 and 12.5) than TEG (12.5 and 18.6). Comparing to the polar and hydrogen forces for a heavy oil (3.0 and 3.4) the 1-hexanol are closer than TEG which could explain way TEG is more difficult to solve into the crude oil.

The glycols could make some unknown bindings, crosslinking, with the asphaltenes or other polar components in the crude oil caused by glycols having two hydroxyl groups. If the glycols solve fully or partly into the crude oil these solvents should be able to connect to the polar components in the crude oil. According to the Hansen solubility parameter all glycols have polar and hydrogen forces in the same range, and these are higher compared to other tested solvents. High polar and hydrogen forces could cause stronger and closer interaction between glycols and polar components in the crude oil as asphaltenes. Glycols could instead of stabilizing asphaltenes in small aggregates and reducing the viscosity, create a denser network of asphaltenes and glycol which increases the viscosity.

8.5.2 Solvents Reducing the Viscosity

The solvents that reduce the dynamic viscosity of the crude oils have more or less the same trend in the different crude oils, Figure 7-1. The solvents have a distinct effect by decreasing the dynamic viscosity with 24-53 %, but overall there is not one specified solvent that has a clear better effect than the other tested chemicals.

In the NIR spectroscopy there are three chemicals in crude oil A that stand out with a bit lower optical density. This is samples with asphaltene dispersant chemicals from AkzoNobel (Chem A, Chem D and Chem E) with an optical density of 0.2547 ± 0.0005 - 0.2717 ± 0.0015 (Appendix G). The optical density of the clean crude oil is 0.3057 ± 0.0001 while the optical density of the sample “A-Toluene” is 0.3027 ± 0.0003. The detected change in optical density could be caused by the solvent affecting the asphaltene particle size.

The sample with the commercial product “Chem D” is presenting the lowest optical density in crude oil B. The crude oil B has an optical density of 1.298 ± 0.014, sample “B-Toluene” lower the optical density to 1.267 ± 0.001 while the sample «B-Chem D» give 1.212 ± 0.001. In crude oil C the product is giving a relatively low optical density. The sample ”C-Chem-D” has an optical density of 0.9980 ± 0.0047 while the clean crude oil C and the sample “C-Toluene” has higher optical density at 1.053 ± 0.007 and 1.043 ± 0.002, respectively.

In crude oil C the sample with 1-hexanol has the lowest optical density of 0.9357 ± 0.0056. 1-hexanol has not the same positive effect on the optical density in crude oil A and B. In crude oil A the optical density increase negligible compared to the clean crude oil and in crude oil B the effect is also negligible compared to the other samples and the clean crude oil itself.

The commercial solvents made for asphaltene dispersant seem to have some effect on the asphaltene particle size. Especially in crude oil A which has a low amount of asphaltenes. The solvent "Chem-D" seems generally to have the best effect of these commercial products even though this is a very small effect compared to the rest of the solvents.

From the NMR spectroscopy result the sample "A-2-Butanone" has the highest average T_2 relaxation time with a value of 18.3 ± 0.1 ms (Appendix H). However, the T_2 relaxation time of all the blended samples reducing the viscosity are relatively alike, 16.7 ± 0.0 ms to 18.3 ± 0.1 ms, and gives no further information.

The 2-butanone has the lowest Hildebrand solubility value of all the tested solvents with active groups, 19.3 $MPa^{0.5}$. The polar force is higher than the hydrogen force (9.0 and 5.1) compared to 1-hexanol (5.8 and 12.5). However, this seem not to have any big influence on the asphaltenes considering the NIR spectroscopy results of samples added 2-butanone, and comparing results between 1-hexanol and 2-butanone.

8.5.3 Effect of Solvent Concentration

The change in dynamic viscosity reduction versus the added amount of solvent is studied in crude oil A and B and presented in Appendix E, E.1 Dynamic Viscosity. Blends of crude oil A added 0.5, 1, 2 and 3 wt % solvent show a linear correlation trend except from a change in between the 0.5 wt % and 1 wt % solvent. The change seems to be relatively alike for all solvents where the first added amount contributes to the biggest change in the dynamic viscosity. Blends of crude oil B added 0.5, 1 and 2 wt % has a linear correlation between the viscosity reduction and added amount of solvent.

The correlation between the density and added amount of solvent for crude oil A and B are linear and presented in Appendix E, E.2 Density. Crude oil C samples with 2 wt % solvent are also presented to illustrate the density differences between the various samples.

8.6 Standards Used in the Experimental Work

Two standard oils, APN 26 and APN 415, with known dynamic viscosity, kinetic viscosity and density were used at the viscometer. This was to make sure that any measurements from the viscometer were trustful.

At the NIR spectroscopy a standard sample was analysed every time the instrument was used. By using a standard any differences in the instrument could be detected and used as a deviation when comparing the samples. Details from the analysed standards are found in Appendix I.

8.7 Sources of Error

The crude oils could lose some of their lighter hydrocarbons during the experimental work. The same will be for volatile solvents. All samples consisting volatile chemicals would have source of error as the samples has been opened to make withdrawals to analyses. However, in the experimental work all samples have been treated as similarly as possible to avoid most of the differences in between the samples.

Maybe a better way of making the samples is by adding an volume amount (%) chemical instead of weight as the densities of the chemicals are different. Thereby the result can be presented based on the added vol % solvent instead of added wt %. The volume amount of added solvent is between 0.549-0.743 vol % for the 0.5 wt % samples. The samples with 1 wt % solvent are found in the range 1.086-1.482 vol % while the 2 wt % samples are found between 1.675-2.950 wt %. Blended samples with 3 wt % solvent are found in the range 3.257-4.245 vol %. The differences are significant and none of the results are based on the volume percent. An overview of the calculated added amount of solvent in volume percent is given in Appendix D.

Even more correct than using vol % could be to add the same amount of molecules or active groups (hydroxyl or carbonyl) for the different solvents, alcohols and ketones. The results are presented above in Figure 7-2 as the effect per molecule. This is maybe the most correct way of presenting it, but the number of added molecules is not the same for all mixtures, and thereby calculated. This is a potential improvement for future work.

The partition factor for chemicals in water-oil has not been looked into. Some of the added solvent could have a better solubility in water then oil. Also, there is a possibility that an added solvent could be part dissolved in the crude oil and part dissolved in the remaining water. For dealing with this potential problem, crude oils with as little water as possible were used in the experimental work.

9 Conclusion

The aim of this thesis was to investigate how chemicals with active groups as alcohols and ketones could reduce the viscosity by dispersing asphaltenes.

Adding a glycol in small amounts increases the dynamic viscosity rather than decreasing. The glycols show some difficulty to solve into the crude oil. The NMR spectroscopy shows that MEG is the least soluble glycol and needs more than 66 hours of shaking at 40˚C. Samples with crude oil A and DEG or TEG are more homogeneous after longer treatment but the dynamic viscosity is still increased.

The solvents reducing the dynamic viscosity have a relatively equal effect. It was expected that the alcohols and ketone should reduce the viscosity better than the reference solvents. 1-hexanol and 2-butanone seem rather to have a dilution effect than a chemical bonding effect to the asphaltenes and polar components in the crude oil as the naphtha, toluene and n-hexane show more or less the same effect. The hydroxyl and carbonyl group creates little or no detectable interactions with the asphaltenes in the crude oil in small amounts ≤ 3 wt %. However, all of the tested solvents, except glycols and water, did contribute to a viscosity reduction by a dilution effect with adding 0.5-3 wt % solvent into a heavy crude oil.

The commercial products did not reduce the viscosity more than the other tested solvents. The asphaltene dispersant products present a viscosity reduction in the same range as samples added toluene. The viscosity reduction product, Solvtreat, has not been reducing the viscosity any more than the other tested solvents.

From the NIR spectroscopy there is no solvent that is clearly better than any other. However, the commercial asphaltene dispersant product Duomeen T (Chem D) show same effect on the asphaltenes in the NIR spectrum at 1600 nm but this is not detected as a viscosity reduction on the crude oil.

Using a glycol, 1-hexanol or 2-butanone in small amounts (≤ 3 wt %) as flow improver are not preferred instead of additive a lighter petroleum product, as naphtha, to reduce the viscosity of the oil.

10 Further Work

The unexpected increase in the viscosity by adding glycols should be tested further. The cause of this change is not known and could be studied closer by adding different amount into the crude oil in an extended range as well as use of other analysis methods as rheometer.

Other analysis methods as infrared spectroscopy (IR) could be used to look for any changes in the asphaltene structures by adding the solvent. In the same way the IR could be used to see if the glycols are binding with the asphaltenes in any way.

Solvents of acids and base, as acetic acid and amine, could be added to study the effect on dynamic viscosity and change in asphaltene aggregation size. These are polar components and should have some ability to connect with the asphaltenes.

Any of the solvents used in this experiment could be mixed and tested as a reduction viscosity chemical. Naphtha or toluene could be blended with a solvent with an active group as alcohol or ketone. The tested chemicals could be studied further by adding bigger amounts into the crude oil. Even though using a bigger amount of chemicals is not interesting in the production, it would be interesting to see if the tested solvents with active groups give any better effect in amounts up to 20 wt %.

The 1-hexanol and 2-butanone molecules could be too small to stabilize the asphaltenes. Other bigger molecules could be tested in small amounts (≤ 3 wt %) as this could affect the stabilizing effect of asphaltenes in a better way than the chemicals tested in this project.

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12 Appendix

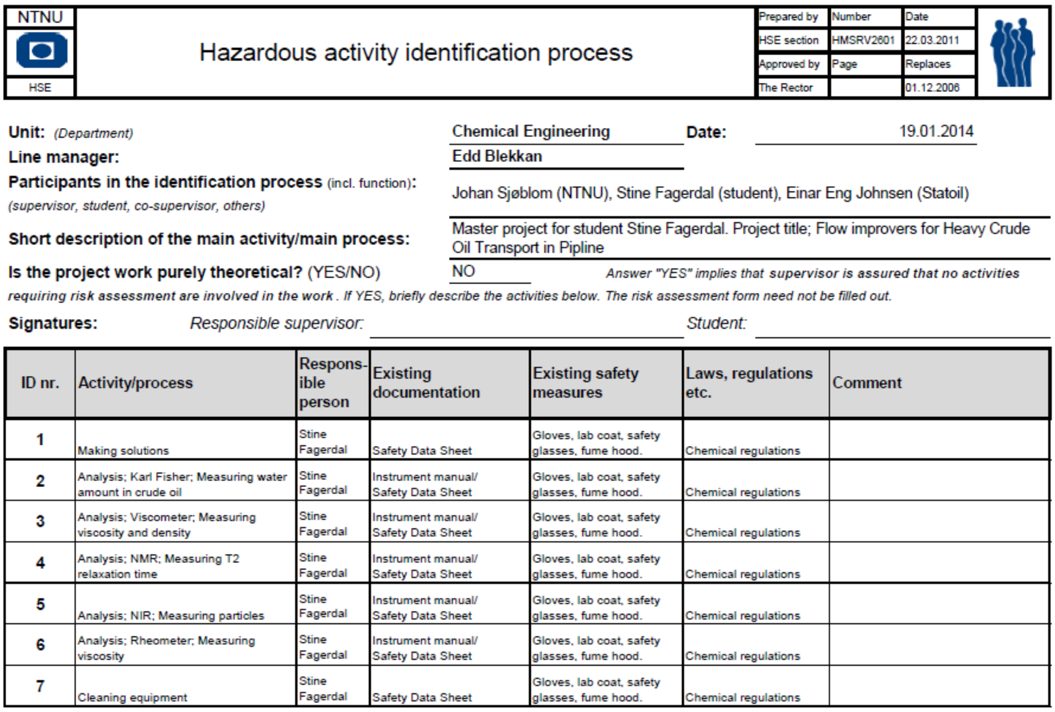
This chapter presents the results and raw data that were not necessary to present in the main report.

Results are presented in Tables and Figures with a text that describes their contents.

12.1 Appendix List

Appendix A Activity and Risk Assessment

Activity and risk assessment of the experimental work are given in Figure A-1 and Figure A-2.



NTNU	Hazardous activity identification process	Prepared by	Number	Date
HSE		HSE section	HMSRV2601	22.03.2011
		Approved by	Page	Replaces
		The Rector		01.12.2006

Unit: *(Department)* Chemical Engineering **Date:** 19.01.2014

Line manager: Edd Blekkan

Participants in the identification process (incl. function): Johan Sjøblom (NTNU), Stine Fagerdal (student), Einar Eng Johnsen (Statoil)
(supervisor, student, co-supervisor, others)

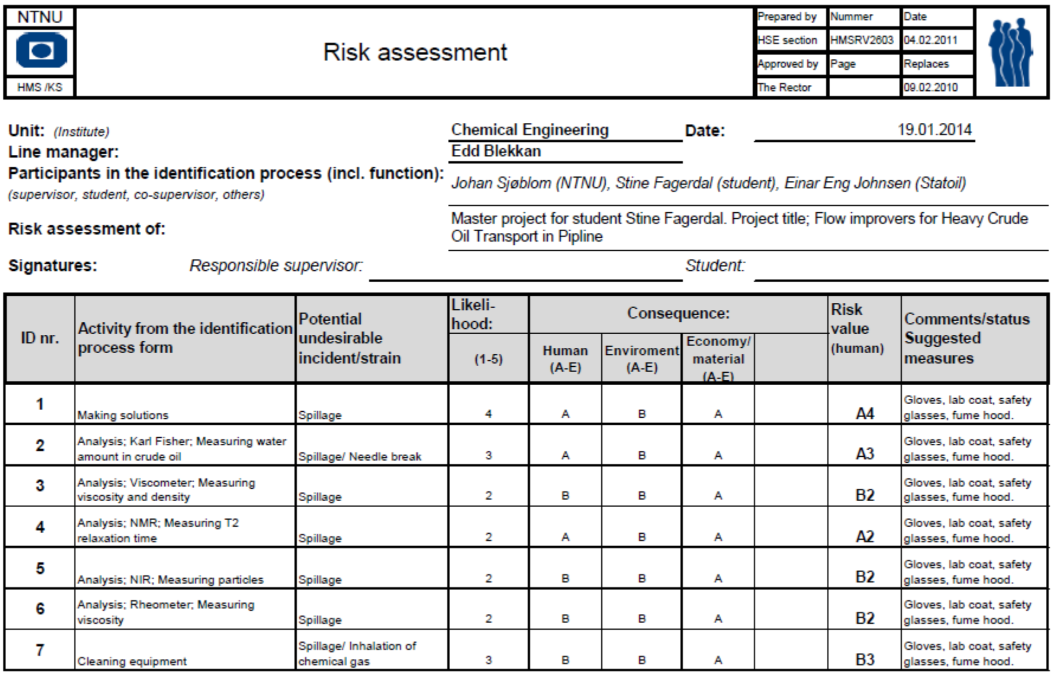
Short description of the main activity/main process: Master project for student Stine Fagerdal. Project title; Flow improvers for Heavy Crude Oil Transport in Pipline

Is the project work purely theoretical? (YES/NO) NO *Answer "YES" implies that supervisor is assured that no activities requiring risk assessment are involved in the work. If YES, briefly describe the activities below. The risk assessment form need not be filled out.*

Signatures: *Responsible supervisor:* *Student:*

ID nr.	Activity/process	Respons-ible person	Existing documentation	Existing safety measures	Laws, regulations etc.	Comment
1	Making solutions	Stine Fagerdal	Safety Data Sheet	Gloves, lab coat, safety glasses, fume hood.	Chemical regulations	
2	Analysis; Karl Fisher; Measuring water amount in crude oil	Stine Fagerdal	Instrument manual/ Safety Data Sheet	Gloves, lab coat, safety glasses, fume hood.	Chemical regulations	
3	Analysis; Viscometer; Measuring viscosity and density	Stine Fagerdal	Instrument manual/ Safety Data Sheet	Gloves, lab coat, safety glasses, fume hood.	Chemical regulations	
4	Analysis; NMR; Measuring T2 relaxation time	Stine Fagerdal	Instrument manual/ Safety Data Sheet	Gloves, lab coat, safety glasses, fume hood.	Chemical regulations	
5	Analysis; NIR; Measuring particles	Stine Fagerdal	Instrument manual/ Safety Data Sheet	Gloves, lab coat, safety glasses, fume hood.	Chemical regulations	
6	Analysis; Rheometer; Measuring viscosity	Stine Fagerdal	Instrument manual/ Safety Data Sheet	Gloves, lab coat, safety glasses, fume hood.	Chemical regulations	
7	Cleaning equipment	Stine Fagerdal	Safety Data Sheet	Gloves, lab coat, safety glasses, fume hood.	Chemical regulations	

Figure A-1: Hazardous activity identification process.



NTNU	Risk assessment	Prepared by	Nummer	Date
HMS /KS		HSE section	HMSRV2603	04.02.2011
		Approved by	Page	Replaces
		The Rector		09.02.2010

Unit: *(Institute)* Chemical Engineering **Date:** 19.01.2014

Line manager: Edd Blekkan

Participants in the identification process (incl. function): *Johan Sjøblom (NTNU), Stine Fagerdal (student), Einar Eng Johnsen (Statoil)*
(supervisor, student, co-supervisor, others)

Risk assessment of: Master project for student Stine Fagerdal. Project title; Flow improvers for Heavy Crude Oil Transport in Pipline

Signatures: *Responsible supervisor:* *Student:*

ID nr.	Activity from the identification process form	Potential undesirable incident/strain	Likeli-hood:	Consequence:				Risk value (human)	Comments/status Suggested measures
			(1-5)	Human (A-E)	Enviroment (A-E)	Economy/ material (A-E)			
1	Making solutions	Spillage	4	A	B	A		A4	Gloves, lab coat, safety glasses, fume hood.
2	Analysis; Karl Fisher; Measuring water amount in crude oil	Spillage/ Needle break	3	A	B	A		A3	Gloves, lab coat, safety glasses, fume hood.
3	Analysis; Viscometer; Measuring viscosity and density	Spillage	2	B	B	A		B2	Gloves, lab coat, safety glasses, fume hood.
4	Analysis; NMR; Measuring T2 relaxation time	Spillage	2	A	B	A		A2	Gloves, lab coat, safety glasses, fume hood.
5	Analysis; NIR; Measuring particles	Spillage	2	B	B	A		B2	Gloves, lab coat, safety glasses, fume hood.
6	Analysis; Rheometer; Measuring viscosity	Spillage	2	B	B	A		B2	Gloves, lab coat, safety glasses, fume hood.
7	Cleaning equipment	Spillage/ Inhalation of chemical gas	3	B	B	A		B3	Gloves, lab coat, safety glasses, fume hood.

Figure A-2: Risk assessment.

Appendix B Chemical Properties

B.1 Chemical Properties

Table B-1 and Table B-2 presents the chemical properties of the solvents used in the experimental work.

Table B-1: Chemical properties of referent solvents and solvents with active groups. Dynamic viscosity is measured at the viscometer. (32) (58)

Chemicals	Viscosity (at 20°C) [mPa·s]	Density [g/cm^3]	Molecule weight [g/mol]	Boiling point [°C]
Naphtha	0.5200	0.7140	103.1	-
Toluene	0.6236	0.8650	92.14	100.6
n-Hexane	0.3143	0.6548	86.18	68.95
Water	1.002	1.000	18.02	99.98
MEG	21.03	1.110	62.07	197.3
DEG	36.04	1.118	106.1	245.3
TEG	48.59	1.125	150.2	288.0
1-Hexanol	5.316	0.8136	102.2	156.5
2-Butanone	0.4246	0.8050	72.11	79.64

Table B-2: Chemical properties of the commercial products used in the experimental work. Dynamic viscosity is measured at the viscometer. (58)

Chemicals	Viscosity (at 20°C) [mPa·s]	Density [g/cm^3]	Molecule weight [g/mol]	Boiling point [°C]
Solvtreat EFI-201	0.3852	0.68-0.74	-	64
Armohib Ai-1000	-	0.865 (65°C)	-	-
Duomeen T	-	0.850 (20°C)	-	-
Ethoduomeen T/13	-	0.940	-	-

B.2 Karl Fischer Titration

The water amount in the various crude oils was detected by the Karl Fischer titration. Results are given in Table B-3.

Table B-3: Results from the Karl Fischer titration.

Sample name	Average [wt %]	Deviation [wt %]
Crude oil A	0.027	± 0.005
Crude oil B	0.15	± 0.03
Crude oil C	0.51	± 0.01

Appendix C Pretest of Crude Oil A and B

C.1 Properties of Pretest Samples

Properties of the pretest samples are presented in Table C-1 and Table C-2 given in wt %, vol %, number of molecules and weight loss during the heating /shaking in wt %.

Table C-1: The properties of series "Pretest A" given in wt %, vol %, number of molecules and weight loss during the heating /shaking in wt %.

Sample series: Pretest A	Wt % solvent	Vol % solvent	Molecule solvent [mol]	Weight loss [wt %]
1 H Crude oil A	-	-	-	0.000
A-1 H	1.998	2.295	0.007820	0.002
A-2 H	2.001	2.299	0.007834	0.000
A-4 H	2.002	2.300	0.007837	0.000

Table C-2: The properties of series "Pretest B" given in wt %, vol %, number of molecules and weight loss during the heating /shaking in wt %.

Sample series: Pretest B	Wt % solvent	Vol % solvent	Molecule solvent [mol]	Weight loss [wt %]
1 H Crude oil B	-	-	-	0.001
B-2 H	2.007	2.396	0.009825	0.001
B-4 H	2.016	2.406	0.009867	0.003
B-6 H	2.016	2.406	0.009867	0.002
B-24 H	2.023	2.414	0.009902	0.007

C.2 Analyses

C.2.1 Viscometer

Dynamic viscosity of “Pretest A” samples is shown in Figure C-1. The shake and heating time has little or no impact on the dynamic viscosity. The ”Pretest A” samples show no significant change in the dynamic viscosity with increasing shake and heating time.

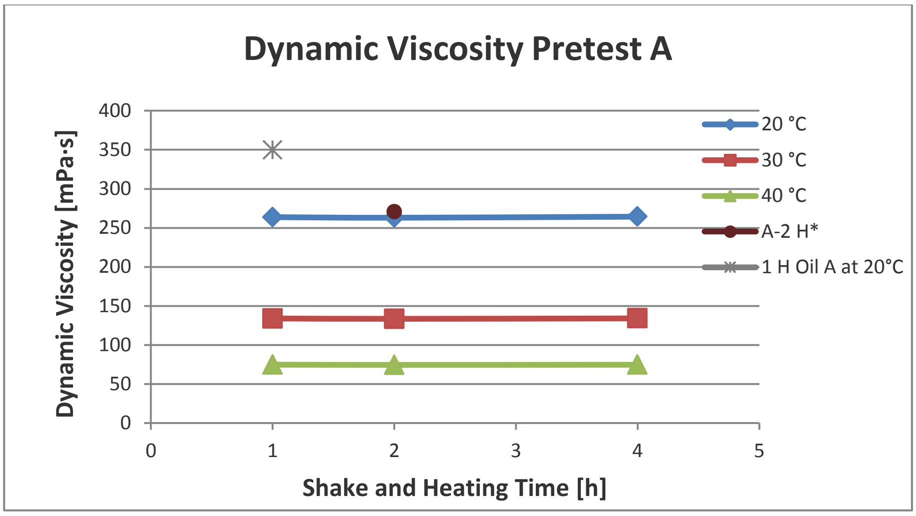


Figure C-1: Dynamic viscosity of “Pretest A”.

Dynamic viscosity of “Pretest B” samples is shown in Figure C-2. The shake and heating time has less impact as the temperature increases. The measurement at 20°C and 30°C shows a small increasing effect of the dynamic viscosity with increased shake and heating time. The biggest change is found between 2 hours to 4 hours. The measurement at 50°C shows a more unaffected straight line.

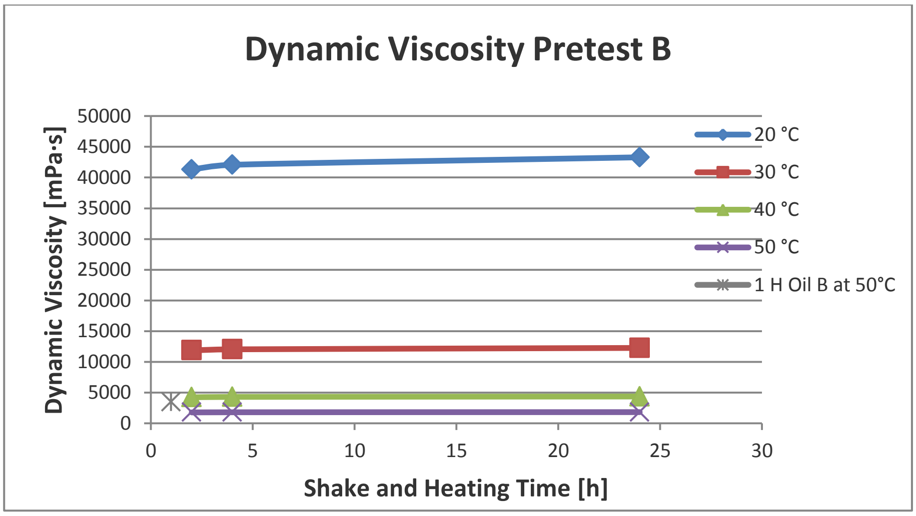


Figure C-2: Dynamic viscosity of “Pretest B”.

Row Data Viscometer

The results from the dynamic viscosity and density of the "Pretest A" samples are presented in Table C-3 to Table C-7. The results are given as an average value from three measured parallels with deviation.

Table C-3: Dynamic viscosity and density given as an average value with deviation for sample "1 H Crude oil A".

Sample: 1 H Crude oil A	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	349.69	± 0.80	0.9382	± 0.0001
30	173.28	± 0.38	0.9317	± 0.0001
40	94.903	± 0.278	0.9253	± 0.0001
30	173.20	± 0.34	0.9317	± 0.0001
20	350.19	± 0.78	0.9382	± 0.0001

Table C-4: Dynamic viscosity and density given as an average value with deviation for sample "A-1 H".

Sample: A-1 H	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	263.74	± 0.61	0.9353	± 0.0000
30	133.96	± 0.41	0.9288	± 0.0001
40	74.824	± 0.268	0.9223	± 0.0001
30	133.99	± 0.47	0.9288	± 0.0000
20	264.65	± 0.96	0.9353	± 0.0000

Table C-5: Dynamic viscosity and density given as an average value with deviation for sample "A-2 H".

Sample: A-2 H	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	263.04	± 0.72	0.9353	± 0.0000
30	133.55	± 0.46	0.9287	± 0.0000
40	74.515	± 0.302	0.9222	± 0.0000
30	133.39	± 0.51	0.9287	± 0. 0000
20	263.24	± 1.00	0.9352	± 0.0000

Table C-6: Dynamic viscosity and density given as an average value with deviation for sample "A-4 H".

Sample: A-4 H	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	264.37	± 0.72	0.9354	± 0.0001
30	134.08	± 0.41	0.9288	± 0.0001
40	74.717	± 0.258	0.9223	± 0.0001
30	133.77	± 0.43	0.9288	± 0.0001
20	264.16	± 0.81	0.9354	± 0.0001

Table C-7: Dynamic viscosity and density given as an average value with deviation for sample "A-2 H*".

Sample: A-2 H*	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	270.64	-	0.9357	-
30	136.88	-	0.9292	-
40	75.644	-	0.9226	-
30	135.55	-	0.9292	-
20	268.19	-	0.9357	-

The results from the dynamic viscosity and density of the "Pretest B" samples are presented in Table C-8 to Table C-11. The results are given as an average value from three measured parallels with deviation.

Table C-8: Dynamic viscosity and density given as an average value with deviation for sample "1 H Crude oil B".

Sample: 1 H Crude oil B	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	3444.8	-	0.9560	-
40	9224.5	-	0.9622	-
30	29270	-	0.9684	-
20	-	-	0.9748	-
50	3430.8	-	0.9560	-

Table C-9: Dynamic viscosity and density given as an average value with deviation for sample “B-2 H”.

Sample: B-2 H	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	1778.1	± 0.1	0.9522	± 0.0105
40	4236.4	± 0.1	0.9586	± 0.0052
30	11872	± 0	0.9649	± 0.0000
20	41302	± 0	0.9714	± 0.0051
50	1766.3	± 0.0	0.9523	± 0.0000

Table C-10: Dynamic viscosity and density given as an average value with deviation for sample “B-4 H”.

Sample: B-4 H	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	1801.6	± 0.2	0.9522	± 0.0158
40	4302.9	± 0.1	0.9586	± 0.0104
30	12044	± 0	0.9650	± 0.0052
20	42081	± 0	0.9714	± 0.0051
50	1791.6	± 0.1	0.9524	± 0.0053

Table C-11: Dynamic viscosity and density given as an average value with deviation for sample “B-24 H”.

Sample: B-24 H	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	1825.3	± 0.0	0.9523	± 0.0053
40	4367.9	± 0.2	0.9587	± 0.0052
30	12271	± 0	0.9650	± 0.0104
20	43299	± 0	0.9714	± 0.0103
50	1815.4	± 0.4	0.9524	± 0.0053

C.2.2 Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy was used in the pretest to study the homogeneity of the samples given different shaking and heating time. Table C-12 presents the average T_2 relaxation time with deviation from three parallels of crude oil A. The average values are used in Figure C-3 to presents the T_2 relaxation time of the samples in “Pretest A”. All of the blended samples have more or less the same relaxation time and are represented with a similar uniform curve.

Table C-12: Average and deviation T_2 relaxation time [ms] of “Pretest A” samples.

Sample	Average T_2 Relaxation Time [ms]	Deviation T_2 Relaxation Time [ms]
1 H Oil A	14.4	± 0.6
A-1 H	16.8	± 0.4
A-2 H	16.4	± 0.1
A-4 H	16.8	± 0.2
A-2 H*	16.2	-
1-Hexanol	734	± 18

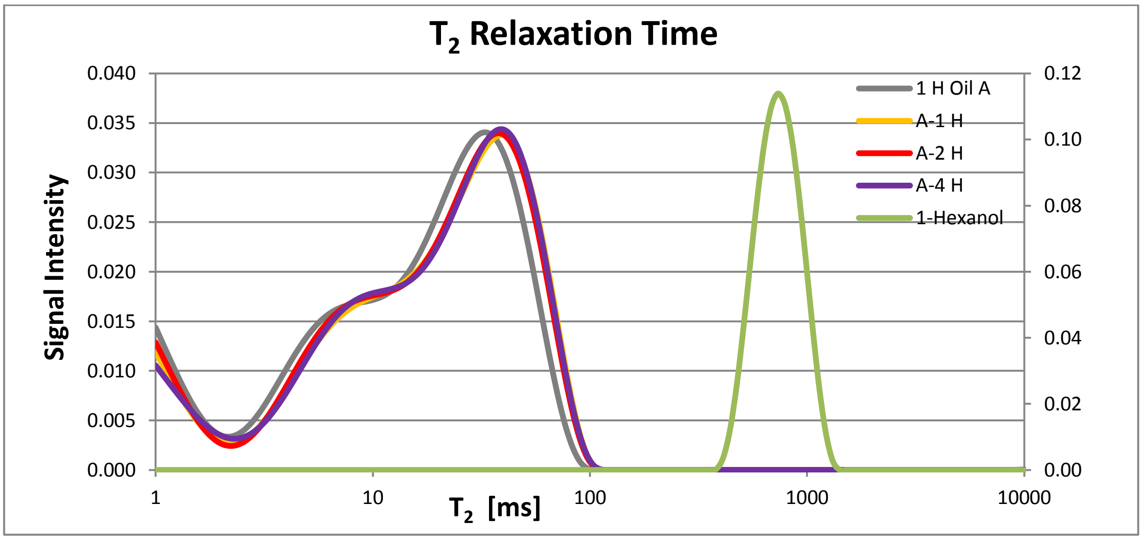


Figure C-3: T_2 relaxation time [ms] of “Pretest A” samples with different heating and shaking times. The pure 1-hexanol is presented with a secondary axis.

Figure C-4 presents the effect of storage time in T_2 relaxation time presented of “A-2 H” sample from “Pretest A” (not stored and stored). The two samples, A-2 H (not stored) and A-2 H* (stored) have identical relaxation time and curve.

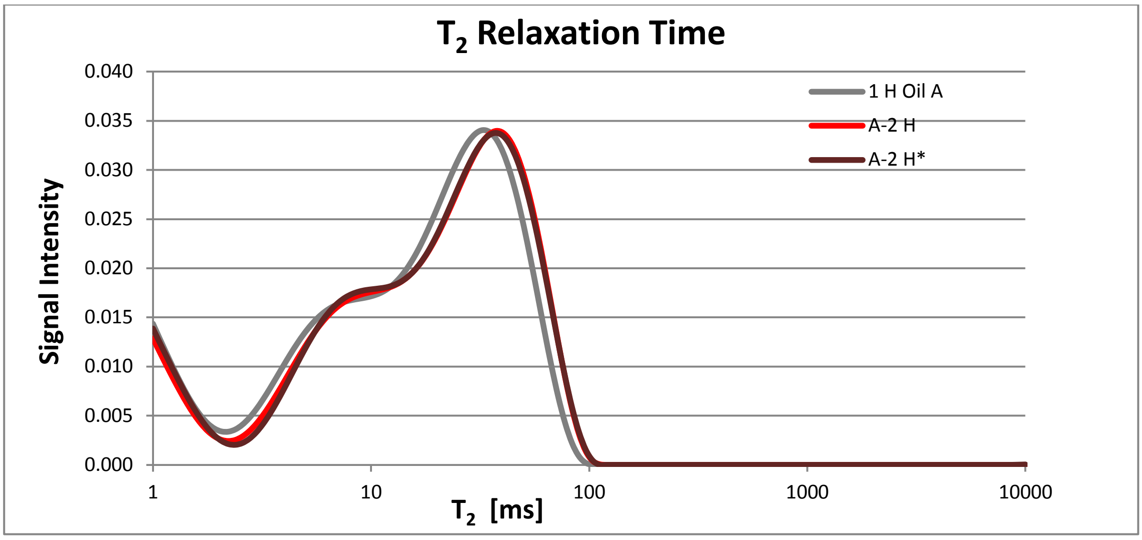


Figure C-4: Effect of storage time in T_2 relaxation time presented of samples “A-2 H” and “A-2 H*”.

Table C-13 presents the average T_2 relaxation time and deviation from two parallels of crude oil B. The average values are used in Figure C-5 to presents the T_2 relaxation time of the samples in "Pretest B". All of the blended samples have more or less the same relaxation time and are represented with a similar uniform curve.

Table C-13: Average and deviation of T_2 relaxation time [ms] of "Pretest B" samples.

Sample	Average T_2 Relaxation Time [ms]	Deviation T_2 Relaxation Time [ms]
1 H Oil B	2.47	± 0.04
B-2 H	2.89	± 0.18
B-4 H	2.84	± 0.02
B-24 H	2.96	± 0.08
1-Hexanol	734	± 18

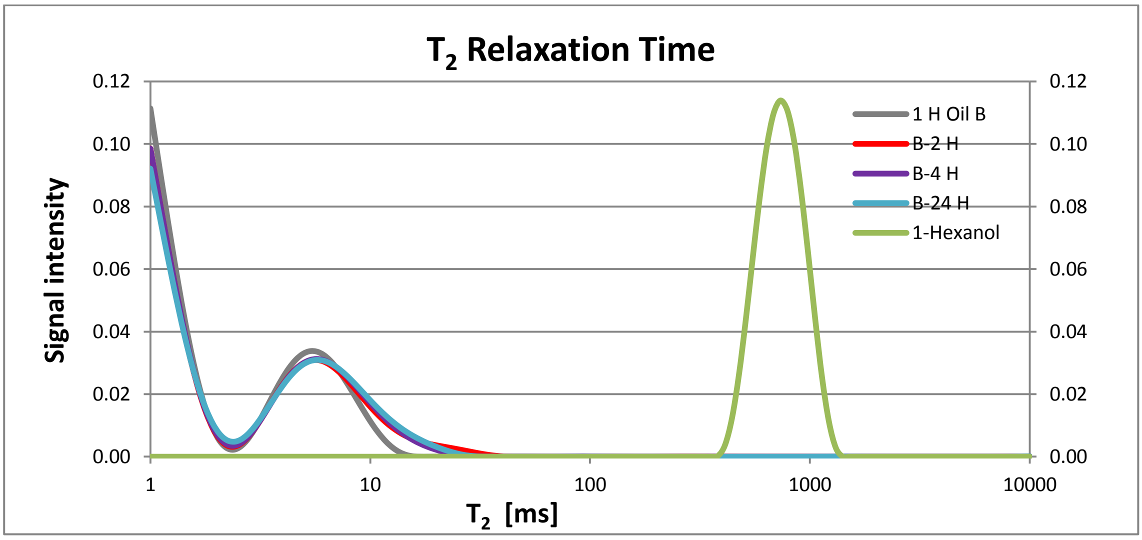


Figure C-5: T_2 relaxation time [ms] of "Pretest B" samples with different heating and shaking times. The pure 1-hexanol is presented with a secondary axis.

Appendix D Properties of the Crude Oil Samples

Properties of the crude oil samples are presented with the added solvents given in wt %, vol %, number of molecules and weight loss during the heating /shaking in wt %.

D.1 Crude Oil A

Properties of crude oil A samples added solvents of 0.5. 1. 2 and 3 wt % are presented in Table D-1 - Table D-4.

Table D-1: The properties of crude oil A with 0.5 wt % solvents given in wt %, vol %, number of molecules and weight loss during the heating /shaking in wt %.

Sample series: A-0.5 wt %	Wt % solvent	Vol % solvent	Molecule solvent [mol]	Weight loss [wt %]
A-Naphtha	0.505	0.662	0.00196	0.002
A-Toluene	0.506	0.549	0.00220	0.001
A-n-Hexane	0.506	0.723	0.00235	0.001
A-1-Hexanol	0.504	0.580	0.00197	0.002
A-2-Butanone	0.503	0.586	0.00279	0.001
A-Solvtreat	0.503	0.692	-	0.001

Table D-2: The properties of crude oil A with 1 wt % solvents given in wt %, vol %, number of molecules and weight loss during the heating /shaking in wt %.

Sample serie: A-1 wt %	Wt % solvent	Vol % solvent	Molecule solvent [mol]	Weight loss [wt %]
A-Naphtha	1.002	1.312	0.003887	0.001
A-Toluene	1.002	1.086	0.004351	0.001
A-n-Hexane	1.002	1.429	0.004651	0.001
A-1-Hexanol	1.003	1.154	0.003928	0.001
A-2-Butanone	1.001	1.165	0.005555	0.002
A-Solvtreat	1.002	1.376	-	0.001

Table D-3: The properties of crude oil A and blends of crude oil A with 2 wt % solvents given in wt %, vol %, number of molecules and weight loss during the heating /shaking in wt %.

Sample series: A-2 wt %	Wt % solvent	Vol % solvent	Molecule solvent [mol]	Weight loss [wt %]
Crude oil A	-	-	-	0.003
A-Naphta	2.001	2.611	0.007761	0.001
A-Toluene	2.001	2.166	0.008688	0.001
A-n-Hexane	2.000	2.840	0.009284	0.002
A-Water	1.999	1.877	0.05547	0.003
A-MEG	2.025	1.716	0.01305	0.001
A-DEG	2.001	1.684	0.007544	0.000
A-TEG	2.003	1.675	0.005335	0.000
A-1-Hexanol	2.005	2.304	0.007852	0.001
A-2-Butanone	2.001	2.323	0.01110	0.001
A-Solvtreat	1.998	2.735	-	0.002
A-Chem A	2.001	2.165	-	0.002
A-Chem D	2.002	2.168	-	0.002
A-Chem E	2.001	2.157	-	0.001

Table D-4: The properties of crude oil A with 3 wt % solvents given in wt %, vol %, number of molecules and weight loss during the heating /shaking in wt %.

Sample series: A-3 wt %	Wt % solvent	Vol % solvent	Molecule solvent [mol]	Weight loss [wt %]
A- Naphta	2.998	3.900	0.01163	0.002
A-Toluene	3.012	3.257	0.01308	0.003
A-n-Hexane	3.003	4.245	0.01394	0.001
A-1-Hexanol	3.014	3.458	0.01180	0.000
A-2-Butanone	2.999	3.476	0.01664	0.002
A-Solvtreat	3.001	4.091	-	0.001

D.2 Crude Oil B

Properties of the crude oil B samples added solvents of 0.5. 1 and 2 wt % are presented in Table D-5 to Table D-7.

Table D-5: The properties of crude oil B with 0.5 wt % solvents given in wt %, vol %, number of molecules and weight loss during the heating /shaking in wt %.

Sample series: B-0.5 wt %	Wt % solvent	Vol % solvent	Molecule solvent [mol]	Weight loss [wt %]
B- Naphta	0.507	0.691	0.002461	0.002
B-Toluene	0.499	0.562	0.002706	0.005
B-n-Hexane	0.500	0.743	0.002902	0.008
B-1-Hexanol	0.503	0.602	0.002460	0.002
B-2-Butanone	0.500	0.605	0.003468	0.005
B-Solvtreat	0.503	0.719	-	0.005

Table D-6: The properties of crude oil B with 1 wt % solvents given in wt %, vol %, number of molecules and weight loss during the heating /shaking in wt %.

Sample serie: B-1 wt %	Wt % solvent	Vol % solvent	Molecule solvent [mol]	Weight loss [wt %]
B- Naphta	0.998	1.358	0.004840	0.004
B-Toluene	1.000	1.125	0.005427	0.003
B-n-Hexane	1.000	1.482	0.005803	0.005
B-1-Hexanol	1.000	1.196	0.004894	0.007
B-2-Butanone	1.003	1.211	0.006952	0.004
B-Solvtreat	0.999	1.426	-	0.005

Table D-7: The properties of crude oil B and blends of crude oil B with 2 wt % solvents given in wt %, vol %, number of molecules and weight loss during the heating /shaking in wt %.

Sample series: B-2 wt %	**Wt % solvent**	**Vol % solvent**	**Molecule solvent [mol]**	**Weight loss [wt %]**
Crude oil B	-	-	-	0.004
B- Naphta	2.076	2.813	0.01008	0.005
B-Toluene	2.002	2.250	0.01086	0.004
B-n-Hexane	2.001	2.950	0.01161	0.004
B-Water	1.998	1.949	0.05545	0.006
B-MEG	2.001	1.762	0.01612	0.005
B-DEG	2.001	1.749	0.009430	0.003
B-TEG	1.998	1.736	0.006654	0.003
B-1-Hexanol	2.004	2.392	0.009808	0.003
B-2-Butanone	2.042	2.462	0.01416	0.003
B-Solvtreat	1.998	2.839	-	0.003
B-Chem A	2.002	2.250	-	0.003
B-Chem D	2.000	2.250	-	0.001
B-Chem E	2.002	2.241	-	0.002

D.3 Crude Oil C

Properties of the crude oil C samples with 2 wt % solvent are presented in Table D-8.

Table D-8: The properties of crude oil C and blends of crude oil C with 2 wt % solvents given in wt %, vol %, number of molecules and weight loss during the heating /shaking in wt %.

Sample serie: C-2 wt %	**Wt % solvent**	**Vol % solvent**	**Molecule solvent [mol]**	**Weight loss [wt %]**
Crude oil C	-	-	-	0.002
C- Naphta	2.004	2.696	0.009719	0.001
C-Toluene	2.002	2.234	0.01087	0.001
C-n-Hexane	1.998	2.924	0.01159	0.001
C-Water	1.999	1.935	0.05548	0.010
C-MEG	2.012	1.758	0.01621	0.002
C-DEG	2.011	1.744	0.009478	0.001
C-TEG	1.998	1.723	0.006654	0.002
C-1-Hexanol	2.001	2.370	0.009793	0.001
C-2-Butanone	1.999	2.392	0.01386	0.001
C-Solvtreat	1.999	2.819	-	0.001
C-Chem A	2.004	2.236	-	0.001
C-Chem D	2.007	2.241	-	0.001
C-Chem E	1.999	2.221	-	0.001

Appendix E Viscometer

E.1 Dynamic Viscosity

The dynamic viscosity [mPa·s] of the crude oils with 2 wt % solvent are presented in this appendix. Crude oil A and C are presented at 20°C while crude oil B is presented at 50°C. Figure E-1 presents the dynamic viscosity of crude oil A with 2 wt % solvent at 20°C. The result is presented as the average value from three parallels.

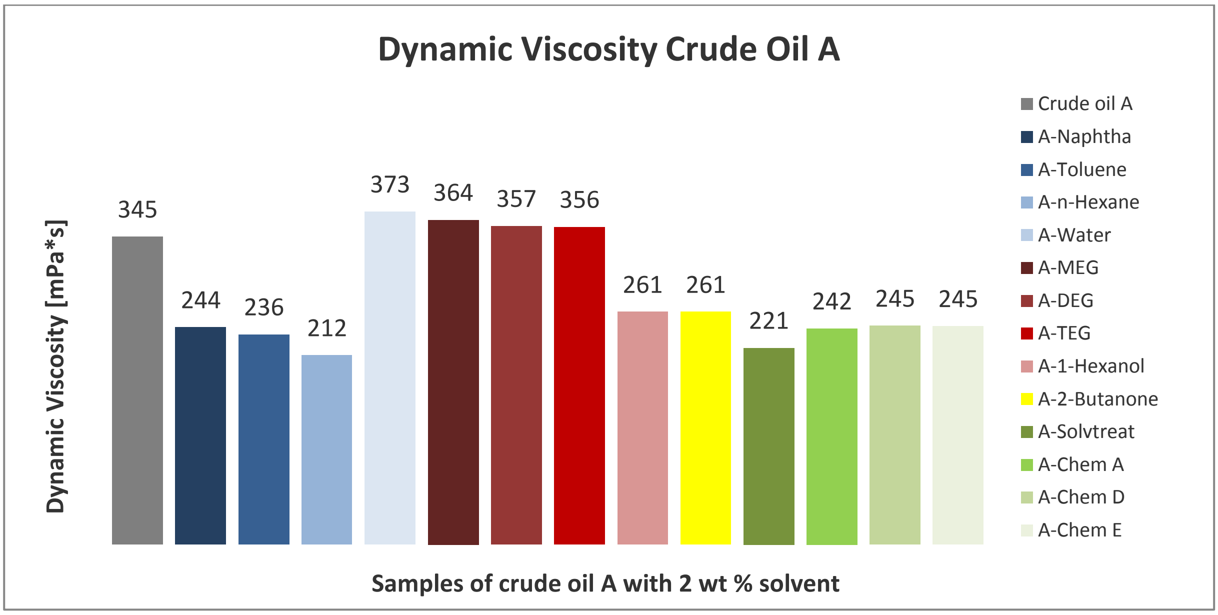


Figure E-1: Dynamic viscosity [mPa·s] given as an average value of crude oil A with 2 wt % solvent at 20°C.

Dynamic viscosity of all samples made from crude oil A is presented in Figure E-2. at 20°C.

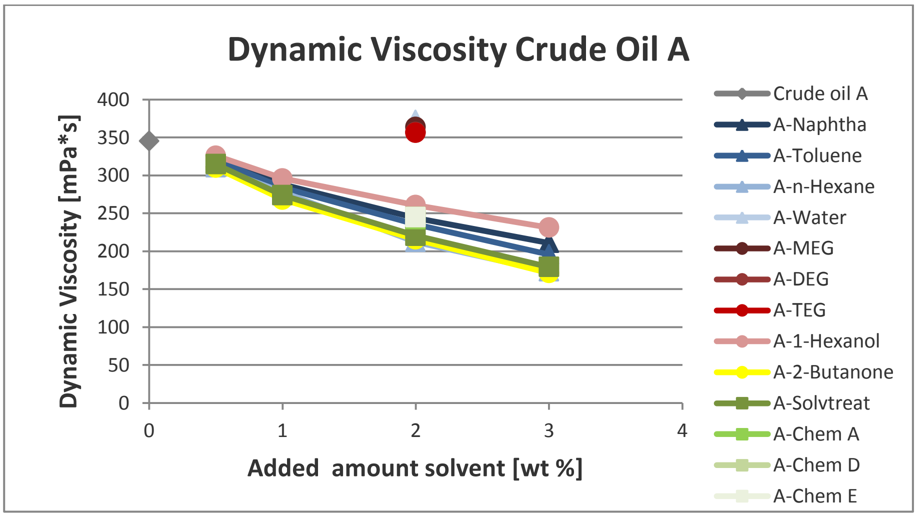


Figure E-2: Dynamic viscosity in range 0-400 mPa·s verses added amount of solvent in crude oil A at 20°C.

Figure E-3 presents the dynamic viscosity of crude oil B with 2 wt % solvent at 50°C. The result is presented as the average value from two parallels.

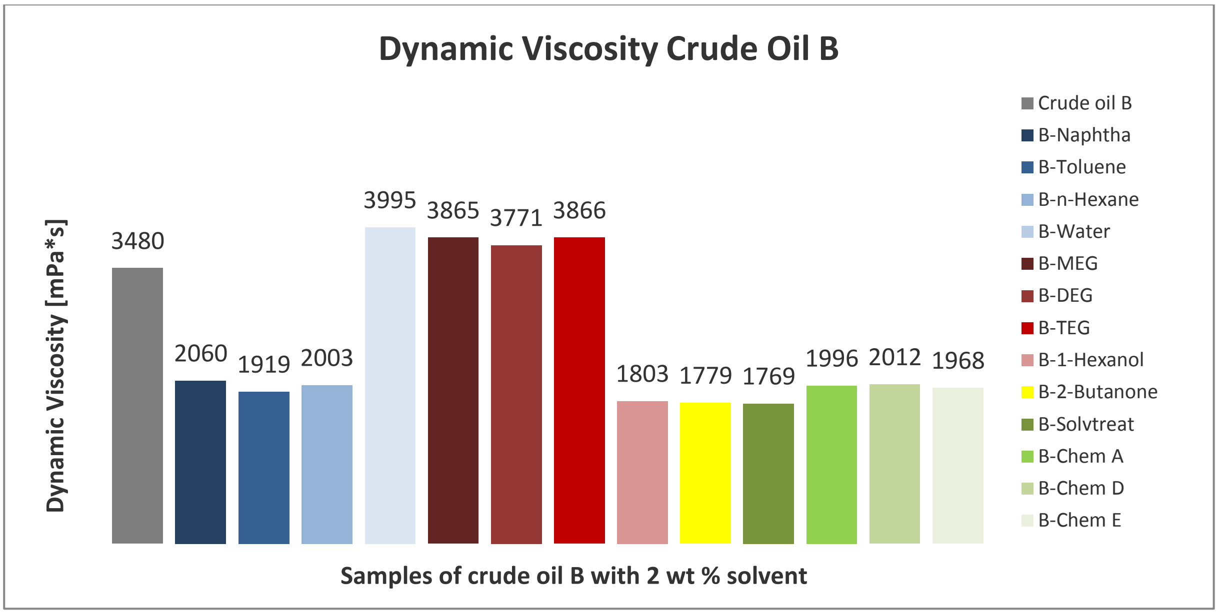


Figure E-3: Dynamic viscosity [mPa·s] given as an average value of crude oil B with 2 wt % solvent at 50°C.

Dynamic viscosity of all samples made from crude oil B is presented in Figure E-4 at 50°C.

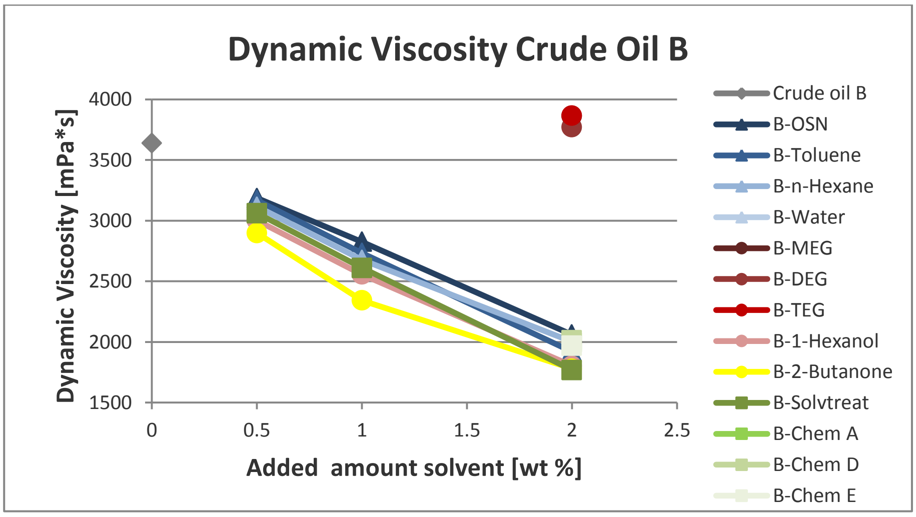


Figure E-4: Dynamic viscosity in range 1500-4000 mPa·s verses added amount of solvent in crude oil B at 50°C.

Figure E-5 presents the dynamic viscosity of crude oil C with 2 wt % solvent at 20°C. The result is presented as the average value from two parallels.

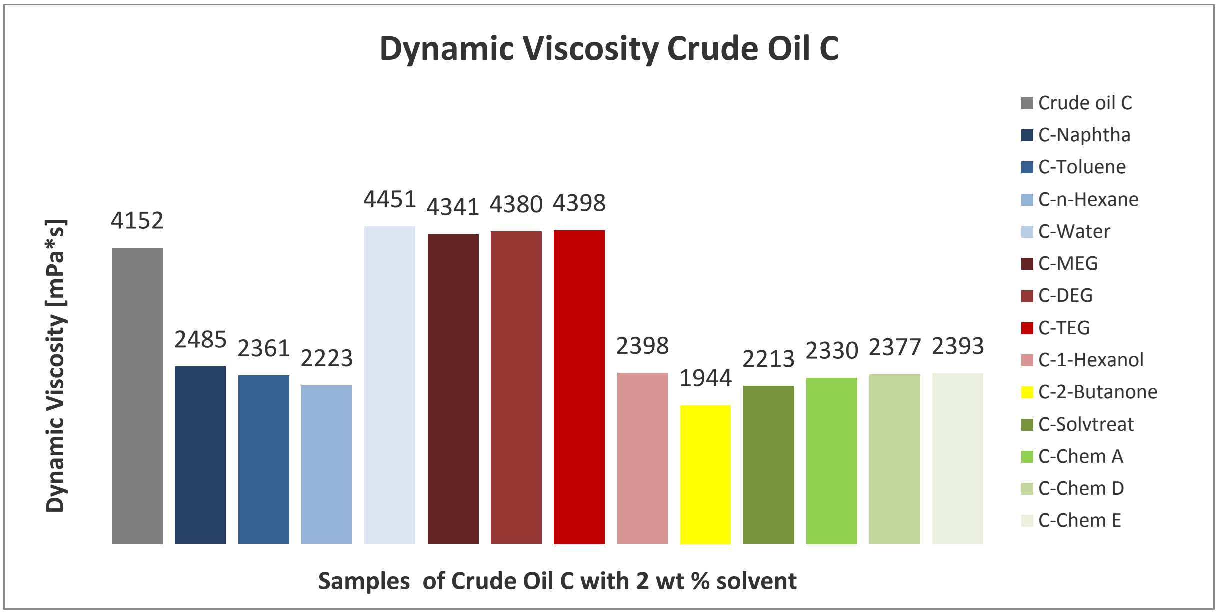


Figure E-5: Dynamic viscosity [mPa·s] given as an average value of crude oil C with 2 wt % solvent at 20°C.

E.2 Density

The densities [g/cm^3] of the crude oils with 2 wt % solvent are presented in this chapter. Crude oil A and C are presented at 20°C while crude oil B is presented at 50°C.

Figure E-6 presents the density of crude oil A with 2 wt % solvent at 20°C. The result is presented as the average value from three parallels.

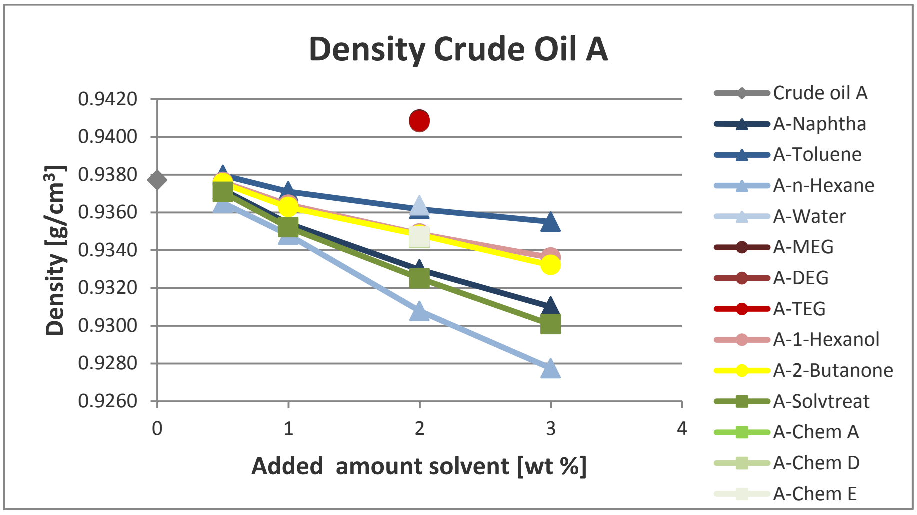


Figure E-6: Density in range 0.9260-0.9420 g/cm^3 verses added amount of solvent in crude oil A at 20°C.

Figure E-7 presents the density of crude oil B with 2 wt % solvent at 50°C. The result is presented as the average value from two parallels.

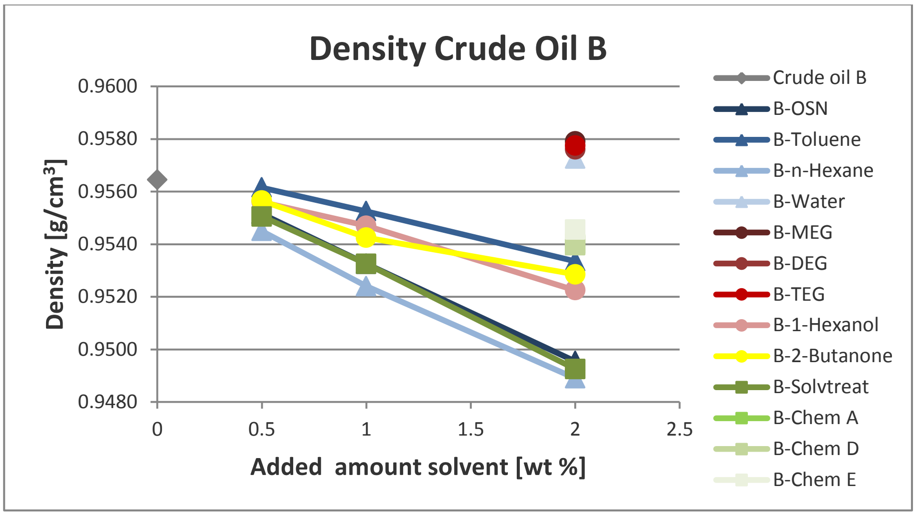


Figure E-7: Density in range 0.9480-0.9600 g/cm^3 verses added amount of solvent in crude oil B at 50°C.

Figure E-8 presents the density of crude oil C with 2 wt % solvent at 20°C. The result is presented as the average value from two parallels.

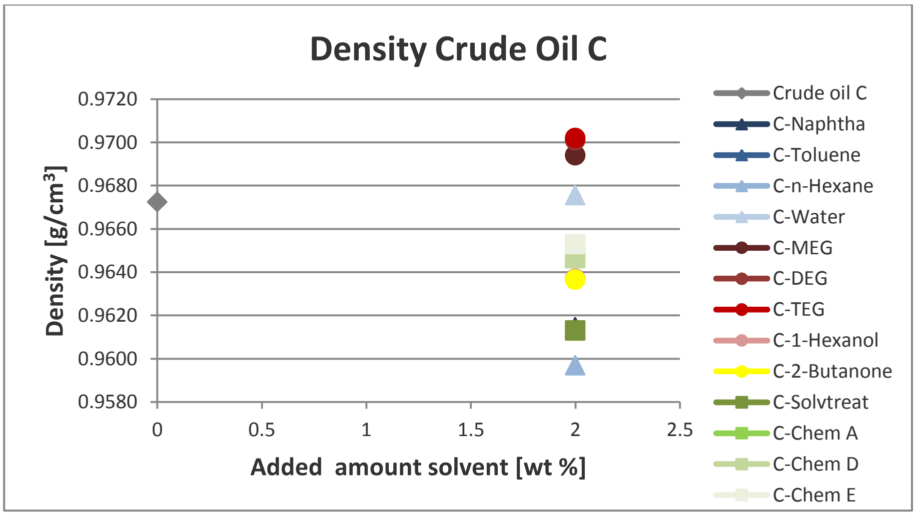


Figure E-8: Density 0.9580-0.9720 g/cm^3 verses added amount of solvent in crude oil C at 20°C.

E.3 Row Data Viscometer

The results from viscometer of the dynamic viscosity and density are given for all samples made in the experimental work.

E.3.1 Crude Oil A

The dynamic viscosity and density of crude oil A samples are presented in Table E-1 to Table E-35. The results are given as an average value from three measured parallels with deviation.

Table E-1: Dynamic viscosity and density given as an average value with deviation of crude oil A.

Sample: Crude oil A	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	345.27	± 0.10	0.9377	± 0.0000
30	171.20	± 0.07	0.9312	± 0.0000
40	93.639	± 0.076	0.9248	± 0.0000
30	171.07	± 0.13	0.9312	± 0.0000
20	345.60	± 0.31	0.9377	± 0.0000

Crude Oil A Samples with 0.5 wt % Solvent

Table E-2: Dynamic viscosity and density given as an average value with deviation of crude oil A with 0.5 wt % naphtha.

Sample: 0.5 wt% A-Naphtha	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	323.55	± 0.35	0.9372	± 0.0000
30	161.62	± 0.09	0.9307	± 0.0000
40	89.014	± 0.051	0.9242	± 0.0000
30	162.07	± 0.53	0.9307	± 0.0000
20	323.54	± 1.01	0.9370	± 0.0003

Table E-3: Dynamic viscosity and density given as an average value with deviation of crude oil A with 0.5 wt % toluene.

Sample: 0.5 wt % A-Toluene	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	320.55	± 0.36	0.9380	± 0.0000
30	160.19	± 0.07	0.9314	± 0.0000
40	87.889	± 0.067	0.9249	± 0.0000
30	159.26	± 0.15	0.9314	± 0.0000
20	318.81	± 0.44	0.9379	± 0.0000

Table E-4: Dynamic viscosity and density given as an average value with deviation of crude oil A with 0.5 wt % n-hexane.

Sample: 0.5 wt % A-n-Hexane	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	310.89	± 0.45	0.9365	± 0.0000
30	156.05	± 0.04	0.9300	± 0.0000
40	86.020	± 0.010	0.9235	± 0.0000
30	155.44	± 0.16	0.9300	± 0.0000
20	309.96	± 0.46	0.9365	± 0.0000

Table E-5: Dynamic viscosity and density given as an average value with deviation of crude oil A with 0.5 wt % 1-hexanol.

Sample: 0.5 wt % A-1-Hexanol	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	325.99	± 0.44	0.9376	± 0.0000
30	162.24	± 0.14	0.9311	± 0.0000
40	89.133	± 0.035	0.9246	± 0.0000
30	162.25	± 0.15	0.9311	± 0.0000
20	326.42	± 0.29	0.9376	± 0.0000

Table E-6: Dynamic viscosity and density given as an average value with deviation of crude oil A with 0.5 wt % 2-butanone.

Sample: 0.5 wt % A-2-Butanone	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	310.25	± 0.47	0.9375	± 0.0001
30	155.75	± 0.10	0.9311	± 0.0000
40	86.093	± 0.052	0.9246	± 0.0000
30	155.57	± 0.18	0.9311	± 0.0000
20	310.31	± 0.45	0.9376	± 0.0000

Tabl. E-7: Dynamic viscosity and density given as an average value with deviation of crude oil A with 0.5 wt % Solvtreat.

Sample: 0.5 wt % A-Solvtreat	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	314.85	± 0.33	0.9371	± 0.0000
30	157.72	± 0.15	0.9306	± 0.0000
40	87.054	± 0.070	0.9241	± 0.0000
30	157.61	± 0.15	0.9306	± 0.0000
20	314.89	± 0.33	0.9371	± 0.0000

Crude Oil A Samples with 1 wt % Solvent

Table E-8: Dynamic viscosity and density given as an average value with deviation of crude oil A with 1 wt % naphtha.

Sample: 1 wt % A-Naphtha	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	288.31	± 0.13	0.9354	± 0.0000
30	145.99	± 0.06	0.9289	± 0.0000
40	81.336	± 0.029	0.9225	± 0.0000
30	145.81	± 0.05	0.9289	± 0.0000
20	288.33	± 0.12	0.9354	± 0.0000

Table E-9: Dynamic viscosity and density given as an average value with deviation of crude oil A with 1 wt % toluene.

Sample: 1 wt % A-Toluene	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	284.13	± 0.13	0.9371	± 0.0000
30	144.26	± 0.03	0.9306	± 0.0000
40	80.405	± 0.008	0.9241	± 0.0000
30	144.02	± 0.01	0.9306	± 0.0000
20	284.05	± 0.05	0.9371	± 0.0000

Table E-10: Dynamic viscosity and density given as an average value with deviation of crude oil A with 1 wt % n-hexane.

Sample: 1 wt % A-n-Hexane	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	277.94	± 0.19	0.9348	± 0.0001
30	141.54	± 0.07	0.9283	± 0.0001
40	78.998	± 0.041	0.9218	± 0.0001
30	141.04	± 0.10	0.9283	± 0.0001
20	277.20	± 0.21	0.9348	± 0.0001

Table E-11: Dynamic viscosity and density given as an average value with deviation of crude oil A with 1 wt % 1-hexanol.

Sample: 1 wt % A-1-Hexanol	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	296.10	± 0.21	0.9364	± 0.0000
30	148.70	± 0.09	0.9299	± 0.0000
40	82.287	± 0.075	0.9234	± 0.0000
30	148.47	± 0.06	0.9299	± 0.0000
20	295.96	± 0.19	0.9364	± 0.0000

Table E-12: Dynamic viscosity and density given as an average value with deviation of crude oil A with 1 wt % 2-butanone.

Sample: 1 wt % A-2-Butanone	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	268.22	± 0.13	0.9363	± 0.0000
30	137.03	± 0.07	0.9297	± 0.0000
40	76.887	± 0.041	0.9233	± 0.0000
30	136.92	± 0.09	0.9297	± 0.0000
20	268.33	± 0.15	0.9363	± 0.0000

Table E-13: Dynamic viscosity and density given as an average value with deviation of crude oil A with 1 wt % Solvtreat.

Sample: 1 wt % A-Solvtreat	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	273.93	± 0.11	0.9352	± 0.0000
30	139.66	± 0.11	0.9287	± 0.0000
40	78.101	± 0.025	0.9222	± 0.0000
30	139.43	± 0.06	0.9287	± 0.0000
20	273.96	± 0.13	0.9352	± 0.0000

Crude Oil A Samples with 2 wt % Solvent

Table E-14: Dynamic viscosity and density given as an average value with deviation of crude oil A with 2 wt % naphtha.

Sample: 2 wt % A-Naphtha	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	243.65	± 0.20	0.9330	± 0.0000
30	125.93	± 0.06	0.9265	± 0.0000
40	71.284	± 0.041	0.9200	± 0.0000
30	125.70	± 0.09	0.9265	± 0.0000
20	243.41	± 0.20	0.9330	± 0.0000

Table E-15: Dynamic viscosity and density given as an average value with deviation of crude oil A with 2 wt % toluene.

Sample: 2 wt % A-Toluene	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	235.62	± 0.25	0.9362	± 0.0000
30	122.32	± 0.11	0.9297	± 0.0000
40	69.486	± 0.054	0.9232	± 0.0000
30	122.07	± 0.11	0.9297	± 0.0000
20	235.29	± 0.26	0.9362	± 0.0000

Table E-16: Dynamic viscosity and density given as an average value with deviation of crude oil A with 2 wt % n-hexane.

Sample: 2 wt % A-n-Hexane	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	212.27	± 0.15	0.9308	± 0.0000
30	111.68	± 0.09	0.9242	± 0.0000
40	64.225	± 0.056	0.9178	± 0.0000
30	111.58	± 0.09	0.9243	± 0.0000
20	212.25	± 0.16	0.9308	± 0.0000

Table E-17: Dynamic viscosity and density given as an average value with deviation of crude oil A with 2 wt % water.

Sample: 2 wt % A-Water	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	373.41	± 1.47	0.9364	± 0.0005
30	184.63	± 0.54	0.9290	± 0.0007
40	100.26	± 0.22	0.9271	± 0.0019
30	183.48	± 1.22	0.9346	± 0.0002
20	372.48	± 2.43	0.9368	± 0.0001

Table E-18: Dynamic viscosity and density given as an average value with deviation of crude oil A with 2 wt % MEG.

Sample: 2 wt % A-MEG	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	364.09	± 0.12	0.9409	± 0.0000
30	179.89	± 0.11	0.9344	± 0.0000
40	98.065	± 0.080	0.9280	± 0.0000
30	179.81	± 0.19	0.9344	± 0.0000
20	364.45	± 0.49	0.9409	± 0.0000

Table E-19: Dynamic viscosity and density given as an average value with deviation of extra treated crude oil A with 2 wt % MEG.

Sample: 2 wt % A-MEG*	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	382.73	± 0.10	0.9416	± 0.0000
30	187.73	± 0.03	0.9351	± 0.0000
40	101.72	± 0.04	0.9287	± 0.0000
30	187.23	± 0.04	0.9351	± 0.0000
20	381.74	± 0.09	0.9417	± 0.0000

Table E-20: Dynamic viscosity and density given as an average value with deviation of crude oil A with 2 wt % DEG.

Sample: 2 wt % A-DEG	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	357.26	± 0.34	0.9408	± 0.0000
30	176.18	± 0.15	0.9342	± 0.0000
40	95.787	± 0.066	0.9278	± 0.0000
30	175.64	± 0.10	0.9342	± 0.0000
20	356.09	± 0.27	0.9408	± 0.0000

Table E-21: Dynamic viscosity and density given as an average value with deviation of extra treated crude oil A with 2 wt % DEG.

Sample: 2 wt % A-DEG*	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	383.60	± 0.12	0.9397	± 0.0000
30	187.47	± 0.03	0.9332	± 0.0000
40	101.21	± 0.05	0.9311	± 0.0000
30	186.81	± 0.04	0.9376	± 0.0000
20	381.81	± 0.11	0.9419	± 0.0000

Table E-22: Dynamic viscosity and density given as an average value with deviation of crude oil A with 2 wt % TEG.

Sample: 2 wt % A-TEG	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	356.21	± 0.62	0.9408	± 0.0000
30	175.66	± 0.27	0.9343	± 0.0000
40	95.485	± 0.129	0.9278	± 0.0000
30	175.13	± 0.27	0.9343	± 0.0000
20	354.86	± 0.59	0.9408	± 0.0000

Table E-23: Dynamic viscosity and density given as an average value with deviation of extra treated crude oil A with 2 wt % TEG.

Sample: 2 wt % A-TEG*	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	382.65	± 0.12	0.9398	± 0.0000
30	187.12	± 0.03	0.9333	± 0.0000
40	101.00	± 0.03	0.9312	± 0.0000
30	186.37	± 0.01	0.9377	± 0.0000
20	381.06	± 0.07	0.9420	± 0.0000

Table E-24: Dynamic viscosity and density given as an average value with deviation of crude oil A with 2 wt % 1-hexanol.

Sample: 2 wt % A-1-Hexanol	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	260.86	± 0.13	0.9349	± 0.0002
30	132.28	± 0.06	0.9284	± 0.0001
40	73.689	± 0.028	0.9219	± 0.0000
30	131.89	± 0.06	0.9284	± 0.0000
20	260.36	± 0.13	0.9350	± 0.0000

Table E-25: Dynamic viscosity and density given as an average value with deviation of crude oil A with 2 wt % 2-butanone.

Sample: 2 wt % A-2-Butanone	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	215.62	± 0.12	0.9348	± 0.0000
30	113.12	± 0.07	0.9282	± 0.0000
40	64.819	± 0.033	0.9217	± 0.0000
30	112.86	± 0.07	0.9282	± 0.0000
20	215.36	± 0.16	0.9348	± 0.0000

Table E-26: Dynamic viscosity and density given as an average value with deviation of crude oil A with 2 wt % solvtreat.

Sample: 2 wt % A-Solvtreat	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	220.58	± 0.39	0.9325	± 0.0000
30	115.32	± 0.18	0.9260	± 0.0000
40	65.863	± 0.093	0.9195	± 0.0000
30	115.04	± 0.20	0.9260	± 0.0000
20	220.20	± 0.32	0.9325	± 0.0000

Table E-27: Dynamic viscosity and density given as an average value with deviation of crude oil A with 2 wt % chem A.

Sample: 2 wt % A-Chem A	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	242.24	± 0.05	0.9346	± 0.0000
30	125.30	± 0.00	0.9281	± 0.0000
40	71.072	± 0.018	0.9260	± 0.0000
30	125.20	± 0.03	0.9325	± 0.0000
20	242.29	± 0.02	0.9368	± 0.0000

Table E-28: Dynamic viscosity and density given as an average value with deviation of crude oil A with 2 wt % chem D.

Sample: 2 wt % A-Chem D	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	245.32	± 0.19	0.9346	± 0.0000
30	126.86	± 0.13	0.9281	± 0.0000
40	72.012	± 0.115	0.9260	± 0.0000
30	127.12	± 0.26	0.9325	± 0.0000
20	246.28	± 0.55	0.9368	± 0.0000

Table E-29: Dynamic viscosity and density given as an average value with deviation of crude oil A with 2 wt % chem E.

Sample: 2 wt % A-Chem E	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	244.93	± 0.11	0.9347	± 0.0000
30	126.46	± 0.03	0.9282	± 0.0000
40	71.618	± 0.029	0.9261	± 0.0000
30	126.38	± 0.06	0.9326	± 0.0000
20	244.94	± 0.12	0.9369	± 0.0000

Crude Oil A Samples with 3 wt % Solvent

Table E-30: Dynamic viscosity and density given as an average value with deviation of crude oil A with 3 wt % naphtha.

Sample: 3 wt % A-Naphtha	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	211.03	± 0.14	0.9310	± 0.0000
30	110.94	± 0.07	0.9245	± 0.0000
40	63.749	± 0.031	0.9180	± 0.0000
30	110.85	± 0.06	0.9245	± 0.0000
20	211.04	± 0.12	0.9311	± 0.0000

Table E-31: Dynamic viscosity and density given as an average value with deviation of crude oil A with 3 wt % toluene.

Sample: 3 wt % A-Toluene	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	195.78	± 0.15	0.9355	± 0.0000
30	103.93	± 0.06	0.9290	± 0.0000
40	60.172	± 0.037	0.9225	± 0.0000
30	103.76	± 0.07	0.9290	± 0.0000
20	195.73	± 0.15	0.9355	± 0.0000

Table E-32: Dynamic viscosity and density given as an average value with deviation of crude oil A with 3 wt % n-hexane.

Sample: 3 wt % A-n-Hexane	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	173.52	± 0.34	0.9277	± 0.0000
30	93.55	± 0.12	0.9212	± 0.0000
40	54.785	± 0.054	0.9146	± 0.0000
30	93.25	± 0.13	0.9212	± 0.0000
20	173.16	± 0.27	0.9278	± 0.0000

Table E-33: Dynamic viscosity and density given as an average value with deviation of crude oil A with 3 wt % 1-hexanol.

Sample: **3 wt % A-1-Hexanol**	**Dynamic viscosity [mPa·s]**		**Density [g/cm³]**	
Temp. [°C]	**Average**	**Deviation**	**Average**	**Deviation**
20	231.39	± 0.12	0.9336	± 0.0000
30	118.53	± 0.02	0.9271	± 0.0000
40	66.653	± 0.010	0.9205	± 0.0000
30	118.40	± 0.02	0.9271	± 0.0000
20	231.24	± 0.09	0.9336	± 0.0000

Table E-34: Dynamic viscosity and density given as an average value with deviation of crude oil A with 3 wt % 2-butanone.

Sample: **3 wt % A-2-Butanone**	**Dynamic viscosity [mPa·s]**		**Density [g/cm³]**	
Temp. [°C]	**Average**	**Deviation**	**Average**	**Deviation**
20	171.43	± 0.19	0.9332	± 0.0000
30	92.439	± 0.090	0.9267	± 0.0000
40	54.311	± 0.082	0.9201	± 0.0000
30	92.344	± 0.092	0.9267	± 0.0000
20	171.43	± 0.20	0.9333	± 0.0000

Table E-35: Dynamic viscosity and density given as an average value with deviation of crude oil A with 3 wt % Solvtreat.

Sample: **3 wt % A-Solvtreat**	**Dynamic viscosity [mPa·s]**		**Density [g/cm³]**	
Temp. [°C]	**Average**	**Deviation**	**Average**	**Deviation**
20	179.31	± 0.33	0.9301	± 0.0000
30	96.020	± 0.147	0.9235	± 0.0000
40	56.057	± 0.084	0.9170	± 0.0000
30	95.929	± 0.155	0.9235	± 0.0000
20	179.31	± 0.35	0.9301	± 0.0000

E.3.2 Crude Oil B

The dynamic viscosity and density of crude oil B samples are presented in Table E-36 to Table E-61.

The results are given as an average value from two measured parallels with deviation.

Table E-36: Dynamic viscosity and density given as an average value with deviation of crude oil B.

Sample: Crude oil B	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	3480.0	± 43.3	0.9565	± 0.0005
40	9449.1	± 138.1	0.9627	± 0.0004
30	30289	± 717	0.9689	± 0.0005
20	-	-	0.9753	± 0.0005
50	3475.1	± 14.9	0.9570	± 0.0000

Crude Oil B Samples with 0.5 wt % Solvent

Table E-37: Dynamic viscosity and density given as an average value with deviation of crude oil B with 0.5 wt % naphtha.

Sample: 0.5 wt % B-Naphtha	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	3186.7	± 4.2	0.9552	± 0.0001
40	8415.3	± 4.4	0.9614	± 0.0000
30	26147	± 98	0.9676	± 0.0000
20	-	-	0.9740	± 0.0000
50	3162.0	± 7.4	0.9552	± 0.0001

Table E-38: Dynamic viscosity and density given as an average value with deviation of crude oil B with 0.5 wt % toluene.

Sample: 0.5 wt % B-Toluene	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	3168.7	± 26.5	0.9562	± 0.0001
40	8328.8	± 94.3	0.9624	± 0.0000
30	25966	± 286	0.9686	± 0.0000
20	-	-	0.9750	± 0.0000
50	3146.2	± 29.0	0.9562	± 0.0001

Table E-39: Dynamic viscosity and density given as an average value with deviation of crude oil B with 0.5 wt % n-hexane.

Sample: 0.5 wt % B-n-Hexane	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	3114.5	-	0.9545	± 0.0003
40	8165.5	-	0.9621	± 0.0015
30	25506	-	0.9683	± 0.0014
20	-	-	0.9735	± 0.0003
50	3094.5	-	0.9547	± 0.0002

Table E-40: Dynamic viscosity and density given as an average value with deviation of crude oil B with 0.5 wt % 1-hexanol.

Sample: 0.5 wt % B-1-Hexanol	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	3002.8	± 6.6	0.9556	± 0.0001
40	7789.9	± 23.9	0.9619	± 0.0000
30	23841	± 37	0.9681	± 0.0000
20	94365	± 311	0.9745	± 0.0000
50	2979.3	± 8.5	0.9556	± 0.0001

Table E-41: Dynamic viscosity and density given as an average value with deviation of crude oil B with 0.5 wt % 2-butanone.

Sample: 0.5 wt % B-2-Butanone	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	2898.2	± 12.6	0.9557	± 0.0000
40	7467.2	± 63.8	0.9619	± 0.0000
30	22712	± 232	0.9681	± 0.0000
20	88728	± 907	0.9745	± 0.0000
50	2878.4	± 13.1	0.9557	± 0.0000

Table E-42: Dynamic viscosity and density given as an average value with deviation of crude oil B with 0.5 wt % Solvtreat.

Sample: 0.5 wt % B-Solvtreat	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	3061.9	± 22.3	0.9551	± 0.0000
40	8034.3	± 96.8	0.9613	± 0.0000
30	24865	± 369	0.9675	± 0.0000
20	-	-	0.9739	± 0.0000
50	3040.3	± 23.6	0.9551	± 0.0000

Crude Oil B Samples with 1 wt % Solvent

Table E-43: Dynamic viscosity and density given as an average value with deviation of crude oil B with 1 wt % naphtha.

Sample: 1 wt % B-Naphtha	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	2825.7	± 5.3	0.9533	± 0.0000
40	7343.8	± 34.1	0.9596	± 0.0000
30	22623	± 4	0.9659	± 0.0000
20	89889	± 806	0.9722	± 0.0000
50	2810.0	± 1.5	0.9534	± 0.0000

Table E-44: Dynamic viscosity and density given as an average value with deviation of crude oil B with 1 wt % toluene.

Sample: 1 wt % B-Toluene	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	2732.9	± 17.0	0.9553	± 0.0000
40	7038.3	± 69.9	0.9616	± 0.0000
30	21376	± 270	0.9679	± 0.0000
20	82773	± 1243	0.9743	± 0.0001
50	2713.6	± 16.1	0.9553	± 0.0000

Table E-45: Dynamic viscosity and density given as an average value with deviation of crude oil B with 1 wt % n-hexane.

Sample: 1 wt % B-n-Hexane	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	2677.1	± 16.3	0.9524	± 0.0000
40	6897.2	± 61.3	0.9587	± 0.0000
30	20920	± 222	0.9650	± 0.0000
20	81623	± 1128	0.9714	± 0.0000
50	2652.5	± 20.6	0.9525	± 0.0000

Table E-46: Dynamic viscosity and density given as an average value with deviation of crude oil B with 1 wt % 1-hexanol.

Sample: 1 wt % B-1-Hexanol	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	2556.1	± 30.0	0.9547	± 0.0003
40	6428.5	± 44.7	0.9610	± 0.0003
30	18951	± 129	0.9674	± 0.0004
20	71630	± 798	0.9739	± 0.0005
50	2529.2	± 22.5	0.9548	± 0.0003

Table E-47: Dynamic viscosity and density given as an average value with deviation of crude oil B with 1 wt % 2-butanone.

Sample: 1 wt % B-2-Butanone	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	2342.6	± 15.2	0.9543	± 0.0000
40	5837.7	± 62.7	0.9607	± 0.0000
30	16988	± 208	0.9670	± 0.0000
20	62795	± 1290	0.9733	± 0.0000
50	2320.7	± 20.2	0.9543	± 0.0000

Table E-48: Dynamic viscosity and density given as an average value with deviation of crude oil B with 1 wt % Solvtreat.

Sample: 1 wt % B-Solvtreat	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	1769.1	± 6.0	0.9493	± 0.0004
40	4271.2	± 29.8	0.9557	± 0.0003
30	12106	± 63	0.9621	± 0.0003
20	42809	± 257	0.9685	± 0.0003
50	1756.1	± 4.1	0.9495	± 0.0002

Crude Oil B Samples with 2 wt % Solvent

Table E-49: Dynamic viscosity and density given as an average value with deviation of crude oil B with 2 wt % naphtha.

Sample: 2 wt % B-Naphtha	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	2060.0	± 3.1	0.9496	± 0.0002
40	5134.9	± 17.2	0.9560	± 0.0001
30	15011	± 47	0.9623	± 0.0001
20	55238	± 53	0.9687	± 0.0000
50	2047.3	± 6.8	0.9497	± 0.0001

Table E-50: Dynamic viscosity and density given as an average value with deviation of crude oil B with 2 wt % toluene.

Sample: 2 wt % B-Toluene	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	1919.1	± 2.4	0.9534	± 0.0003
40	4670.0	± 14.8	0.9598	± 0.0002
30	13361	± 39	0.9661	± 0.0003
20	47936	± 279	0.9724	± 0.0003
50	1903.8	± 3.0	0.9535	± 0.0001

Table E-51: Dynamic viscosity and density given as an average value with deviation of crude oil B with 2 wt % n-hexane.

Sample: 2 wt % B-n-Hexane	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	2003.1	± 24.8	0.9489	± 0.0002
40	4948.6	± 69.1	0.9553	± 0.0002
30	14501	± 182	0.9616	± 0.0002
20	52461	± 1019	0.9680	± 0.0002
50	1995.4	± 24.5	0.9490	± 0.0002

Table E-52: Dynamic viscosity and density given as an average value with deviation of crude oil B with 2 wt % water.

Sample: 2 wt % B-Water	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	4035.4	± 40.4	0.9573	± 0.0002
40	11026	± 154	0.9634	± 0.0003
30	36037	± 729	0.9697	± 0.0005
20	-	-	0.9761	± 0.0004
50	4028.3	± 55.3	0.9566	± 0.0009

Table E-53: Dynamic viscosity and density given as an average value with deviation of crude oil B with 2 wt % MEG.

Sample: 2 wt % B-MEG	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	3864.6	± 22.5	0.9579	± 0.0005
40	10512	± 70	0.9642	± 0.0005
30	34294	± 237	0.9704	± 0.0005
20	-	-	0.9767	± 0.0005
50	3842.8	± 8.7	0.9580	± 0.0005

Table E-54: Dynamic viscosity and density given as an average value with deviation of crude oil B with 2 wt % DEG.

Sample: 2 wt % B-DEG	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	3770.5	± 67.9	0.9576	± 0.0000
40	10187	± 226	0.9638	± 0.0000
30	32899	± 850	0.9701	± 0.0000
20	-	-	0.9764	± 0.0000
50	3745.9	± 80.1	0.9577	± 0.0000

Table E-55: Dynamic viscosity and density given as an average value with deviation of crude oil B with 2 wt % TEG.

Sample: 2 wt % B-TEG	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	3865.5	± 58.0	0.9578	± 0.0001
40	10468	± 192	0.9640	± 0.0002
30	34363	± 772	0.9702	± 0.0002
20	-	-	0.9766	± 0.0002
50	3847.3	± 65.9	0.9578	± 0.0002

Table E-56: Dynamic viscosity and density given as an average value with deviation of crude oil B with 2 wt % 1-hexanol.

Sample: 2 wt % B-1-Hexanol	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	1802.9	± 10.4	0.9523	± 0.0000
40	4294.5	± 17.3	0.9587	± 0.0000
30	11964	± 61	0.9650	± 0.0000
20	41851	± 371	0.9714	± 0.0000
50	1785.6	± 8.0	0.9523	± 0.0000

Table E-57: Dynamic viscosity and density given as an average value with deviation of crude oil B with 2 wt % 2-butanone.

Sample: 2 wt % B-2-Butanone	**Dynamic viscosity [mPa·s]**		**Density [g/cm³]**	
Temp. [°C]	**Average**	**Deviation**	**Average**	**Deviation**
50	1779.2	± 10.6	0.9529	± 0.0004
40	4194.7	± 24.8	0.9593	± 0.0003
30	11646	± 103	0.9658	± 0.0002
20	39904	± 139	0.9723	± 0.0002
50	1771.0	± 15.7	0.9531	± 0.0003

Table E-58: Dynamic viscosity and density given as an average value with deviation of crude oil B with 2 wt % Solvtreat.

Sample: 2 wt % B-Solvtreat	**Dynamic viscosity [mPa·s]**		**Density [g/cm³]**	
Temp. [°C]	**Average**	**Deviation**	**Average**	**Deviation**
50	1769.1	± 6.0	0.9493	± 0.0004
40	4271.2	± 29.8	0.9557	± 0.0003
30	12106	± 63	0.9621	± 0.0003
20	42809	± 257	0.9685	± 0.0003
50	1756.1	± 4.1	0.9495	± 0.0002

Table E-59: Dynamic viscosity and density given as an average value with deviation of crude oil B with 2 wt % chem A.

Sample: 2 wt % B-Chem A	**Dynamic viscosity [mPa·s]**		**Density [g/cm³]**	
Temp. [°C]	**Average**	**Deviation**	**Average**	**Deviation**
50	1995.8	± 4.5	0.9540	± 0.0000
40	4893.3	± 3.3	0.9604	± 0.0000
30	14175	± 22	0.9667	± 0.0000
20	51369	± 43	0.9730	± 0.0000
50	1980.6	± 4.5	0.9540	± 0.0000

Table E-60: Dynamic viscosity and density given as an average value with deviation of crude oil B with 2 wt % chem D.

Sample: 2 wt % B-Chem D	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	2012.4	± 6.9	0.9540	± 0.0000
40	4945.2	± 14.4	0.9603	± 0.0000
30	14366	± 8	0.9666	± 0.0000
20	52461	± 112	0.9730	± 0.0000
50	1999.5	± 6.2	0.9540	± 0.0000

Table E-61: Dynamic viscosity and density given as an average value with deviation of crude oil B with 2 wt % chem E.

Sample: 2 wt % B-Chem E	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
50	1968.1	± 17.6	0.9546	± 0.0007
40	4835.4	± 46.5	0.9609	± 0.0006
30	13837	± 142	0.9672	± 0.0006
20	50257	± 574	0.9735	± 0.0006
50	1952.2	± 19.0	0.9546	± 0.0007

E.3.3 Crude Oil C

The dynamic viscosity and density of crude oil C samples are presented in Table E-62 to Table E-75. The results are given as an average value from two measured parallels with deviation.

Crude Oil C Samples with 2 wt % Solvent

Table E-62: Dynamic viscosity and density given as an average value with deviation of crude oil C.

Sample: Crude oil C	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	4152.4	± 21.7	0.9673	± 0.0001
30	1627.4	± 3.1	0.9608	± 0.0000
40	732.05	± 1.06	0.9542	± 0.0001
30	1623.5	± 4.1	0.9608	± 0.0000
20	4110.7	± 13.8	0.9673	± 0.0000

Table E-63: Dynamic viscosity and density given as an average value with deviation of crude oil C with 2 wt % naphtha.

Sample: 2 wt % C-Naphtha	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	2485.3	± 10.5	0.9615	± 0.0000
30	1040.3	± 2.5	0.9549	± 0.0000
40	491.62	± 0.86	0.9481	± 0.0000
30	1039.1	± 2.4	0.9549	± 0.0000
20	2481.4	± 8.3	0.9615	± 0.0000

Table E-64: Dynamic viscosity and density given as an average value with deviation of crude oil C with 2 wt % toluene.

Sample: 2 wt % C-Toluene	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	2361.3	± 6.1	0.9653	± 0.0002
30	1000.0	± 0.8	0.9587	± 0.0001
40	476.53	± 0.28	0.9519	± 0.0001
30	998.91	± 1.59	0.9587	± 0.0001
20	2362.6	± 4.8	0.9653	± 0.0001

Table E-65: Dynamic viscosity and density given as an average value with deviation of crude oil C with 2 wt % n-hexane.

Sample: 2 wt % C-n-Hexane	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	2222.6	± 16.2	0.9597	± 0.0001
30	944.75	± 4.01	0.9531	± 0.0001
40	451.73	± 1.61	0.9463	± 0.0001
30	943.32	± 5.03	0.9531	± 0.0001
20	2223.2	± 14.6	0.9597	± 0.0001

Table E-66: Dynamic viscosity and density given as an average value with deviation of crude oil C with 2 wt % water.

Sample: 2 wt % C-Water	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	4450.6	± 15.5	0.9676	± 0.0001
30	1735.7	± 7.1	0.9612	± 0.0002
40	780.19	± 5.29	0.9546	± 0.0001
30	1732.9	± 9.1	0.9611	± 0.0002
20	4395.2	± 13.5	0.9676	± 0.0001

Table E-67: Dynamic viscosity and density given as an average value with deviation of crude oil C with 2 wt % MEG.

Sample: 2 wt % C-MEG	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	4340.9	± 17.7	0.9694	± 0.0000
30	1697.3	± 0.3	0.9629	± 0.0000
40	763.96	± 1.08	0.9563	± 0.0000
30	1696.8	± 0.5	0.9630	± 0.0000
20	4284.6	± 13.3	0.9695	± 0.0000

Table E-68: Dynamic viscosity and density given as an average value with deviation of crude oil C with 2 wt % DEG.

Sample: 2 wt % C-DEG	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	4379.6	± 5.8	0.9701	± 0.0001
30	1705.8	± 0.7	0.9636	± 0.0000
40	764.91	± 0.65	0.9570	± 0.0000
30	1700.2	± 0.9	0.9636	± 0.0001
20	4302.3	± 2.1	0.9701	± 0.0000

Table E-69: Dynamic viscosity and density given as an average value with deviation of crude oil C with 2 wt % TEG.

Sample: 2 wt % C-TEG	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	4398.4	± 5.6	0.9702	± 0.0000
30	1714.2	± 0.3	0.9637	± 0.0000
40	767.48	± 0.36	0.9570	± 0.0000
30	1705.6	± 0.8	0.9637	± 0.0000
20	4320.3	± 2.1	0.9702	± 0.0000

Table E-70: Dynamic viscosity and density given as an average value with deviation of crude oil C with 2 wt % 1-hexanol.

Sample: 2 wt % C-1-Hexanol	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	2397.8	± 9.7	0.9637	± 0.0000
30	1005.6	± 1.3	0.9571	± 0.0000
40	476.06	± 0.47	0.9503	± 0.0000
30	1004.5	± 1.7	0.9571	± 0.0000
20	2395.0	± 7.4	0.9637	± 0.0000

Table E-71: Dynamic viscosity and density given as an average value with deviation of crude oil C with 2 wt % 2-butanone.

Sample: 2 wt % C-2-Butanone	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	1943.8	± 0.0	0.9637	± 0.0000
30	846.24	± 1.03	0.9570	± 0.0000
40	412.64	± 0.59	0.9502	± 0.0001
30	845.24	± 0.43	0.9570	± 0.0000
20	1943.6	± 0.5	0.9637	± 0.0000

Table E-72: Dynamic viscosity and density given as an average value with deviation of crude oil C with 2 wt % Solvtreat.

Sample: 2 wt % C-Solvtreat	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	2212.9	± 9.5	0.9613	± 0.0001
30	940.10	± 2.61	0.9547	± 0.0001
40	449.56	± 1.19	0.9479	± 0.0000
30	938.69	± 3.30	0.9547	± 0.0001
20	2214.1	± 9.0	0.9613	± 0.0001

Table E-73: Dynamic viscosity and density given as an average value with deviation of crude oil C with 2 wt % chem A.

Sample: 2 wt % C-Chem A	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	2330.1	± 9.5	0.9650	± 0.0001
30	987.47	± 3.41	0.9584	± 0.0001
40	471.31	± 1.26	0.9516	± 0.0001
30	986.62	± 3.82	0.9584	± 0.0001
20	2329.1	± 11.3	0.9650	± 0.0001

Table E-74: Dynamic viscosity and density given as an average value with deviation of crude oil C with 2 wt % chem D.

Sample: 2 wt % C-Chem D	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	2376.5	± 7.4	0.9647	± 0.0005
30	1005.8	± 0.8	0.9582	± 0.0003
40	479.09	± 0.27	0.9515	± 0.0002
30	1004.7	± 1.4	0.9583	± 0.0002
20	2378.2	± 5.2	0.9649	± 0.0002

Table E-75: Dynamic viscosity and density given as an average value with deviation of crude oil C with 2 wt % chem E.

Sample: 2 wt % C-Chem E	Dynamic viscosity [mPa·s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation
20	2393.1	± 20.3	0.9653	± 0.0001
30	1010.7	± 5.4	0.9587	± 0.0001
40	480.67	± 2.03	0.9519	± 0.0001
30	1009.3	± 6.3	0.9587	± 0.0001
20	2393.9	± 18.1	0.9653	± 0.0001

Appendix F Rheometer

Table F-1 presents the average dynamic viscosity of the clean crude oils and the crude oil samples with 2 wt % hexanol, “A-1-Hexanol”, “B-1-Hexanol” and “C-1-Hexanol”, from the rheometer.
In addition the average dynamic viscosity from the viscometer is given with the deviation between the measured values.

Table F-1: Average dynamic viscosity from rheometer, viscometer and the deviation between the measurements given in percent.

Sample	Temp [°C]	Average Dynamic Viscosity Reometer [mPa·s]	Average Dynamic Viscosity Viscometer [mPa·s]	Deviation [%]
Crude Oil A	20	389.08	345.27	11.26
A-1-Hexanol	20	257.86	260.86	-1.16
Crude Oil B	50	3806.3	3480.0	8.6
B-1-Hexanol	50	1707.7	1802.9	-5.6
Crude Oil C	20	4240.6	4152.4	2.1
C-1-Hexanol	20	2431.4	2397.8	1.4

Figure F-1 presents the dynamic viscosity of the clean crude oils and the crude oil samples with 2 wt % hexanol, “A-1-Hexanol”, “B-1-Hexanol” and “C-1-Hexanol”, versus the shear rate. The dynamic viscosity remains unchanged with increased shear for all the samples.

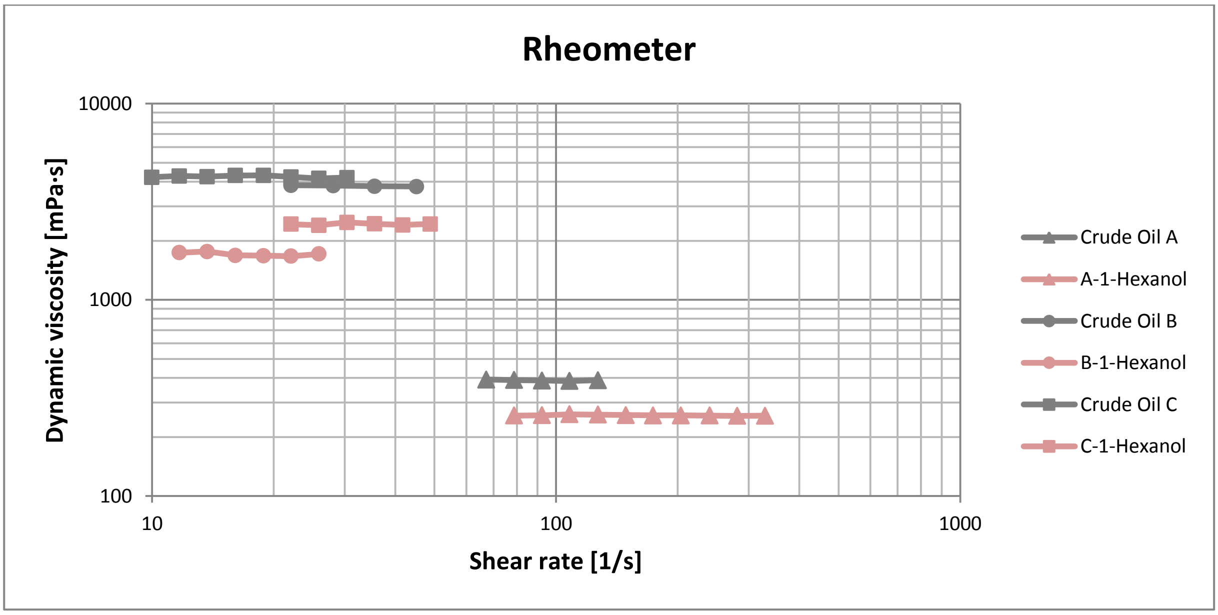


Figure F-1: Dynamic viscosity [mPa·s] of the clean crude oils and three blended samples versus shear rate [1/s].

Appendix G Near Infrared Spectroscopy

The average optical density and deviation from three parallels of all blended samples of crude oil A, B and C are presented in Table G-1, Table G-2 and Table G-3.

Table G-1: Samples from crude oil A given with average optical density and deviation at 1600 nm.

Sample	Average Optical Density	Deviation Optical Density
Crude oil A	0.3057	± 0.0001
A- Naphta	0.3022	± 0.0043
A-Toluene	0.3027	± 0.0003
A-n-Hexane	0.3013	± 0.0018
A-Water	1.384	± 0.002
A-MEG	0.9648	± 0.0007
A-DEG	0.7701	± 0.0008
A-TEG	0.6521	± 0.0003
A-1-Hexanol	0.3190	± 0.0002
A-2-Butanone	0.3081	± 0.0004
A-Solvtreat	0.3048	± 0.0004
A-Chem A	0.2717	± 0.0015
A-Chem D	0.2547	± 0.0005
A-Chem E	0.2629	± 0.0009

Table G-2: Samples from crude oil B given with average optical density and deviation at 1600 nm.

Sample	Average Optical Density	Deviation Optical Density
Crude oil B	1.298	± 0.014
B- Naphta	1.239	± 0.003
B-Toluene	1.267	± 0.001
B-n-Hexane	1.235	± 0.007
B-Water	1.630	± 0.011
B-MEG	1.234	± 0.002
B-DEG	1.234	± 0.004
B-TEG	1.274	± 0.002
B-1-Hexanol	1.271	± 0.008
B-2-Butanone	1.268	± 0.006
B-Solvtreat	1.246	± 0.002
B-Chem A	1.245	± 0.002
B-Chem D	1.212	± 0.001
B-Chem E	1.247	± 0.002

Table G-3: Samples from crude oil C given with average optical density and deviation at 1600 nm.

Sample	Average Optical Density	Deviation Optical Density
Crude oil C	1.053	± 0.007
C- Naphtha	1.022	± 0.004
C-Toluene	1.043	± 0.002
C-n-Hexane	1.052	± 0.007
C-Water	1.247	± 0.002
C-MEG	0.9396	± 0.0046
C-DEG	1.062	± 0.006
C-TEG	1.038	± 0.001
C-1-Hexanol	0.9357	± 0.0056
C-2-Butanone	1.034	± 0.009
C-Solvtreat	1.053	± 0.003
C-Chem A	1.002	± 0.002
C-Chem D	0.9980	± 0.0047
C-Chem E	1.063	± 0.005

Appendix H Nuclear Magnetic Resonance Spectroscopy

An excerpt of crude oil A with 2 wt % solvent were analysed with the NMR spectroscopy. The average T_2 relaxation time with deviation from three parallels is given in an overview in Table H-1. All tested samples have a higher T_2 relaxation time than the clean crude oil.

Table H-1: Average T_2 relaxation time with deviation.

Sample	Average T_2 Relaxation Time [ms]	Deviation T_2 Relaxation Time [ms]
Crude oil A	14.3	± 0.2
A- Naphta	17.2	± 0.0
A-Toluene	17.5	± 0.1
A-n-Hexane	18.1	± 0.3
A-Water	15.9	± 0.1
A-MEG	15.0	± 0.1
A-MEG*	15.6	± 0.1
A-DEG	14.5	± 0.1
A-DEG*	15.1	± 0.1
A-TEG	14.6	± 0.2
A-TEG*	15.4	± 0.1
A-1-Hexanol	16.7	± 0.0
A-2-Butanone	18.3	± 0.1

The result from the T_2 relaxation analyses are presented in Figure H-1 and Figure H-2. The results of the total signals are normalised in all Figures. In Figure H-1 the samples have more or less the same shape on the curves. "A-Toluene" represents the highest signal while the "A-Water" curve has a second peak at a later relaxation time.

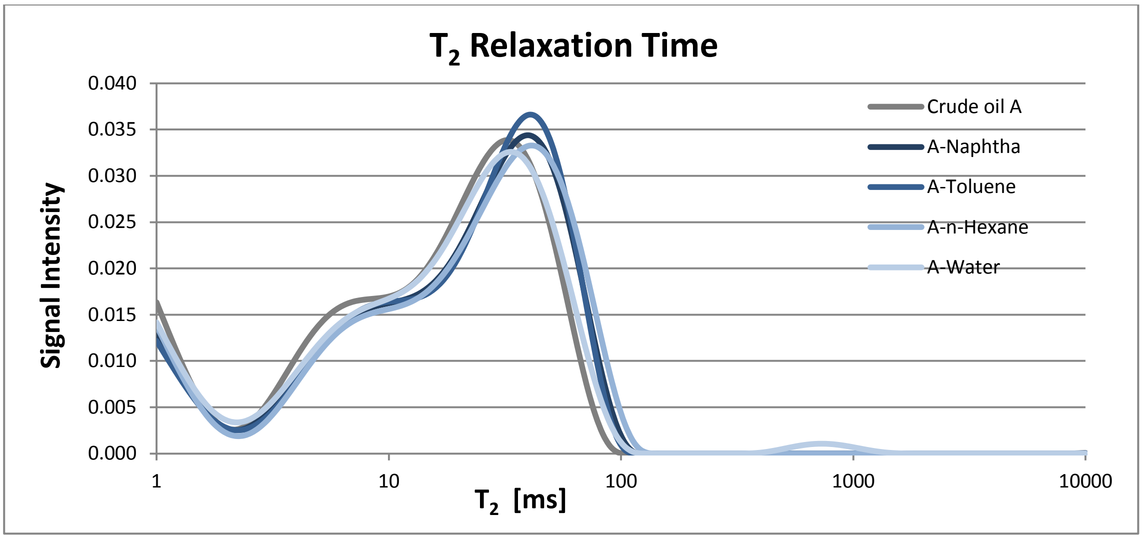


Figure H-1: Crude oil A and blends of oil A with 2 wt % reference solvent measured with NMR spectroscopy.

In Figure H-2 the samples have more or less the same shape on the curves. “A-Butanone” represents the lowest signal in the beginning and the highest signal on its peak compared to the other samples. The samples “A-MEG”, “A-DEG” and “A-TEG” have a curve with a second signal at a later relaxation time.

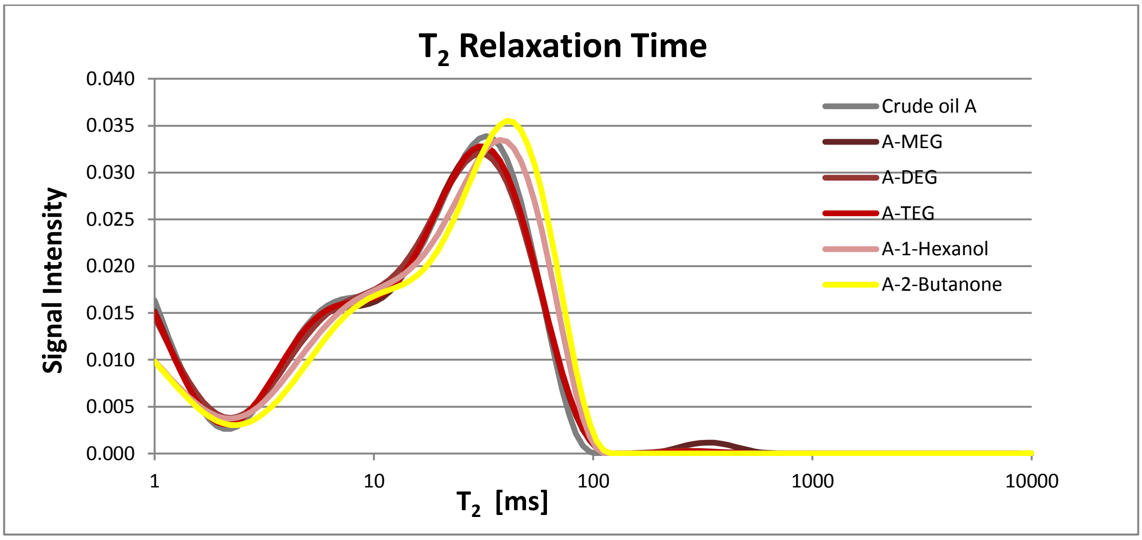


Figure H-2: Crude oil A and blends of oil A with 2 wt % active group solvents measured with NMR spectroscopy.

The samples with glycols and water are presented in Table H-2. In addition the samples with glycols are presented after been treated for 66 hours. The table gives the location of the second peak represented with the relaxation time interval and the peaks size in proportion compared to the total curve areal.

Table H-2: An excerpt of samples with a curve with a second signal. The second peak is given with its T_2 relaxation time interval and proportion compared to the total curve areal in vol %.

Sample	T_2 [ms]	Proportion [vol %]
A-Water	330.9 - 1754	1.1
A-MEG	172.3 - 734.8	1.1
A-MEG*	160.2 - 511.3	0.7
A-DEG	138.6 - 683.4	0.3
A-DEG*	-	0.0
A-TEG	149.0 - 591.1	0.2
A-TEG*	-	0.0

A selection of the samples showing curves with a second peak are presented separately in Figure H-3 to Figure H-9. The results of the total signals are normalised in all Figures. In addition the samples with glycols are measured a second time after been treated for 66 hours. The secondary peak of the curve from sample “A-Water” has a lower T_2 relaxation time than the pure water.

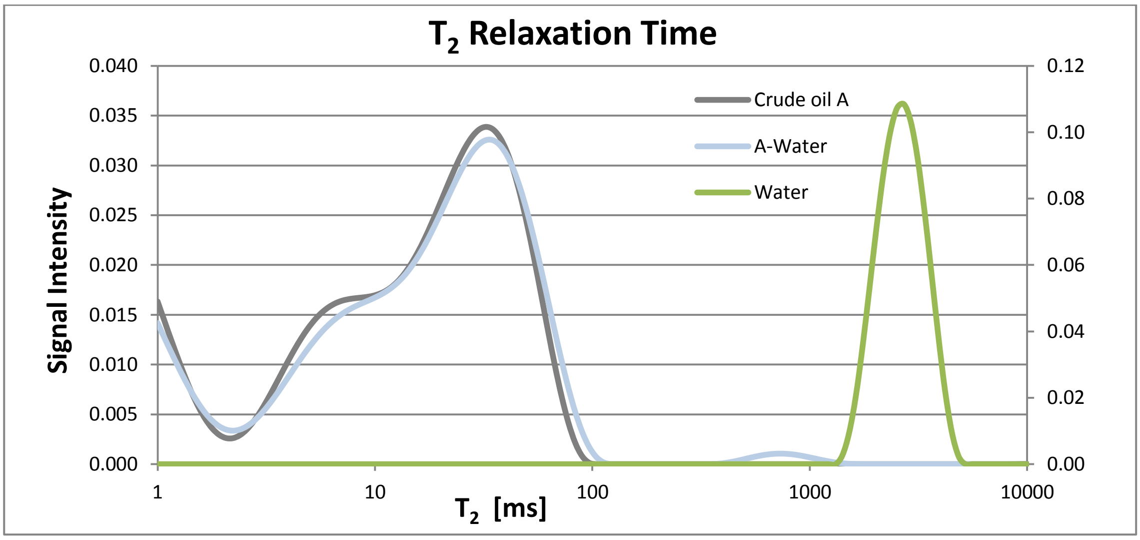


Figure H-3: Sample “A-Water” presented with the clean crude oil and clean water measured with NMR spectroscopy. The pure water is presented with a secondary axis.

The secondary peak of the curve from sample “A-MEG” has more or less the same T_2 relaxation time as the pure MEG.

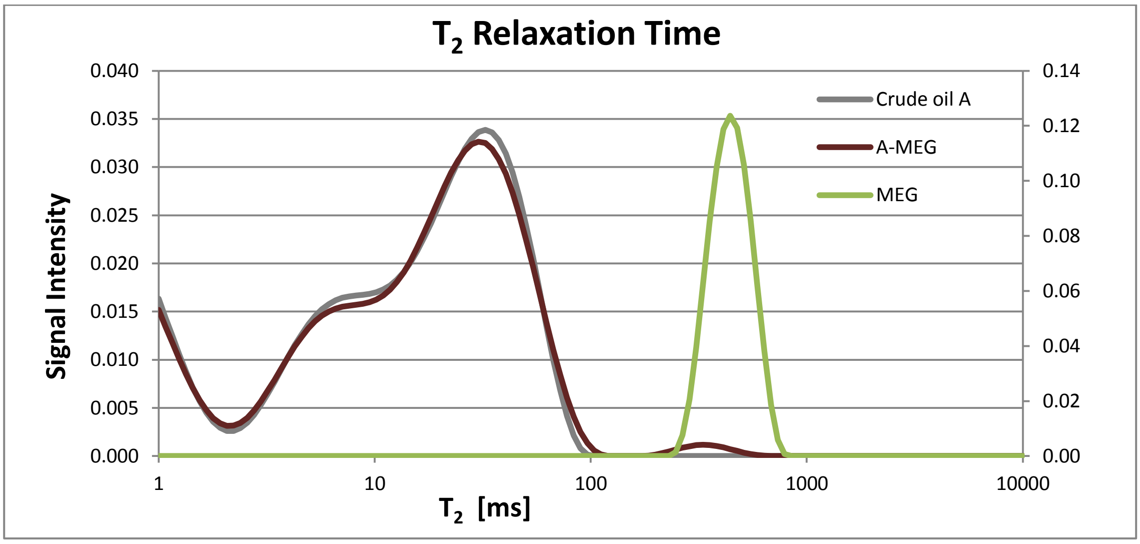


Figure H-4: Sample “A-MEG” presented with the clean crude oil and clean MEG measured with NMR spectroscopy. The pure MEG is presented with a secondary axis.

There is still a secondary signal of the curve from sample “A-MEG*” after been treated in 66 hours. The secondary peak of the curve from sample “A-MEG*” has more or less the same T_2 relaxation time as the pure MEG.

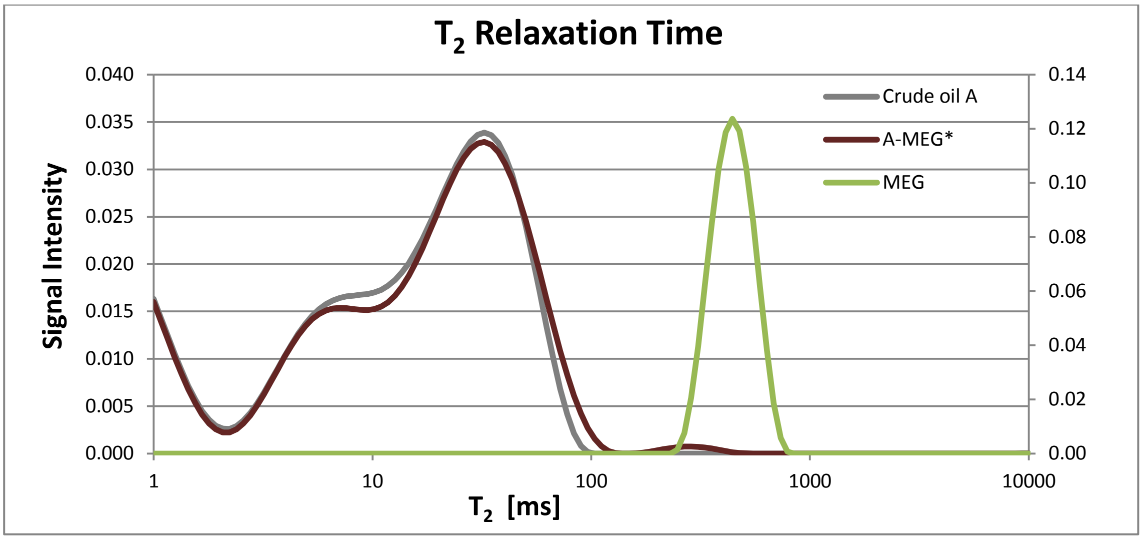


Figure H-5: Sample “A-MEG*” presented with the clean crude oil and clean MEG measured with NMR spectroscopy. The pure MEG is presented with a secondary axis.

The secondary peak of the curve from sample “A-DEG” has more or less the same T_2 relaxation time as the pure DEG.

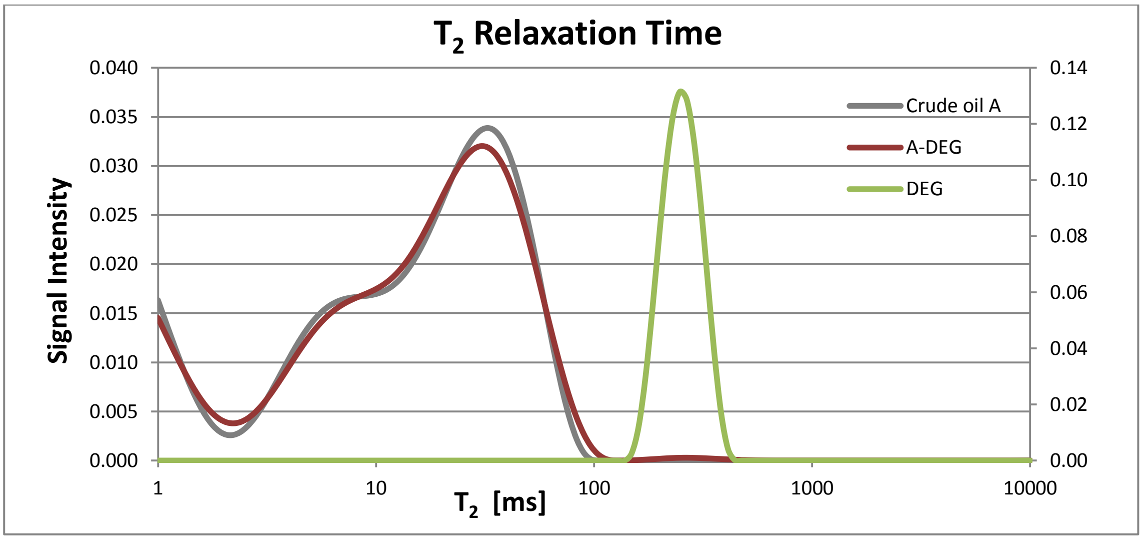


Figure H-6: Sample “A-DEG” presented with the clean crude oil and clean DEG measured with NMR spectroscopy. The pure DEG is presented with a secondary axis.

There is no detectable secondary signal of the curve from sample “A-DEG*” after been treated in 66 hours.

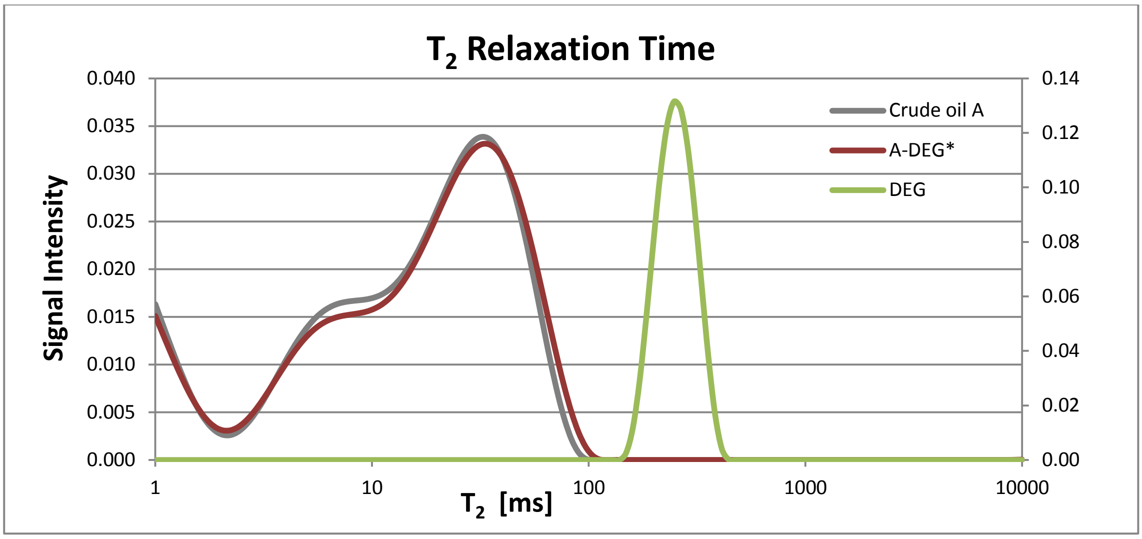


Figure H-7 Sample “A-DEG*” presented with the clean crude oil and clean TEG measured with NMR spectroscopy. The pure DEG is presented with a secondary axis.

The secondary peak of the curve from sample “A-TEG” has more or less the same T_2 relaxation time as the pure TEG.

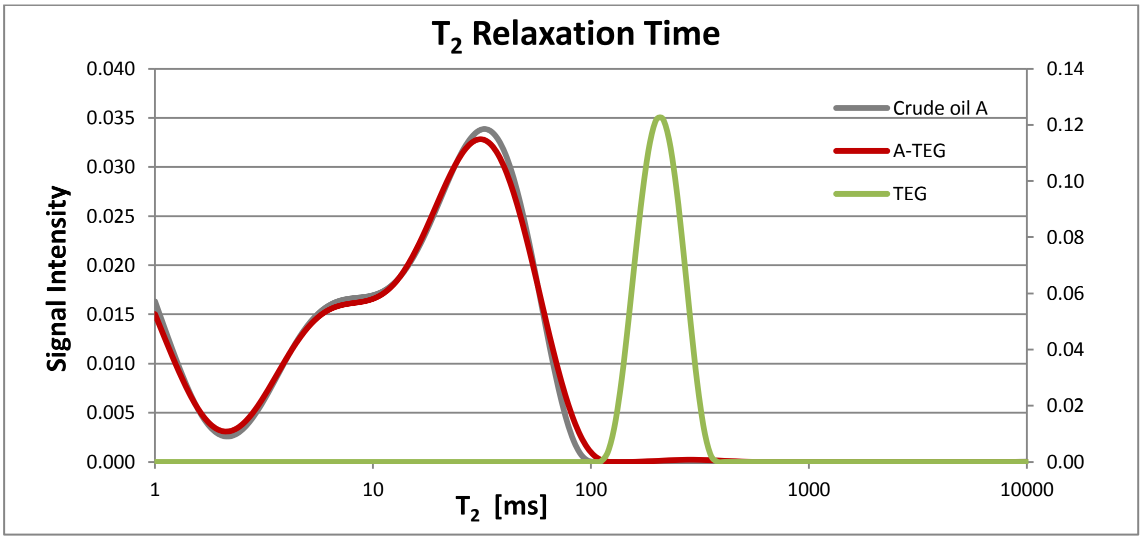


Figure H-8: Sample “A-TEG” presented with the clean crude oil and clean TEG measured with NMR spectroscopy. The pure TEG is presented with a secondary axis.

There is no detectable secondary signal of the curve from sample “A-TEG*” after been treated in 66 hours.

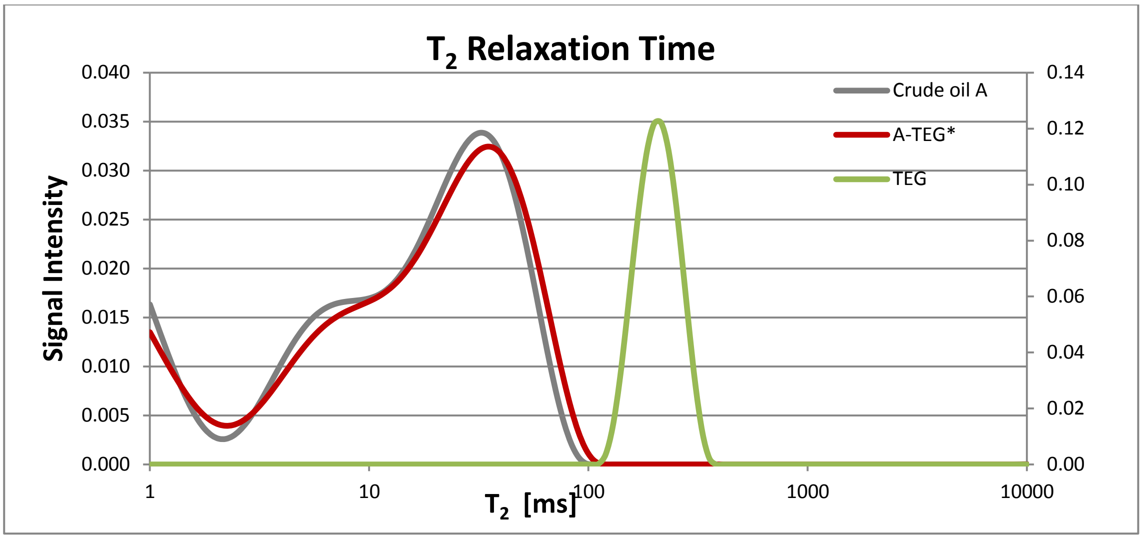


Figure H-9: Sample “A-TEG*” presented with the clean crude oil and clean TEG measured with NMR spectroscopy. The pure TEG is presented with a secondary axis.

Appendix I Standard Oils

I.1 Viscometer

Two standards oils, APN 26 and APN 415, with stated values were measured at the viscometer. The average dynamic viscosity, kinematic viscosity and density with deviation from two parallels are given in Table I-1 and Table I-2. The stated values (collared grey) for viscosity are only given with four significant numbers while the instrument is operating with five significant numbers.

Table I-1: Theoretical and measured average value for viscosity and density of the APN 26 standard oil. The deviation is given between the stated value and the measured average value.

Sample: APN 26	Dynamic Viscosity [mPa·s]		Kinematic Viscosity [mm²/s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation	Average	Deviation
20	50.33		61.35		0.8203	
20	50.276	± 0.03	61.327	± 0.01	0.8199	± 0.0002
25	39.88		48.81		0.8171	
25	39.903	± 0.01	48.860	± 0.02	0.8167	± 0.0002
40	21.54		26.67		0.8077	
40	21.544	± 0.00	26.687	± 0.1	0.8073	± 0.0002
60	11.07		13.92		0.7952	
60	11.072	± 0.00	13.931	± 0.01	0.7948	± 0.0002

Table I-2: Theoretical and measured average value for viscosity and density of the APN 415 standard oil. The deviation is given between the stated value and the measured average value.

Sample: APN 415	Dynamic Viscosity [mPa·s]		Kinematic Viscosity [mm²/s]		Density [g/cm³]	
Temp. [°C]	Average	Deviation	Average	Deviation	Average	Deviation
20	1122		1326		0.8460	
20	1123.5	± 1	1328.8	± 1	0.8455	± 0.0002
25	804.9		954.8		0.8430	
25	806.73	± 0.9	957.53	± 1.4	0.8425	± 0.0002
40	332.7		398.9		0.8341	
40	333.91	± 0.6	400.59	± 0.8	0.8336	± 0.0003
60	127.4		155.0		0.8222	
60	127.78	± 0.2	155.51	± 0.3	0.8217	± 0.0003

I.2 Near Infrared Spectroscopy

Spectrums of standards used to detect deviations in the NIR instrument are presented in Figure I-1.

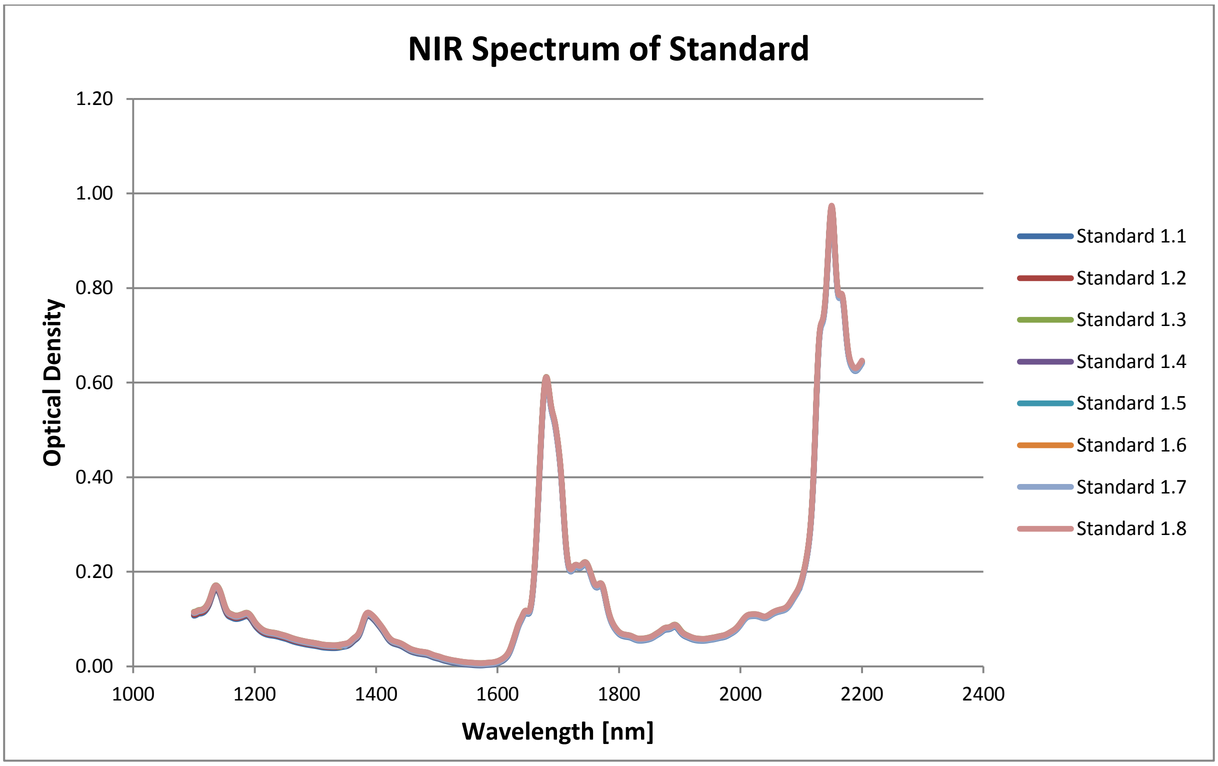


Figure I-1: Spectrum of standards presented with optical density in range 0-1.20 and wavelength between 1100-2200 nm.

Table I-3 presented standards with average optical density and deviation from three parallels at 1600 nm.

Table I-3: Average optical density and deviation of Standards at 1600 nm.

Standard	Average Optical Density	Deviation Optical Density
Standard 1.1	0.006527	± 0.000065
Standard 1.2	0.007957	± 0.000337
Standard 1.3	0.01118	± 0.00019
Standard 1.4	0.009747	± 0.001349
Standard 1.5	0.009863	± 0.000513
Standard 1.6	0.01045	± 0.00026
Standard 1.7	0.008233	± 0.000325
Standard 1.8	0.01119	± 0.00013