

**ASPHALTENE CHARACTERIZATION
OF A
MALAYSIAN CRUDE OIL**

By

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FINAL PROJECT REPORT

**Submitted to the Chemical Engineering Programme
in Partial Fulfillment of the Requirements
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
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BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

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July 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



MICHELLE LISA JOHN

ABSTRACT

Asphaltenes are the most polar fraction of petroleum that can precipitate due to changes in pressure, temperature and composition which may be encountered during petroleum production and transportation. The precipitated asphaltenes can subsequently deposit on the surfaces of production/transportation pipelines and clog the pipeline partially or completely. Why asphaltenes deposit on a metal surface remains a poorly understood topic. This study is to determine the onset of asphaltene precipitation with respect to varying pressures and temperatures. High-pressure NIR was used to study the aggregation of asphaltenes by pressure depletion. What would be established is data displaying optimum operating conditions in which asphaltene deposition can be minimized or mitigated altogether. With this knowledge, operators can then be wary of the limits in the operating conditions to prevent asphaltene fouling in pipelines.

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CHAPTER 1

INTRODUCTION

1.1 Background

One of the major unsolved complex systems confronting the petroleum and natural gas industries at present is the untimely deposition of heavy organic compounds present in the oil. The production, transportation and processing of petroleum, bitumen, and other heavy-organic-containing hydrocarbons could be significantly affected by flocculation and deposition of asphaltene, resin, paraffin / wax , diamondoid, organo-metallics, etc. in the reservoir rock tubulars, oil well, pumps, storage vessels, transfer pipelines, and refinery and upgrading equipment with devastating economic consequences.

One question of interest in the oil industry is "when" and "how much" heavy organics will flocculate out under certain conditions. Since petroleum crude generally consists of a mixture of hydrocarbons and heavy organics it has become necessary to look at each of its constituents as a polydisperse or discrete mixture interacting with one another.

The kind and amount of depositions of heavy organics from petroleum fluids vary depending on the hydrocarbons present in oil and the relative amounts of each family of heavy organics.

The heaviest and most polar fraction of the crude oil is named asphaltenes, and gives rise to a variety of nuisances during crude oil production. It is widely recognized that flocculation and deposition of asphaltenes may occur when the thermodynamic equilibrium is disturbed. This may come as a result of changes in pressure and temperature [1-3], as a result of compositional alterations when blending fluid streams [4], or due to injection of gas during enhanced oil recovery (EOR) operations. The most serious precipitation problem is the creation of a formation damage [5], i.e.

partial or complete blockage of the inflow zone around a well, and thereby loss of productivity. Another possible problem is adsorption of asphaltenes on to the reservoirs mineral surfaces, whereby the wettability of the reservoir is changed from water-wet to oil-wet [6] and thereby reducing the potential oil recovery. In addition, the asphaltenes may deposit on the steel walls in the production line, or be transported along in the pipeline only to accumulate in separators or other fluid processing units. Clean up of deposited asphaltenes in the field may necessitate well shut-in and loss of oil production. Hence, preventing asphaltene flocculation is preferable from both an operational and economical viewpoint.

1.2 Problem Statement

Asphaltenes are generally defined as the fraction that soluble in aromatic solvents such as benzene or toluene and insoluble in light normal alkanes such as n-pentane or n-heptane. Asphaltenes are typically stable in a live fluid at reservoir condition. Once the drilling and production starts, the change in pressure, composition and temperature, can cause asphaltenes to destabilize.

Asphaltene 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.

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. The conditions of asphaltene deposition are controlled by factors such as pressure, temperature, composition and flow regime. 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.

1.3 Objectives and Scope of Study

The objective of this study is to determine the stability of asphaltene in its responses to different operating conditions. The author would like to establish the characteristics of asphaltene in different pressures and temperatures that may occur in the production of petroleum. What would be established is data displaying optimum operating conditions in which asphaltene deposition can be minimized or mitigated altogether. With this knowledge, operators can then be wary of the limits in the operating conditions to prevent asphaltene fouling in pipelines.

CHAPTER 2

LITERATURE REVIEW

2.1 Crude Oil Composition

Even though crude oils are a continuum of tens of thousands of different hydrocarbon molecules, the proportions of the elements in crude oils vary over fairly narrow limits.

Nevertheless, a wide variation in properties is found from the lightest crude oils to the highly asphaltenic crudes. The carbon content normally is in the range 83-87%, and the hydrogen content varies between 10 and 14%. In addition, varying small amounts of nitrogen, oxygen, sulfur and metals (Ni and V) are found in crude oils [1].

Due to the complex composition of crude oils, characterization by the individual molecular types is not possible, and elemental analysis is unattractive 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 [2-9]. Knowledge of the distribution of major structural classes of hydrocarbons in crude oils is needed in various fields in the petroleum industry. Examples are studies related to reservoir evaluation, migration and maturity, degradation processes, processing, and environmental effects [10].

The SARA-separation 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 the saturates (S), aromatics (A), resins (R), and the asphaltenes (A). Instead of molecules or atoms, certain *structures* are here considered the components of the crude oil, and the SARA-separation can be seen to give information somewhat between that obtained by elemental analysis and analysis for individual molecules [1].

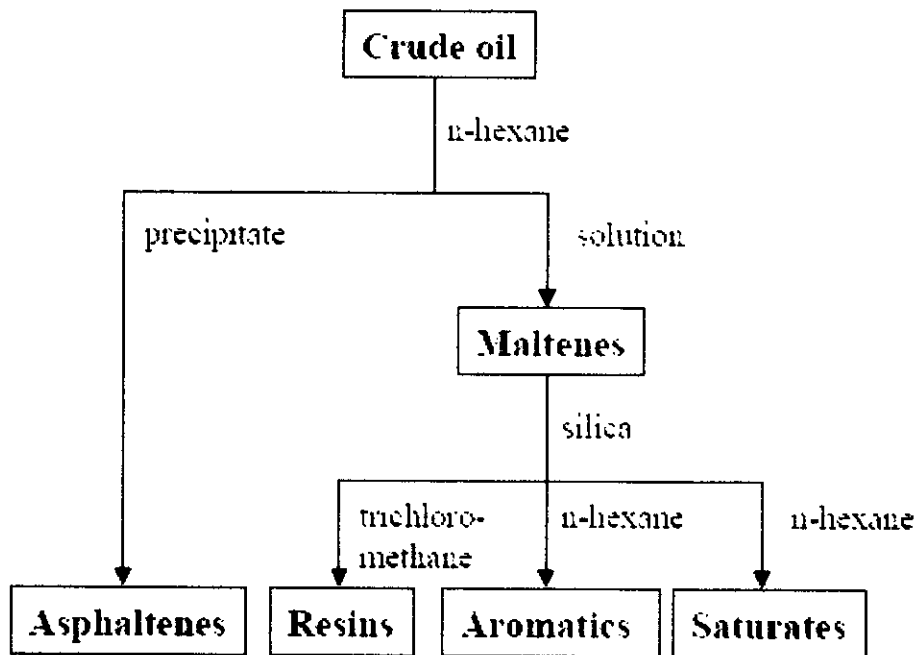


Figure 1 SARA Separation scheme

Saturates: The saturates (aliphatics) are non-polar hydrocarbons, without double bonds, but including straight-chain and branched alkanes, as well as cycloalkanes (naphthenes). 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 the saturates generally are the lightest fraction of the crude oil. Wax is a sub-class of the 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 [12-14].

Aromatics: The term aromatics refer to benzene and its structural derivatives. 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.

Resins: This 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 [1, 15, 16]. Since the resins are defined as a solubility class, overlap both to the aromatic and the asphaltene fraction is expected.

Despite the fact that the resin fraction is very important with regard to crude oil properties, little work has been reported on the characteristics of the resins, compared to for instance the asphaltenes. However, some general characteristics may be identified.

Resins have a higher H/C ratio than asphaltenes, 1.2-1.7 compared to 0.9-1.2 for the asphaltenes [16]. Resins are structural similar to asphaltenes, but smaller in molecular weight (< 1000 g/mole). Naphthenic acids are commonly regarded as a part of the resin fraction.

Asphaltenes: 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 asphaltene fraction contains the largest percentage of heteroatoms (O, S, N) and organometallic constituents (Ni, V, Fe) in the crude oil. The structure of the asphaltenes has been the subject of several investigations, but is now believed to consist of polycyclic aromatic clusters, substituted with varying alkyl side chains [15]. Figure 2 shows a hypothetical asphaltene monomer molecule. The molecular weight of asphaltene molecules has been difficult to measure due to the asphaltenes tendency to selfaggregate, but molecular weights in the range 500-2000 g/mole are believed to be reasonable [17-21]. Asphaltene monomer molecular size is in the range 12-24 Å [1, 18].



Figure 2 Hypothetical Asphaltene Molecule [22]

It is important to keep in mind that knowledge about the chemical composition of crude oils, gained from for instance a SARA-analysis, cannot fully explain the crude oil behaviour with regard to emulsion stability, asphaltene deposition etc. Equally important is information of the structure of the crude oil, which is a result of interactions between the continuum of chemical constituents in the oil. The interactions between the heavy end molecules, the asphaltenes and resins, play the most significant role in this sense.

2.2 Asphaltene Chemistry

The word asphaltene was coined in France by Boussingault [20] in 1837. Boussingault described the constituents of some bitumens found at that time in eastern France and in Peru. He named the fraction of distillation residue, which was insoluble in alcohol and soluble in essence of turpentine, “asphaltene”, since it resembled the original asphalt. The strong interest in developing a better understanding of the solution behaviour of asphaltenes, has been motivated by their impact on production, transportation, refining and utilization of petroleum. The asphaltene fraction is composed of the heaviest and components in crude oils. Separated solid asphaltenes usually appears brown to black in colour and has no

definite melting point but decomposes when the temperature exceeds 300-400 °C. It has been shown that changes in temperature [21, 22], pressure [1, 23-25] and oil composition [26] can cause asphaltene precipitation.

Asphaltenes are operationally defined as the non-volatile and polar fraction of petroleum that is insoluble in *n*-alkanes (i.e. pentane or heptane). As a result, asphaltenes constitute a solubility class of crude oil components, rather than a chemical class. The molecular weight, polarity and aromaticity of precipitated asphaltenes generally increase with increasing carbon number of *n*-alkane precipitant. A schematic diagram representing the range of heavy compounds precipitated by mixing crude oil with *n*-pentane and *n*-heptane is shown in Figure 3.

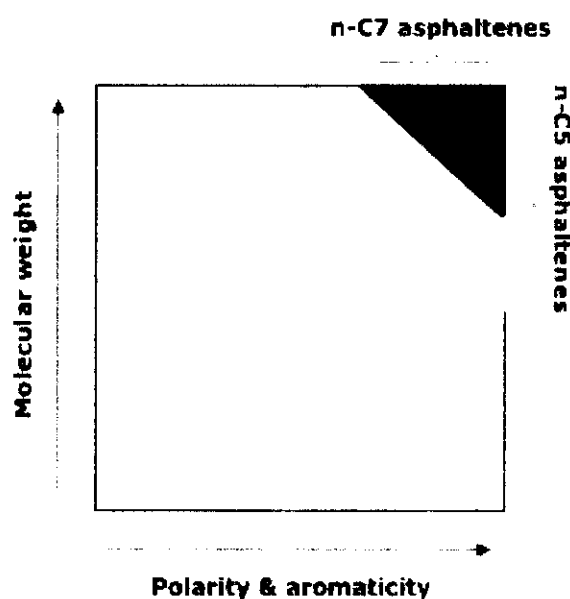


Figure 3 Hypothetical diagram representing the molecular characteristics of the asphaltenes precipitated from petroleum by *n*-alkane addition.

A number of investigators have constructed model structures for asphaltenes, resins, and other heavy fractions based on physical and chemical methods. Physical methods include IR, NMR, ESR, mass spectrometry, X-ray, ultra-centrifugation, electron microscopy, small angle neutron scattering, small angle X-ray scattering, quasi-elastic

light scattering spectroscopy, VPO, GPC, etc. Chemical methods involve oxidation, hydrogenation, etc.

While asphaltenes are recognised to be remarkably polydisperse in heteroatomic functionality, molecular weight, and carbon backbone structure, some common features have been established. Asphaltenes are characterized by fused ring aromaticity, small aliphatic side chains, and other elements including sulphur, oxygen, nitrogen, and metals such as vanadium and nickel. The heteroatoms accounts for a variety of polar groups such as aldehyde, carbonyl, carboxylic acid and amide, which are found in the asphaltene molecules. The aromatic carbon content of asphaltenes is typically in the range of 40 to 60 %, with a corresponding H/C atomic ratio of 1.0-1.2. A large percentage of these aromatic carbon rings are interconnected in the molecular structure and, consequently, the asphaltene molecule appears flat or planar. Figure 4 shows a suggested asphaltene structure. Yen and co-workers [29, 30] proposed a macrostructure model, where the asphaltenes was depicted as stacks of flat sheets of condensed aromatic systems, which was interconnected by sulphide, ether, of aliphatic chains. Espinat et al. [31] suggested the asphaltene molecules to be disc-like with polyaromatic fused ring cores containing polar functional groups. It is currently accepted that asphaltenes consist of aromatic compounds with π - π interactions, which undergo acid-base interactions and self associate through hydrogen bonding [32, 33].



Figure 4 Hypothetical molecular structure of the asphaltenes. (Downhole Asphaltene Remediation Technology)

Several major problems associated with the recovery and refining of petroleum [34-39], are related to the aggregation and precipitation of asphaltenes. Investigations have shown that asphaltene particles may self-associate, and form aggregates in the presence of aromatic hydrocarbons [26]. The degree of association is largely dependent upon the aliphatic/aromatic ratio of the solvent. Due to the aggregation phenomena, measurements of the true molecular weight and the aggregate size are inherently difficult and have resulted in numerous research efforts. The size of the aggregate structure has been suggested to lie between 2 and 25 nm in diameter [40-42]. The molecular weight obtained have ranged from a few hundred to several million g mol^{-1} , however, the most recent values from several different types of asphaltenes tend to suggest values from 600-1500 g mol^{-1} [43-49].

The aggregation is thought to occur through hydrogen bonding, however there is some inconsistency in the description of asphaltene self-association [30, 50-52], and both micelles and colloids are used in reference to asphaltenes. An asphaltene colloid is defined as a submicron particle consisting of several asphaltene molecules bound by π -bond interactions between polyaromatic clusters. Asphaltene micelles are considered analogous to a surfactant micelle, where the association of molecules is driven by hydrophobic-hydrophilic interactions. The terms “aggregate” and “micelle” are often used interchangeably in the literature. It has been shown that resins are essential in dissolving the asphaltenes in the crude oil. They are thought to attach to the asphaltene micelles/aggregates with their polar groups, and stretch their aliphatic groups outward to form a steric-stabilisation layer around asphaltenes [53, 54]. However, there still remains the debate about whether the micelle in petroleum is homogeneous insofar as it is composed only from asphaltenes, or if both asphaltene and resin molecules constitute a mixed micelle [30, 54].

Resins are defined as the non-volatile and polar fraction of crude oil that is soluble in *n*-alkanes (i.e., pentane) and aromatic solvents (i.e., toluene) and insoluble in liquid propane. They are structurally similar to asphaltenes, on the other hand, molar mass is lower, hydrogen/carbon ratio higher, and the heteroatom content lower. Long et al.

[28] showed that once resins were removed from the crude by adsorption chromatography, the remaining oil phase could no longer stabilise the asphaltenes.

Asphaltenes are also known to self-associate due to pressure depletion [1-3, 55]. At high pressures in the reservoir, the asphaltenes are dissolved in the monophasic crude oil. When the pressure is reduced the molar volume and the solubility parameter difference between asphaltenes and the crude oil increases towards a maximum at the bubble point of the crude oil. As a result of the reduced solvating power, the asphaltenes may start to precipitate at some onset pressure higher than the bubble point. Prior to the precipitation a stepwise association of the asphaltene molecules will take place. The final precipitation is due to a strong attraction between the colloidal particles and the formation of agglomerates. Once gas evolves, the light alkane fraction of the liquid phase is reduced, and thereby the solvating power for asphaltene molecules increases. The relative change in asphaltene solubility has been shown to be highest for light crude oils that are undersaturated with gas, and which usually contain only a small amount of asphaltenes. This gives the surprising result that light reservoir oils, which are low in asphaltenes are considered to be more likely to experience asphaltene related field problems than heavier, less undersaturated, asphaltenic oils.

A possible way of avoiding asphaltene precipitation is by adding chemicals that act in a way similar to resins by dispersing the asphaltenes in solution. Gonzales et al. [56] investigated the peptization of asphaltenes in aliphatic solvent by various oil-soluble amphiphiles including long-chain alkylbenzene, alkyl alcohol, alkylamine and *p*-alkylphenol. They found that the head group of the amphiphile influenced the effectiveness of the amphiphiles. Chang and Fogler [32, 33], using a series of alkylbenzene-derived amphiphiles as the asphaltene stabilisers, investigated the influence of the chemical structure on the asphaltene solubilisation and the strength of the amphiphile-asphaltene interactions. The results showed that the polarity of the amphiphile head group and the length of the alkyl tail controlled the amphiphile effectiveness. Increasing the acidity of the amphiphile head group could promote the amphiphile ability to stabilise asphaltenes, probably through acid – base interactions between the asphaltene and the amphiphiles. León et al. [57] showed results from

adsorption studies on asphaltene particles, where the adsorption isotherms of two amphiphiles (nonylphenol and nonylphenolic resin) were compared to a native resin. The adsorption isotherm for the natural resins was characterised by the continuous increase in the amount of adsorbed resins, and there was no indication of a plateau similar to the ones shown by the amphiphiles. This type of isotherm was explained by the penetration of substrate micropores by resin molecules, which lead to the partial breakdown of the asphaltene macrostructure.

In addition to the resins, other molecules in the petroleum mixture have also shown a tendency to stabilise the asphaltene particles/aggregates. Auflem et al. [58] showed that natural and synthetic naphthenic acids have a tendency to disperse the asphaltenes, and reduce the asphaltene particle size. This was proposed to occur through acid-base interactions between the naphthenic acids and asphaltenes, whereby the naphthenic acid would disperse the asphaltenes in solution in a similar way as the resins.

Naphthenic acids are classified as monobasic carboxylic acids of the general formula RCOOH, where R represents a cycloaliphatic structure. The classification contains a wide variety of structures with carbon number from C₁₀ to C₅₀, and from 0 to 6 saturated rings [59]. In crude oil production, the problems related to naphthenic acids arise from the processing conditions. As the pressure drops during production and carbon dioxide is lost from solution, the pH of the brine increases, which in turn leads to dissociation of the naphthenic acid ($\text{RCOOH} \rightarrow \text{RCOO}^- + \text{H}^+$). As a result, the following may occur: i) deposition of naphthenates [60] in oil/water separators, desalters, tubing or pipelines following complexation of naphthenic acids with metal cations present in the aqueous phase and, ii) formation of stabilised emulsions due to naphthenic acids and naphthenates accumulating at the w/o interface [61] and thereby stabilising colloidal structures.

2.3 Emulsions and Emulsion Stability

Emulsions have long been of great practical interest due to their widespread occurrence in everyday life. They may be found in important areas such as food,

cosmetics, pulp & paper, pharmaceutical and agricultural industry. Emulsions are also found in the petroleum industry, where they are typically undesirable and can result in high pumping costs, reduced throughput and special handling equipment. An emulsion is usually defined as a system consisting of a liquid dispersed in another immiscible liquid, as droplets of colloidal sizes ($\sim 0.1-10 \mu\text{m}$) or larger. If the oil is the dispersed phase, the emulsion is termed oil-in-water (o/w) emulsion, conversely, if the aqueous medium is the dispersed phase, it is termed a water-in-oil (w/o) emulsion. This classification is not always appropriate and other types as, for instance, multiple emulsions of the type o/w/o, may also be found. In the emulsified state, the interfacial area between the dispersed droplets and the bulk phase represents an increase in the systems free energy. Consequently, the emulsions are not thermodynamically stable, and will seek to minimise the surface area by separating into the different phases. For an emulsion to separate, the droplets must merge with each other, or with the homophase continuum that gradually forms.

Processes that facilitate the separation are sedimentation/creaming, flocculation and coalescence [62-64], as shown in Figure 5. Creaming and sedimentation create a droplet concentration gradient due to a density difference between the two liquid phases, which result in a close packing of the droplets. Aggregation of droplets may be said to occur when they stay very close to one another for a far longer time than if there were no attractive forces acting between them. The size and shape of the individual droplets are for the most part retained. 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.

Electrical double layer repulsion, or steric stabilisation by polymers and surfactants with protruding molecular chains, may prevent the droplets to come into contact with

each other. Also, polymers, 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 closed packed particles has considerable mechanical strength, and the most stable emulsions occur when the contact angle is close to 90° , so that the particles will collect at the interface. Particles, which are oil-wet, tend to stabilise w/o emulsions while those that are water-wet tend to stabilise o/w 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 sufficiently high concentration.

Other factors that usually favour emulsion stability are 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 termed Ostwald ripening [65]. Special features of surfactant association into liquid crystalline phases with lamellar geometries that facilitates the stabilisation may also occur [66].

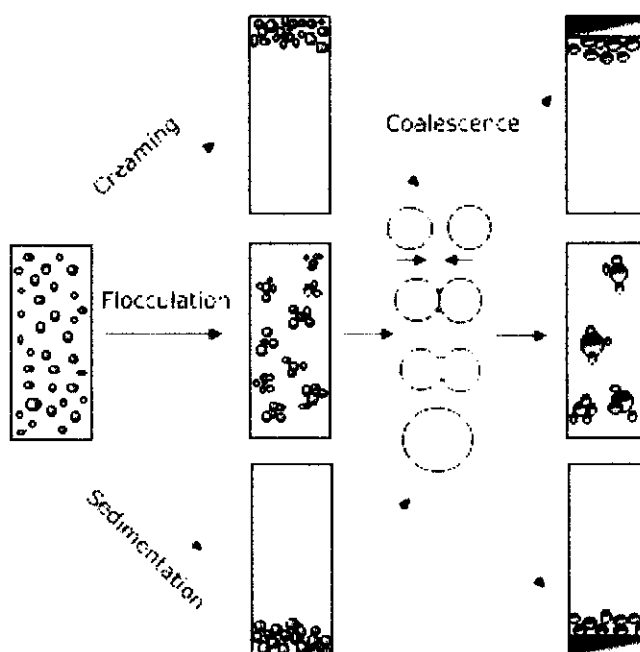


Figure 5 Processes taking place in an emulsion leading to emulsion breakdown and separation.

2.4 Stabilization of Water-In-Crude Oil Emulsions

The oil industry has an interest in crude oil emulsions for two main reasons: i) Water-in-crude oil emulsions can form in the processing of fluids from hydrocarbon reservoirs to the refinery or in production facilities during extraction and cleaning. The emulsified water adds significant volume to the crude oil, causes corrosion in the pipelines and increases the cost of transportation and refining. ii) Water-in-crude oil emulsions can form in oceanic spills. These emulsions are very stable and the oil phase is difficult to recover, leading to great environmental damage. Due to their colour and semisolid consistency, they are often named chocolate mousse.

In order to devise optimum treatment for water-in-oil emulsions, it is vital to understand how they are stabilized. The predominant mechanism whereby petroleum emulsions are stabilized is through the formation of a film with elastic or viscous properties. This film is thought to consist of a physical, cross-linked network of asphaltenic molecules, which aggregate through lateral intermolecular forces to form primary aggregates or micelles at the oil-water interface [8, 9, 67-73]. In addition, adsorption of solid particles from wax, clays, inorganic material or naphthenates may contribute to the film strength. Hence, the emulsion stability arises from a physical barrier that hinders the film to break when insufficient energies are involved in collisions between droplets.

Asphaltenes are thought to be peptized in the oil phase by the resinous components, and are hence prevented from precipitation. However, when water is introduced to the crude oil, the asphaltenic aggregates in the oil phase adsorb to the new oil-water interface. The resins are likely shed and do not participate in the stabilizing film [74], Figure 6. Eley et al. [75] showed that the stability of water-in-crude oil emulsions was related to the asphaltene precipitation point. The most stable emulsions occurred when the asphaltenes were on the verge of precipitation or above.

Kilpatrick et al [74] have shown that the resins are unnecessary in the stabilization of the asphaltenic film. The exact conformation in which asphaltenes organize at oil-water interfaces and the corresponding intermolecular interactions have yet to be agreed upon. The often suggested explanations are either H-bonding between acidic

functional groups (such as carboxyl, pyrrolic and sulfoxide), electron donor-acceptor bonding between transition metal atoms and electron-rich polar functional groups, or some other type of force such as π -bonding between delocalised π electrons in fused aromatic rings. The relative strength and importance of each in forming the viscoelastic film and their consequent roles in stabilising water-in-oil emulsions have still not been fully explained.

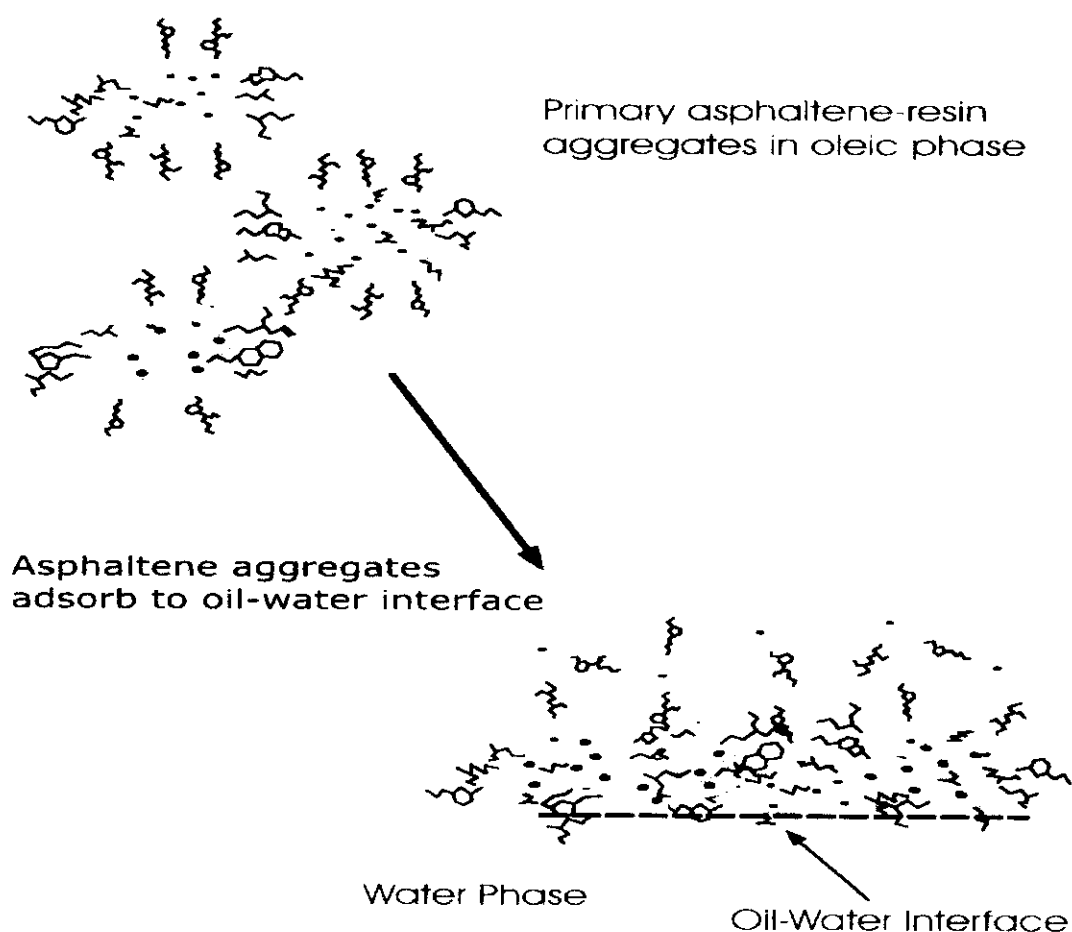


Figure 6 Proposed stabilising mechanisms for asphaltenes in petroleum by resin molecules.

2.5 Destabilisation of Crude Oil Emulsions

The destabilisation of crude oil emulsions forms an integral part of crude oil production. Stable emulsions are typically 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 separation tools are typical equipment used in the destabilisation of crude oil 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. Also, the capital cost of implementing or changing a chemical emulsion-breaking program is relatively small and can be accomplished without a shutdown. The separation rate of a w/o emulsion depends upon the matching of the demulsifier with the process residence time, the concentration and the stability of the emulsion, the temperature, the process vessel, the mixing energy and the type of stabilising mechanisms. Through building up more fundamental knowledge concerning the processes involved in stabilising and breaking the emulsions, the development and use of environmentally friendlier chemicals is facilitated. Also, the optimisation of type and amount of chemicals employed, contributes to reducing the oil content in the produced water offshore.

Commercial demulsifiers are typically mixtures of several components, which have various chemical structures and cover a wide molecular weight distribution. Some typical chemical structures used as demulsifiers are listed by Jones et al. [77] and Djuve et al. [78]. Each component of the demulsifier typically possesses a different partitioning ability and a different interfacial activity, and thus should provide a range of properties such as: i) Strong attraction to the oil/water interface, with the ability to destabilise the protective film around the droplet. ii) The ability to function as a wetting agent, changing the contact angle of solids. iii) The ability to act as flocculants and, iv) promotion of film drainage and thinning of the interdroplet

lamella by inducing changes to the interfacial rheological properties such as decreased interfacial viscosity and increased compressibility [73, 79, 80]. Krawczyk [81] showed that demulsifiers with equal partitioning between the aqueous and oil phase, gave the best destabilising efficiency. This balance would lead to a maximum in the surface adsorption of demulsifier and a minimum in interfacial tension. However, partitioning would not be a dominant factor when other effects such as dissolution of the interfacial material or their flocculation by the demulsifier occur.

When two water droplets approach each other, the capillary pressure acting normal to the interface causes liquid to be squeezed out of the film into the bulk. This liquid flow results in a viscous drag on the surfactants in the sublayer, and the adsorbed emulsifier are carried away towards the film periphery, thereby creating a nonuniform concentration distribution. Demulsifier molecules may then occupy the empty spaces available for adsorption, and due to the high interfacial activity of the demulsifier, the interfacial tension gradient is reduced. This leads to a strong increase in the rate of film thinning, and ultimately, when the film thickness decreases below some critical value, the film ruptures and the droplets coalesce.

Strong attraction to the oil/water interface is often dependent on diffusibility and interfacial activity of the demulsifier. For fast diffusion to the interface, the molecular weight of the demulsifier becomes important. The demulsifiers relative solubility in oil is also important for mass transport to the interface, and where this is inadequate, carrier solvents (e.g. alcohols or benzene derivatives) are often used. At the interface, the demulsifier may influence the droplet interfacial film material by displacement, complexation, changing the solubility in the continuous phase, changing the viscosity of the interfacial film, or through quick diffusivity and adsorption, thus inhibiting the Gibbs-Marangoni effect, which counteracts film drainage.

In residual emulsions, the droplets are finely dispersed and widely distributed, and the flocculating ability of the demulsifier is required to gather up the droplets. Then, high molecular weights highly branched demulsifiers, with an affinity for the water droplet, are necessary. For emulsions with particle-stabilised films, demulsifiers,

which act as wetting agents, may prove effective. The demulsifier may adsorb on to the solids, causing them to be more oil or water wettable, and thereby more easily transported into the continuous phase away from the interface. In some situations the demulsifiers have been used as inhibitors, i.e. injected before the emulsification process has taken place. This gives the demulsifier the chance to compete with the emulsifying agent in the process of covering the interface as the emulsifying process occurs, and thereby hinder the formation of a stabilising film. One should however, not forget to clarify the effect of concentration of the injected chemicals on the emulsion stability, as too much chemicals injected may result in an overtreat where the emulsion is actually stabilised, or a new emulsion type is created. Also, the injected demulsifiers should be checked to be compatible with other chemicals (corrosion inhibitors, scale inhibitors and flow enhancers) used in the stream as well as the components in the produced stream itself.

The effect of increased temperature is the sum of changes in several parameters. For instance, changes in the solubility of the crude oil surfactants or injected treating chemicals may occur as a result of increasing temperature. The density of the oil is reduced faster than the density of water as temperature increases, thereby accelerating the settling. Bulk viscosity of the crude oil decreases with increasing temperature, hence facilitating an increased collision frequency between water droplets, in addition to increasing the settling rate. Essential for the coalescence, especially in flocculated systems, is the influence of the interfacial viscosity. Depending on the type of interface the interfacial viscosity may decrease, increase or remain unchanged with increased temperature [77]. With highly paraffinic crudes found in the North Sea, waxes are strongly correlated to the stability of emulsions. The wax may contribute to the stability through particle stabilisation, or from increasing the viscosity of the crude oil. Therefore, melting and crystallisation sequence of wax is of importance for the stabilising properties of these compounds [82]. High operational temperatures may however result in high losses of light end molecules, and consequently an increased potential for asphaltene deposition.

Electrical resolution of crude oil emulsions is possible since the systems are relatively non-conducting. In 1965 Waterman [83] summarised the main behaviours of a drop, or a pair of drops under an electric field. The mechanism promoting separation are the result of either forces between particles resulting from induced dipoles charges (dipole coalescence), or forces that result from interactions between unidirectional field and particles having a net charge (electrofining). The principle behind the electrically induced coalescence is often divided into: i) non interacting droplets approaching each other, ii) deformation of droplets and formation of plane-parallel films, and iii) thinning of the films to a critical thickness at which the film becomes unstable, ruptures and the two drops unify and form a single large droplet. Important features of a typical electrocoalescer are: The electric field (AC or DC), frequency, and set up for electrodes. The electrocoalescers in the oil and petroleum industry uses both AC and DC electric fields for the separation of water-in-oil emulsions [84]. One problem is that most of the equipment in the market today is big and bulky, and it would therefore be of interest to develop small portable devices, incorporating features such as an optimum applied field strength combined with centrifugal force, to further enhance the separation.

CHAPTER 3 METHODOLOGY

3.1 Characterization of Crude Oil

Oil used in this study is Angsi !35

Table 1 Characterization of Angsi !35

CHARACTERISTIC	UNIT	VALUE
Density	kg/l	0.8238
API	Degree	40.17
Basic Sediment and water	Vol %	<0.025
Water content	Vol %	< 0.025
Total Acid Number	mgKOH/g	0.478
Flash Point	^o C	<25
Pour Point	^o C	+30
ASTM Color	-	>8.0
Total Sulphur	Wt %	0.0392
Salt	Lb/1000bbbls	11.5
Nitrogen	Ppm wt	170
Ash	Wt %	0.002
Wax	Wt %	14.1
Kinematic viscosity @ 40 ^o C	cSt	4.313

Kinematic Viscosity @ 70 ^o C	cSt	2.376
Characterisation factor		12.5
Gross Calorific Value	MJ/kg	45.85
Mercury	Ppb wt	8
Asphaltenes	Wt%	<50
Sodium (Na)	Ppm wt	<1
Potassium (K)	Ppm wt	<1
Copper (Cu)	Ppm wt	<1
Lead (Pb)	Ppm wt	<1
Iron (Fe)	Ppm wt	<1
Nickel (Ni)	Ppm wt	2
Vanadium (V)	Ppm wt	<1
Arsenic (As)	Ppm wt	<1

3.2 Standard Procedure for Separating Asphaltenes from Crude Oil

The ASTM recommended procedure for separating asphaltenes from crude oil (ASTM D2007-80) is a widely-recognized standard. The author has chosen follow this procedure, with some modifications, in order to ensure that the results are comparable to those obtained in other laboratories. The ASTM procedure specifies adding a volume of n-pentane that is 40 times the volume of the aliquot of oil. The principal modification is to use n-heptane instead of n-pentane as the standard precipitant. Step-by-step instructions for asphaltene separation are provided in this standard procedure.

Determine sample size

Most crude oils contain from 1 to 10 grams of n-heptane asphaltenes per 100 ml of oil. To ensure accurate determination of asphaltene content, as much oil should be used as possible. In most cases, 20 ml of oil should be adequate.

Mix crude oil with precipitant

1. Accurately measure a volume of oil into a glass flask.
2. Add 40 times that volume of n-heptane (or other asphaltene precipitant, as needed) to the flask. Seal the flask with a stopper and shake the mixture thoroughly. If a rubber stopper is used, wrap it with aluminum foil to avoid direct contact of stopper with the solvent or its vapor.
3. Equilibrate the mixture for two days at ambient conditions. Shake the flask at least twice during this aging period.

Filter to separate solid asphaltenes from oil/precipitant mixture

After aging for two days, a funnel filter assembly can be used to separate precipitated asphaltenes from the oil/precipitant mixture:

4. Select and pre-weigh a weighing vessel and filter paper. Start with an 0.22 μ m filter. See additional instructions below (Steps 11-16) if mixture does not pass through the 0.22 μ m filter.
5. Install filter paper into the funnel filter assembly. Use a prefilter immediately beneath it to prevent direct contact of the filter paper with metal supporting net. Direct contact can lead to development of cracks in the brittle membrane filter and thus cause leakage. Use a strong spring clamp to tightly hold the assembly together.
6. Pour about 100 ml of the oil/precipitant mixture into the funnel cup and seal the cup with aluminum foil to reduce evaporation during filtration.
7. As long as the mixture passes through the filter rapidly, continue add mixture to the funnel cup. Repeat until the filtration rate becomes very slow. It will be easier to recover asphaltenes if you allow them to accumulate on a single filter. (If the deposited layer is too thin, the asphaltenes may be difficult to remove from the filter after drying due to adhesion or from the weighing boat due to electrostatic forces.)
8. Before removing the filtered asphaltenes, rinse the funnel cup with several aliquots of the n-alkane precipitant. Rinsing should be done just as the last of the mixture passes through the filter, before the deposited asphaltene layer begins to dry and crack. After the final rinse, continue to pull a vacuum until the deposited asphaltene dries enough to form cracks.
9. Turn off the vacuum pump. Loosen the clamp with one hand while holding the funnel assembly together with the other hand. Carefully peel off the entire filter paper and asphaltenes, placing them in the weighing boat. If any asphaltene remains on the bottom rim of funnel cup, use a spatula to transfer them to the weighing boat.
10. Pre-weigh another piece of filter paper and repeat Steps 5 through 10 until all of the mixture has been filtered. Upon successful filtration of the whole mixture through an 0.22 μ m filter, proceed to Step 18 for routine determinations or Step 15 for more precise measurements.

Dry and weigh the asphaltenes

11. Dry the filtered asphaltenes and filter papers in the hood for several days. Check the total weight of the weighing boat, filter papers, and asphaltenes every few hours. If the weight change is less than 0.0001g over a 12 hour period, the asphaltenes are dry.

Determine the amount of asphaltene in the oil

12. The weight of the asphaltenes can be determined by subtracting the weight of the weighing boat and all filter papers from total weight. The asphaltene content is calculated by:

$$\text{asphaltene content (g/100ml)} = \frac{\text{weight of dried asphaltene (g)}}{100 \text{ crude oil volume (ml)}} \times 100$$

13. Use a spatula to transfer the dried asphaltenes to a glass vial and seal it with a Teflon-lined cap. In most cases, only about 80-90% of the separated asphaltene can be collected in the vial. The powdery remainder often cannot be removed from the filters and weighing vessel.

3.3 Near Infra-red Spectroscopy

William Herschel is credited as the father of near-IR techniques, for his discovery of the near infrared region as early as 1800. The molar absorptivity of NIR bands permits operations in the reflectance mode, and hence the measurements can be made directly on the material itself. The measurements are thus rapid and non-invasive [93], and there is usually no need for extensive sample preparation. Also, the NIR spectra contain information on both chemical composition and physical properties of the sample [94]. This permits not only the identification of compounds, but also total characterization of samples and determination of non-chemical parameters.

The near infrared region is found between the visible and middle infrared regions (MIR) of the electromagnetic spectrum. According to the American Society for Testing and Materials (ASTM), it is defined as the spectral region spanning 780 - 2526 nm (12820 - 3959 cm^{-1}). Light absorption in this region is primarily due to overtones and combinations of fundamental vibration bands occurring in the NIR region. This makes NIR an excellent choice for hydrocarbon analysis, where functional groups such as methylenic, olefinic and aromatic C-H give rise to various C-H stretching vibrations that are mainly independent of the rest of the molecule. The intensity of the overtone and combination bands is marked lower than for the fundamental bands. When dealing with organic compounds, as for crude oils, the most prominent NIR bands are those related to O-H, C-H and N-H groups. Main absorption bands of NIR spectra are given in Table 2.

Table 2 Near Infrared Spectroscopy Adsorption Bands

<i>Absorption band</i>	<i>Wavelength region [nm]</i>
O - H First overtone	1400 - 1450
O - H Combinations	1900 - 1975
C - H Second overtone	1125 - 1225
C - H Combinations first overtone	1350 - 1450
C - H First overtone	1625 - 1775
C - H Combinations	1950 - 2450

In addition to molecular absorption, the NIR spectra are dependent upon several physical parameters, where the most prominent is scattering from particles. As the particle size changes it causes a change in the amount of radiation scattered by the sample [95], and this is reflected in the NIR spectra as a shift of the baseline. A typical representation of the baseline shift in a system as a consequence of change in particle sizes are shown in Figure 7.

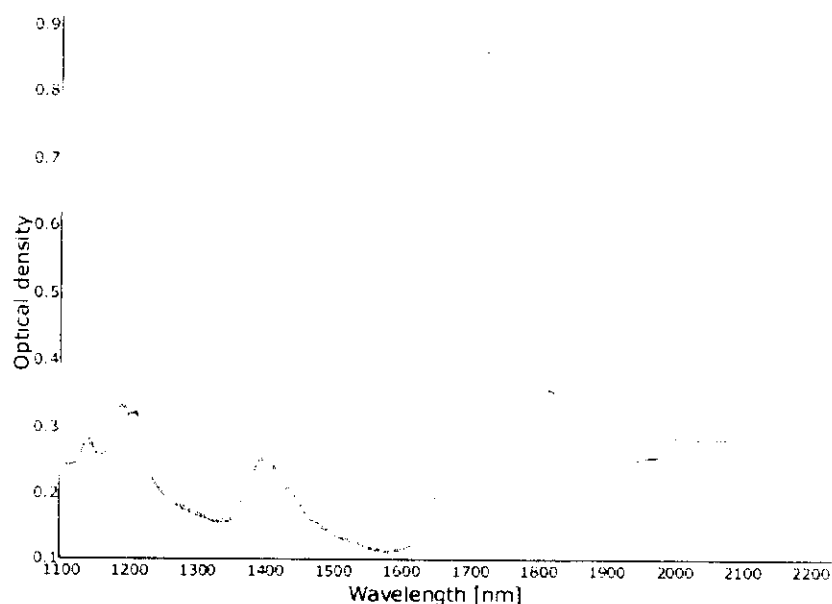


Figure 7 Optical density, a sum of scattering and absorption of transmitted light, plotted against wavelength for several NIR spectra. .

The system consists of asphaltene particles in model oil (heptane/toluene 70/30 vol. %) and is measure at defined time intervals after injection of a chemical. The

lowering of the baseline is a measure of decreased scattering as the chemical disperses the particles

For slightly lossy dielectric spheres in the Rayleigh limit ($r/\lambda \leq 0.05$), the scattering and absorption processes contribute separately to the extinction coefficient [96]. That is

$$\sigma_{\text{tot}} = \sigma_{\text{sc}} + \sigma_{\text{abs}}$$

where σ_{tot} , σ_{sc} and σ_{abs} are the total, scattering and absorption cross-sections, respectively. The ratio of scattering to absorption scales with r^3 , indicating the importance of particle size on the total light extinction. The relation between optical density (OD), light intensity (I), particle diameter (N) and particle cross section (σ_{tot}) is given as

$$OD = \log\left(\frac{I_0}{I}\right) = 0.434 \cdot N \cdot \sigma_{\text{tot}}$$

where I_0 and I are the intensities of incident and transmitted light, respectively. The effect of multiple scattering is not accounted for in this equation. Details on light scattering in the near infrared region can be found in the literature [98-100].

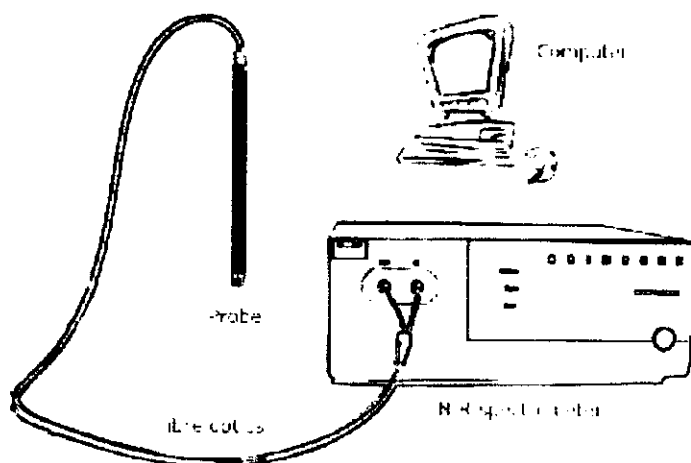


Figure 8 The near infrared spectrometer setup.

CHAPTER 4

RESULTS AND DISCUSSION

The asphaltene aggregation behaviour was studied by use of a high-pressure NIR system shown in Figure 8. The figure below shows a scanned picture of the NIR spectra for one of the experimental runs.

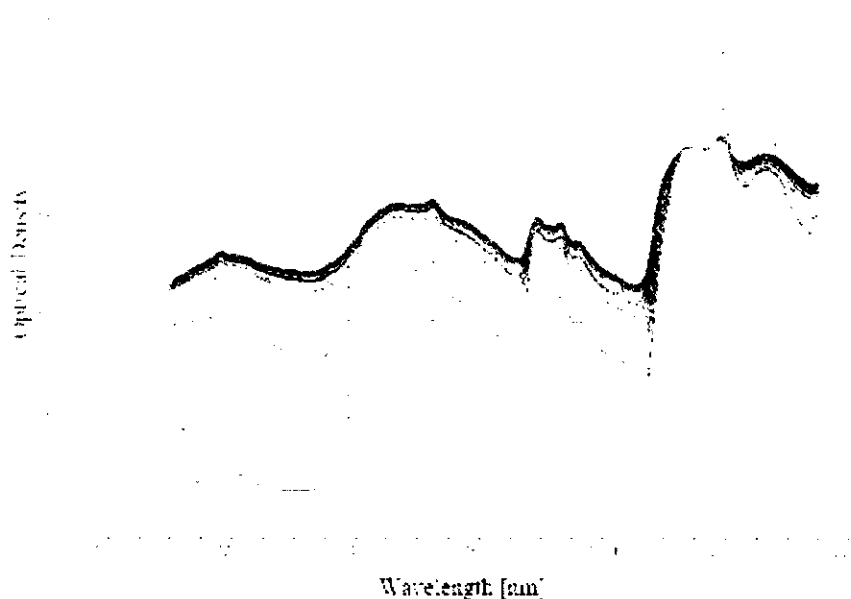


Figure 9 Example of NIR spectra from experiment

Both a recombined crude oil and model systems of pentane, toluene and asphaltene were studied. The model systems were constructed such as to be at the verge of asphaltene precipitation. Two systems of 1.2 wt% asphaltene in 35 wt% and 40 wt% pentane-toluene solvents were made. The crude oil contained 0.8 wt% asphaltenes and had a reservoir bubble point pressure of 155 bar. The systems were pressurized to 300 bar and charged to the high pressure rig at temperatures of 100°C and 150°C. The systems were then depressurized in steps, and the resulting NIR spectra at each pressure level were analyzed. The system was allowed about 20 minutes to

equilibrate at each pressure level. It was found that at the asphaltene aggregation onset pressure a distinct shift in the baseline of the spectrum was seen. Lowering the pressure even further, the bubble point was detected by NIR spectra displaying low absorbance due to gas evolution.

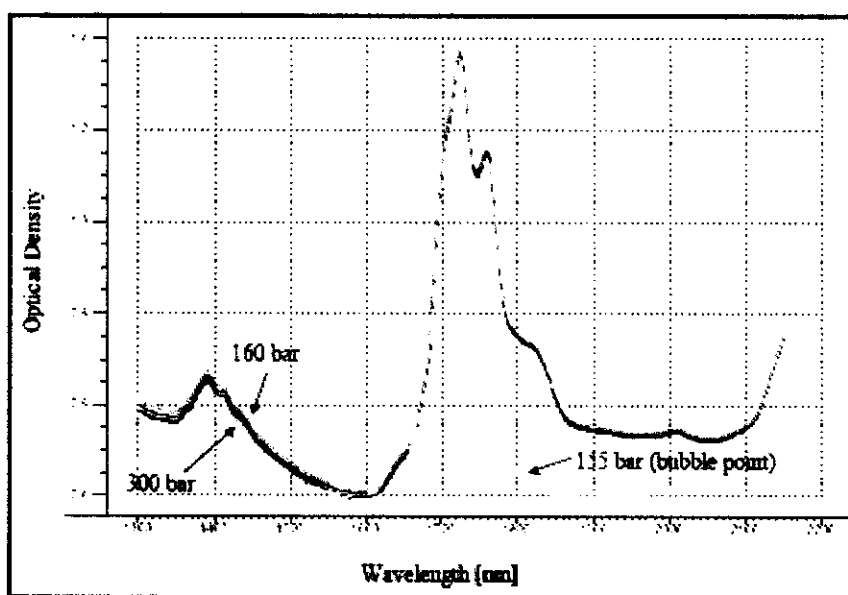


Figure 10 Overlain spectra for pressure from 300 bar -160 bar

Starting from 300 bar, first a decrease in optical density with pressure depletion due to the compressibility of the crude oil was seen. As soon as aggregates started to grow, the optical density increased due to increased light scattering. Although this was difficult to see directly from the spectra, the pressure depletion path is indicated along with the detected asphaltene aggregation onset pressure at 180 bar.

Performing the same type of experiments on the model systems (containing only asphaltenes in addition to solvents) produced the same type of results, thus confirming that the shift in the score plot indeed was caused by asphaltene aggregation.

Depressurisation of a model system without asphaltenes showed no shift in the score plot. Table 3 summarises the experimental conditions, detected onset pressures and bubble points for the systems studied. The bubble point pressures for the low temperature model systems were too low to be detected. As expected, the onset

pressure for the 40 wt% pentane solvent was higher than for the 35 wt% pentane system. In addition, the onset pressure at 150°C was found to be higher than that at 100°C.

Table 3 Bubblepoint and asphaltene aggregation onset pressures

System	Temperature (°C)	Bubblepoint (bar)	Onset pressure (bar)
Crude oil	100	155	180
35 wt% pentane	100	<2.5	20
35 wt% pentane	150	10	30
40 wt% pentane	100	<2.5	40
40wt% pentane, no asphaltene	150	14	-

Table 4 Asphaltene deposition with respect to depleting pressures for crude oil system

Pressure	300	275	250	225	200	175	150	125	100
wt %	0	0.05	0.2	0.4	0.8	0.7	0.6	0.5	0.4

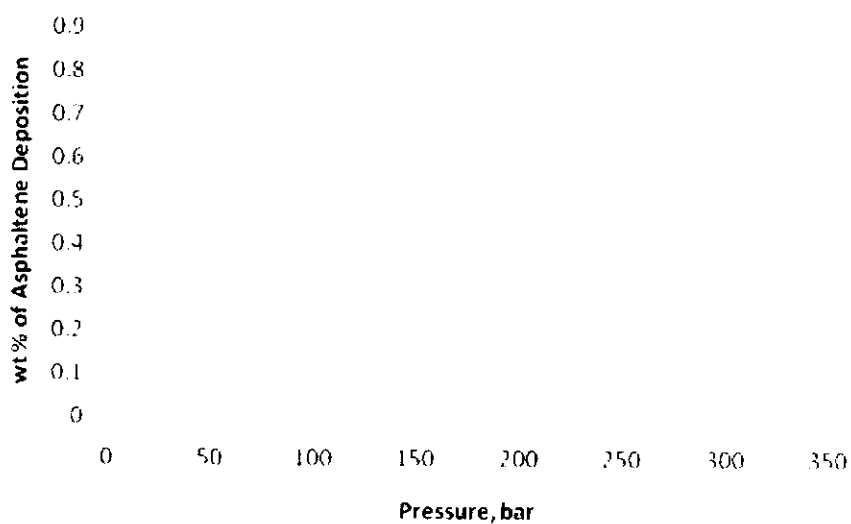


Figure 11 Pressure effect on amount of asphaltene deposition in the crude oil.

CHAPTER 5

CONCLUSION

The asphaltene precipitation behavior in the pressure depletion process has been examined for the Angsi 135 crude oil. Two systems of 1.2 wt% asphaltene in 35 wt% and 40 wt% pentane-toluene solvents were made. Samples were analyzed using the NIR spectroscopy method to determine the onset of asphaltene precipitation over a pressure depletion from 300 bar to 100 bar and temperatures of 100°C and 150°C.

The crude oil contained 0.8 wt% asphaltenes and had a reservoir bubble point pressure of 155 bar. The systems were then depressurized in steps, and the resulting NIR spectra at each pressure level were analyzed.

The pressure depletion path is indicated along with the detected asphaltene aggregation onset pressure at 180 bar. As expected, the onset pressure for the 40 wt% pentane solvent was higher than for the 35 wt% pentane system. In addition, the onset pressure at 150°C was found to be higher than that at 100°C.

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