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Emulsions (w/o and o/w) of Heavy
Crude Oils.
Characterization, Stabilization,
Destabilization and Produced
Water Quality

Thesis for the degree of philosophiae doctor

Trondheim, November 2008

Norwegian University of
Science and Technology
Faculty of Natural Science and Technology
Department of Chemical Engineering



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PREFACE

This thesis is submitted for fulfillment of the PhD degree at the Norwegian University of Science and Technology (NTNU) and is based on experimental work performed at the Ugelstad Laboratory at the Department of Chemical Engineering in the period September 2004 to September 2008. The work was supervised by Professor Johan Sjöblom.

I received my BSc in Chemical Engineering in June 2002 at Sør-Trøndelag University College. In 2004 I received my MSc in the field of surface, colloid and polymere chemistry on the subject “a study of the relationship between viscosity and emulsion stability for heavy crude oils” at the Ugelstad Laboratory (Department of Chemical Engineering, NTNU).

This study has been two folded within the scope of a Joint Industrial Program JIP1 on Particle Stabilized Emulsions/Heavy Crude Oils, financed by the industry, and within the scope of the project Treatment of Produced Water financed by Norwegian Research Council, through the Petromaks program, and several industry partners. The thesis consists of five papers or manuscripts.

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First of all, I would like to thank Professor Johan Sjöblom for the opportunity to do my PhD at the Ugelstad Laboratory, for excellent supervision and for all his effort in establishing a modern and well-equipped laboratory within the field of colloid and surface chemistry.

The participants in the JIP 1 consortium consisting of StatoilHydro, ABB, British Petroleum, Shell, Total, Mærsk, Champion Technologies, Chevron, ENI, Petrobras, Vetco Gray, Aibel and Aker Kværner have contributed considerably through their sponsorship and useful discussions. Thanks to Norwegian Research Council, through the Petromaks program, and several industry partners: StatoilHydro, Shell Technology Norway AS, Total E&P Norge AS, ChevronTexaco Energy Technology Company, Aibel, Champion Technology and DNV as a part of the Treatment of Produced Water project.

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And finally, a warm thank to my family, and in particular my daughter Filippa and my husband Are. It would not have been possible for me to complete this thesis without you.

LOVE YOU ♥

ABSTRACT

Water is invariably produced with crude oil. If there is high pressure and enough shear forces when crude oil and produced water flow through the production path, stable emulsions may be formed. This scenario may particularly be present during the production of heavy oils where steam is used to reduce the viscosity of heavy oil or in cases where submersible pumps are used to artificially lift the produced fluids. To efficiently design and operate heavy oil production systems, knowledge about properties that will influence the formation of emulsions and destabilization mechanisms of emulsions systems is necessary. If the water is not removed from the crude oil it will lead to quality problem and economical losses. On the other side knowledge about produced water characteristics is important to help operators increase production, but knowledge about the impacts of discharging produced water in marine environment is important as well. Produced water is mainly salty water trapped in the reservoir rock and brought up along with oil or gas during production. It can contain very minor amounts of chemicals added downhole during production. These waters exist under high pressures and temperatures, and usually contain oil and metals. Because of this, they must be treated prior to being discharged.

This work was developed within the aims of the projects “Particle Stabilized Emulsions/Heavy Crude Oils” and “Treatment of Produced Water”, and has been two folded with an attempt to investigate both emulsions of heavy crude oils and the produced water issue to see how different crude oil properties will influence on the quality of produced water. A matrix of thirty different crude oils has been used in this study. The influence of viscosity, temperature and dilution on the emulsion stability was investigated in Paper 1. Paper 2 investigates the stability of water/crude oil systems correlated to the physicochemical properties of the oil phase, and summarizes the characterization of thirty crude oil systems with respect to bulk properties, interfacial properties, spectroscopic signatures, and emulsion stability. The experimental results were compared to a simplified theoretical model which described the destabilization process by taking drag forces and dielectrophoretic forces into account. In addition to highlighting previous results and discussing these based on recent experience, new results are presented in Paper 3. The focus in Paper 3 is on viscous responses and their influence on the emulsion stability measurements in the laboratory coalescer. A new semi-empirical model which explains the experimental findings is presented. The model

accounts for varying water cuts, magnitudes of the electrical field, and a broad range of oil viscosities, both for different crude oils and for oils at different temperatures. Paper 4 aims to achieve a better understanding of stability and flow properties of w/o emulsions investigating both a heavy crude oil and a waxy crude oil. The motivation for this work was to get a better understanding of emulsion transport of hydrate particles. The presence of paraffin wax in crude oil and gas condensate fluid is known to cause significant flow assurance problems related to wax deposit buildup and gel formation. In the last paper, Paper 5, knowledge from the characterization studies of the different crude oils have been used to see if there is any relationship between the crude oil properties and the quality of the produced water, investigated by means of transmission profiles from Turbiscan LAb measurements. Correlations were made by using multivariate data analysis.

LIST OF PUBLICATIONS

Paper 1

“Emulsions of Heavy Crude Oils. I. Influence of Viscosity, Temperature and Dilution”

Pål V. Hemmingsen, Anne Silset, Andreas Hannisdal, Johan Sjöblom

Journal of Dispersion Science and Technology, 26(5), 615-628, 2005

Paper 2

“Stability of Water/Crude Oil Systems Correlated to the Physicochemical Properties of the Oil Phase”

Andreas Hannisdal, Pål V. Hemmingsen, Anne Silset, Johan Sjöblom

Journal of Dispersion Science and Technology, (2007), 28(4), 639-652

Paper 3

“Emulsions of Heavy Crude Oils. II. Viscous Responses and Their Influence on Emulsion Stability Measurements”

Anne Silset, Andreas Hannisdal, Pål V. Hemmingsen, Johan Sjöblom

Paper 4

“Characterization of the formation, flowability, and resolution of Brazilian crude oil emulsions”

Kristofer Paso, Anne Silset, Geir Sørland, Marcelo Goncalves, Johan Sjöblom

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Paper 5

“A Multivariate Analysis on the influence of indigenous crude oil components on the quality of produced water. Comparison between bench and rig scale experiments”

Anne Silset, Geir Rune Flåten, Herman Helness, Esa Melin, Gisle Øye and Johan Sjöblom

ADDITIONAL PUBLICATIONS

“Plasmachemical Modifications of Asphaltenes”

Gisle Øye, Anne Silset, Magne Knag, Bodhild Øvrevoll, Johan Sjöblom

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“Quartz Crystal Microbalance Monitoring of Asphaltene Adsorption/Desorption”

Dorota Dudasova, Anne Silset, Johan Sjöblom

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”Stability Mechanisms of Crude Oil Emulsions – A Review” (oral presentation by P.V.H)

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2006

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1. INTRODUCTION TO CRUDE OIL AND PETROLEUM PROCESSING

1.1 History

The oil history began over five thousand years ago. In the Middle East, oil seeping up through the ground was used in waterproofing boats and baskets, in paints, lighting and even for medication [1]. The modern petroleum history began in the later years of the 1850s with the discovery, in 1857, and subsequent commercialization of petroleum in Pennsylvania in 1859 [2]. The first oil well structures in open waters were built in the Gulf of Mexico. They were constructed from a piled jacket formation, in which a framed template had piles driven through it to pin the structure to the sea bed at water depths of up to 100 m. A support frame was added for the working parts of the rig such as the deck and accommodation. These structures were the fore-runners for the massive platforms that now stand in very deep water and in many locations around the world. There have been land oil wells in Europe since 1920s. It was not until the 1960s the exploration in the North Sea really began, without success in the early years. They finally struck oil in 1969 and have been discovering new fields ever since. The subsequent development of the North Sea is one of the greatest investment projects in the world [1].

Petroleum is the most important substance consumed in modern society. It provides not only raw materials for the ubiquitous plastics and other products, but also fuel for energy, industry, heating, and transportation. The word petroleum, derived from the Latin *petra* and *oleum*, means literally rock oil and refers to hydrocarbons that occur widely in the sedimentary rocks in the form of gases, liquids, semisolids, or solids. From a chemical standpoint, petroleum is an extremely complex mixture of hydrocarbon compounds, usually with minor amounts of nitrogen-, oxygen-, and sulfur-containing compounds as well as trace amounts of metal-containing compounds [3].

The fuels that are derived from petroleum supply more than half of the world's total supply of energy. Gasoline, kerosene, and diesel oil provide fuel for automobiles, tractors, trucks, aircraft, and ships. Fuel oil and natural gas are used to heat homes and commercial buildings,

as well as to generate electricity. Petroleum products are the basic materials used for the manufacture or synthetic fibers for clothing and in plastics, paints, fertilizers, insecticides, soaps, and synthetic rubber. The use of petroleum as a source of raw material in manufacturing is central to the functioning of modern industry [3]. Figure 1.1 shows the distribution of proved reserves of crude oil in 2007. Proved reserves of oil are generally taken to be those quantities that geological and engineering information indicates with reasonable certainty can be recovered in the future from known reservoirs under existing economic and geological conditions [4].

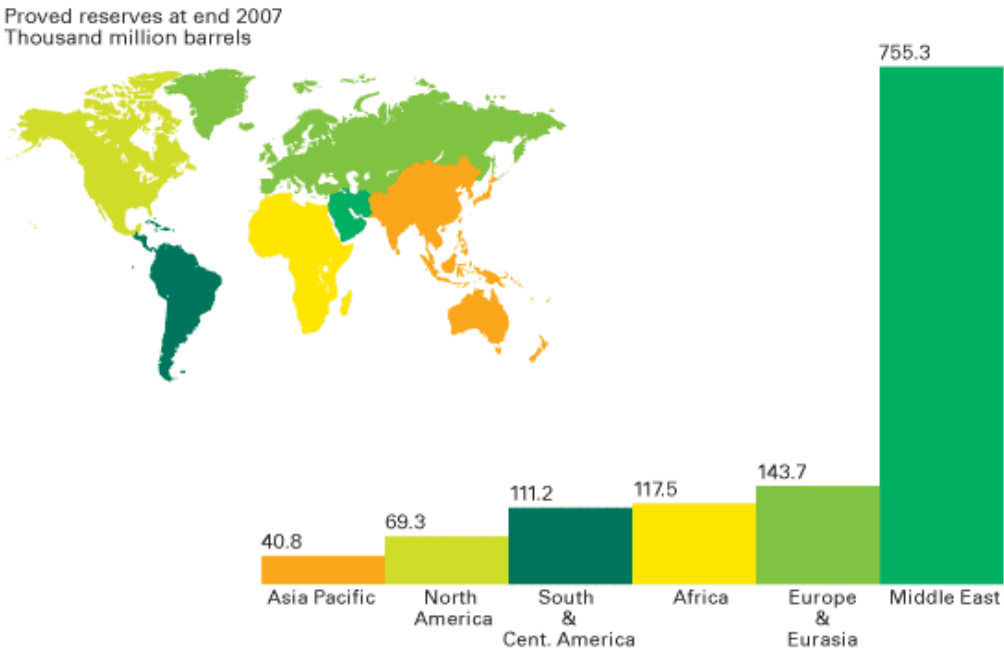


Figure 1.1: Colour coded map of the world and associated bar chart, showing proved oil reserves at end 2007 in thousand million barrels. The Middle East has the greatest proved oil reserves at 755.3 thousand million barrels. This is followed by Europe and Eurasia, with 143.7 thousand million barrels, Africa (117.5), South and Central America (111.2), North America (69.3) and finally Asia Pacific with 40.8 thousand million barrels [4].

1.2 Origin

Two schools of thought exist about the origin of petroleum: an Eastern school suggesting that its origin is biogenic resulting from the decay of organic biological matter and stored in sedimentary basins near the Earth’s surface, and a Ukrainian-Russian school proposing that it is abiogenic with inorganic origin deep within the Earth’s crust dating back to the creation of Earth [5, 6]. The two theories have been intensely debated since the 1860s, shortly after the

discovery of widespread occurrence of petroleum. The idea of abiogenic petroleum origin proposes that large amounts of carbon exist naturally in the planet, some in the form of hydrocarbons. Hydrocarbons are less dense than aqueous pore fluids, and migrate upward through deep fracture networks. From the idea of biogenetic origin petroleum is a naturally occurring hydrocarbon mixture, but hydrocarbons that are synthesized by living organisms usually account for less than 20% of the petroleum [7]. The remainder of the hydrocarbons in petroleum is produced by a variety of processes generally referred to as diagenesis, catagenesis, and metagenesis. These three processes are a combination of bacteriological action and low-temperature reactions that convert the source material into petroleum. During these processes, migration of the liquid products from the source sediment to the reservoir rock may also occur. The biogenic origin of petroleum is a mainstream theory adopted by the majority of petroleum reservoir engineers, geologists and scientists. It is supported by field observations, laboratory experiments and basin models used to explain known economic occurrence of natural gas, crude oil and asphalt [3].

Hydrocarbons and their associated impurities occur in rock formations that are usually buried thousands of feet below the surface. These reservoir rocks must possess fluid-holding capacity (porosity) and also fluid-transmitting capacity (permeability). A variety of different types of openings in rocks are responsible for these properties in reservoir rocks (figure 1.2). Petroleum migrates to a pool or field, displacing the water, in which the oil or gas occupies pore space in the rock. A hydrocarbon reservoir has a distinctive shape, or configuration, that prevents the escape of hydrocarbons that migrate into it.

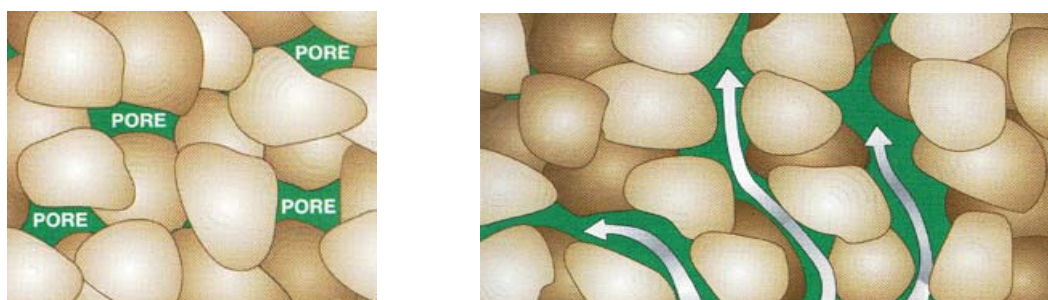


Figure 1.2: The figure shows pores as small open spaces on the left hand side and connected pores that give good rock permeability on the right hand side [8].

These reservoir shapes, or traps, can be classified into two types: structural traps and stratigraphic traps. Structural traps form because of a deformation in the rock layer that contains the hydrocarbons. Two examples of structural traps are fault traps and anticlinal

traps (figure 1.3). Strategic traps form when other beds seal a reservoir bed or when the permeability changes within the reservoir bed itself [3, 8].

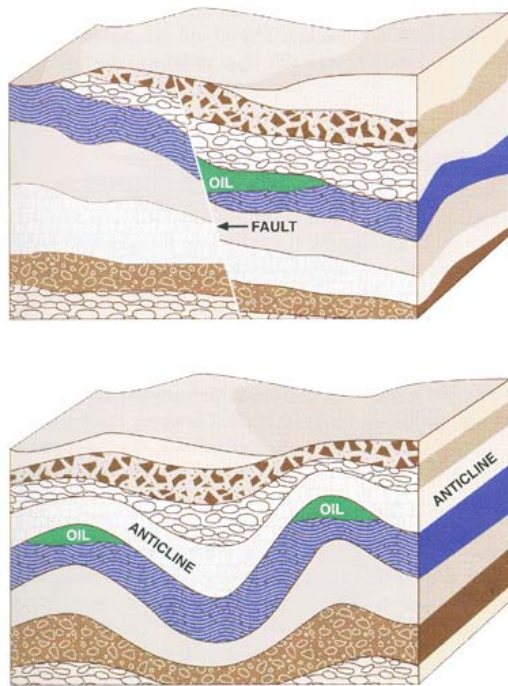


Figure 1.3: Two typical petroleum traps: fault trap and anticline trap. The lightest compounds (gas) is on the top, while oil, and water if present, is found further down in the formation leading to gas, oil and water zones [8].

1.3 Crude oil

Crude oil is the name given to all organic compounds which are liquid under reservoir conditions. They can partly solidify at the surface after expansion and cooling [9, 10]. Crude oil is not a uniform material with a simple molecular formula. It is a complex mixture of gaseous, liquid, and solid hydrocarbon compounds, occurring in sedimentary rock deposits throughout the world. The composition of the mixture depends on its location. Two adjacent wells may produce quite different crudes and even within a well the composition may vary significantly with depth. Nevertheless, the elemental composition of crude oil varies over a rather narrow range [11]:

C	83.0-87.0	wt.%	O	0.05-1.5	wt.%
H	10.0-14.0	wt.%	S	0.05-6.0	wt.%
N	0.1-2.0	wt.%	Metals	<0.01	wt.%

Although at first sight these variations seem small, but the various crude oils are extremely different. The high fraction of C and H suggests that crude oil consists of hydrocarbons, which indeed has been proven to be the case. From detailed analysis it appears that crude oil contains alkanes, cycloalkanes (naphthenes), aromatics, polycyclic aromatics, sulfur-containing compounds, nitrogen-containing compounds, oxygen-containing compounds, etc. The larger part of crude oil consists of alkanes, cycloalkanes, and aromatics. Both linear and branched alkanes are present. In gasoline applications the linear alkanes are much less valuable than the branched alkanes, whereas in diesel fuel the linear alkanes are desirable. Cycloalkanes are often called naphthenes. Aromatics have favorable properties for the gasoline pool. However, currently their adverse health effects are receiving increasing attention. The most important binuclear aromatic is naphthalene. The heavier the crude the more polycyclic aromatic compounds it contains. Heavy crudes render less useful products. The amount of sulfur may at first sight seem low. However, its presence in petroleum fractions has many consequences for the processing of these fractions. The presence of sulfur is highly undesirable, because it leads to corrosion, poisons catalysts, and is environmentally harmful. The nitrogen content of crude oil is lower than the sulfur content. Nevertheless, nitrogen compounds deserve attention because they disturb major catalytic processes. The oxygen content of crude oil is usually low, and oxygen occurs in many different compounds. A distinction can be made between acidic and non-acidic compounds. Organic acids and phenols belong to the class of acids. Metals are present in crude oil only in small amounts. Even so, their occurrence is of considerable interest, because they deposit on and thus deactivate catalysts for upgrading and converting oil products. Part of the metals is present in the water phase of crude oil emulsions and may be removed by physical techniques. The other part is presented in oil-soluble organometallic compounds and can only be removed by catalytic processes. Most of the metal-containing compounds are present in the heavy residue of the crude oil. The metal contents vary widely and the most abundant metals are nickel, iron, and vanadium [11].

1.4 Recovery

The first stage in extraction of crude oil is to drill a well into the underground reservoir. Often many wells are drilled into the same reservoir, to ensure that the extraction rate is economically viable (figure 1.4). In addition, some wells (secondary wells) may be used to

pump water, steam, acids or various gas mixtures into the reservoir to raise or maintain the reservoir pressure, and so maintain an economic extraction rate. If the underground pressure in the oil reservoir is sufficient, the oil will be forced to the surface under this pressure (primary recovery). Natural gas is often present, which also supplies needed underground pressure (primary recovery). In this situation, it is sufficient to place an arrangement of valves (the Christmas tree) on the well head to connect the well to a pipeline network for storage and processing. Over the lifetime of the well the pressure will fall, and at some point there will be insufficient underground pressure to force the oil to the surface. Secondary oil recovery uses various techniques to aid in recovering oil from depleted or low-pressure reservoirs. Sometimes pumps, such as beam pumps and electrical submersible pumps are used to bring the oil to the surface. Other secondary recovery techniques increase the reservoir pressure by water injection, natural gas reinjection and gas lift, which inject air, carbon dioxide, or some other gas into the reservoir [3].

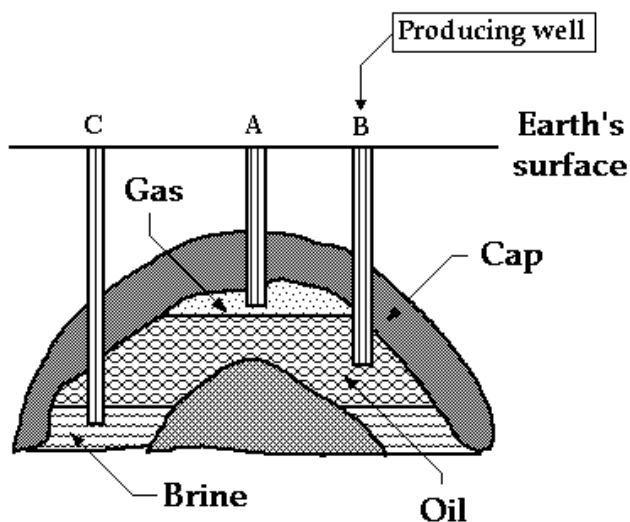


Figure 1.4: The oil and gas are found in so called reservoir rock, sealed by a non-penetrable cap. The lightest compounds (gas) is on top, while oil, and water if present, is found further down in the formation leading to gas, oil and water zones [12].

Enhanced oil recovery (EOR, tertiary oil recovery) relies on methods that reduce the viscosity of the oil to increase. Tertiary recovery is started when secondary oil recovery techniques are no longer enough to sustain production. For example, thermally enhanced oil recovery methods are those in which the oil is heated, making it easier to extract; usually steam is used for heating the oil. The viscosity (or the API gravity) of petroleum is an important factor that must be taken into account when heavy oil is recovered from a reservoir. In fact, certain

reservoir types, such as those with very viscous crude oils and some low-permeability carbonate (limestone, dolomite, or chert) reservoirs, respond poorly to conventional secondary recovery techniques. A significant amount of laboratory research and field testing has been devoted to developing enhanced oil recovery methods as well as defining the requirements for a successful recovery and the limitations of the various methods [3]. The quality of the well product and separation of oil and water will be discussed more in detail in chapter 2.

1.5 Transportation

Most oil fields are at a considerable distance from the refineries that convert crude oil into usable products, and therefore the oil must be transported in pipelines and tankers (figure 1.5). This gives possibilities for changes in temperature, pressure and composition during transportation. Flow assurance of the multiphase system is of therefore of great importance, both from an economical and environmental point of view.



Figure 1.5: Figure to the left shows typical tiebacks from wellhead to the platform. For successful transport of produced fluids knowledge about “flow assurance” is important [13]. Figure to the right shows oil pipeline in Saudi Arabia [14].

However, most crude oils need some form of treatment near the reservoir before it can be carried considerable distances through the pipelines or in tankers. Fluids produced from a well are seldom pure crude oil. In fact, the oil often contains quantities of gas, saltwater, or even sand. Separation must be achieved before transportation. Separation and cleaning usually take place at a central facility that collects the oil produced from several wells. Another step that needs to be taken in the preparation of crude oil for transportation is the removal of excessive

quantities of water. Crude oil at the wellhead usually contains emulsified water in proportions that may reach 80% to 90%. It is generally required that crude oil to be transported by pipeline contain substantially less water than may appear in the crude at the wellhead. In fact, water contents from 0.5% to 2.0% have been specified as the maximum tolerable amount in a crude oil to be moved by pipeline. It is therefore necessary to remove the excess water from the crude oil before transportation [3, 15-17].

Flow assurance (the successful transportation of produced fluids in long pipelines in a harsh environment) is a major hurdle for technical and economic success in deep water. The challenge is to move the produced oil, gas, and water from wells located at the bottom of the sea floor to platforms located in more shallow water. The fluids are subjected to cold ocean temperatures and large pressure changes that may cause them to be unstable and thereby create problems (figure 1.6) [13].

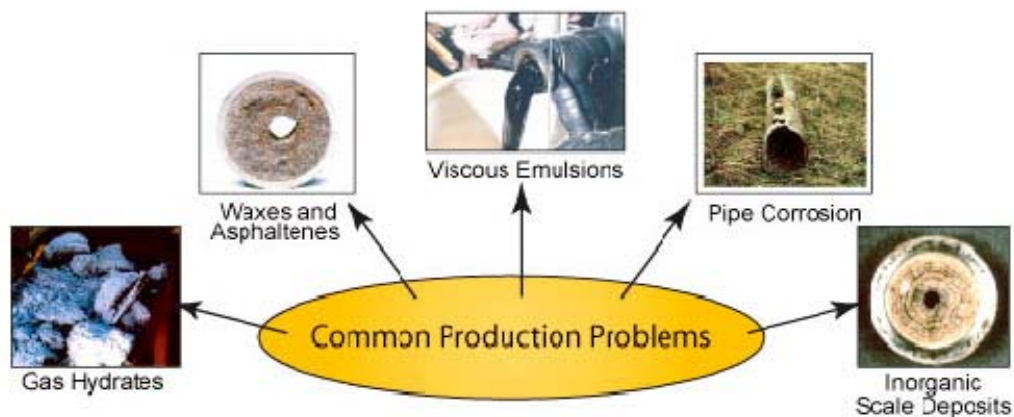


Figure 1.6: The figure illustrates expensive production problems caused by fluid chemistry during production of crude oil [13].

1.6 Refining

Crude oil is rarely used in its raw form but must be processed into its various products, generally as a means of forming petroleum products with hydrogen content different from that of the original feedstock such as gasoline, diesel fuel, asphalt base, heating oil, kerosene, and liquefied petroleum gas. Crude oil is separated into fractions by fractional distillation. The fractions at the top of the fractionating column have lower boiling points than the fractions at

the bottom. The heavy bottom fractions are often cracked into lighter, more useful products. All of the fractions are processed further in other refining units (figure 1.7) [3, 11].

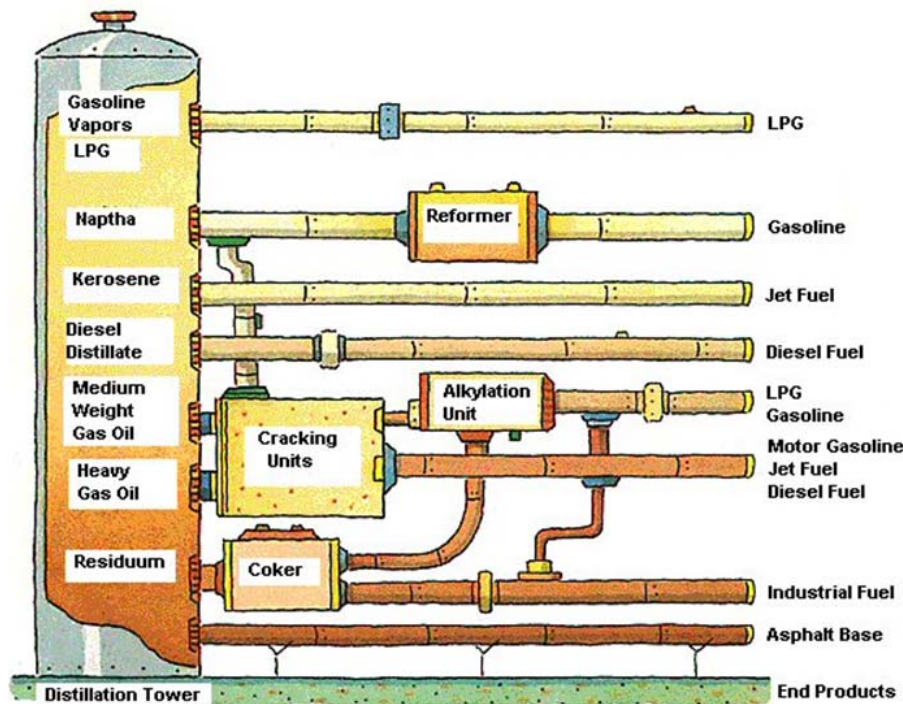


Figure 1.7: Representation of a distillation tower showing many of a refinery's many important processes [18].

Each refinery has its own range of preferred crude oil feedstock from which a desired distribution of products is obtained. Figure 1.8 shows the relative placement of different processes within the refinery. According to Speight [3], refinery processes can be divided into three major types:

Separation: division of crude oil into various streams (or fractions) depending on the nature of the crude material.

Conversion: production of saleable materials from crude oil, usually by skeletal alteration, or even by alteration of the chemical type of the crude oil constituents.

Finishing: purification of various product streams by a variety of processes that accomplish molecular alteration, such as reforming.

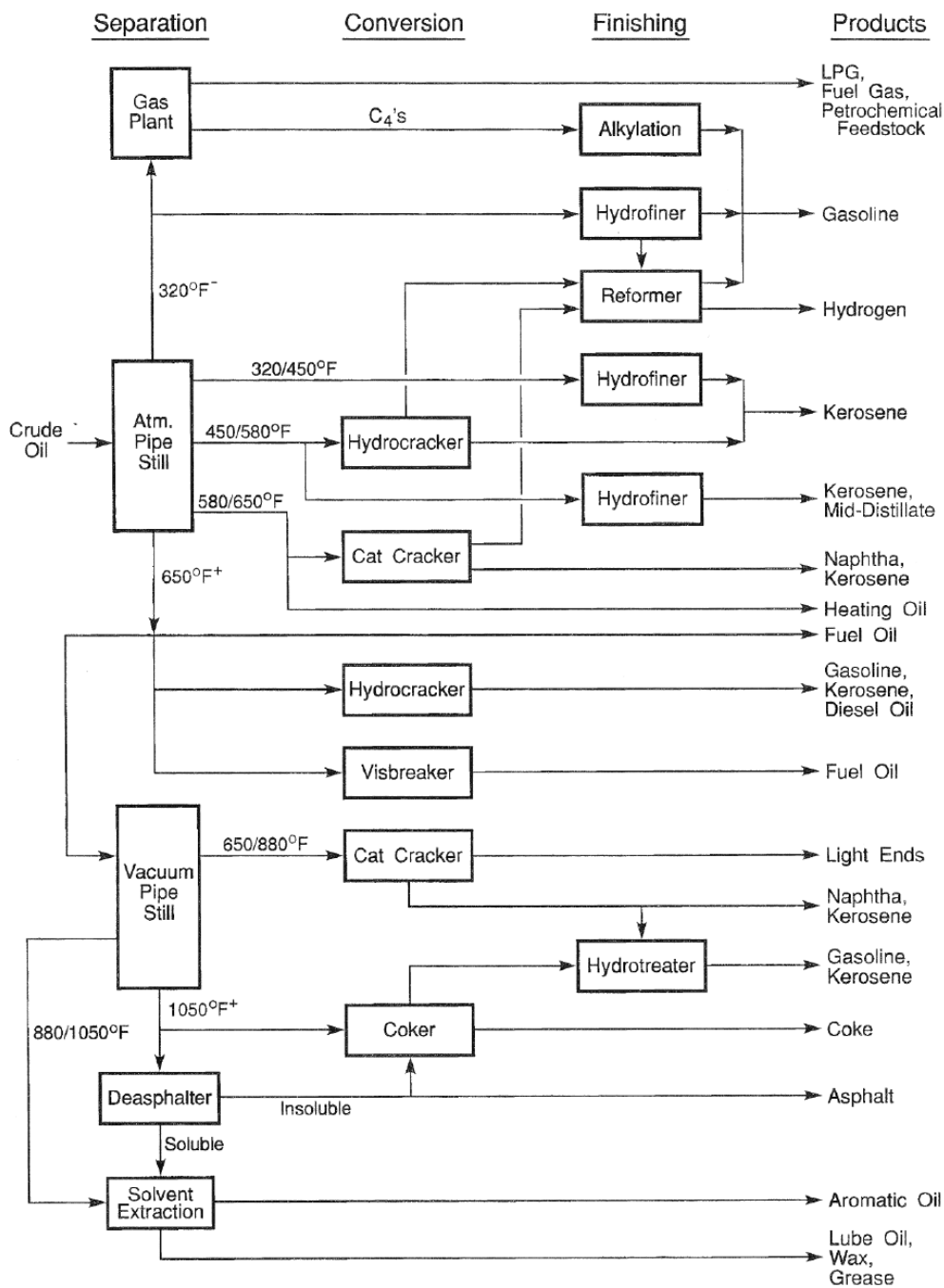


Figure 1.8: Flow scheme of the relative placement of unit operations in a refinery [3].

1.7 Challenges

The problems encountered in production of petroleum are highly dependent on the properties of the processed fluids and the reservoir rock. In some parts of the world, operators face challenges due to high wax content, in other parts due to asphaltenes, sulfur, co-produced

reservoir material etc. Problems can be found in all stages of operation. Problems can be due to rheological properties of the fluids, deposition and plugging, erosion, corrosion, catalyst poisoning, emulsion formation etc.

Precipitation and/or deposition of organic or inorganic material at pipe walls, in reservoirs or in equipment like heat exchangers, hydrocyclones etc can cause serious problems with respect to flow conditions and efficiency of the process. Type of solids encountered during petroleum production can be: waxes, asphaltenes, hydrates, diamondoids, scales, calcium naphthenate, sulfur, and many more. The temperature in deep water, usually near 40°F (4.4°C), can create flow problems in risers and export pipelines. In the next sections problems related to wax, asphaltenes and naphthenates are discussed in more detail.

1.7.1 Wax

Wax deposition in pipelines and risers is an ongoing challenge to operators, and can have a significant effect on oil production efficiency. Build-up in pipelines can cause increased pressure drops, resulting in reduced throughput and thus reduced revenue. In more extreme cases, pipelines/processing facilities can plug, halting production and leading to potentially huge losses in earnings.

The wax present in petroleum crudes primarily consists of paraffin hydrocarbons (C18 - C36) known as paraffin wax and naphthenic hydrocarbons (C30 - C60). Hydrocarbon components of wax can exist in various states of matter (gas, liquid or solid) depending on their temperature and pressure. When the wax freezes it forms crystals, and crystals from paraffin wax are known as macrocrystalline wax. Those formed from naphthenes are known as microcrystalline wax. As the clean waxy crude flows through a cold pipe or conduit (with a wall temperature below the cloud point of the crude) crystals of wax may be formed on the wall. Wax crystals could then grow in size until the whole inner wall is covered with the possibility of encapsulating oil inside the wax layers. As the wax thickness increases, pressure drop across the pipe needs to be increased to maintain a constant flow rate. As a result, the power requirement for the crude transport will increase. The arterial blockage problems of clean waxy crude can be efficiently controlled by insulation and heating of the pipe to a temperature above its cloud point. Most of the existing wax deposition problems of the clean

waxy crudes are due to the lack of proper insulation and heating systems. As a result application of chemical anti-foulants and frequent use of pigging operation have become necessary. Regular paraffinic or waxy crudes are widespread in the world and the major complex systems problems related to the production, processing, and transportation of these medium-gravity fluids is not just crystallization of their wax content at low temperatures, but the formation of deposits which do not disappear upon heating and will not be completely removed by pigging (figure 1.9) [3, 9, 10, 19, 20].



Figure 1.9: Pigging to remove wax from a subsea transfer line. Pigging devices fit the diameter of the pipe and scrape the pipe wall as they are pumped through the pipe [20].

1.7.2 Asphaltenes

Some crude oils contain large amounts of asphaltenes, which can destabilize due to large pressure drops, temperature changes, shear (turbulent flow), solution carbon dioxide (CO_2) or other changes in oil composition. Asphaltene deposition can present a major flow assurance challenge. Deposition can occur in various parts of the production system including well tubing, surface flow lines and even near the wellbore (figure 1.10). Crude oils that are susceptible to pressure-induced asphaltene precipitation are generally highly undersaturated; that is, the subsurface formation pressure is much higher than the bubble point. The crude oil can experience a large pressure drop without evolving gas. Once gas evolves, the light alkane fraction of the liquid phase is reduced, thus increasing the solvating power of the oil, thereby stabilizing asphaltenes.



Figure 1.10: Asphaltene deposition in a pipeline [20].

Particles, even in small amounts, can also cause huge problems for separation of water-in-oil emulsions as they gradually concentrate in the interfacial layer in separators. Speight [3] has viewed the effect of asphaltenes and resin constituents on recovery and refining processes. Asphaltene deposition and fouling of flowlines/facilities can greatly reduce productivity and increase operational costs through the requirement for frequent chemical treatment and removal of deposits [3, 9, 10, 20, 21].

1.7.3 Naphthenate

Deposition of metal naphthenates in process facilities is from an operational point of view one of the most serious issues related to the production of acidic crudes. The problem arises from pressure drop and degassing of carbon dioxide during the transport of the fluids from the reservoir to the topside, leading to dissociation of naphthenic acids at the interface between the crude and the co-produced water. Consequently, the naphthenic acids may react with metal cations in the water to form naphthenates. These electrochemically neutral compounds might then start to agglomerate in the oil phase, normally in combination with inorganic materials, and further adhere and accumulate to process unit surfaces. This may lead to costly shutdown periods during which the deposits have to be removed. Metal naphthenate deposition in topside facilities is becoming a common problem in a number of fields where acidic crudes are being processed. Calcium naphthenate deposits in a separator are illustrated in figure 1.11 [9, 10, 22-28].



Figure 1.11: Calcium naphthenate build-up in separator [29].

StatoilHydro researchers and operational staff have worked intensively with chemical suppliers to find ways of preventing and treating the problem. For many years, the accepted view was that calcium naphthenate deposition resulted from a reaction between natural naphthenic acids in the oil and calcium ions in the formation water. This still holds true. But nobody was able to identify which naphthenic acids are active in the process, quantify them, and unravel their elusive molecular structure. However, in the summer of 2002 ConocoPhillips and StatoilHydro made a decisive breakthrough from a study of advanced analytical data. Although initially confidential, both partners have now agreed to publish their findings. The crucial revelation hinges on the identification of a new family of naphthenic acids with molecular weights three times higher (1227 to 1235 g/mol) than the average molecular weight of naphthenic acids in crude oil (430 g/mol). The ARN acid family (as it is called) is also unique in the sense that the acids are four-protonic, whereas the other acids encountered in Heidrun crudes (which constitute over 99.99 per cent of the total) are mono-protonic [23]. The structure of ARN was refined by Ugelstad Laboratory in 2006 (figure 1.12) [30].

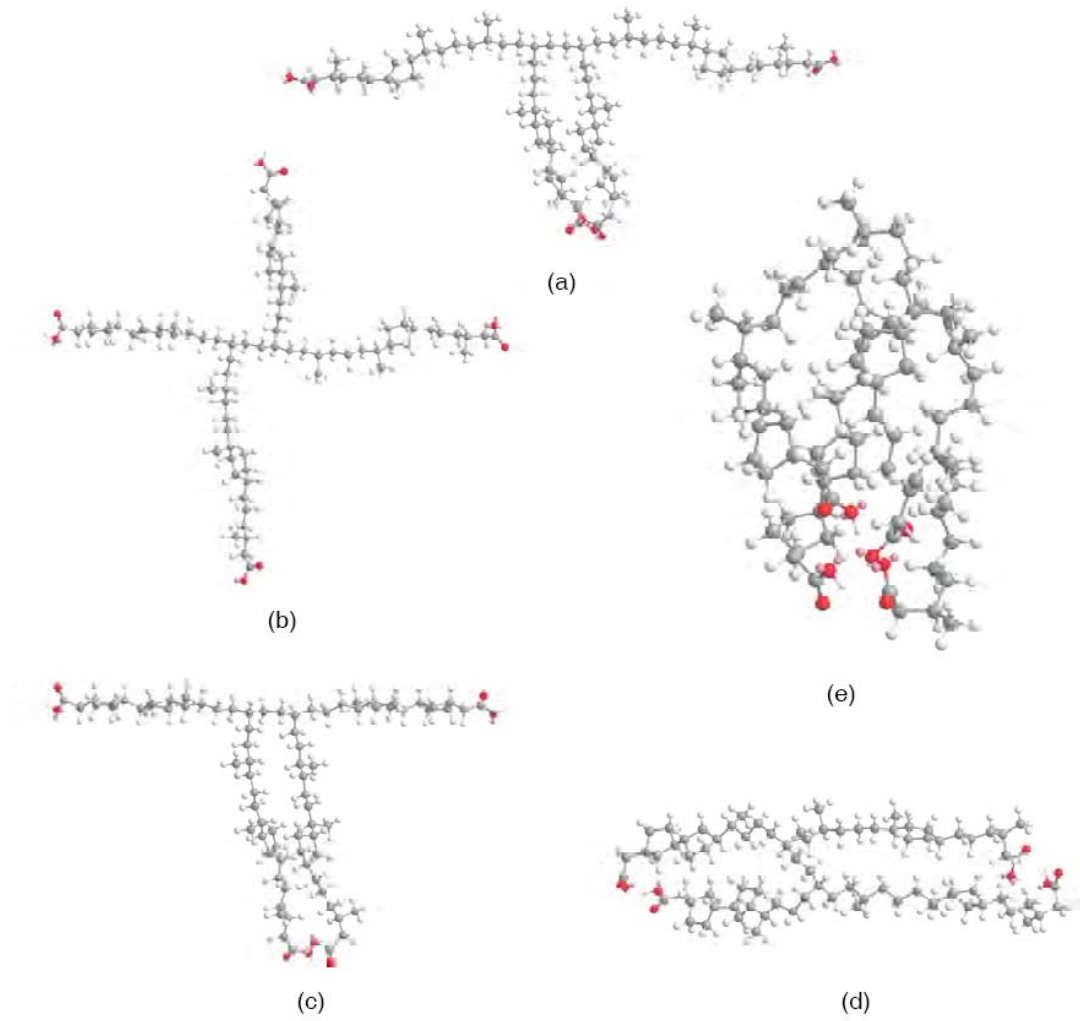


Figure 1.12: The structure of ARN (C80 tetraacids) responsible for naphthenate deposition problems refined by Ugelstad Laboratory in 2006 [30].

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2. HEAVY CRUDE OILS AND EMULSION STABILITY

2.1 Heavy crude oils

Crude oils are often divided into conventional crude oils, heavy crude oils, and extra heavy crude oils. Specific gravity (SG) has been, since the early years of the industry, the principal specification of crude oil products [1]. The American Petroleum Institute (API) gravity is of more common use (figure 2.1). It refers to density at 60°F (15.6°C) and its relationship with specific gravity is given by:

$$^{\circ}\text{API} = (141.5/\text{SG}) - 131.5 \tag{2.1}$$

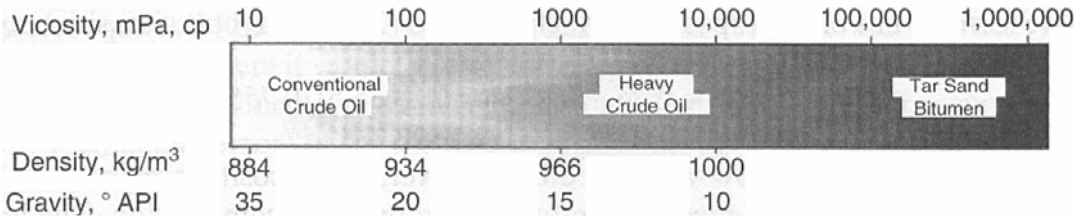


Figure 2.1: Classification of petroleum by °API gravity and viscosity [1].

The hydrocarbon value hierarchy is shown as a graph of monetary value versus American Institute of Petroleum (API) gravity (figure 2.2). Note that high °API values characterise light hydrogen-rich deposits, while low °API cover heavy, carbon-rich deposits such as heavy oil. These range from carbon-rich deposits, such as coal and heavy oil, to hydrogen-rich accumulations like natural gas and natural gas liquids (NGL) [2-4].

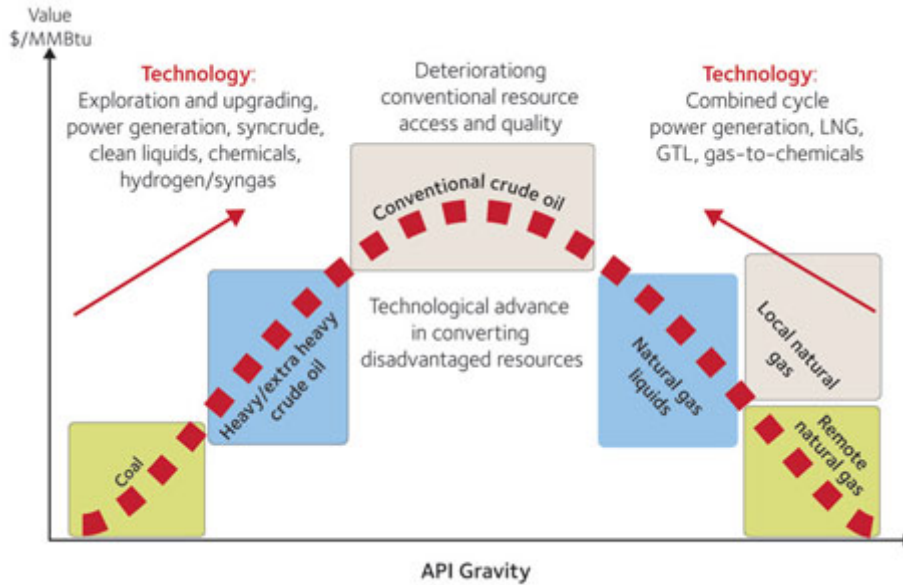


Figure 2.2: The graph shows monetary value vs API gravity. Vast quantities of relatively underdeveloped energy resources remain in the ground [2].

Classifying heavy crude oils on the basis of gravity is useful for the refining industry, because the API gravity correlates with fundamental refining value drivers. However density itself is not usually the biggest problem in oil production processes, where viscosity is by far more important. Heavy oils have much higher viscosity (and lower API gravity) than conventional petroleum, and primary recovery of these petroleum types usually requires thermal stimulation of the reservoir. The generic term heavy oil is often applied to a crude oil that has less than 20°API and usually, but not always, sulfur content higher than 2% by weight. Further, in contrast to conventional crude oils, heavy crude oils are darker in color and may even be black [1].

2.2 SARA

Due to the complex composition of crude oils, characterisation by the individual molecular types is not possible, and elemental analysis is ineffective because it gives only limited information about the constitution of petroleum due to the constancy of elemental composition. Instead, hydrocarbon group type analysis is commonly employed [5]. The SARA fractionation is an example of such group type analysis, separating the crude oils in four main chemical classes based on differences in solubility and polarity. The four SARA

fractions are saturates (S), aromatics (A), resins (R), and the asphaltenes (A). Figure 2.3 shows the SARA group type fractionation, as described by Aske et al. [5, 6].

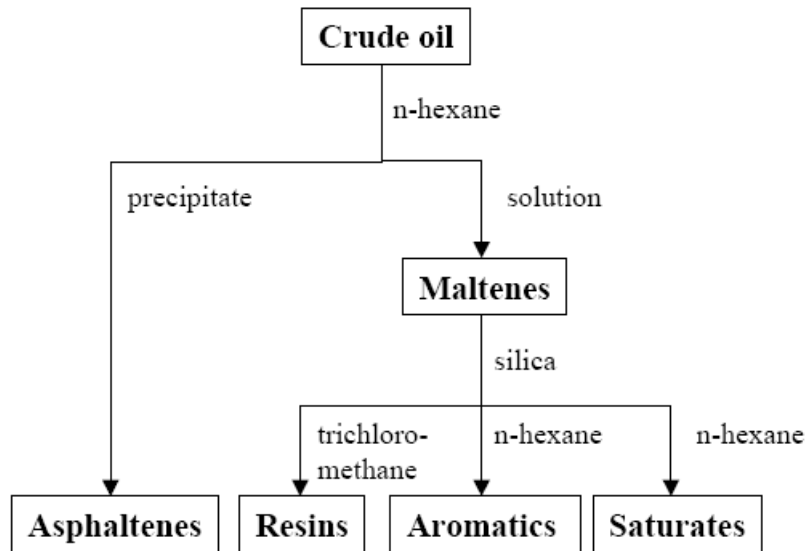


Figure 2.3: SARA fractionation scheme [6].

Saturates (aliphatics) are non-polar hydrocarbons, without double bonds, but including straight-chain and branched alkanes, as well as cycloalkanes (naphtenes). Cycloalkanes contain one or more rings, which may have several alkyl side chains. The proportion of saturates in a crude oil normally decreases with increasing molecular weight fractions, thus saturates generally are the lightest fraction of the crude oil. Wax is a sub-class of saturates, consisting primarily of straight-chain alkanes, mainly ranging from C₂₀ to C₃₀. Wax precipitates as a particulate solid at low temperatures, and is known to effect emulsion stability properties of crude oil systems [5, 6].

The term **aromatics** refer to benzene and its structural derivates. Aromatics are common to all petroleum, and by far the majority of the aromatics contain alkyl chains and cycloalkane rings, along with additional aromatic rings. Aromatics are often classified as mono-, di-, and tri-aromatics depending on the number of aromatic rings present in the molecule. Polar, higher molecular weight aromatics may fall in the resin or asphaltene fraction [5, 6].

The **resin** fraction is comprised of polar molecules often containing heteroatoms such as nitrogen, oxygen or sulphur. The resin fraction is operationally defined, and one common definition of resins is as the fraction soluble in light alkanes such as pentane and heptane, but insoluble in liquid propane [5]. Since the resins are defined as a solubility class, overlap both to the aromatic and the asphaltene fraction is expected. Resins have a higher H/C ratio (1.2-1.7) than asphaltenes (0.9-1.2) [6, 7], and the resins are structurally similar to asphaltenes, but lower in molecular weight (< 1000 g/mole). Naphthenic acids are commonly regarded as a part of the resin fraction [7].

The **asphaltene** fraction, like the resins, is defined as a solubility class, namely the fraction of the crude oil precipitating in light alkanes like pentane, hexane or heptane. This precipitate is soluble in aromatic solvents like toluene and benzene. The molecular nature of the non-volatile fractions of petroleum has been the subject of numerous investigations [1], but determining the actual structures of the constituents of the asphaltene fraction has proven to be difficult. It is the complexity of the asphaltene fraction that has hindered the formulation of the individual molecular structures. Nevertheless, various investigations have brought to light some significant facts about asphaltene structure. There are indications that asphaltenes consist of condensed aromatic nuclei that carry alkyl and alicyclic systems with heteroelements (N, O and S) and organometallic constituents (Ni, V, Fe) scattered throughout in various, including heterocyclic locations (figure 2.4 and 2.5). Since the asphaltenes have a great tendency to self-associate the literature is full of different molecular weights reported. Depending on type of solvent and physic conditions, molecular weights are reported in the range from about 1000 to 18000 g/mol and more [5, 8, 9]. Lately, mean molecular weights of approximately 750 g/mol have been reported, which are believed to be a good estimate of the asphaltene monomer molecular weight [7].

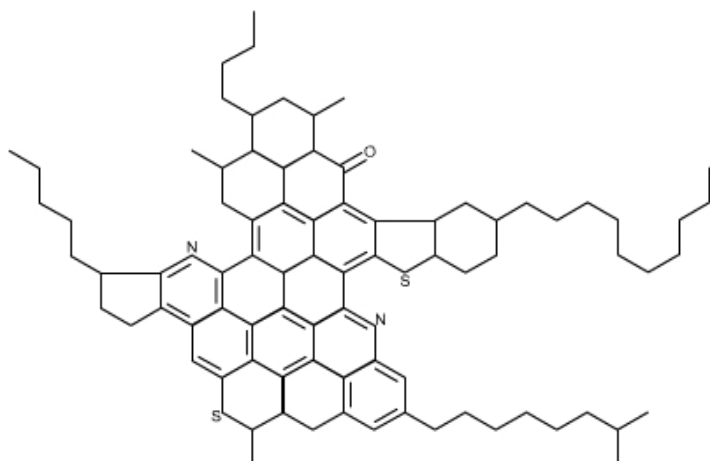


Figure 2.4: The figure shows a hypothetical asphaltene molecule [8].

Other basic generalizations have also been noted: with increasing molecular weight of the asphaltene fraction, both aromaticity and the proportion of heteroelements increase [10-12]. In addition, the proportion of asphaltenes in petroleum varies with source, depth of burial, the specific (or API) gravity of the crude oil, and the sulfurcontent of the crude oil as well as nonasphaltene sulfur [10]. However, many facts of asphaltene structure remain unknown.

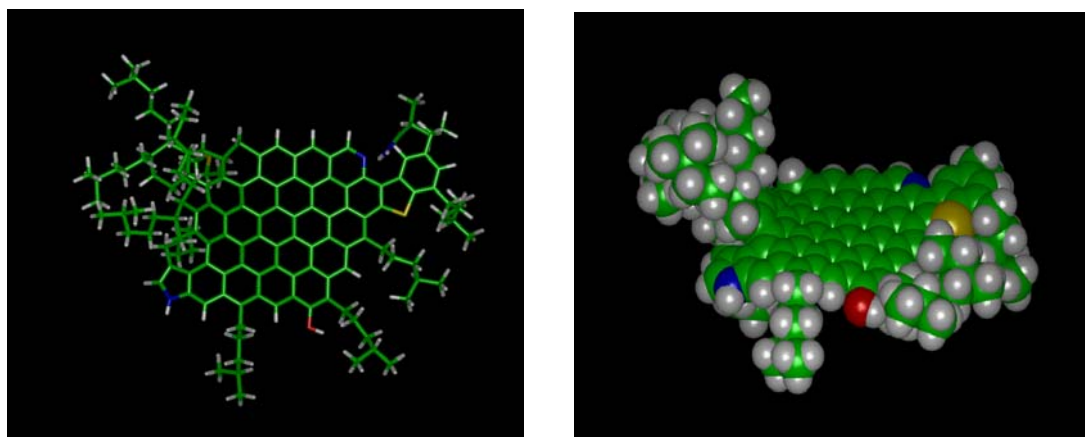


Figure 2.5: 3D picture of Carboznanis model of Venezuelan crude asphaltene molecule [13].

2.3 Emulsions and stabilizing mechanisms

An emulsion is a mixture of two immiscible (unblendable) liquids. One liquid (the dispersed phase) is dispersed in the other (the continuous phase). Usually the polar liquid is aqueous, while the less polar phase is an organic oil. In order to have an emulsion (both oil-in-water and water-in-oil) one of these two phases must be dispersed in the other in the form of small droplets. In addition an interfacial film surrounding the droplets must guarantee sufficient

kinetic stability. Multiple emulsion types may also occur, for instance oil droplets dispersed in water droplets, that in turn are dispersed in continuous oil phase (o/w/o) constitute an oil-in-water-in-oil emulsion. The size of the water droplets in a crude oil emulsion can be even higher than 100 μm , which is large compared to the common definition of the upper limit of colloidal size (1-10 μm) [14].

If oil is dispersed in water without any amphiphile or other kind of stabilizer added, the stability will be very poor. The oil droplets will collide and the collisions will lead to droplet fusion, i.e. coalescence. The rate with which individual droplets move due to gravity is proportional to (i) the density difference between the dispersed and the continuous phase, (ii) the square of the droplet radius, and (iii) the inverse of the viscosity of the continuous phase. Emulsions break-down can occur by various mechanisms, as illustrated in figure 2.6. Creaming or sedimentation occurs as a result of the density difference between the phases. Droplets can also flocculate, which means that they enter the so-called “secondary minimum”, an energetically stable situation where the droplets are close to each other but still retain their integrity. Flocculation is the process in which emulsion drops aggregate, without rupture of the stabilizing layer at the interface. Flocculation may also occur under conditions when the van der Waals attractive energy exceeds the repulsive energy and can be weak or strong, depending on the strength of inter-drop forces. Creaming, sedimentation and flocculation are all reversible phenomena and the original state can often be regained by application of high shear. A much more severe phenomenon is coalescence, a process in which droplets merge into each other. Coalescence is an irreversible phenomenon [14].

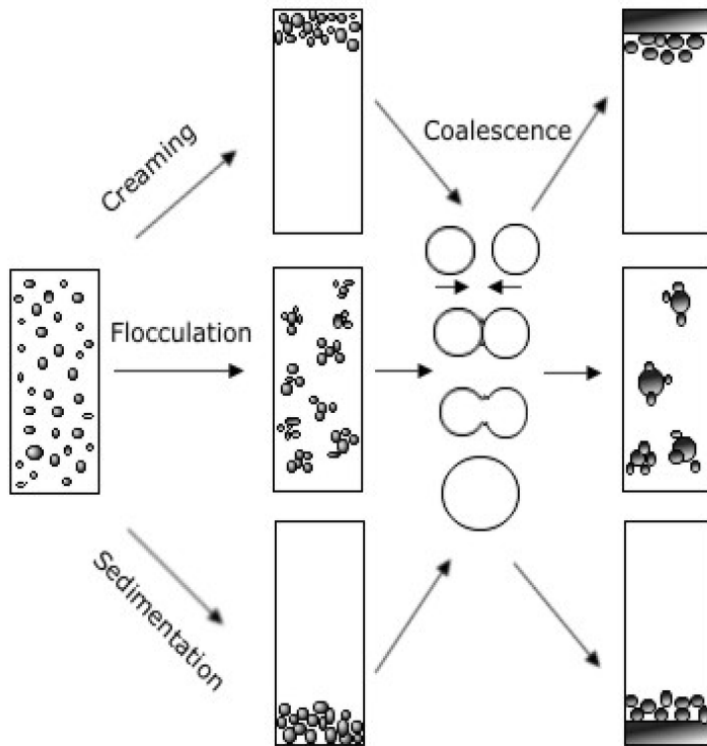


Figure 2.6: Mechanisms for the destabilization of emulsions. Different processes can occur simultaneously [14].

The mechanism of coalescence occurs in two stages; film drainage and film rupture. In order to have film drainage there must be a flow of fluid in the film, and a pressure gradient present. However, when the interfacial film between the droplets has thinned to below some critical thickness, it ruptures, and the capillary pressure difference causes the droplets to rapidly fuse into one droplet. Hence, the properties of the thin film are of uttermost importance for the separation. If the droplets deform, the area of the interface increases and consequently the drainage path in the film also increases, resulting in lower drainage rates [14].

Electrical double layer repulsion, or steric stabilization by polymers and surfactants with protruding molecular chains, may prevent the droplets to come into contact with each other. Polymer, surfactants or adsorbed particles can create a mechanically strong and elastic interfacial film that act as a barrier against aggregation and coalescence. A film of close packed particles has considerable mechanical strength, and the most stable emulsions occur when the contact angle is close to 90°C , so that the particles will collect at the interface. Solide particles diffuse to the o/w interface, forming rigid structures that can sterically inhibit droplet coalescence. Particles, which are oil-wet, tend to stabilize w/o emulsions. In order to

stabilise the emulsions the particles should be least one order of magnitude smaller in size than the emulsion droplets and in sufficient high concentration.

The indigenous crude oil components contribute to the formation of a viscoelastic film on the crude o/w interface, and the dominating mechanism whereby crude oil emulsions are stabilised is through the formation of a viscoelastic, physically cross-linked network of asphaltene aggregates at the o/w interface. The ability of asphaltenes and resins to form elastic crude o/w interfaces is an important factor regarding emulsion stability. Other factors that usually favour emulsion stability, is low interfacial tension, high viscosity of the bulk phase and relatively small volumes of dispersed phase. A narrow droplet distribution of droplets with small sizes is also advantageous, since polydisperse dispersions will result in a growth of large droplets on the expense of smaller ones, an effect called Ostwald ripening. Special features of surfactant association into liquid crystalline phases with lamellar geometries that facilitate the stabilisation may also occur [7, 15-22]

The formation of an interfacial film consisting of surface-active material present in the crude oils plays a fundamental role with regard to emulsion stability. The surface-active material adsorbes to the o/w interface reduces the interfacial tension and allows the droplets to stand tangential stresses because of the creation of interfacial gradients. These gradients will oppose the stretching trying to restore a uniform interfacial tension state and the interface will behave elastically. This phenomenon is called Gibbs-Marangoni effect (figure 2.7) [5, 23].

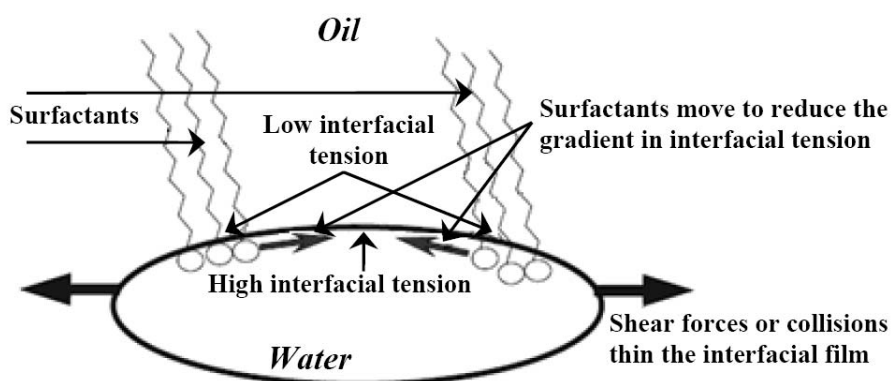


Figure 2.7: Gibbs-Marangoni effect at the o/w interface [5].

2.4 Emulsion resolution in electrostatic processes and separation facilities

The destabilisation of crude oil emulsions forms an integral part of crude oil production. Generally, these emulsions have to be broken to reach specified values of product quality, both for oil and produced water. Exporting oil not fulfilling the quality criteria ($<0.5\%$ w/o), results in large economic penalties.

Stable emulsions are often broken using gravity or centrifugal settling, application of high electric fields and addition of destabilising chemicals (demulsifiers). Other methods such as pH adjustment, filtration, membrane separation and heat treatment techniques, may also be used. Gravity settling tanks, cyclones, centrifugal separators and other kinds of mechanical separator tools are typical equipment used in the destabilisation of crude oils emulsions. However, this hardware is of considerable volume as well as expensive to install on offshore platforms typical for North Sea conditions. It is therefore of great economical benefit whenever the installations can be kept at a minimum in size and number. Chemical destabilisation is therefore a very common method for destabilising emulsions. Several demulsifiers exist on the market, and their type and dosage depend on the specific conditions of the field development. In the last years electrostatic destabilization of water-in-oil emulsions has received more and more attention, since it has potential to drastically reduce the use of heat, which is energy consuming, and of chemical emulsion breakers, which may be detrimental from an environmental point of view. Electrostatics cannot completely replace emulsion resolution methods such as time, temperature and chemical methods [24].

The electrocoalescence technology is governed by the effect of electrostatic forces and the effect of shear flow (flow conditions). When an electric field is applied to a water-in-oil emulsion, a suspended droplet is subjected to different forces, see figure 2.8. The theoretical background will not be described more in detail and for further information the reader should consult the literature [25-31].

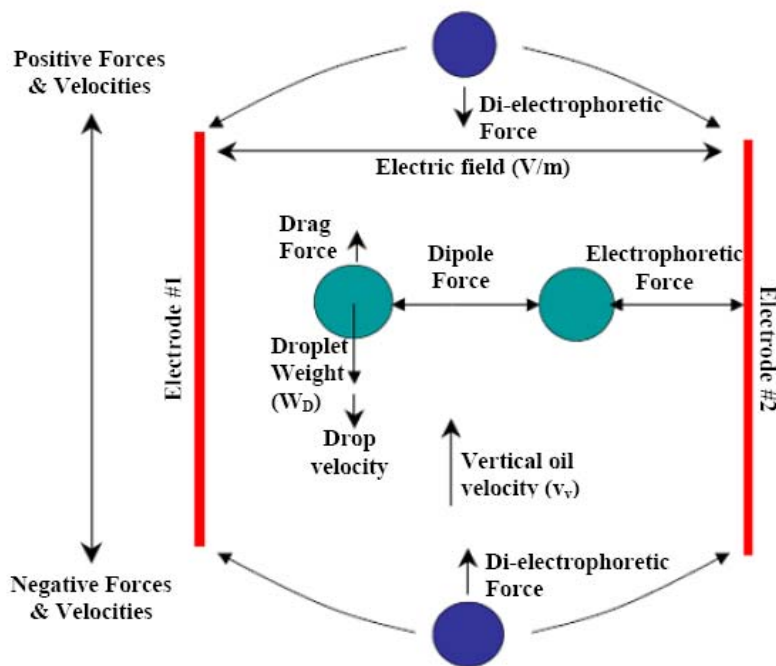


Figure 2.8: Electrocoalescence forces, modified form [25, 32].

A variety of electrostatic treatment techniques available to the designer and operator include AC, DC, AC/DC, modulated and pulsed fields. When an electrostatic method is selected, an understanding of the water droplet behavior within a voltage field will aid the designer to optimize the treatment rate, temperature, chemical dosage and applied voltage. In an AC type electrostatic field, the driving force for droplet coalescence is based on the dipole of the water molecule. Applying voltage to an AC-electrode aligns the water molecules creating a chain of water droplets with positive and negative poles. Droplets that are close together will migrate towards each other and coalesce. In a DC electrostatic field, a sustained movement of electrons charges the water droplet interface. The ability to charge the droplet interface is primarily dependent on the voltage magnitude and the oil conductivity. Studies have shown that higher DC voltage levels are capable of delivering a significant charge to even the smallest water droplets and thereby promoting coalescence. Furthermore, the DC field promotes droplet stretching that ruptures the outer film and enhances the droplet coalescence rate. In general, for electrostatic treatment processes, crude oil is considered a non-conductive continuous phase. Pure organic components may be treated electrostatically; however the low conductivity generally reduces the droplet charge and hinders droplet movement, coalescence and separation. In highly refined oils where the conductivity is extremely low, AC and DC electrostatic fields rely on the dipole of the dispersed water to promote droplet coalescence.

However, in DC treatment processes, the oil conductivity is essential in delivering a charge to the dispersed water droplets. The DC field transfers a charge to dispersed water droplet proportional to the voltage gradient and the oil conductivity. Small-scale lab studies have shown that a limited increase in the oil conductivity can improve water droplet coalescence by a significant amount in some crude oils. Unfortunately, high oil conductivity requires an increase in the connected power supply and limits the voltage gradient developed between electrodes [33].

Due to the high viscosity of the continuous oil phase and the low density difference between oil and water phases, sedimentation of water drops in heavy crude oil is extremely time consuming. Conventional solutions for heavy oil applications include one, or often a combination of: (1) increasing the residence time in separators, (2) application of heat, and (3) increasing the drop size and distribution. Due to the squared dependence of sedimentation velocity and drop size (Stokes law, simplified system), any drop growth upstream of a separator will result in a dramatic improvement in the performance of gravity separators. Drop growth (or flocculation) can be achieved with the use of chemical additives like flocculants, electrostatic coalescers (separators), or in-line electrostatic fields [34]. The electrostatic coalescers are common in heavy crude oil production, and there are three main separators available on the market today; VIEC (Vessel Internal Electrostatic Coalescer) and LOWACC (Low Water Content Coalescer) from Aibel and CEC (Compact Electrostatic Coalescer) from AkerKværner. The technologies are compared and evaluated with regard to compactness, electrical consumption, robustness, and capacity, quality of outlet and need of chemicals.

VIEC - Vessel Internal Electrostatic Coalescer: It consists of isolated high voltage modules fitted in a separator wall, targeting the oil/water emulsion phase. Figure 2.9 illustrates a typical VIEC module. The high voltage electrostatic field makes water droplets in oil coalesce, so that they will separate more easily. The VIEC is tolerant of any combination of oil, water and gas. Therefore it can be installed even in the first stage separator without surveillance of process conditions. The performance improvement can be realized as cleaner oil, less heating, less chemical consumption or a combination. The VIEC can also improve the performance of subsea processing and thereby enable smaller equipment or ultimately water free oil transport with wellhead water injection. Norsk Hydro has found the VIEC so

interesting that it is being installed in the first stage separator on the Troll C platform, which produces over 220,000 BPD of oil. The VIEC will reduce the water content in the oil from 13 to less than 5% and also improve water treatment capacity and separator control. The installation on Troll C will qualify the equipment for future use subsea [25, 35].

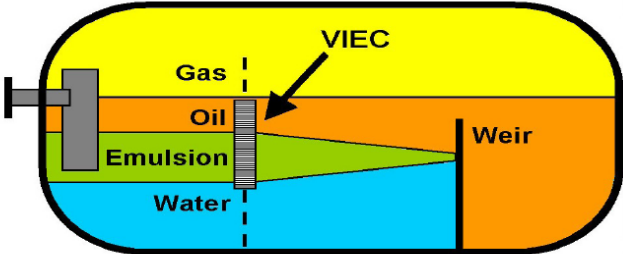


Figure 2.9: VIEC modul [35].

LOWACC - Low Water Content Coalescer: The LOWACC is installed after the VIEC to improve the outlet oil quality (figure 2.10 and 2.11). The LOWACC consists of two corrugated electrode plates where the oil flow through and where smaller droplets can coalesce further (purification stage). LOWACC, together with VIEC, enables one-step separation and heavy-oil separation by exposing the emulsion of water in oil to an electrostatic field. The water droplets contained in the oil phase are coalesced into bigger droplets and separates easily. Due to insulation of the electrodes, short-circuiting is avoided. The LOWACC is designed to be used in both high and low pressure separators, and separators with difficult separation or heavy emulsions [25, 35].

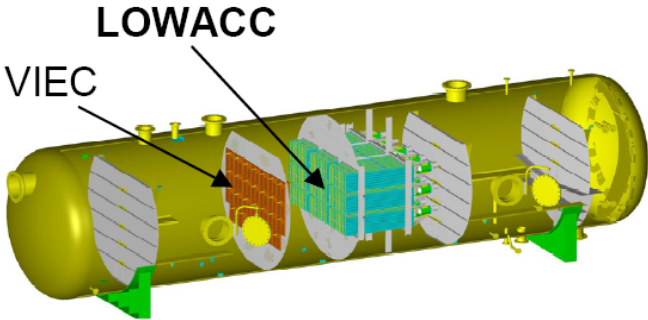


Figure 2.10: VIEC and LOWACC installed in a separator. Both are placed in the same separator to achieve full separation using only one vessel [35].

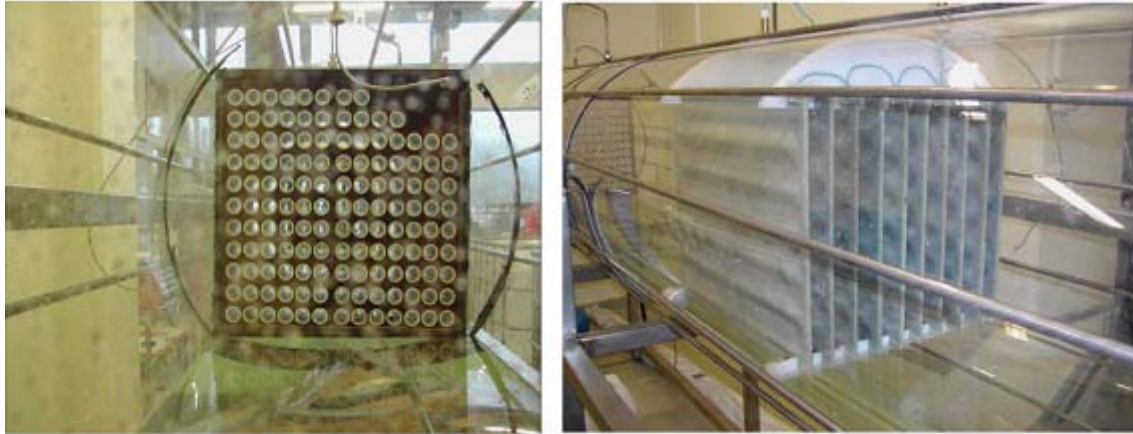


Figure 2.11: The VIEC (left picture) is an energized plate with holes installed at the inlet of a normal separator tank. The electric field set up inside the holes enhances coalescence. The LOWACC (right picture) consists of two corrugated electrode plates where the oil flow through and where smaller droplets can coalesce further (purification stage) [35].

CEC - Compact Electrostatic Coalescer: CEC is an inline coalescer and are installed upstream the separator. Figure 2.12 show CEC internals and figure 2.13 show typical flow schematics for CEC system. The CEC consists of many concentric electrodes inside each other. CEC enhances separation by applying a high voltage alternating electric field to an emulsion. This coalesces and aggregates the entrained water droplets so that they readily settle out in a downstream separator. Coalescence occurs quickly under turbulent flow conditions and minimises the need for emulsion-breaking chemicals. It also leaves the oil with less than 0.3% water content, which is somewhat below the normal refinery requirement because of its salinity. The world's first CEC installation was on Glitne in late 2001. Several years later, this remains in perfect working order after keeping the water-in-oil content well below 0.3% while reducing the need for chemical additives [2, 25, 36].

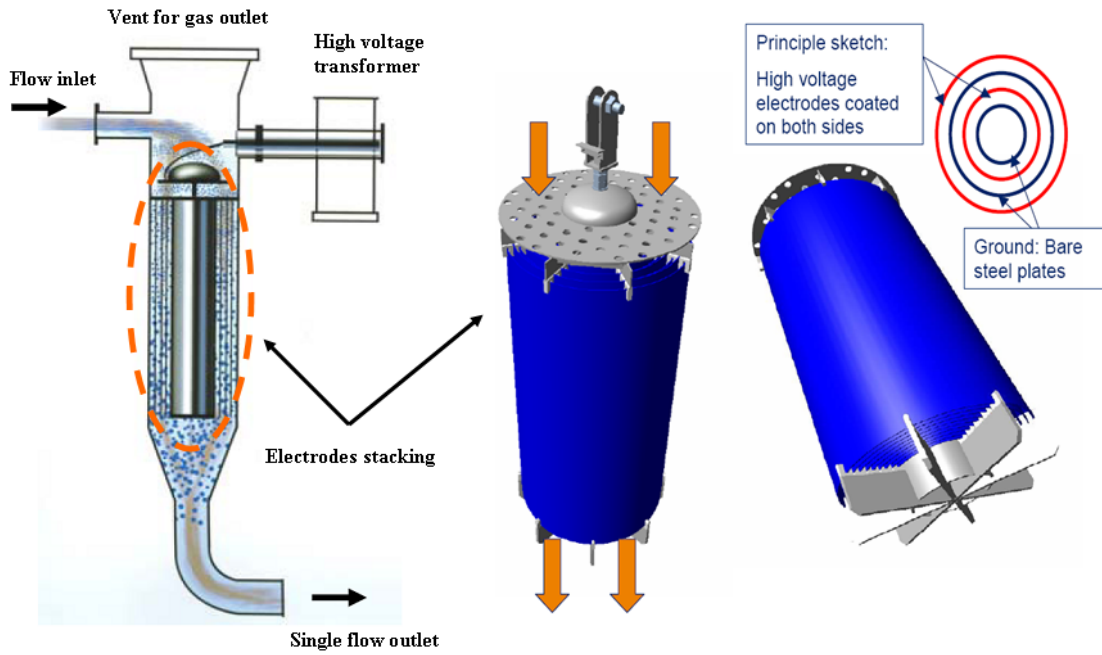


Figure 2.12: Illustration of the construction of a CEC unit with the electrodes stacking inside. Crude oil and water in dispersed state enter the CEC at the top. The droplet size of the water droplets has increased when the dispersion exits at the bottom [37].

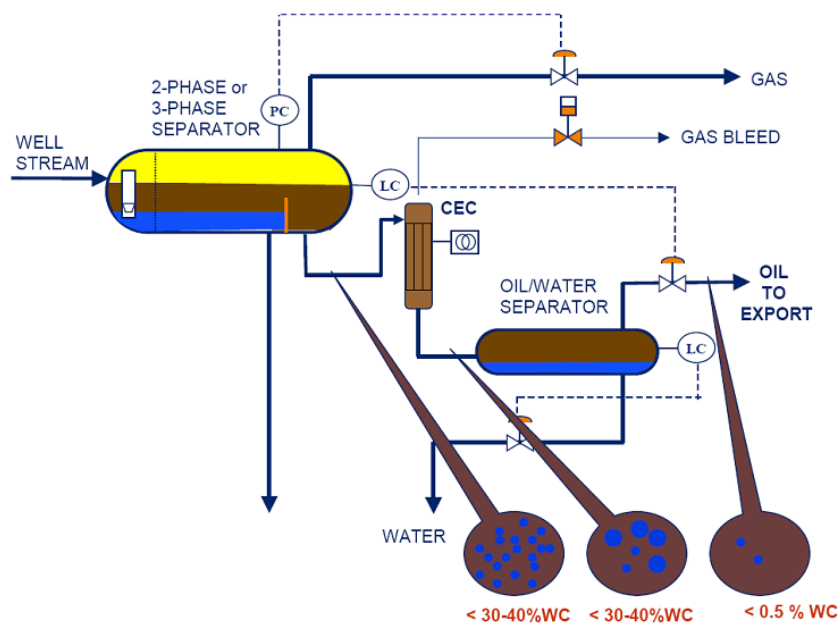


Figure 2.13: Typical flow schematics for CEC system [37].

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3. THE PRODUCED WATER ISSUE

3.1 The origin of produced water

In subsurface formations, naturally occurring rocks are generally permeated with fluids such as water, oil, or gas (or combinations of these fluids). It is believed that the rock in most oil-bearing formations was completely saturated with water prior to the invasion and tapping of petroleum [1]. The less dense hydrocarbons migrate to trap locations, displacing some of the water from the formation in becoming hydrocarbon reservoirs. Thus, reservoir rocks normally contain both petroleum and hydrocarbons (liquid and gas) and water. Sources of this water may include flow from above or below the hydrocarbon zone, flow from within the hydrocarbon zone, or flow from injected fluids and additives resulting from production activities. This water is frequently referred to as “connate water” or “formation water” and becomes produced water when the reservoir is produced and these fluids are brought to the surface. Produced water is any water that is present in a reservoir with the hydrocarbon resource and is produced to the surface with the crude oil or natural gas [2].

When hydrocarbons are produced, they are brought to the surface as a produced fluid mixture. The composition of this produced fluid is dependent on whether crude oil or natural gas is being produced and generally includes a mixture of either liquid or gaseous hydrocarbons, produced water, dissolved or suspended solids, produced solids such as sand or silt, and injected fluids and additives that may have been placed in the formation as a result of exploration and production activities [2]. To maintain the hydraulic pressure in the petroleum reservoir, which is reduced as soon as production is started, seawater is commonly pumped into the reservoir water layer below the hydrocarbons (Figure 3.1). This pressure maintenance due to water injection causes high extensions in recoverable hydrocarbons but simultaneously contributes to increased water production [3].



Figure 3.1: Re-injection of separated water from an offshore installation [3].

3.2 The composition of produced water

Produced water is not a single commodity. The physical and chemical properties of produced water vary considerably depending on the geographic location of the field, the geological formation with which the produced water has been in contact for thousands of years, and the type of hydrocarbon product being produced. Produced water properties and volume can even vary from one field to another, within the field, and throughout the lifetime of a reservoir. On the other hand, oil fields usually start producing reservoir water at a rather early stage of production at low water to oil ratios. Later, as fields mature, the ratio between water and oil can reach high values (up to 10:1), and the composition of the produced reservoir water changes, but significantly less than in gas fields. Also, oil field production is often enhanced by injection of water, to maintain the reservoir pressure. When the injected water breaks through into the production stream, it dilutes the formation water and discharged produced water progressively approaches the injected water in composition and character [4]. The produced water and hydrocarbon production profile for a typical oilfield is illustrated in figure 3.2. The figure demonstrates the significant change in the water/oil ratio when the oilfield reach maturity and water by far becomes the biggest fraction of the production [3].

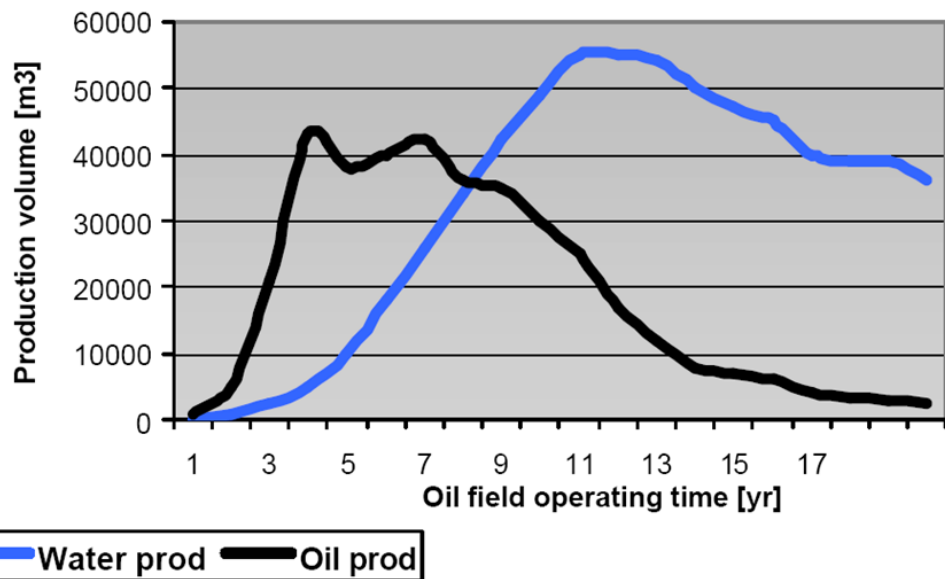


Figure 3.2: Typical production profile for an oilfield in the North East Atlantic [3].

The composition of produced water in general can be identified as residual concentrations of chemical additives from the production line, dispersed oil-in-water emulsions and dissolved organic compounds along with traces of heavy metals and inorganic compounds. More specifically, the main compounds of concern in addition to the dispersed oil are semi-soluble hydrocarbons such as benzene, toluene, ethylbenzene and xylene (BTEX), polycyclic aromatic hydrocarbons (PAH), naphthalenes, phenanthrenes and dibenzothiophenes (NPD), organic acids, phenol and alkylated phenols, traces of chemicals additives and natural low-radioactive elements. The main strategy for reducing the pollution from produced water has traditionally been to reduce the content of dispersed oil. One of the reasons behind this strategy is that good removal of dispersed oil has also resulted in substantial removal of soluble hydrocarbons [2].

Table 1 shows typical concentrations of pollutants in treated offshore produced water samples from the Gulf of Mexico (composite data from many different platforms) [2, 5]. The first column of data represents the performance for a very basic level of treatment (best practicable technology, or BPT) while the second column of data represents a more comprehensive level of treatment (best available technology, or BAT). The data show that many constituents are present. The organic and inorganic components of produced water discharged from offshore wells can be in a variety of physical states including solution, suspension, emulsion, adsorbed particles, and particulates.

In addition to natural components, produced waters from oil production may also contain groundwater or seawater injected to maintain reservoir pressure, as well as miscellaneous solids and bacteria. Most produced waters are more saline than seawater [6]. They may also include chemical additives used in drilling and producing operations and in the oil/water separation process. Treatment chemicals are typically complex mixtures of various molecular compounds. These mixtures can include:

- Corrosion inhibitors and oxygen scavengers to reduce equipment corrosion;
- Scale inhibitors to limit mineral scale deposits; biocides to mitigate bacterial fouling;
- Emulsion breakers and clarifiers to break water-in-oil emulsions and reverse breakers to break oil-in-water emulsions;
- Coagulants, flocculants, and clarifiers to remove solids; and
- Solvents to reduce paraffin deposits [7]

In produced water, these chemicals can affect the oil/water partition coefficient, toxicity, bioavailability, and biodegradability [8]. With increased development of subsea oil fields in the North Sea and the Gulf of Mexico, many of these additives will be required in larger amounts, to assure flow assurance in subsea pipelines [2, 9].

Table 1: Produced water characteristics following treatment [2].

Constituent	Concentration after BPT-Level Treatment (mg/L) ^a	Concentration after BAT-Level Treatment (mg/L) – Gas Flotation Treatment ^b
Oil and grease	25	23.5
2-Butanone	1.03	0.41
2,4-Dimethylphenol	0.32	0.25
Anthracene	0.018	0.007
Benzene	2.98	1.22
Benzo(a)pyrene	0.012	0.005
Chlorobenzene	0.019	0.008
Di-n-butylphthalate	0.016	0.006
Ethylbenzene	0.32	0.062
n-Alkanes	1.64	0.66
Naphthalene	0.24	0.092
p-Chloro-m-cresol	0.25	0.010
Phenol	1.54	0.54
Steranes	0.077	0.033
Toluene	1.901	0.83
Triterpanes	0.078	0.031
Total xylenes	0.70	0.38
Aluminum	0.078	0.050
Arsenic	0.11	0.073
Barium	55.6	35.6
Boron	25.7	16.5
Cadmium	0.023	0.014
Copper	0.45	0.28
Iron	4.9	3.1
Lead	0.19	0.12
Manganese	0.12	0.074
Nickel	1.7	1.1
Titanium	0.007	0.004
Zinc	1.2	0.13
Radium 226 (in pCi/L)	0.00023	0.00020
Radium 228 (in pCi/L)	0.00028	0.00025

^a BPT = best practicable technology.

^b BAT = best available technology.

Source: EPA (1993).

3.3 Impact of produced water on the environment

A great deal of scientific research has been carried out to determine the consequences of long-term exposure of produced water on the environment. Some of this research has given alarming results. The previous sections outline the many chemical constituents found in produced water. These chemicals, either individually or collectively, when present in high concentrations, can present a threat to aquatic life when they are discharged or to crops when the water is used for irrigation. Produced water can have different potential impacts depending on where it is discharged. For example, discharges to small streams are likely to have a larger environmental impact than discharges made to the open ocean by virtue of the

dilution that takes place following discharge. Numerous variables determine the actual impacts of produced water discharge. These include the physical and chemical properties of the constituents, temperature, content of dissolved organic material, humic acids, presence of other organic contaminants, and internal factors such as metabolism, fat content, reproductive state, and feeding behavior [2, 10].

In the year 2000 produced water totaled about 150 million m³ and approximately 3500 metric tons of oil was discharged to the sea [11]. Discharges will increase in the years ahead, primarily because of increased water production from the major fields, and because the use of chemicals is greater in fields with seabed completions. Each year, the Norwegian Petroleum Directorate prepares short-term and long-term forecasts for production, costs, investments, and discharges and emissions. These are based on data obtained from the operators. Measures to reduce the discharges have been inadequate to reverse the trend of an increasing discharge of produced water, which is mainly a consequence of more and more of the production taking place from old fields where production of water increases. The measures have, however, helped to reduce the discharge of oil per produced unit of water (Figure 3.3) [12].

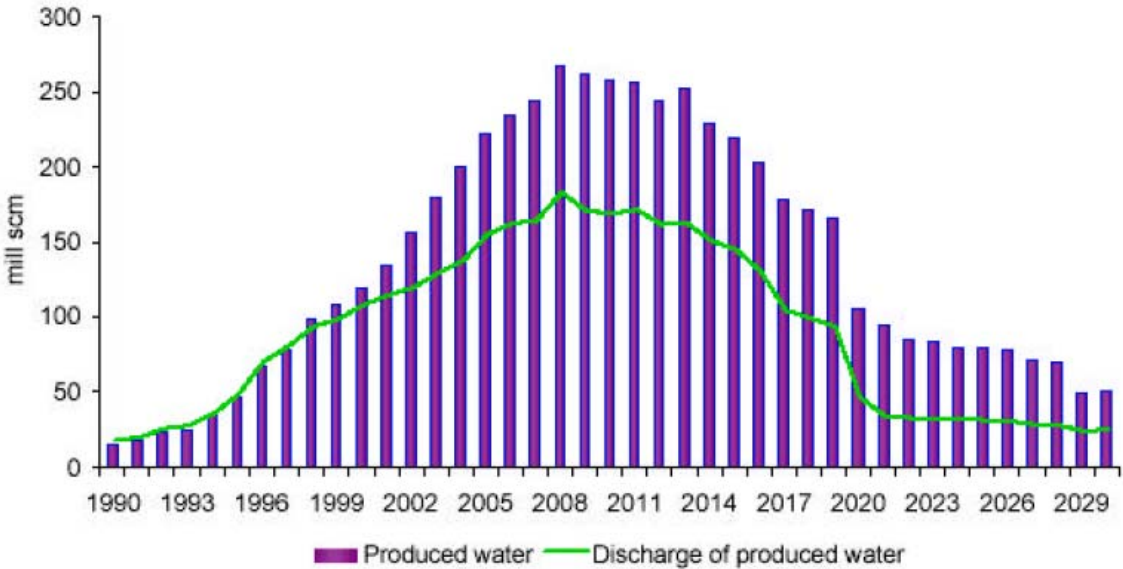


Figure 3.3: Forecast of water production and discharge on the Norwegian continental shelf [3, 12].

The quantity of produced water in figure 3.3 that is not discharged to sea is re-injected into the reservoir or to another formation suitable for disposal. The long-term effects of such contaminants on the environment are not fully documented and understood. Some research programmes are completed and several new studies are underway to map possible

consequences for living organisms. Dilution aspects and movement of species in the oceans makes definite conclusions hard to make. There are so many variables that the modelling is extremely complex. Results from recent research show however that fish exposed to alkyl phenols have disturbances in both organs and fertility. These results are serious and have triggered further investigations [3].

A common legislation for produced water discharges to sea from offshore installations has been 40 mg/l (ppm) oil-in-water. The Oslo Paris Convention (OSPAR) has agreed that the maximum discharge limit is reduced to 30 ppm oil-in-water for the petroleum companies operating in the North-East Atlantic and that the overall oil discharges in produced water are reduced by 15% from 1999 levels. In Norway, the oil operators have agreed to implement a policy of zero harmful discharge within 2005. There shall be no harmful discharges from any new installation, and existing installations shall continuously work against a practically achievable zero harmful discharge [13].

In Norway the Pollution Control Authority (SFT) together with The Norwegian Oil Industries Association (OLF) has developed a produced water management tool, the Environmental Impact Factor (EIF), to meet the zero-discharge strategy. The EIF is a model for optimising the activities taken to reduce the most harmful components in produced water for each offshore installation. EIF considers all the contaminants in the produced water [3, 14-16].

3.4 Treatment of produced water

3.4.1 Conventional technologies for water treatment

During petroleum production, vast volumes of liquids have to be managed each day. Deferred production causes high economical losses and therefore continuous operations are always strived for. The capacity, reliability and performance of the produced water management system is often critical for continuous oil production particularly in mature oil field where the water production can greatly exceed the oil production. The water production system needs to be designed to receive continuously increasing quantities of water as oil production continues.

Gravity based separation – flotation: Produced water treatment has traditionally taken place in gravity based equipment, where the difference in the density of the two liquids to be separated is utilized. Such separation is commonly performed in huge horizontal tanks at different pressures. Flotation of the lighter components (oil) can be enhanced by means of finely distributed gas bubbles going out of solution (pressure reduction) and parallel plate packages installed diagonally in the separation vessel.

The EPCON Compact Flotation Unit (CFU) is a reliable and highly efficient technology for separating water, oil and gas to achieve a high standard of treated water (figure 3.4). It requires no external energy and the CFU also has a smaller volume and shorter retention time than traditional flotation units currently in use. The EPCON CFU is a well-proven environmental solution to treat the increasing volumes of produced water, and major operators worldwide have tested and/or installed the technology [17].

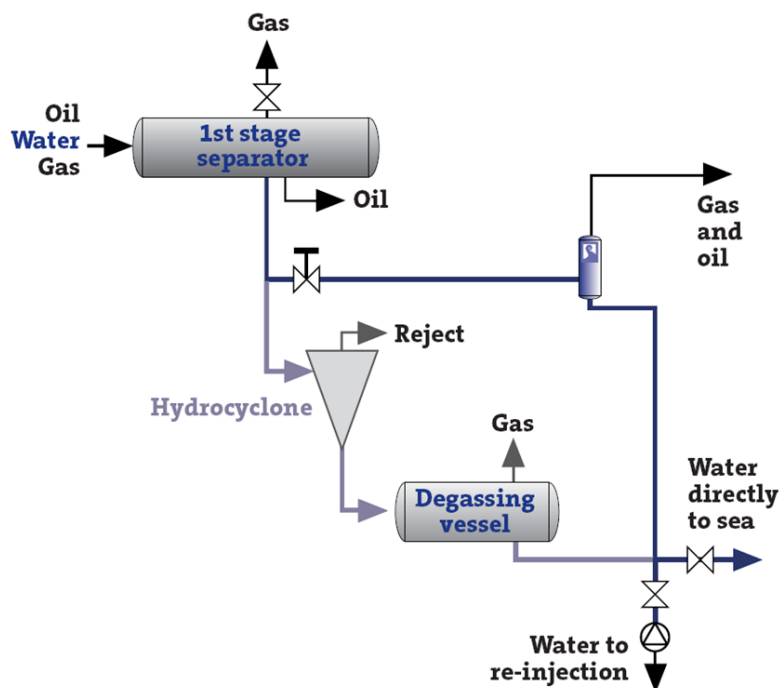


Figure 3.4: A typical EPCON CFU installation working in parallel with a traditional water-treatment system to increase total produced water treatment capacity [17].

Several combined processes, including gas flotation and induced centrifugal inertia forces, act on the fluid components of different specific gravities. The small oil droplets are made to agglomerate and coalesce, facilitating separation from the water. The separation process is aided by internal devices in the chamber and a gas flotation effect caused by the release of

residual gas from the water. Process optimization can also be achieved by the introduction of external gas and/or flocculants. The separated oil and gas is removed in a continual process via an outlet pipe at the top of the vessel [17].

Separation techniques based on filtration: A well known technique for separating non soluble components is by filtration. Several principles for handling produced water have been considered including microfiltration membranes and media filters. Such treatment technologies are potentially advantageous because of very good separation degrees can be achieved. However microfiltration has found very limited practical application because of cost and poor operability, very high energy consumption and degradation of the filters elements with use.

Cyclonic separation methods: The continuous demand for higher treatment capacity in very limited space has resulted in improved treatment methods. The most commonly used technology in offshore production since around 1990 is the static hydrocyclone that utilizes available pressure for enhanced speed in gravity separation (figure 3.5). The advantages for this equipment type are high reliability (no moving parts), low maintenance, requires very little space, and gives good separation effect and high capacity. Produced water is pumped tangentially into the conical portion of the hydrocyclone. Water, the heavier fluid, spins to the outside of the hydrocyclone and moves toward the lower outlet. The lighter oil remains in the center of the hydrocyclone before being carried toward the upper outlet.

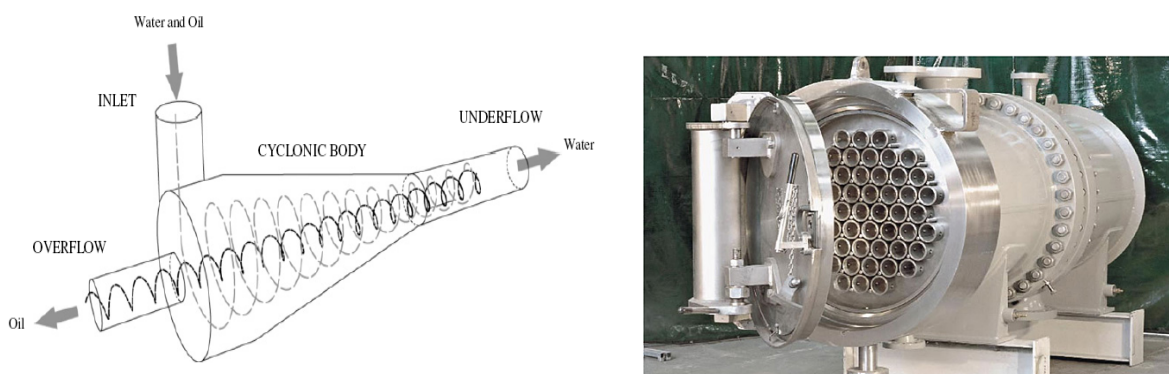


Figure 3.5: Schematic of hydrocyclone on the left hand side and multiple hydrocyclones inside a vessel on the right hand side [18].

New challenges in handling produced water: Gravity based separation techniques have together with static hydrocyclones been the most extensive method for treating produced water. Other types of equipment have also been utilized, mostly in special cases with difficult operating treatment characteristics or small volumes, though to a less extent. Even if produced water systems more or less have functioned as intended with respect to the design specifications, the future has brought new considerations regarding what is sufficient treatment. A good alternative for disposal of produced water would be to send it back into the reservoir where it came from as part of the pressure support, or to another suitable formation. Unfortunately this requires extensive treatment prior to re-injection and due to high costs it is an economically viable alternative mainly for fields with large water production. Re-injection could also cause degradation of the reservoir production quality and productivity.

3.4.2 Produced water management

Based on the serious uncertainties connected to the long-term environmental effects from produced water discharges and in order to be preventive of possible environmental damage legislation is now being tightened. On the Norwegian continental shelf in the North-East Atlantic, the government and the oil companies have agreed to zero harmful discharge in produced water by the end of 2005. The petroleum industries operating in the area are investigating several ways of meeting the new requirements.

Subsea separation: In order to reduce the necessary processing capacity in the petroleum treatment plant, it could be advantageous to separate as much as possible of the water fraction from the well stream at an early point in the production sequence. By placing first stage water/oil separation process equipment on the sea bottom it will not be necessary to transport all the water to the platform processing facility. The Platform facility is greatly simplified with significant weight reduction. The water separated at the seabed can be injected into a shallower well formation. Figure 3.6 presents a graphic illustration of the Troll Pilot subsea installation in the Norwegian continental shelf.

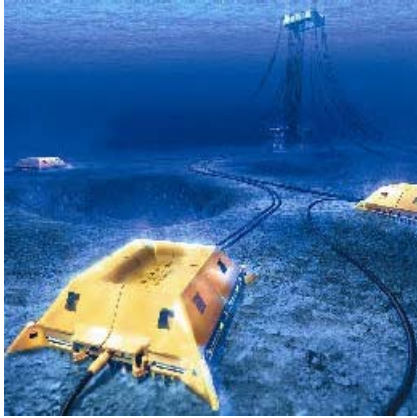


Figure 3.6: The Troll pilot subsea unit [3].

Downhole technology: A further step in reducing the water-cut from the production stream is to locate oil/water separation process equipment down in the production wells. This technique has been investigated extensively the last years. The produced water is separated from the oil and gas. It is then pressurised by downhole hydraulic pumps and re-injected into the reservoir. The technology is still only in pilot design. It is still very expensive. The complexity increases with reservoir depth. Vertical Downhole Oil/Water Separation (DOWS) systems have been used to some extent world wide in the last years. A new more complex horizontal separation system is under pilot testing pilot testing in Norway.

Water shut-off methods: In order to reduce the water flow to the well production zones, there are two traditional methods utilized. During mechanical shut-off, cement or mechanical devices blocks the water pathway by plugging the perforated production section. The chemical shut-off includes injection of polymers into the reservoir that increases the water viscosity, forms a stable gel and thereby restricts the water flow ability.

Sidetracking: An increase in water production for example as a consequence of water breakthrough in the production zone could be stopped by pulling the well internals, closing down the perforated zone (mechanical shut-down) and drilling to a new section. Figure 3.7 illustrates several sidetrack wells drilled off from the old original.

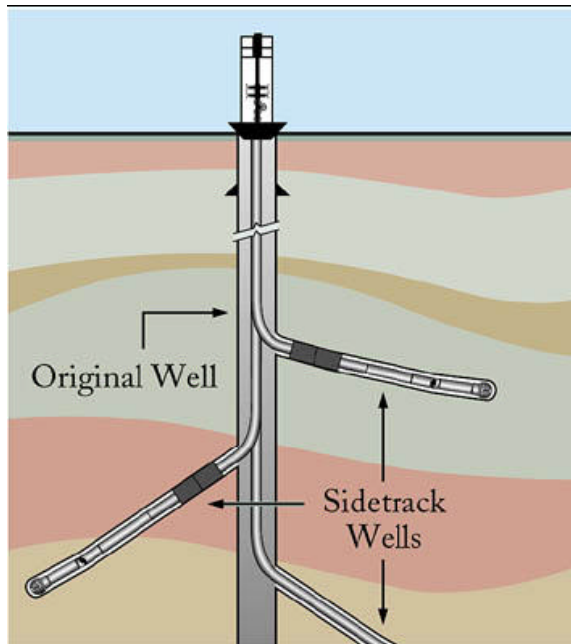


Figure 3.7: Illustration of sidetrack wells [3].

3.4.3 Recent produced water treatment developments

As there is still no economically practical method for disposal of all the produced water via re-injection or various recycle methods, a range of innovative wastewater technologies have been developed or are under development. The different technologies all have their operating characteristics that make them suitable for only certain produced waters or operating characteristics. There is a major focus on new techniques to remove dissolved components from produced water.

Separation by filtration: Utilization of membranes has been considered for treatment of oily wastewater to reduce dissolved components. The new systems include the use of nano filtration membranes. However, although the filtration method has very good separation effect, the high costs and complexity of these treatment techniques means that applications are only experimental.

Water treatment by extraction: Another technology that has been widely tested on both pilot and full scale on the Norwegian continental shelf is rooted in the solvent properties of supercritical liquids (CTour). The process utilizes liquid condensate (NGL) from the gas scrubbers and injects it into the produced water upstream of the hydrocyclones. The dispersed

and dissolved hydrocarbons, which have higher solubility in the condensate, go into the condensate phase and are separated in the hydrocyclones. This equipment has undergone extensive pilot testing and its field tests are imminent. The process is very sensitive to the available condensate quality.

Enhanced oil separation by means of coalescence: Several modern produced water treatment methods are based on the coalescing of dispersed oil droplets, often prior to cyclonic separation. The devices are installed upstream of the cyclonic vessels to increase oil droplet diameters which will result in better separation degree in the hydro cyclones. The process of coalescence could be accelerated by different means. One method is to install a special fibre media in the pipelining or the hydrocyclone vessels that attracts oil droplets and promotes coalescence into larger aggregates. These systems have no effect on removing dissolved hydrocarbons, but are simple and easily retrofitted. The fibre media is sensitive to fouling and any abrasive elements (sand) in the water. Other processes include combinations of chemical injection (coagulation/flocculation) and mechanical agitation in specially built vessels. Compact flotation units are hybrid cyclone/degassers that could replace standard degasser equipment.

Methods based on adsorption: Adsorption has proven a successful area in maintaining compliance with produced water discharges. Unfortunately most processes involve filters and therefore are restricted in volume or require advanced regeneration processes which could be both energy demanding and expensive. The adsorption techniques include activated carbon filters with regeneration by wet air oxidation and oil-adsorbing media canisters based on resins, polymer and clay technologies [3].

Many of the commercially available produced water treatment technologies are for dispersed oil removal. Most of them are able to treat large water volumes from the oil fields with short retention times. Hydrocyclones is today the most used technology on North Sea platforms. Recent technological innovations in dispersed oil removal seem to have either concentrated on increasing hydrocyclone removal efficiencies (coalescers, CTour) or developing more compact and efficient flotation processes, for example, by combining flotation with cyclonic separation. New types of filtration processes may also emerge (TORR). In dissolved hydrocarbon treatment, there seem to be no good treatment alternatives available for produced water treatment on oil platforms with large water flows. CTour is a promising technology and

removes the majority of the environmentally most harmful hydrocarbons. However, its efficiency is not good for lighter hydrocarbons and requirements for the quality and quantity of the condensate used in the process limits its general applicability. Many other methods that are effective for dissolved hydrocarbon removal like adsorption and MPPE are judged to be unsuitable (due to size, adsorbent disposal etc.) for treatment of large volumes of produced water in offshore applications. Although membranes are now widely used in water and waste water treatment (and other applications), the petroleum industry seems to be skeptical to the process due to problems with fouling and regeneration (cleaning) in earlier field trials. It is a challenge to develop a process for dissolved organics removal which is also compact enough for use on offshore oil-fields. Biological treatment is judged to require too much space and oxidation is hardly mentioned in overviews.

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4. MULTIVARIATE DATA ANALYSIS

4.1 Principal Component Analysis (PCA)

Principal component analysis (PCA) is a projection method that helps researchers visualise the most important information contained in a data set. PCA finds combinations of variables that describe major trends in the data set. Mathematically, PCA is based on an eigenvector decomposition of the covariance matrix of the variables in a data set. Given a data matrix \mathbf{X} with m rows of samples and n columns of variables, the covariance matrix of \mathbf{X} is defined as (equation 4.1) [1, 2]:

$$\text{cov}(X) = \frac{X^T X}{m-1} \quad (4.1)$$

The result of the PCA procedure is a decomposition of the data matrix \mathbf{X} into principal components called score and loading vectors (equation 4.2) [1, 2]:

$$X_{n \times m} = t_1 p_1^T + t_2 p_2^T + t_i p_i^T + \dots + t_k p_k^T + E_{n \times m} \quad (4.2)$$

Here, t_i is the score vector, p_i is the loading vector and \mathbf{E} is the residual matrix. The score and loading vectors contain information on how the samples and variables, respectively, relate to each other. The direction of the first principal component (t_1, p_1) is the line in the variable space that best describes the variation in the data matrix \mathbf{X} . The direction of the second principal component is given by the straight line that best describes the variation not described by the first principal component and so on. Thus, the original data set can be adequately described using a few orthogonal principal components instead of the original variables, with no significant loss of information. Plotting the first and second principal component against each other, the score plot is obtained (figure 4.1) [1, 2].

Loading plot or “mapping of variables” can be viewed as the bridge between the variable space and the principal component space. Like score vectors, loading vectors can be plotted against each other. The loadings show how well a variable is taken into account by the model

components. The loadings can be used to understand how much each variable contributes to the meaningful variation in the data, and to interpret variable relationships. They are also useful to interpret the meaning of each model component [2].

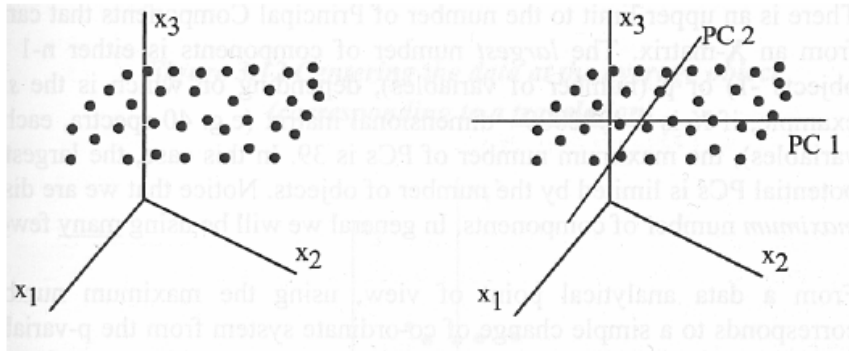


Figure 4.1: The figure shows how the principal component axis are defined in order to construct the score plot [2].

4.2 Outlier detection

Some samples can have values that are extremes compared to the other samples in the matrix. They may not be representative for the system at all, or they may be due to errors in measurements. Such samples will often be found in the outskirts of the main “swarm” in the score plot and are referred to as outliers (Figure 4.2). Outliers can be of the “mild” type as to the left in the figure or the “extreme” type to the right. Other ways to detect samples that are very different or have a high influence on the models is to look at the leverage. The leverage is based on the idea that anything can be lifted out of balance if the lifter has a long enough lever. This means that the principal component axes in the score plot can be influenced by a sample that has a high leverage and thus give a bad model [1, 2].

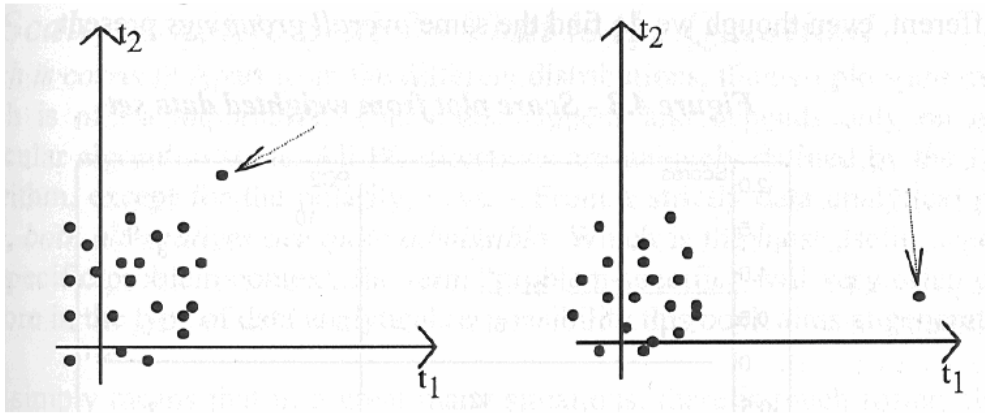


Figure 4.2: The plot shows an example of how outliers are detected in the score plot [2].

A sample with high leverage that falls near the PC axis can reinforce the PC model. Special attentions must therefore be paid to samples located far from the other samples in the score plot or have a high leverage (i.e. higher influence). Such samples may contain valuable information or the discrepancy is due to non-representative samples. To decide if a sample is an outlier and should be deleted from the data set, or an extreme that is important in order to get the true picture one have to carefully evaluate the specific samples and preferentially have detailed knowledge of the system under investigation [1, 2].

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5. EXPERIMENTAL TECHNIQUES

Different analytical techniques have been utilized in this doctoral work. This chapter focuses on the main experimental techniques that I have used, and will provide a theoretical background for the different methods. Emphasis will be on practical aspects and interpretation of results. The different techniques that have been used for the characterization of the different crude oils (SARA - precipitation of asphaltenes and fractionation of maltenes by HPLC, density, interfacial tension (IFT), interfacial elasticity and TAN) will not be treated in this chapter. Instead the reader is addressed to the experimental section of each paper where they have already been thoroughly described to get an insight.

5.1 Critical Electric Field (Ecritical)

Electro-coalescers are commonly used in the oil industry to enhance the separation of water from crude oil. The electro-coalescer applies an electric field of $1\text{-}10\text{ kV cm}^{-1}$ through the flowing water-in-oil emulsion to enhance the flocculation and coalescence of the dispersed water droplets. Basically, the water droplets increase their sizes through the electro-coalescer, and thereby the water sedimentation rate is increased. There is a variety of factors influencing the electrically-induced coalescence, such as the dielectric properties of the dispersed and the continuous phase, the volume fraction of the dispersed phase, conductivity, size distribution of the dispersed droplets, electrode geometry, electric field intensity, the nature of the electric field (AC or DC), etc. An electric field cell containing a small volume of sample has been developed for the determination of emulsion stability (figure 5.1). The method is similar to the one employed by Aske et al. [1]. The cell for determining the critical field consist of a Teflon plate with a hole in the center ($r = 5\text{ mm}$), and a brass plate on each side. The distance between the plates varies from 0.1 mm up to 1.0 mm , and the upper brass plate has holes for sample injection. The brass plates are connected to a computer-controlled power supply (Agilent Model 6634B) that can deliver a maximum of 100 V DC [1].

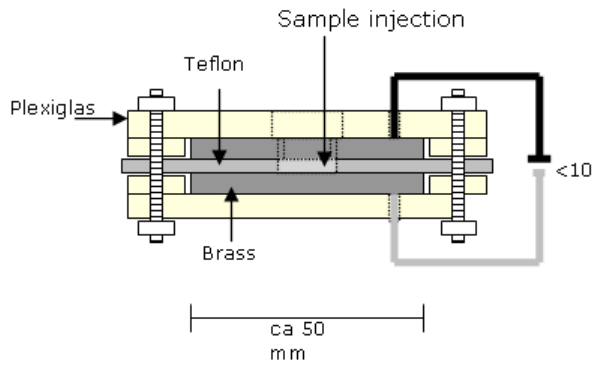


Figure 5.1: Illustration of the critical electric field cell used to measure emulsion stability of water-in-oil emulsions [2].

The power supply can stepwise increase the voltage and measure the current passing through the emulsion. A sudden increase of the current will indicate that the electric field has broken the emulsion and that there will be a free transport of ions between the electrodes. The corresponding electric field is the $E_{critical}$ value. Figure 5.2, illustrates how emulsions behave under the influence of the applied field [2]:

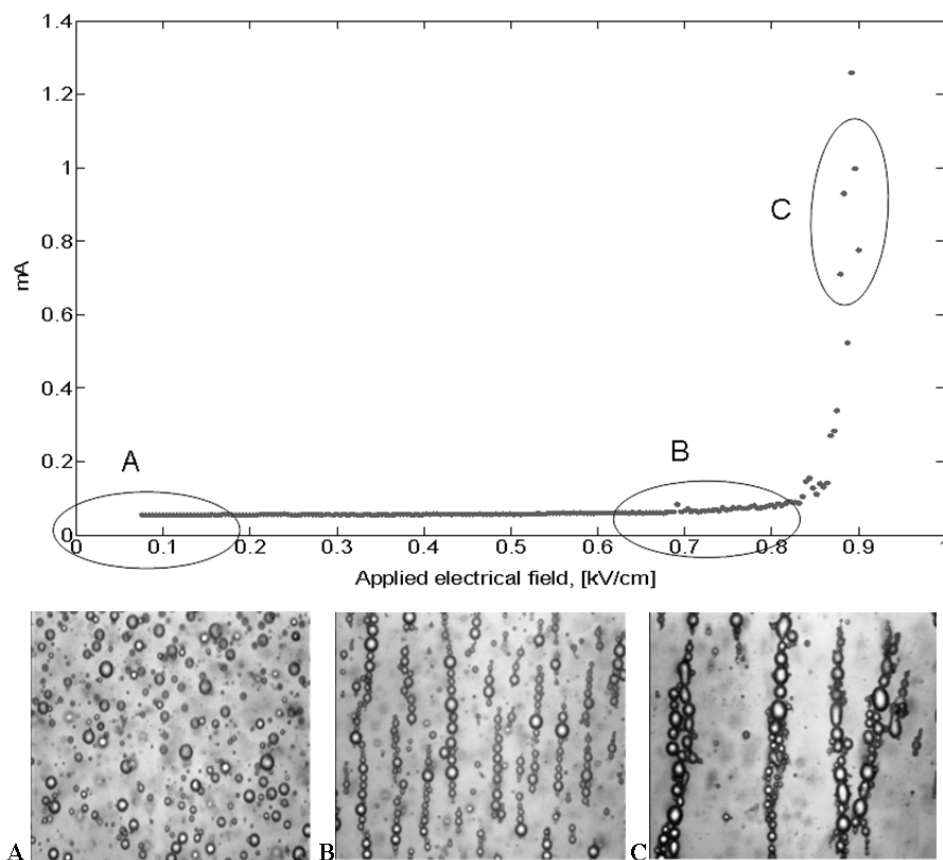


Figure 5.2: Configuration of the emulsion droplets when increasing the applied electrical field [2].

A: When no field is applied, the water droplets are randomly distributed according to Stokes law of sedimentation and Brownian motion. In addition, some degree of droplet flocculation may be present.

B: As the field increases, the droplets line up between the electrodes due to polarisation of the aqueous droplets containing electrolyte.

C: Finally, at some point, the applied electric field causes irreversible rupture of the interfacial films between the droplets. The droplets coalesce, resulting in a water-continuous bridge between the electrodes. The ions of the water phase contribute to a sudden increase in the conductivity. The emulsion stability is hence defined as the strength of the field when the conductivity suddenly rises.

5.2 Rheometry

Rheometry refers to the measuring techniques used to determine the rheological properties of materials, where rheology is the flow of fluids and deformation of solids under various kinds of stress and strain. Rheometry is an extremely useful tool for determining the flow properties of various materials by measuring the relationships between stress, strain, temperature, and time. Most rheometer models belong to three specific categories. These are the rotational rheometer, the capillary rheometer, and the extensional rheometer. The most commonly used of these is the rotational rheometer, which is also called a stress/strain rheometer.

In rotational methods the test fluid is continuously sheared between two surfaces, one or both of which are rotating. These devices have the advantage of being able to shear the sample for an unlimited period of time, permitting transient behavior to be monitored or an equilibrium state to be achieved, under controlled rheometric conditions. Rotational methods can also incorporate oscillatory and normal stress tests for characterizing the viscoelastic properties of samples. Rotational measurements fall into one of two categories: stress-controlled or rate-controlled. In stress-controlled measurements, a constant torque is applied to the measuring tool in order to generate rotation, and the resulting rotation speed is then determined. If well-defined tool geometry is used, the rotation speed can be converted into a corresponding shear rate. In rate-controlled measurements, a constant rotation speed is maintained and the resulting torque generated by the sample is determined using a suitable stress-sensing device,

such as a torsion spring or strain gauge. Some commercial instruments have the capability of operating in either stress-controlled or rate-controlled modes.

A range of different measuring geometries is available as accessory of rheometers, which can extend the measurement range. Most rheometers depend on the relative rotation about a common axis of one of three tool geometries: concentric cylinder, cone and plate, or parallel plates (figure 5.3).

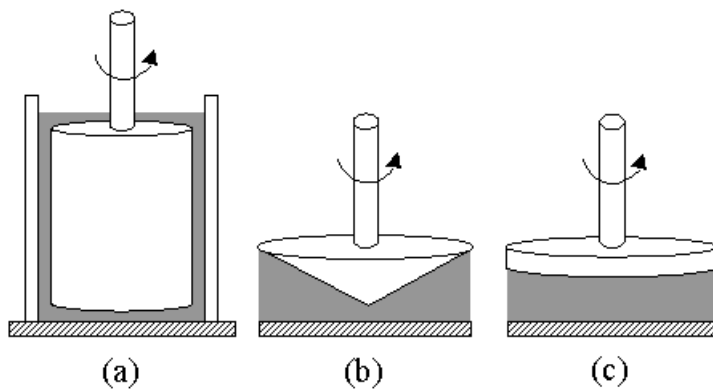


Figure 5.3: Schematic diagram of basic tool geometries for the rotational rheometer: (a) concentric cylinder, (b) cone and plate, (c) parallel plate [3].

The rheometric measurements carried out in this thesis were performed using a Anton Paar Physica MCR 301 and MCR 100 rheometers using a concentric cylinder geometry [3-5].

The evaluation of shear stress with the shear rate for materials can be described by several behaviours (figure 5.4):

- Newtonian fluids: The apparent viscosity is independent of the shear rate.
- Shear thinning (pseudoplastic) fluids: These fluids present a decrease of the apparent viscosity when the shear rate increases.
- Shear-thickening (dilatant) fluids: Contrary to the former cases, the apparent viscosity of these fluids increases with the shear rate.
- Bingham plastic fluids: An important characteristic of these materials is the presence of a yield stress. Below this yield stress, a material exhibits solid like characteristics, and we must apply a yield stress above this value to make the material flow [3].

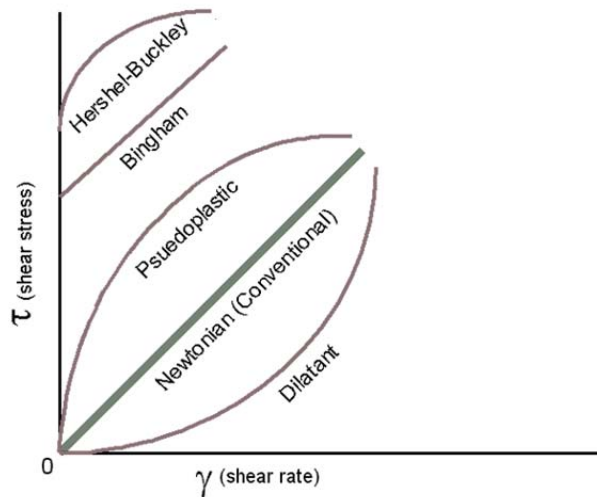


Figure 5.4: Newtonian and non-Newtonian phenomena [6].

5.3 Nuclear Magnetic Resonance (NMR)

5.3.1 Introduction to the principle of NMR

Nuclei with an odd number of protons and neutrons possess a property called spin. In quantum mechanics spin is represented by a magnetic spin quantum number. Spin can be visualised as a rotating motion of the nucleus about its own axis. As atomic nuclei are charged, the spinning motion causes a magnetic moment in the direction of the spin axis. The magnetic moments or spins are constrained to adopt one of two orientations with respect to B_0 , denoted parallel and anti-parallel. The angles subtended by these orientations and the direction of B_0 are labelled theta in figure 5.5 a). The spin axes are not exactly aligned with B_0 , they precess around B_0 with a characteristic frequency as shown in figure 5.5 b). This is analogous to the motion of a spinning top precessing in the earth's gravitational field. Atomic nuclei with the same magnetic spin quantum number as ^1H will exhibit the same effects spins adopt one of two orientations in an externally applied magnetic field.

The Larmor equation expresses the relationship between the strength of a magnetic field, B_0 , and the precessional frequency, F , of an individual spin (equation 5.1):

$$\gamma B_0 = F \quad (5.1)$$

The proportionality constant to the left of B_0 is known as the gyromagnetic ratio of the nucleus. The precessional frequency, F , is also known as the Larmor frequency [7].

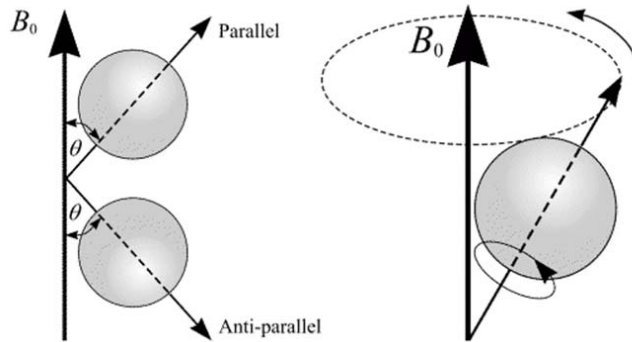


Figure 5.5: a) In the presence of an externally applied magnetic field, B_0 , nuclei are constrained to adopt one of two orientations with respect to B_0 . As the nuclei possess spin, these orientations are not exactly at 0 and 180 degrees to B_0 . b) A magnetic moment precessing around B_0 . Its path describes the surface of a cone [7].

At any given instant, the magnetic moments of a collection of ^1H nuclei can be represented as vectors, as shown in figure 5.6. Every vector can be described by its components perpendicular to and parallel to B_0 . For a large enough number of spins distributed on the surface of the cone, individual components perpendicular to B_0 cancel, leaving only components in the direction parallel to B_0 . As most spins adopt the parallel rather than the antiparallel state, the net magnetisation M is in the direction of the B_0 field [7].

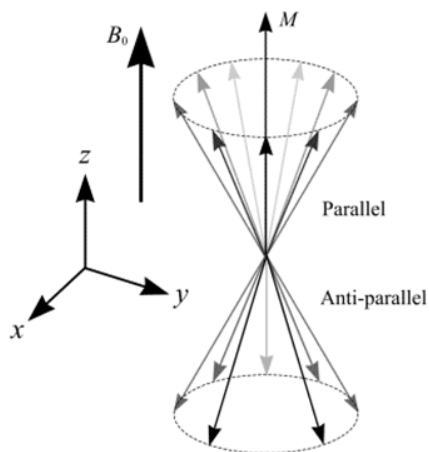


Figure 5.6: A collection of spins at any given instant in an external magnetic field, B_0 . A small net magnetisation, M , is detectable in the direction of B_0 [7].

Suppose the direction of B_0 is aligned with the z-axis of E. The plane perpendicular to B_0 contains the x and y-axes. In order to detect a signal from ^1H nuclei, radio frequency (RF) energy must be applied. RF energy at the Larmor frequency causes nuclear spins to swap between parallel and anti-parallel states. This has an oscillatory effect on the component of M parallel to the z-axis. RF energy, like all electromagnetic radiation, has electric and magnetic field components. Suppose the magnetic field component is represented by B_1 and lies in the x-y plane. The x-y components of M will be made coherent by the B_1 field giving a net x-y component to M and hence effectively causes M to tilt from the z direction into the x-y plane. This phenomenon is described further in figure 5.7 [7].

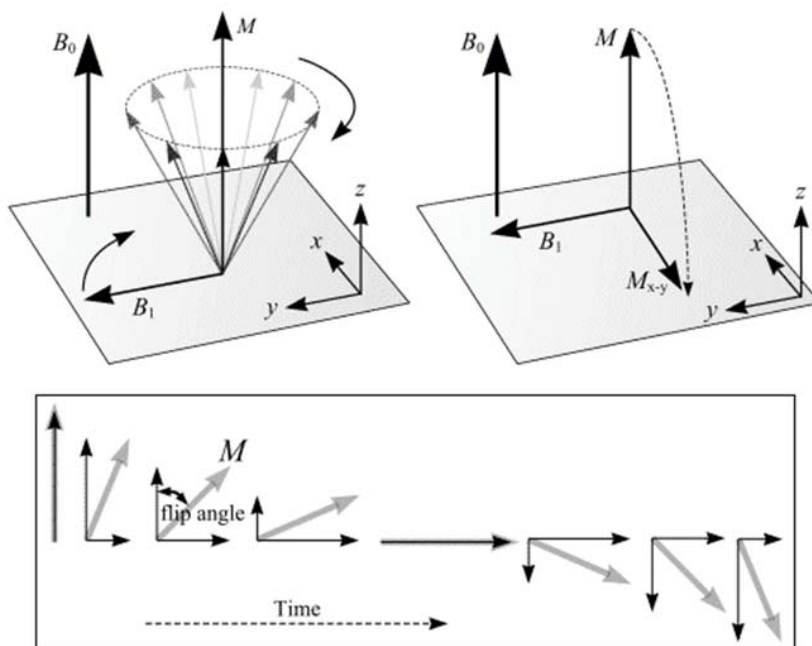


Figure 5.7: Top: The effect of RF radiation on the net magnetisation M is to produce a second magnetic field M_{x-y} . M is tilted from its original longitudinal z-axis orientation, along the direction of the external magnetic field B_0 , into the transverse x-y plane. Bottom: An illustration of flip angle, which is the angle through which M has rotated away from the z-axis [7].

Figure 5.8 a) shows the situation after an RF pulse is applied that causes the net magnetisation vector M to flip by 90 degrees. M lies in the x-y plane and begins to precess about the B_0 axis. M will induce an electromotive force in a receiver coil according to Faraday's law of magnetic induction. This is the principle of NMR signal detection. It is from this received RF signal that an MR image can be constructed. Figure 5.8 b) shows a graph of the voltage or signal induced in a receiver coil versus time. Such a graph, or waveform, is termed free induction decay (FID). The magnitude of the generated signal depends on the number of

nuclei contributing to produce the transverse magnetisation and on the relaxation times (see next section) [7].

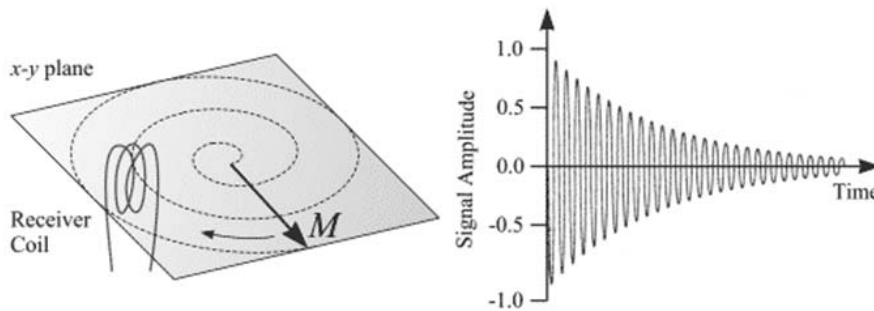


Figure 5.8: a) After a 90 degrees RF pulse, M lies in the x-y plane and rotates about the z-axis. The component of M in the x-y plane decays over time. An alternating current, shown in figure b), is induced in the receiver coil [7].

The return of M to its equilibrium state (the direction of the z-axis) is known as relaxation. There are three factors that influence the decay of M : magnetic field inhomogeneity, longitudinal T_1 relaxation and transverse T_2 relaxation. T_1 relaxation (also known as spin-lattice relaxation) is the realignment of spins (and so of M) with the external magnetic field B_0 (z-axis). T_2 relaxation (also known as T_2 decay, transverse relaxation or spin-spin relaxation) is the decrease in the x-y component of magnetisation [7].

5.3.2 Determination of droplet size via NMR

Droplet sizes and droplets size distribution can be investigated via NMR with different procedures. In Paper 1 pulse field gradient spin-echo nuclear magnetic resonance (PFGSE NMR) was used, which is a method to measure self-diffusion of molecules. The self-diffusion pattern of the components is measured with the aid of pulsed field gradients. In a carefully designed experiment, the “effective” gradient strength (k) is varied so that large signal attenuation is obtained. By doing so, the NMR signal attenuates due to diffusion according to equation 5.2:

$$E = E_0 \exp(-kD) \tag{5.2}$$

where E is the intensity of the signal and $k = \gamma^2 g^2 \delta^2 (4\Delta - \delta/\pi^2)$. Here γ is the gyromagnetic constant, Δ the time between the gradient pulses, g the field gradient strength and δ the length of the field gradient pulse. Thus, in the case of a single diffusing species the logarithm of the normalized signal attenuation (E/E_0) versus k results in a straight line with slope D , where D is the diffusion coefficient, which is obtained by a non-linear least-square fit of equation 5.2 to the data. However, inherent in many systems is the effect of polydispersity on the echo attenuation. This effect is considered by integrating over a distribution of diffusion coefficient $P(D)$ according to equation 5.3:

$$E = E_0 \int_0^{\infty} P(D) \exp(-kD) dD \quad (5.3)$$

The determination of the droplet size distribution was performed using the method outlined by Balinov et al. [8]. The NMR echo attenuation of the various water droplets in the emulsion can be written as equation 5.4:

$$E_{obs} = \frac{\int_0^{\infty} R^3 P(R) E(D, R, g, \Delta, \delta) dR}{\int_0^{\infty} R^3 P(R) dR} \quad (5.4)$$

Where, R is the droplet radius, $P(R)$ is the size distribution function and $E(D, R, g, \Delta, \delta)$ the echo attenuation of a spherical cavity of radius R . The definition of $E(D, R, g, \Delta, \delta)$ is given in ref. (25). For the size distribution Balinov et al. [8] used the log-normal distribution function given by equation (5.5):

$$P(R) = \frac{1}{2R\sigma\sqrt{2\pi}} \exp\left[-\frac{(\ln 2R - \ln d_0)^2}{2\sigma^2}\right] \quad (5.5)$$

Where d_0 is the median diameter and σ is the standard deviation.

5.4 Turbiscan analysis

Turbiscan LAB Expert equipment uses multiple light scattering techniques to detect and determine the destabilising phenomena suffered by the dispersed systems (suspensions and emulsions) as they age. With this technology, the destabilising phenomena of the dispersed systems are detected around 50 times more quickly than by simple observation. This equipment enables users to discriminate between the different destabilising phenomena that a dispersed system may suffer (coalescence, flocculation, sedimentation, creaming), and analyse these phenomena quantitatively. This equipment enables users to study dispersed systems that contain dispersed particles or phase of a size ranging from 0.1 up to 1000 μm in all kinds of dispersing media (water, alcohol, organic solvents, oils, isoparaffins, etc.). The Turbiscan equipment allows dispersed concentration systems of up to 95% (for emulsions) to be studied without the need for dilution. This is very important, as diluting the sample itself means variations in the stability of the dispersed systems [9, 10].

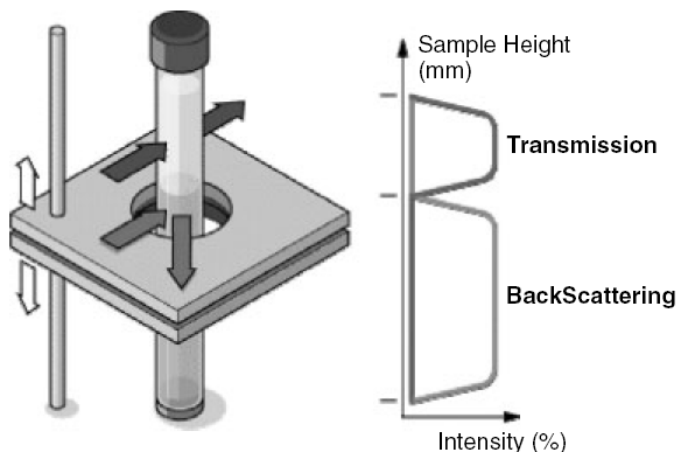


Figure 5.9: Turbiscan LAB Expert measurement principle [9].

The detection head is composed of a pulsed near-infrared light source ($\lambda = 880\text{nm}$) and two synchronous detectors. The transmission detector receives the light, which goes through the sample, while the backscattering detector receives the light scattered backward by the sample, acquiring data every 40 μm while moving along the 55 mm cell height (figure 5.9). The acquisition along the product is then repeated with a programmable frequency to obtain a superimposition of product profiles characterising, whether they are identical or not, the stability or instability of the product. Thermo-regulation allowing measurements to be carried out at controlled temperatures, from +5 $^{\circ}\text{C}$ above the ambient to +60 $^{\circ}\text{C}$ [9, 10].

5.5 Coulter Counter method

The Coulter Counter method was used in this work to measure droplet sizes and droplet size distribution of oil droplets dispersed in water. A Coulter Counter of the type COULTER® Multisizer II was used. The COULTER® Multisizer II is a flexible, multichannel, particle analyser, designed to give high resolution and precision over a wide range of sample sizes and materials. It can provide particle size distribution analysis within the overall range 0.4 μm to 1200 μm

Coulter Counter is a device used for counting and sizing particles and cells. Precisely it is a methodology for counting, measuring and evaluating microscopic particles suspended in a fluid. It is named for its inventor Wallace H. Coulter who developed it for the purpose of counting blood cells [11]. This method is also known as the Aperture-Impedance Method, since the “sensing zone” in this method is an aperture [12]. In the classical Coulter Counter, a conducting medium containing the particles to be analyzed is pumped through a small aperture, which is the sensing zone or the coulter aperture, while the impedance over the aperture is monitored [13]. The working principle of a Coulter Counter is illustrated in figure 5.10.

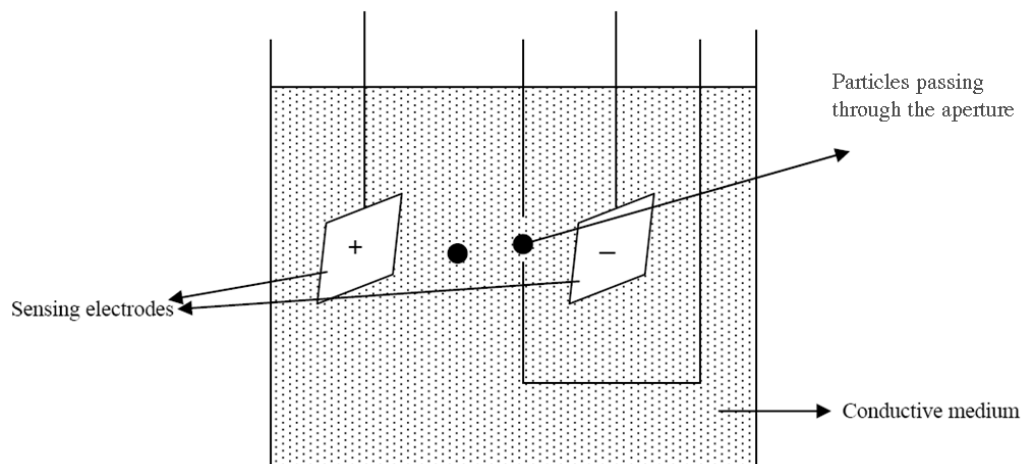


Figure 5.10: Schematic diagram showing the working principle of the coulter counter [13].

When there is no particles present in the aperture, the resistance offered by the aperture is very low because of the presence of the conducting electrolyte. Now consider the case when a particle enters the aperture; it flows through the aperture, this highly resistive sphere displaces the conducting electrolyte in the aperture by an amount equal to its volume hence increasing

the resistance of the aperture or in other words, the impedance across the electrodes. This impedance increase manifests itself as an increase in voltage across the electrodes, which can be detected by instrumentation circuits and processed by the computer.

Since the amount of electrolyte displaced by the particles in the aperture depends upon the size of the particles, different sized particles produces different increase in the resistances and hence different voltage levels [12]. Using count and pulse height analyzer circuits, the number of particles and volume of each particle passing through the sensing zone can be measured. If the volume of liquid passing through the aperture can be precisely controlled and measured, the concentration of the sample can also be determined [11, 14].

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6. MAIN RESULTS

This chapter highlights the most important results and conclusions in each paper collected at the end of this thesis.

Paper 1: Emulsions of Heavy Crude Oils I. Influence of Viscosity, Temperature and Dilution

The focus in this paper was to investigate the influence of viscosity, temperature and dilution for different emulsions of heavy crude oils. Twenty-seven crude oils from light conventional to heavy crude oils have been systematically analyzed with regard to viscosity, density, molecular weight, SARA, emulsion stability and droplet size distribution.

Rheology measurements show that some of the crude oils show Bingham plastic type flow behaviour at temperatures below 20 °C, indicating content of waxes. Analysis of the critical electric field cell shows that the $E_{critical}$ value depends on the applied field gradient. At low applied field gradients, the droplets are given more time to organize themselves into the water-continuous bridges, resulting in a lower $E_{critical}$ value than when the applied field gradient is higher. The $E_{critical}$ also increases at lower water cut, due to the increased distances the droplets must move to form linear chains between the two electrodes. $E_{critical}$ measurements of emulsions of diluted crude oils show that in general, the emulsion stability decreases with increased dilution. However, some systems show regions where the emulsion stability is independent of the dilution ratio or viscosity of the crude oil. The emulsion stability also shows temperature dependence according to Arrhenius law. Correlations between viscosity and emulsion stability indicate that an increase in emulsion stability correlates well with an increase in viscosity, and the viscosity correlates well with the SARA data of the crude oils.

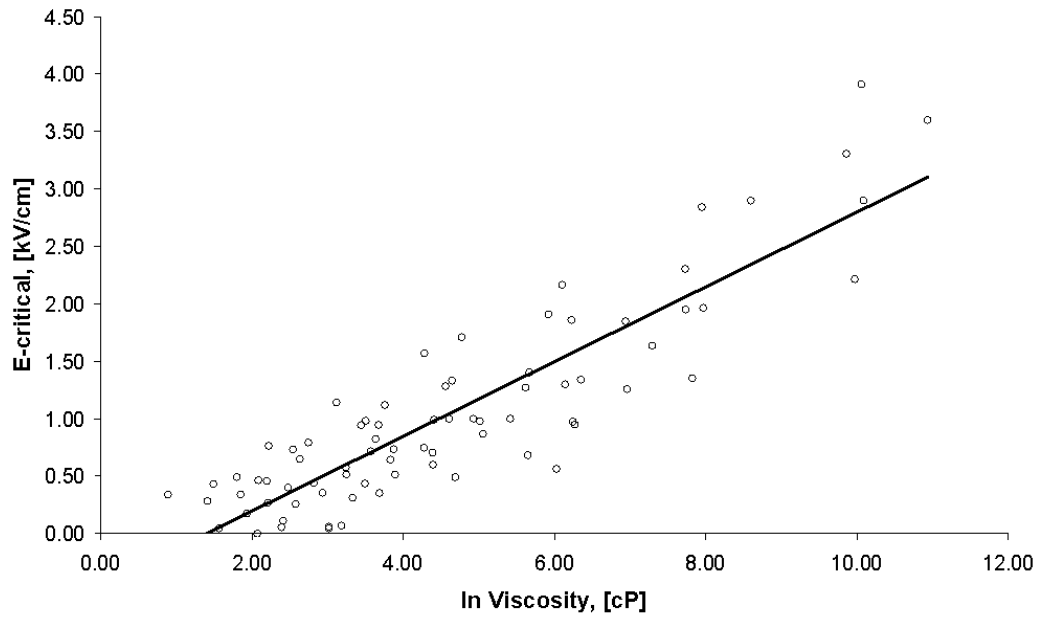


Figure 6.1: ln viscosity versus ecritical measured by the Ecritical cell. The figure shows good correlation between emulsion stability and viscosity.

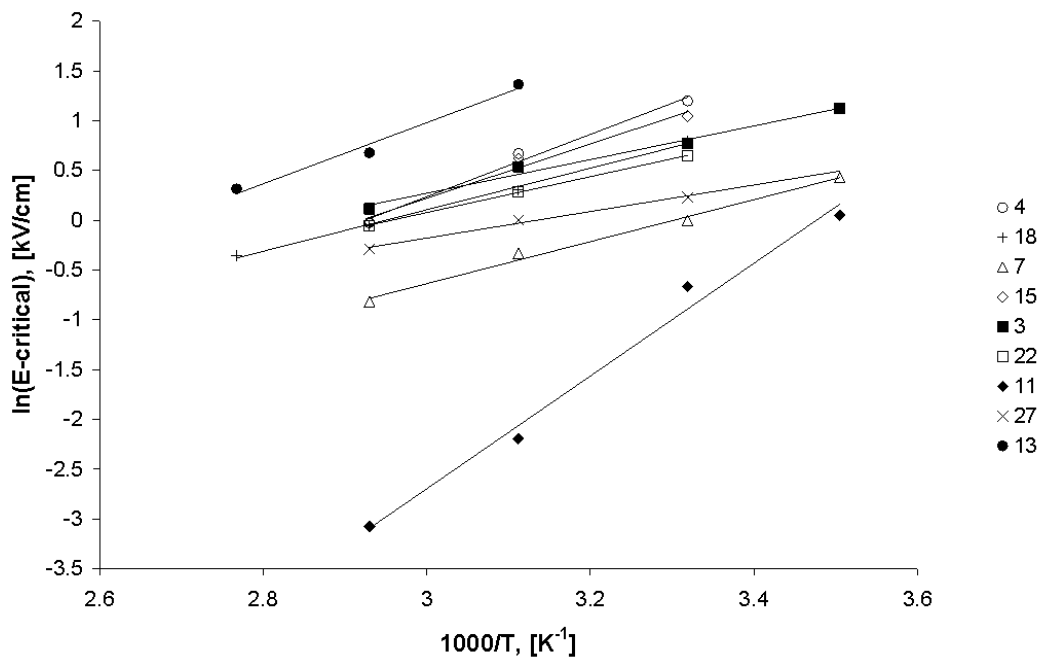


Figure 6.2: Arrhenius plot of Ecritical for nine different crude oils, which indicate that the emulsion stability shows temperature dependence according to Arrhenius law.

Paper 2: Stability of Water/Crude Oil Systems Correlated to the Physicochemical Properties of the Oil Phase

A characterization of thirty crude oils was performed to investigate the relative level of influence that individual parameters have over the overall stability of w/o emulsions. The crude oils were analyzed with respect to bulk and interfacial properties and the characteristics of their w/o emulsions. As expected, a strong covariance between several physicochemical properties was identified.

The characteristic time for droplet approach was predicted from a simplified force balance which modeled drag forces by Stokes' law and dielectrophoretic forces by a point-dipole approximation. Atten (*J. Electrostatics*, 30, 1993) had previously presented expressions for the characteristic time of droplet approach in a constant electrical d.c. field (equation 1). The comparison of the experimental time for destabilization with the theoretical time of droplet approach is showed in figure 6.3 (left) for a water-in-heavy oil emulsion with droplet size of 6 μm . Given enough time, the water-in-heavy oil emulsions could be destabilized even at very low electric field magnitude (0.4 kV/cm). The time for destabilization seemed to follow the $\tau_{\text{exp}} \propto (E_0)^{-2}$ relationship as predicted by equation 6.1:

$$\tau_{\text{theo}} = \frac{8\eta}{15\epsilon E_0^2} \left[\left(\frac{\pi}{6\phi_W} \right)^{5/3} - 1 \right] \quad (6.1)$$

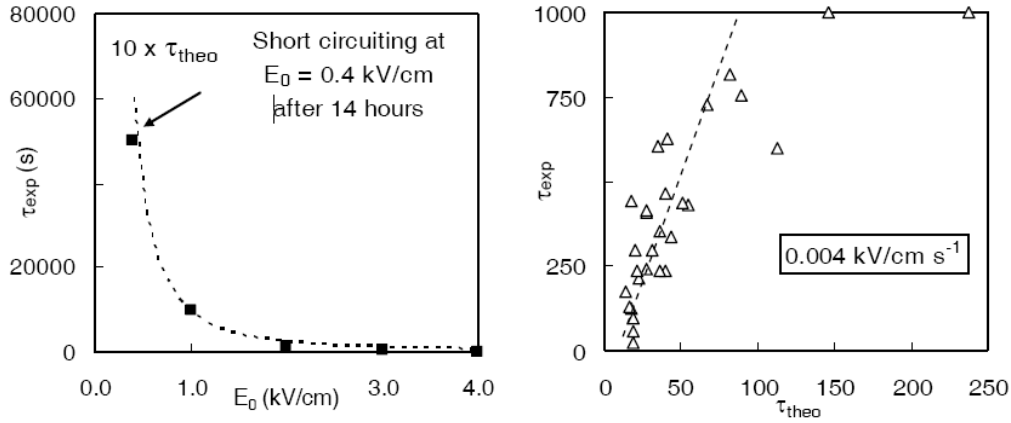


Figure 6.3: Time for destabilization compared to the theoretical time for droplet approach in an electric DC field. Destabilization of a water-in-heavy crude oil emulsion with constant electric field magnitude (left). Destabilization of 30 water-in-crude oil emulsions at a field rate of 0.004 kV/cm s⁻¹ (right).

The expression for the characteristic time was modified for a constantly increasing field magnitude (equation 6.2). Figure 6.3 (right) shows the experimental time for destabilization compared to the theoretical time for 30 water-in-crude oil emulsions at one of the studied field rates (0.004 kV/cm s⁻¹). Surprisingly, the simple model captured the difference between the 30 crude oils reasonably well also at other field rates (showed in paper).

$$\tau_{theo} = \left(\frac{8\eta}{5\varepsilon} \right)^{1/3} \left(\frac{dE_0}{dt} \right)^{-2/3} \left[\left(\frac{\pi}{6\phi} \right)^{5/3} - 1 \right]^{1/3} \quad (6.2)$$

It was proposed that the destabilization of static water-in-heavy crude oil emulsions in an electric field was predominantly retarded by the viscosity of the oil phase. When droplets approach each other in an inhomogeneous electric field the field magnitude increases greatly. Strong dielectrophoretic forces disintegrate the films and result in coalescence. The relative contribution from film stability to the overall emulsion stability may therefore be low.

Paper 3: Emulsions of Heavy Crude Oils II. Viscous Responses and Their Influence on Emulsion Stability Measurements

The stability of heavy crude oil emulsions were studied in a parallel-plate D.C. laboratory coalescer. Particularly, viscous responses and their influence on the emulsion stability measurements were investigated. In addition to highlighting previous results from the same experimental setup and discussing these based on recent experience, new results were presented. These included experiments at different temperatures and volume fractions of water (ϕ_w). A new semi-empirical model for the characteristic time of the destabilization process was presented (equation 6.3).

$$\tau_{theo} = \ln \eta \left(\frac{8}{5\varepsilon} \right)^{1/3} \left(\frac{dE_0}{dt} \right)^{-2/3} \left[\left(\frac{\pi}{6\phi_w} \right)^{5/3} - 1 \right]^{1/3} \quad (6.3)$$

The new model clearly performed much better than the previous model, especially for very viscous crude oils. The logarithmic viscosity (η) of the continuous phase successfully predicted the behaviour of 30 heavy crude oil emulsions in D.C. electric fields. The magnitude of the electric field was constantly increased with a step rate dE_0/dt until destabilization occurred. The relative contribution from the coalescence step was at its maximum for experiments at low field rates, whereas the relative contribution from the flocculation step dominated for experiments performed for high dE_0/dt . Experimental results at different step rates confirmed that the term $(dE_0/dt)^{-2/3}$ properly explained the magnitude of the electric field in the destabilization process. Figure 6.4 shows a) the old model versus b) the new model.

Studies of the performance of industrial electrocoalescers (to be published) have showed that simple electrostatic theory can potentially explain complex separation phenomena when the resistance to the coalescence step is reduced by an efficient demulsifier. The ultimate goal is to build a model for both the laboratory setup and the industrial coalescer so that laboratory experiments can be used to predict the behavior of the industrial process.

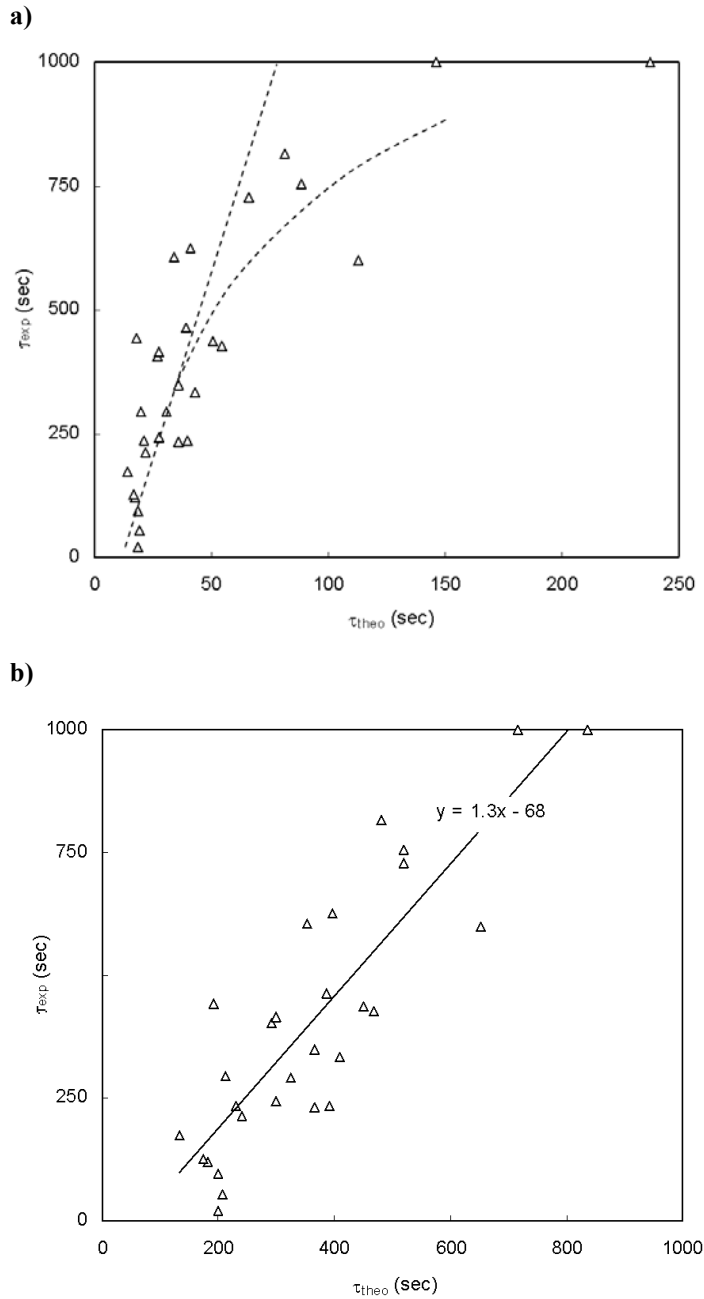


Figure 6.4: a) The characteristic time of destabilization (τ_{exp}) of emulsions ($\phi_w = 0.3$, $T = 40^\circ\text{C}$) in the D.C. field is compared to the theoretical (τ_{theo}) value of droplet approach as predicted from the old model. The experimental time was given by the measured CEF value and dE_o/dt ($0.004\text{ kV/cm s}^{-1}$). **b)** The characteristic time of destabilization (τ_{exp}) of emulsions ($\phi_w = 0.3$, $T = 40^\circ\text{C}$) in the D.C. field is compared to the theoretical (τ_{theo}) value of droplet approach as predicted from the new model Equation 6.3. The experimental time was given by the measured CEF value and dE_o/dt ($0.004\text{ kV/cm s}^{-1}$).

Paper 4: Characterization of the formation, flowability, and resolution of Brazilian crude oil emulsions

The presence of paraffin wax in crude oil and gas condensate fluids is known to cause significant flow assurance problems related to wax deposit buildup and gel formation. At low temperature conditions, waxy crude oils form w/o emulsions with rheological properties similar to heavy w/o emulsions. When paraffin wax crystals are abundant in the continuous phase, the rheological flow properties are characterized by shear thinning flow behaviour, and increasing viscosities with increasing water cut. The stability and flow properties of w/o emulsions were investigated using two Brazilian crude oils: a heavy crude oil (A) and waxy crude oil (B). Stable emulsions were formed with the heavy crude oil at water cuts up to 50%, while the waxy oil formed stable emulsions with water cuts as high as 70% (figure 6.5). Electrocoalescence measurements indicate decreasing Ecritical values with increasing temperature, resulting from a reduced viscosity of the continuous phase as well as dissolution of paraffin wax.

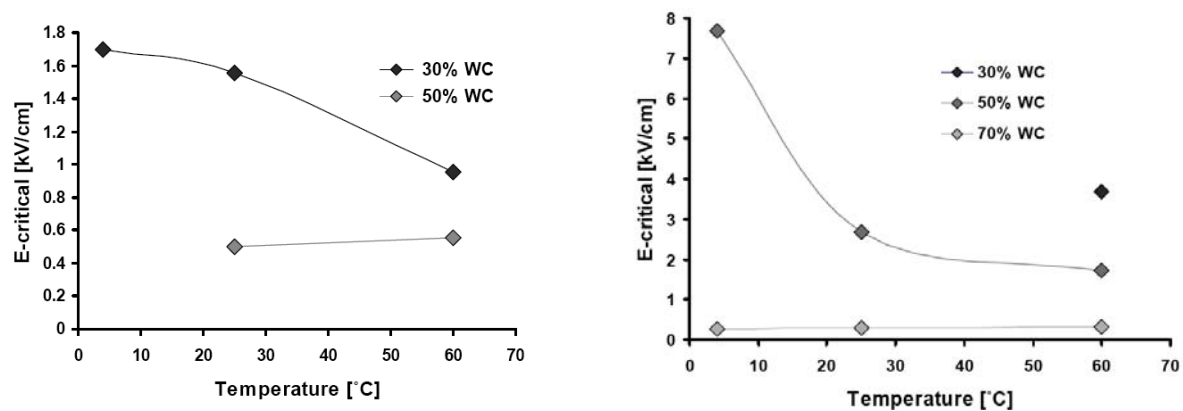


Figure 6.5: Ecritical values measured at different water cuts and temperatures. The figure on the left hand is emulsions formed from the heavy crude oil, while the figure on the right hand is emulsions formed for the waxy crude oil.

The superior stability of the waxy emulsions is likely a consequence of the greater abundance of asphaltenes and the lesser abundance of resins (demonstrated by SARA analysis). Because of the solubilizing effect of resin molecules, asphaltene molecules are more likely to be present in a particulate state in the waxy oil as compared to the heavy oil. Asphaltene particles impart stability to oil-water interfaces, providing resistance to water droplet coalescence and increasing the emulsion stability. At low temperature conditions, molecular asphaltene

adsorption onto precipitated wax crystals may also contribute to emulsion stability by increasing the water wettability of the wax crystals, thereby promoting adsorption onto the oil-water interface

The mechanical shear stress response with respect to absolute strain is shown in figure 6.6 for the gelled fluids. The measured shear stress is shown to initially increase in an elastic-like response, until a maximum shear stress is attained. For the waxy emulsions, a single shear stress peak is observed, indicative of cohesive gel failure. Beyond the maximum, the network structure of the gel becomes degraded with additional shear, and the measured shear stress decreases. Gel breakage was investigated at low shearing rates in order to emulate the rheological conditions associated with flow startup in gelled oil pipelines. A third-order kinetic breakdown model was assumed.

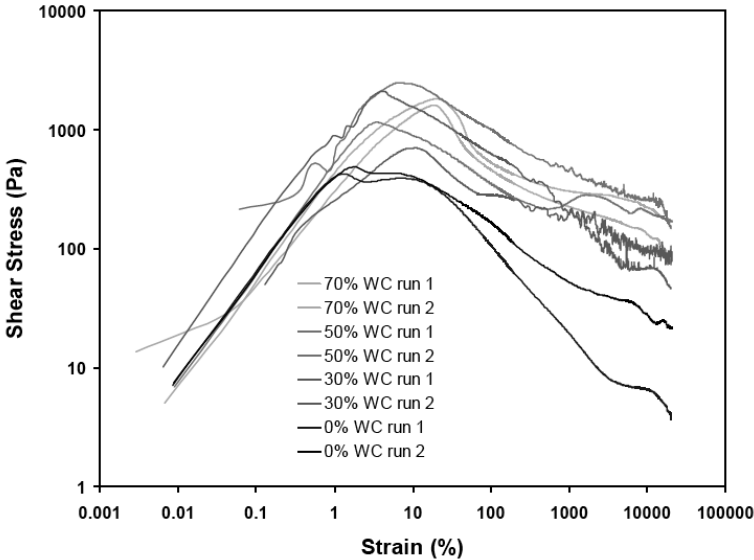


Figure 6.6: Measured shear stress responses when a shear rate of 0.1 s^{-1} is imposed on the wax-oil gels and wax-oil emulsion gels formed from crude oil B at 4°C .

Paper 5: A Multivariate Analysis on the influence of indigenous crude oil components on the quality of produced water. Comparison between bench and rig scale experiments

The focus in this paper was to investigate if there is any correlation between the physio-chemical properties of the crude oils and the quality of the produced water. Both bench and rig scale experiments have been performed.

As an approach to study produced water quality at bench scale, oil and brine water (3.5 wt %) have been mixed together, and transmission profiles from the separation process have been investigated by means of Turbiscan LAB. Results for all thirty crude oils are shown in figure 6.7.

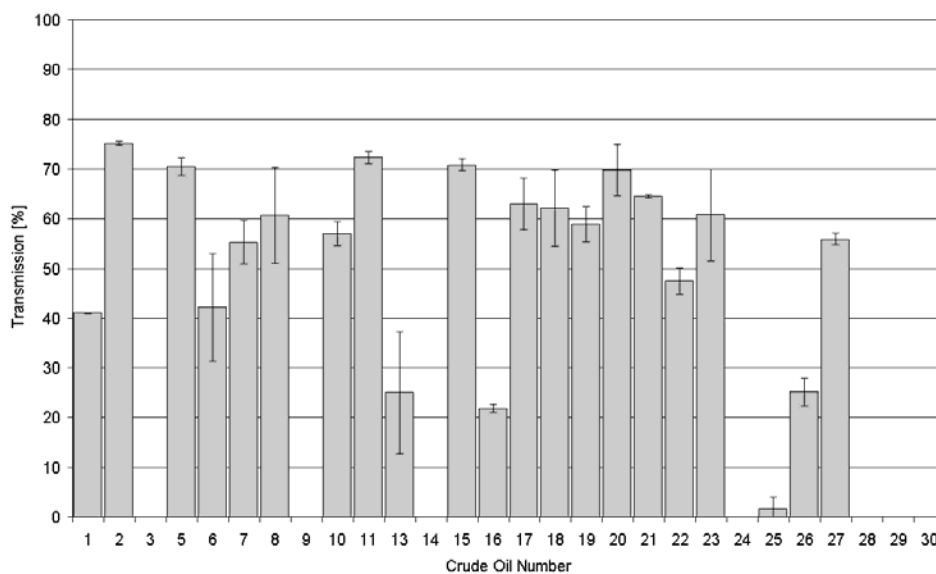
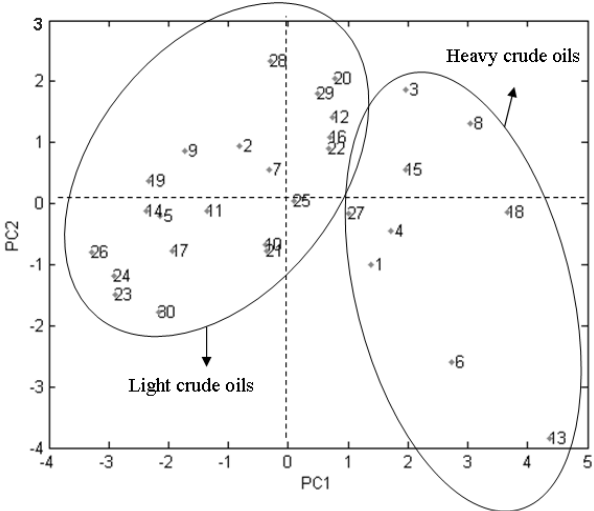


Figure 6.7: Average of maximum transmission for all 3 parallels with error bar from the Turbiscan LAB analysis.

The correlations between transmission profiles and crude oil characteristics were made by using principal component analysis (PCA). The results from the multivariate data analysis of the physio-chemical properties show that the crude oils group according to if they are light or heavy (figure 6.8 a). Results from the multivariate data analysis of the physio-chemical properties together with the transmission profiles show that the crude oils group according to if they are light or heavy and according to if they get high or low transmission (figure 6.8 b).

It is not so clear to see which of the physio-chemical properties that gives high transmission (good produced water quality), but based on results from the larger scale experiments the droplet sizes are a very important parameter.

a)



b)

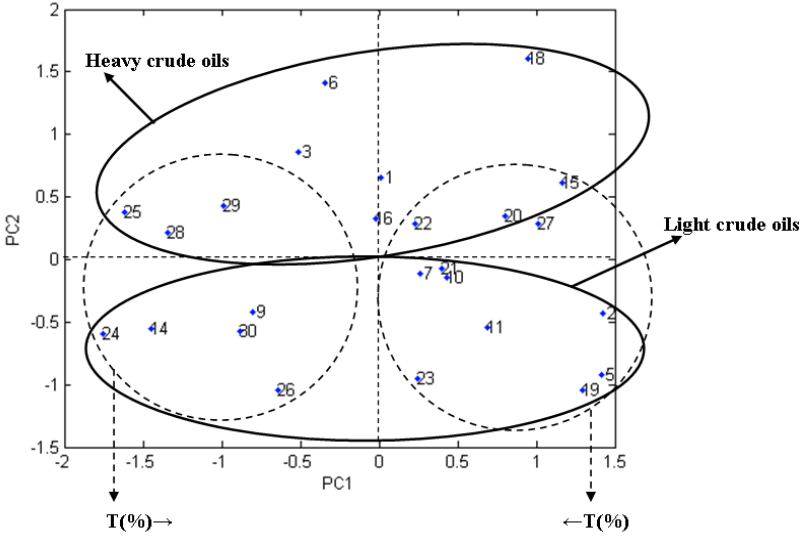


Figure 6.8: a) Score plot of the physio-chemical properties of the crude oils from principal component analysis
 b) Score plot of the physio-chemical properties together with transmission profiles of the crude oils from principal component analysis.

A Vortoil K-liner hydrocyclone connected to a mixing rig has been used to separate oil and water in larger scale experiments. Six crude oils have been investigated at the separation rig, and both droplet size distribution and dispersed oil concentration have been performed. Effect of droplet sizes on the quality of the produced water from the larger scale experiments is clearly seen. Figure 6.9 shows the differences between the different oils for droplets in the

same size range, and this difference is more pronounced for small droplet sizes. This indicates that other crude oil characteristics than viscosity, which directly influence on the droplet size, is important for the separation of small droplets. For small droplets the density seems to be an important factor.

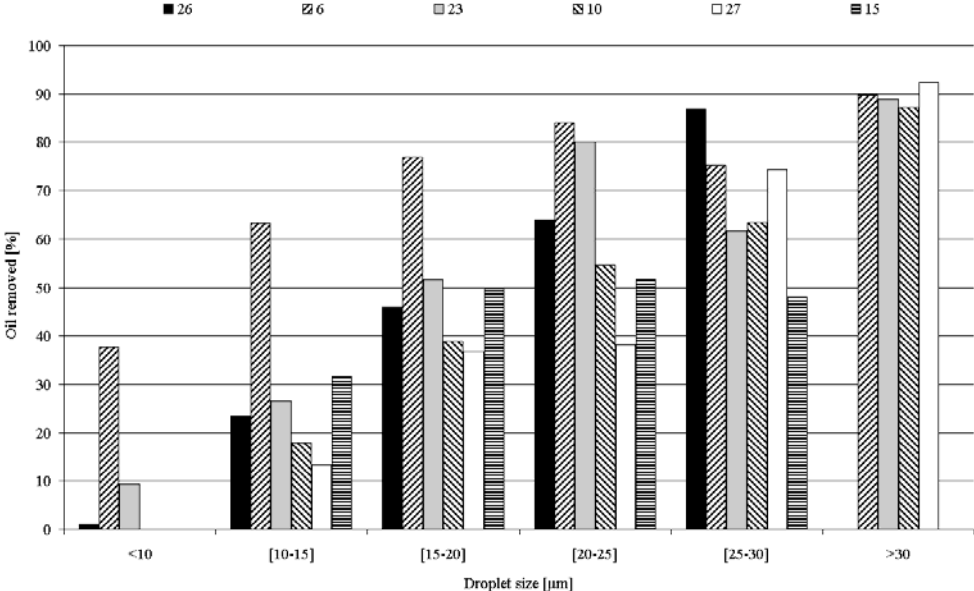


Figure 6.9: The figure shows the amount of oil removed when the droplets are grouped according to size.

7. CONCLUDING REMARKS

In this thesis two important topics related to crude oil processing have been treated: Heavy crude oil emulsions and the produced water problematic. This chapter summarizes the five papers written during my time as a Ph.D student at the Ugelstad Laboratory, and tries to draw some final conclusions of the work.

The main focus in paper 1, 2, and 3 was to increase the understanding of the stability of water/crude oil systems. In paper 1 the influence of viscosity, temperature and dilution on the emulsion stability was investigated. Paper 2 shows how the physiochemical properties of the oil phase influence on the emulsion stability, while paper 3 goes more in detail into viscous responses and their influence on emulsion stability measurements in the laboratory coalescer. Based on findings in paper 1 and 2 a new semi-empirical model has been developed, and is presented in paper 3. The model accounts for varying water cuts, magnitudes of electrical field, and a broad range of viscosities, both for different crude oils and for oils at different temperatures. The results obtained in paper 4 clearly indicate that the presence of emulsified water is shown to drastically increase fluid viscosities and cause shear thinning rheological behavior. High viscosities result in poor emulsification at low temperatures, as is evidenced by the instability of high water cut emulsions prepared at 4 °C. Therefore, in order to create tight emulsions in a pipeline transportation system, fluid emulsification should occur at relatively high temperature conditions, and well before the fluid enters the hydrate formation envelope. Optimally, water cuts should be maintained at or below 30% in order to assure complete emulsion stability. In the last paper results from the characterization work of the heavy crude oils done in paper 1-3 have been used to study o/w emulsions. The motivation for this study was to see how different crude oil properties influences on the produced water quality. From experimental results it is concluded that droplet size, high oil/water density differential and viscosity have a significant impact on separation efficiency in the large scale separation experiments as well as in the bench scale experiments. Based on the findings in paper 5 I will recommend to continue the work within the investigation of droplet sizes and droplet size distribution of o/w emulsions. The NMR technique seems to be promising to this purpose, and should be further investigated.

Paper I-V are not included due to copyright