

Effect of Crude Oil Vanadyl Porphyrin Content and Blending on Heat Exchanger Fouling

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Declaration of Originality

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Abstract

Fouling in the pre-heat train of crude oil distillation unit is a normal occurrence in oil refineries. With the increasing trend of heavy crude oil processing, blending of oils becomes a norm practice in a refinery. Fouling could be enhanced if incompatible oils were blended together. Also, heavy oils typically contain high trace metals composition and their effect towards fouling is yet to be explored. This study has been looking into the effect of changes in the original composition and inter-molecular stability of crude oils towards fouling. A batch system was designed and developed to produce a deposit sample from 3 crude oils of industrial interest. The reactor was successfully commissioned and an operating procedure was established.

In the first part of the work, various concentrations of Vanadium were added to crude oils and subjected to high temperature in the test section. The resultant deposits and liquid products were analysed for their molecular structure and weight distribution. Analysis by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) shows the added Vanadium are largely concentrated in the deposits. The amount of deposits produced increases with the concentration of Vanadium in the original samples. Analyses by Size Exclusion Chromatogram (SEC), Gas Chromatography (GC) and UV-Fluorescence Spectroscopy (UVF) show larger and more complex molecules in deposits from oils with high concentration of Vanadium.

In the second part, the compatibility regions of crude oil blends were established prior to analysis in the reactor. More deposits were produced from incompatible oil blends though these were lighter and less complex than that of compatible blends. Also, oils that were blended from the incompatible region produced deposits of bigger molecular weight distributions and more complex structures. Results of Thermo-Gravimetric Analysis (TGA) confirmed those of SEC's and UVF's of which more volatile components were recorded in active blended deposit samples.

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1. Introduction

1.1. Background

The history of oil-refining goes back to mid-1850's in Pennsylvania, USA, when crude oil was deemed to be a nuisance by-product in salt mining industries. The refined oil products, particularly kerosene were used as burning lamp oil in households, and naphtha which found its way mainly as solvents in small commercial applications [1]. Nowadays, oil-refining process has turned into a big industrial-scale commercial entity largely due to the increasing demand of energy within the past century. This trend of growing need of energy shows no sign of stopping as reported in International Energy Outlook (IEO) 2011 where world energy consumption is predicted to increase by 118%, from 354 quadrillion Btu in 1990 to 770 quadrillion Btu in 2035 [2]. Even though the source of energy has significantly varied in forms in the past decades, the consumption of liquid fuels maintained to be at the top of the pyramid and projected to remain as the largest source of energy at least until 2035 [2,3]. The production of liquid fuels through both conventional (crude oil, condensates) and unconventional (shale oil, extra heavy oil, oil sands) resources is expected to grow by 26.6 million barrels per day from 2008 to 2035. Energy production via unconventional oil resources has become rather competitive and attractive of late due to its potential economic feasibility along with certain advancement in refining processes technology.

The variety and complexity of crude oils of various origins make refining process one of the most intricate processes in energy production. Crude oils are exceedingly complex mixtures of numerous compounds with varying proportions of carbon and hydrogen. They range in consistency from low viscosity liquids to tar-like solids, and in colour from clear to black. An 'average' crude oil contains about 84% carbon, 14% hydrogen, 1-3% sulphur, and less than 1% each of nitrogen, oxygen, metals, and salts [4]. A heavy crude oil however usually contains more carbonaceous materials, sulphur and metals. A crude oil is typically characterised through its American Petroleum Institute (API) scale, which

based on the specific gravity of the oil. Generally, a heavy oil is defined as having API gravity less than 22° and extra heavy oil is classified at below 10° API [5]. Crude oils in between 20° to 30° API gravity are categorised as medium-heavy and these oils are normally blended with lighter crude oils to make them fit for refining purposes. Not many refineries are currently processing oil heavier than 20° API due to the complexity in desalting, handling and transportation - these oils require diluents for desalting and heated storage and transportation equipment for mobility assurance. High concentrations of sulphur, metals such as nickel and vanadium, and basic nitrogen increase the difficulty in processing as they affect the operability of equipment and the overall yield of products.

An oil refinery complex contains a number of major processing units, typically processing crude oils in hundred thousands of barrels per day. The heart of all these processing units is the crude oil distillation unit, CDU. Within the CDU, a mixture of heated crude oils is distilled and separated into its valuable products before being transferred downstream for further processing. The distillation of crude oil is an energy intensive process and accounts for a large fraction of the energy used in a refinery. In order to reduce this huge energy consumption, refineries typically utilise a series of heat exchangers commonly known as the 'crude preheat train' to provide the heating requirement prior to the CDU. This sequence of heat exchangers works by exchanging heat between the input and output streams from various distillation fractions [6].

Far more often than not, the heat exchangers are plagued with unwanted deposits accumulated on the crude oil side of the heat transfer surfaces. The presence of these deposits leads to operating problems and affects the efficiency of the heat recovery systems. Consequently, extra fuel input into the furnace is required, thereby causing a significant negative impact on the refinery economics. It was reported that for a 100,000 barrel per day unit, a loss of 1 °C in the furnace inlet temperature translates to around 450 kW of extra power requirement and would result in USD\$ 40 000 per annum in additional fuel cost [7]. As a result of extra fuel burning, increasing amount of CO₂ emission poses environmental issue of fouling which consequently carries economic penalty to the refinery operators. This penalty due to the energy and environmental impact of fouling has increasingly pushed interest and motivation within the oil industry to further understand fouling behaviour through fundamental research, evaluation of mitigation strategies and also strategic operability of heat exchangers [8-11].

Fouling may be defined as the formation and accumulation of undesired solid material at heat transfer surfaces which impede the transfer of heat and increase the resistance to fluid flow [12]. There is no generic solution or mitigation step that can be employed by refinery operators, mainly due to the complex nature of crude oil itself. A set of actions in one case may be inappropriate in another. Asphaltenes, the heaviest and most complex part of crude oil are widely believed to be one of the main factors associated to fouling. Other components such as waxes, salts, solids and inorganic species, for instance trace metals, can also generate deposition. It is widely agreed however that fouling deposits consist of heavy hydrocarbon components, but the origins of this deposit and the driving factor of foulant deposition is very much an area that commands further research and investigation.

This particular study has focused on the effect of changes in the original composition and inter-molecular stability of crude oils towards the behaviour of fouling. The role of metallic trace element towards deposition of foulant has never been studied in comprehensive manner by researchers in this field. As the trend of heavy crude oil processing continues, the effect of trace metals on fouling propensity needs to be investigated. The presence of metallic compounds is more pronounced in medium and heavy oils, and these species have been reported to increase thermal coking rate on heated surfaces. Vanadium components in particular draw interest as this metal exists in most crude oils in various types and structures. Its presence has been shown to increase agglomeration rate and size of heavy hydrocarbons when subjected to heat. This study has been focusing on the effect of Vanadium, specifically vanadyl porphyrin compound towards deposition process on heat transfer surfaces, with the aim of finding out how its presence at various concentrations affect the characteristics as well as the amount of deposits. Different concentration levels of vanadyl porphyrins were added to crude oil samples before subjected to heat and pressure. The resultant deposits were analysed for their molecular structures and mass distributions.

Most refineries have their own strategies in processing crude oils and marketing their products, hence blending of oils is a common practice and often a heavy oil is added as part of the blending mixtures. It is a well-known fact that blending oils change their stability and may induce or worsen fouling behaviour [13-15]. The effect of blending and blending order on fouling behaviour has been investigated both quantitative and qualitatively.

A batch reactor system was designed and constructed especially for this study. The reactor is designed to provide ample samples for analysis at conditions as close as possible to that of refineries. A selection of characterisation techniques were used in this study, namely Inductively Coupled Plasma Mass Spectrometry, (ICP-MS) for trace metal analysis, Size Exclusion Chromatography (SEC) and Gas Chromatography for molecular weight estimation, UV-Fluorescence Spectrometry (UVF) for molecular structure analysis, and Thermo-Gravimetric Analysis (TGA) for proximate analysis to provide data for comprehensive understanding on the characteristics of the deposits.

1.2. Research Objectives

The general objective of this study is to investigate the effect of changes in crude oil composition and properties towards the fouling behaviour of the oils, with the ultimate goal of providing better insights of heat exchanger fouling in refineries. Four crude oils of different properties and geological origins were selected and put under study. A series of specific objectives has been developed as outlined in the specific component studies below:

1. *Design and development of a batch fouling reactor.*

The requirement of developing a custom-built reactor is essential for sampling purposes. A system that is capable of producing deposits consistently in a systematic and orderly system needs to be established. The design of the reactor must allow samples to be introduced, processed and collected at conditions that methodical analyses such as material balance calculations and deposits characterisations are made possible.

In this study, samples were pressurised and subjected to high temperature for a certain period in batches at static condition. The reactor was designed largely based on an existing system in the laboratory which was used for producing fouling samples in a previous study [16]. A number of modifications were made based on constraints and limitations posed by the existing system.

2. *To study the effect of Vanadium towards deposition of foulants.*

The presence of trace metals in crude oils may affect the production of deposits to certain extent. Their influence towards deposition process has not been singled out and studied in details when other factors such as operating temperatures and pressures had been studied extensively. The selection of Vanadium in this study is seen as a good start in investigating the effect of trace metals towards fouling as these compounds presence in oil commonly, more so in heavy crude oils. The results of this study may contribute towards a more comprehensive understanding of crude oil fouling outlook and may be elaborated further into much detailed and specific analysis.

The Vanadium metal was introduced in the form of vanadyl porphyrin compound into crude oil samples at different range of concentrations and was later subjected to heat and pressure in the reactor. Quantitative and qualitative assessments were performed on the resultant products. Two crude oils were subjected to analysis in an attempt to show the behavioural variance of fouling for different type of crude oils.

3. *To study the effect of certain crude oil blends and order of blending on fouling process.*

Fouling propensity is believed to enhance if incompatible crude oils are blended together. Blending of crude oils may happen at the first instance when oils are stored in refineries. The manner of which these oils are blended may also affect the severity of fouling propensity. It is essential that crude oils blending strategy is performed in the correct manner to minimise depositions on heat exchanger surfaces. Analysis of deposits may also provide insights on how the original crude oil samples affect the characteristics of these deposits.

In this particular study, two different blends of three crude oil samples were examined for their fouling behaviour. The liquid and deposit products were analysed using the techniques listed earlier. The nature of deposits formed within the compatibility behaviour of these blends were explored and presented in this study.

1.3. Structure of the thesis

The thesis is divided into 8 chapters in total. Chapter 1 discusses the background and motivation of the study along with the specific objectives of the research work. Literature survey for pre-heat train fouling in refineries and current state-of-the art of research in heat exchanger fouling are presented in Chapter 2.

Chapter 3 covers the detail technical background and description of the experimental apparatus used in this study. The procedures employed for each technique were also discussed along with the technical constraints that they might have on analysing the sample.

The detail design and development work, along with the commissioning activities of the fouling reactor is presented in Chapter 4. This chapter also discusses the results of the commissioning, which was further used in developing the standard operating procedure of the reactor.

Chapter 5 focuses on the evaluation and the development of methodology for trace metal analysis with ICP-MS. Assessments of the sample preparation procedures have also been discussed and presented in the chapter.

Chapter 6 presents the work conducted on the effect of adding vanadyl porphyrin on the amount of deposit produced and the compositional changes in the liquid and deposit products. The work on crude oil blending is presented in Chapter 7. The compatibility of the oils was established and the resultant experiment products were characterised by SEC, UVF and TGA.

A summary and the main concluding remarks of the study are presented in Chapter 8. This chapter also discusses the recommendations and some modifications towards the design of the reactor that may be considered for future work.

2. Background and Literature Review

This chapter discusses the background of heat exchanger fouling and literature studies conducted on the factors and consequences of crude oil fouling, the effect of crude oil blending and Vanadium content towards deposition, as well as reviews characterisation techniques employed for analysis of fouling deposits.

2.1. Overview of Crude Oil Fouling in Preheat Train

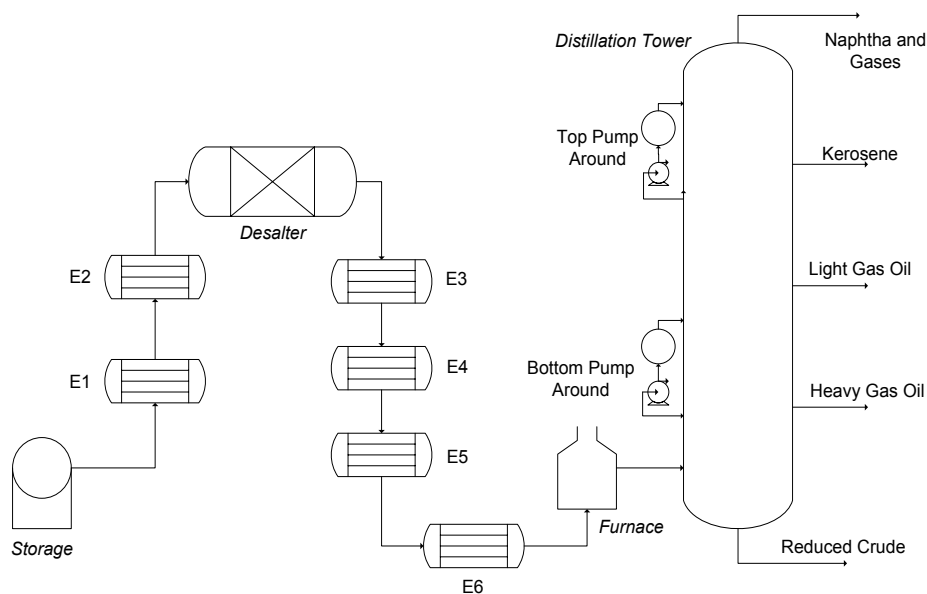


Figure 2.1 Schematic diagram of a typical crude oil distillation unit consists of heat exchanger trains, a desalter unit and a furnace. Reproduced from [8].

Fouling of heat exchangers is a common occurrence in oil refineries. It is very much a well-known problem such that during the design stage of heat exchanger, allowance has to be made to take into account of heat thermal loss and change in flow hydrodynamics due to deposition of materials on the heated surfaces [17-19]. A strategy also must be

drawn out to cater for periodic shutdowns for cleaning and removal of deposits inside these heat exchangers. This particular study is looking into fouling behaviour at heat exchanger trains prior to crude distillation unit, CDU. If fouling occurs in the preheat train, the required temperature might not be met, which reduces the efficiency of separation.

Figure 2.1 shows a simplified schematic diagram of such unit in an oil refinery [8]. Prior to entering the CDU, temperature of the crude oils must be at a certain value that is required for optimum separation in the distillation column. To achieve this temperature, a series of heat exchangers is typically installed upstream of the furnace. The temperature of oil reaching this furnace must be met to reduce the furnace duty as well as to ensure the furnace operates within its own designed capacity.

To ensure the oil mixture flows downstream of the tank, heating is necessary prior to desalter unit up to temperature of 150 °C. A desalter is used specifically to remove dissolved salts typically chlorides of sodium, calcium and magnesium, as well as suspended solids and particulates. If these materials are not removed, the downstream heat exchangers will be susceptible to particulate and inorganic fouling. These types of fouling hence are normally found in heat exchangers upstream of the desalter [20].

As the crude flows towards the furnace, it becomes hotter and chemical reactions start to take place inside the heat exchangers. According to various references in the literature [21-25], chemical reactions within crude oils dominate fouling mechanism at high temperature regions forming heavier components which subsequently translate into coke formed on the heated surfaces. In general, fouling within the preheat train may be categorised into two types; prior to desalter unit inorganic fouling tends to dominate whereas downstream of desalter, fouling is governed by organic components of the oils.

This variation of behaviour has resulted in complications in finding a general solution in handling fouling issue in refineries. Apart from the compositional effect discussed earlier, several other factors may contribute towards fouling, including operating temperature of heat exchanger, crude oil compatibility, flow behaviour and the effect of tubes geometry [8]. It has also been reported that fouling in heat exchangers can be caused by the presence of impurities such as water and rust, iron sulphide and corrosion products as well as configuration and network design of the heat exchangers itself [19,27,28].

2.2.Impacts of Fouling towards Refinery Operation

The prime concern on the effect of fouling is the transfer of heat from one fluid stream to another. The formation and growth of deposits causes decline in thermal and hydrodynamic performance of heat exchangers with time. In addition, as the deposits accumulate in the flow passages of a heat exchanger, the flow area is reduced. For a constant throughput, this means the velocity of the flow is increased and subsequently increases the pressure drop in the heat exchanger. Increased pressure drop may cause significant increases in pumping costs and associated maintenance cost [22].

As mentioned in Chapter 1, crude oil fouling implies a major cost penalty in oil refineries, costing millions of pounds every year. In general, fouling in refineries introduces four major types of economic penalties [8,22,26];

- *Capital expenditure*

Almost all refineries are designed with an allowance that fouling will occur at some stage during its operation. This inclusion increases the design surface area of the heat exchanger, and therefore its installed capital cost. If a special material is used to reduce corrosion of the heat exchanger, the extra cost may be quite substantial.

- *Additional energy requirement and environmental impact*

The extra layer of deposits formed at the heat transfer surface area would subsequently reduce the heat transfer efficiency of the exchanger. This in turn leads to a decline in furnace inlet temperature which later corresponds to the additional fuel required in the furnace. Burning more fuel leads to additional CO₂ release into the atmosphere. If a substantial increase in pressure drop occurs as a result of fouling, a significant increase in energy requirement for pumping is required. This usually involves secondary energy, for example electricity, which has a relatively high price.

- *Production loss due to shut down*

A plant has to be shutdown for cleaning to return the exchanger to normal operation. With experience, a scheduled shutdown is usually planned to minimise costs in terms of lost production. However, unscheduled turnaround can occur if fouling causes a rapid deterioration in operating efficiency. The likely production of off-grade material during the interval between the problem being noticed and the decision to stop production also can cause further loss.

- *Maintenance cost*

Fouling may also represent considerable maintenance costs, which include cost for cleaning the equipment affected and cost of anti-foulant additives. The extra cost for maintaining the pumps due to more frequent usage may be substantial in the long run. The disposal of the carbonaceous deposit materials which contains sulphur, nitrogen and metals, leads to undesirable ecological effects to the environment which potentially requires subsequent care and maintenance.

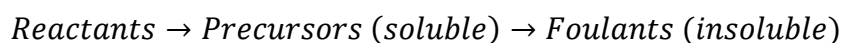
Van Nostrand *et al.* [30] conducted a study on the economic penalties associated with fouling of all US refineries based on a hypothetical and typical refinery operation. The data demonstrate that the total of fouling related costs are in the region of 1360 million US dollar per annum. This figure was later adjusted to account for inflation and is estimated at around 4500 million US dollar per annum [8]. This significant economic impact of fouling further emphasises the importance of investigating its fundamental aspects.

2.3. Types of Fouling

There are several basic mechanisms in which fouling deposits may be created and each of them depends upon certain variables. Fouling is typically classified in terms of knowledge available about initiation process, transport, attachment, removal and ageing of the fouling layers. Eipstein [12] and Bott [21,22] categorised fouling into five general groups; *particulate*, *corrosion*, *chemical reaction*, *crystallisation* and *biological fouling*. Apart from biological fouling, each of this type of fouling may be found in crude oil processing. These fouling categories are further discussed as follows:

1. *Particulate fouling* – particulates that are commonly found in crude oils including sand, silts, clay and small suspended particles contribute towards fouling especially in heat exchangers upstream of desalter. These materials form deposits as they settle on wall surfaces due to factors such as dead flow region or crevices on surfaces.

2. *Corrosion fouling* – this fouling is formed due to adhesion of corrosion products onto the heat exchanger wall causing by the corroded materials that may be formed due to the high acidity of oils being processed. The presence of corrosion products may trigger further deposition of other materials and may promote fouling of different mechanisms.
3. *Chemical reaction fouling* – thermal decomposition of crude oil components is caused by various chemical reactions that happen either in the bulk or on the wall surface itself. This type of fouling usually occurs at high temperature, up to 400 °C. Chemical reaction fouling involves the organic components of crude oils that react with each other at high temperature. General mechanism of fouling typically involves the following steps [31];



Identification of fouling precursors is important in chemical reaction fouling due to the many possibilities of reactions that might take place. Examples of mechanism of which fouling deposits formed through chemical reaction is further discussed in this chapter.

4. *Crystallisation fouling* – this type of fouling occurs when salts dissolved in crude oils reach supersaturated stage and nucleate out of the solution as crystals. The precipitate crystals subsequently deposited on the heated surfaces which may initiate further deposition processes.

A number of studies have been carried out on the mechanism of chemical reaction fouling [21,31-33]. Eipstein [12] defines chemical reaction fouling as a deposition process in which a chemical reaction forms either the deposits or their precursors, and the reaction does not take place with the wall itself. Figure 2.2 shows a general multi-step idealisation of the mechanism of this type of fouling [34]. Precursor *A* may transport to the surface and undergo reaction to form deposit *C* on the wall. On the other hand, *A* could undergo chemical reaction in the bulk to form foulant *B* and transport via mass transfer to the

surface and subsequently adhere on the wall to form deposit C. Hence, characterisation of the deposit is vital to correlate the importance of these precursors towards fouling.

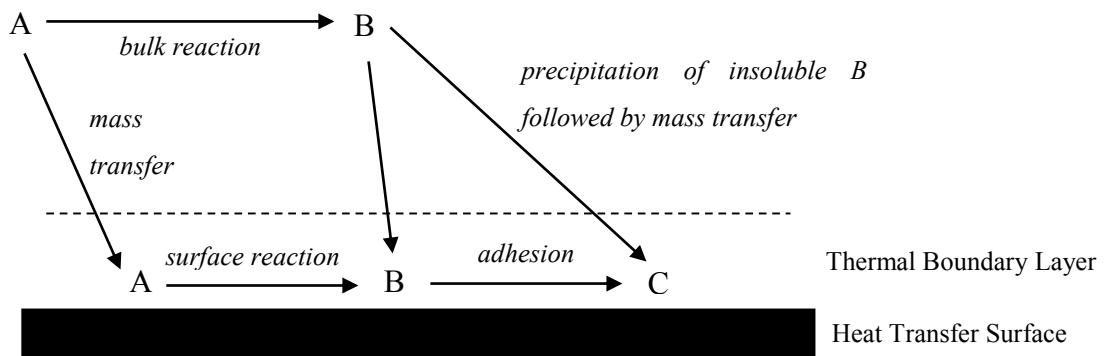


Figure 2.2 Mechanism of chemical reaction fouling. Reproduced from [34].

In chemical reaction fouling, the specific fouling species are hard to identify because components such as trace elements, short-lived radicals and high molecular mass hydrocarbon components may combine to make the chemistry involved in this type of fouling exceedingly complex. There may be a large number of possible reactants, precursors and reactions forming the deposits. For crude oil streams, the precursors or foulant are believed to originate from the following species [34]:

- i) Asphaltenes or resins precipitation due to changes in composition, temperature or pressure.

Asphaltenes are the heaviest fraction in crude oil, containing more carbonaceous materials than other components. Their precipitation from bulk solution is thought to be the key factor of which deposition occurs in heat transfer surfaces [8]. Details of asphaltenes and its contribution towards fouling is discussed further in Section 2.4.5.

- ii) Insoluble gum forms during storage due to oxygen ingress.

The formation of insoluble gums take place when polyperoxide components form at moderately low temperature due to autoxidation process from oxygen

ingress during storage [31]. The presence of oxygen increases the formation rate of gums in the bulk oil, initiating further the deposit formation when the oils are heated in heat exchangers.

- iii) Soluble sulphur species react with heat transfer surface.

Sulphur exists in most of crude oils at varied concentrations. An increase level of sulphur has been known to increase the iron sulphide content in deposits [34] which is thought due to an increase of corrosion rate. The corrosion products, mainly iron sulphides and iron oxides deposited on heated surface and turned into heavier deposits upon heating.

- iv) Coke forms due to thermal decomposition of oil components.

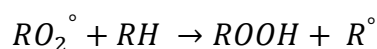
Formation of coke in heat exchangers is mainly caused by thermal decomposition and aging of oil constituents at high temperature [31,34]. Coke is characterised by its high carbon content, which usually end up in fouling deposits and potentially induce more formation of deposits on the heat transfer surfaces.

Reactions may take place in stages where precursors are formed at low temperatures, and then as temperatures are raised in the exchanger, these components will convert in time to form a more solid, coke-like material. This particular type of fouling is likely to occur in crude oil pre-heat train due to the high temperature profile in the exchangers that can reach as high as 400°C. Watkinson [31] classifies chemical reaction fouling for organic fluids into three general classes of reactions: *autoxidation*, *polymerisation* and *thermal decomposition*.

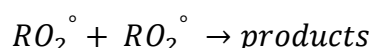
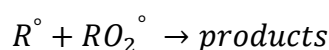
Autoxidation of hydrocarbons has been the focus in several papers as it has been identified as the main source of deposits formation in heat exchanger fouling [34-38]. The chemistry of this process has been studied extensively and listed below are the complex reactions leading to deposit formation [34]:

Initiation: Formation of radicals, R° , $ROOR^\circ$ and RO_2°

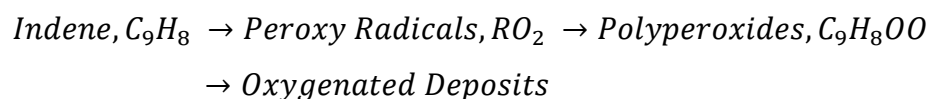
Propagation: $R^\circ + O_2 \rightarrow RO_2^\circ$



Termination: $R^\circ + R^\circ \rightarrow products$



Initiation steps may be caused by thermal decomposition of the hydrocarbon, RH or by its reaction with metal ions, catalysts or UV light. The larger molecular species formed in the termination steps may form part of the depositing species. An example that may be given here is an autoxidation process of indene model compounds forming deposits after being subjected to heat [31]. The formation of radicals gives way for more complex polyperoxides components which later turned into insoluble oxygenated deposits when subjected to heat.



Deposition in this system is mainly attributed to thermal condensation and cracking reactions. The formation of radicals through autocatalytic oxidation process may be induced by several factors, including the presence of trace metals [31]. This research work is looking into providing an insight on the effect of metal i.e. Vanadium towards the formation of fouling deposits that might be related to the chemical reaction fouling process.

Polymerisation fouling occurs typically at moderate temperatures involving component like styrene in a low oxygen condition. Thermal decomposition on the other hand happens at high temperatures and normally involves formation of coke from thermal degradation of materials on heat transfer surfaces, for example decomposition of insoluble gums from the bulk solution forming heavier fractions. This type of fouling has

been thought to be closely linked to crude oil incompatibility or phase separation-related areas [31]. However, little work has been performed so far to establish the solubility limit or phase equilibrium regions of crude oils especially when more than one oils are blended together. This research work however will not focus into bridging these gaps, nevertheless an attempt has been made to provide an understanding in establishing a compatibility map of certain crude oil mixtures on fouling process.

2.4. Factors Influencing Crude Oil Fouling

A combination of observations and experience of industrial operations together with research involving crude oil fouling has identified several factors that contribute towards foulant deposition. Operating process variables such as bulk and surface temperature, flow velocity and tube channel geometry have been proved to play significant roles in determining the extent of fouling [24,39-41]. The presence of impurities or foreign species in the process crudes such as corrosion products, trace metals and inorganic components has also been identified as key influential factors. In addition, changes in the crude oil properties during processing have been proved to increase fouling propensity [42-45]. Other factors which may be significant include residence time of crude in the heat exchanger, the effect of desalter operations and the condition of the heat exchanger surface, i.e. metal type and roughness of surface finish.

Crude oil is a highly complex solution made up of many species of hydrocarbons and inorganic components. Asphaltenes is the heavier fraction of crude oil and believed to be one of the major factors of heat exchanger fouling. Asphaltenes can be defined in terms of the solubility class fraction of a crude oil; being insoluble in light *n*-alkanes such as *n*-heptane and soluble in aromatic solvents e.g. toluene [46-48]. Their presence in crude oils gives crude oil its characters in terms of its chemical and physical properties, including phase changes, viscosity, and interfacial properties [49,50]. Asphaltenes do not have any well-defined chemical or physical properties such as molecular weight, melting point, boiling point, vapour pressure, and solubility. It is proposed that typically asphaltenes consist of $82 \pm 3\%$ carbon; $8.1 \pm 0.7\%$ hydrogen, 0.3-4.9% oxygen, 0.3–10% sulphur, and 0.6–3.3% nitrogen [51]. The presence of asphaltenes in crude oils, especially at high concentrations is widely believed to promote fouling.

2.4.1. Surface and Bulk Temperature

Temperature effects on fouling rates are frequently modelled based on the modified Arrhenius equation, as follows:

$$\frac{dR_f}{dt} = A \exp\left(\frac{-E_{act}}{RT_f}\right) \quad \text{Equation 2.1}$$

where dR_f/dt is the fouling rate, A is the pre-exponential parameter fitted to the data, E_{act} is the activation energy and T_f is the film temperature i.e the temperature of the interface between the bulk fluid and the surface of deposit. This equation can only be used when other factors such as velocity, geometry and fluid composition are kept constant. Crittenden et al [52] established a correlation between the fouling rate and tube wall temperature and observed activation energy values of 33 kJ mol⁻¹ for light crude oils and 21 kJ mol⁻¹ for heavy oils. It must be noted that these values are obtained based on temperature at the wall. Both bulk and surface temperatures affect the fouling rate. The rate increases strongly with both surface and bulk temperature [26]. Fouling rate could be correlated using a modified film temperature, which gave more weight to surface temperature, T_s than to the bulk temperature, T_b :

$$T_f = 0.3T_b + 0.7T_s \quad \text{Equation 2.2}$$

The film temperature reflects the temperature in the thermal boundary region near the surface where reaction and adhesion processes may occur. However, it is not necessarily the best parameter to correlate fouling rates in every situation as it largely depends on the fouling precursor; for example, suspended asphaltenes or impurities in crude oil. In the case of asphaltenes as precursor, fouling rate is much higher at a lower bulk temperature value as shown by Asomaning *et al* [24]. Asphaltene solubility in bulk increases with temperature, hence the suspended asphaltene concentration decreases with an increasing bulk temperature. This would lead to a decrease in the fouling rate with bulk fluid temperature at a constant surface temperature. However, asphaltene can be stable at low temperature and destabilised when the oil is heated up. This may be related to changes in phase as suggested by modelling work of Artola *et al* [53]. On the other hand, for

particulate fouling (due to suspended impurities) the solubility of foulant does not change significantly with bulk fluid temperature. Hence, fouling rates will increase with the bulk temperature at a given surface temperature.

2.4.2. Bulk Flow Velocity

Bulk flow velocities play a major role in the formation fouling layers. The fouling rate normally depends on whether fouling is controlled by chemical reaction on the surface, by mass transfer of precursors from bulk fluid to the surface or by adhesion on the probe surface. If fouling is controlled by chemical reaction or by adhesion on the surface, the fouling rate is inversely proportional to the bulk velocity [54]. In a typical crude pre-heat train, fouling in general decreases with increasing velocity. Saleh *et al.* [39] observed that at film Reynolds numbers of 2500 – 4500, an increase in bulk velocities results in decreased fouling rates. Watkinson [26] also reported that fouling rate generally decreases as the velocity increases to the power of -0.35. In this scenario, fouling mechanism is thought to be dominated by chemical reaction or by adhesion of foulants at the surfaces.

In contrast, if fouling is controlled by mass transfer of reactants or products of reactions from the bulk fluid to the wall region, an increase in bulk velocity may result in an increase in fouling rate [8,54]. The mass transfer coefficient from the bulk to the near-wall region would increase as a result of increased turbulence, raising the fouling rate. The effect of flow rates on fouling is very complicated in that the exact mechanism of fouling must be identified in order to predict what effect flow velocity has on the fouling rate.

2.4.3. Oxygen, Nitrogen and Sulphur contents

When crude oil is subjected to heat, the presence of oxygen in crude oil can lead to autoxidation reactions. These reactions may trigger the formation of free radicals which subsequently form insoluble gums, as discussed in section 2.3. Watkinson [34] reported that the presence of dissolved oxygen, even at low concentration of 10 ppmw in the oil, can have significant effects on fouling through gum formation. This result was also observed in work by Asomaning [40] in which two sets of fouling rate-experiment were performed; one with oil saturated with oxygen and nitrogen, and the other with oil with

an addition of species containing oxygen. Fouling rates in the presence of dissolved oxygen are observed to be 10 times higher than those found in nitrogen saturation set up. The addition of species containing oxygen also increased the extent of fouling, but the effect is rather insignificant compared to that of dissolved oxygen.

Sulphur species are known to exist in fouling deposits, in most cases in the form of iron sulphide. Sulphur exists in crude oil either as aromatic or aliphatic sulphide [8]. The effects of sulphur on fouling are very species-dependent. Free sulphur, disulphides, polysulphides and benzene thiol have been reported to promote instability in stored fuel oils [55]. In crude oil, aliphatic sulphur is the most thermally reactive functional group. Thermal cracking of hydrocarbons is usually initiated by carbon free radicals and hydrogen sulphides formed via the breaking of carbon-sulphur bonds. If insoluble asphaltenes come in contact with a hot surface, the reactive sulphides will initiate the cracking of asphaltenes to form insoluble coke. The presence of iron sulphide can be explained by the reaction of hydrogen sulphides with surfaces containing Iron, which forms corrosion products and could also be the precursor for fouling.

The effect of nitrogen species towards fouling is less detrimental in comparison to the effects of Oxygen and Sulphur. However, species such as pyrroles have been shown to form gums in fuel oils, shale oils and naphthas [55] through complex polymerisation reactions. A recent study has suggested that basic nitrogen content above 200 ppm in the crude oil usually indicate that the crude will not foul, whereas concentration below 100 ppm will give rapid fouling problem in the heat transfer surface. Crude oils with basic nitrogen content of 100-200 ppm are found to have immediate fouling potential in the heat transfer surface [56].

2.4.4. Trace Metals

Vanadium and nickel are the two most common metals found in crude oil. Other metals such as iron, copper and zinc may also be present in significant amounts. A high concentration of these metals in crude oil is usually linked with the asphaltene content in the distillation residue [8]. Crittenden *et al.* [39] performed elemental analysis on fouling deposits obtained from pre-heat train and the results show a significant amount of inorganic species. Eaton and Lux [57] conducted TGA analysis of several fouling samples and discovered concentration of ash of up to 54% indicating serious influence

of inorganic species towards deposition. However, the linkage between these metals found in deposits and their presence in crude oil is rather inconclusive. The contribution of these metals towards fouling will be further discussed in Section 2.5.

2.4.5. Asphaltenes Precipitation and Deposition

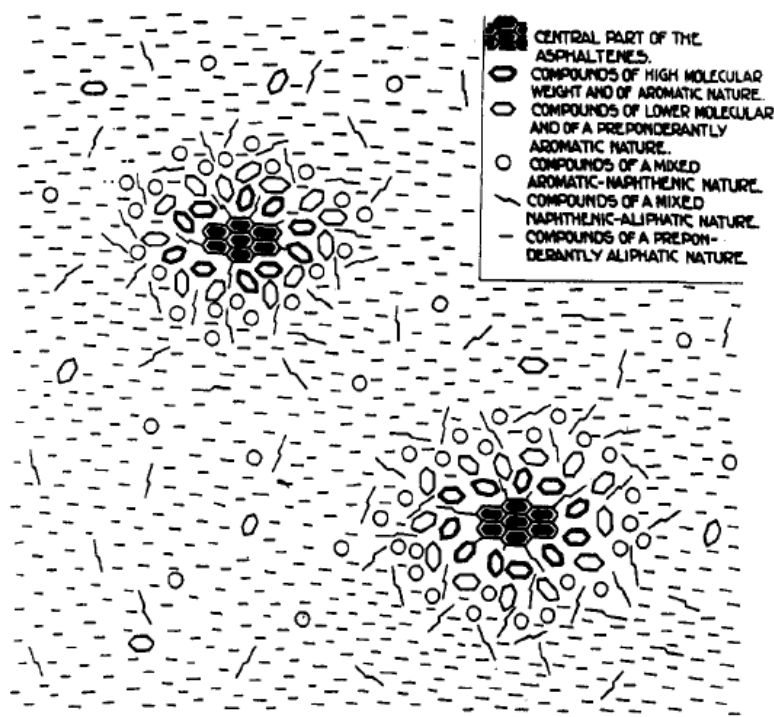


Figure 2.3 Model of asphaltene micelles as proposed by Pfeiffer et al. Reproduced from [62].

The occurrence of asphaltenes in crude oils has been the subject of a large number of studies [60,61]. Many reported that asphaltenes exist in crude oil as partly dissolved and partly in colloidal/micellar forms, a model firstly proposed by Pfeiffer and Saal [62]. The crude oil structure according to this model is arranged such that asphaltenes are at its centre surrounded by components of high molecular weight components with high aromaticity, as shown in Figure 2.3. These components are surrounded by lighter constituents with less aromatic nature and gradually surrounded by lighter components to the point that intermicellar phase is formed.

This model was later simplified by Wiehe [63] into four types of component classification as shown in Figure 2.4. Asphaltenes (A) are thought to be sub-microscopic

solids dispersed in the oil by surfactant-like property of resins (R). This dispersion is dissolved in crude oil by small ring aromatics (a) which is a solvent for the resin-asphaltene micelle but at the same time opposed by the non-solvents, the saturates (s). By disturbing the delicate balance of the structure, for example increasing saturates or decreasing resins and/or aromatics, probability of asphaltene precipitation in the bulk solution is increased. This concept has also been supported by findings from Rogel [64] through investigation of resin-asphaltene interaction via thermodynamic molecular modeling approach. The model, which was developed without employing any experimental data, predicts reduction in size of aggregates and increasing value of critical micelle concentration with the presence of resins. Sedghi et al. [65] also confirmed this behaviour through measurement of conductivity of charged carriers in asphaltenes to probe their aggregation behaviour. It was found that resins tend to aggregate and associate with asphaltenes to increase their stability in crude oil solution.

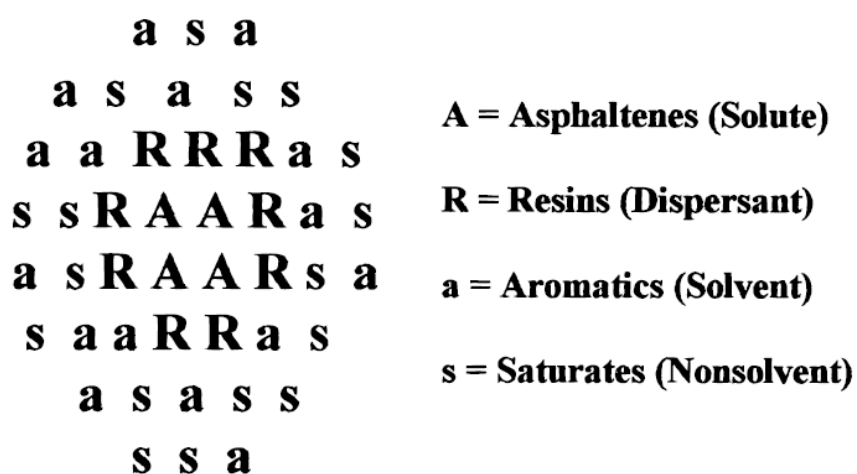


Figure 2.4 Schematic diagram of physical model for crude oil compositional structure. Reproduced from [63].

Often, as an initial estimation for crude oil stability, the Colloidal Instability Index, CII of a crude oil is measured to evaluate its tendency to foul [66]. This index predicts the stability of asphaltenes by measuring the compositional balance of crude oil components i.e. the ratio of the amount of saturates and asphaltenes over the resins and aromatics (SARA);

$$CII = \frac{\text{Asphaltenes} + \text{Saturates}}{\text{Resins} + \text{Aromatics}} \quad \text{Equation 2.3}$$

As this index measures the ratio of asphaltenes and its non-solvent (saturates) to that of its peptizers (resins and aromatics). A higher value correlates to a more stable oil. It was reported that values above 0.9 correspond to unstable asphaltenes and values below 0.7 indicate crude oils with stable asphaltenes. Any CII that falls between these two numbers is within the uncertain region of stability.

Dickakian *et al.* [13] suggested that the predominant mechanism for pre-heat train fouling is asphaltene incompatibility with crude oil. This incompatibility initiates precipitation of some asphaltenes in the crude oil. Suspended asphaltenes are generally deposited on heat transfer surface, and then carbonised into infusible coke. The major factors governing precipitation of asphaltenes appear to be alterations in the crude composition as a result of crude-blending, fluid injection and changes in pressure and temperature [58,59]. Blending of crude oils leads to either immediate asphaltene destabilisation, hence high fouling possibility for the crude blends, or non-instantaneous asphaltene flocculation which gives relatively low fouling potential. Wiehe [42] demonstrated how incompatibility of certain crudes can be determined and predicted based on asphaltene solubility in heptane/toluene mixture. This model is called Oil Compatibility Model, OCM. The fundamental hypothesis of the model is the dispersed phase of asphaltenes-resins has the same flocculation stability parameter regardless of whether the oil is blended with non-polar solvents or with other crude oils. Two parameters can be defined to characterise crude oil blends, namely Insolubility Number, I_N , and Solubility Blending Number, S_{BN} . I_N represents the percentage of toluene in the hexane/toluene mixture that is required to prevent asphaltene precipitation, i.e. the degree of insolubility of asphaltenes in the oil. S_{BN} measures the ability of an oil to dissolve asphaltene and is defined as follows:

$$S_{BN} = I_N \left(1 + \frac{100}{H_D} \right) \quad \text{Equation 2.4}$$

The parameter H_D represents the ratio of crude oil to heptane volume required for precipitation to occur when the oil is contacted with an increasing volume of heptane. Once the blending parameters for each crude oil have been determined, the compatibility of the blends may be established by calculating the Solubility Blending Number of the mixture, S_{BNmix} . This can be calculated from the volumetric average of the oil mixture through Equation 2.5.

$$S_{BNmix} = \frac{V_1 S_{BN1} + V_2 S_{BN2}}{V_1 + V_2} \quad \text{Equation 2.5}$$

where

V_1 is volume of crude oil 1

V_2 is volume of crude oil 2

S_{BN1} is solubility blending number of crude oil 1

S_{BN2} is solubility blending number of crude oil 2

The S_{BNmix} varies according to volume of the crude oils being mixed together. If the two crude oils are incompatible, the S_{BNmix} would have, at certain oil ratio, an incompatible region that is characterised by the relationship below:

$$S_{BNmix} < I_{Nmax}$$

At values of S_{BNmix} lower than the maximum I_N of the two crude oils, the oil blend becomes incompatible and susceptible to asphaltene precipitation, hence increasing the possibility of fouling deposition on heat transfer surfaces. For a compatible pair of crude oils, the S_{BNmix} must be higher than the largest I_N of any of the crude oil. It should be emphasized that the order of blending is critical to the compatibility of the blend. An example of compatibility region established from the OCM model is presented in Figure 2.5.

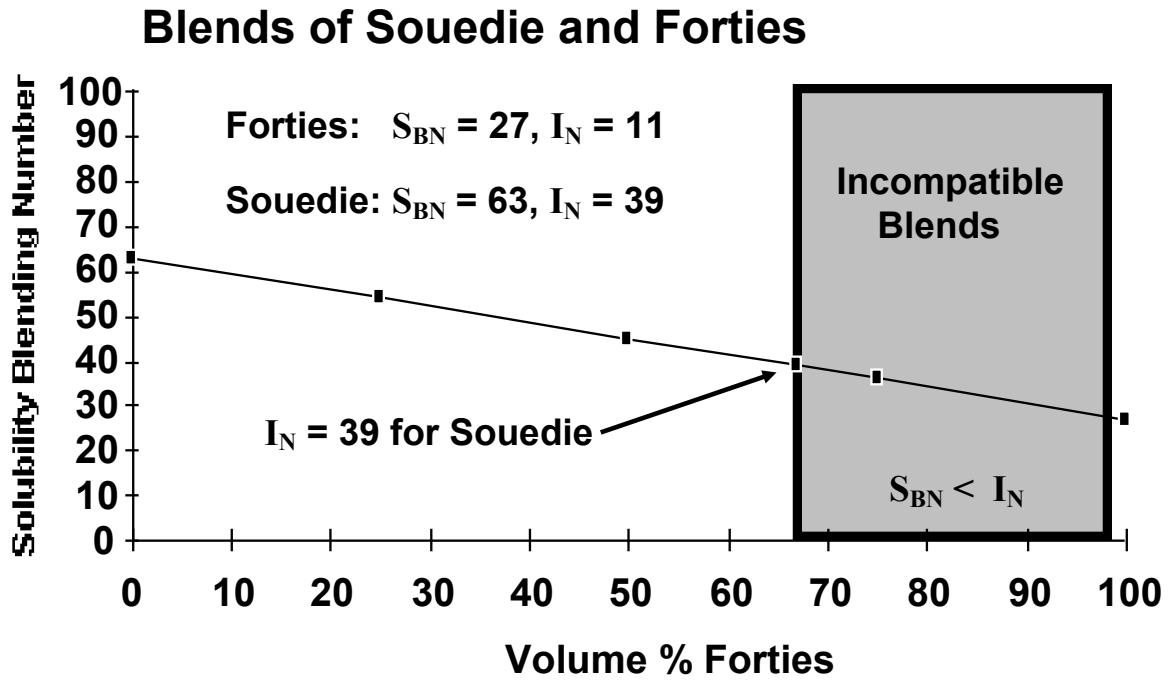


Figure 2.5 The compatibility mapping for the blend of Souedie and Forties crude oils. Reproduced from [42].

In this blend, the incompatible region starts when the volume percentage of Forties crude oil goes above 67 vol%. This is the case if Forties oil is added into a container with Souedie crude oil. If the order of blending is reversed, the blend will immediately be incompatible and instantaneous precipitation of asphaltenes will occur, increasing the probability of fouling.

It has also been shown that in some crude oil blends, high fouling rate is observed in the compatible region that is near to the incompatible region [67]. In addition, there are some crude oils that are self-incompatible. These oils contain insoluble asphaltenes that form even without blending oils [68]. For these crude oils, the Solubility Blending Number, S_{BN} is equal to the Insolubility Number, I_N as H_D cannot be determined hence has a value of 0. Most of self-incompatible oils have a high paraffinic content, which acts as a non-solvent for asphaltenes in the solution. There are more than 10 identified self-incompatible oils thus far and when processed, the propensity of fouling is high.

Stark *et al.* [44] measured the stability of asphaltenes in crude oil via an Asphaltene Stability Index (ASI) test which determines the onset of flocculation by a heptane-

titration system. The index corresponds to the onset of asphaltene flocculation and the transmittance of the laser used in the detection system. Oils with high fouling potential have been found to have ASI values 1 to 0, and oils with low fouling potential have been found to have ASI values of 2.5 or higher. Crudes are compatible if the ASI of the blend is higher than that of the individual crudes.

The compatibility of crude oils can also be determined through the measurement of refractive index (RI) of an oil blend at different blending ratios. The concept was first documented by Buckley et al. [69] in which the measurement of RI for mixtures of several crude oils with n-heptane was performed to predict the onset of asphaltene precipitation. In a later work, Buckley discussed how the stability of asphaltenes in a certain crude oil can be measured through the difference between the RI values of the oil sample and the point at which precipitation is first observed [70]. Based on this work, Alvarez et al. [71] extended the technique to predict the compatibility behaviour of a crude oil blend. The assessment of formation of a denser phase upon blending was performed with ellipsometry of which the RI value was measured. Samples were blended and centrifuged to separate the denser phase, thought to be the precipitated asphaltenes, and the bottom and top section were measured for their densities. The bottom part of the mixture showed a greater density values suggesting an agglomeration of solid particles. The weight of solid formed at the bottom of the centrifugal flask was also quantified and the difference in weights amongst the blend ratios was determined. The results showed a good agreement with the compatibility region established through OCM model by Wiehe, as well as an agreement towards fouling behaviour of near-incompatible region. The effect of crude oil blending towards fouling behaviour will be discussed in detail in Section 2.6.

2.5. Trace Metals in Crude Oils and Their Contribution towards Fouling

Inorganic elements, especially trace metals, in crude oils are believed to be concentrated in the asphaltene fraction [72,73]. Asphaltenes and resins may contain up to 100% of the trace element content of crude oil [70]. Even though the presence of metals in crude oil is normally at very low concentration, they often have detrimental consequences in refinery processes. Among the most important of these are corrosion of the refinery

process equipment and catalyst poisoning during the cracking process [74-77]. They are thought to contribute to fouling problems as well, but this area is still lacking research. This particular work will be looking into the effect of metals, especially Vanadium towards deposition.

A literature review by Jones [78] on the occurrence of trace metals and other elements in crude oils concluded that Nickel and Vanadium are the only metallic elements present at high concentration levels of at least at 10 ppm. These two elements have been studied extensively because of the presence of Nickel and Vanadium porphyrins, which are believed to originate from chlorophyll (or haemoglobin), hence indicating a biogenic origin of petroleum [79,80]. However non-porphyrins Nickel and Vanadium may also be present in crude oils, especially in the asphaltic component of the oil. The exact molecular forms in which these metals exist in crude oils are still discussed widely amongst researchers of the field, but according to Yen [81] the metallic compounds in crude oil can be classified into five different categories:

- i) Metallo-porphyrin chelates (vanadyl and nickel porphyrins, chlorophyll and other hydroporphins).
- ii) Transition metal complexes of mixed ligands (non-porphyrins) such as vanadium, nickel, chromium and iron.
- iii) Organo-metallic compounds such as mercury, antimony and arsenic.
- iv) Carboxylic acid salts of polar functional groups of resins, e.g. molybdenum.
- v) Colloidal minerals such as sodium chloride and silica.

Amongst these compounds, the metallo-porphyrins, **i)** and non-porphyrins **ii)** are the two most important classes as they are found most frequently in crude oils. Biggs *et al.* [82] isolated these porphyrin and non-porphyrin components and observation through HPLC found that the metallo-porphyrins are smaller molecular size compounds compared to the non-porphyrin metals. Vanadyl porphyrin is one of the metal compounds most commonly found in petroleum fluids. Structural-wise, Vanadium is bonded to four nitrogen atoms in a porphyrin cycle as well as to a single Oxygen atom, as shown in Figure 2.6a. The most typical types of identified in petroleum samples are the Etio form

(Figure 2.6b) and the DPEP form (Figure 2.6c). Other forms such as the Benzo type also exist but are not as abundant as the other two [83]. These porphyrins are fully characterised and separation is possible via chromatography [84]. They decompose if subjected to thermal treatment or exposed to a mixture of reactive gases such as H_2 and H_2S .

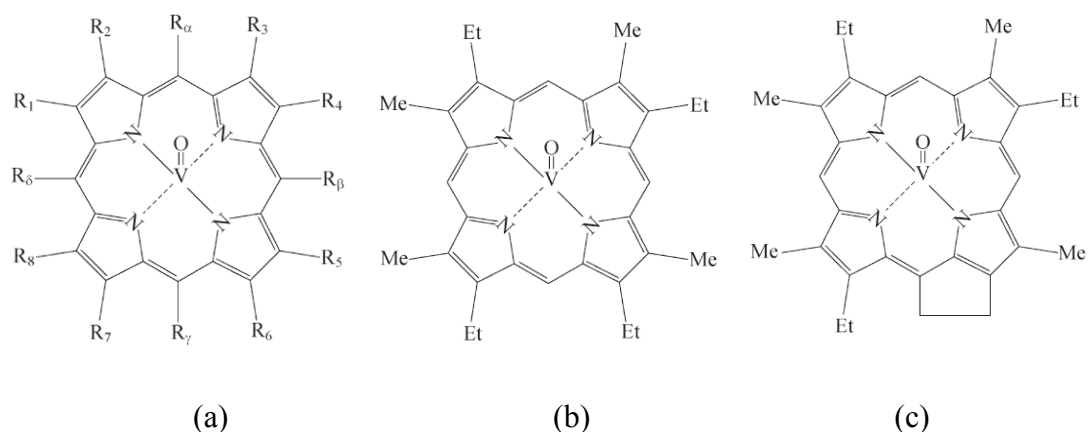


Figure 2.6 Different forms of vanadyl porphyrins; (a) general (b) etio (c) DPEP. Reproduced from [83].

Several works have been conducted to investigate the distribution of metals, especially in petroleum fluids. Reynolds et al. [85] separated seven atmospheric residual samples into their SARA fractions and observed that most of the Vanadium and Nickel (up to 98%) are concentrated in the resins and asphaltene fractions. A similar observation was reported by Pena et al. [86] in which the distribution of vanadyl porphyrins in a Mexican heavy crude oil was studied. The oil sample was fractionated into three fractions; maltenes, residual (deasphalted oil) and asphaltenes. Atomic absorption spectroscopy (AAS) results found that most of the Vanadium concentrated in the asphaltene fraction with DPEP, Etio and Benzo types of porphyrins identified in all three fractions.

Nalwaya *et al* [87] fractionated asphaltenes into different polarity classes and observed that metal elements especially Iron, Nickel and Vanadium concentrated in the most polar fraction of asphaltenes. This in turn, determines the degree of difficulty of asphaltene dissolution in the solvent used (methylene chloride), in which a lower rate of dissolution

was observed for the more polar fraction. It was demonstrated that the presence of metal elements, especially Iron, Nickel and Vanadium, primarily determines the asphaltene polarity. The levels of these metals were significantly higher in the most polar fraction. It was also observed that the addition of ferric ions in the crude oil increased asphaltene yield during fractionation, suggesting that an increase in metal concentration in the solution will further promote asphaltene precipitation.

Kaminski *et al* [88] performed a similar fractionation and mixed the heavier fraction with a salt of EDTA in an attempt to remove metals from the asphaltenes via chelation. The dissolution rate of asphaltenes increased significantly, suggesting that metal content has a direct effect on asphaltene dissolution. It was noted that very little of the Nickel and Vanadium was removed via chelation despite the presence of these elements in the original asphaltene fraction, whereas larger amounts of Iron and Aluminium were removed. This can be attributed to the tightly bound nature of Nickel and Vanadium incorporated in porphyrins molecules.

The contribution of trace metals towards deposition has not been widely investigated. Implication of vanadyl porphyrins towards agglomeration of asphaltenes was first discussed by Tynan *et al.* [89] considering that this porphyrin structures are capable of forming additional ligand structures with heteroatoms. Cayton [90] studied the methods of controlling thermal coking and discovered several coke promoter compounds. It was reported that certain metals such as Molybdenum, Vanadium, Nickel and Cobalt have been found to promote thermal coking at high temperature hydrocarbon processes. Yudin *et al.* [91] conducted a kinetic study of asphaltene aggregation of four different types of crude oils with various concentrations of Vanadium and discovered that the kinetic of aggregation increases as the concentration of Vanadium increases. It was also observed that the size of agglomerates increases with the concentration of Vanadium.

Whilst not many works have been done in the area of trace metals contribution towards fouling, considerable amount of research has been conducted in finding the optimum ways of selectively removing Vanadium from crude oils [83]. The most common method used commercially is through coking, which captures the Vanadium in the coke by-products [92]. Even though deasphalting process gives Vanadium-rich products, it is however non-selective and complete removal would produce high asphalt products that could be non-economical if removed totally from the process fluids [93]. Thus far, only

catalytic removal of metals can perform selective removal but it comes at a high operating cost for refineries. By removing Vanadium from process stream, improvement on the efficiency of certain equipment may be achieved but its effect towards fouling behaviour has not been highlighted.

2.6. Effect of Oil Blending towards Fouling

Blending of crude oils is a normal practice in oil refineries. This is usually done to achieve the target API number specific to the refinery strategy in getting the required products distributions. It has been reported in several studies how blending of incompatible oils increases the likelihood of fouling in process streams [42-45]. The parameters required to determine the compatibility behaviour of a crude oil via OCM model have been described in Section 2.4.5. The premise behind this model is through the work of de Boer [94] and Andersen [95], who investigated the onset of asphaltene precipitation through addition of asphaltenes to non-solvent and developed the solubility parameter.

Stark and Asomaning [44] studied the fouling behaviour of individual crude oils and their blends and found that compatible blends give an increase in asphaltene instability. In general, this was the case if blending were made between high asphaltene crude oil and lighter oil with low asphaltene content. However, there were cases in which a compatible blend may be established between a high asphaltic crude oil and a lighter oil. To model and collect the data of fouling due to blending in refineries is rather difficult due to several factors, as pointed out by Yeap et al [96]. Data gathered from a refinery usually involves many variables, not just the blending ratio/order strategy, but factors such as operating temperature and pressure, fluctuations of operating conditions, hydraulic effects and location of the heat exchangers, which also play important roles in fouling. Data collected over long periods usually involve several changes in the crude oil slate. Additionally, refinery operators prefer not to publish any data related to the operation of their processing equipment. As such, investigations of fouling behaviour due to blending of oils are often conducted in laboratory scale to achieve better control over the variables and therefore acquire more accurate results.

Hong and Watkinson [97] studied the fouling behaviour of blends from Cold Lake vacuum residue and Athabasca atmospheric tower bottoms that are rich in asphaltenes,

at 17.7% and 13.5% respectively, with several diluents of aromatic contents ranging from 0.5 to 25% in a flow loop with an annular test section. It was found that fouling was much higher when the aliphatic diluent was used, and decreases as the aromaticity of the diluent was increased. Hong also concluded that higher asphaltene content does not guarantee a higher degree of fouling. Instead, it is the incompatibility of crude oils that drives fouling by asphaltenes. A similar observation was made and reported by Van den Berg et al. [98] who assessed the blending strategy in a refinery based on crude oils compatibility and their historical behaviour towards fouling. A blending model was established from the characteristics of individual crude oils such as their origin, evolution and maturity and then grouped together through combination of these geological data and their assay parameters. The analysis showed that crude oil from a similar kerogen type (related to origin of crude oil) and maturity levels are always compatible. Some crude oils were also found to behave as fouling ‘cleaning’ agent if blended within their compatible behaviour.

Derakhshesh et al [99] studied the correlation between crude oil stability (from ASTM D7517), with the fouling factor values and the thickness of the fouling layer formed on a stainless steel test section. Tests were conducted for neat crude oil samples as well as crude oil with added diluent at various volume ratios. The results showed that as the, the volume of diluent increased the stability of oil decreased with the higher fouling factor recorded for sample with the lower stability value. The thickness of the fouling layer formed at the test section increased as the fouling factor increased. Additionally, Derakhshesh and colleagues also characterised the foulant layer for its elemental content and discovered that at the higher fouling rate (thicker deposit), the fraction of carbon is higher. The results, amongst other studies on crude oil compatibility, indicate that blending of incompatible oil mixtures will lead to increase fouling propensity. Characterisation of deposits specifically formed from crude oil blends requires further in-depth study and is further discovered in this project.

2.7. Characterisation of Fouling Deposits

Characterisation studies of fouling deposits and heavy coke materials have been reported in the literature. These analyses include full elemental analysis, volatiles and ash content,

metal content, solubility tests, molecular structural features and molecular weight distribution [100-106]. Bennett *et al.* [56] produced a list of different analytical techniques on fouling deposit characterisation, based on the objective of the study. Because of the wide range of possible contributing species and due to the nature of deposits, characterisation of fouling samples has to be performed by several analytical techniques. For example, analytical methods for determination of molecular weights of fouling deposits often show large variations leading to constant discussions amongst researchers in the field. One analytical technique may only provide limited information of a certain sample especially those containing heavy hydrocarbon constituents. For example, coherent estimates of molecular weight for heavy crude oil fractions e.g. fouling deposits, with Gas Chromatography (GC) are constrained by its low upper range limit and may require added information from other analytical techniques. The usage of Size Exclusion Chromatography (SEC) has been reported to provide extra information for heavy samples such as coal tar pitch and crude oil asphaltenes fractions [100]. In addition to GC and SEC, several other techniques such as High Performance Liquid Chromatography (HPLC) and Matrix Assisted Laser Desorption Ionisation-Mass Spectrometry (MALDI-MS) have been widely used in determining the molecular mass of deposit samples.

In this particular study, information on samples' molecular structures had been investigated through UV-Fluorescence Spectroscopy. Composition of samples was analysed through approximate analysis with Thermogravimetric Analyser (TGA) whereas Inductively Coupled Plasma spectrometers (ICP) had been used for trace metals analysis. By combining data from each analytical techniques, comprehensive information of each deposit may be acquired to provide greater understanding on the fouling behaviour of the crude oil samples. This is particularly important to draw out an insight on how changes made on the original crude oil samples affect the characteristics of the deposit products. Debates and discussions of results generated from these equipment are very much still ongoing especially on the capability of these instruments in detecting components of high molecular weights.

2.7.1. Size Exclusion Chromatography

Determination of molecular weight distribution of hydrocarbon liquids via size exclusion chromatography has been studied in several studies [103,107-122]. SEC has been applied

extensively for characterisation of coal-based samples because of its ability to estimate molecular mass distribution up to 15,000 u [100]. SEC chromatograms typically produce bimodal distribution with the early eluting peak corresponding to large molecular mass whilst the later peak corresponding to smaller molecular masses. A sample is dissolved in a solvent (mobile phase) such as THF, NMP and CHCl_3 , carried through along the column where molecular size separation occurs based on the level of penetration of molecules with the column packing. Since the technique separates components by their sizes rather than mass, its application for materials such as asphaltenes requires calibration with components of various molecular weights and sizes.

The application of SEC heavily relies on the solubility of sample in the eluent i.e. the choice of solvent. A poor selection of solvent may lead to interaction between samples and column packing affecting the elution behaviour. These phenomena had been identified and discussed in several publications [108,123-126]. Several solvents had been used in the past especially Tetrahydrofuran (THF). It has been reported however that elution time of components in THF is structure dependent [110]. Moreover, in analysing heavy materials such as coal tar pitch and petroleum coke THF is a poor solvent as it does not dissolve some of the larger mass components [111,112]. Furthermore, Herod et al. [113] observed that the separation of components was affected by the surface interaction between THF and the column packing materials. The use of toluene, the solvent employed for asphaltene fraction definition, is deemed unsuitable due to similar interaction effects [109]. Chloroform, being one of the most powerful solvents is a possible candidate but Paul-Dauphin [114] and Sato [115] discovered that elution behaviour gives the reverse effect for the standard material polycyclic aromatic hydrocarbon (PAH), i.e. higher molecular weight corresponds to higher molecular mass. The practice of utilizing NMP as solvent was first documented by Lafleur and Nakagawa [116] and since then has been used in characterizing coal-derived samples in several research works [117-122]. NMP is a good solvent in dissolving coal-derived samples completely but not for certain petroleum-based fluids. Berrueco et al [109] investigated the feasibility of using a mixture of NMP and Chloroform as the eluent phase and discovered an improvement in the solubility of petroleum samples as well as reduced the sensitivity towards structural features of samples compares to when using NMP alone. The presence of NMP in the mixture blocks surface interactions between the packing materials and sample molecules.

SEC is an indirect technique of molecular separation that requires calibration. For the NMP/CHCl₃ system, a series of polystyrene (PS) and polymethylmethacrylate (PMMA) materials were used as calibration standards. The elution times of these standards are very much indistinguishable, showing the independency of molecular structure towards the elution behaviour of materials in the eluent. The full calibration analysis has been reported in detail by Berrueco et al. [109]. By adding CHCl₃ to the eluent, solubility of crude oil-based samples was achieved as well as reductions of the structure dependence of elution times of standard polymers.

Certain studies claimed that the excluded peak of SEC chromatograms represent the aggregation of molecules in the sample mixture [123,125]. However, several efforts made to disaggregate this fraction and therefore prove that it was actually composed of aggregates of smaller molecules were unsuccessful. The dilution level of samples used in SEC is very high, making it unlikely for aggregation to take place [117, 124]. When a wide range of diluted samples were injected into the SEC system, the relative proportions of the two peaks of the bimodal chromatograms remained unchanged, contrary to what would be expected if aggregation were taking place.

2.7.2. Gas Chromatography

Analysis of fuel-based materials via Gas Chromatography (GC) is normally limited to about 400 amu [101]. Typically a capillary GC is chosen to analyse hydrocarbon based samples that are sufficiently volatile to be below the temperature of column coating or analyte degradation. Higher mass components are usually not volatile enough to elute through the column or be vaporised in the injector. Analysis of a coal tar that has molecular mass range above 300 amu produced a rapid fall of peaks after ~250 amu, indicating the onset of a loss of aromatics of greater mass in the GC column system [100]. It has been shown however that the molecular mass detected in high temperature GC (HTGC) columns may be extended through application of polymer that can withstand the high temperature environment [127]. Coupling a high temperature GC with a mass spectrometer (GC-MS) also has been proved to increase the detection capability of a GC system [113,128,129].

HTGC is typically used in developing distillation distribution of crude oil through simulated distillation analysis (SimDis). SimDis is a comparative analysis of which a

sample is analysed for its distillation fraction through sample calibration of n-alkanes standards [101]. Analysis of petroleum residual samples with HT-SimDis GC did reach a column temperature up to 425 °C, which corresponds to atmospheric equivalent boiling point, AEBP of 847 °C [130]. This particular analysis may be used to analyse the volatility of samples as well as their boiling point classification, which could be useful in characterising the molecular mass range at the lighter end of fouling deposit samples. However at this range of temperature, other reactions such as pyrolysis would occur and might affect the final results.

2.7.3. UV Fluorescence Spectroscopy

UV-Fluorescence (UV-F) spectroscopy is used to investigate the aromatic ring structure of samples. UV-F cannot be used to classify specific structural features of aromatic systems. The analysis is used to observe the change in spectral behaviour that correlates to the change in size of the aromatic ring systems. There are a number of possible structural changes that can cause the shift of spectra, for example loss of aromatic substituent groups containing heteroatoms and loss of alkyl and alkoxy substituents [101]. Three types of fluorescence spectra may be generated in the form of emission, excitation and synchronous spectra. The synchronous spectra, which are generated from simultaneous change of the excitation and emission wavelengths with a fixed difference in wavelength between both, are typically used in analyzing coal and petroleum-derived samples. Application of UV-fluorescence spectroscopy to characterise the structural features of fused aromatic rings in these samples has been investigated in several research works [111,131-134].

Analysis of an SEC system with UV-F detector has shown that coal and petroleum-derived molecules do not fluoresce significantly at mass of >3000 u [135]. This result indicates even though the molecules may be able to absorb UV-light, they do not fluoresce at the selected wavelength and hence are not detected in the spectra. UV-F analysis however still provides significant input towards the molecular structure of coal and petroleum-based samples. Al-Muhareb et al. [108] studied the spectral shift of crude oil residue fraction in various solvents of different polarity and observed increased aromatic systems with increased of solvent polarity. Leyva et al. [136] compared the relative magnitude of aromatic ring systems in several asphaltene samples and discovered minor differences amongst the spectra perhaps due to the limitation of UV-F to fluoresce

molecules of high aromaticity. Venditti [16] characterized fouling deposit samples originated from oil refineries as well as of laboratory bench test unit extensively. It was observed that heavy materials with larger molecular mass range detected by SEC corresponded to larger aromatic ring systems as indicated by the UV-F analysis. This correlation is important to associate the linkage between molecular weight and molecular structure of samples especially for components of high complexity such as crude oil fouling deposits.

2.7.4. Inductively-Coupled Plasma Techniques

Quantification of trace metals in hydrocarbon materials samples has been investigated by several techniques, namely inductively coupled plasma with mass spectrometer (ICP-MS), inductively coupled plasma with optical emission spectroscopy (ICP-OES) and atomic absorption spectrometry (AAS) [101,137]. Atomic absorption spectrometry is a single element monitoring technique and has been used for determination of metals in organic compounds in several works [138-141]. This technique has been gradually replaced by the ICP methods due to their higher sensitivity, multi-elemental capability, high sample throughput and low sample consumption.

The two ICP methods mentioned above have been widely used in determining trace metals content in coal-based and biomass samples. These techniques require sample preparation or digestion to dissolve the metal into solution and separate the organic components that bound these elements. The two preparation methods, i.e. open and closed digestions, were studied by Lachas et al [142] for coal based samples. It was discovered that certain volatile elements are lost during the open digestion. The study also found that the decrease in sample size does not affect the accuracy or the precision of the ICP analysis, as long as the original sample matrix contains low concentration of trace elements and the solutions contain adequate dissolved elements. The techniques were replicated by Richaud et al. [143] and up to 17 elements in several coal and biomass samples were successfully analysed using the two ICP techniques. Herod et al [144] studied the partitioning of trace elements of coal tar pitch and coal liquefaction extracts and reported larger fractions of trace elements in the larger molecular mass fraction. A separate study by Richaud et al. [145] concluded that the trace elements in coal derived fluids may be present in association with organic components but majority of the metals are associated with mineral matter.

Analysis of trace metals distributions in petroleum-based samples has also been reported in a number of publications. Kumar et al. [146] evaluated the trace metals composition of a naphtha fraction determined by ICP-MS and AAS. The results produced from both techniques showed good agreement amongst themselves for most of the elements, especially for Nickel, Vanadium and Lead. Bettinelli et al. [147] analysed a fuel oil sample, digested via acid mineralisation (HNO_3 and H_2O_2) in a microwave, with ICP-MS instrumentation and produced good accuracy and precision relative to the standard materials of NIST 1634b (trace elements in fuel oil) and NIST 1619 (sulphur in residual fuel oil). De Souza et al. [148] conducted a study on determination of trace elements in a crude oil sample via ICP-OES. Samples were digested with nitric acid in a microwave as well as in an ultrasonic bath. The results were also compared to the NIST 1634b reference material and showed good agreement for most of the elements. Recoveries of 90% to 105% were recorded and indicated reliable sample preparation technique. Wondimu et al. [149] performed similar analysis of sample digestion through combination of HNO_3 and H_2O_2 with ICP-MS instrumentation of NIST 1634b sample. The effect of sample size and reagent composition and volume towards elements recoveries was studied. It was reported that also using 250 mg sample, as opposed to 1 g recommended by NIST, the produced results were in good agreement with the certified values for most elements.

2.7.5. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is used to estimate the proximate composition of deposit samples. An ASTM method is available for proximate analysis of coal and coke materials with a TGA system [150]. This analysis provides the total ash content, volatile loss and fixed carbon content and has been proved to be a valuable tool for characterising deposits [16,106]. A high content of ash in a deposit is indicative of a high inorganic content, suggesting predominance of inorganic fouling. The results of TGA when coupled with full elemental analysis, provide information on the extent of organic contribution towards deposition. C/H value indicates whether the organic components of the deposit are waxy (>2.0), asphaltenic (1.0-1.2) or coke-like (<1.0) [151]. The results from TGA may be used to evaluate the volatility of samples but the results may differ from other values obtained from a more controlled experimental condition/apparatus, such as a wire mesh reactor, where factors such as uneven heating rate on samples and

secondary reactions of volatiles may be reduced. This method is however is well-established with large database available in the literature. Results that are internally consistent with low standard deviations amongst repeats may be used as comparative analysis of samples.

2.8. Summary

The discussion within this chapter has been focused on the general understanding of thermal fouling in pre-heat train of a crude oil distillation unit in which the contributing factors and impacts were presented in detail. The fouling issue is well recognised by refinery operators with several mitigation and operating strategies already in place to reduce its economic impact towards operation. The status of research on the effects of trace metals especially Vanadium and Nickel towards fouling has been studied and discussed. A comprehensive analysis on fouling behaviour through blending of crude oils has also been presented amongst other work on asphaltene stability in individual crude oils and their blends. It is noted that some areas required deeper insights and investigations and these have been looked further in the current study;

Contribution of Vanadium towards deposition has been studied. With the current trend of heavy crude oil processing, the impact of having higher concentrations of Vanadium in the processed oil shall be assessed. Understanding of fouling behaviour and characterisation of deposits of Vanadium-rich oil have been established to provide better insights of chemical reaction fouling with the presence of Vanadium at high temperature regions.

Characterisation of deposits generated from both incompatible and compatible crude oil blends requires further assessment in order to understand the contributing materials of fouling deposits originated from the blend. It has been proved and reported in the literature how incompatible oils increase fouling propensity, but the compositional and characterisation of deposits are still lacking understanding.

3. Experiment Methods and Instrumentation

This chapter discusses the research methodology and detailed background of the analytical instruments used in the study. Descriptions of the crude oil samples used are presented here along with the sample preparation procedure prior to each analysis, particularly on the trace element analysis with the ICP instruments. The constraints and limitations of each analytical technique are also noted and discussed, providing clearer view on the discussions of results that follows in the ensuing chapters.

3.1. Crude Oil Samples

Three crude oils of different origins and characteristics were selected for this particular work. Their properties are listed in Table 3.1.

Table 3.1 Properties of crude oil samples used in the study

	Crude A	Crude B	Crude D
API Gravity [°]	28	24	46
Asphaltenes [%] ^a	6.7 ^a	5.4 ^a	0.06
Vanadium [ppm]	68 ^b	47 ^b	2
Nickel [ppm]	18 ^b	22 ^b	3 ^b
Sulphur [wt%]	2.81	3.62	0.03
Viscosity at 80 °C [cP]	5677	7826	878
Viscosity at 100 °C [cP]	3903	4914	638
Acidity [mg KOH/g]	0.22	0.10	0.08

^adetermined independently in laboratory through ASTM D6560

^bdetermined independently in laboratory via ICP-MS analysis

These values are obtained from a crude oil assay library [152] and some were verified independently wherever possible in the laboratory. The asphaltenes content were determined following the ASTM D6560 [47] procedure whereas concentration of Nickel and Vanadium were obtained via ICP-MS analysis. The detailed procedures are presented later in the chapter.

The crude oil samples originated from three different regions, ranging from Asia Pacific to Middle Eastern. Crude A and B fall under medium-heavy, sour type oils while Crude D is a sweet, light crude oil registering API gravity of 45°. This range of oils suited the requirement needed to provide sufficient data and information for the study as they represent the typical type of oil currently used in oil refineries.

3.2. Sample Production and Preparation

There were a number of analyses conducted throughout the study particularly on characterisation of the samples. Most of the methods discussed here are adopted from previous experimental analysis in the research group whereas some are referred from established standard methods in literature.

3.2.1. Fouling Reactor

As previously mentioned, a batch reactor was specifically designed and built for this study. Detail construction of the reactor is presented in the following Chapter 4. Briefly, the reactor consists of a heated test section where deposit samples were produced, connected to a feeding line where sample and pressure were introduced, and a discharge line where excess oil and pressure were relieved. The preparation of samples prior to each run was done separately; particularly in the case of crude oils blending and mixing of vanadyl porphyrin to ensure a standard procedure was followed. The detail procedure of each is presented in the respective chapters.

3.2.2. Asphaltenes Determination

The crude oil was fractionated into the two parts following the ASTM D6560 (IP 143). 10 g of sample mixed with 250 mL of heptane was placed in a reflux set-up with heptane for 60 minutes. This step was vital to precipitate out the asphaltenes fraction. The solution is later left to cool to room temperature for 90 to 150 minutes before being vacuum-filtered with a 2.5 μm filter paper to separate the heptane insoluble from the maltenes fraction. Afterwards, the maltenes fraction was recovered using a rotating evaporator and a subsequent drying step in an oven. To recover the asphaltenes fraction, the heptane insoluble along with the filter paper, were washed with hot toluene in a Soxhlet set-up as illustrated in Figure 3.1. The filter paper with heptane insoluble was placed inside an extraction chamber. The flask was heated resulting in evaporation of toluene that consequently moved up into the condenser. The condensed liquid trickled down into the extraction chamber containing the insoluble heptane fraction. The chamber was filled with hot liquid toluene and washed back down into the flask. This process was repeated until the toluene inside the extraction chamber became clear. At the end of extraction, the mixture in the flask were collected and placed in a vacuum oven to recover the asphaltenes fraction. Subsequent weighing and drying were repeated until the weight became constant.

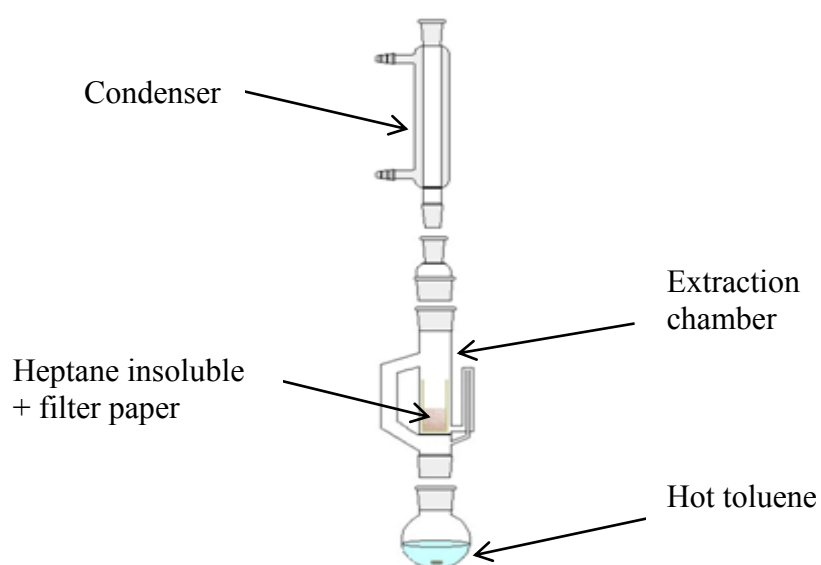


Figure 3.1 The Soxhlet set-up for asphaltenes extraction with hot toluene.

3.2.3. Trace Element Analysis

Since concentration of metals in crude oils is generally very small, trace element analysis was performed to quantify the amount of metals present in the samples. The quantification analysis by ICP requires sample dissolution in an acidic solution. This step is important in order to remove the carrier matrix of mineral and/or carbonaceous materials. Dissolution of the hydrocarbons is done in the presence of strong acids, which is also served to dissolve the trace elements. There are two digestion methods commonly used in sample preparation; wet-ashing and microwave acid-leaching methods [137,153]. Wet-ashing is an open digestion technique, with two means of heating via a hot plate and a muffle furnace. It had been reported that this method gives rise to loss of volatile components, such as Arsenic and Selenium due to the high temperatures required during acid extraction [154-157]. The microwave or closed digestion technique on the other hand involves microwave heating of samples contained in PTFE vessels. This method was developed to prevent losses of analytes and to minimise contamination in the samples. It also requires much less time than the wet-ashing method.

The reagents used for all ICP analyses, namely sulphuric acid (98% w/w), nitric acid (69% w/w), hydrofluoric acid (40% w/w), perchloric acid (70% w/w) and hydrogen peroxide (30% w/w) were all of AristAR® and/or AnalaR® grades. Deionised, distilled water was used throughout the work for washing and rinsing of the vessels, and preparation work for dilution of acids. All labwares, except for the platinum crucibles used in sample digestion, were cleaned using acetone and 10% HNO₃ solutions. The platinum crucibles were cleaned in a beaker containing 20% perchloric acid solution and heated on a hot plate at 180°C for 3 hours.

3.2.3.1. Wet-ashing Digestion

20 mg of sample was weighed and placed in a platinum crucible. 100 µl of concentrated sulphuric acid (98% w/w) was added and the crucibles were placed on a hot plate at 150 °C for 3 hours in a fume cupboard. Concentrated sulphuric acid was used to digest the volatile organic complexes such as vanadyl porphyrins [155]. It reacts with these organometallic links and retains the volatile metals as sulphates. The crucibles were then moved into a muffle furnace and left overnight at 520 °C leaving completely ashed samples. The ashed products were treated with perchloric acid (60% w/w) and

hydrofluoric acid (40% w/w) at 300 µl and 500 µl respectively. They were placed on a hot plate at 250°C for approximately 45 minutes until the content reached incipient dryness. Hydrofluoric acid was used to dissolve the silicates component in the samples. It ensures the destruction of these minerals, reacting to produce volatile SiF₄ and water. Perchloric acid is a powerful oxidising agent and ensures the complete evaporation of fluorides which would otherwise damage the glassware of the ICP instrumentations. The residue was later dissolved in dilute nitric acid, at 2% w/w for ICP-MS and 10% w/w for ICP-OES, by reheating them on a hot plate at 150°C. The final analyte was made up to 10 ml with 2%/10% nitric acid, which was the background matrix required for ICP analysis. HNO₃ is an excellent matrix for ICP-MS as all the elements present in HNO₃ are present in plasma or in the air. The plasma of ICP mainly consists of argon ions and few percentages of H⁺, O⁺ and N⁺ ions from air. Hence, no new atoms are introduced that could potentially increase the polyatomic interferences [137].

3.2.3.2. Microwave Digestion

20 mg of sample was placed in a clean 7 ml PTFE vessel with a screw top. 1 ml of concentrated nitric acid (69% w/w) was added to each vessel and sealed before being fitted-in into a carousel. The distribution of vessels on the carousel was made as evenly as possible to make sure each vessel was subjected to similar amount of heat inside the microwave. The heating programme was set at 300 W for 1 minute followed by a 2-minute rest, 5 minutes at 500 W and 10 minutes at 600 W. After 5 minutes rest under ventilation, the carousel was taken out and placed in a freezer at -180°C for 1 hour. This was to minimise the loss of volatiles and gases during opening. The sample was then set to room temperature before transferred into a 10 ml volumetric flask and topped up to the volume with 2%/10% HNO₃. The yellowish solution was finally filtered to remove remaining solids to prevent detrimental effects to the ICP instrumentations.

3.2.3.3. Dilution Factor

The results of ICP are recorded as concentration of trace metals in liquid form. To obtain the concentration in solid, a correction factor called dilution factor (DF) has to be applied to the results. This is due to sample preparation procedure in which dilution is required to ensure the total dissolved solid (TDS) in the samples satisfy the ICP requirement. If the TDS is too high (TDS is typically less than 0.2%) [153], the likelihood of blockage

at the orifices inside the instrument's ionisation chamber is increased. This would subsequently reduce the sensitivity and accuracy of readings. DF can be defined as:

$$DF = \frac{V_s \times d}{M_s} \quad \text{Equation 3.1}$$

where, V_s is the volume of the sample in ml

d is the dilution multiple (no. of times sample is diluted)

M_s is the mass of sample in grams

3.2.3.4. Limit of Detection

The limit of detection, LOD is the lowest value at which one can confidently say that a particular element exists in the sample. The LOD is calculated statistically and defined as the concentration equal to three times the standard deviation of the background matrix i.e. procedural blank, multiplied by the DF and quoted as the concentration in solid for each preparation procedure. LOD may be defined as follows:

$$LOD = 3 \times \frac{(Std_{RCpb})}{(RC_{10ppb} - RC_B)} \times [Std_{10ppb}] \times DF \quad \text{Equation 3.2}$$

where, Std_{RCpb} is the standard deviation of the raw data counts of the procedural blank

RC_{10ppb} is the mean of raw data counts of the 10 ppb calibration standard

RC_B is the mean of raw data counts of the calibration blank

Std_{10ppb} is the concentration of the calibration standard 10 ppb solution

DF is the dilution factor

It is clear that LOD depends on the instrument sensitivity, sample preparation variables and sample interferences. If the concentration of a particular element is calculated below its LOD, the value is considered to be unreliable and therefore typically not reported.

3.3. Analytical Techniques

Characterisation of samples was performed via several techniques with the aim of understanding the build-up structure and content of the deposit samples as well as the liquid counterparts. The analysis in particular is looking into the molecular structure of the samples, their molecular weight distribution, the relative molecular mass between samples, and the trace metal content of oils and products.

3.3.1. Size Exclusion Chromatography

Size Exclusion Chromatography (SEC) is a liquid chromatography technique used to analyse the molecular mass distribution of sample by means of separating the molecules based on their sizes. Separation happens as a result of the different degrees of penetration. Samples containing mixtures of molecules are dissolved in a solvent and eluted through a stationary phase, typically a column packed with polymer beads, at different rates. This results in the separation of a solution based on their molecular sizes. Molecules of comparatively smaller size are slowed in their progression in the column as they enter into the stagnant mobile phase within the pores of the packing. Consequently, the large molecules move more rapidly through the column and the mixtures are separated into its components. As a result, SEC chromatograms typically give bimodal distributions in which the early eluting peak, or excluded peak, corresponds to the larger molecular components of the sample that are not resolved by the column. This peak might also indicates molecules with special molecular arrangement with different spatial conformation e.g. fullerenes [109]. The void volume of the column is determined by the

earliest eluting time of the sample which also corresponds to the volume of the eluent that surrounds the column packing. The second peak, or the retained peak, relates to the smaller molecular components of that particular sample and resolved by the column porosity. The limit of permeation of the column corresponds to the latest elution time and no peak shall appear after this limit, which suggests separation is done based on the size of molecules. Figure 3.2 shows a typical chromatogram produced by an SEC system.

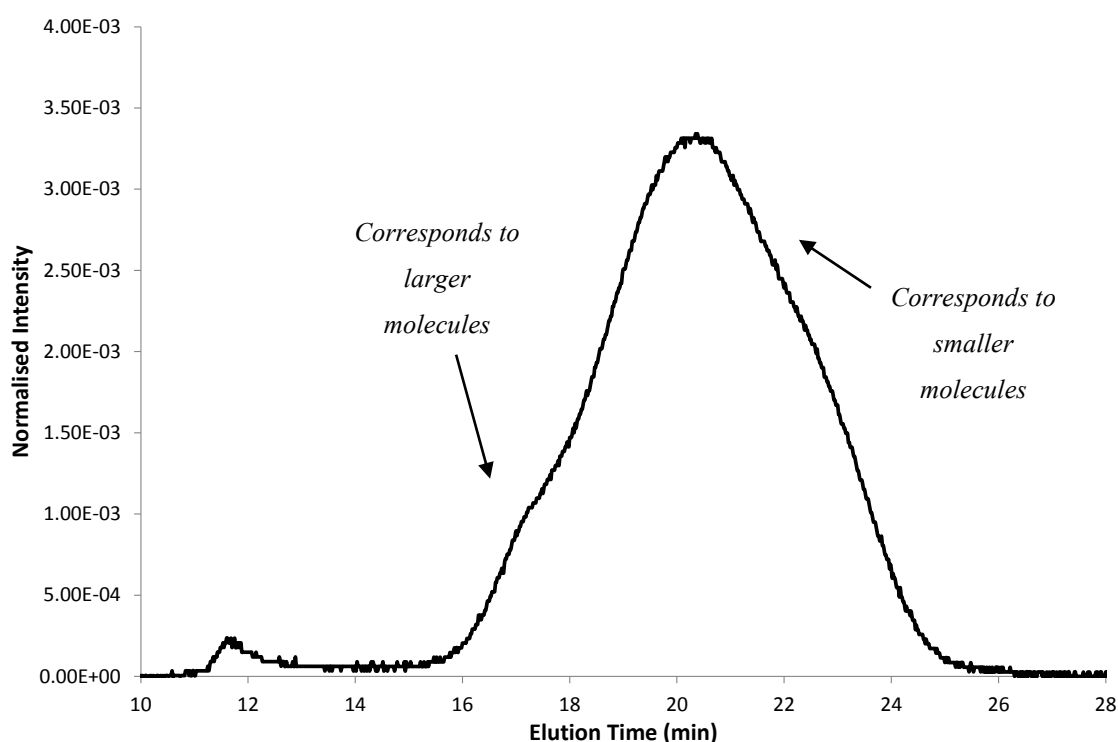


Figure 3.2 Size exclusion chromatogram of a crude oil sample in a NMP:CHCl₃ eluent. Signal intensity is plotted against the elution time.

For this particular study, a 300 mm long, 7.5 mm ID packed Mixed-D column of 0.5 micron polystyrene/polydivinylbenzene particles from Polymer Laboratories, UK has been used. During operation, the temperature of the column was kept at 80 °C with mixtures of NMP and CHCl₃ at 6:1 ratio used as eluent and pumped at 0.5 mL min⁻¹. Detection was done through a UV-absorbance detector from Perkin-Elmer (model LC290) and the wavelength was set at 300 nm during measurement. Since SEC is not an absolute technique, direct estimation of molecular mass is not possible, hence calibration of the column is necessary. This was carried out using known molecular mass compounds

such as polymers. Calibration was performed with a range of standards consists of polystyrenes (PS), polycyclic aromatic hydrocarbons (PAH) and heterocyclic nitrogen and oxygenated compounds. The calibration curves are defined as follows and the corresponding plots are presented in Appendix 3.1:

$$\text{Log MW} = 9.7674 - 0.3521t \quad \text{for } 11 < t < 20 \text{ min (PS standards)} \quad \text{Equation 3.3}$$

$$\text{Log MW} = 5.473 - 0.1471t \quad \text{for } 20 < t < 24 \text{ min (PAH, O and N standards)} \quad \text{Equation 3.4}$$

The chromatograms are typically plotted against the elution time instead of the molecular weight due to the first excluded peak being out of the linear calibration line. This fraction of samples is not resolved by the column and cannot be corresponded to a particular molecular weight range. The measure of molecular size of a sample depends on its hydrodynamic volume in the solvent used to elute the column which may varies from one study to another. This relates to the solvation effects of the sample in that particular solvent and the molecular size may not necessarily equate the molecular weight [101]. By plotting the response signal against elution time, a qualitative comparison may be made between different samples rather than quantitative comparison that are not representative to the correct molecular weight values. The plot against molecular weight produce a curve that is in reverse order to that of elution time, as shown here in Figure 3.3 for the same sample presented in Figure 3.2. In this example, the second peak corresponds to a higher molecular weight which is not necessarily corresponds to the values of the x-axis as this fraction of the sample is not resolved by the column.

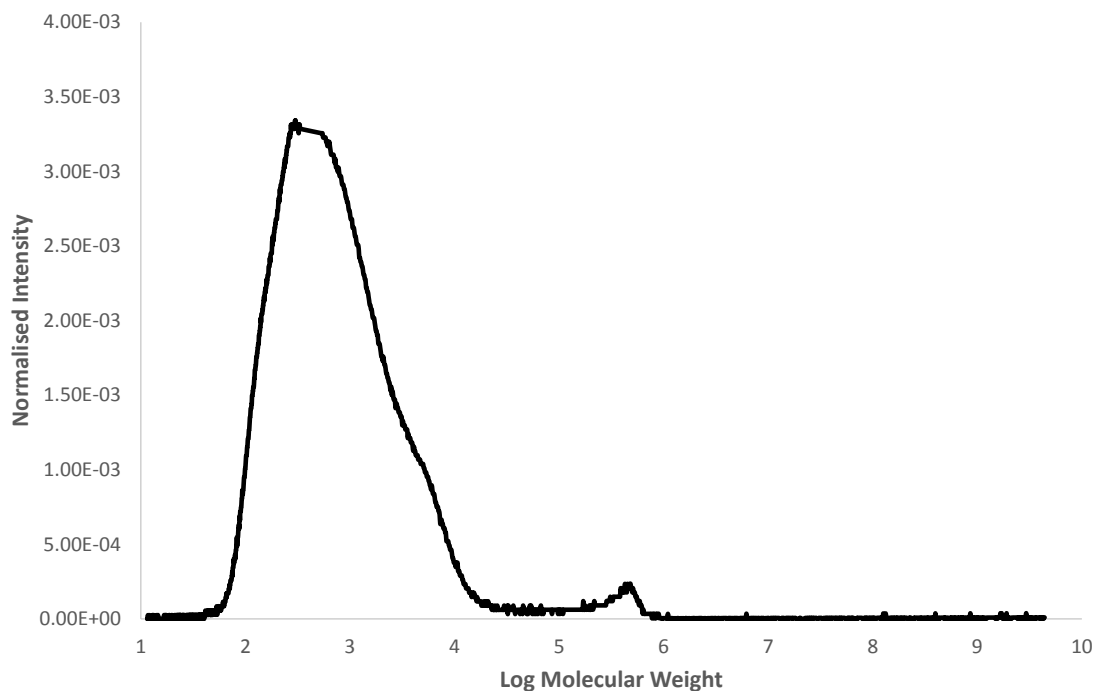


Figure 3.3 Size exclusion chromatogram of a crude oil sample in a NMP:CHCl₃ eluent. Signal intensity is plotted against the log of molecular weight.

Prior to the first sample injection, a mixture containing the standard compounds was injected to ensure that the elution times of these compounds were within the calibrated regions. Previous work in the laboratory [103,109,117,158] has shown good agreement in the description of the molecular mass of SEC-retained materials between the calibration of the SEC system with standards and the mass range of the low mass peak observed by MALDI-MS. These works mainly involved characterisation of coal tar pitch and petroleum-based samples with various types of solvents as the eluent phase. Work with pure NMP, pure chloroform and THF of heavy hydrocarbon liquid samples had been studied comprehensively [102,114,159,160] albeit some limitations posed by these solvents. THF has shown to be limited by its solubility power as well as discrepancies posed between the samples and calibration data of PS and PAH standards. Pure NMP also only partially dissolved heavy hydrocarbon samples which limit the analysis to the light band of molecular weight range of samples analysed. Pure chloroform is best in dissolving petroleum-derived samples but it cannot eliminate interactions between the samples and the column packing, hampering the use of this solvent. Work by Berrueco

et al. [109], also reported by Venditti [16], utilised the mixture of NMP and chloroform in analysing crude oil based samples and had significantly improved the performance of SEC. It is however worth to note the complete solubility of deposit samples still was not achieved at the ratio of 6:1 NMP:CHCl₃ used in this work.

3.3.2. UV-Fluorescence Spectroscopy

Analysis of the molecular structure of samples has been analysed using UV-Fluorescence spectroscopy (UV-F). This technique offers the possibility of qualitative but not quantitative analysis of information on the relative concentrations and sizes of fused aromatic ring systems in heavy hydrocarbon samples. The UV region of light spectrum provides information about conjugated π - electronic systems, especially the aromatic systems. The requirement of only small amounts of sample by this technique is well-suited for characterising the limited amount of samples available for this study.

The principle of UV-F is based on the relaxation of molecules excited to higher energy state, by absorption of incident light, to the ground energy state. Upon light incident, an organic molecule is excited to a higher vibrational energy level of excited energy state before losing its energy due to molecular collisions. This subsequently dropped the molecule to lower vibrational energy level in the ground energy state. The return to lower various vibrational energy levels typically emits visible light. This transition between electronic energy levels provides the information of the structure of the various vibrational levels by analysing the different frequencies of the emitted light.

Three types of spectra can be obtained from a UV-F spectroscopy; emission, excitation and synchronous. Emission spectra are obtained by exciting samples at a fixed wavelength while recording the emission over the available spectrum. Excitation spectra are acquired by varying the excitation wavelength over the available spectrum, while fixing the measurement at a pre-selected emission wavelength. Synchronous spectra are produced by sweeping the excitation and emission wavelengths with a fixed wavelength difference typically at 20 nm, over the entire range of wavelength. Typically, when analysing a hydrocarbon-based sample, the synchronous spectra is the most significant information required as it combines the emission and excitation UV-fluoresce spectra simultaneously and indicates the structural complexity of the sample. The individual emission and excitation spectra of complex hydrocarbon system normally give similar

fluorescence characteristics, hence not much information can be gathered from the two individually.

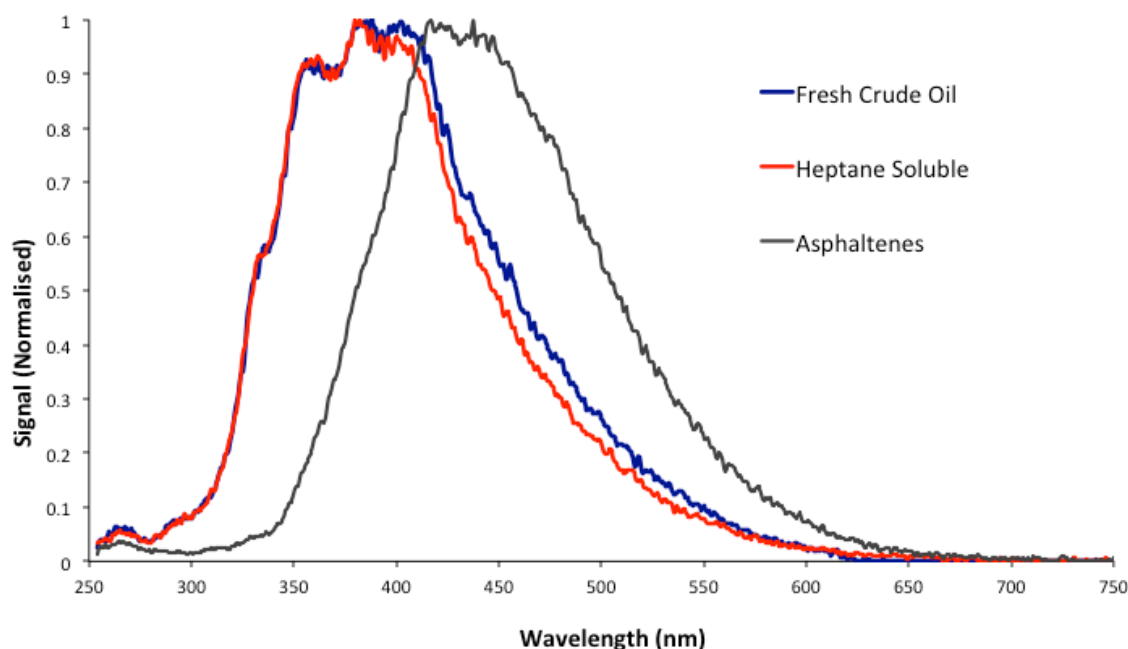


Figure 3.4 Synchronous UV-fluorescence spectra of a crude oil and its maltenes and asphaltenes fractions

Typical synchronous UV-fluorescence spectra of hydrocarbon are shown in Figure 3.4. A clear difference in terms of the shift of each spectrum is observed here indicating structural difference amongst the three samples. A shift towards longer wavelength signifies components of higher structural complexity particularly on the aromaticity of the sample. Smaller conjugated aromatic systems fluoresce at the shorter wavelength end of the spectrum, whereas larger aromatic clusters give fluorescence at longer wavelength. This shift also indicates the presence of condensed linear aromatic systems and the presence of heterocyclic S, O and N rings [161]. The intensity of fluorescence however decreases with cluster size, hence molecules of large clusters are invisible by this technique. UV-fluorescence spectroscopy has already been used for characterisation of coal-derived products [162,163]. Li *et al* [162] discovered that the use of UV-fluorescence spectroscopy, in conjunction with SEC, has allowed tracing the changes in

UV-fluorescence spectroscopic properties of coal tars with increasing molecular mass. For petroleum-based samples, Venditti *et al* [106] analysed synchronous UV-F spectra of fouling deposits solubility fractions. Three fractions were analysed; NMP-insoluble, chloroform-insoluble and toluene-insoluble fractions. There was a shift towards longer wavelengths, from NMP-insoluble to the chloroform-insoluble fractions which suggests that chloroform has the lowest ability in dissolving large aromatic components.

In this particular study, a Perkin-Elmer LS55 luminescence spectrometer with a slit width of 5 nm was used to record the emission, excitation and synchronous spectra. Scanning was performed at 500 nm min⁻¹ with constant wavelength difference set at 20 nm to obtain the synchronous spectra. Samples were diluted in chloroform to avoid the effect of self-absorbance and placed in a quartz cell with 1 cm path length. Samples were first scanned for the synchronous spectra until the intensity of the fluorescence was reduced by further dilution with chloroform. The other two spectra were later obtained from the same solution. The spectra are peak-normalised for comparative analysis with other sample of interests.

3.3.3. X-ray Fluorescence Spectroscopy

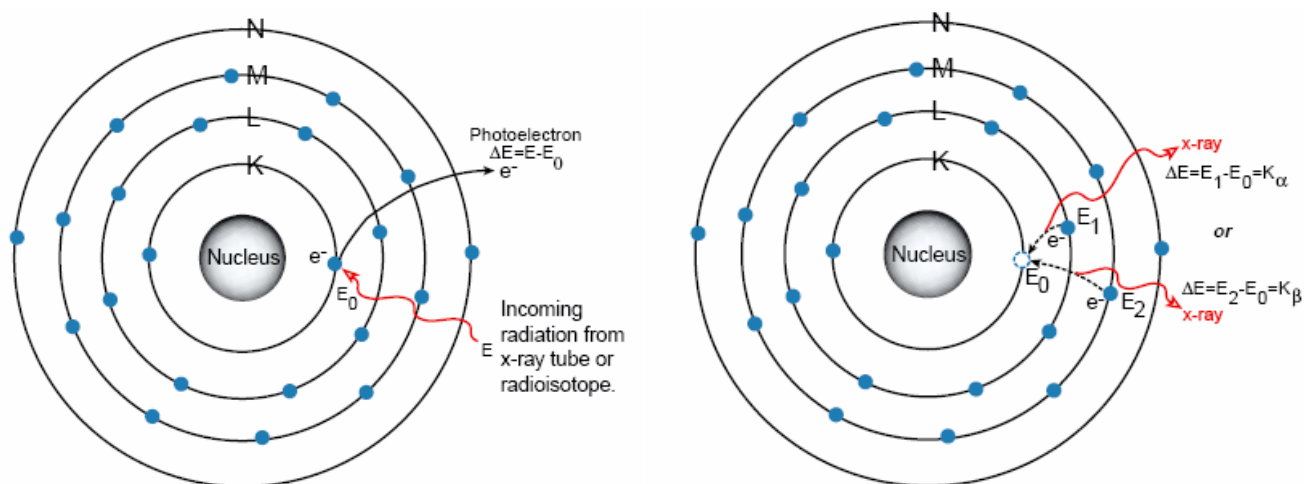


Figure 3.5 (a) Radiation of X-ray photons excites an electron from an inner shell, (b) The vacancy is filled by an electron from a higher energy level, and the energy difference is released as secondary X-ray photon. Reproduced from [137].

X-ray Fluorescence spectroscopy (XRF) is a non-destructive, multi-elemental analysis which utilises an X-ray beam to irradiate photons of a sufficiently high energy onto the samples. This incident photon results in the excitation of an inner shell electron, producing an electronically excited ion. This in turn causes the de-excitation of another electron from a higher energy level to fill the vacancy, as shown here in Figure 3.5. The energy difference between the two shells appears as a secondary (fluorescent) X-ray photon emitted by the atom. These photons have a narrow energy bandwidth and are specific for the particular electron transition and characteristic of the ionized element. The intensity of the fluorescent beam indicates the element concentration in the sample. These released photons are captured by a detector and displayed as an X-ray spectrum²⁴.

XRF is a fast and cost-effective technique but it is less sensitive than ICP methods. Results are often accurate, provided adequate calibration standards are available. When no such standards can be found, semi-quantitative (standardless) analysis remains possible. A full quantitative analysis requires a standard sample that has the similar background matrix to that of the samples. XRF is very sensitive to the matrix of analysed samples. Spectral and matrix interferences must be taken into account during analysis, especially from the underlying substrates. The measurements are typically susceptible to errors in particular from metal substrates. A correction for matrix effects must be applied and the sample itself has to be homogeneously distributed over the sample dish [137,153].

Contrary to ICP techniques, XRF instruments do not readily measure elements in ppm level i.e. mass per mass units. The method usually reports the amount of element in a sample layer in mass per unit area. This is because X-rays are typically measured for a known spatial area and the count rate of X-rays is a function of both mass fraction and thickness of the specimen layer. For example, if samples of different thickness, containing the same concentration of a particular element by weight were analyzed by XRF, the thicker film would yield a higher measurement count rate. This limits the precision of measurement to quantitatively analyze and compare to calibration standards on a mass per mass unit basis [137]. All XRF analyses were performed on S4 Explorer X-ray Spectrometer from Bruker AXS. Samples are placed in PTFE cups covered at the bottom (substrate) with polypropylene film of 4 μ thickness. Samples layers are distributed as evenly and as thinly as possible to reduce the effect of heterogeneity on the fluorescence intensity. The operating conditions of the XRF spectrometer are presented in Table 3.2.

Table 3.2 XRF instrumental parameters and operating conditions.

Component/Parameter	Setting
X-ray frequency	Max. 63 Hz
X-ray Tube Nominal current	Max. 50 mADC
X-ray Tube Nominal power	Max. 1000 W
Anode material	Rhodium
Sample Size (diam.)	50 mm
Sample Height (max.)	46 mm
Detector Gas Inflation	Argon

3.3.4. Inductively Coupled Plasma Optical Emission Spectroscopy

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is a mature and robust multi-elemental analytical technique suitable for trace determination of many elements in various types of samples. This instrument consists of three main parts; the plasma torch assembly, the sample introduction system and the spectrometer. ICP is chiefly used as excitation source for optical emission spectrometry. The torch in ICP is essentially made up of three concentric quartz tubes, which produce a plasma region at the tip of the torch [153] as shown in Figure 3.6. This plasma is produced from flowing gases, typically argon, and maintained by energy coupled to it from a radio frequency generator. The sample is introduced into the plasma from the most inner concentric tube to produce a high velocity jet of gas that punches a cooler hole through the centre of the plasma.

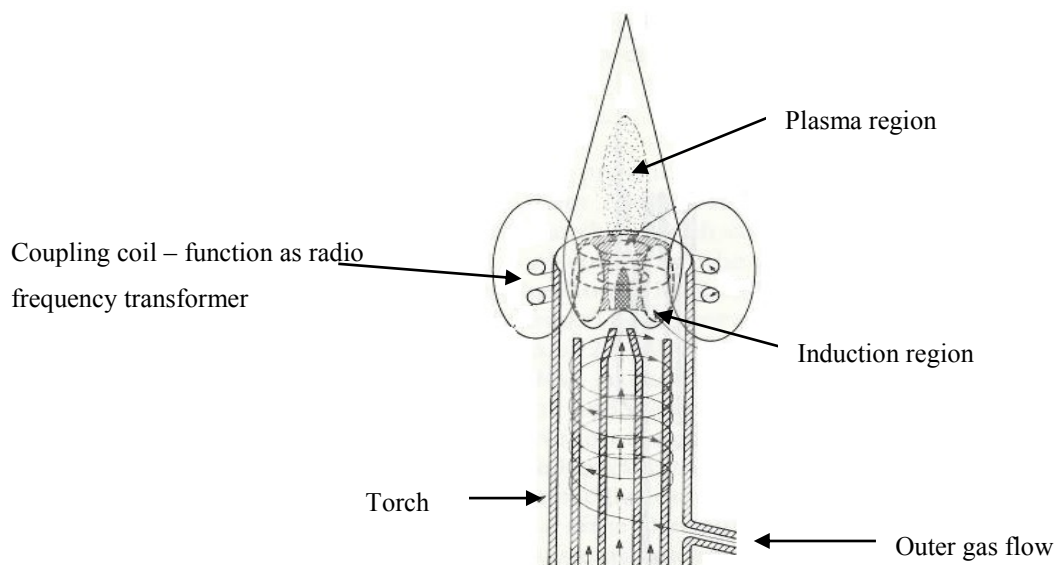


Figure 3.6 Schematic of ICP torch, gas flows and the induced magnetic field. Reproduced from [153].

In ICP-OES the sample is excited in a high temperature plasma condition to produce visible line spectra characteristic of the element present. The concentration of the elements is determined by comparing the intensities of the line spectra obtained against the spectra from standard solutions [164]. It allows simultaneous determination of 20 – 60 elements with detection limits down to low $\mu\text{g l}^{-1}$ levels. Unfortunately, ICP-OES lacks the sensitivity and often the selectivity to accurately determine trace element content in very dilute solutions. Often, the spectral interference (high background levels) reduces its sensitivity and limits the range of elements that can be accurately determined in many sample types [154].

The ICP-OES requires any sample to be in solution. The sample introduction system is normally equipped with a peristaltic pump, a pneumatic nebuliser and a spray chamber. The fluid sample is pumped into the nebuliser via the peristaltic pump. The nebuliser then generates an aerosol mist and injects humidified argon gas into the chamber along with the sample. This mist accumulates in the spray chamber, where the larger droplets settle out as waste and the finest particles are subsequently swept into the torch assembly. These small droplets carry only about 1% of the solution into the torch, whereas the rest is pumped away as waste [153,155].

ICP-OES analyses were carried out on Optima 7000 DV with cyclonic spray chamber from Perkin Elmer. The calibration of the ICP-OES was done with multi-element solutions made from single element solutions supplied by Merck. Each sample determination was the mean of three separate sequential determinations and a reagent blank correction was made. The instrumental parameters and operating conditions are listed in Table 3.3.

Table 3.3 ICP-OES instrumental parameters and operating conditions

Parameter	Setting
Forward power	650 W
Reflected power	< 10 W
Plasma gases	All argon
Nebuliser gas flow	0.800 l min ⁻¹
Auxiliary gas flow	0.800 l min ⁻¹
Coolant gas flow	7.5 l min ⁻¹
Torch	Fassel type
Detector	Photomultipliers
Solution uptake flow rate	1.0 ml min ⁻¹
Washout time	45 s
Integration time	5 s
Calibration Mode	External calibration
Standard matrix	10% HNO ₃
Standard concentration	0, 5, 20 ppm

3.3.5. Inductively Coupled Plasma Mass Spectroscopy

Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) is a very sensitive multi-elemental technique. The fundamental difference between ICP-OES is that the plasma is not used to generate photons of light, but to generate trace metal ions instead. The aerosol is introduced into the plasma via pneumatic nebuliser and these droplets undergo successive process of volatilisation, atomisation and ionisation. Its efficient ionisation, coupled with the sensitive detection of the mass spectrometer, results in parts per trillion detection limits that are generally 2-3 orders of magnitude lower than the ICP-OES [153]. Similarly to ICP-OES, the quantification of the trace elements is obtained by external calibration curves using multi-element standard aqueous solutions. Although it is a very sensitive technique, ICP-MS has some limitations regarding the interpretation of results. Due to the utilisation of a mass spectrometer, some ionic interference is inevitable. There are three types of interferences in ICP-MS [154]:

- i) *Isobaric overlap* - this interference occurs when isotopes of different elements have the same mass to charge ratio (m/z). For example, ^{48}Ti and ^{48}Ca .
- ii) *Doubly charged ions* - interference when ions such as M^+ and N^{2+} with a mass ratio $N/M = 2$, so that the m/z ratio is the same for both elements. For example, $^{130}\text{Ba}^{2+}$ and $^{65}\text{Cu}^+$.
- iii) *Molecular ions interference* - occurs when some of the components of the plasma or solution forms a polyatomic cluster with O, Ar or Cl with an m/z value the same to that of the metal ions. For example, ^{75}As and $^{40}\text{Ar}^{35}\text{Cl}$; ^{51}V and $^{16}\text{O}^{35}\text{Cl}$.

ICP-MS is also relatively intolerant to high levels of Total Dissolved Solid (TDS) in the final analyte solution. This should be generally below 0.02% (200 ppm). If the solution is not dilute enough, this will generate unstable plasma conditions and ionisation will not be as effective. All ICP-MS analyses reported here were carried out using a PQ 2+ STE instrument from Fison Instruments, equipped with a Galan V-groove nebuliser and a Gilson Minipuls 3 peristaltic pump. A standard Pentium 4 PC provided overall system control. The instrument was optimised for multi-element determination from 6Li to 210Pb. Each sample determination was the mean of three separate sequential determinations and a reagent blank correction was made. Signal drift was monitored by

running the 10 ppb standard solution after every 5 samples. The instrumental operating parameters used in this study are provided in Table 3.4.

Table 3.4 ICP-MS instrumental parameters and operating conditions

Parameter	Setting
Forward power	1350 W
Reflected power	< 3 W
Plasma gases	All argon
Nebuliser gas flow	0.900 l min ⁻¹
Auxiliary gas flow	1.5 l min ⁻¹
Coolant gas flow	14.0 l min ⁻¹
Sampling cone	Ni 1 mm Orifice
Skimmer	Ni 0.7 mm Orifice
Solution uptake flow rate	0.8 ml min ⁻¹
Dwell time	300 µs
Sample time	66 s
Washout time	60 s
Number of repeats	3 standards and samples, 5 blanks, 1 drift
Calibration Via	Multi element standards
Standard matrix	2% HNO ₃
Standard concentration	0, 1, 5, 10, 20, 100 ppb
Drift monitor	10ppb multi-element solution

3.3.6. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) were conducted to assess the ash content of deposit samples and also to evaluate the proximate elemental composition of the samples. A non-isothermal analysis was used in this study. Approximately 5 mg of sample were used in each run with the loss of weight recorded throughout the heating and cooling procedure. The programme used in this analysis is as follows:

1. Hold with nitrogen gas at 40 mL min⁻¹ for 5 minutes at 50 °C to allow the weight to stabilise before heating.
2. Heat from 50 °C to 105 °C at 20 °C min⁻¹.
3. Hold for 35 minutes at 105 °C.
4. Heat from 105 °C to 900 °C at 10 °C min⁻¹
5. Hold for 30 minutes at 900 °C.
6. Cool from 900 °C to 850 °C.
7. Hold for 80 minutes at 850 °C and after 40 minutes (when the weight was stabilised) the gas was switched to air at 40 mL min⁻¹ to burn out the fixed carbon.

3.3.7. Gas Chromatography

Gas Chromatography (GC) with flame ionisation detector (FID) was used to evaluate the molecular composition of samples. The analysis of fuel-derived materials with GC posed limitations in terms of the low upper limit of molecular mass that can be solved by the column [100]. A tar sample can be analysed only up to about 300 amu with capillary column GC, which is a real constraint if full molecular weight range analysis were to be done on petroleum-based samples. A simulated distillation (SimDis) programme following the standard method of ASTM D2887 was used in this analysis. With calibration of column performed using a standard gas oil, the lower molecular mass range of the samples can be analysed. The percentage of samples resolved by the column is quantified for each sample, and the results are being compared to those of SECs.

The samples were analysed using a Perkin Elmer Clarus 500 Chromatographer with FID detector. The calibration curve is presented in Appendix 3.2. An SGE capillary column type HT-5 of 0.1 µm film thickness and 25 m long was used. The carrier gas used was helium and operation was done in split mode with split ratio of 1:20. The programme was set and calibrated to which the boiling point distribution below 450 °C were recorded

and quantified. Samples were dissolved in chloroform and set to a concentration level of 0.1 mg mL^{-1} . The test was performed three times for accuracy of the measurement. The programme started at $35 \text{ }^{\circ}\text{C}$ and with a constant increase of temperature at a rate of $15 \text{ }^{\circ}\text{C min}^{-1}$ until it reached $350 \text{ }^{\circ}\text{C}$. This temperature was maintained for 2 minutes before a second ramp to $380 \text{ }^{\circ}\text{C}$ at a rate of $25 \text{ }^{\circ}\text{C min}^{-1}$. The temperature was maintained for 10 minutes before the run ended.

4. Design and Construction of Fouling Reactor

This chapter describes the development stages, detail design and the motivation behind the commission of the fouling reactor used in this study. The flowsheet, detail construction and the performance requirements of the reactor is discussed in detail together with the operating procedure, sample preparation and sample collection procedures. The preliminary results during commissioning are also presented followed by the discussion of the final assembly of the fouling reactor.

4.1. Introduction

Previous work done in this laboratory was largely based on deposit samples produced in a batch micro-bomb reactor. Figure 4.1 shows a schematic diagram of the reactor. Deposits were produced in a $\frac{1}{2}$ inch bored-through Swagelok[®] union-tee, connected to a control head via $\frac{1}{4}$ inch tube, which also channels pressurised nitrogen gas into the system. The reactor was heated in a fluidised-sand bath and shaken throughout to induce thermal homogeneity in the sample. The top of the pressure line was cooled by a heat exchanger which condenses vapours and protects the pressure transducer from exposure to high temperature environment. The reactor has successfully produced deposits from a number of crude oil samples over a range of operating conditions, i.e. 250 - 400 °C, at 60 - 80 bar. Characterisation of the deposits has been carried out using techniques such as SEC and UV-F and is reported elsewhere [16].

The existing design of micro-bomb reactor however has some limitations with regards to its operating conditions. In each experiment, the union-tee was loaded with liquid sample and pressurised to the required operating pressure with nitrogen gas. This creates a two phase system inside the reactor and the condition was maintained throughout the experiment. Experiments were carried out at relatively high pressure due to the

volatilisation of sample at low pressure. It has been reported that at 40 bar, around 40% w/w of sample was lost. In order to minimise this problem, most experiments were conducted at 80 bar, which is significantly higher than the operating pressure found in most refineries. The current fouling reactor has been designed with the specific aim of minimising this limitation.

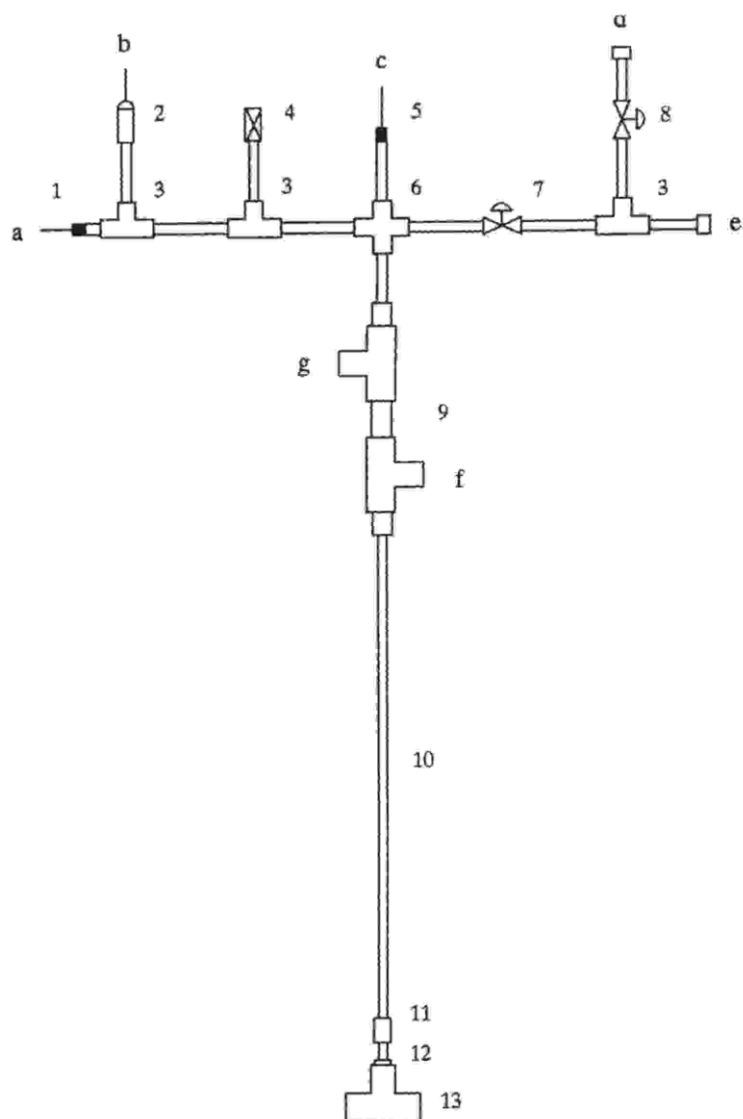


Figure 4.1 A schematic diagram of Micro-bomb reactor

Legend: [1] Thermocouple; [2] Pressure Transducer; [3] Union Tee; [4] Auto-pressure Relief Valve; [5] Thermocouple; [6] Union Cross; [7] Ball Valve; [8] Needle Valve; [9] Heat Exchanger; [10] Vertical Pressure Extender; [11] Union Connector.

4.2. Background and Overview of Fouling Reactor

Figure 4.2 shows the full schematic diagram of the fouling reactor. The performance requirement of the reactor is summarised in Table 4.1. These operating temperature and pressure were chosen based on the industrial-recommended procedures laid out by Bennett *et al* [56] for experimental fouling research. The reactor can be divided into two sections; the ‘hot’ and ‘cold’ sections, as shown in the simplified diagram in Figure 4.3. The ‘cold’ part acts as the supply and control section of the system. This section consists of a sample reservoir (6) and a nitrogen gas supply (1) that acts as pressure feeder into the system. The reservoir is capable of housing 50 cm³ of crude oil at a time and its role is to supply oil sample during start up. Prior to each experiment, samples were de-gassed with nitrogen in the reservoir. The entire process line was also purged with nitrogen to establish an air-free condition along the system before each run.

Table 4.1 Performance requirement of fouling reactor

Working temperature	up to 400 °C
Working pressure	up to 70 bar
Reaction volume	5 ml
Pressure transducers temperature	< 100 °C

The ‘hot’ part of the reactor consists of the main test section (12) where deposits were produced. Crude oil samples were displaced into the test section using nitrogen gas from a gas cylinder and at the same time the system was pressurised to the required pressure. Once the working pressure was reached, the test section was heated up to the set temperature by a heating tape controlled via a heating tape controller. The temperature measurements of the test section were measured using K-type thermocouples. Assembly of the test section is presented in Section 4.3.1.

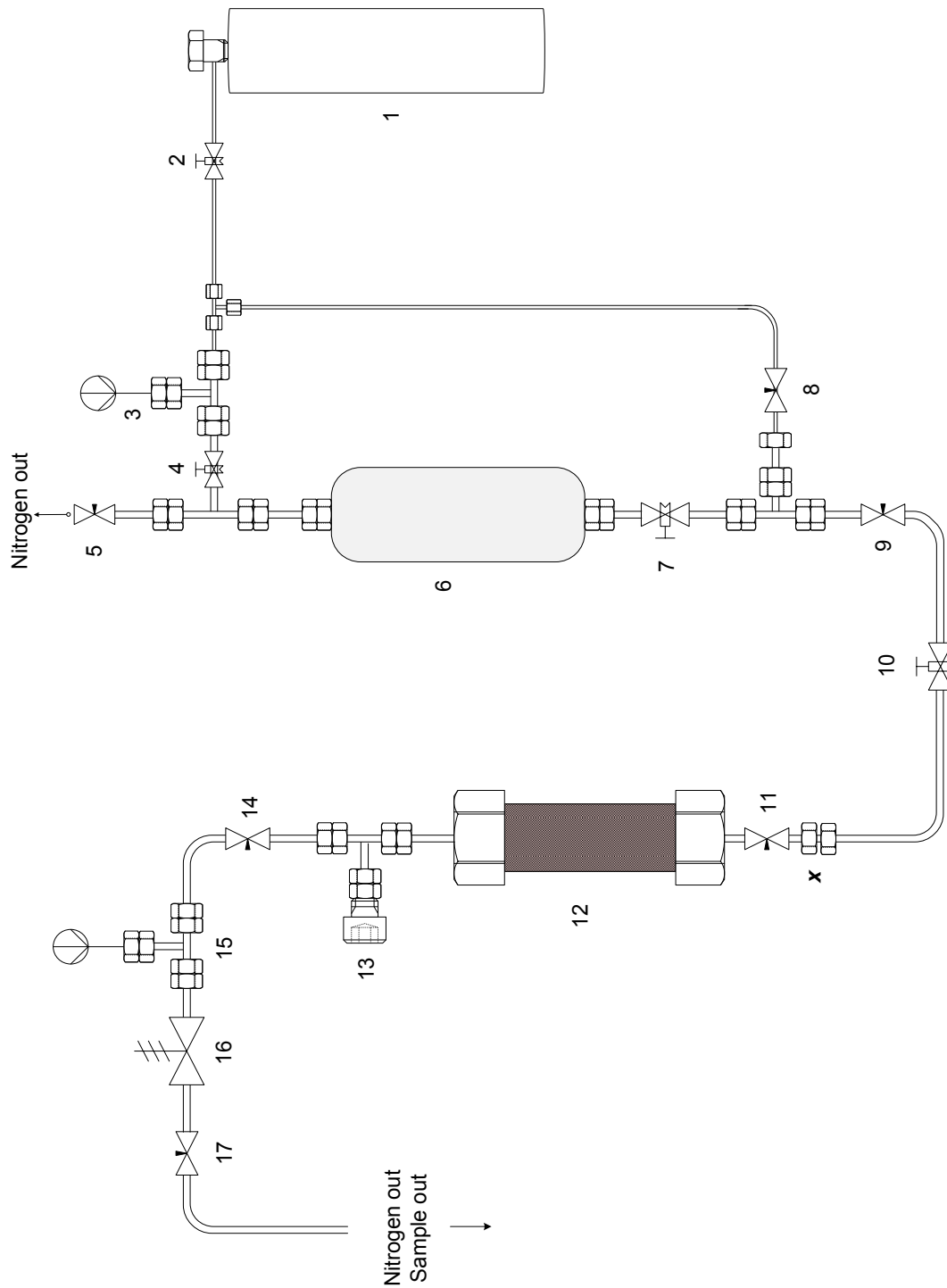


Figure 4.2 Schematic diagram of the fouling reactor final assembly.

Legend: [1] Nitrogen gas cylinder; [2] Ball valve; [3] Pressure transducer; [4] Needle valve; [5] Needle valve; [6] Sample cylinder; [7] Ball valve; [8] Needle valve; [9] Needle valve; [10] Ball valve; [11] Needle valve; [12] Test section; [13] Thermocouple assembly; [14] Needle valve; [15] Pressure transducer; [16] Pressure relief valve; [17] Needle valve.

Each section is equipped with standard industrial pressure transducers (3 and 15) to monitor the pressure along the line. A flush-diaphragm type transducer with cooling element from Swagelok is used in the ‘hot’ section to increase its temperature rating and to protect the transducer from the process fluids. The pressure of the system was displayed by a remote panel digital indicator system with multiple signal inputs. The signals were processed and recorded by a standard desktop computer through a data acquisition board using LabView software.

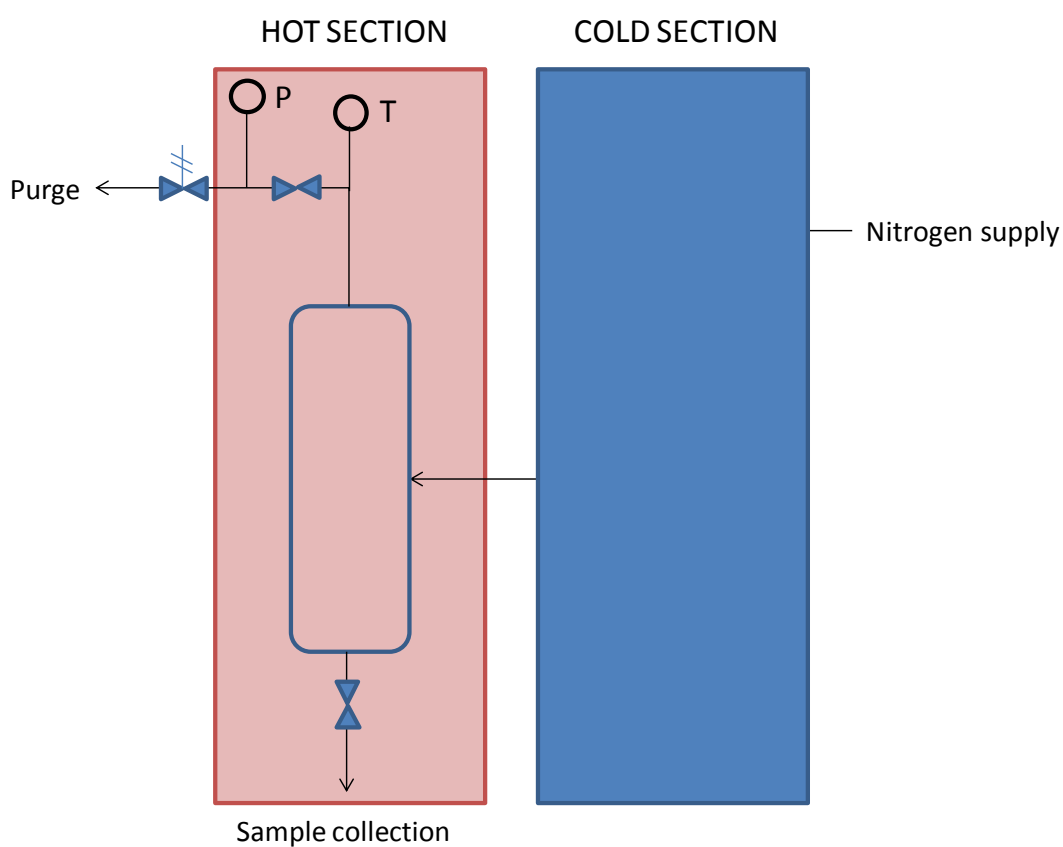


Figure 4.3 Schematic diagram of the fouling reactor distinguishing the cold and hot sections

Once the reactor reached the required temperature, the two sections were separated by closing the needle valve (11). At the end of each experiment, the valve at the top of the test section (14) was closed. These two steps were vital to ensure that the rest of the process fluids did not contaminate the products recovered. The liquid product was collected via the bottom needle valve (11) whereas the deposits formed inside the tube

were collected mechanically using a spatula. At the end of each experiment, the test section and the rest of the process line were washed with chloroform. The collected products are labelled and stored for further analysis. The full operating procedure are presented as follows:

1. Leakage Test and Purging of Reactor

- The pressure transducers 3 & 15 are connected to the display box. Ensure that the pressures reading are displayed correctly i.e. at 0 barg.
- Leakage test is performed on the system. Set the pressure at least at 10 bar higher than the desired operating pressure.
- Once the leakage test is completed, valve 5 is opened and the reactor is purged with Nitrogen gas for 10 minutes. Once purging is done valve 2 and 17 are closed.
- Place the heating tape around the test section and connect it to the heating tape controller. Apply insulation cloth around the test section and make sure the tape and the knots are secured without any loose ends.

2. Filling and Purging of Sample

- Close valves 5, 7 and 8.
- Open the connection at the top of the sample cylinder. Fill the cylinder with sample using a funnel and once done the fitting is reconnected.
- Open the gas cylinder and valve 2 to run a leakage test around the tank, especially at the fitting where reconnection was made.
- Depressurise the tank by slowly opening valve 5. Once done, close valve 4 and 9.
- Open valve 7 followed by valve 2.
- Open the regulator of Nitrogen cylinder slowly until the pressure reads about 5 - 6 barg.
- Release the pressure slowly by opening valve 8 (regulator at this point is only slightly opened).
- Check the flow of Nitrogen at valve 5. When opening valve 8, transducer 3 will reach a point where it gives constant reading. This means bubbling is taking place.

Try to maintain the pressure at 5-6 barg by regulating valve 8 and the regulator.
Let the flow i.e. sample purging run for 20 minutes.

- After 20 minutes, close the regulator until transducer reading drops to 0 barg.
- Close valve 5 immediately.

3. Sample Flow and Heating up of Test Section

- Ensure valves 4, 5, 8 and 17 are closed. Open valve 6 and check that valves 9, 10, 11 and 14 are opened.
- Open the regulator and valve 2 until transducer 3 gives reading at around 10 barg. Close the regulator afterwards.
- Open valve 4 slowly until the readings between the two transducers are balanced.
- Open valve 17 slowly and close immediately when sample is seen to drip out of the tube.
- The pressure of the system is increased to the required test condition and valves 11 and 14 are closed once pressure is reached.
- Turn on the heating tape and set the controller to the desired temperature.
- Record the pressure values on both transducers. Monitor the pressure increase with every increment of test section temperature.
- The pressure and temperature of test section are monitored regularly.

4. Sample Collection

- Once experiment is finished, turn off the heating tape controller and let the test section to cool down to room temperature. After the temperature has reached room temperature, slowly depressurise cold section of the system by opening valve 5. Unwrap the heating tape from the test section.
- Open valve 17 to dispose the rest of the sample and open the connection downstream of valve 14.

- Detach the connection at position 'x'. Open valve 11 to collect the liquid product. Open valve 14 to recover the rest of liquid sample. Record the weight on a measuring balance.
- Disassemble the test section from both ends. Collect the resultant deposit products and weigh on a measuring balance.
- Wash the test section with chloroform. Recover the chloroform insoluble fraction and record the weight.

4.3.Details of the Design and Development of Fouling Reactor

The final design of the reactor is the result of series of trial runs made throughout the commissioning stage. As mentioned earlier, the limitation posed by micro bomb reactor's operability had been the key factor when designing the fouling reactor. The free volume above the sample in micro bomb reactor affects the volatilisation of light compounds hence the requirement of running at high pressure. To minimise or eliminate this free volume, the test section of the fouling reactor has to be entirely filled with sample, allowing the possibility of operating at lower pressure. It is also essential to have a free space along the process line to allow for the thermal expansion of the crude oil sample. This is necessary to make sure that the pressure build up inside the reactor is controlled. Having taken into account these constraints, the system was designed and assembled for preliminary tests. The following sub-sections discuss the details of the design prior to commissioning, which includes description of the reactor assembly, the temperature and pressure controls and measurement, and the safety measures employed in the reactor.

4.3.1. Test Section Assembly

The test section is made of a ½ inch (12.7 mm) outer diameter carbon steel tube with a thickness of 0.048 inch (1.2 mm). Stainless steel tube was initially used but difficulties in producing fouling layers were encountered during commissioning. It was thought that even without the effect of fluid hydrodynamic, deposition of foulant species were retarded with the absence of surface roughness on the heat transfer surfaces. Furthermore, most of the shell and tube heat exchangers are made of carbon steel, hence the test section was later changed to this type of material.

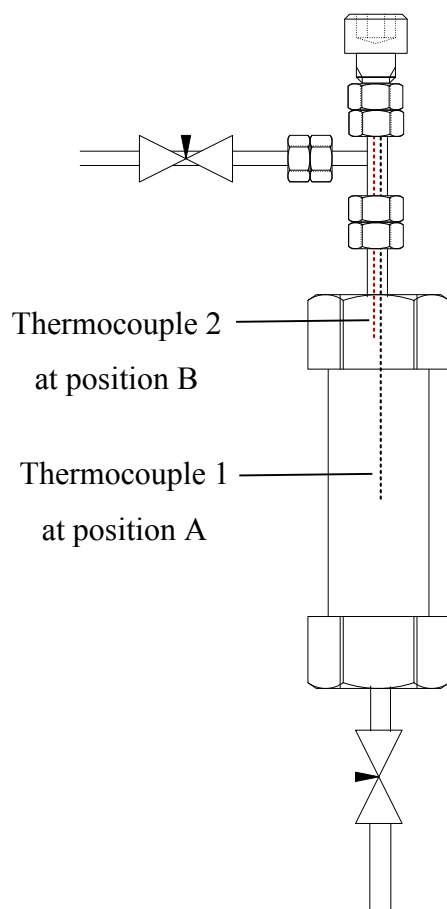


Figure 4.4 Thermocouple set-up during commissioning of reactor. Thermocouple 1 is the control temperature which reads the temperature of the bulk liquid.

The test section can withstand pressure up to 197 bar at temperature of 538 °C. The length of the test section tube is 1000 mm which translates into 8 cm³ of sample. This length can be varied, if needed be, depending on the amount of sample required for analysis. Both ends are connected to ¼ inch (6.35 mm) outer diameter stainless steel tube, and a 1.0 mm K-type thermocouple is positioned inside the test section from the top end. A special assembly with multiple thermocouples was used during the commissioning stage to calibrate the temperature profiles of the test section, as shown in Figure 4.4. Another thermocouple is attached to the outer wall of the test section, which measures the wall temperature of the tube as well as to control the heating of the test section. As discussed in Section 2.4.1, the effect of bulk and surface temperature are quite significant towards fouling with surface temperature being the more important parameter. With this set-up,

the temperature distribution inside the test section may be recorded to investigate whether a significant temperature profile exist along the tube that might affect the distribution of deposits on the tube surface. A shell and tube heat exchanger in refineries typically experienced this temperature profile especially over the length of the tubes where distribution of foulants are not evenly spread along the tube as well as between the tubes themselves.

The temperature is controlled by a standard heating tape controller with an output of 55Vac, 400W and an input of 230Vac, 5A. The heating tape used is a ½” x 4’ standard insulated tape with a power of 313 W from Omega Engineering, UK. The heating tape covers the whole part of the tube including the upper part of the thermocouple assembly and the connecting tube leading to the needle valve attached at the bottom of the test section. It is essential to include this volume since the products collected at the end of each experiment would include fluids contained in this section. The total volume of the heated section is totalled up to 10.5 mL.

4.3.2. Volumetric Thermal Expansion

Upon heating, the crude oil sample inside the test section undergoes volumetric thermal expansion. The extent of expansion depends on the density of the process fluid at temperatures before and after heating. In order to work out the expansion of the samples, the coefficient of thermal expansion, β for each crude oil is computed. β is defined as:

$$\beta = \frac{\left(\rho_o / \rho_l \right)^{-1}}{T_l - T_o} \quad \text{Equation 4.1}$$

Where, ρ_o is density of fluid at temperature T_o

ρ_l is density of fluid at temperature T_l

Three different types of crude oils Crude A, Crude B and Crude D were used as samples in this study. The densities at different temperatures for each oil were obtained from a

crude oil data library provided by PETRONAS. The coefficient of volume expansion for each crude oil was then computed from these data. The amount of volume change was calculated and the result is tabulated in Table 4.2.

Table 4.2 Coefficient of thermal expansion for Crude A, B & D and volume changes at $dT = 285\text{ }^{\circ}\text{C}$

Sample	Coefficient of thermal expansion, β	Percentage of change in volume
Crude A	1.42×10^{-3}	41%
Crude B	1.32×10^{-3}	38%
Crude D	1.97×10^{-3}	57%

It is worth noting that the β value for each crude oil is based on the density values from $15\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$ at atmospheric pressure. If a closed volume were heated, the maximum expansion is observed for Crude D at 57% volume change. This expansion would result in an unacceptable increment of pressure inside the test section. To avoid this pressure increase, the oil is allowed to expand into the process line. The whole configuration encompasses a total volume of 78 cm^3 and with a starting volume sample of 30 cm^3 , there is an ample amount of free volume for the expansion to take place. However, the whole system would still need to be calibrated to investigate the actual increment in pressure. The results of this calibration activity are discussed and presented Section 4.4.1.

4.3.3. Safety Considerations

The apparatus is designed to operate up to temperature of $400\text{ }^{\circ}\text{C}$ and 80 bar pressure. The design pressure and temperature were set at values 10% higher than the operating values. An automatic relief valve is installed in the reactor assembly and set at 70 bar release pressure. In the event of over-pressure, the pressure will be released and any process fluid discharged will be contained. To increase the safety feature, the reactor is enclosed in a steel cabinet placed over a laboratory bench. A 1/8 inch-thick steel plate is

used as the material for the cabinet. An extractor fan with ventilation tube is attached to the top of the cabinet and channelled into a fume cupboard. The vent is used to extract out any gases accumulated inside the cabinet especially during sample collection. This is particularly important when running crude oil samples with significant amount of sulphur where H_2S is produced and requires venting when the reactor is opened after an experiment.

4.4. Commissioning of Fouling Reactor

With all the construction parts assembled and the apparatus placed in the safety cabinet, the fouling reactor was tested for calibration of temperature measurement and controlling system, leakage testing, system pressure calibration, sample feeding control, and products collection procedure. Series of changes were made on the initial design following these trial runs in which the details are presented in the following sections.

Table 4.3 Physical and chemical properties of Paratherm NF.

Typical properties	
Chemical name	Hydrotreated mineral oil
Appearance	Water white liquid
Odour	Odourless
Viscosity @ 60 °F (mm ² /s)	64
Density @ 60 °F (kg/m ³)	886
Flash point (D93), °C	157
Average volume expansion, %100 °C	9.9
Average molecular weight	340
Boiling point, °C	260

In view of safety, it was decided to conduct the first set of trial runs with an inert, non-fouling fluid that requires minimal maintenance and has a relative ease of operation. Paratherm NF is a mineral-oil based heat transfer fluid mainly used in chemical reactors and electrical heaters applications. The chemical and physical properties of the fluid are listed in Table 4.3. It has low viscosity, high heat transfer coefficient and relatively good thermal stability. The fluid is also very soluble in common solvents such as toluene and chloroform which would make it easier for cleaning purposes.

4.4.1. Commissioning Runs

The commissioning activities were divided into three stages. The first stage was conducted with Paratherm NF to evaluate the operating procedure of the system. The second stage involved the evaluation of temperature measurement and control system as well as the assessment of sample thermal expansion upon heating. The third stages of commissioning assessed the repeatability and consistency of runs through analysis on the recoveries of experiment products.

4.4.1.1. Evaluation of Operating Procedure

The first sets of runs were conducted to evaluate the practicality of the start-up/shut-down procedure and the feasibility of sample loading and products collection. These experiments were conducted without applying any heating on the sample. 40 cm³ of Paratherm NF were loaded into the sample reservoir, bubbled through with nitrogen gas and channelled into the test section using the same nitrogen supply. Once the test section was filled, it was depressurised for sample collection and the apparatus was then disassembled for cleaning.

It was found that during degassing, the flow of nitrogen was difficult to control via the cylinder pressure regulator. The ball valve (4) initially attached to the nitrogen feeding line was then replaced with a needle valve to ensure a better control of flow without any problem of over-pressure and loss of sample. It was also discovered that a ball valve (2) is required to isolate the nitrogen cylinder from the rest of the set-up to make sure that the pressure regulator is giving the correct reading of the reactor.

The amount of liquid sample collected at the end of each run was weighed. The weights were found to vary significantly in between the runs. It was also noticed that during sample loading the pressure readings of the two transducers showed different values at times. It was thought that the check valve at the top of the test section might have caused these irregularities to occur. When displacing and pressurising the reactor, sample was loaded at increasing rate of pressure until it reached a point where the end of the pressure line was filled. A check valve was in placed to prevent the sample to flow back into the test section. The valve caused the pressure of the ‘cold’ section to be slightly higher than the ‘hot’ part as more pressure was introduced from the gas cylinder. This might also have caused the inconsistencies on the amount of liquid products recovered between similar runs. The check valve was later replaced with a needle valve (14) that would allow free mixing and movement of samples and nitrogen gas, hence provides better sample loading. The instalment of this valve was also to ensure the pressure transducer was reading the pressure in the correct section of the reactor.

4.4.1.2. Evaluation of Temperature Control and Measurement

The temperature measurement and control system consists of multiple temperature probes, a heating tape controller and digital indicators for the purposes of monitoring and controlling the heating of the test section. The pressure readings of both sections are indicated via a multiple-display box which is connected to the pressure transducers. Three sets of test runs were performed, with two sets using Paratherm NF and one set with a crude oil sample. The first set was conducted to investigate the behaviour of the system pressure towards a gradual increase of temperature in the test section. The second set of runs was also to check the increment in pressure with respect to temperature, but the pressure was further increased with nitrogen gas to the required reaction condition. The final runs were conducted to study the thermal expansion of crude oil samples, in particular samples that were to be used in this study.

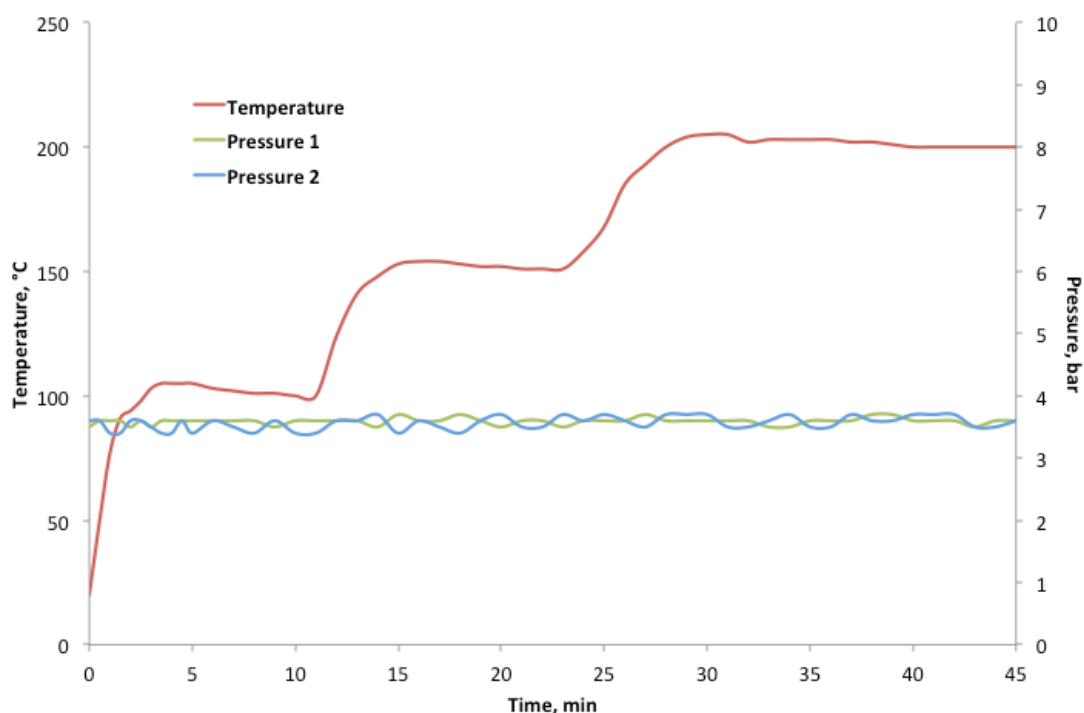


Figure 4.5 The plot of temperature and pressure profiles with 3 different temperature set points (100°C, 150°C and 200°C)

As in the previous experiments, 40 cm³ of sample was used. The temperature and pressure evolutions of the first set of experiment are shown in Figure 4.5. The set-point temperature was initially set at 100 °C. As the Paratherm NF is loaded into the test section, the initial readings for both pressure transducers are at 3.5 bar. Upon heating, the temperature of the test section increased gradually to 100 °C within 3 minutes. The pressure inside the reactor however remained at around 3.5 bar as displayed by both transducers. The temperature was then increased to 150 °C, and again there were no significant increase in the pressure readings. The temperature was finally increased to 200 °C with no increment in pressure recorded inside the reactor. This is largely due to the fact that there is a relatively large free volume overhead especially inside the sample reservoir which allowed the Paratherm NF to expand. Even though expansion of Paratherm NF took place inside the test section, this extra allowance of volume compensated for this volume increment.

The second set of test-run was conducted to investigate the effect of temperature increase towards pressure, but this time the pressure inside the reactor were further increased with

nitrogen. The plot of this exercise is shown in Figure 4.6. The temperature was set at 250°C with starting pressure of 3.7 and 3.4 bars. Once the temperature had reached the set-point, it was observed that the pressure inside the reactor remained unchanged. The pressure was then increased to 10 bar and later to 20 bar. The increment of pressure was recorded in accordance to the set value with no apparent increase through sample expansion was observed. This phenomenon may be explained as in the previous experiment; the extra volume overhead allows the expansion to occur inside the reactor.

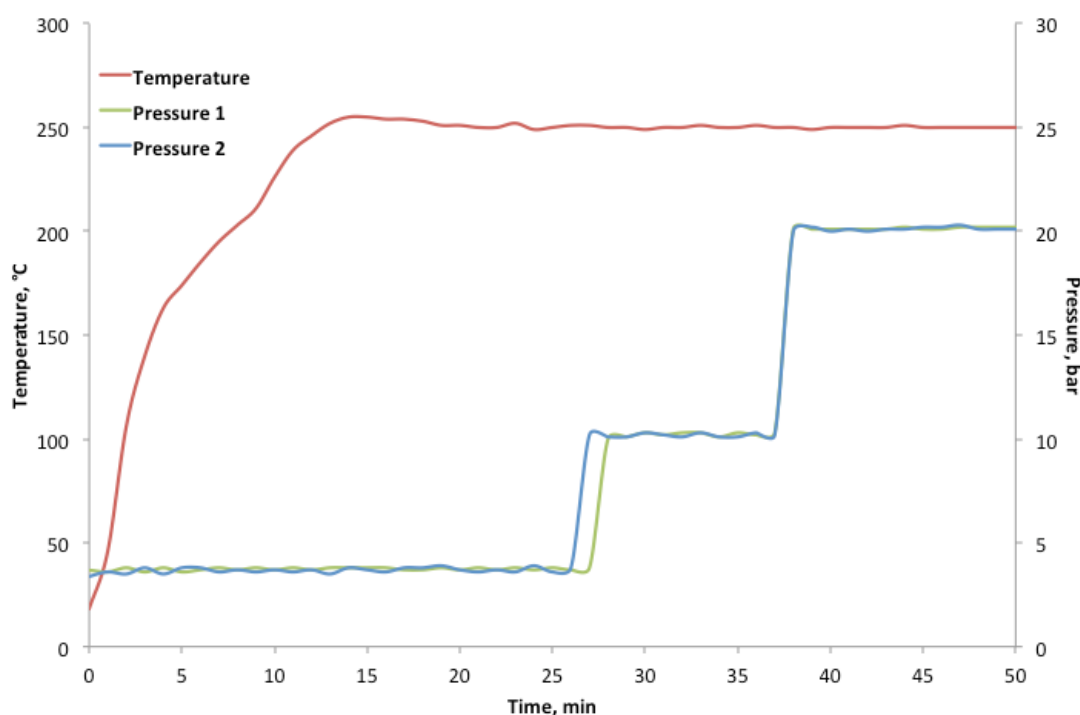


Figure 4.6 The plot of temperature and pressure profiles with staged increment in pressure of 10 and 20 bar.

After the initial test runs with Paratherm NF were performed successfully, the next stage was to run the reactor using a crude oil sample. Even though runs with Paratherm NF suggested that the pressure increment inside the reactor upon heating is negligible, a test run with crude oil is necessary as the thermal expansion coefficient is higher compared to that of Paratherm NF. The β value for Paratherm NF is 9.9 % per 100 °C whereas the crude oil samples used for this study have a range of β values between 15 to 25 % per 100°C.

The experiment was conducted at 250 °C and reactor pressure of 20 bar. Crude A with thermal expansion coefficient value of 16% per 100 °C was used as sample. Even though this value is higher than that of Paratherm NF, it was presumed that the thermal expansion would not affect the increment of pressure inside the reactor. The experiment was run for 275 minutes and the pressure and temperature profiling are shown in Figure 4.7.

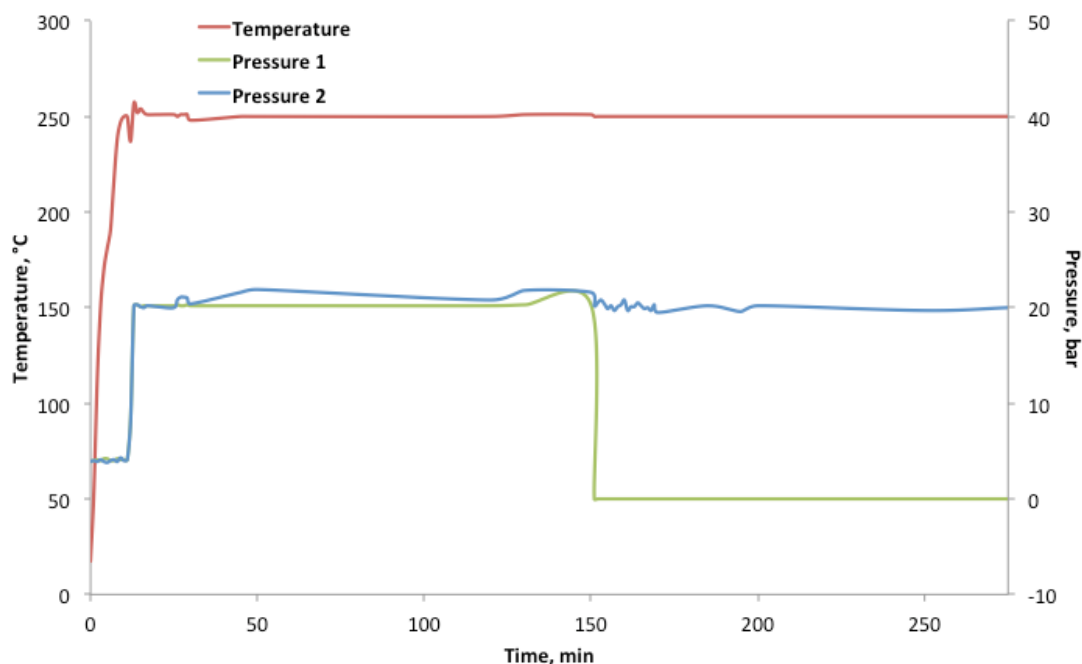


Figure 4.7 The pressure and temperature profiles for run of Crude A at 250°C and 20 bar.

The plot shows the overall profile of the operating conditions for this run. The reactor was heated up to 250 °C without any significant increase in pressure, as shown in the earlier runs with Paratherm NF. The pressure was then increased to 20 bar after 15 minutes in which both transducers responded accordingly. After 25 minutes of operation, the needle valve at the bottom of the test section was closed to separate the cold and hot section apart. The reading of pressure transducer 2, which reads the pressure in the test section, increased slightly at around 1 bar. This is probably due to the formation of gaseous products e.g. hydrogen sulphide and volatilisation of lighter components in the sample. After 150 minutes, the cold section was depressurised to atmospheric pressure.

Pressure inside the test section responded slightly but it stayed at around 20 bar until the reactor is turned off.

This series of test runs again showed that the pressure inside the reactor did not increase with the increase in temperature. The tests also demonstrated the stability of the test section temperature once it had reached the set-point value. This shows a good control of temperature was achieved during experiments. It was also noted that no deposits were formed after these trial runs with crude oil. Further runs were later carried out in which details are discussed in the succeeding chapters.

Along with the temperature-pressure calibration, the distribution of temperature in the test section was also investigated. The temperature gradient was expected to occur along the test section especially at both ends of the tube due to the different wall thickness. In order to perform this measurement, a multiple thermocouple set-up was employed, as shown in Figure 4.4, and the temperature readings at both positions were recorded. Figure 4.8 and Figure 4.9 show the plots of the temperature values at different temperature set-points, ranging from 300 °C to 400 °C for 7-hour and 24-hour reaction time. It was observed that apart from a small amount of deposits formed at 400 °C with 7 hour running period, there were no deposits produced in each of the run. The temperature at point 'B' was always lower than the set-point temperature i.e. bulk temperature at the middle of the test section. This temperature reacted accordingly towards changes in the set-point and the difference between these two values was almost constant throughout the experiment for both reaction periods. The difference in temperature may be explained by the fact that both ends are connected to the process line via tube reducers which are of thicker built compared to the test section tube. It was later discovered that the difference in temperature did affect the distribution of deposits formed at the wall to certain degree, but the most fouled part was not always happened at the hottest section of the tube.

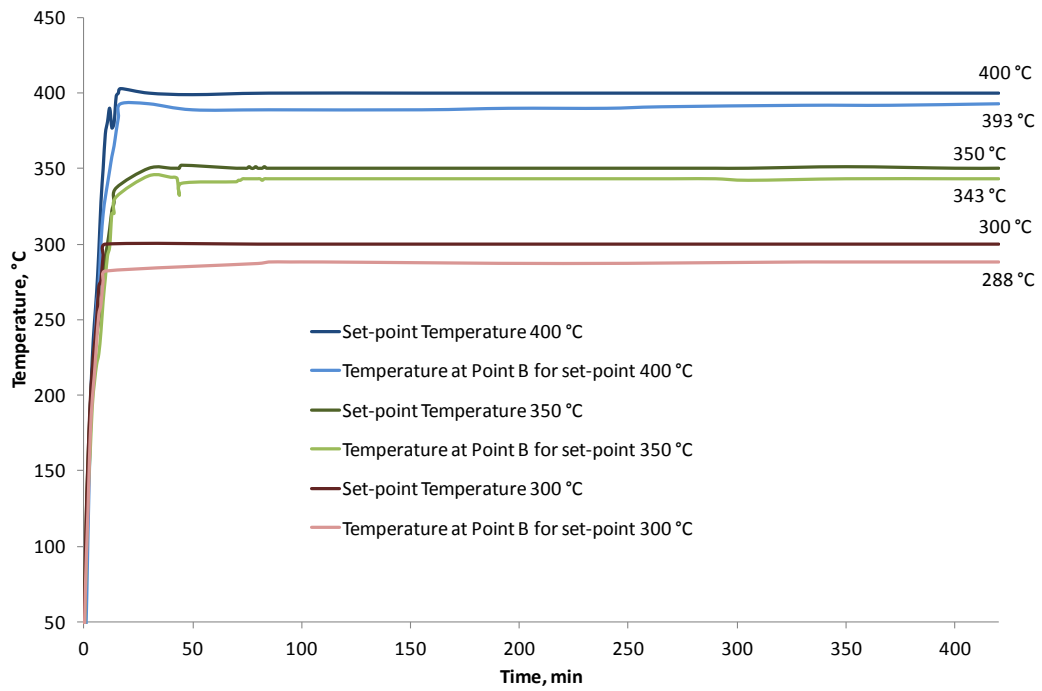


Figure 4.8 Plots to show the temperature profile of the test section at different set-point temperature values for experimental period of 7-hour.

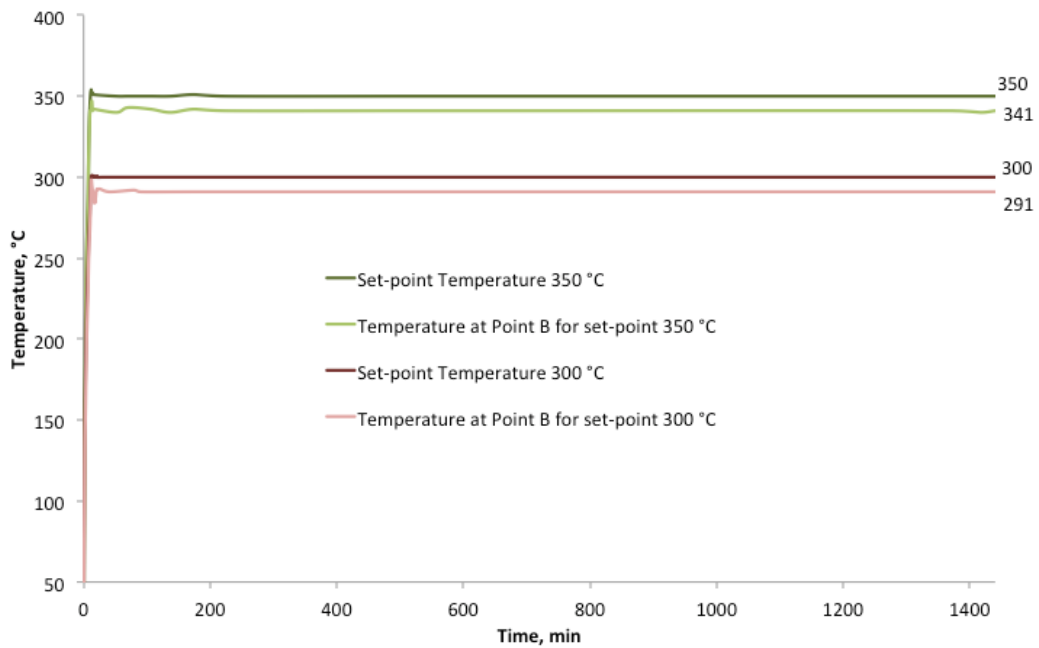


Figure 4.9 Plots to show the temperature profile of the test section at different set-point temperature values for experimental period of 24-hour.

4.4.1.3. Repeatability Tests

With temperature and pressure calibrated and after the required changes were made in the configuration of the reactor, the next step was to work out the optimum operating condition for the system in producing deposit samples. This optimum condition was to be tailored to the 3 crude oil samples that were going to be used in this particular study. Typical operating parameters of heat exchangers in the industrial pre-heat train range from 200 °C to 330 °C and pressures about 150-600 psi (10-40 bar). The worst fouling however occurs at the high temperature end of heat exchanger, hence recommended operating temperatures for a laboratory scale fouling reactor often quoted in the range of 260-320 °C wall temperatures and bulk temperatures of 200-260 °C. The suggested pressure is relatively high, at around 300-1000 psi (20-70 bar) in order to prevent boiling. On this basis, the first set of test runs were conducted at this range of parameters with the aim of generating consistent results.

The first reactor configuration was put up for tests using Crude A as sample. The main aim for these test runs was to achieve repeatable results in between similar runs in terms of the amount of deposits and liquid products recovered. This repeatability test consisted of variation in operating temperature, pressure and reaction running time based on the results of earlier tests, as well as the operating conditions of the micro-bomb reactor. The test was conducted to achieve the final design at which consistent amount of deposits and liquid products were produced at similar operating condition. In the test runs conducted for temperature and pressure calibration presented earlier, no significant amount of foulants were deposited at 300 °C and 350 °C bulk temperature. It was also noticed that at 300 °C, in terms of formation of deposits, similar results were obtained at 7-hour and 48-hour reaction times in which no deposits produced in either of the run. It was however observed that some soot-like particles were deposited at the wall of the test section after washing with chloroform. Based on this observation, it was decided to change the test section from stainless steel to carbon steel and to conduct a repeatability test at higher bulk temperature i.e. 400 °C at 7-hour reaction time. Table 4.4 summarises the results of the first repeatability tests (Run #14 is a blank control run). At the end of each run, the weights of liquid product and the carbonaceous chloroform-insoluble particles were recorded.

Table 4.4 Summary of the first repeatability test with Crude A. Sample was heated at 400 °C for 7 hour reaction period at initial pressure of 15 bar.

Run #	Bulk Temp.	Pressure Final	Amount of Liquid Product	Amount of Chloroform Insoluble
14	22 °C	15.0 bar	10.54 g	0 g
15	400 °C	24.0 bar	5.79 g	0.116 g
16	400 °C	24.2 bar	6.41 g	0.147 g
17	400 °C	23.5 bar	4.54 g	0.114 g

The results showed good consistencies amongst the runs on the amount of chloroform-insoluble recovered. This fraction distributed rather evenly along the wall (the wall temperature is recorded at 5-8 °C higher than the bulk) and it probably acts as precursor for the formation of deposits. The fact that more consistent results were obtained after the change-out from stainless steel to carbon steel tube suggest that roughness of the heat transfer surfaces may contribute towards deposition process. Several publications has discussed about this influence especially when the hydrodynamic effects such as fluid flow velocity and shear stress are taken into account [165-166]. Surface roughness can give significant impact on the mass and heat transfer of materials particularly in a turbulent flow condition. The transfer rate can be either increased or decreased depending on the nature of the roughness i.e. the size, shape distribution and orientation of the roughness element [167]. It has been reported that as the fouling layer formed, the initial fouling rate can reach negative values due to the effect of limited mass transfer rate towards the surface. As the dynamic of surface roughness changes due to formation of more layers over time, the fouling rate may increase causing thicker layer of deposits. The effect of surface roughness however was not taken into account in this study, nevertheless it contributed towards the formation of fouling layers on the test section.

On the other hand, the amount of liquid products recovered was rather inconsistent, ranging from 4.5 to 6.4 g (43 - 61% of initial amount) with the rest was most likely gas. Similar issues were discovered during commissioning stage in which the replacement of

the check valve to a needle valve was made. The increment of pressure at the end of each experiment was found to be consistent, which suggest that the gaseous products formed were at similar level. It was thought that this discrepancy might be the results of nitrogen gas being trapped inside the test section during sample loading, especially at the thermocouples T-junction as shown in Figure 4.10 (a). This entrapped gas probably prevented the sample to fill up the top part of the test section which would further cause inconsistency on the amount of sample being heated. This might have also contributed to the fact that the recovered amount was much less than the total volume of the test section, with no apparent loss of products discovered anywhere else. The configuration was later modified to the configuration presented in Figure 4.10 (b) and is positioned at an incline in order to ensure that the whole test section is fully loaded with sample.

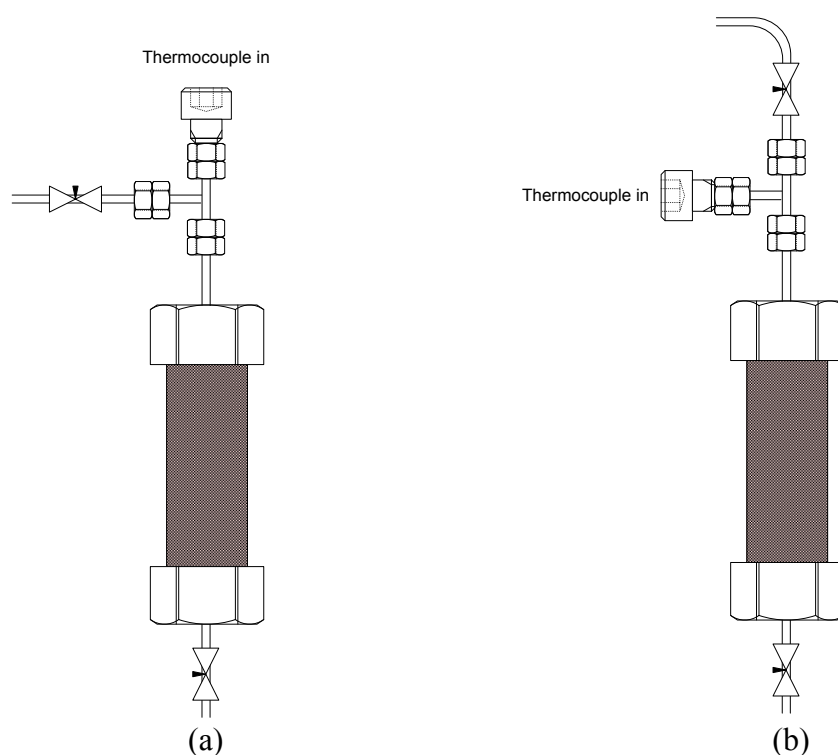


Figure 4.10 (a) Initial configuration of the thermocouple fitting during commissioning stage (b) Modified configuration after commissioning

Table 4.5 Summary of the second repeatability test with Crude A. Sample was heated at 400 °C for 4 hour reaction period at initial pressure of 15 bar.

Run #	Pressure Final	Amount of Liquid Product	Amount of Chloroform Insoluble
19	41.0 bar	8.21 g	0.161 g
20	42.9 bar	8.22 g	0.163 g
21	50.6 bar	7.83 g	0.201 g

The latest configuration was later checked for consistency at 400 °C bulk temperature and cold pressure of 15 bar. Similar analysis as in the first repeatability test was performed; the liquid product and chloroform-insoluble fraction were recovered and the amounts were recorded. The summary of these runs and the results are presented in Table 4.5.

Compared to the first test, this set of runs gave better consistencies in most of the examined parameters. Repeatable results were achieved especially on the amount of liquid products recovered and the chloroform-insoluble fraction. Bigger increments in pressure were also recorded compared to the first test which suggests more gaseous products were produced from relatively larger volumes of sample. Run 21 however gave a higher pressure increase than the other two runs. It was noticed that the wall temperature for this particular run was relatively higher, measured at 440 °C compared to around 410 - 415°C in the other two. This is thought to be caused by two reasons:

- i) the heating tape used in Run 21 is a heavy-insulated type which has a coat of insulation thread. This coating gives an extra layer between the tape and the tube wall hence more power is required to provide the heat to the bulk liquid. This would in turn give higher value of temperature at the wall and consequently higher increment in pressure;
- ii) the wall temperature was measured using a needle thermocouple wrapped inside the heating tape. This was thought to be not a good practice since the

thermocouple might be reading the temperature of the heating tape rather than the temperature of the wall.

This configuration seemed to give good consistencies in terms of the amount of products recovered but the control and measurement of the reaction temperature had to be improved. A ring thermocouple was later installed to measure the wall temperature and connected to the heating tape controller. This would give a more accurate representation of the wall temperature and a better control for the heating of the test section.

As in the previous configurations, the modified reactor was tested for consistency. In this set of test runs, the temperature was controlled at the wall rather than the bulk. The bulk temperature was recorded to assess the temperature gradient from the wall to the bulk liquid. The wall temperature was set at 340 °C and reaction initial pressure of 10 bar. Since there were no significant amounts of deposits formed at shorter reaction period, the duration was increased to 24 hour. Table 4.6 summarises the results of the third repeatability test.

Table 4.6 Summary of the third repeatability test. Crude A sample was heated at 340 °C for 24 hour reaction period.

Run #	Pressure Final	Amount of Liquid Product	Amount of Chloroform Insoluble
31	13.2 bar	9.31 g	0.055 g
32	12.8 bar	9.56 g	0.049 g
34	13.5 bar	9.57 g	0.047 g

The three identical runs showed good agreement between them in terms of the products distribution. The heating of test section was found to be consistent and a better control of temperature was achieved. Figure 4.11 shows the temperature profile of the bulk and the tube wall. The bulk liquid temperature showed a very good consistency between the runs with a steady temperature difference around 5 – 7 °C lower than at the wall. The increment in pressure after each experiment was also found to be consistent, albeit less

increment compared to the runs in previous consistency tests. This indicated less gaseous products were formed during the experiment largely due to the fact that a lower reaction temperature was utilised in this set of runs.

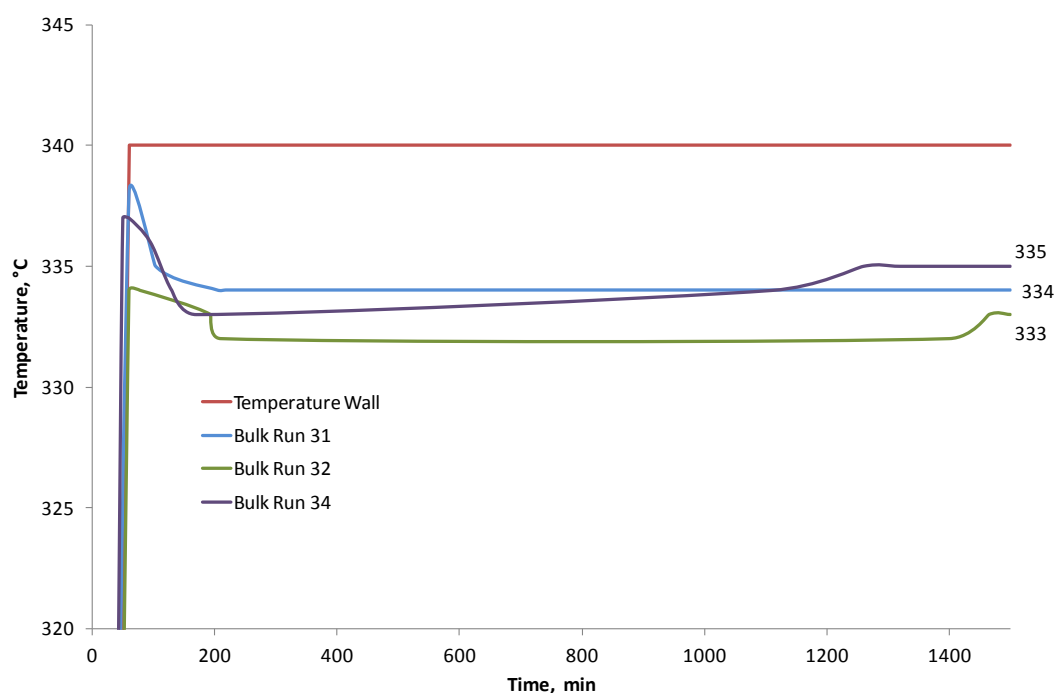


Figure 4.11 Temperature profile of the bulk and wall temperatures of three identical runs at 340 °C wall temperature.

4.5. Development of Standard Experiment Run

Once the commission activities were completed, the next set of test was to conduct experiments to develop a standard operating parameter of the system. The main aim was to produce consistent amount of deposits between repeats of identical runs. The selection of operating condition was made based on the available data gathered during commissioning. Experiments conducted at 400 °C for duration of 7 hours produced a small quantity of deposits on the test section wall. This temperature however is too high compared to the typical heat exchanger operating temperatures in refineries. On the other hand, experiments conducted at 300 °C and 350 °C for duration of 24 hour did not yield any deposit product. It was decided to run several experiments at 350 °C at a longer

period i.e. 48 hour to assess the formation of deposits on the test section wall surfaces. Table 4.7 shows the summary of the results.

The amount of deposits and liquids formed were quite consistent in between the repeats with low standard deviations. The mass balance closures in each run were calculated at 91% to 93%, recording sample loss of 7% to 9%. These values are much less compared to those recorded in the micro bomb reactor. This result indicates that the target of reducing sample loss through volatilisation in the new system had been achieved. This also marks the success in developing a new system in producing deposit samples for this particular system. The operating parameters of the system were then finalised at 350 °C wall temperature, 10 bar initial pressure and experiment duration of 48 hours.

Table 4.7 Summary of the run of Crude A conducted at 350 °C wall temperature at 10 bar operating pressure for reaction period of 48 hour.

Run #	Pressure Final	Amount of Liquid Product	Amount of Deposits	Amount of Chloroform Insolubles
35	18.2 bar	9.52 g	0.173 g	0.067 g
36	17.8 bar	9.32 g	0.182 g	0.097 g
37	19.5 bar	9.43 g	0.196 g	0.083 g

4.6. Summary & Conclusions

After three stages of commissioning activities, the final configuration of the fouling reactor was finally realised. The initial configuration was deemed to be not practical for the research purposes due to its failure in producing repeatable results, largely caused by the poor control of reaction temperature and the inconsistent amount of sample loaded into the test section. A better control of temperature was acquired through the installation of a ring thermocouple attached to the outer wall of the test section which provides better stability and accuracy in the temperature measurement. The wall temperature was found

to be at 5 – 7 °C higher than the bulk temperature. A temperature profile along the test section was also calibrated in which the top and bottom parts are found to be at 7 – 12 °C lower than the middle section temperature. The current configuration was deemed to be able to produce repeatable results. It was also concluded that the reactor set-up was able to produce deposits on consistent basis at 350 °C wall temperature and 10 bar operating pressure for 48 hours running period.

5. Evaluation and Development of Method for Trace Element Analysis

In this chapter, the evaluation and development of trace element analysis methodology are presented and discussed. Two ICP-based techniques i.e. ICP-OES and ICP-MS were assessed with two sample digestion procedures of closed and open digestions. Each analysis was evaluated with two standard reference materials and used as indicators of the feasibility of the techniques as well as the sample preparation procedures. Four deposit samples from different units of a refinery were also analysed to measure the possibility and of the digestion procedures in extracting the metals out of the organic components.

5.1. Introduction & Samples

ICP is a very powerful method in quantifying trace element concentrations of a material. The two most common techniques are ICP-MS and ICP-OES, which could detect trace elements in a sample up to parts per billion levels. These two methods require sample pre-treatment prior to analysis which usually involves sample digestion in organic solvents or acid solutions. The pre-treatment is necessary to destroy the organic constituents and solid particles of the sample to ensure safe operations of the ICP. Presence of solids would increase the probability of damaging the nebuliser instrumentation. There are various methods available in the literature for the determination of metals in crude oils and residual fuels but these are mainly tailored for Atomic Absorption Spectroscopy (AAS). Along with these standard methods, a number of studies had been performed within this research group on trace element determination, mainly focusing on coal and biomass samples [142-145]. Two sample preparation techniques, open and closed digestion, had been proved viable in determining trace element contents. Details of the digestion procedures have been presented in Chapter 3.

The evaluation of these techniques towards their abilities in producing reliable results for petroleum-based samples was duly performed in this study. The results were compared in terms of their efficiencies in extracting trace elements and also consistencies in producing repeatable results. The concentration of trace metals, especially Vanadium in this study, may be accurately determined by the techniques based on the readings recorded for the known element concentrations of standard reference materials from National Institute for Standards and Technology (NIST).

In these preliminary studies, two types of samples were used. The first set of samples consists of two standard reference materials from NIST. The first standard is a certified sub-bituminous coal, SRM 1635 which has certified values for 14 elements and the other standard is SRM 1634c, a fuel oil reference material which consists of 5 certified elements. The certified values of each element are measured via two or more independent methods such as AAS and ICP-OES. The second set of samples consists of heat exchangers foulant deposits obtained from four different locations of an oil refinery. Table 5.1 shows the origins of each sample and the operating conditions of the respective heat exchangers. These deposits provided the best possible ground for the evaluation study as most of the subsequent analyses ultimately involved deposit samples produced from the laboratory-scale fouling reactor.

Table 5.1 Summary of deposit samples from refineries used in the preliminary trace element analysis. The location and origin of deposits, the operating temperatures and types of process fluids are presented.

Sample	Unit type	Sample location	Temperature	Feed processed
PHTD	Pre-heat train	Tube side	$T_{in} = 158^{\circ}\text{C}$ $T_{out} = 166^{\circ}\text{C}$	Desalted crude oil
KPHTD	Kerosene pre-heat train	Tube side	$T_{out} = 240\text{-}260^{\circ}\text{C}$	Kerosene
DA	Desulphuriser train	Shell side	Shell side = 288°C Tube side = 315°C	Vacuum gas oil
DB	Residue processing	Tube side	Shell side = up to 370°C	Crude oil vacuum residue

5.2. Results of XRF Analysis

XRF analysis was performed prior to the full qualitative analysis with ICP techniques. The analysis was conducted as a screening analysis to identify the elements present in the deposit samples. These elements were classified according to their concentration levels and later selected for ICP analyses based on this classification. Briefly, samples that were lumped together were carefully broken up to evenly distributed pieces using a PTFE rod to minimise contamination. These samples were then placed in the XRF cell and distributed evenly to fully cover the thin polypropylene film at the bottom. Samples were lightly pressed to make it as compact as possible and measured to be at 5 mm thickness. Summary of the XRF analyses can be found in Table 5.2.

Table 5.2 Concentrations of elements in refinery deposit samples quantified by XRF spectrometer.

Element	PHT		KPHT		DA		DB	
	Conc. (vol %)	Stat. error	Conc. (vol %)	Stat. error	Conc. (vol %)	Stat. error	Conc. (vol %)	Stat. error
Al	0.49	0.72%	1.19	0.47%	0.99	0.04%	7.30	0.05%
As	0.51	0.20%	0.70	0.16%	1.21	0.06%	0.71	0.06%
Ba	0.84	0.39%	0.51	0.48%	0.19	0.57%	6.09	0.20%
Br	0.14	0.18%	0.53	0.10%	0.32	0.23%	0.15	0.15%
Ca	13.01	0.06%	5.56	0.10%	0.78	0.14%	5.88	0.23%
Cl	1.70	0.30%	3.73	0.20%	4.34	0.15%	0.45	0.08%
Co	0.52	0.14%	0.47	0.14%	0.07	0.66%	0.16	0.13%
Cr	0.08	0.50%	0.15	0.37%	1.93	0.14%	0.11	0.08%
Er	0.30	0.15%	0.28	0.16%	0.41	0.32%	0.26	0.30%
Fe	28.31	0.04%	30.97	0.04%	38.85	0.57%	30.28	0.04%
K	0.13	0.65%	0.45	0.36%	0.21	0.37%	0.28	0.08%
Mg	0.67	0.58%	2.89	0.29%	0.32	0.21%	0.80	0.56%
Mn	0.31	0.25%	0.34	0.24%	0.53	0.08%	0.32	0.19%
Mo	0.27	0.10%	1.86	0.04%	0.53	0.25%	1.69	0.16%
Na	9.65	0.29%	4.48	0.42%	4.72	0.23%	0.52	1.13%
Ni	0.21	0.53%	0.45	0.35%	0.55	0.13%	3.86	0.09%
P	1.18	0.36%	0.31	0.70%	0.76	1.11%	1.89	0.60%
Pb	0.82	0.13%	1.10	0.11%	0.90	0.12%	0.56	0.26%
Pd	0.06	1.15%	0.08	1.07%	0.15	0.11%	0.08	0.46%
Re	0.41	0.07%	0.37	0.05%	0.92	0.64%	0.56	0.22%
S	36.69	0.05%	20.29	0.07%	38.40	0.93%	27.11	0.39%
Si	0.87	0.49%	18.95	0.11%	2.11	0.89%	4.52	0.12%
Sr	0.52	0.08%	0.25	0.12%	0.31	0.63%	0.47	0.21%
Ti	0.23	0.41%	0.50	0.27%	0.09	0.75%	0.25	0.18%
V	0.24	0.34%	0.33	0.28%	0.09	0.23%	4.41	0.22%
Zn	1.71	0.06%	3.10	0.05%	n.d	n.d	1.08	1.07%
Zr	0.13	0.12%	0.13	0.14%	0.28	0.11%	0.17	0.12%

The method used here was a semi-quantitative as full qualitative analysis was not possible due to the unavailability of calibration standard. The elements present in each sample were identified and later categorised into major, minor or trace concentration levels. The result showed that each sample contained high concentrations of Iron and Sulphur. Iron is most likely originated from the corrosion products of the heat exchanger materials and was later deposited on the heat transfer surfaces. The origin of Sulphur is thought to be from the process fluids itself, mainly came from the processed crude oils that contain high percentage of sulphur compounds. It was noted that there were relatively high percentages of Calcium and Sodium in deposit PHTD and Calcium, Chlorine, Sodium and Silicon in deposit KPHTD. These elements might be originated from the entrained water (brine) collected during production process or during transport. Sediments and sands trapped in the crude oils were the most likely sources of Silicon. These two deposits are particularly concentrated with these elements due to the location of the heat exchangers themselves. The two exchangers are located in the pre-heat train, which principally is the first processing unit encountered by the crude oil in a refinery. This particular oil refinery might have employed a desalter unit in its train, however some inorganic materials might have still been entrapped in the treated fluids resulting in their deposition on the heat exchangers wall.

On the other hand, deposits DA and DB were mostly concentrated by Iron and Sulphur compounds. DB in particular contained relatively high concentrations of Aluminium, Barium, Nickel and Vanadium metals compared to the other deposits. This is particularly interesting especially in the case of Nickel and Vanadium. As discussed in Chapter 2, these two metals have been found to be mainly concentrated in the heavier part of crude oil. As DB comes from a heat exchanger processing a vacuum residue stream, it is no surprise that these metals were found at higher concentrations than in the other deposits.

Based on these results, the elements detected were grouped into the three categories according to their concentration levels, as shown in Table 5.3. Elements that were detected above 10% were classified as major elements, from 2% to 10% were minor and those below 2% were considered as trace elements. Nickel and Vanadium were detected at trace values in most of the deposit samples except in DB. The XRF spectrometer is rather useful in providing the background information of the elements present in the deposit samples. In view of this, the full quantitative analysis was later conducted using ICP-OES and ICP-MS.

Table 5.3 Classification of elements detected by XRF Spectrometer.

Sample	Major Elements	Minor Elements	Trace Elements
PHTD	Fe, Ca, S	Na	Al, As, Ba, Br, Cl, Co, Cr, Er, K, Mg, Mn, Mo, Ni, P, Pb, Pd, Re, Si, Sr, Ti, V, Zn, Zr
KPHTD	Fe, S, Si	Ca, Cl, Mg, Na, Zn	Al, As, Ba, Br, Co, Cr, Er, K, Mn, Mo, Ni, P, Pb, Pd, Re, Sr, Ti, V, Zr
DA	Fe, S	Cl, Na, Si	Al, As, Ba, Br, Ca, Co, Cr, Er, K, Mg, Mn, Mo, Ni, P, Pb, Pd, Re, Sr, Ti, V, Zr
DB	Fe, S	Al, Ba, Ca, Ni, Si, V	As, Br, Co, Cr, Er, K, Mg, Mn, Mo, P, Pb, Pd, Re, Sr, Ti, Zn, Zr

5.3. ICP-OES Analysis

Having established the elements classification through XRF spectrometer, full quantitative analyses were performed using the ICP instruments. Detailed descriptions on the background instrumentations of both techniques are discussed in Chapter 3. ICP-OES analysis was conducted on the reference materials and the four deposit samples via two sample digestion procedures, the wet-ashing (open) and microwave (closed) digestions. These procedures were analysed for their extraction efficiencies and their consistencies in producing repeatable results between the replicates. The results of ICP-OES were later compared to the ones of ICP-MS.

5.3.1. Open and Closed Digestions of Standard Reference Materials

The standard reference materials (SRM) were subjected to both digestions methods in which the details can be found in section 3.2.3. 20 mg of sample of three replicates were prepared for each technique with dilution factor (DF) of 500. Previous works in the laboratory had found that no significant differences were discovered on the recovery of the elements for different sample sizes. These are applicable to both ICP techniques as long as the total dissolved solid (for ICP-MS) and the dilution factors of the final solutions remained constant [142]. To ascertain reproducibility, analysis of each sample was performed twice. The results of the ICP-OES of the two standards are reported in Table 5.4.

Table 5.4 A comparison of ICP-OES measured values of reference coal 1635 and fuel oil 1634c with certified values. All values are in ppm (mg.kg^{-1}).

	SRM 1635			SRM 1634c		
	Open Digestion	Closed Digestion	<i>Certified Values</i>	Open Digestion	Closed Digestion	<i>Certified Values</i>
As	n.d.	n.d.	0.42 ± 0.15	n.d.	n.d.	0.14 ± 0.001
Cd	n.d.	n.d.	0.03 ± 0.01	n.d.	n.d.	-
Cr	3.82 ± 0.46	2.10 ± 0.78	2.5 ± 0.3	1.56 ± 0.50	n.d.	-
Cu	4.1 ± 0.1	2.05 ± 0.7	3.6 ± 0.3	-	-	-
Fe	2511 ± 70	2427 ± 102	2390 ± 50	-	-	-
Ni	5.96 ± 0.81	2.68 ± 1.45	1.74 ± 0.10	26.54 ± 5.67	14.51 ± 1.61	17.54 ± 0.21
Pb	25.02 ± 9.18	18.53 ± 2.45	1.9 ± 0.2	-	-	-
Se	n.d.	1.30 ± 0.96	0.9 ± 0.3	n.d.	n.d.	0.102 ± 0.004
V	8.91 ± 2.20	4.56 ± 0.55	5.2 ± 0.5	34.88 ± 5.41	20.29 ± 2.74	28.19 ± 0.40
Zn	39.34 ± 4.62	163.8 ± 11.0	4.7 ± 0.5	252.3 ± 10.3	345.5 ± 128.7	-

[‘n.d.’ denotes not-determined, ‘-’ denotes no data available/element not analysed]

The error analysis was performed on the repeated experiments. Samples of three replicates were measured for their standard deviations and reported as the experimental errors. Looking at the SRM 1635 results, most of the elements were measured at higher concentrations compared to the certified values. Good agreements however were obtained for Iron in both digestion procedures. The measured values of Arsenic, Cadmium and Selenium were mostly below the limit of detection (LOD) of the equipment hence no values were recorded. As discussed earlier, ICP-OES often has low sensitivity in determining low-level element concentrations, as shown here for these elements. When the results between the closed and open digestion were compared, no conclusive remark could be made as both methods showed lack of accuracy towards the certified values. As for the SRM 1634c standard, similar trends to those of SRM 1635 were observed for the analysed elements. The experimental values showed no agreement to the certified values for all elements; in fact Arsenic and Selenium were not measured at all by the ICP-OES in both digestion techniques.

5.3.2. Open and Closed Digestions of Deposit Samples

Within the same batch of samples, 20 mg of sample deposits were weighed and digested with three replicates each. The results for all four samples are summarised in Table 5.5 and Table 5.6. Results of DA and DB samples for both digestion methods show that Arsenic and Selenium were detected at concentrations below the LOD of the equipment. The same observation was also found for PHTD and KPHTD samples. Again, this may be explained by the lack of sensitivity in ICP-OES in determining elements at very low concentrations especially in dilute solutions. Comparing the results of both digestion methods in all deposit samples, open digestion seemed to produce higher concentrations for most of the elements. One explanation that could be drawn from this observation was that the combination of mineral acids used in extracting the metal elements in open digestion procedure, as discussed in Section 3.2.3.1, is very powerful such that complete dissolution of organic materials in the sample was achieved. Results of the open-digested samples of the standard reference materials were also found to be superior to that of closed-digested samples. The values however were recorded at higher concentrations compared to the certified values. This might suggest that some factors such as sample contamination might have occurred during analysis, which for some reasons was more acute in the open-digested samples.

Table 5.5 ICP-OES analysis of samples DA and DB in parts per million (ppm).

Element	DA		DB	
	Open Digestion	Closed Digestion	Open Digestion	Closed Digestion
As	n.d.	n.d.	n.d.	n.d.
Cd	4.4 ± 0.9	4.2 ± 0.4	n.d.	n.d.
Cr	1137 ± 71	94.1 ± 2.6	115.1 ± 5.2	55.7 ± 0.7
Cu	219.9 ± 13.8	12.6 ± 1.3	78.6 ± 2.1	3.94 ± 0.11
Ni	302.3 ± 15.9	191.4 ± 3.8	3293 ± 182	2142 ± 4
Se	n.d.	n.d.	n.d.	n.d.
V	14.9 ± 1.8	6.8 ± 0.4	3980 ± 340	2620 ± 5
Zn	29.1 ± 8.8	1090 ± 100	1120 ± 90	1980 ± 130

Table 5.6 ICP-OES analysis of samples PHTD and KPHTD in parts per million (ppm).

Element	PHTD		KPHTD	
	Open Digestion	Closed Digestion	Open Digestion	Closed Digestion
As	n.d.	n.d.	n.d.	n.d.
Cd	5.3 ± 0.6	4.5 ± 0.3	11.5 ± 1.6	10.7 ± 0.6
Cr	154.3 ± 25.6	54.8 ± 15.5	186.5 ± 45.3	51.9 ± 5.5
Cu	56.3 ± 5.8	37.9 ± 5.4	12.6 ± 2.1	9.2 ± 0.6
Ni	320.2 ± 15.3	255.6 ± 58.6	452.6 ± 24	407.6 ± 15.4
Se	n.d.	n.d.	n.d.	n.d.
V	215.6 ± 45.2	117.2 ± 20.8	263.4 ± 13.2	206.6 ± 13.7
Zn	4880 ± 260	4610 ± 340	6850 ± 270	5550 ± 350

The open digestion procedure is more susceptible to external contamination, either from the ashing container or the muffle furnace, but at the same time the elements are more liable to loss through volatilisation or retention in the container itself. Overall comparison

made amongst all samples showed that samples that had been prepared through open digestion procedures gave values higher than the closed digestion technique, as well as the standard reference materials. It is more likely that these samples were exposed to contamination rather than elemental loss during preparation. Having analysed these data, further analyses on the SRM and deposits samples were performed with ICP-MS to evaluate the performance of the two digestion procedures and at the same time to compare the performance of the two ICP-based techniques.

5.4. ICP-MS Analysis

As in the ICP-OES analysis, two sets of samples were analysed, the standard reference materials (SRM 1635 and 1634c) and the heat exchanger deposit samples. Due to the limited amount of samples available, only deposits DA and DB were analysed by ICP-MS. By contrast to the ICP-OES, the final solution is diluted in 2% HNO₃ solution mainly to protect the nebuliser prior to the plasma in the ICP-MS. Four different batches of samples at dilution factor of 500 were prepared using different combination of acids as presented in Table 5.7

Table 5.7 Description of different batches for ICP-MS analysis

Sample batch	Digestion method	Reagents used
1	Closed	HNO ₃
2	Closed	HNO ₃ and H ₂ O ₂
3	Open	H ₂ SO ₄ , HClO ₄ and HF
4	Open	H ₂ SO ₄ , HNO ₃ and HF
5	Open	H ₂ SO ₄ , H ₂ O ₂ and HF

A previous study done in this research group on fuel oil reference material utilised a mixture of HNO₃ and hydrogen peroxide, H₂O₂ as oxidising agents in the closed digestion procedure [142]. The mixture had been proved to successfully extract most of the elements in the reference materials but failed to produce reliable results for Vanadium. On the other hand, closed digestion with HNO₃ alone on coal and ash standard reference

materials was found out to be inadequate in extracting trace elements from the organic matrix in both standards [143]. With Vanadium being the element of interest in this study, a comparative analysis was performed on the digestion procedure using both reference materials and heat exchanger deposit as samples. The first set of samples was digested with mixture of HNO_3 and H_2O_2 whilst the second set used HNO_3 as reagent.

For the open digestion method, different reagents were tested in order to investigate the effect of HClO_4 towards the measurement of Vanadium concentration. The count of Vanadium ions in the mass spectrometer detector is specifically confronted due to polyatomic interference from the chlorine and oxygen ions originated from the acid. The polyatomic ion species formed between chlorine and oxygen ions $^{35}\text{Cl}^{16}\text{O}^+$ may interfere directly with the peak of Vanadium ^{51}V ions. Even though the acid solution is brought to incipient dryness during sample preparation, any residual chlorine may still interfere with the measurement of Vanadium. Other possible interferences that may arise from chlorine ions are Arsenic ^{75}As with $^{40}\text{Ar}^{35}\text{Cl}^+$ and Selenium ^{77}Se with $^{40}\text{Ar}^{37}\text{Cl}^+$ ions, both due to interaction with Argon plasma gas. Two other oxidising agents HNO_3 and H_2O_2 were used as alternatives for HClO_4 . Samples were prepared in separate batches and the result of each is discussed in the following sections.

5.4.1. Open and Closed Digestions of Standard Reference Materials 1635

The results obtained for the coal reference standard is presented in Table 5.8. The error values are calculated from the three replicates made within the batch. The blank samples readings are presented in Appendix 5.1. Comparing the results between Batch 1 and 2 of the closed-digested samples, both batches produced similar concentration for most of the elements, except for Nickel and Copper. This suggests that the combination of HNO_3 and H_2O_2 is as good as HNO_3 alone in digesting the organic components of the coal reference material.

When comparing the certified values with the experimental results, it becomes clear that determination of Arsenic, Selenium and Chromium was more accurate than the rest of the elements. As previously illustrated in the literature, HNO_3 was not adequate to break up the organic constituents of the coal matrix, and as shown here, neither is the mixture of HNO_3 and H_2O_2 .

Table 5.8 ICP-MS analysis of sub-bituminous SRM 1635 (in ppm)

Element	Certified values	Closed Digestion		Open Digestion		
		Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
V 51	5.20 ± 0.5	3.11 ± 0.04	3.15 ± 0.09	4.92 ± 0.03	4.72 ± 0.04	4.37 ± 0.05
Cr 52	2.50 ± 0.3	2.12 ± 0.19	2.20 ± 0.03	2.81 ± 0.07	1.89 ± 0.13	1.85 ± 0.06
Ni 60	1.74 ± 0.1	1.12 ± 0.03	2.65 ± 0.07	1.79 ± 0.04	0.93 ± 0.03	1.78 ± 0.04
Cu 63	3.60 ± 0.3	3.64 ± 0.05	4.35 ± 0.06	3.63 ± 0.05	4.68 ± 0.08	5.35 ± 0.14
As 75	0.42 ± 0.15	0.46 ± 0.01	0.35 ± 0.02	0.30 ± 0.01	0.27 ± 0.01	0.29 ± 0.02
Se 78	0.90 ± 0.3	0.95 ± 0.09	0.93 ± 0.04	0.06 ± 0.06	0.05 ± 0.08	0.16 ± 0.09
Cd 111	0.03 ± 0.01	0.02 ± 0.004	0.04 ± 0.004	0.04 ± 0.002	0.02 ± 0.005	0.02 ± 0.004

Compared to the closed-digested samples, the open digestion batches, Batch 3, 4 and 5, produced considerably better extraction for most of the elements except for Arsenic and Selenium. These two elements are rather volatile and it is likely that some of the elements were lost during sample preparation. The rest of the elements, in particular Vanadium and Nickel, fared better to the certified values, although Vanadium was below the certified concentration. With the exception of Vanadium in Batch 6 and Nickel in Batch 5, the results were within the range of certified values. Vanadium polyatomic interference with $[^{35}\text{Cl}^{16}\text{O}]^+$ ions did not take place in all batches as each determination was below the certified values of 5.20 ± 0.5 . Also, the blank samples did not show any sign of contamination or polyatomic interference. This indicates that the chloride ions were eliminated in the preparation process. In the case of low detection of Nickel in Batch 4, it is thought that HNO_3 failed to completely oxidise the organic constituents that bound Nickel metal in the reference material. The other two batches however show very good agreement towards the certified value. Overall, when comparing the general extraction capability amongst the batches throughout the elements being examined, Batch 3 with HClO_4 produced better matching of the certified values for each element. HClO_4 is a very powerful oxidising agent which could oxidise organic materials rapidly and the combination of HClO_4 with HF increases the efficiency of digestion as a result of increased boiling temperature of the mixture [156].

The results of SRM 1634c samples are displayed in Table 5.9. The extraction ability and elements recoveries of the closed digestion procedure has proved to be superior compared to the open digestion batches. Vanadium and Arsenic in particular are quantified at ranges close the certified values in the closed-digested batches especially in Batch 1. This result shows that HNO₃ alone is adequate in breaking up the organic constituents that bound the metal elements in the sample. The concentrations of Vanadium in open-digested samples are comparable between each other, which again suggest the absence of polyatomic interference in the HClO₄-prepared samples. On the other hand, the results of open-digested samples were recorded at concentrations below the certified values for most of the elements. This may be due to the robust conditions that the sample had to go through during the preparation step that led to the loss of the elements. The opposite however was observed for similar analysis through ICP-OES technique. To further understand if this phenomenon is due to techniques or the digestion procedures itself, analysis of refinery deposit samples were conducted.

Table 5.9 ICP-MS analysis of fuel oil SRM 1634c (in ppm)

Element	Certified values	Closed Digestion		Open Digestion		
		Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
V 51	28.19 ± 0.4	28.20 ± 0.11	28.99 ± 0.12	26.54 ± 0.27	24.11 ± 0.23	25.60 ± 0.20
Cr 52	<i>n.a.</i>	1.17 ± 0.03	0.91 ± 0.01	0.79 ± 0.02	0.60 ± 0.04	0.53 ± 0.02
Ni 60	17.54 ± 0.21	16.66 ± 0.16	16.20 ± 0.10	16.23 ± 0.09	15.35 ± 0.15	14.70 ± 0.17
Cu 63	<i>n.a.</i>	0.56 ± 0.01	0.36 ± 0.01	0.87 ± 0.01	0.90 ± 0.01	0.35 ± 0.03
As 75	0.143 ± 0.006	0.144 ± 0.001	0.131 ± 0.005	0.117 ± 0.006	0.124 ± 0.005	0.093 ± 0.006
Se 78	0.102 ± 0.004	0.125 ± 0.059	0.116 ± 0.055	0.005 ± 0.004	0.108 ± 0.094	0.054 ± 0.039
Cd 111	<i>n.a.</i>	0.004 ± 0.001	0.007 ± 0.003	0.005 ± 0.001	0.009 ± 0.002	0.007 ± 0.005

When comparing the results of both reference materials, the sub-bituminous coal SRM 1635 recorded better element recoveries in the open digestion procedure compared to the closed digestion technique. On the contrary, the elements in the fuel oil reference SRM 1634c were recovered at closer accuracy to the certified values in the closed digestion procedure compared to the open-digested samples. This observation suggests that the organic matrix that fringed the metal constituents in the fuel oil reference is of a lesser force compared to the bonds that made up the coal reference material.

5.4.2. Wet-ashing and microwave digestions for deposit samples

The heat exchanger deposits DA and DB were analysed and the results are summarised in Table 5.10 and Table 5.11. Comparing the results of DA via both closed digestion procedures, most of the elements are generally quantified at similar level of concentrations except for Cadmium. However it was noted that the standard deviations of the elements in Batch 2 were higher, which shows poor repeatability and consistency within the analysis. This result once again shows that digestion with HNO₃ alone is sufficient and fully capable of extracting metal components consistently in crude oil based materials. The results of the open digested samples however gave lack of agreement amongst the three batches with no particular method stands out in terms of consistencies between the results. Vanadium, Chromium, Arsenic and Selenium were quantified at lower concentrations compared to those of Batches 1 and 2. Once again this could be explained by loss of elements through volatilisation during sample preparation.

The results of deposit DB shows fairly similar features to that of DA with Vanadium, Arsenic and Selenium in particular quantified at higher concentrations in the closed digestion procedure. Chromium however was recovered at higher concentrations in the open digested samples which may be explained by the nature of the deposit itself. Compared to deposit DA, DB is composed of heavier components consists of high carbonaceous materials as it comes from the vacuum distillation processing unit. Chromium is probably bound at much higher force within the organic constituents which are digested more efficiently via the robust procedure of open digestion method. Whilst Batch 1 showed better results for the closed digested samples, the open digested batches were relatively comparable with each other apart from Selenium, which was successfully quantified in Batch 3. Again, there was also no evidence to suggest the polyatomic interference for Vanadium in Batch 3 samples with HClO₄ ions.

Table 5.10 ICP-MS analysis of sample DA (in ppm)

Element	Closed Digestion		Open Digestion		
	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
V 51	17.5 ± 3.5	17.9 ± 9.3	14.0 ± 1.1	17.3 ± 3.2	16.5 ± 0.8
Cr 52	1203 ± 125	1208 ± 523	871 ± 61	824 ± 106	782 ± 46
Ni 60	280 ± 45	218 ± 152	244 ± 41	212 ± 28	234 ± 39
Cu 63	216 ± 22	188 ± 52	210 ± 54	177 ± 21	185 ± 5
As 75	12.2 ± 1.1	13.8 ± 8.8	9.49 ± 0.38	9.14 ± 1.64	10.2 ± 0.9
Se 78	18.5 ± 2.1	21.6 ± 10.7	0.35 ± 0.07	< LOD	< LOD
Cd 111	3.16 ± 0.38	1.75 ± 0.41	3.51 ± 1.27	2.84 ± 0.41	3.21 ± 0.04

Table 5.11 ICP-MS analysis of sample DB (in ppm)

Element	Closed Digestion		Open Digestion		
	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
V 51	3641 ± 103	3520 ± 242	3225 ± 45	3302 ± 109	3323 ± 31
Cr 52	83.6 ± 8.9	88.6 ± 17	99.9 ± 6.4	97.7 ± 10.5	97.1 ± 15.6
Ni 60	2540 ± 140	2731 ± 234	2769 ± 228	2555 ± 134	2534 ± 18.8
Cu 63	69.5 ± 2.3	70.8 ± 13.9	63.7 ± 1.3	64.5 ± 2.0	64.7 ± 1.1
As 75	2.21 ± 0.42	2.17 ± 0.25	1.85 ± 0.35	2.15 ± 0.40	2.10 ± 0.24
Se 78	4.51 ± 0.16	4.51 ± 0.50	1.31 ± 0.24	< LOD	< LOD
Cd 111	1.52 ± 0.38	1.96 ± 0.76	2.71 ± 0.88	1.89 ± 0.35	1.91 ± 0.15

5.5. Summary & Conclusions

It was concluded that quantification of trace metals in crude oil samples is possible through both ICP techniques and sample digestion procedures to certain agreement. The results of ICP-MS are proven to be more reliable in terms of consistency among the repeats and closer accuracy towards the certified values. The ability of the instrument to reach lower limit of detection (LOD) allows better accuracy on the quantification of elements with minimal instrumental issues such as background spectral interferences in ICP-OES. The closed digestion procedure generated results much closer to the certified values on both Standard Reference Materials. This is mainly attributed by the various steps involving three different mineral acids at high temperatures in the open digestion procedure which results in loss of certain elements through volatilisation. This result also suggests that the heat exchanger deposits were mainly comprised of carbonaceous materials that could be dissolved efficiently with a strong oxidising agent i.e. HNO_3 without the necessity of using other acids such as HF to dissolve any silica-based materials. This subsequently avoids any secondary issues such as polyatomic interferences of elements and possible equipment damage from the residual acids [7]. The combination of ICP-OES and open digestion procedure seemed to generate inconsistent results amongst the samples. The balance between the effect of sample contamination and spectral interference could not be established. It was concluded that the ICP-MS with closed digestion procedure would be used as the technique for quantification of trace element of crude oil derived samples in this particular study.

6. Effect of Vanadyl Porphyrin on Deposition

As discussed in Chapter 2, a large amount of inorganic species concentrates in the heavier part of crude oils, especially in the asphaltenes fraction. The most common and abundant metal compounds found in crude oils are Vanadium and Nickel. They can be found in various forms with the porphyrin compounds being one of the most common types. These metals are mainly found in parts per million level. Even at this low level of concentration, they may pose some serious operational issues in refineries such as the deactivation of catalyst in the catalytic cracking unit by Vanadium. With the current trend of heavy crude oil processing, the inorganic composition of oil has become an increasingly significant trait in crude oil analysis. The effect of these metals towards fouling however has not been studied in much detail, whereas more studies have been dedicated to the organic side of heat exchanger fouling.

In this chapter, the effect of vanadyl porphyrin towards deposition of foulant on heat transfer surfaces is studied and discussed. Two crude oil samples, Crude A and Crude D were subjected to analyses. Crude A represents a medium-heavy oil sample and Crude D corresponds to a light crude oil. A systematic approach was taken wherein various concentrations of vanadyl porphyrin were introduced in each crude oil and subjected to heat and pressure in the fouling reactor. The amount of deposits and liquid produced were quantified and subsequent analyses by ICP-MS, SEC, UV-F Spectroscopy and GC were carried out. Details of the analyses are presented in the following sections which includes the preliminary study on the development of sample preparation procedures for ICP analysis.

6.1. ICP-MS Analysis of Crude A and Crude D

Having proven that the closed digestion technique and ICP-MS instrumentation produced reliable results, as discussed in Chapter 5, the concentration of Vanadium in both crude oils and their maltenes and asphaltenes fractions were quantified. The fractionation procedure is presented in the following section.

6.1.1. Asphaltenes Content of Crude A and Crude D

Both crude oils were fractionated into the two parts following the ASTM D6560 (IP 143) standard procedure. The procedure used in this study is presented in Section 3.2.2. The asphaltenes determination analysis was repeated at least twice for each crude oil. The amount of asphaltenes for Crude A was determined to be at $6.39 \pm 0.23\%$ whereas for Crude D was at $0.08 \pm 0.01\%$. These values are relatively close to the amount reported in the literature for both Crude A and D at 6.7% and 0.07% respectively [152]. The amount of maltenes for Crude A was calculated at $80.1 \pm 0.1\%$ whereas for Crude D was determined at $88.7 \pm 0.1\%$. The smaller concentration of asphaltenes and higher amount of maltenes in Crude D proves that the oil mainly consists of lighter components relative to Crude A. The percentages of sample recovery of these analyses ranged from 85 – 89%. It is thought that some components of the sample were probably lost during sample transfer, sample drying and vaporisation of volatile components during reflux.

6.1.2. ICP-MS analysis of Crude A

Four elements namely Arsenic, Nickel, Selenium and Vanadium were picked as elements of choice for this analysis. The concentration of Vanadium and Nickel in particular are of interest since these elements are consistently found in crude oils and the reference values are available in the assay of each crude oil. The other two elements are certified values in the reference standard, SRM 1634c, hence were chosen for references. The recoveries of each element are presented here and they gave good consistency between repeats in each sample, especially for the lighter Crude D Figure 6.1 shows the comparative plots of each fraction for Vanadium and Nickel. The errors were calculated between three replicates of sample.

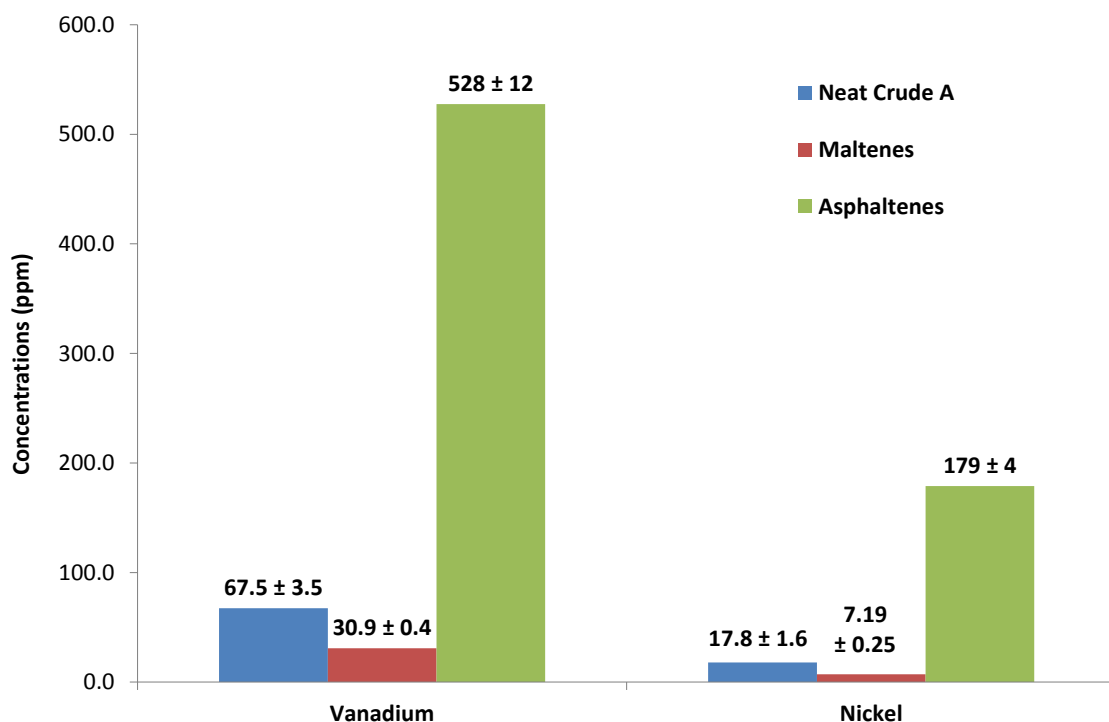


Figure 6.1 Concentration of Vanadium and Nickel in Crude A and its fractions measured by ICP-MS.

The mass balance of the two metals was calculated with a closure of $92 \pm 3\%$ for Vanadium and $95 \pm 4\%$ for Nickel in between the repeats, taken into account the recovery of maltenes and asphaltenes fractions of 85%. The total amount of Vanadium in Crude A is found to be at around 68 ppm. For a medium-heavy crude oil, this is a typical amount that could be expected. The bulk of it is concentrated in the asphaltenes fraction, at a concentration of 530 ppm, whilst the maltenes part of the oil contains about 31 ppm of Vanadium. The same trend can be seen for Nickel with most of the metal concentrated in the asphaltenes fraction. This finding illustrates that Vanadium and Nickel concentrate in the heavier part of crude oils as reported by many in literatures. As discussed in Section 2.5, these two metals are commonly found as the most abundant in crude oils, and the porphyrin types of each are often found in the same fraction when analysed [84]. Analysis by Ali et al. [73] showed that the vanadyl porphyrins are mainly of Etio and DPEP homologues, whereas nickel porphyrins are mainly of the Etio types. These two compounds however are similar in many of the physical properties to the material they are associated to, which in this case the polar asphaltenes molecules. Since the physical

properties of these porphyrins are largely similar, they most likely would give comparable effects in the fouling behaviour of a certain crude oil sample.

6.1.3. ICP-MS Analysis of Crude D

Identical analysis was performed for the lighter Crude D with similar elements chosen for quantitative analysis. Only two replicates however were made for the asphaltenes fraction due to the small amount recovered during fractionation. The results are summarised in Figure 6.2.

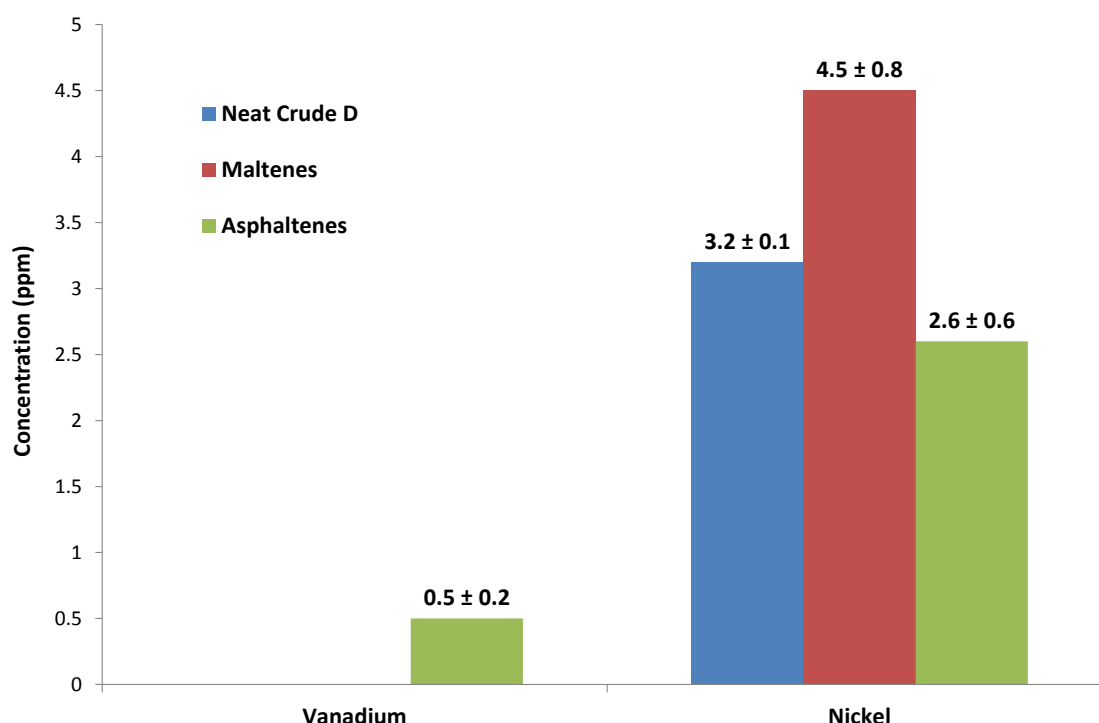


Figure 6.2 Concentrations of Vanadium and Nickel in Crude D and its fractions measured by ICP-MS.

As expected, the amount of trace metals in Crude D are much less compared to the heavier Crude A. In fact, the concentration of Vanadium in the oil and the maltenes fraction were recorded below the limit of detection of the equipment. Most of the Vanadium concentrated in the asphaltenes fraction as observed in Crude A. The amount however was comparatively small, recorded at around 0.5 ppm. The opposite was observed for concentration of Nickel in the oil, which gave higher concentration in the

maltenes fraction as oppose to the asphaltenes. This is perhaps due to the building block of the Nickel metals in Crude D are made of lighter components. The Nickel compounds are most likely attached to the small aromatic components that are soluble in heptane rather than in the bigger aromatics systems of asphaltenes.

6.2. Fouling Reactor Deposit Analysis

This analysis focused on the effect of added Vanadium concentration in both Crude A and D towards the formation of deposits in the fouling reactor. The resulting products were analysed for their molecular weight distribution and aromatic ring structures along with quantification of Vanadium in each product. Characterisation of the products is essential in order to monitor and investigate the effect of additional Vanadium towards the compositional balance of the original crude oils to establish the role of Vanadium on deposition process in each sample. The partitioning of Vanadium in the products were established as part of overall mass balance analysis. Crude A and Crude D were separately mixed with vanadyl porphyrin at 5 different concentrations and each of these oil compositions was studied for their foulant deposition in the fouling reactor. Various types of vanadyl porphyrin compounds are available commercially both in liquid and solid forms. The particular porphyrin used in this study is 5, 10, 15, 20 - tetraphenyl 21H, 23H - porphine vanadium (IV) oxide. The molecular information of the compound is shown in Table 6.1 and Figure 6.3 shows the molecular structure. This particular porphyrin is chosen as it is one of the simplest forms of vanadyl porphyrin with no intricate structures attached to its core or periphery that might affect the stability of the neat crude oil upon mixing. It is also in a solid form with no solvent associated to it, as any solvent present would pose the risk of altering the intermolecular equilibrium of the oil and therefore its stability. The presence of these vanadyl compounds is illustrated by Speight et al [51]. Introduction of vanadyl porphyrin complex into the samples was presumed to affect the fouling behaviour as it is typically associated with asphaltenes molecules. A hypothetical structure of crude oil asphaltenes is presented in Figure 6.4, in which the porphyrin compounds of Vanadium and Nickel are proposed as one of the asphaltenes building blocks. The porphyrin structures are thought to be linked at the peripheral of asphaltenes molecules hence made it susceptible for reactions with other hydrocarbon compounds.

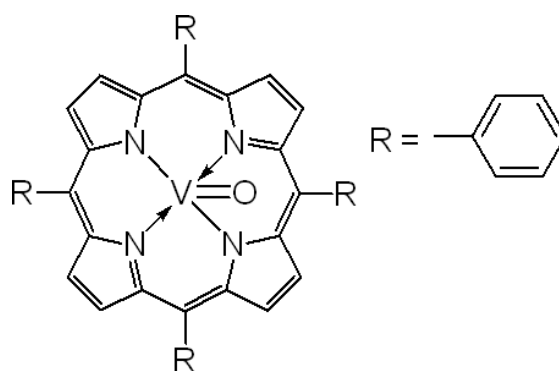


Figure 6.3 Molecular structure of vanadyl porphyrin used in the study.

Table 6.1 Physical properties of vanadyl porphyrin used in the study.

Name	5, 10, 15, 20 - Tetraphenyl 21H, 23H - porphine vanadium (IV) oxide
Empirical Formula	C ₄₄ H ₂₈ N ₄ OV
Molecular Weight	679.66 g mol ⁻¹

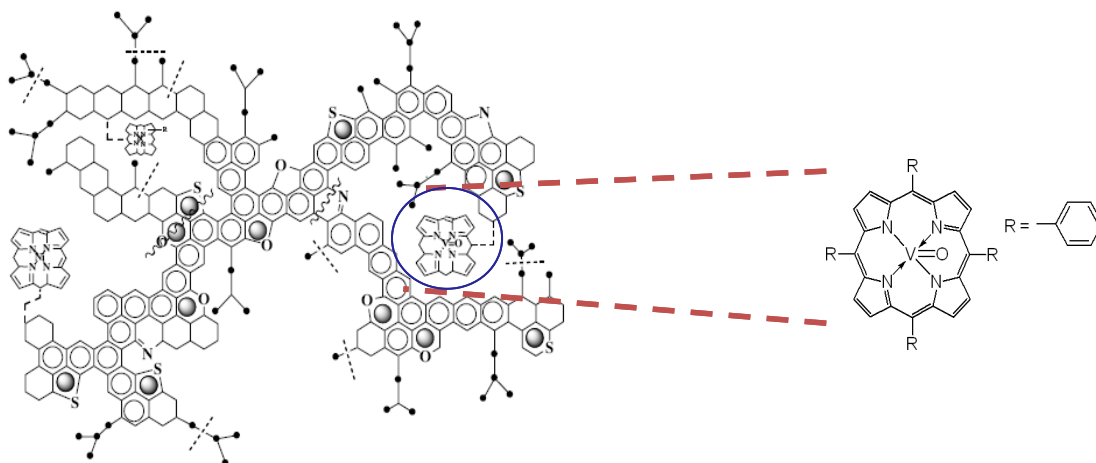


Figure 6.4 Hypothetical molecular structure of asphaltenes and the associated vanadyl porphyrin. Reproduced from [54].

6.2.1. Sample Preparation

Five samples at different concentrations of added Vanadium were prepared i.e. at 35, 75, 350, 550 and 750 ppm (weight) in each of the crude oils. 30 mL of oil was prepared for each run. Out of this volume, 10.5 mL of sample was heated in the test section, as measured during commissioning. To ensure that the solid porphyrin was properly dissolved in the oil, samples were stirred and heated on a magnetic stirrer at 40°C for 20 minutes. The same procedure was done for a blank run without any additional Vanadium porphyrin to ensure each sample underwent similar sample preparation procedure. The concentration of Vanadium of each sample was later quantified, along with the deposit and liquid products, in the subsequent ICP-MS analysis.

All experiments were conducted in the fouling reactor with test conditions of 350 °C wall temperature, 10 bar pressure and running time of 48 hour. At the end of each experiment, the liquid products and deposits were collected and quantified. Afterwards, the test section was washed with chloroform and the chloroform insoluble fraction attached to the wall was recovered. This fraction was not classified as deposits, instead is categorised as heavy coke material that was not characterised in the subsequent analyses. Each mixture of oil and vanadyl porphyrin sample was run in the reactor twice for repeatability analysis. To ease discussion, each sample has been given a sample name i.e. A1 to A6 for Crude A and D1 to D6 for Crude D as listed in Table 6.2. These names correspond to concentration of the added Vanadium.

6.2.2. Amount of Deposits

The results of runs with Crude A are presented in Table 6.2. Figure 6.5 and 6.6 show the plots of these data at different concentrations of added Vanadium in the original samples.

Table 6.2 Amount of deposit, liquid and chloroform insoluble fractions for Crude A and the corresponding additional Vanadium.

Sample No.	Crude Oil Sample	Amount of Deposit, g	Amount of Liquid, g	Amount of Chloroform Insoluble, g
A1	A	0.184 ± 0.012	9.42 ± 0.10	0.036 ± 0.002
A2	A + 35 ppm V	0.195 ± 0.016	9.20 ± 0.08	0.046 ± 0.002
A3	A + 75 ppm V	0.185 ± 0.014	9.39 ± 0.12	0.033 ± 0.001
A4	A + 350 ppm V	0.156 ± 0.013	9.42 ± 0.11	0.045 ± 0.002
A5	A + 550 ppm V	0.484 ± 0.013	7.81 ± 0.06	0.035 ± 0.001
A6	A + 750 ppm V	0.776 ± 0.025	7.04 ± 0.08	0.030 ± 0.001

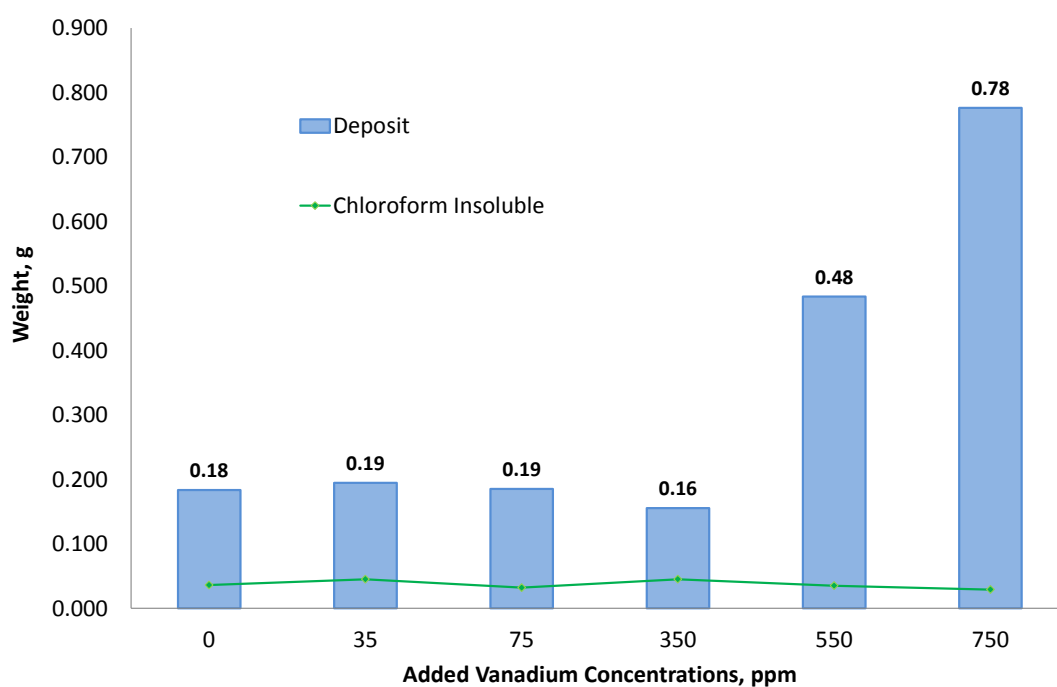


Figure 6.5 Comparisons of the amount of deposit and chloroform insoluble collected after runs of neat Crude A and Crude A with additional Vanadium.

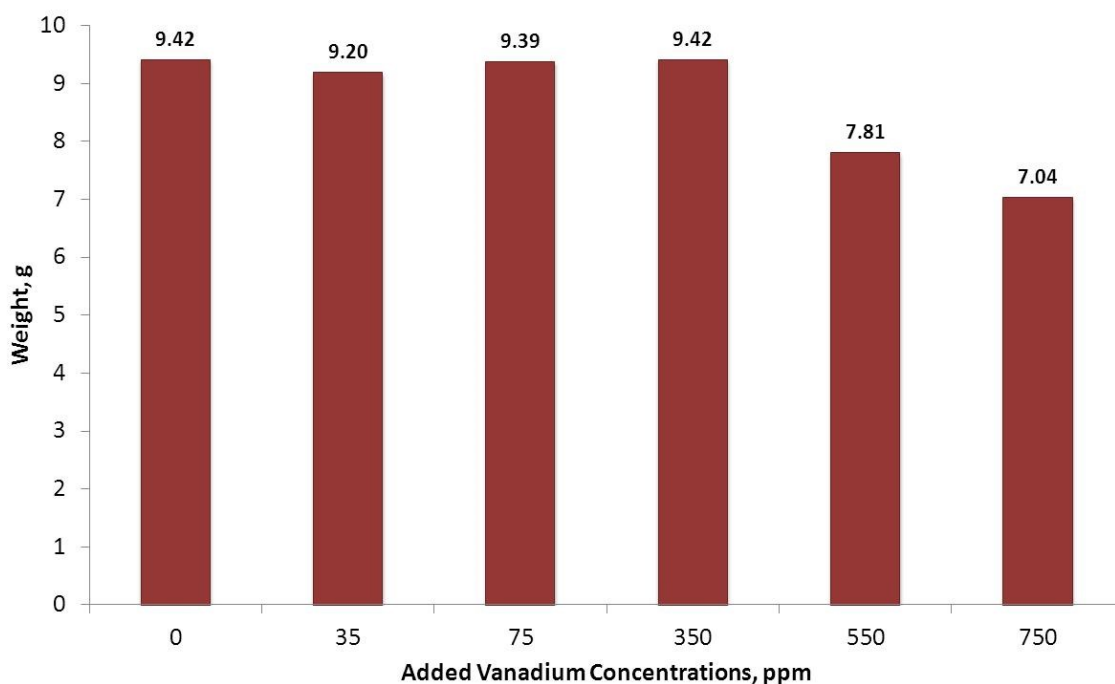


Figure 6.6 Comparisons of the amount of liquid product recovered for neat Crude A and its corresponding additional Vanadium.

The amount of deposits formed from individual run of Crude A was recorded at 0.184 g. Figure 6.5 shows that the amount of deposits formed from samples with added Vanadium of 35, 75 and 350 ppm were comparable to this value. The deposit amount however increased significantly for sample A5 and further increased for sample A6. This indicates that for this particular oil, the addition of extra vanadyl compounds at small concentration did not affect the amount of deposit produced at the end of each run. It is important to note that the original amount of vanadium in Crude A is 67 ppm, and a typical heavy crude oil of API gravity below 20 has a range of vanadium concentration of 300 – 1500 ppm [78]. For Crude A, an addition of Vanadium concentration up to 514% of the original concentration did not have an effect on the amount of deposits produced. The corresponding liquid products recovered at the end of each run, presented in Figure 6.6, also showed a similar trend in which comparable amount of liquid were recovered for experiment for sample A1 up to sample A4. This value however dropped for sample A5 and further decreased for sample A6. This suggests that at high concentration of Vanadium, fouling behaviour of the crude oil changes and formation of deposits can be expected to escalate further if more vanadyl porphyrin compounds were added. The

reduced amount of liquid product corresponds to the increment on the amount of deposits for sample A5 and A6. The presence of Vanadium triggers further the deposition of fouling materials on heated surfaces especially at high concentrations of Vanadium. At high concentrations, Vanadium seemed to induce the formation of fouling precursor and precipitation of compounds from the bulk liquid and subsequently adhered to the heated surface area. Vanadyl porphyrins have been known to undergo electrophilic substitution in the presence of nitrogen through nitration process in a relatively acidic condition [168]. Alkene oxygenation of hydrocarbon compounds have also been reported to occur in the presence of vanadyl porphyrin complexes, promoting further thermal cracking of hydrocarbons [169]. These reactions might have possibly promoted further the reactivity of hydrocarbons through thermal cracking forming heavy deposits especially at higher concentration of vanadyl porphyrins. The structural and molecular weight analysis of these products will be discussed in the following section. The chloroform insoluble fraction is the deposit collected at the tube wall after washing with chloroform. The amount collected was quantified for mass balance analysis of the system. This fraction, regarded as coke, is the heavier product of the reactor. As depicted in Figure 6.5, the amount collected was relatively similar for all crude oil samples.

Similar analysis was performed for Crude D, a much lighter crude oil compared to Crude A. The results are summarised in Table 6.3 and comparative plots of the samples tested are presented in Figure 6.7 and Figure 6.8.

Table 6.3 Amount of deposit, liquid and chloroform insoluble fractions for Crude D and the corresponding additional vanadyl porphyrin.

Sample No.	Crude Oil Sample	Amount of Deposit, g	Amount of Liquid, g	Amount of Chloroform Insoluble, g
D1	D	No deposit	7.25 ± 0.14	None recovered
D2	D + 35 ppm V	No deposit	7.37 ± 0.28	None recovered
D3	D + 75 ppm V	No deposit	7.14 ± 0.18	None recovered
D4	D + 350 ppm V	0.023 ± 0.011	6.99 ± 0.17	None recovered
D5	D + 550 ppm V	0.172 ± 0.024	5.97 ± 0.14	None recovered
D6	D + 750 ppm V	0.475 ± 0.016	5.06 ± 0.10	None recovered

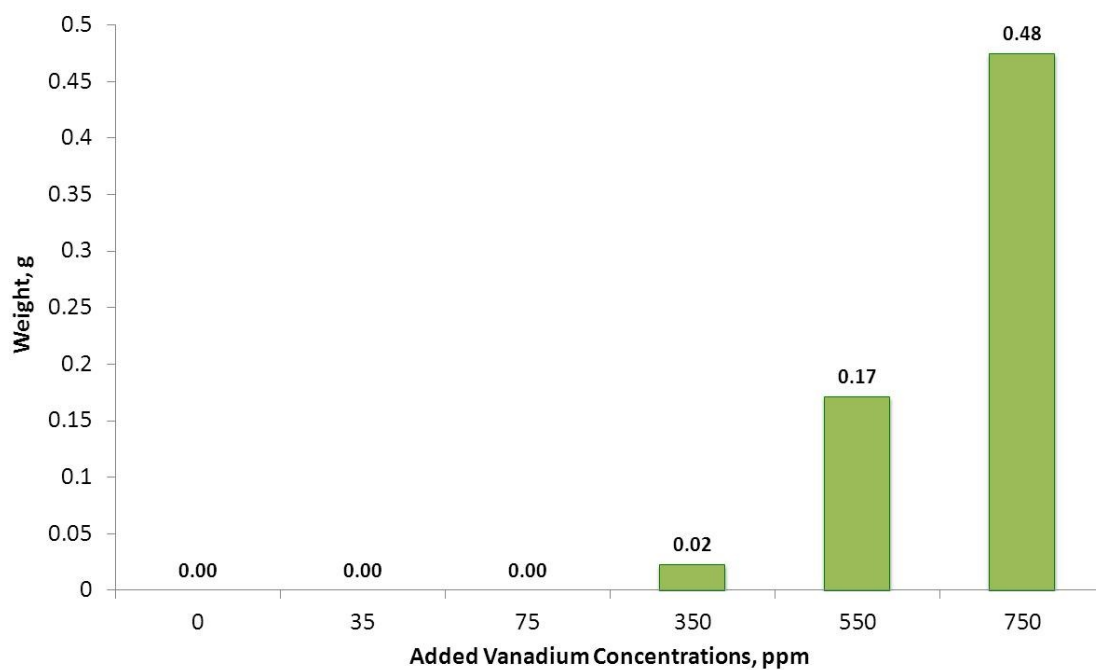


Figure 6.7 Plots of the amount of deposit collected after runs of neat Crude D and Crude D with additional vanadyl porphyrin.

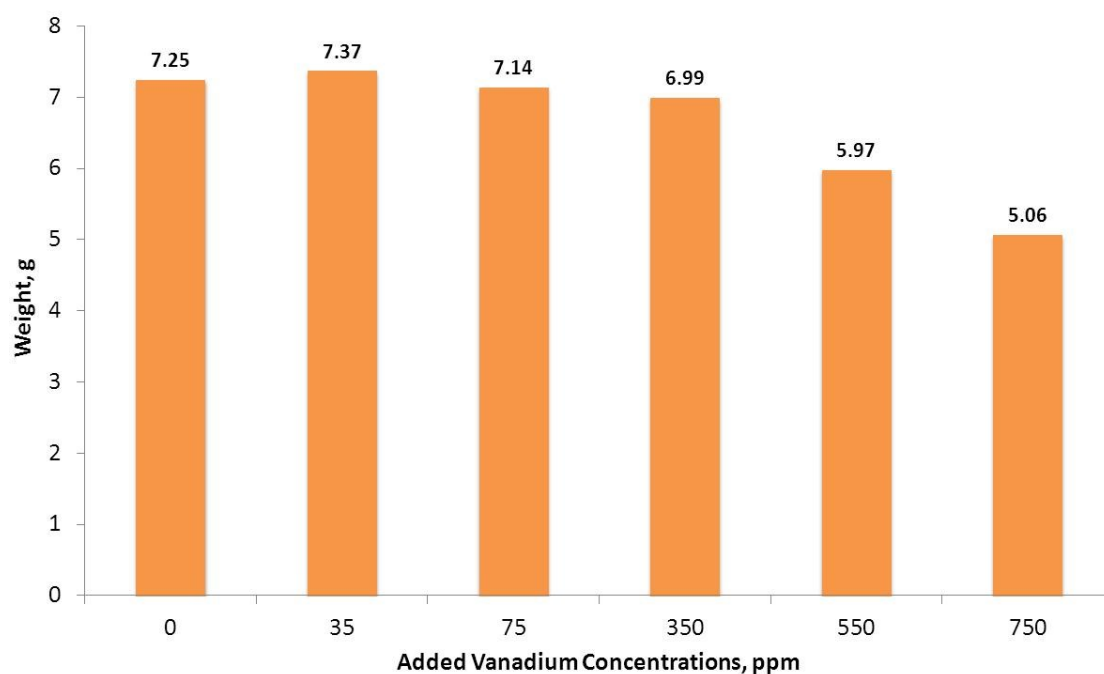


Figure 6.8 Bar charts to show the amount of liquid product recovered for neat Crude D and Crude D with additional vanadyl porphyrin.

The individual run of Crude D did not produce any deposit in the reactor. Addition of Vanadium at 35 and 75 ppm seemed to not have any effect on the fouling behaviour of Crude D. A small amount of deposits however was collected for sample D4. This trend of deposit formation is rather similar to that of heavier Crude A in which a sharp increase in the amount of foulant produced was observed at 550 ppm of added Vanadium from 350 ppm. This supports the earlier discussion of which fouling behaviour following to introduction of vanadyl porphyrins is only significant at high concentrations. The amount of deposits produced became more significant for sample D6. If compared to the amount of deposits produced from the similar concentration for Crude A, the value was much less. From the naked eye observation, the deposits formed for Crude D looked more waxy and contained less coke-like materials compared to those of Crude A. There was no chloroform insoluble fraction recovered after the runs with Crude D. This is most likely due to the composition of Crude A which contains relatively heavier components with more asphaltenes and larger aromatic compounds. The characterisation of both deposits will be presented later in the chapter.

The corresponding liquid products for analysis of Crude D is presented in Figure 6.8. The amount collected for sample D1, D2 and D3 were reasonably close to each other. Thereafter, the amount of liquid product decreased as the concentration of Vanadium increased. As observed in the previous analysis of Crude A, more components in the bulk liquid were precipitated and attached at the heated wall surface in the more Vanadium-concentrated oils. The amount of liquid recovered at the end of each experiment was less compared to its counterpart from Crude A. This is thought to be due to the formation of more gaseous products for Crude D samples. Crude D is composed of much lighter components and at the experiment temperature and pressure, this lighter component vaporised into gas hence reducing the amount of liquids recovered.

Mass balance analysis performed on Crude A recorded up to 26% samples loss upon recoveries of each product, whereas Crude D gave up to 48% loss as shown in Table 6.4. The highest loss was recorded at sample with the highest concentration of Vanadium in each crude oil. Since the gaseous products were not recovered, the poor recoveries were most likely due to the loss of these gaseous components during sample collection. Higher percentages were recorded for Crude D due to its relatively lighter nature compares to Crude A.

Table 6.4 Percentages of sample loss for each run of neat Crude A and Crude D and with added Vanadium.

Samples	Percentage of sample loss		Samples	Percentage of sample loss
A1	8.54%		D1	31.2%
A2	10.4%		D2	30.1%
A3	8.84%		D3	32.3%
A4	8.72%		D4	33.5%
A5	20.9%		D5	41.7%
A6	25.6%		D6	47.5%

6.2.3. Characterisation of Liquid and Deposit Products by ICP-MS

Each deposit and liquid products were subjected to ICP-MS for full elemental quantitative analysis. Both products were digested via closed digestion technique with concentrated nitric acid. Two batches of analysis were performed and three replicates were prepared in every batch. The concentration of Vanadium was expected to be higher in the deposit products as the heavier hydrocarbon compounds were thought to be most likely accumulated in the deposits. Table 6.5 displays the concentration of Vanadium in both liquid and deposit products for neat Crude A and Crude A with added Vanadium and these values are visualised in Figure 6.9.

As expected, the results showed that most of the Vanadium was concentrated in the deposit fraction of the products. As the amount of the added vanadyl porphyrin increased, the amount quantified in both products increased. The increment in the liquid products however was not as steep as those of deposits. Comparing the values between the products of Sample A3 and A4, there is a relatively sharp increase in the concentration of Vanadium in the deposit compared to the increment in the liquid product. The concentration of Vanadium in the deposit gradually increased from sample A1 to A3 with the sudden jump in sample A4 due to the corresponding increment in the amount of vanadyl porphyrin added to the sample. This behaviour however was not observed in the liquid product, which showed a gradual increase in the concentration of Vanadium. Most of the added Vanadium in sample A4 accumulated in the deposit, while the amount of

deposits formed for sample A4 was similar to those of sample A1, A2 and A3. This shows that the nature of deposits among these four samples were different. It also indicates that the deposits may be made up of several crude oil components, and in this particular case the added Vanadium contributed towards the deposit composition but it did not ensure increment in the amount of deposit with an increase in concentration of Vanadium. This behaviour however was not observed after a certain amount of added Vanadium, which this study placed at 350 ppm and above, in which the amount of deposit formed increased along with the concentration of Vanadium in the deposits. It should be noted that the standard deviation of Vanadium concentration in the deposits fractions was rather high. This is perhaps due to the non-uniformity of Vanadium distribution within the deposits formed in the reactor. Some Vanadium complexes most likely attached to certain locations in the tube more than others, as observed during the recovery of the deposit in which certain locations fouled more than other parts in the tube. The most fouled region however was not always found at the hottest part of the test section i.e. at the middle part but also recovered at the upper, relatively colder part of the tube.

Table 6.5 Concentration of Vanadium in the liquid and deposit products of Crude A and Crude A with additional vanadyl porphyrin

Sample No.	Sample	Concentration of Vanadium in Liquid Product, ppm	Concentration of Vanadium in Deposit Product, ppm
A1	Crude A	39.1 ± 1.1	333 ± 37
A2	Crude A + 35 ppm V	72.8 ± 2.6	359 ± 42
A3	Crude A + 75 ppm V	109 ± 2	404 ± 17
A4	Crude A + 350 ppm V	152 ± 3	683 ± 163
A5	Crude A + 550 ppm V	203 ± 3	866 ± 176
A6	Crude A + 750 ppm V	255 ± 2	886 ± 107

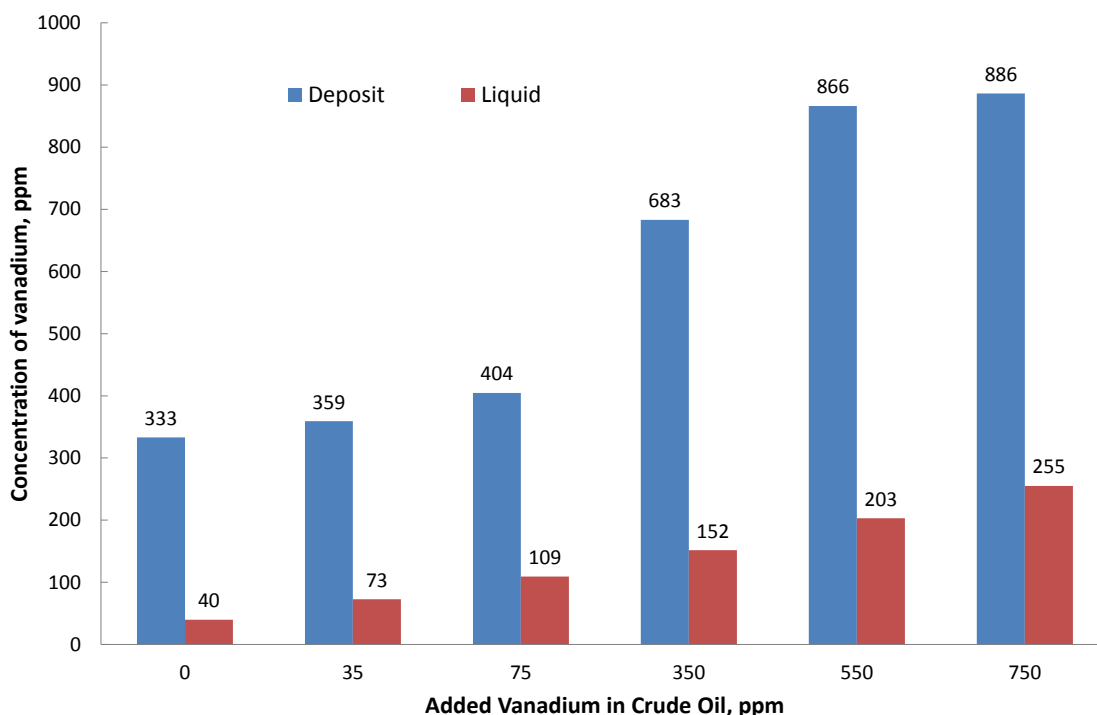


Figure 6.9 Concentrations of Vanadium in the liquid and deposit products of neat Crude A and Crude A with additional Vanadium.

Analysis of the lighter Crude D was conducted in a similar manner. Summary of the results are tabulated in Table 6.6 and the corresponding bar chart is displayed in Figure 6.10. The amount of Vanadium in the liquid product for sample D1 was not recorded as it was below the LOD of the equipment. It was observed that as the concentration of added vanadyl porphyrin increased, the concentration of Vanadium in the liquid (and deposit for sample D4, D5 and D6) increased. Similar to the trend exhibited in Crude A samples, a gradual increase on the concentration of Vanadium in the liquid fraction was recorded. The amount however was not as high as their counterparts in Crude A samples. This is largely due to the fact that the original amount of Vanadium in Crude D is lower than Crude A, and also as observed for samples D4, D5 and D6, most of the elemental Vanadium were concentrated in the deposit fractions. Also, it was observed that the concentrations of Vanadium in Crude D deposit products were higher compared to those of Crude A samples. There were more deposits produced from Crude A samples and they were made of more carbonaceous components as oppose to the deposits from Crude D. This relatively higher content of carbon made the concentration of Vanadium lesser in Crude A deposits.

Table 6.6 Concentration of Vanadium in the liquid and deposit products of Crude D and Crude D with additional vanadyl porphyrin

Sample No.	Sample	Concentration of Vanadium in Liquid Product	Concentration of Vanadium in Deposit Product
D1	Crude D	<LOD	NA
D2	Crude D + 35 ppm V	19.1 ± 1.1	NA
D3	Crude D + 75 ppm V	50.2 ± 1.2	NA
D4	Crude D+ 350 ppm V	77.1 ± 1.9	872 ± 20
D5	Crude D + 550 ppm V	102 ± 2	1344 ± 21
D6	Crude D + 750 ppm V	138 ± 3	1573 ± 28

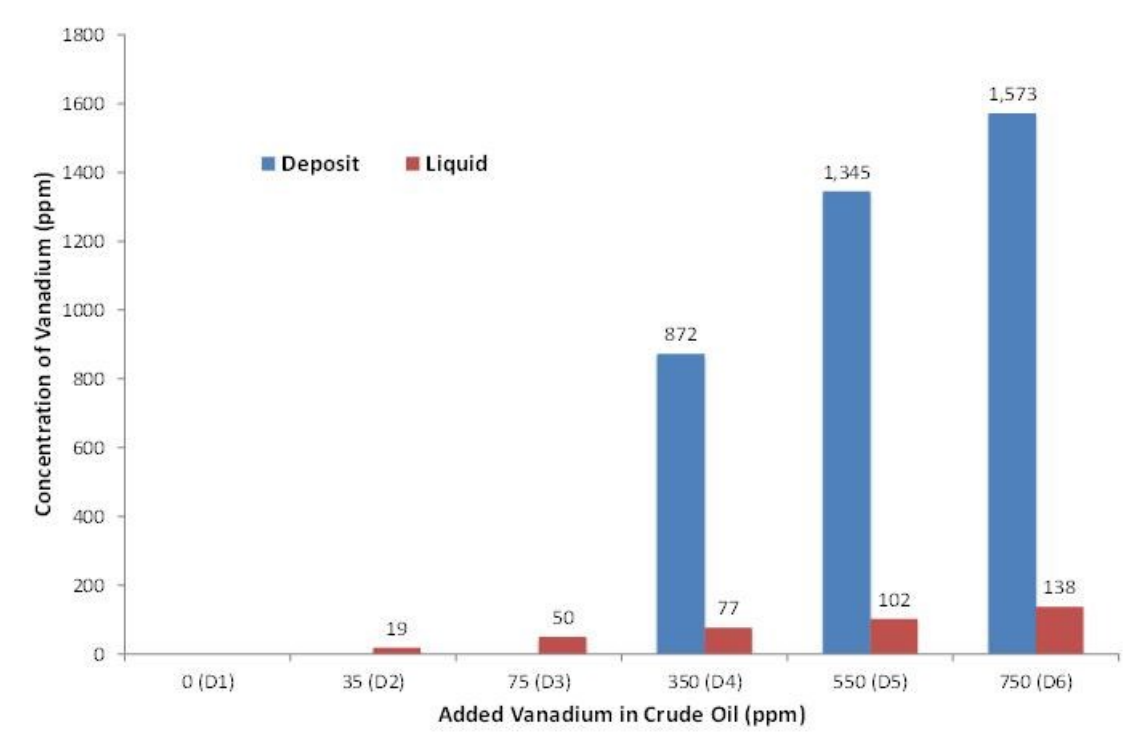


Figure 6.10 Concentrations of Vanadium in the liquid and deposit products of neat Crude D and Crude D with additional Vanadium.

Calculation of mass balance on Vanadium between the amount quantified in products and the concentration added in Crude A samples gave closures in between 58% to 81%. The lower percentages were recorded for samples at higher concentrations of added

Vanadium. These closures did not take into account the amount of Vanadium in the insoluble chloroform fraction. The concentrations of Vanadium in the chloroform insoluble fractions were not quantified as the samples recovered were not sufficient for the trace element analysis. In addition, the nature of this material, which was very powdery, made it liable to static interference during sample preparation hence reduces the accuracy of measurements. Having said that, the concentrations of Vanadium in the insoluble fractions may be calculated, assuming that there was no loss of Vanadium in the gaseous product. Throughout samples A1 to A6, this fraction contained the highest concentration of Vanadium amongst the reactors' products. It was found that the fraction originated from sample A6 contained the highest concentration of Vanadium at 98,104 ppm (10 wt%) whereas sample A1 contained the lowest amount at 6,407 ppm (0.7 wt%). These values are relatively high as the amount recovered for each sample was very low, with the highest at 0.046 g. Nevertheless, this analysis suggests that majority of the Vanadium ended up in the heavy insoluble fractions implying that Vanadium metal complexes concentrated in this heavy carbonaceous compounds that formed through thermal degradation of hydrocarbons on the wall surfaces. For Crude D samples, the closures were calculated from 64% to 88%, with lower percentages recorded for samples with higher concentration of added Vanadium. Crude D produced less amount of chloroform insoluble therefore better recoveries of Vanadium were observed.

The higher amount of volatiles escaped during experiment may contribute towards the higher percentages of Vanadium in the deposits of samples A5, A6, D5 and D6. These samples recorded the highest losses of light hydrocarbon volatiles amongst others, which in turn translated into higher concentrations of Vanadium in the deposit products. As discussed in Section 2.5 and 6.2, the vanadyl porphyrins complexes are associated to the heavier fractions of crude oil which presence at higher concentrations in these samples. The loss of volatiles directly increased the concentration of Vanadium in the heavier deposit products as these porphyrins complexes accumulated in the heavier hydrocarbon components. This is however may be further examined by quantifying the amount of volatiles which allows the recovery of Vanadium in this fraction as well as the chloroform insoluble.

6.2.4. Characterisation of Liquid and Deposit Products by SEC

In order to investigate the molecular weight distribution of the products, each sample was subjected to SEC analysis. Each sample was diluted in NMP/ CHCl_3 solution at 6:1 ratio and filtered through a 1.0 micron PTFE filter disc to separate out the undissolved solids. To investigate the effect of adding vanadyl porphyrins into Crude A, the chromatograms of samples A2 to A6 are plotted against the neat Crude A as shown in Figure 6.11. All chromatograms showed bimodal distribution behaviour, which is typical for a petroleum-derived sample in NMP-based solution. The first peak, appearing at a shorter elution times usually corresponds to materials of larger apparent molecular size and is not resolved by the column as it appears before its exclusion limit. This peak can also be due to rigid 3-D structures that cannot get into the column's porosity. The second, broader peak represents the materials that are resolved by the column porosity and corresponds to molecular compounds of smaller molecular sizes. All chromatograms of A1 to A6 produced similar elution behaviour especially for the retained peak. It was observed that addition of vanadyl porphyrin did not change the nature of chromatograms. Detection of porphyrins via UV-vis had been reported in several literatures but with the presence of complex hydrocarbons, absorption of the metallo-porphyrins is masked by these components [73].

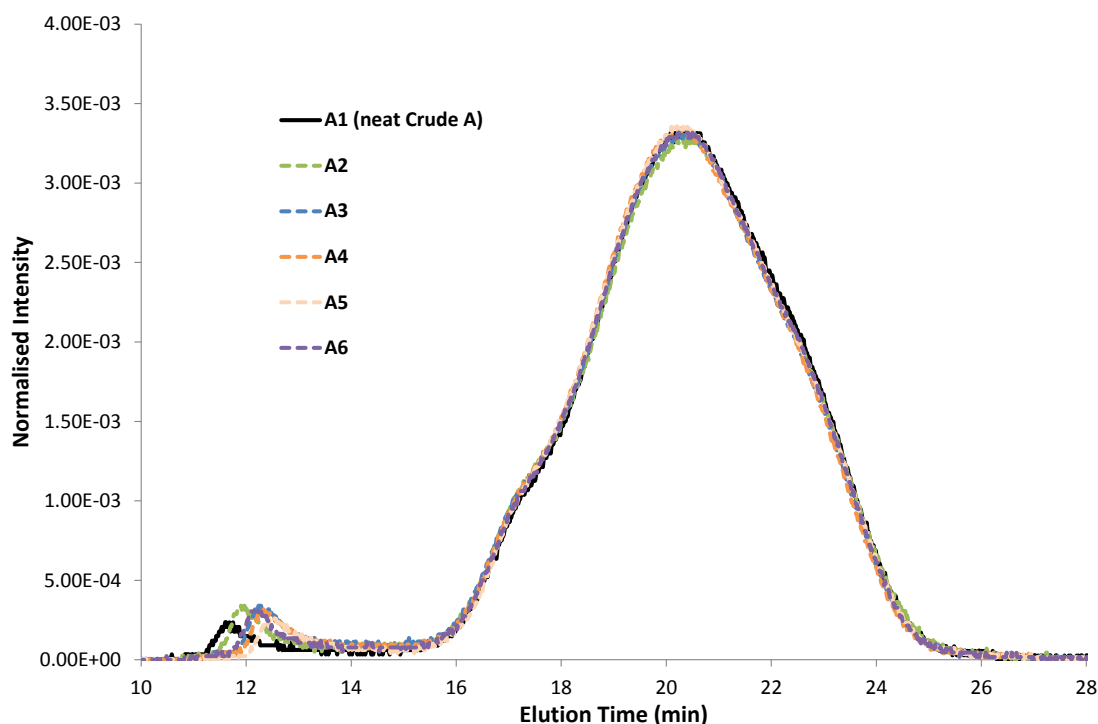


Figure 6.11 Comparison of size exclusion chromatograms of neat Crude A (A1) and sample A2 to A6.

The chromatograms of sample A1 and the resultant liquid and deposit products are presented in Figure 6.12. The elution peaks for these chromatograms fell at three different retention time ranges, but showed considerable overlapping. The retained peak of original sample A1 (neat Crude A) gave a shorter retention time than the two products, which indicated a presence of heavier materials (larger molecular weight) in the sample. The chromatogram of the deposit fraction was expected to give a shift towards heavier molecular weight region. These results however only showed the fraction of products soluble in the NMP/ CHCl_3 mixture. A certain amount of sample that was not soluble in the mobile phase was removed during filtration to avoid damage to the column. This is particularly relevant for the deposit sample as it means that the insoluble heavy coke fraction was not analysed and therefore only a partial molecular weight distribution is represented. It was likely that the insoluble fraction were of larger molecular weight than what was observed by SEC. The fact that about 9% of original samples were loss as volatiles in the reactor might have also contributed towards the shift to shorter retention time for the original A1 sample. Comparison made between the liquid and deposit

chromatograms however showed that the retained peak for the supernatant liquid shifted towards longer elution times, which implied smaller molecular sizes and weight distribution than that of the deposit fraction. This result suggests that the liquid product became lighter due to precipitation of heavier components on the heated tube surface to form a deposit layer on the wall. Similar behaviour was observed for the other samples, A2 to A5 as shown in Figure 6.13 – Figure 6.17.

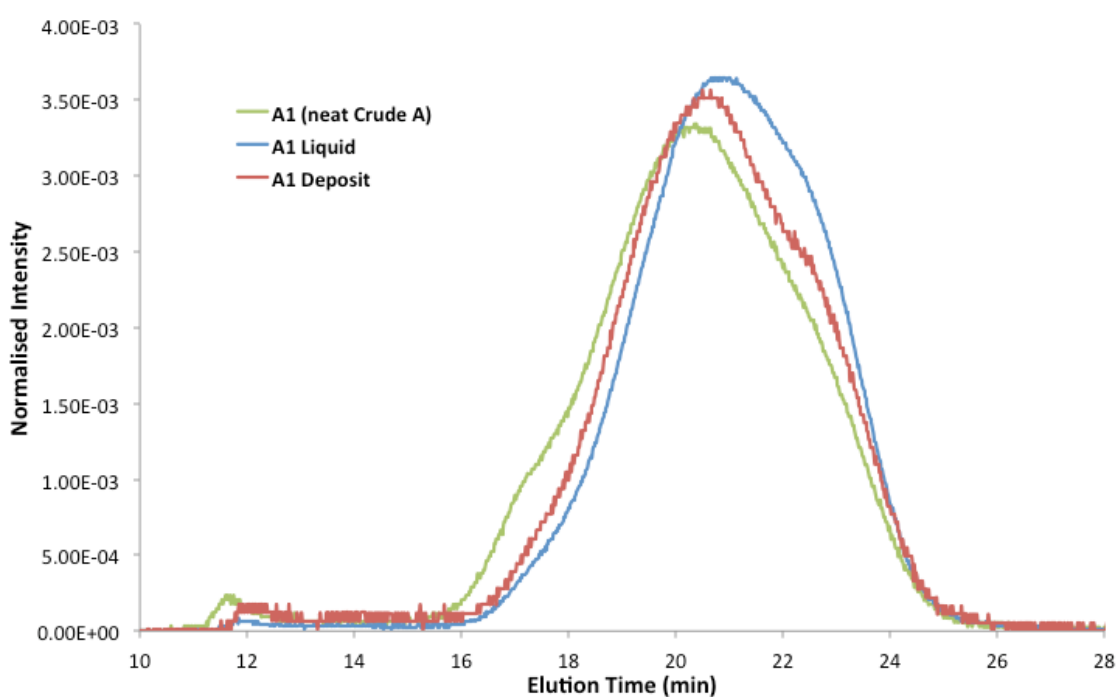


Figure 6.12 Size exclusion chromatograms of Sample A1 and the corresponding liquid and deposit products at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

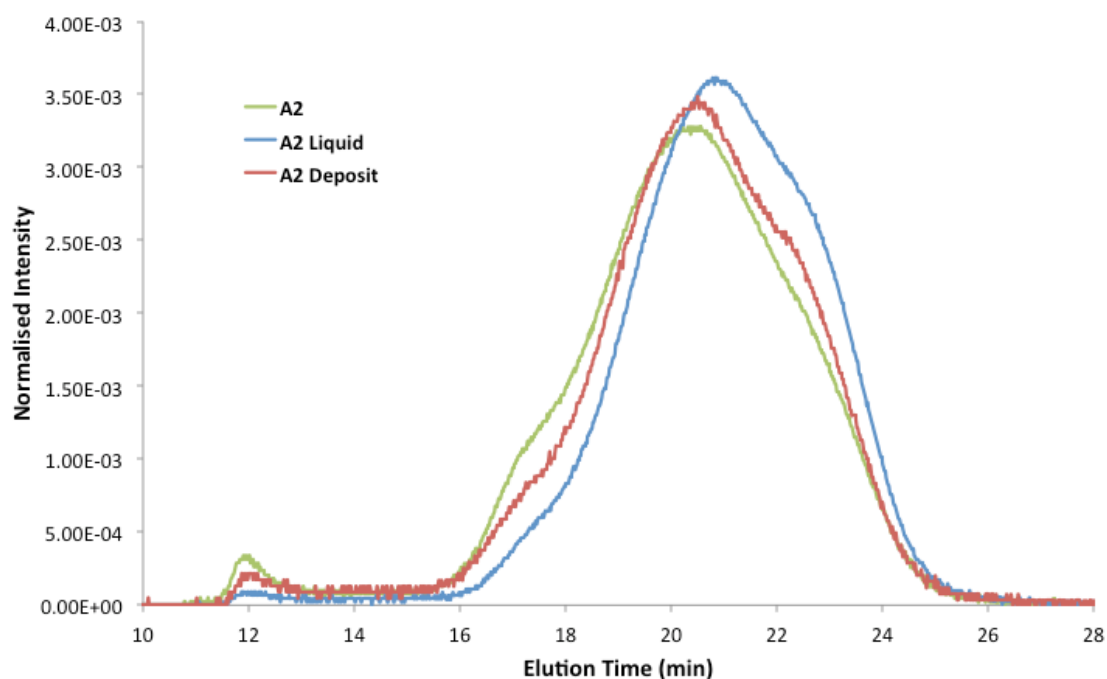


Figure 6.13 Size exclusion chromatograms of Sample A2 and the corresponding liquid and deposit products at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

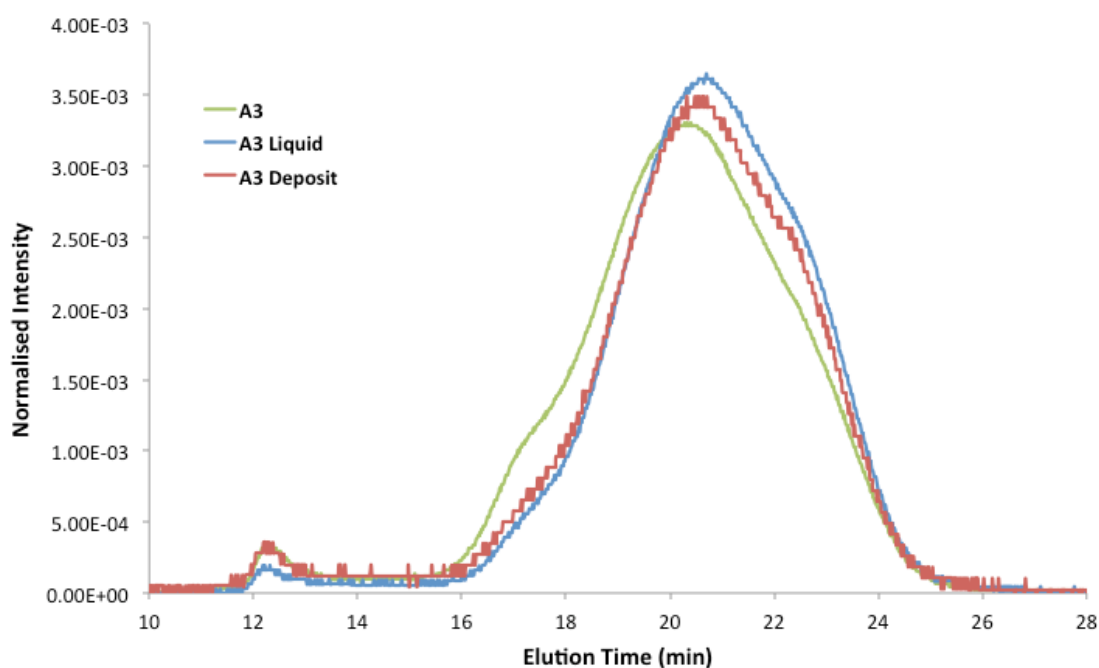


Figure 6.14 Size exclusion chromatograms of Sample A3 and the corresponding liquid and deposit products at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

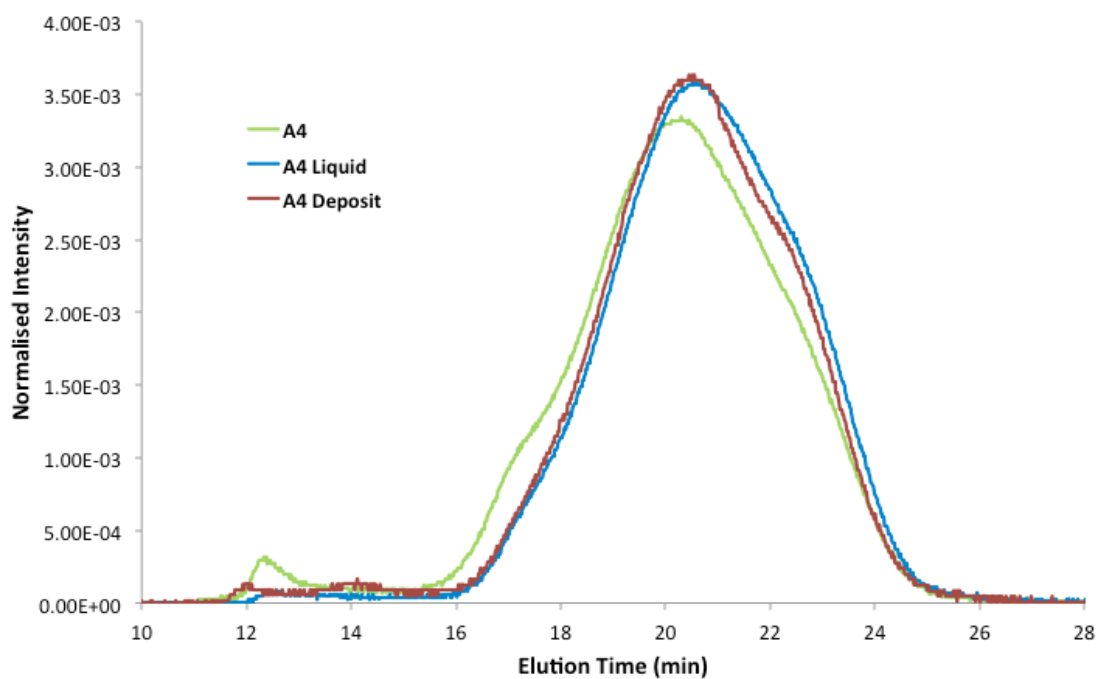


Figure 6.15 Size exclusion chromatograms of Sample A4 and the corresponding liquid and deposit products at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

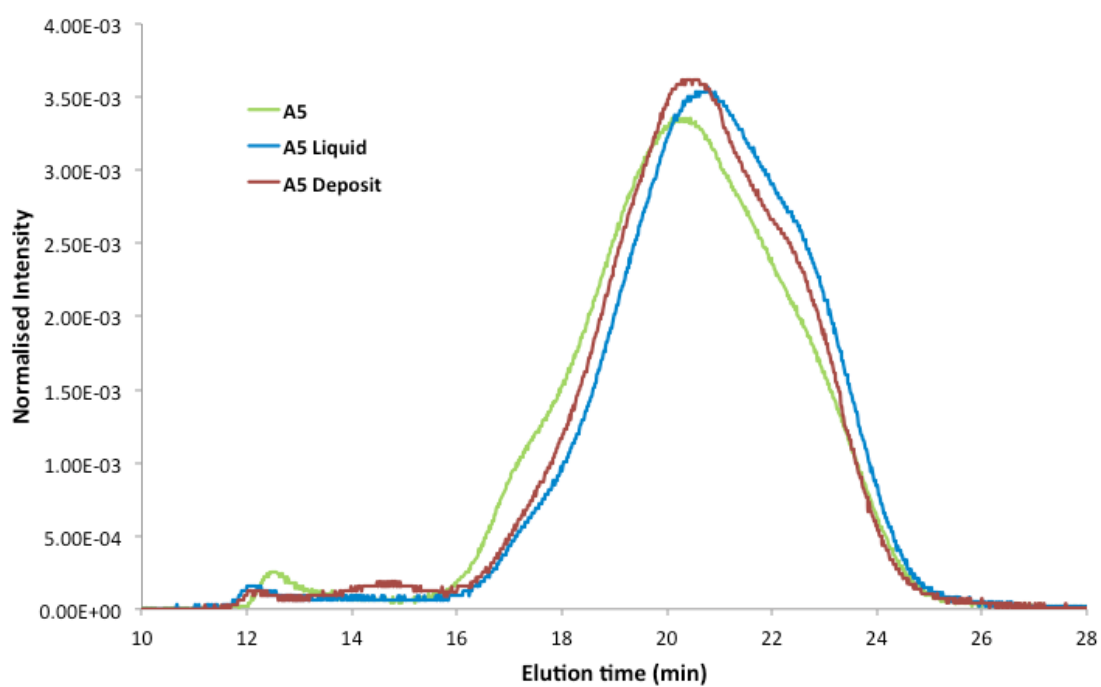


Figure 6.16 Size exclusion chromatograms of Sample A5 and the corresponding liquid and deposit products at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

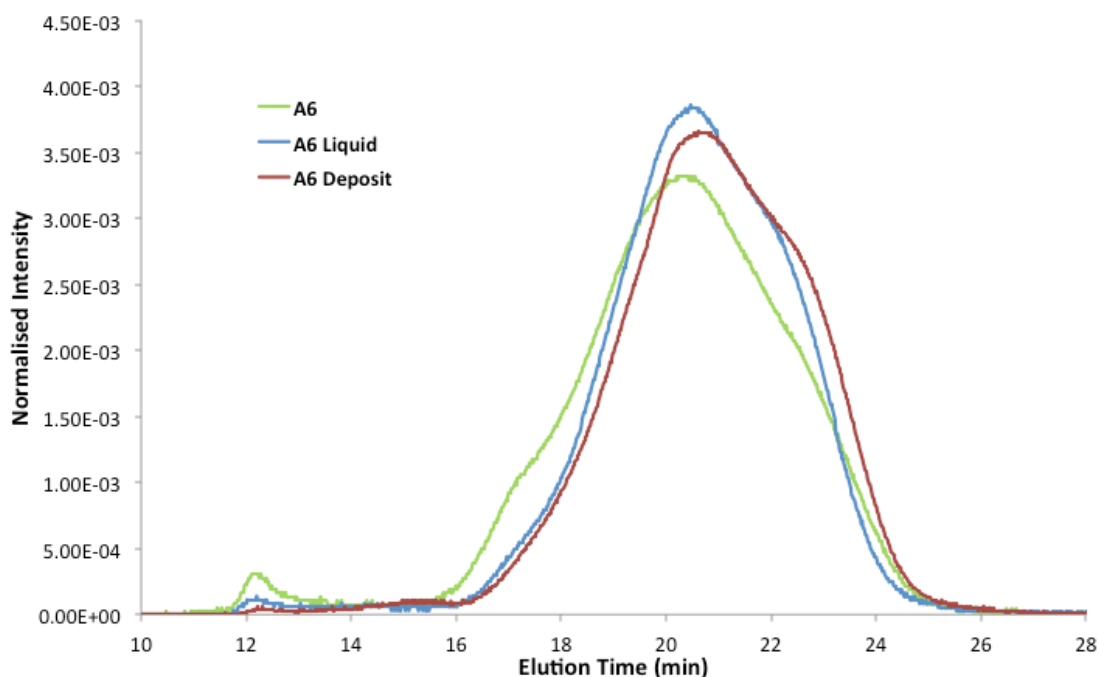


Figure 6.17 Size exclusion chromatograms of Sample A6 and the corresponding liquid and deposit products at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

Chromatograms of sample A6 (Figure 6.17) show a slightly different behaviour than the other samples. As a reminder, this sample contained the highest concentration of added Vanadium amongst the samples, produced the higher amount of deposits and also has the higher concentration of Vanadium in the deposit fraction. The retained peak of the deposit sample shifted towards a longer elution time compared to the one of liquid sample. This indicates that the soluble part of A6 deposits consisted of smaller components than the supernatant liquid, which is against the postulated outcome. This may be explained largely due to the fact that a considerable amount of the deposit sample was not soluble in the NMP/ CHCl_3 solution. To see how the deposit fractions compare against each other, the chromatograms for each sample are plotted together as shown in Figure 6.18. The plots showed a minor difference in the elution time of sample A6 deposits compared to the other chromatograms in which a longer residence time was observed. Chromatograms of the other five samples were comparatively similar, suggesting that the molecular mass of these deposits were within a particular molecular weight distribution range. The deviation of A6 deposit signified two contradicting phenomena; either the deposit was built of smaller molecular weight components or it was made of heavier carbonaceous materials which were not dissolved in the NMP/ CHCl_3 mixture. In

order to investigate the composition of these six deposits, a Simulated Distillation analysis with gas chromatography (GC) was performed. The discussion of this analysis is presented later in the chapter.

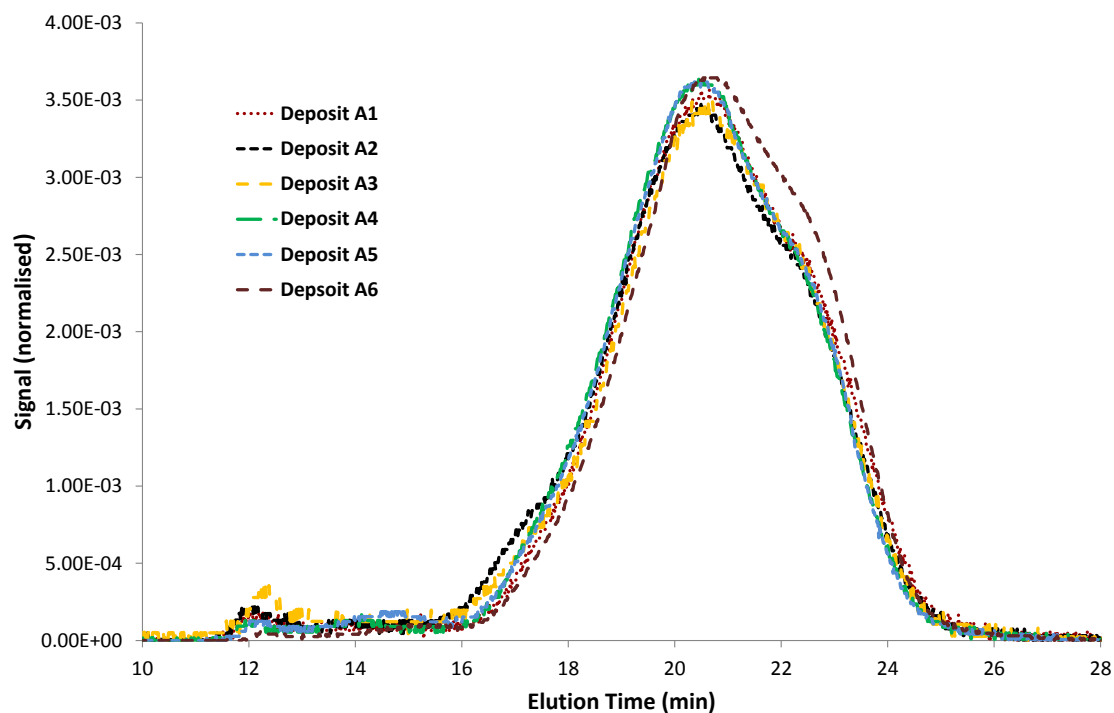


Figure 6.18 Size exclusion chromatograms of deposit products of Sample A1-A6 for experimental run at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

The complementary plots of the liquid products for Sample A1 to A6 are displayed in Figure 6.19. The chromatograms were rather identical with the retained peak shoot up at similar time, at around 16 minutes. The plots of liquid products for the less Vanadium concentrated samples, i.e. A1 and A2, however showed a shift towards longer elution times compared to the rest of the liquid products. These samples seemed to follow a similar elution path, apart from between 21 – 23 minutes, whereas the other chromatograms were observed to be grouped into a different period of slightly earlier elution time. This suggests that liquid products extracted from more Vanadium-concentrated sample contained slightly heavier materials which were possibly originated from components of increasing molecular size in the bulk liquid that were not large enough yet to be deposited onto the heated surface materials. Having said that, the

differences between these chromatograms however were rather small, hence further characterisation shall be made to complement this observation.

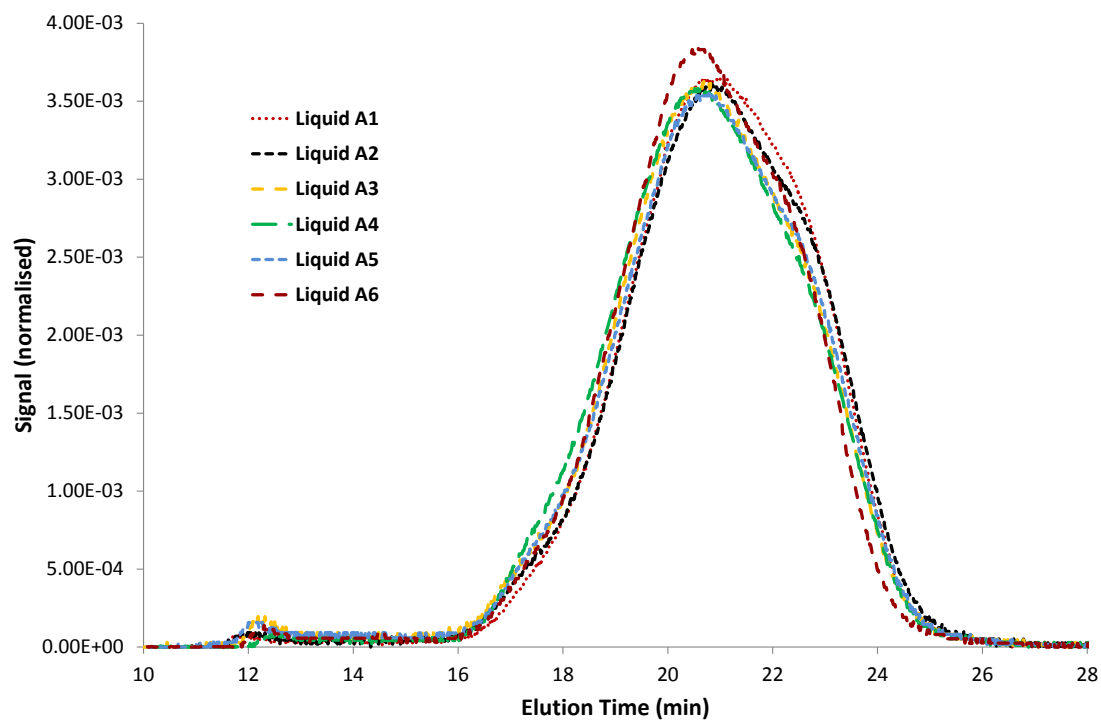


Figure 6.19 Size exclusion chromatograms of liquid products of Sample A1-A6 for experimental run at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

Table 6.7 Summary of the solubility test in 6:1 NMP/CHCl₃ solution for sample A1 to A6 deposit products

Deposit Sample	Solubility (%)
A1	64 ± 3.0
A2	65 ± 2.0
A3	59 ± 4.8
A4	63 ± 3.2
A5	58 ± 4.6
A6	48 ± 3.1

A solubility test was performed in each deposit to quantify how much of these samples are actually analysed in the SEC. Summarily, 3 mg of sample was dissolved in 5 mL of 6:1 NMP/CHCl₃ solution in a small vial and placed in a mixer for 30 minutes. The whole solution was filtered through a 1.0 micron PTFE filter disc and the weight difference before and after filtering was recorded. Table 6.7 shows the summary of the analysis. Apart from deposit of sample A6, the solubility of each deposit was determined at around 60%. Only about 48% of the A6 deposit sample was dissolved in the NMP/CHCl₃ mixture, which suggests that it contained a higher amount of heavier carbonaceous materials that was insoluble in the solvent mixture. This observation supports the SEC analysis of the products of sample A6 in which the chromatogram of the deposit shifted towards the smaller molecular weight range when compared to that of the liquid product. As expected, the sample analysed in SEC only showed the partial picture of the deposit fraction due to this limitation in sample solubility.

Analysis for Crude D and its corresponding products were performed to mirror the analysis of Crude A. Crude D is a lighter oil hence the chromatograms were anticipated to shift towards longer elution time. The chromatograms of liquid fractions of each sample were expected to be eluted earlier than the original samples as some lighter fractions escaped during the experiment. Figure 6.20 shows the chromatograms of samples D1 to D6. The chromatograms of D2, D3 and D4 matched the elution behaviour of neat Crude D. There seemed to be differences in the elution times of sample D5 and D6 compared to the other samples especially around 20 – 22 minutes. These peaks were most likely caused by the presence of vanadyl porphyrins in the two samples. Crude D is a much lighter crude oil compared to Crude A and absorbance of UV light by vanadyl porphyrins were made possible due to the lighter nature of hydrocarbons matrices of the oil.

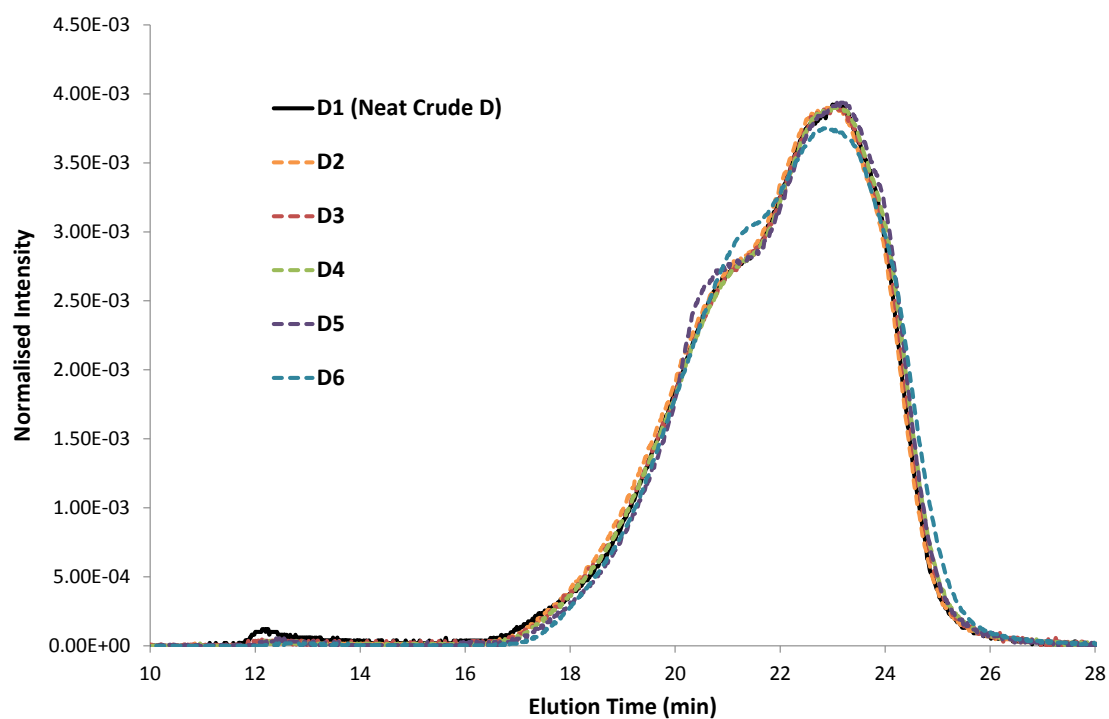


Figure 6.20 Comparisons of size exclusion chromatograms of neat Crude D (D1) and samples D2 to D6.

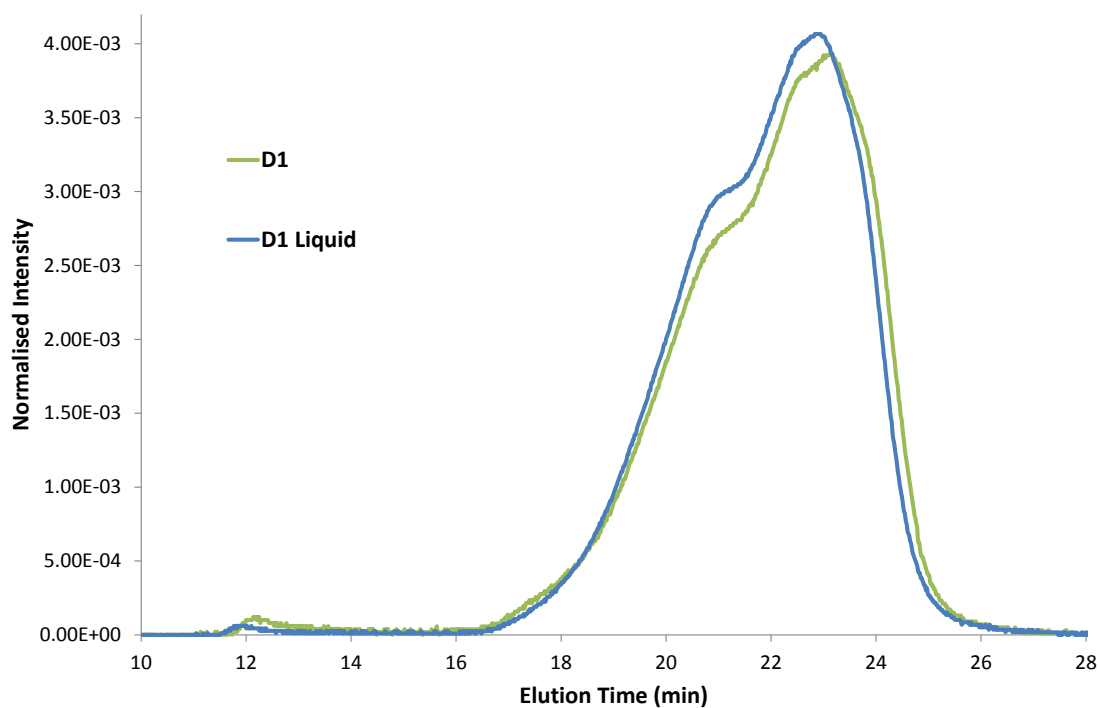


Figure 6.21 Size exclusion chromatograms of Sample D1 and the corresponding liquid product at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

Figure 6.21 shows the chromatograms of sample D1 (neat Crude D) and the resultant liquid product. The retained peak of the original D1 sample gave a longer elution time compared to the supernatant liquid product. The maximum intensity of the supernatant liquid peak was recorded at about 0.5 minute earlier than the peak of the original D1 sample. This suggests the absence of some components in the liquid product which were originally present in the original D1 sample. This could be explained through the escape of some lighter components in the gaseous state after each experiment. The absence of these components has made the average molecular weight of the liquid slightly higher, shown here by the shift of the retained peak towards a shorter retention time. In addition, there could be some thermal reactions to produce a heavier liquid product. Similar observation was seen for D2 and D3 samples as displayed in Figure 6.22 and Figure 6.23. The release of lighter components as gaseous products was observed in both sets of experiments and were clearly represented in the chromatograms of the liquid products against the original D2 and D3 samples.

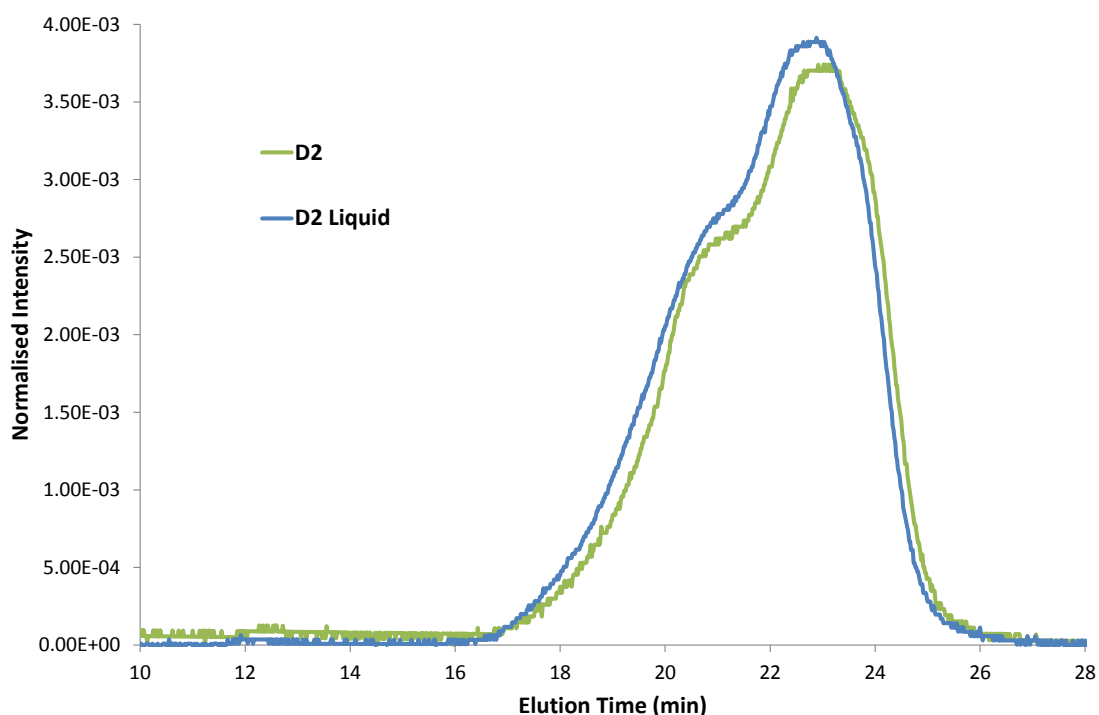


Figure 6.22 Size exclusion chromatograms of Sample D2 and the corresponding liquid product at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

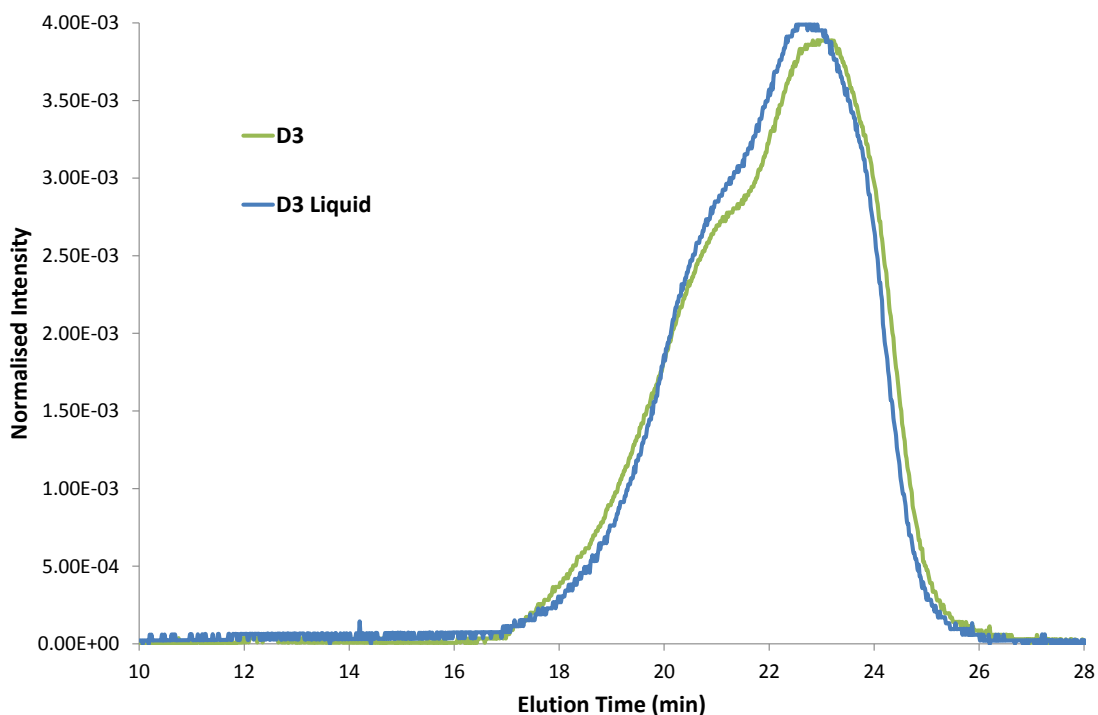


Figure 6.23 Size exclusion chromatograms of Sample D3 and the corresponding liquid product at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

Contrary to samples D1 to D3, samples D4, D5 and D6 produced some deposits at similar operating conditions. As discussed earlier in the chapter, these deposit fractions were made of lighter fractions than deposits of Crude A in terms of its solubility behaviour towards CHCl_3/NMP solvent mixture, hence higher percentages of Crude D deposits were analysed by the column. The chromatograms of these deposits were expected to produce shifts towards heavier molecular weight range. The solubility fraction in the solvent mixture however was difficult to quantify due to the small amount of sample produced from the reactor and the relatively minute fraction of insoluble materials that may be extracted from the syringe filter. This would lead to large amount of statistical and experimental errors in the analysis. The SEC chromatograms of the deposit fractions relative to their respective liquid and original sample fractions are presented in Figure 6.24 to 6.26. The retained peak of each deposit gave comparatively shorter elution time compared to the chromatograms of both liquid fractions and the original samples. This translates into the proposition that the deposits contained components of larger molecular weight compared to the liquid products. Certain amount of the oil constituents agglomerated and formed a layer of deposit at the heated wall which was proven to be a heavier fraction than the rest of the bulk supernatant liquid.

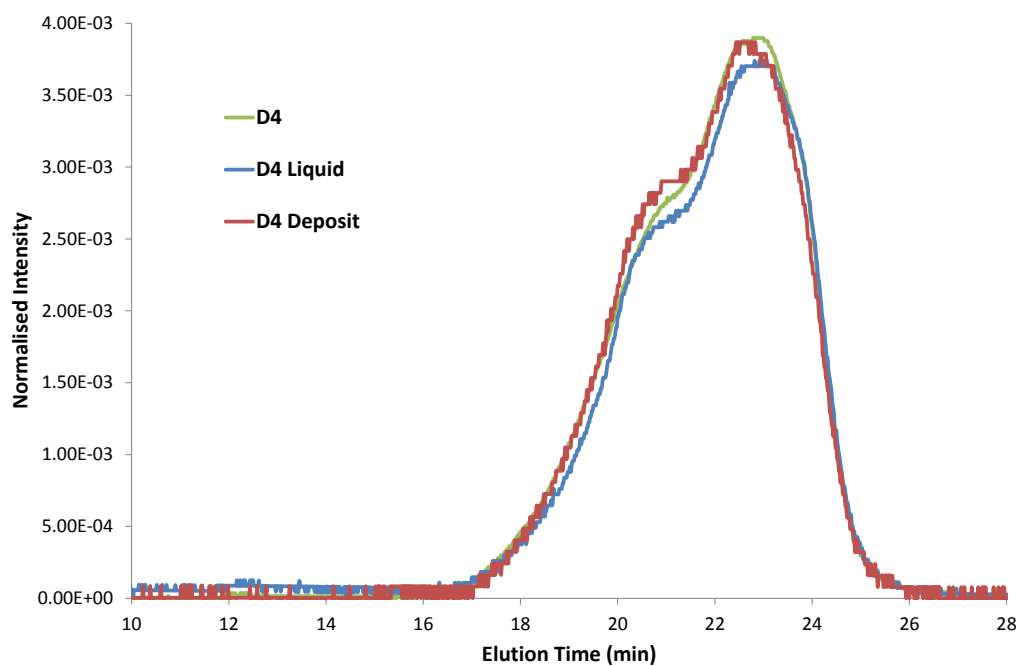


Figure 6.24 Size exclusion chromatograms of Sample D4 and the corresponding liquid and deposit products at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

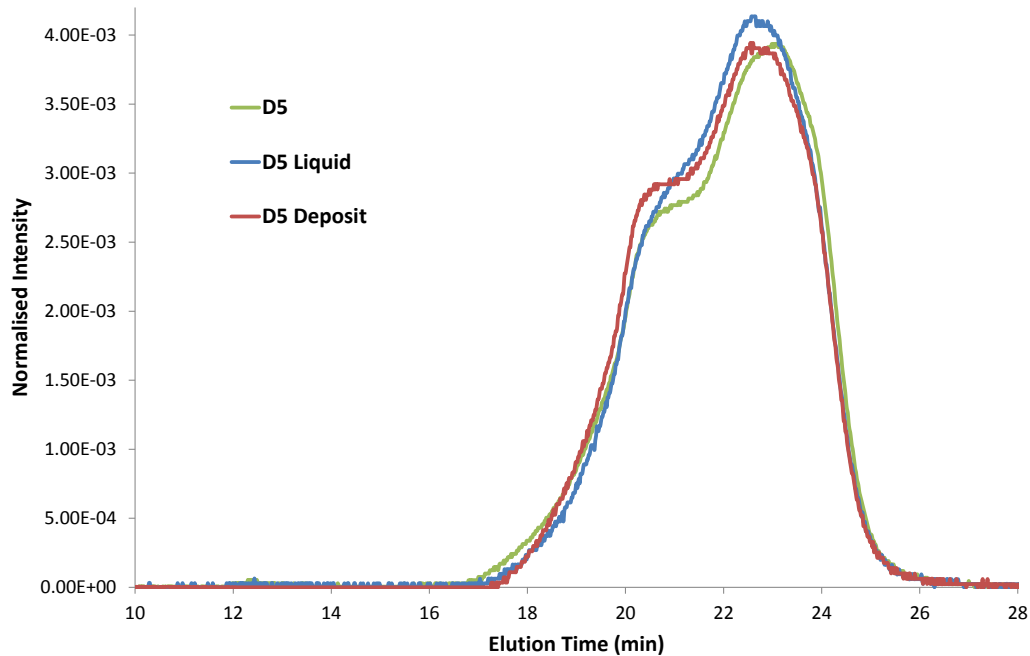


Figure 6.25 Size exclusion chromatograms of Sample D5 and the corresponding liquid and deposit products at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

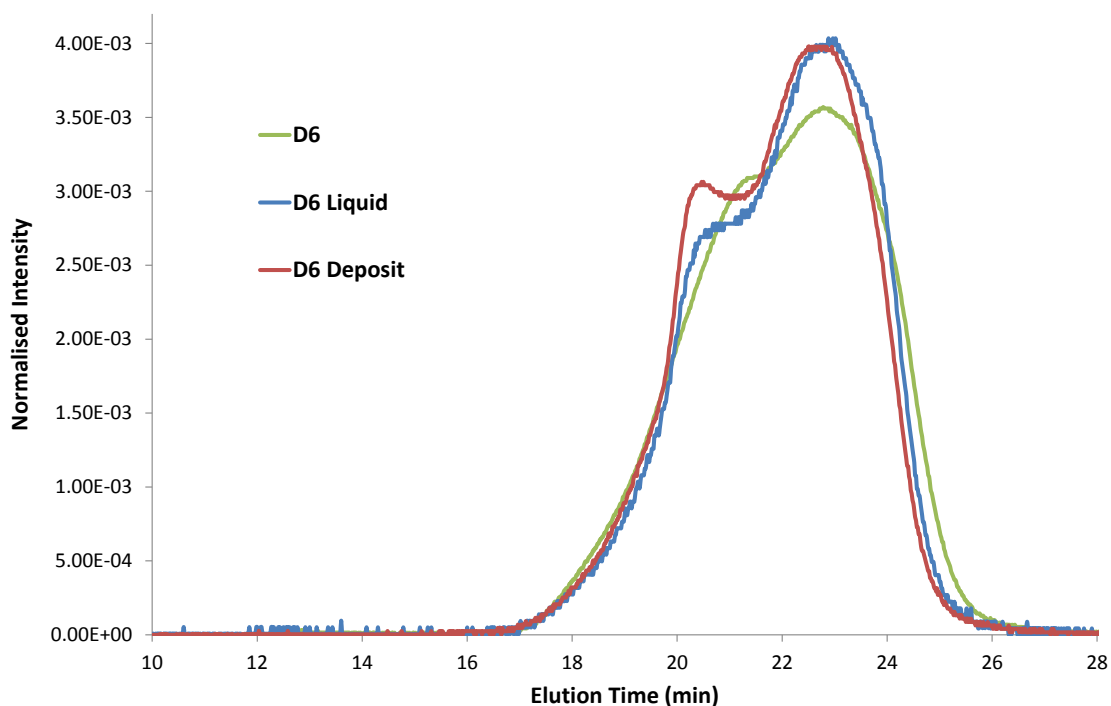


Figure 6.26 Size exclusion chromatograms of Sample D6 and the corresponding liquid and deposit products at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

It is interesting to examine how the deposits compare to each other in an attempt to see the effect of the added Vanadium on the molecular weight distribution of these fractions. In Figure 6.26, the chromatogram of D6 deposit fraction produced a distinct second peak at around 20 minutes of elution time. This peak was also seen in the chromatogram of the liquid product of the same sample albeit at a lower intensity. In fact, the chromatogram of D5 deposit in Figure 6.25 showed the extra shoulder peak at around the same elution time. The small peak however was absent in the chromatogram of D4 deposit sample which contained less concentration of added Vanadium. As discussed earlier, the increment in the intensity of the peak was most likely contributed by the increased concentration of vanadyl porphyrin in the original crude oil. The comparison between the chromatograms of the three deposit fractions are presented in Figure 6.27, which clearly shows an increased intensity of the shoulder peak as the concentration of added Vanadium in the deposits increased.

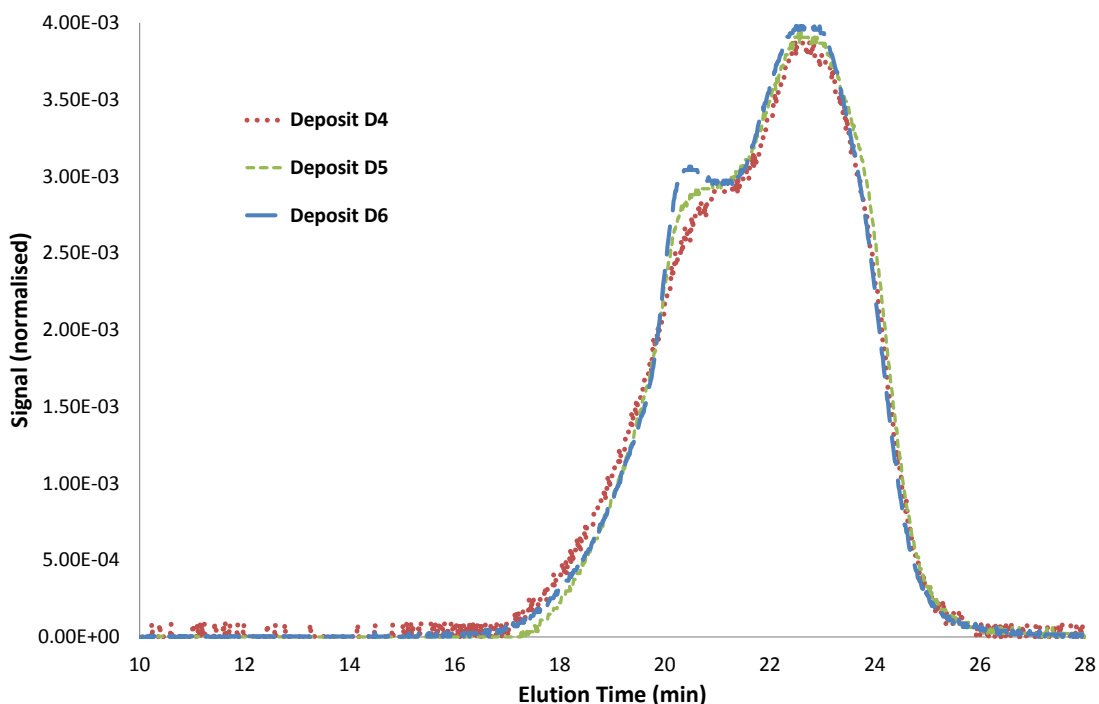


Figure 6.27 Size exclusion chromatograms of deposit products of sample D4, D5 and D6 for experimental runs at 350 °C and 10 bar for 48 hour. Detection is via UV-A at 300 nm.

6.2.5. Characterisation of Liquid and Deposit Products by UVF

To investigate the change in the molecular structure of the crude oil samples after heating, analysis through UV-fluorescence spectroscopy was performed. The changes in the structure, particularly in the sizes of fused aromatic rings systems, may be detected via the synchronous spectra of the fluoresced UV light. The main discussion that follows involves investigation on the difference of spectra from the products and the original sample.

Based on the SEC results, the fluorescence spectra for deposit samples were expected to produce characteristics of larger aromatic ring structures compare to the liquid products. The spectra for neat Crude A, sample A1 and its corresponding products are shown in Figure 6.28. These spectra showed marked differences between the three samples in terms of the aromatic chromophores of the fractions. The deposit appeared to have the larger aromatic systems as its spectrum shifted towards longer wavelengths compared to the other two fractions. Moreover, the normalised peak of the deposit fraction showed

lower intensity at small aromatic chromophores, i.e. at 360 nm, than to the liquid and original fractions, which suggests that these components most probably underwent condensation reactions to form larger aromatic ring systems. The liquid product contained smaller aromatic ring systems than the original sample, which can be explained through the migration of large rings towards the deposit as well as, to certain degree, thermal cracking of molecules forming smaller components. This observation is in agreement with the result of SEC in which heavier molecular fractions are mainly concentrated in the deposit product.

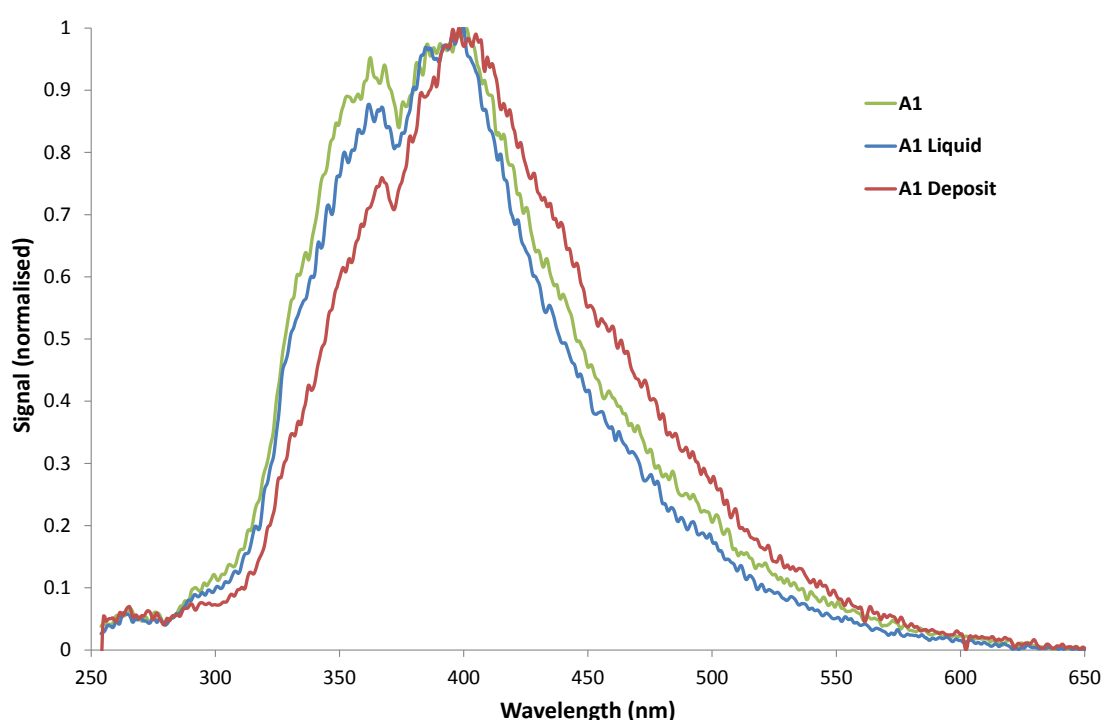


Figure 6.28 Synchronous UV-Fluorescence spectra of sample A1 and its corresponding liquid and deposit fractions.

The normalised synchronous spectra of samples A2, A3, A4 and A5 gave similar pattern to that of A1 sample. The spectra for samples A2 and A5 are shown in Figure 6.29 and Figure 6.30. The spectra for both deposit products gave a shift towards longer wavelengths suggesting that the fractions were made up of larger aromatic rings. Both liquid products shown here fluoresced at shorter wavelengths in comparison to the original crude oil samples. This indicates that the supernatant liquids contained smaller polynuclear aromatic systems. This is consistent with the results of SEC analysis in which smaller molecular weight materials were observed for the liquid products for all ranges of Vanadium concentration in Crude A.

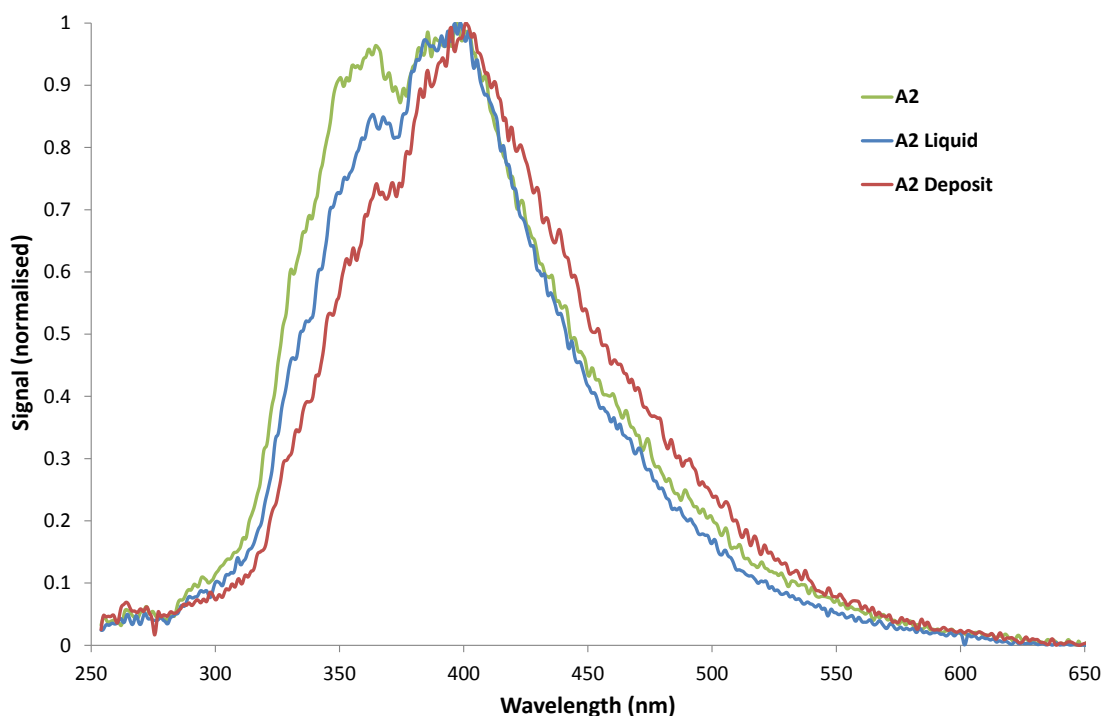


Figure 6.29 Synchronous UV-Fluorescence spectra of sample A2 and its corresponding liquid and deposit fractions.

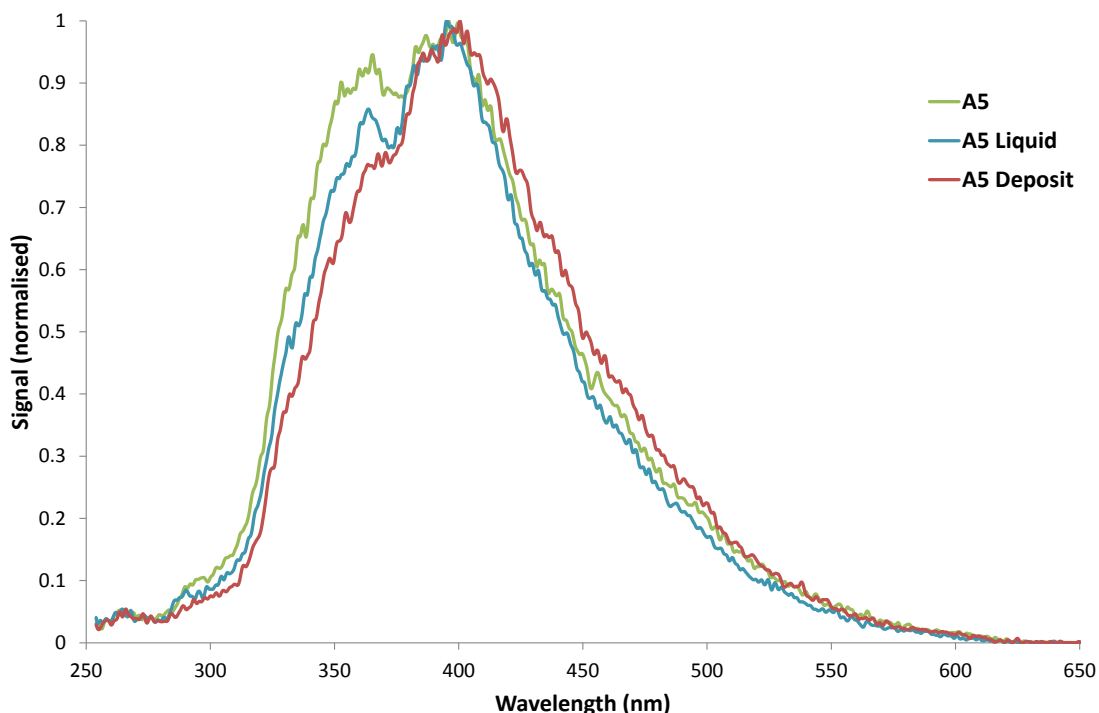


Figure 6.30 Synchronous UV-Fluorescence spectra of sample A5 and its corresponding liquid and deposit fractions.

On the other hand, comparison between the spectra of liquid products for sample A1 to A6, as shown in Figure 6.31, showed no significant differences or any qualitative distinctions between the samples. In contrast, synchronous spectra of the deposit products gave a certain trend relative to the concentration of added vanadyl porphyrin as portrayed in Figure 6.32. A6 deposit, which contained the higher amount of Vanadium, fluoresced at the shorter range of wavelength whereas the deposit of original crude, A1 shifted towards the longest wavelength suggesting that smaller aromatic chromophores formed in the A6 deposit. This observation may be clarified through the partial solubility of the deposit in chloroform. As discussed in the earlier part of this chapter, only a certain amount of deposits were soluble in chloroform with A6 being the least soluble fraction. The spectra shown here represent to a certain degree the conjugated aromatic ring systems in the samples. Nevertheless, the results are in agreement with the molecular weight analysis in the SEC in the sense that smaller aromatic rings corresponds to the smaller molecular mass distribution.

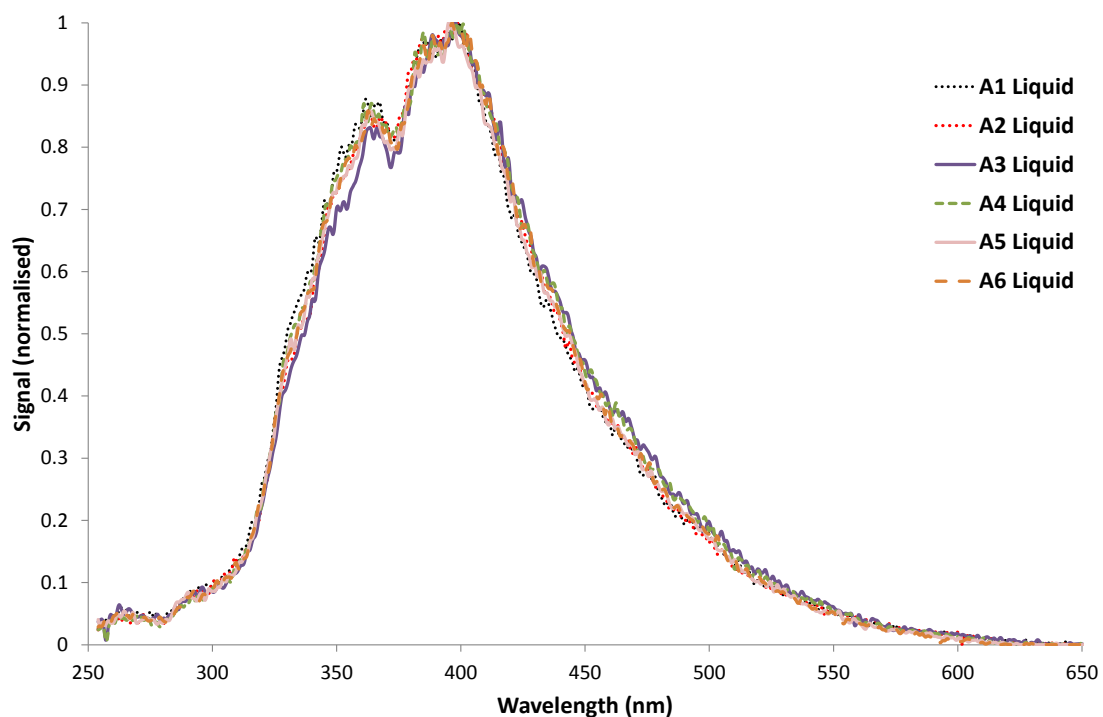


Figure 6.31 Synchronous UV-Fluorescence spectra of liquid products for sample A1 to A6

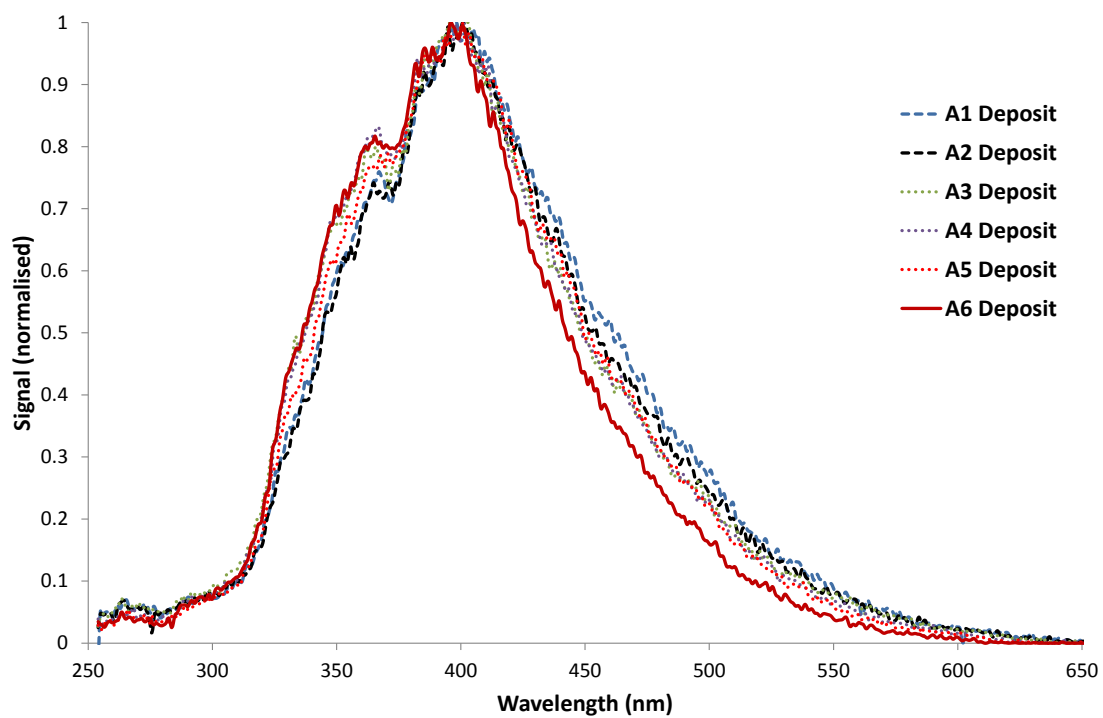


Figure 6.32 Synchronous UV-Fluorescence spectra of deposit products for sample A1 to A6.

Mirror analysis was performed for Crude D samples at similar concentration levels of added vanadyl porphyrin. The spectra of native Crude D and its liquid product are shown in Figure 6.33. The spectrum of Crude D appeared to be having several more peaks than those of Crude A. The peaks at 300, 325 and 350 nm, which were absent in Crude A, suggests that Crude D samples contained a higher concentration of smaller aromatic chromophores. Crude D and its liquid product were qualitatively similar in their aromatic components distribution with no apparent difference in terms of the height of the peaks and their fluorescence behaviour. Crude D however seems to fluoresce more between 400 – 500 nm suggesting the presence of bigger aromatic chromophores. Similar behaviour was observed for Sample D2 and D3 where both original crude oil and liquid products produced comparable spectra with no significant difference in their fluorescence activities. Results of Sample D4, D5 and D6 however showed relative distinction amongst the unheated sample and their respective liquid and deposit products. The three samples gave similar fluorescence behaviour with the most significant wavelength shift occurring for the deposit products, shown in Figure 6.34 for Sample D6.

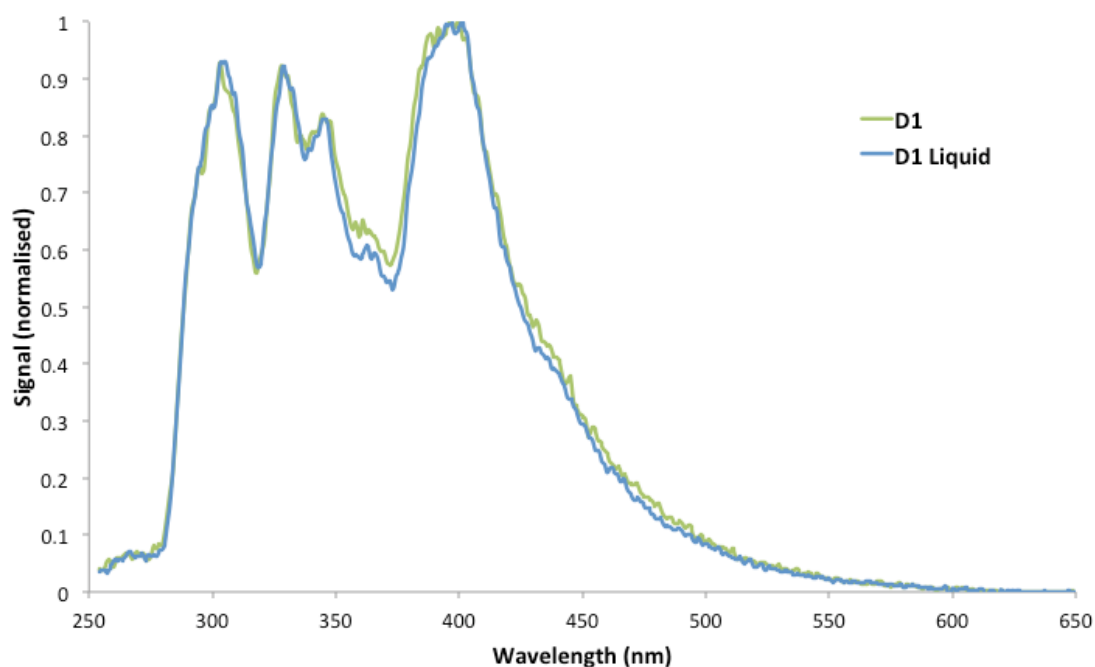


Figure 6.33 Synchronous UV-Fluorescence spectra of sample D1 and its corresponding liquid fraction.

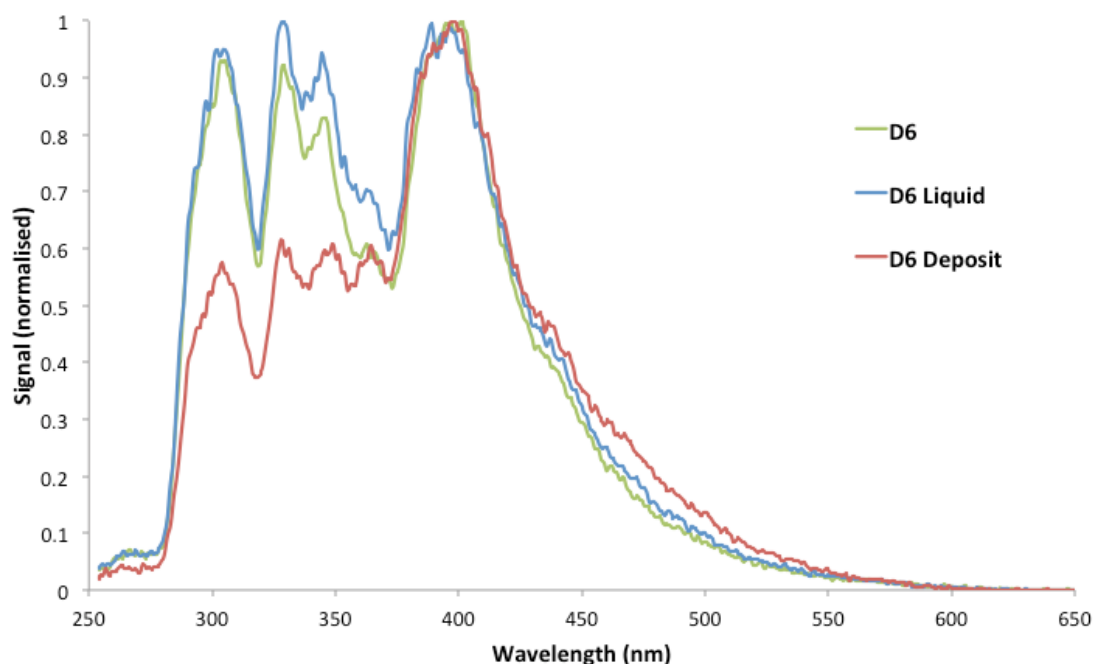


Figure 6.34 Synchronous UV-Fluorescence spectra of sample D6 and its corresponding liquid fraction and deposit fractions.

The three spectra produced peaks at similar wavelength throughout. At shorter wavelength, between 250 nm and 375 nm, the liquid product gave the higher signal values suggesting a bigger distribution of smaller aromatic chromophores. Whereas at longer wavelength, the spectra for deposit product gave the highest intensity corresponding to a larger range of bigger aromatic chromophores. Taking into account the results of SEC, which gave biggest molecular weight distribution in the deposit fraction, this results further support the deduction that bigger conjugated aromatic chromophores were produced in the deposit sample and correspond to the heavier part of the product distributions.

The spectra of each deposit product is plotted against each other and displayed in Figure 6.35. Deposit D6 contained larger molecular weight distribution hence was expected to produce larger molecular aromatic ring structures. The spectra of the deposit, which contained the higher concentration of Vanadium, as presumed, fluoresced towards longer wavelength suggesting that it comprised of bigger conjugated aromatic chromophore systems than the other two deposit products. This observation reinforced the findings in the analysis of Crude A that as the concentration of Vanadium metal increased, the

formation and accumulation of bigger aromatic chromophores in the deposit product increased. Again, the result is in agreement with the observation in SEC analysis in which D6 deposits shows larger molecular weight distribution that might have been contributed by the larger aromatic ring systems in this particular sample.

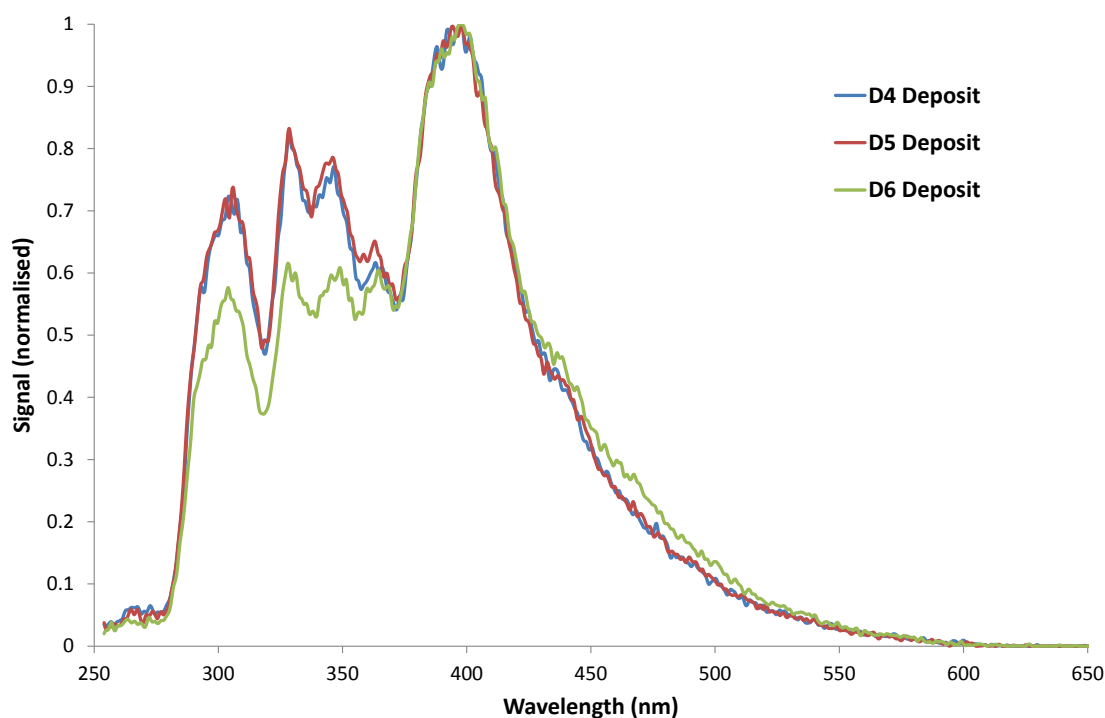


Figure 6.35 Synchronous UV-Fluorescence spectra of deposit products for sample D4, D5 and D6.

6.2.6. Characterisation of Liquid and Deposit Products by GC

The samples were subjected to Gas Chromatography (GC) analysis to further examine their molecular characteristics. As discussed in Chapter 2, GC is normally chosen as a method to analyse hydrocarbons components and their derivatives of up to 400 amu [100]. GC analysis was performed largely to investigate the constituents and the relative volatility of each sample, and also to support the analytical findings from the other characterisation instrumentations. It is important to stress here that, as in the previous analysis, the results of GC are used as a comparative analysis between the products and their original samples. In this analysis, simulated distillation analysis was performed and

the results were categorised into the fractional distillation composition as a mean of quantifying the lights and heavies in the samples. A gas oil was used as a calibration standard with compositional boiling point ranges from 115 °C to 475 °C. Two runs were conducted for each sample in which around 2-5% deviations were recorded in between the runs.

Because of the limitation posed by GC, only a certain amount of these samples were analysed. The amount analysed can be quantified by measuring the relative difference of the area under the chromatograms between the sample and the standard gas oil. It was predicted that only certain percentages of the samples would be analysed by the column especially the heavier deposit products. Figure 6.36 shows the percentages of these samples resolved by the GC column. To ensure consistency amongst the different analytical techniques, all samples were diluted in chloroform. About 20.2% of the original Crude A was detected by the GC. The liquid products contained higher concentrations of smaller molecular weight components in comparison to the original crude oil, as suggested by the higher percentages of sample being eluted through the GC column. This is in agreement with the SEC results presented earlier in the chapter. In general, more of the liquid products were analysed by the column as compared to the deposit products, the highest being the liquid product of A1 i.e. the product of original Crude A. The percentages then remained at a constant value as the concentration of vanadyl porphyrin increased at about 21%. On the other hand, the percentage of analysed sample of the deposit fraction decreased as the concentration of added Vanadium increased. This is particularly the case for A6 sample in which only 8% of the sample was within the detection capacity of the GC. Comparing with the SEC result, the A6 deposit gave the lighter molecular weight distribution amongst the deposit products. The GC results subsequently support the observation that a certain amount of A6 deposits, particularly the heavy fraction was not dissolved in chloroform, and therefore had not been analysed.

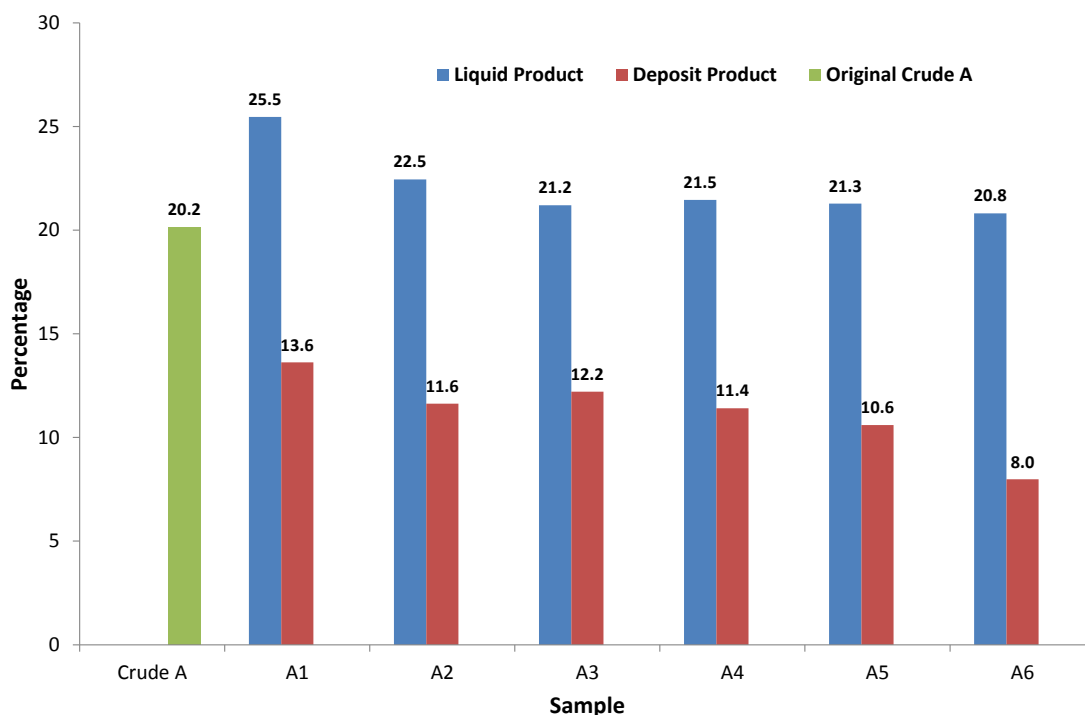


Figure 6.36 Percentages of Crude A, liquid and deposits products of A1 to A6 analysed in GC.

To further analyse the GC-resolved fraction of the samples, the result is characterised into its distillation fraction. Figure 6.37 shows these fractions, namely naphtas, kerosene, diesel, fuel oils and residue, for each liquid product and the original Crude A. Crude A gave the higher percentage of diesel at 26% and a rather uniform value for the other fractions. The liquid product of Crude A i.e. the A1 liquid sample gave a higher percentage of naphta fraction and a lower values of residue compared to its native oil. The same result was observed for liquid product of A2. The rest of liquid products however gave a different fractional polarity in which higher percentages of heavier fractions and lower percentages of lighter fragments were observed. Again, as observed by the SEC analysis, the more vanadium-concentrated samples tend to have higher percentages of heavier molecular weight components. The agreement between these two independent analyses showed the contribution of Vanadium towards production of heavier components in the fouling products.

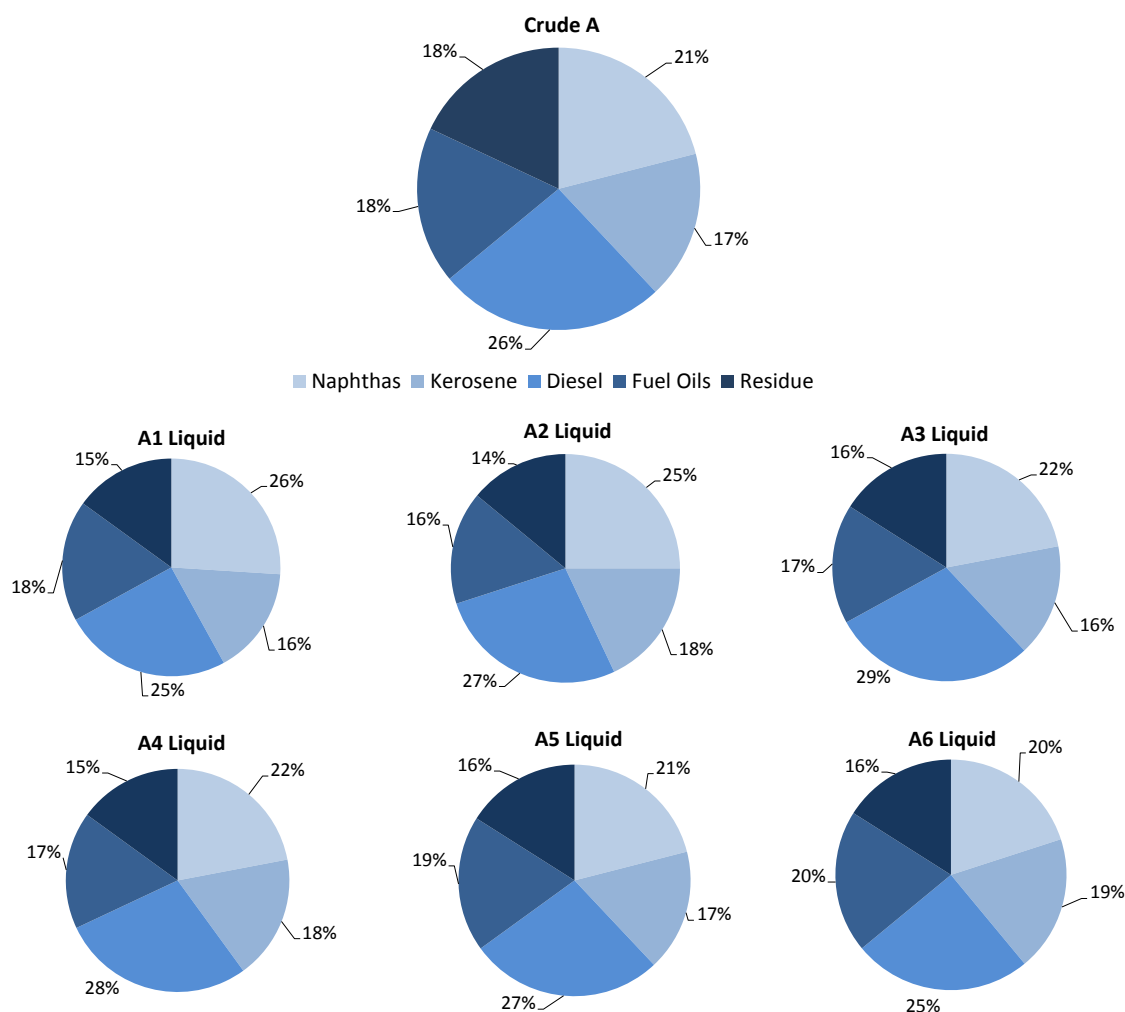


Figure 6.37 Distillation fractions of Crude A and the liquid products of sample A1 to A6 as analysed by GC.

Similar analysis was performed for the deposit samples as shown in Figure 6.38. Noticeably, the light fractions in all samples were at lower percentages compared to their counterparts in the liquid products. The heavier residue fractions on the other hand were recorded at higher percentages than those of the liquid products. Even though only up to 14% of these deposits samples was analysed in GC, the results suggest that the deposits were largely made up of heavier molecular compounds relative to the liquid products. Comparison made amongst the deposit samples meanwhile shows relative similarity in the fractional distribution amongst sample A1 to A5. Sample A6 however yielded a higher naphtha fraction and a lower residue fraction. Only about 8% of A6 deposit was analysed by GC, which suggests that a large fraction of the sample consists of high

molecular weight components. This observation is in agreement with the result of SEC in which A6 deposit sample gave the smaller molecular weight distribution amongst the deposit products.

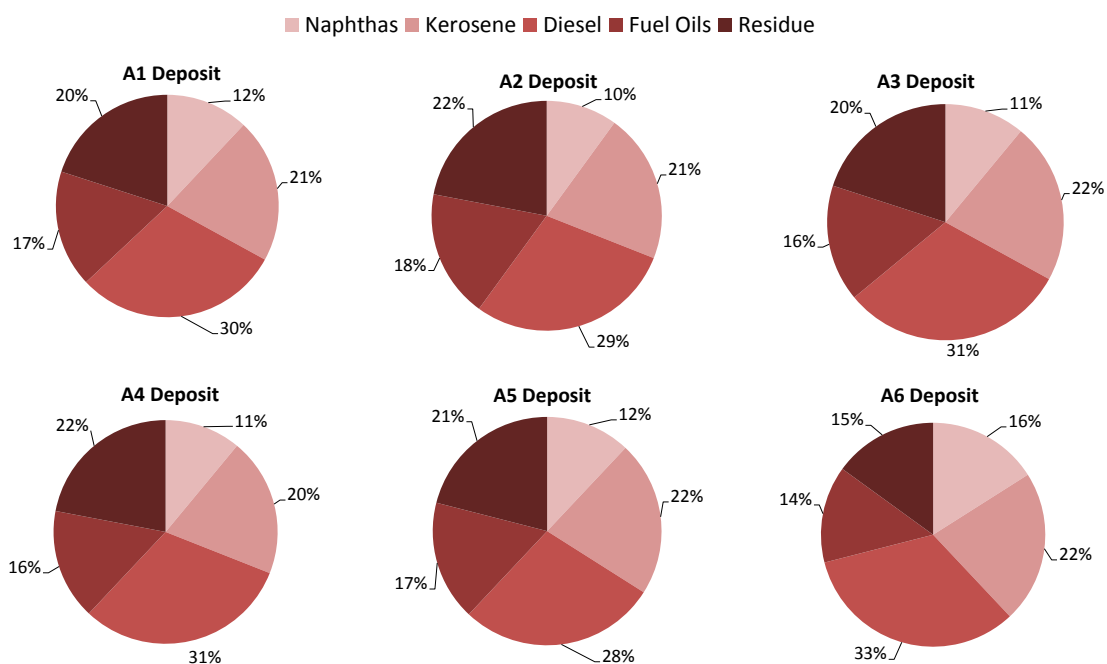


Figure 6.38 Distillation fractions of the deposit products of sample A1 to A6 as analysed by GC

Analysis for Crude D samples was conducted in a similar manner. A major difference between the results of the two crude oil samples was the percentages of analysed sample in GC. Being the lighter oil, Crude D samples gave higher percentages to that of Crude A as shown in Figure 6.39. Up to 49% of the sample was resolved by the GC column as opposed to about 26% for Crude A samples. About 33% of native Crude D was analysed by GC and is slightly higher than the amount quantified for the liquid products of sample D1 (30%) and D2 (31%). This could be due to the loss of some lighter components as gaseous products in the reactor which resulted in heavier supernatant liquid products. Barring sample D3, similar behaviours were observed in the SEC analysis of these two samples - the liquid products shifted towards shorter elution times, i.e. heavier molecular weight distributions. On the other hand, liquid products for sample D4 onwards gave

higher analysed percentages compares to the native Crude D. This is somewhat anticipated as the heavier components of Crude D are believed to be accumulated in the resultant deposit products. As the concentration of Vanadium in the oil increased, the quantity of liquid being analysed by the GC column increased with the opposite observed in the deposit products.

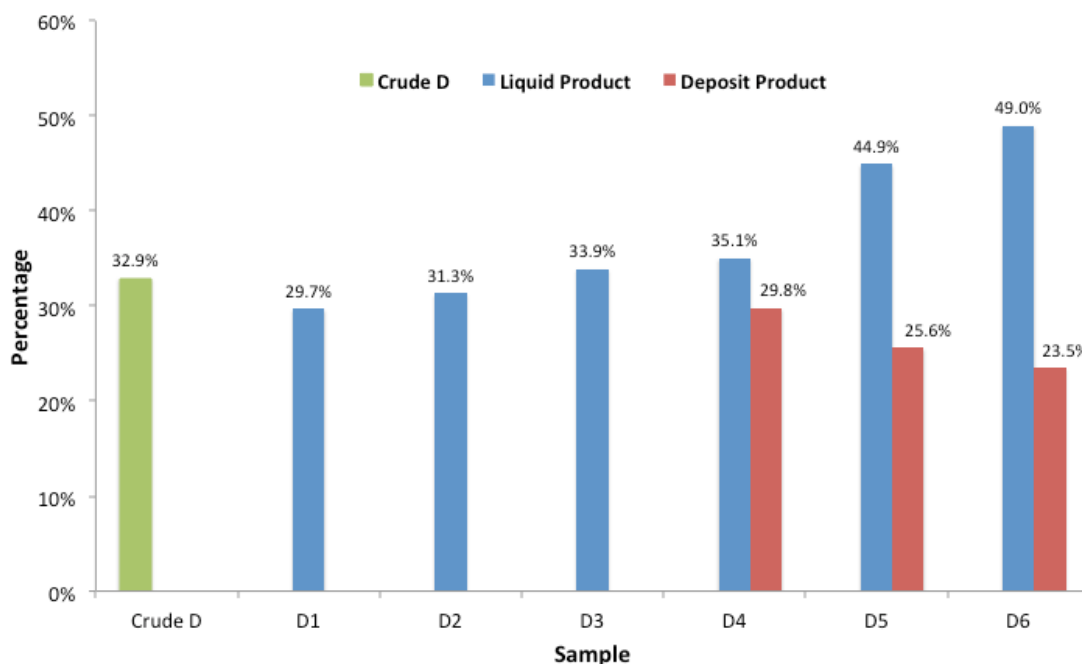


Figure 6.39 Percentages of Crude D, liquid and deposits products of D1 to D6 analysed in GC.

The distillation fractions of each liquid product of Crude D are shown in Figure 6.40. Sample D1 up to D4 showed similar fractional percentages with the original Crude D sample. Whereas for sample D5 and especially sample D6, higher percentages of naphthas fractions were observed. Sample D6 in particular recorded lower percentages of heavier fractions i.e. fuel oils and residues, and higher percentages of lighter fractions i.e. naphthas and kerosene. This observation to a certain extent provides an explanation towards the higher percentages of liquid product of D6 being analysed by the GC column. It contained a higher quantity of lighter products as oppose to the rest of the liquid products.

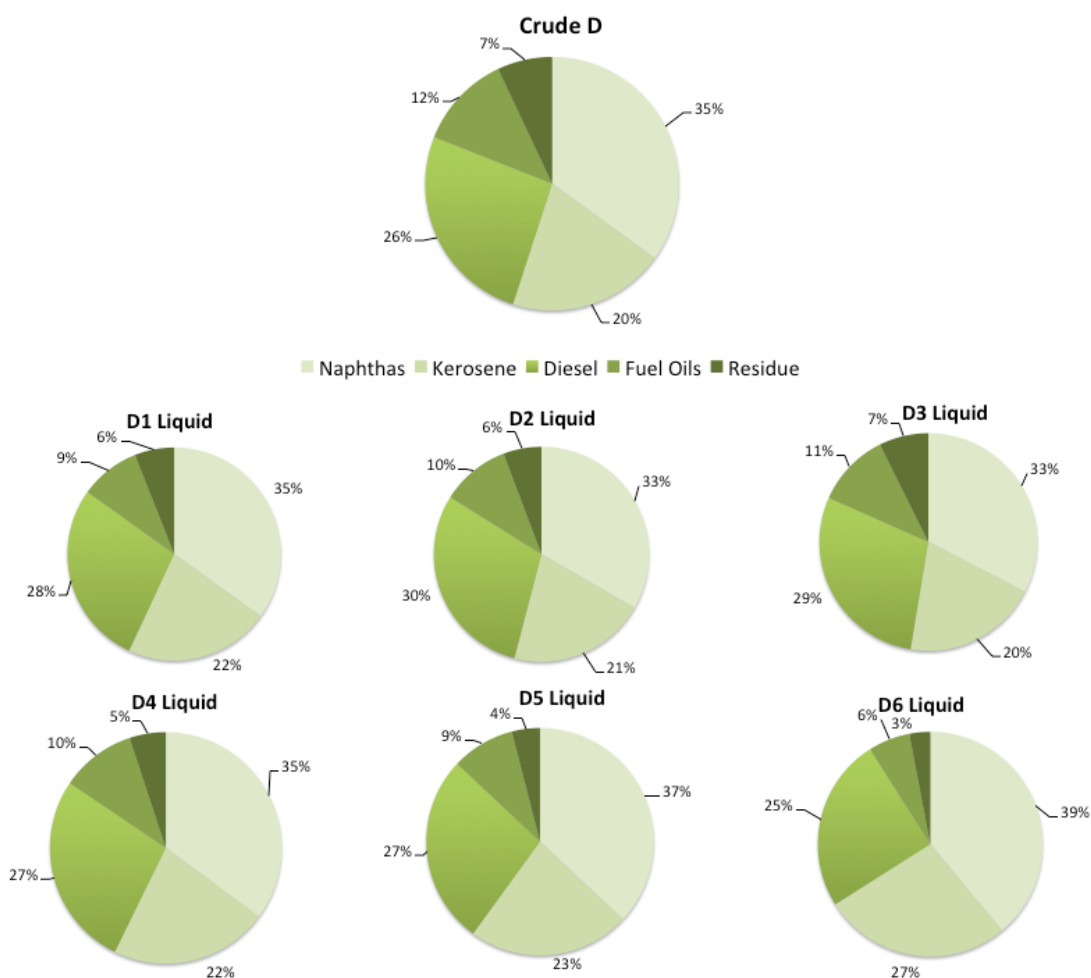


Figure 6.40 Distillation fractions of Crude D and the liquid products of sample D1 to D6 as analysed by GC.

The fractional distribution of Crude D deposit products is presented in Figure 6.41. The three samples show significant differences in each fraction especially for the naphthas, kerosene and diesel fractions. D6 deposit sample recorded 29% of naphthas and kerosene as opposed to 54% and 49% for sample D4 and D5 respectively. The amount of heavier fractions i.e. fuel oils and residue were relatively similar for deposits D4 and D5 whereas higher amount was quantified for D6 deposits. It can be concluded through this observation that at higher concentration of Vanadium, the resultant deposit products are heavier compared to samples with lower Vanadium content.

The GC results summarily are in agreement to the SEC analysis in the sense that heavier molecular weight distributions were observed in the deposit products compared to the original sample and the liquid products. Also, as the concentration of Vanadium

increased, the resulting deposit fraction tends to give smaller distribution of light components particularly in the case of Crude D. Although Crude A did not pose similar behaviour, most probably due to the weak solubility in chloroform, the GC results however supported the observation in SEC that a considerable amount of the heavy hydrocarbon in the deposit products, particularly deposit A6, were not characterised due to the limitation of the analytical instrumentation.

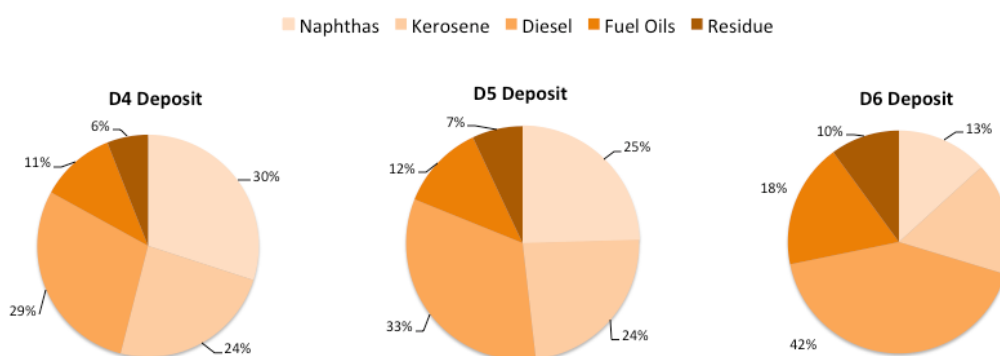


Figure 6.41 Distillation fractions of the deposit products of sample D4 to D6 as analysed by GC.

6.3. Summary & Conclusions

Several conclusions can be drawn from this study on the effect of Vanadium metal towards the formation of deposit in the fouling reactor. Firstly, it was observed that higher amount of deposits was produced for samples with higher concentrations of added Vanadium. This is correct for both crude oils being studied. Crude A produced higher quantities of deposits than the lighter Crude D. The neat Crude A produced about 0.18 g of deposit (1.7% of the total heated amount) whereas neat Crude D did not produce any fouling materials. This could be due to higher percentages of heavier hydrocarbon materials in Crude A. For Crude A, the amount of deposit produced only increased after 550 ppm added Vanadium was introduced in the original crude oil. A similar behaviour was observed for Crude D as deposits were only produced at 350 ppm added Vanadium with a sharp increase at 550 ppm of Vanadium. The effect of Vanadium towards the amount of deposit was only significant at high concentration of this metal. The increment

of the amount of deposits between neat crude oil run and run at 550 pmm of added vanadyl porphyrin was 0.60 g for Crude A and 0.48 for Crude D. This indicates that heavier crude oil is affected more by the addition of porphyrin, but more samples have to be included to further support this observation.

Quantification of Vanadium in the liquid and deposit products showed that most of the added Vanadium were concentrated in the deposit. As the concentration of vanadyl porphyrin increased, the amount found in the deposit increased. The concentration of Vanadium in deposits of Crude D was found to be higher than those of Crude A most likely due to less carbonaceous elements present in the lighter Crude D deposits.

Characterisation of the products with SEC of Crude A samples suggests that the deposits contained larger molecular weight distribution than the liquid products. This was the case apart from A6 deposit, which contained the most Vanadium, due to the fact that most of the sample did not dissolve in chloroform. Analysis of Crude D products gave similar weight distribution behaviour for all of the samples with deposit of Sample D6 proved to be the heavier amongst the products. Further analysis with UVF results showed that the deposits contained bigger conjugated aromatic chromophores than the liquids in both crude oil samples. When the spectra of deposit products were compared across all samples, the spectrum of A6 deposit contained smaller chromophores than the rest of the deposits, again due to the poor solubility of A6 deposit in chloroform. Results of Crude D on the other hand showed that deposit of D6 sample contained the largest aromatic chromophores than the other deposit products. These results are in agreement to those of SECs with the observation that heavier products are composed of larger conjugated aromatic ring systems. Results of SEC and UVF confirmed that the presence of Vanadium promoted the formation of heavier and more complex components in fouling deposits.

Characterisation with GC was conducted to further analyse the chloroform soluble fraction of samples but limited to only the lighter fraction of deposits. Nevertheless analysis of the distillation fractions showed good agreement with the results of SEC with the heaviest fraction was found in the deposit products. Deposits of both Crude A and D gave the smallest analysed percentages in GC amongst the products. As the concentration of Vanadium increased, the percentages for the liquid products of Crude D increased whereas the values for the deposit decreased. This trend however was only observed for

the deposit products of Crude A but not for the liquid in which the percentages analysed were roughly equivalent to each other. This was most likely due to the limitation of the GC itself, which only shows partial molecular distribution of the samples, and the poor solubility of samples in chloroform.

These samples may be further analysed by other analytical techniques such as FTIR and MALDI-MS in order to get more comprehensive views on the characteristics of each liquid and deposit products. FTIR provides information on the functional groups especially the carbon and hydrogen bonds and may be useful as indicators towards changes in aromatic substitution patterns hence changes in the molecular structures. It may be used to complement the results of UVF spectrometer. On the other hand, MALDI-MS would be useful to support the findings of SEC in qualifying the molecular weight of samples especially in the lower molecular weight region. Samples eluted from SEC may be fractionated by several elution time groups and could be further analysed by MALDI-MS and compared by its molecular weight.

It is concluded that the objective of this study had been fulfilled with the establishment of the effect of Vanadium towards deposition process. Characterisation of each deposit product had pointed to the general agreement that Vanadium does enhances fouling process on heated surfaces forming molecules of bigger masses and more complex in structures.

7. Effect of Crude Oil Blending on Deposition

Three crude oils, Crude A, Crude B and Crude D were selected for this particular study. These oils are of industrial interest and are parts of a crude oil blend processed in a refinery. The main aim of this specific study is to investigate the fouling behaviour of these oils upon blending. The applicability of oil compatibility model, OCM of Wiehe [42] on these oils was assessed. The oils were first mapped for their compatibility to establish the fouling propensity behaviour upon blending. Two blends were investigated for their deposition characteristics i.e. blend of Crude A and Crude D as well as Crude B and Crude D. Both sets of blends were found to be incompatible at certain blending ratios between the crude oils. Having determined these regions of incompatibility, each blend was subjected to high temperatures and pressure in the fouling batch system at selected mixing ratios. The resultant products were characterised for their compositional and structural changes and the amounts of deposits were quantified. In addition to the blending ratio, the order in which the crude oils are mixed is believed to affect the deposition of materials on the wall of the reactor. Each blend was subjected to high temperature in the test section described in Chapters 3 and 4 and characterisations with SEC, UV-F and TGA were carried out on the products. The following sub-chapters discuss the findings of each study in detail.

7.1. Crude Oil Compatibility

To assess the compatibility of Crude A, Crude B and Crude D, the OCM model by Wiehe et al was used, details of which have been described in Chapter 2. In order to establish the compatible matrix of the blend, each crude oil was examined for their individual solubility parameters; the solubility blending number, S_{BN} and insolubility number, I_N as presented in Section 2.4.5.

To determine these two numbers, the onset of asphaltene precipitation by a mixture of test liquid was determined for each crude oil. The test liquids were composed of heptane and toluene at various volume ratios. The volume of test liquid at each test was fixed at 1 mL and the ratio of heptane and toluene was varied from 0% to 100% of heptane. Two sets of test liquid mixtures were prepared at 20% and 50% of crude oil volume to the volume of test liquid. These mixtures were prepared in a vial and placed on a vial shaker for 10 minutes to ensure the test liquids were well-mixed with the oil. Each mixture was then placed under an optical microscope to check for the precipitation of asphaltenes, characterised by the presence of asphaltene agglomerates, shown as an example in Figure 7.1. At each mixture, the minimum volume of toluene and the test liquid that kept asphaltenes in solution were recorded. These parameters were used in Equation 7.1 to determine each crude oil's insolubility and solubility blending numbers.



Figure 7.1 Agglomerates of asphaltenes precipitated at a solution composition of 20% toluene and 80% heptane for Crude B shown by an optical microscope (1 cm: 10 micron).

$$\frac{100 V_T}{V_{TL}} = I_N + \frac{100 V_{oil}}{V_{TL}} \left[\frac{I_N - S_{BN}}{100} \right] \quad \text{Equation 7.1}$$

where V_T is volume of toluene
 V_{TL} is volume of test liquid
 V_{oil} is volume of crude oil

Through Equation 7.1, if the minimum volume percentage of toluene in the test liquid to keep asphaltenes soluble, V_T is plotted against 100 times the volume ratio of oil to test liquid, $100 V_{oil}/V_{TL}$, the data will fall on a line. The y-axis intercept will be equal to the Insolubility Number. The x-axis intercept can be determined experimentally through heptane dilution tests, H_D which quantify the maximum amount of heptane, V_H that can be added to the crude oil without precipitating asphaltenes. Briefly, heptane was gradually added to 5 mL of crude oil sample until the point of precipitation was detected through a spot test. The spot test was carried out as follows;

- i) A drop of sample was placed on a 5 micron filter paper to the point that a darker ring was observed at the centre of the spot indicating asphaltene precipitation.
- ii) The point was tested with further dilution through a number of trials. In the first trial, heptane was added in 5 mL increments until a defined inner spot is detected.
- iii) This test was repeated in a second trial with amount of heptane equal to 4 mL less than the amount when asphaltenes were detected in the first trial. The amount of heptane was added in 1 mL increments until a definite change in the spot was observed.
- iv) Further dilutions were made in the third trial at value 0.8 mL less than the amount added in the second trial, with 0.2 mL increments of heptane until asphaltenes ring were observed.
- v) The final value is taken as the average between the amount of heptane added when the ring was observed in the third trial and the higher amount of heptane

added without detecting asphaltenes. The summary of results for Crude A, B and D is presented in Table 7.1.

To obtain the two blending parameters, a graphical representation of the results is made, shown in Figure 7.2. Each crude is clearly represented by the three lines plotted through the two points obtained from the precipitation tests and the one point from heptane dilution test. Extrapolation of each line was made to obtain the values of Insolubility Number, I_{BN} at the y-intersect. These values are found to be at 38.7, 49.2 and 14.5 for Crude A, Crude B and Crude D respectively. The Solubility Blending Number, S_{BN} , and Heptane Dilution number, H_D , for each oil are calculated through Equation 7.2 and the results are summarised in Table 7.2.

$$S_{BN} = I_N \left[1 + \frac{100}{H_D} \right] = I_N \left[1 + \frac{V_H}{V_{oil}} \right]_{V_T=0} \quad \text{Equation 7.2}$$

Table 7.1 Precipitation of Asphaltenes of Crude A, B and D at crude oil to test liquid mixture ratio of 1:4 and 1:1. V_H is obtained through heptane dilution test to quantify the minimum amount of heptane needed to precipitate asphaltenes.

Crude	V_H (mL)	V_{oil} (%) in Mixture	Percentage of toluene in test liquid at precipitation
A	3.2	20	$35 \pm 3\%$
		50	$25 \pm 2\%$
B	3.0	20	$45 \pm 4\%$
		50	$32 \pm 3\%$
D	7.0	20	$10 \pm 2\%$
		50	$7 \pm 1\%$

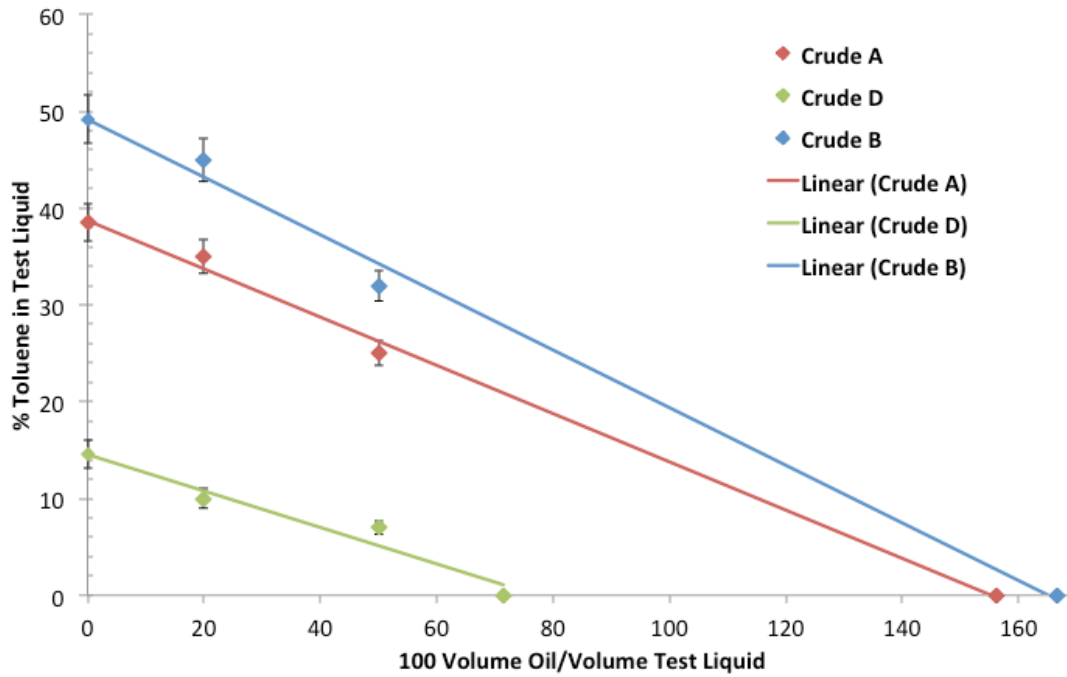


Figure 7.2 The plots of percentage of toluene in Test Liquid versus the ratio of oil to Test Liquid for Crude A, B and D.

Table 7.2 Heptane Dilution value and Solubility Blending Number for Crude A, B and D.

Crude Oil	H_D	S_{BN}
A	156.3	84
B	166.7	78
D	71.4	35

Once the blending parameters for each crude oil were determined, the compatibility of the blends was established. The Solubility Blending Number of the mixture, S_{BNmix} can be calculated from the volumetric average of the oil mixture through Equation 7.3.

$$S_{BN} = \frac{(V_1 S_{BN1} + V_2 S_{BN2})}{(V_1 + V_2)} \quad \text{Equation 7.3}$$

where V_1 is volume of crude oil 1
 V_2 is volume of crude oil 2
 S_{BN1} is solubility blending number of crude oil 1
 S_{BN2} is solubility blending number of crude oil 2

The S_{BNmix} varies according to volume of the crude oils being mixed together. If the two oils are incompatible, the blend would have, at certain oil ratio, an incompatible mix. At values of S_{BNmix} lower than the maximum I_N of the two crude oils, the oil blend becomes incompatible and susceptible to asphaltenes precipitation, hence increasing the possibility of fouling deposits on heat transfer surfaces. In this particular work, two sets of oil blends are put under study, namely blend of Crude A and D, and blend of Crude B and D. The compatibility/incompatibility regions of the two blends were mapped out as shown in Figure 7.3 and Figure 7.4.

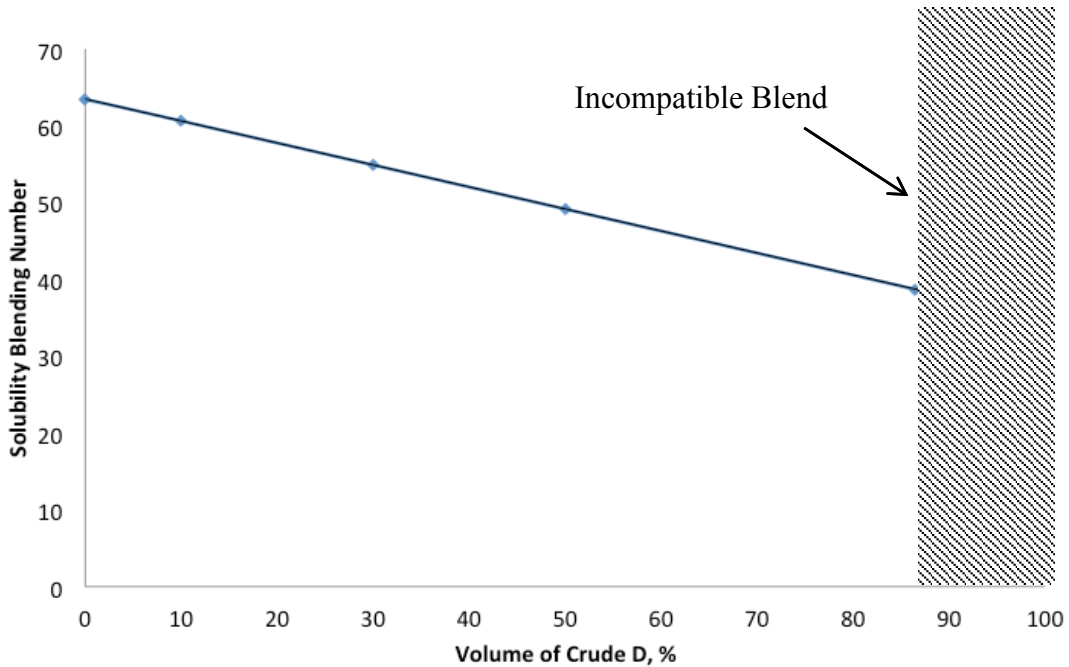


Figure 7.3 Graphical representation of blending behaviour of Crude A and Crude D. Shaded area represents the incompatibility region of the blend.

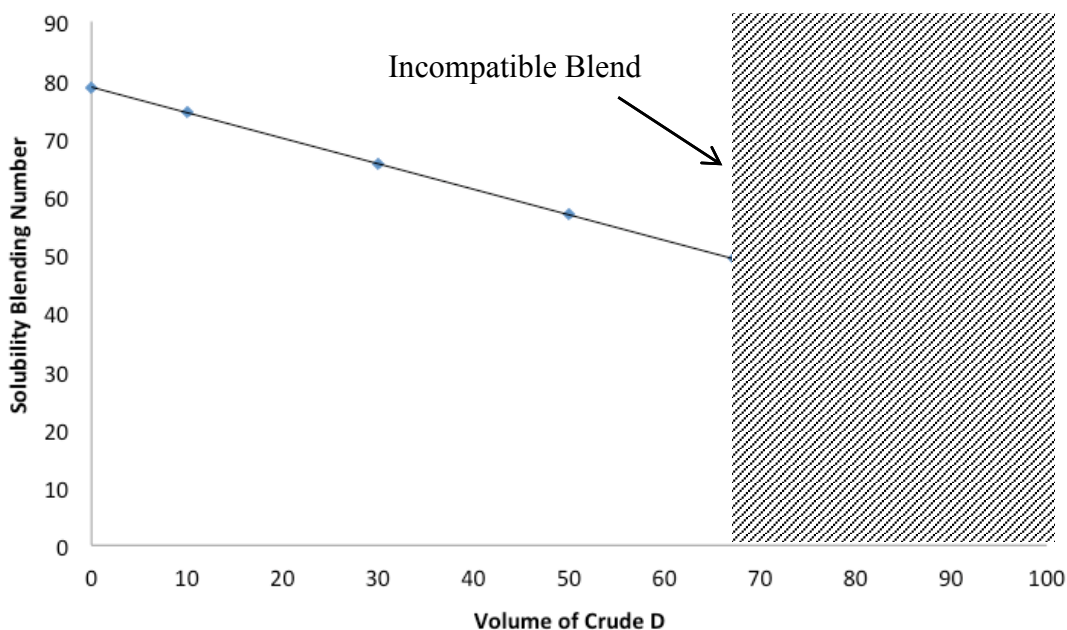


Figure 7.4 Graphical representation of blending behaviour of Crude B and Crude D. Shaded area represents the incompatibility region of the blend.

For each set of blends, there is an incompatibility region since the Insolubility Number of Crude A (38.7) and Crude B (49.2) are greater than the Solubility Blending Number of Crude D (38). For the blend of Crude A and Crude D this region is predicted at fractions of Crude D higher than 86 vol %, as depicted in Figure 6.3. When Crude D is added to Crude A, the mixture remains compatible up until the point where the Solubility Blending Number of the mixture equals the Insolubility Number of Crude A at 38.7. This incompatible region is where asphaltenes start to precipitate out of the mixture and most likely pose problems of deposition on heat surfaces when heated. A similar approach can be made for blend of Crude B and Crude D and for this blend, the incompatibility region is notably larger than that of Crude A and D due to a higher Insolubility Number of Crude B. If Crude D is poured into a container containing Crude B, the mixture is deemed compatible until the Solubility Blending Number of the mixture decreases to 49.2, which is the Insolubility Number of Crude B. This point corresponds to Crude D volume percentage of 67 vol %, at which asphaltenes start to precipitate and flocculate in the solution.

Different asphaltene precipitation behaviour takes place if the order of blending is reversed, i.e. Crude A or Crude B is added to Crude D. The act of blending may be represented graphically through Figure 7.3 and Figure 7.4 – if mixing is performed such that the heavier crude oils are added into Crude D (from right to left hand side of graph), the blend would be inside the incompatible region. The molecular balance that holds asphaltenes in the solution is immediately disturbed hence making the blend incompatible and resulting in a larger probability of fouling.

As discussed in Section 2.4.1, the bulk and surface temperatures play significant roles towards asphaltenes stability in crude oil solution as both affect the fouling rate. When the effect of oil compatibility is taken into account of which many industrial heat exchangers operations experience, the fouling propensity of the oil blends becomes more elaborate as another perspective of asphaltenes solubility and precipitation may be viewed thermodynamically. Artola et.al [53] studied the phase behaviour of a crude oil system using model compounds by modelling the p-T diagram and asphaltenes solubility using the statistical associating fluid theory (SAFT) equation of state. The asphaltenes precipitation boundary was established and it was found that the precipitation is initiated by the thermodynamic instability of the liquid-liquid phase separation which may occur due to mixing of oils or changes in the temperature or pressure of the fluid system. Hence, when certain crude oils are mixed regardless of their compatibility behaviour, one can expect that precipitation of asphaltenes may take place when temperature and pressure of the fluid mixtures change due to changes in the phase equilibria stability. For this particular study however, the effect of changes in temperature and pressure of the oil blends towards fouling behaviour were not taken into consideration.

Once the solubility parameters and compatibility behaviour of both blends were established, each blend was studied for its fouling behaviour. The study was done in two different modes, by varying the ratio of crude oils and by blending the crude oils in different order. The amount of deposits produced for each sample was quantified before the deposits were subjected to analysis by SEC, UVF and TGA. To ease the discussion that ensues, the mixing process of blending Crude D into Crude A is called ‘passive’ blending to represent the approach of blending, going from the compatible towards the incompatible region. The reverse action is called ‘active’ blending as asphaltenes are thought to precipitate out of the solution once Crude A is mixed into Crude D.

7.2. Fouling Behaviour of Crude A and Crude D Blend: Passive Blending

Six samples with different oil ratios were selected within both compatible and incompatible regions of the blend. These ratios were 50:50, 40:60, 30:70, 20:80, 10:90 and 5:95 of Crude A:D. The latter two samples are within the blend narrow incompatible region. 30 mL sample were prepared for each blend, for example in the 40:60 blending ratio, 18 mL of Crude D was poured into a container with 12 mL of Crude A. Before the sample was fed into the test section, it was stirred for 20 minutes to ensure that both crude oils had blended well. Immediately after mixing, the sample was fed into the test section. All experimental runs were performed for 48 hours at 350 °C wall temperature and operating pressure of 10 bar.

7.2.1. Solubility of Deposits

Prior to the analyses by SEC and UVF, the deposit samples were quantified for their solubility in the NMP/CHCl₃ mixture at 6:1 volume ratio. Briefly, 3 mg of sample was dissolved in 5 mL of 6:1 NMP/CHCl₃ solution in a small vial and placed in a mixer for 30 minutes. The whole solution was filtered through a 1.0 micron PTFE filter disc and the weight difference before and after filtering was recorded. The results are tabulated in Table 7.3.

Table 7.3 Summary of the solubility test in 6:1 NMP/CHCl₃ solution for deposits samples of Crude and Crude D from passive blending action.

Deposit Sample	Solubility (%)
Crude A	64 ± 2.0
50 A : 50 D	67 ± 2.3
40 A : 60 D	70 ± 3.8
30 A : 70 D	73 ± 3.2
20 A : 80 D	78 ± 2.6
10 A : 90 D	82 ± 3.1
5A : 95 D	89 ± 2.8

It was observed that as the concentrations of lighter Crude D in the original samples increased, the solubility of the resultant deposit products increased. Deposits from Crude A gave the lowest solubility behaviour amongst the samples. It seemed that the addition of Crude D increased the solubility of deposits with the highest recorded for deposits originated from the 5A:95D blending ratios. This information is particularly valuable when evaluating the results of SEC and UVF of each deposit.

7.2.2. Amount of Deposit

Figure 7.5 summarises the amount of deposit produced for each oil ratio. The values reported are averages taken for two runs with errors calculated through standard deviations amongst the repeats.

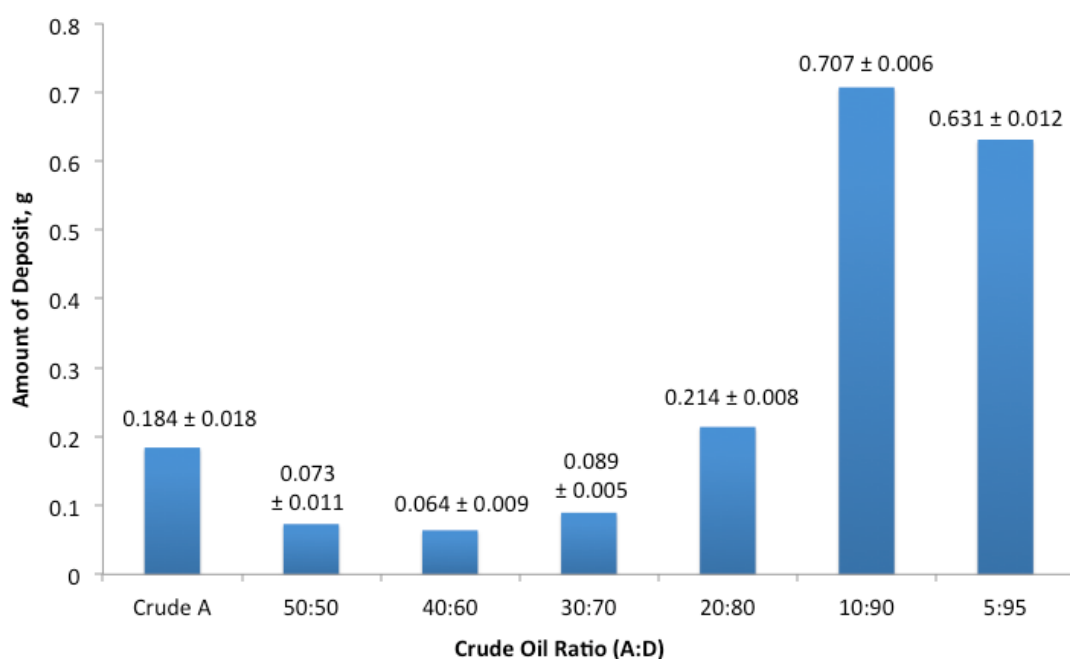


Figure 7.5 Amount of deposit produced for each oil ratio of Crude A and Crude D in passive blending action.

The amount of deposits recovered for oil ratios of 50:50 to 30:70 were similar to each other. These ratios are within the compatible region of the blend. Referring back to the amount of deposits produced in the individual runs of each crude oil, these amounts were relatively lower than the amount produced for neat Crude A (0.0184 g) whilst no deposits

were formed for neat Crude D. The presence of Crude D at these volume ratios somewhat deterred the deposition of foulants on the test section heated wall. For the case of 20:80 blending ratio, a marked increase in the amount of deposits was observed. This ratio is quite close to the incompatible blend region; it is thought that some amount of asphaltenes might have precipitated out of the crude oil mixture and deposited on the test section wall, suggesting the fouling behaviour of nearly incompatible blend.

A further increment in the deposits was observed once the ratios entered the incompatible blending region, i.e. at oil ratios of 10:90 and 5:95. The amount of deposits collected at the end of each experiment was found to be substantially higher than those outside the incompatible region with the highest one recovered from the 10:90 blending ratio. The value decreased slightly at the 5:95 ratio, probably due to the decreasing amount of Crude A asphaltenes in the solution. Further analysis on the compositional and structural characteristics of the deposits was made to investigate their build up at molecular level.

7.2.3. Characterisation by SEC

For characterisation with SEC and UV-F, 3 mL of samples were prepared in a vial for each blend ratio. For example at 30:70 blending ratio, 2.1 mL of Crude D was added into a vial containing 0.9 mL of Crude A. Samples were later placed in a vial shaker for 20 minutes to ensure the oils were well-mixed. Solutions for SEC were prepared by diluting a drop of each sample with NMP/CHCl₃ solvents at volume 6:1 ratio. Further dilution was made if the UV absorbance signal detected by SEC was too high. Figure 7.6 shows SEC chromatograms for each blend ratio. The difference in molecular weight distribution of crude blends with different compositions is apparent. As the volume of Crude D increased, the range of molecular weight moved towards a lighter distribution. As the volume of heavier Crude A decreased, the lighter components of Crude D dominated the overall molecular mass of the mixture.

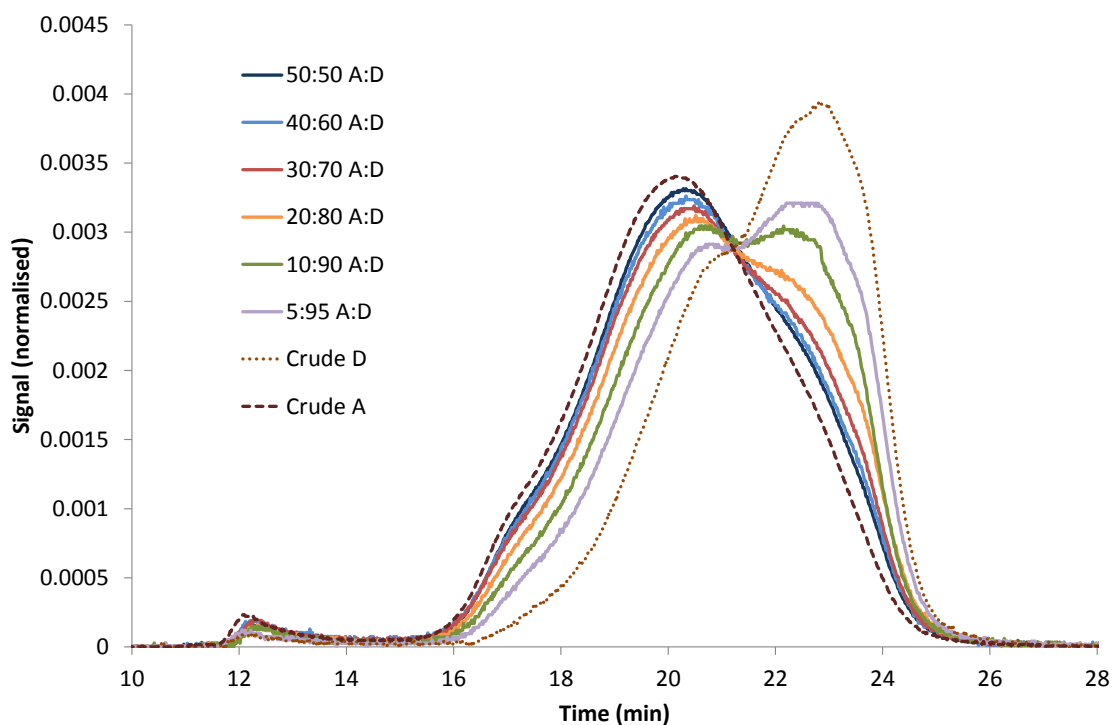


Figure 7.6 SEC chromatograms indicating molecular weight distribution of neat crudes and crude oil blends prior to heating in fouling reactor.

Figure 7.7 shows the chromatograms of the deposits from 50:50 to 5:95 oil blending ratio. The latter two blending ratios gave a shift towards longer elution time suggesting that these deposits contain smaller molecular weight distributions than the other fouling products. The amount of lighter Crude D were higher in the last two blends hence lighter deposits products were produced. The concentration of heavy hydrocarbons in Crude A were diluted by lighter hydrocarbons of Crude D but at the same time precipitations and agglomerations of asphaltenes were immediate and induced further accumulation of lighter hydrocarbons into deposits. These deposits may be built up of longer carbon chain materials rather than heavier aromatic chains from the crude oils. The paraffinic and naphthenic hydrocarbons were not deposited when Crude D was heated on its own, but as it was mixed with heavier oil such as Crude A significant amounts of deposits were produced, particularly when the blend was within its incompatible region.

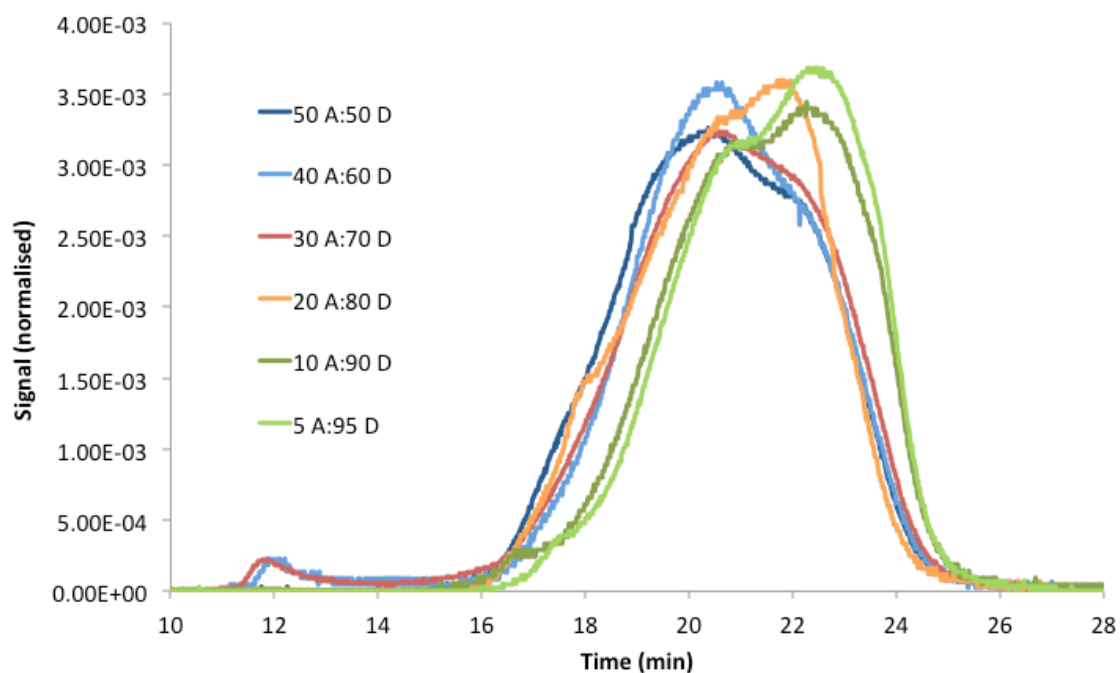


Figure 7.7 Size Exclusion Chromatograms of the deposit samples of Crude A and Crude D blends for passive blending action.

The chromatograms of 50:50, 40:60 and 30:70 blending ratios produced peaks with maximum intensities at similar retention times of around 20 minutes. These chromatograms, when compared to the chromatogram of deposit of neat Crude A, showed similar retention times apart from deposits of 50:50 blending ratio that gave slightly earlier elution time, as shown in Figure 7.8. This indicates that deposits produced from the blend within its compatible region somewhat have similar molecular weight distribution to that of deposit from neat Crude A. The solubility of deposits from Crude A however was lower than that of 50:50 blending ratio, hence the fractions of Crude A deposits that were evaluated here was of lighter molecular components than those of the blend.

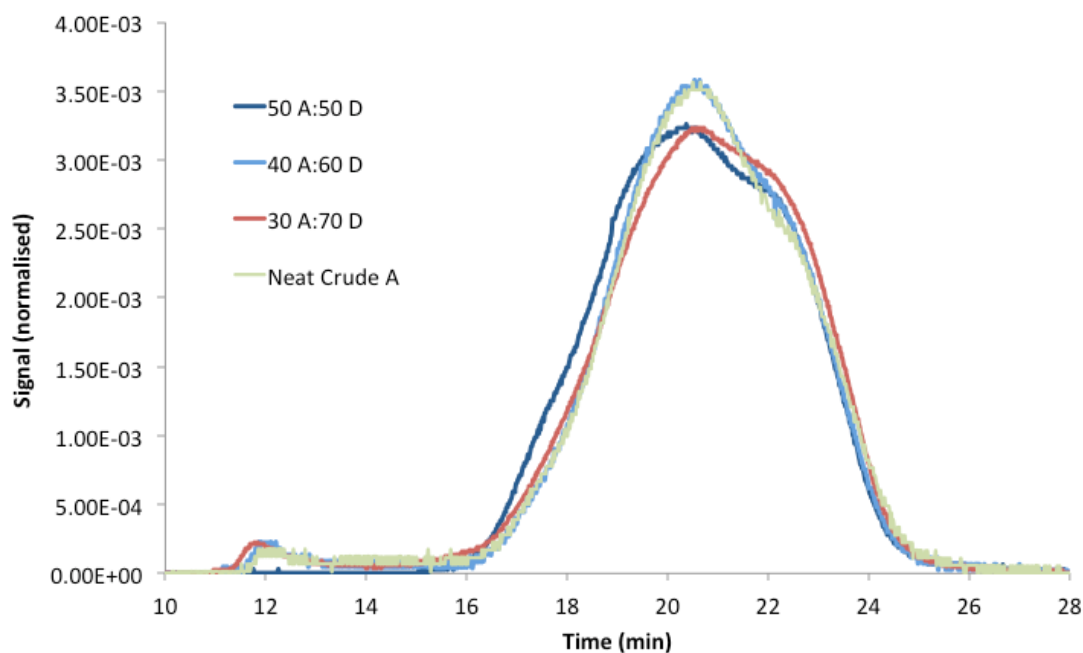


Figure 7.8 SEC chromatograms of deposits produced from compatible region of Crude A and D blend and deposit from neat Crude A.

The deposits from 20:80 blend produced a chromatogram with elution times in between the two compatibility regions. The chromatograms gave a slight shift towards longer elution time with a peak at 22 minutes. This behaviour is most likely due to the fact that this ratio is near the incompatible region of the crude oil blend, hence giving characteristics of the two regions. As shown in the previous section, this blend produced an increased amount of deposits compared to the other compatible blends. This observation shows that fouling at near-incompatible region produced deposits with characters of both compatible and incompatible regions. This supports the discussion in Section 2.4.5 of which certain crude oil blends may show characteristics of nearly-incompatible blend that could potentially give severe fouling in heat exchangers.

7.2.4. Characterisation by UVF

Changes in the molecular structure of these deposits were investigated by UVF spectroscopy. Figure 7.9 shows the synchronous spectra of neat Crude A and Crude D as well as the spectra of the selected blending ratios. The difference of spectral shifts between each sample at both short and long wavelength is clear, suggesting different molecular structure of each blending ratio in both small and large aromatic rings systems.

Crude A gives the larger aromatic ring structures and Crude D gives higher intensity at smaller fused aromatic ring systems, with the ratios of each blend lying in between the two oils.

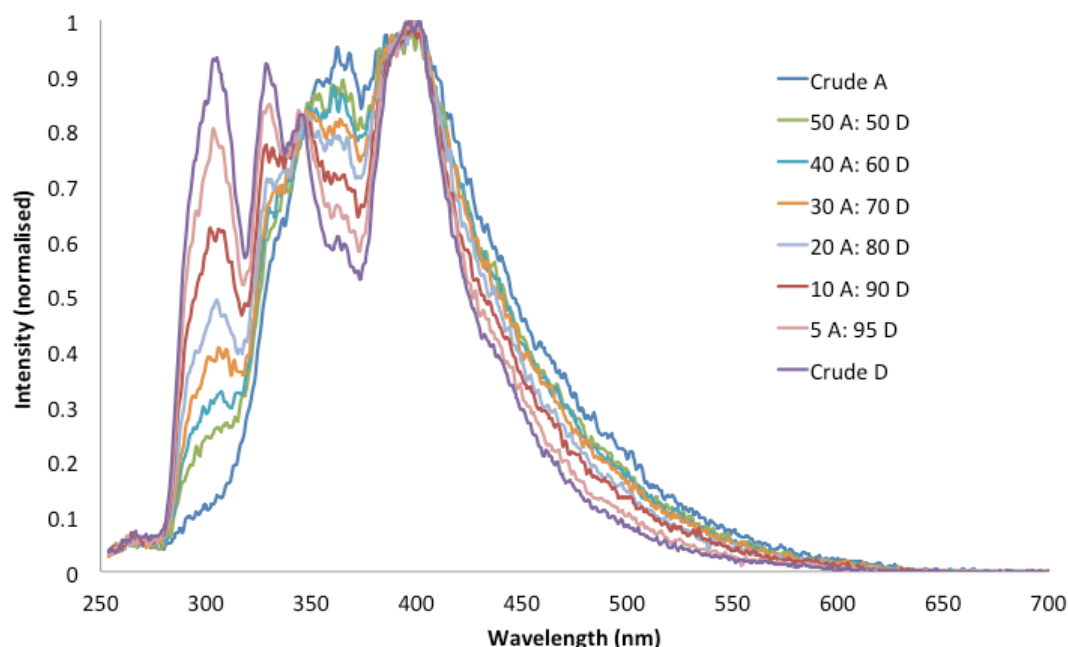


Figure 7.9 Synchronous UVF spectra of Crude A, Crude D and their blends at various blending ratios.

Analysis of the deposit samples showed a consistent agreement with the results of the native samples, as shown in Figure 7.10. The two deposits produced in the incompatible region, which contained the higher volume percentage of lighter Crude D, gave higher intensity at short wavelengths, which corresponds to smaller aromatic chromophores. Deposits originated from blends containing the higher Crude A percentages, i.e. at 50% and 40%, contained larger conjugated aromatic rings as both fluoresced the higher at longer wavelengths. Even though the quantities of deposits produced in the compatible region were much less compared to those in the incompatible region, these deposits appeared to be more carbonaceous. Deposits produced in the incompatible region were less heavy and appeared to be of lighter components. Taking into account the shear force exerted by the flow of fluid in a normal shell and tube heat exchanger, these deposits may be removed more efficiently than those of heavier and more carbonaceous foulants. Further studies may be performed to observe the effect of this stress on the deposition and removal rates of deposits.

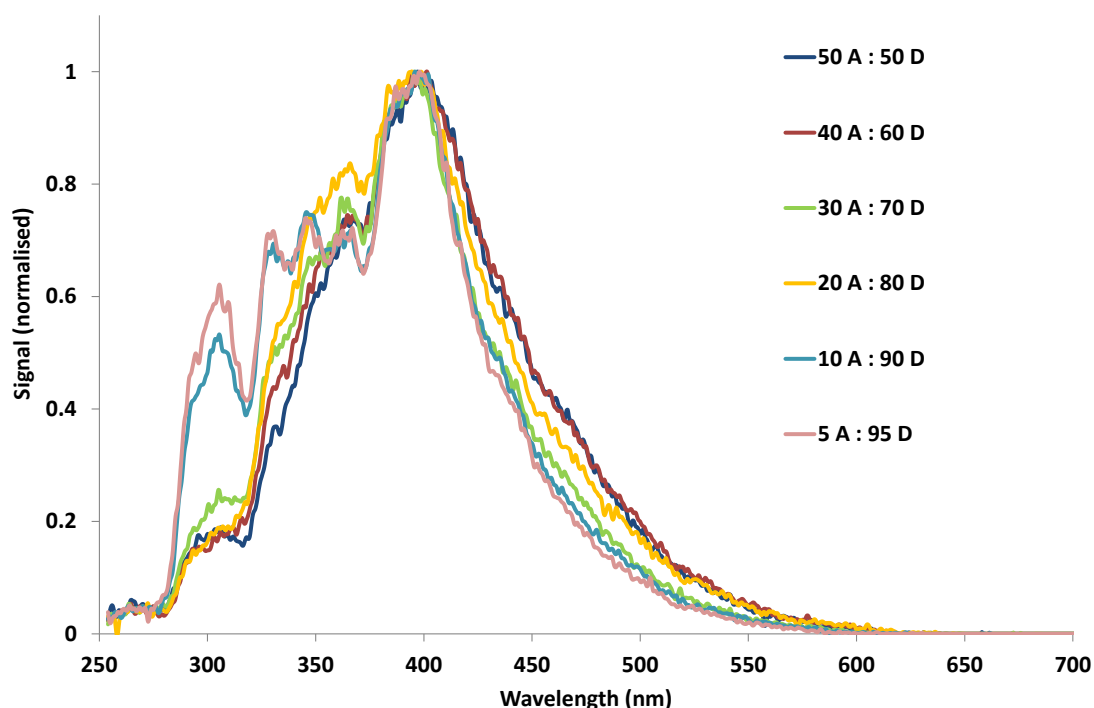


Figure 7.10 Synchronous UVF Spectra of deposit products of blends of Crude A and Crude D at various volume ratios in passive blending action.

Comparison made between the synchronous spectra of both products and its original sample showed consistent and similar trend amongst the blending ratios in terms of the spectral shifts of the three samples. Examples shown in Figure 7.11 and Figure 7.12 are for samples of 50:50 and 5:95 blending ratios. The former showed an apparent shift between the three samples, with larger aromatic ring structures found in the deposit product. The supernatant liquid spectrum was similar to the original sample with an exception in the short wavelength region (280 to 375 nm) in which a shift towards longer wavelengths was observed for the liquid product suggesting relatively bigger aromatic ring structure in the sample.

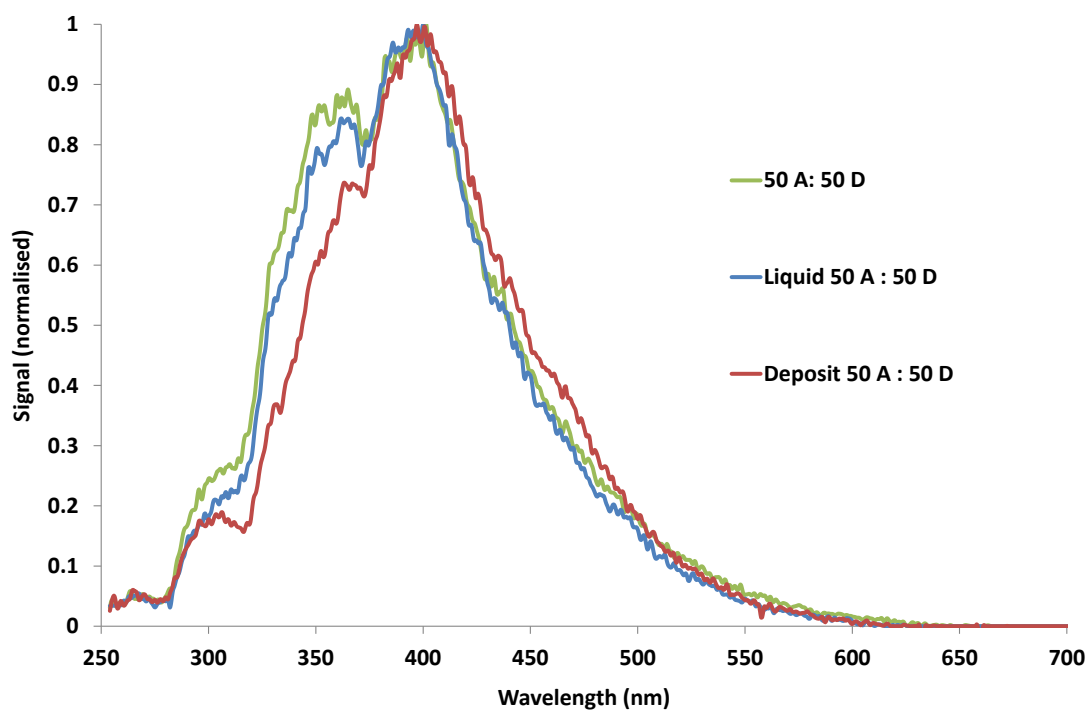


Figure 7.11 Synchronous UVF spectra of the original 50A:50D blend and the corresponding liquid and deposit products.

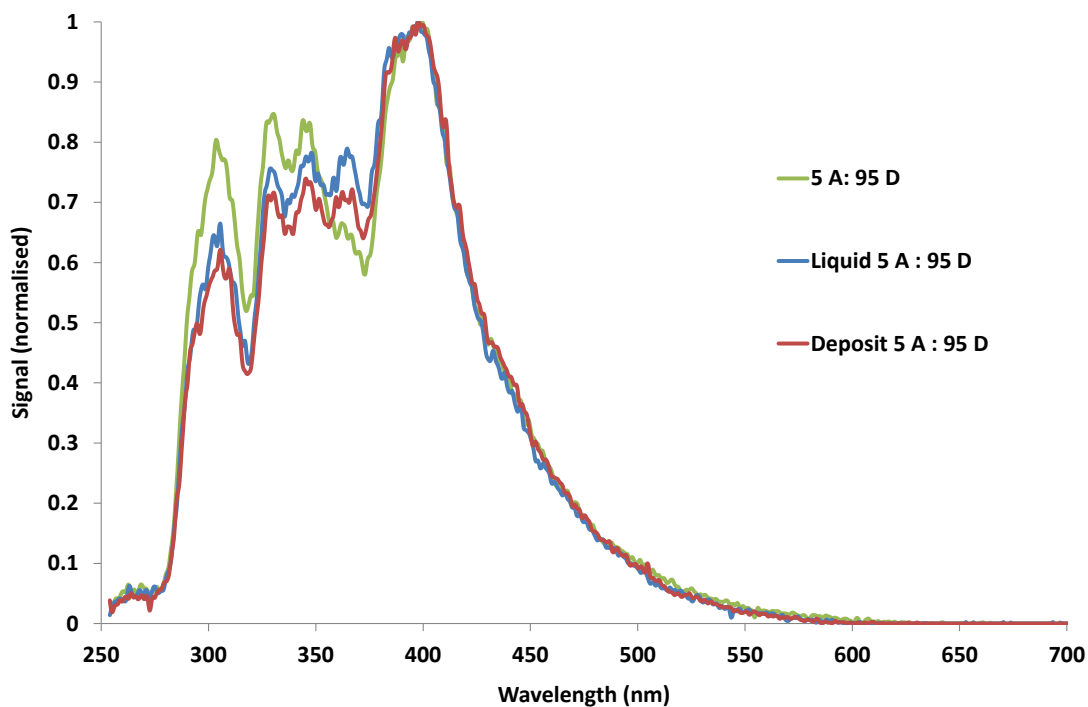


Figure 7.12 Synchronous UVF spectra of the original 5A:95D blend and the corresponding liquid and deposit products.

For the 5:95 blending ratio, the difference in spectral shift between the original sample and the products was less apparent in the long wavelength region (375 to 700 nm), in fact they were very similar to each other. The shorter wavelength region showed a more distinct difference in the intensity of the signal detected by the spectrometer. A higher intensity was found in the original sample whereas the deposit recorded the lower signal. This is not to be mistaken by higher quantity of smaller aromatic ring structure in the original sample but it is an indication that the conjugated ring systems in the sample gave the higher fluorescence ability.

These results show that even though larger amount of deposits were formed at higher concentration of Crude D, the nature of deposits were lighter in both molecular weight and structures. The asphaltene molecules that precipitated out of the solution upon blending in the incompatible region triggered further agglomerations of lighter components when heated. This can be relate to chemical reaction fouling phenomenon of which the asphaltene acted as precursor of fouling, enhancing the formation of deposits on the heat transfer surfaces.

7.2.5. Characterisation by TGA

Thermogravimetric analysis (TGA) was performed on each sample as a proximate analysis to investigate the volatile matter and the fixed carbon contents. The heating programme in TGA is presented in Chapter 3, Section 3.3.6. An example of the temperature and weight profiles is presented in Appendix 7.1. The amounts of ash produced were also recorded at the end of the TGA cycle along with sample weight loss throughout the selected heating programme. The results may be used to estimate the relative compositional proportions of heavy materials and volatile matter of deposits and liquid products for the selected crude oil blending ratios. Figure 7.13 shows the percentages of ash, fixed carbon and volatiles loss of deposit produced from each of the blending ratio.

Upon heating to 370 °C, TGA gave 27 – 89% of weight loss. At this temperature, most of the volatile components would be released to the atmosphere. The larger loss was recorded for the deposits produced from highest percentage of Crude D i.e. 95 vol% at 89%. This was expected due to the lighter nature of Crude D. This supports the results of SEC and UVF which suggested smaller and lighter molecular weight distributions and

structures in this particular sample. At the other end, deposits from 50:50 blending ratio yielded the lower percentage of volatile loss (27%). The higher fixed carbon contents were recorded in the 30%, 40% and 50% of Crude A. Since all samples were subjected to the same temperature, the higher content of fixed carbon was most likely due to the higher percentages of heavier Crude A in the original samples. The percentage of ash however was rather inconclusive indicating that fouling due to inorganic components in the sample was not contributory.

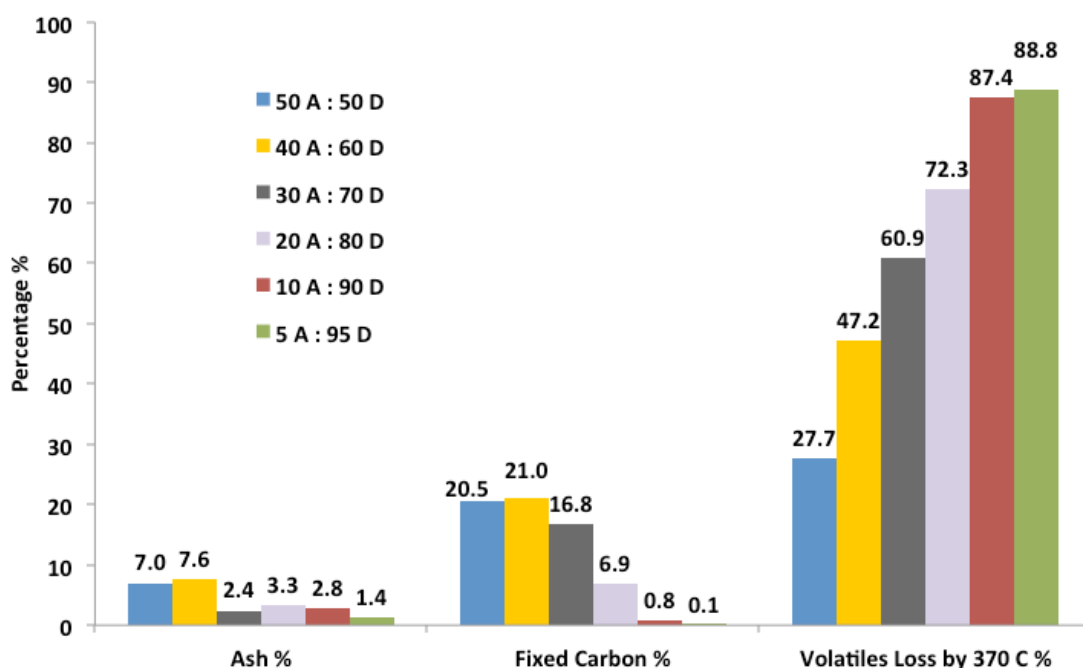


Figure 7.13 Percentages of ash, fixed carbon and volatiles loss at 370 °C in the deposits produced from passive blending of Crude A and Crude D.

7.3.Fouling Behaviour of Crude A and Crude D Blend: Active Blending

The same blending ratios of Crude A and Crude D were selected for this study, but in these experiments Crude A was poured into Crude D during sample preparation. Similar sample preparation procedure to that of passive blending was performed. All runs were conducted at 350 °C wall temperature and pressurised to 10 bar for 48 hour. In this blending action, a different set of results were expected since the precipitation of asphaltenes would be rather instantaneous as the heavier oil was introduced into the

lighter oil resulting in immediate imbalance of the asphaltenes suspension in the bulk solution.

7.3.1. Solubility of Deposits

Similar solubility test described in Section 7.2.1 were conducted for deposits of active-blended samples of Crude A and Crude D blend. The results are shown in Table 7.4.

Table 7.4 Summary of the solubility test in 6:1 NMP/CHCl₃ solution for deposits samples of Crude A and Crude D from active blending action.

Deposit Sample	Solubility (%)
Crude A	64 ± 2.0
50 A : 50 D	66 ± 3.3
40 A : 60 D	69 ± 2.1
30 A : 70 D	74 ± 2.2
20 A : 80 D	80 ± 3.6
10 A : 90 D	84 ± 2.1
5A : 95 D	88 ± 2.2

As observed in the passive-blended deposits, the solubility of the active-blended deposits increased as the concentrations of lighter Crude D in the original samples increased. The relative differences between the two blending actions were relatively small and within the experimental errors. Differences in the molecular weight distributions and structures were evaluated to further understand the nature of these deposits.

7.3.2. Amount of Deposit

The amount of deposit produced for this particular set is plotted in

Figure 7.14. In this blending action, the effect of compatibility of the blend became less apparent as each blend has gone through the incompatible part of the blend. It was promptly noted that compared to passive blending, the amounts of deposit produced in the 40:60, 30:70 and 20:80 blending ratios were relatively larger. This result indicates that once the blend had been through the incompatible region, deposition on heated

surface was enhanced from the precipitated asphaltenes that came out of the solution immediately upon blending. This was however not the case for the 50:50 blending ratio. The amount recovered here was comparable to that from passive blending. It is thought that the volume of lighter Crude D, which acted as the solvent in this blend, was too low to give any precipitation behaviour of the asphaltenes. The fact that this blend is deep inside the compatible region of the blend also supports this observation.

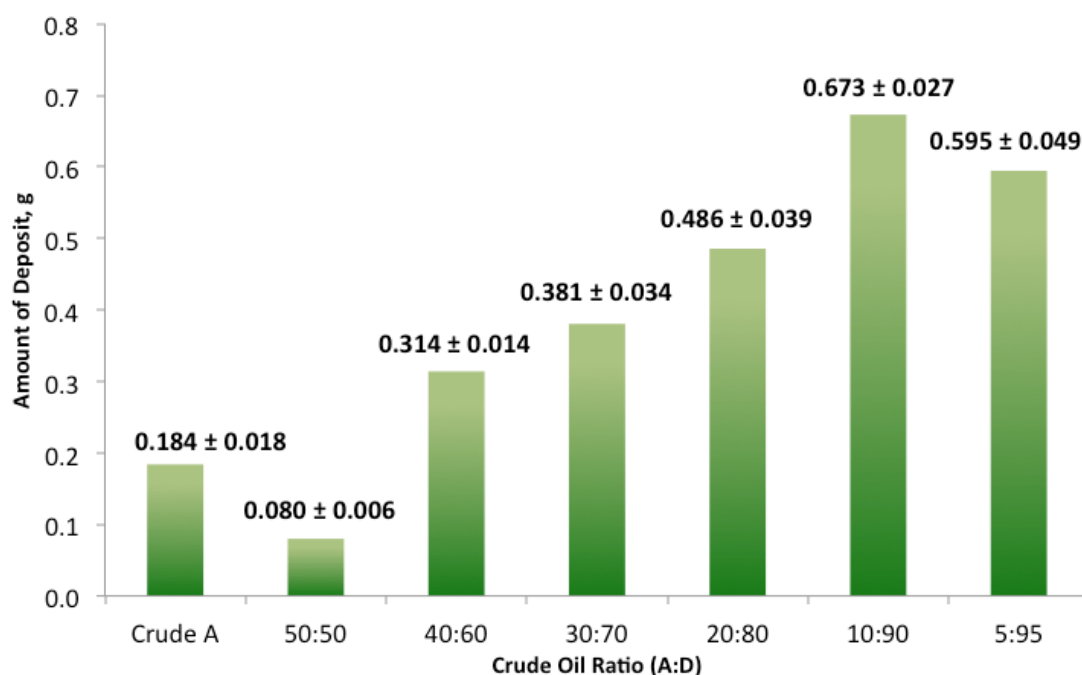


Figure 7.14 Amount of deposit produced for each oil ratio of Crude A and Crude D in active blending action.

Similar to the passive blending, the higher amounts of deposits were produced in the 10:90 and 5:95 blending ratios, albeit at slightly lower quantities than in passive blending, with the higher amount recorded at 10:90 ratio, averaged at 0.67 g. A lower mean quantity was recorded for 5:95 blending ratio most likely due to a lower amount of Crude A asphaltenes in this ratio. This observation again supports the hypothesis of which asphaltenes become the main precursor that promotes formation of deposits as it precipitated out of the bulk solution upon blending.

7.3.3. Characterisation by SEC

SEC chromatograms of the deposit products are shown in Figure 7.15. The chromatograms can be divided into three different groups with the larger molecular weight distribution found in the deposit from 50:50 blending ratio. Deposits from 20% to 40% of Crude A were clustered into similar weight distribution group given that the elution times for all three samples were identical. The last two blending ratios at the higher volume percentage of Crude D eluted at longer retention times and found to be in similar range of molecular weight distribution. These two samples contained the lighter components amongst the deposits, understandably as the percentages of lighter Crude D in the original samples were higher. Similar behaviour was observed in the passive-blended deposits. The amounts of asphaltenes were relatively less in these samples, however more deposits were formed from lighter components that agglomerated and adhered to the heated wall triggered by the incompatibility behaviour of the blends. This observation suggests that even at low concentrations of asphaltenes, deposition of foulant can still occur. In fact, if it involves crude oils in their incompatible region, the amount of deposits produced can be larger.

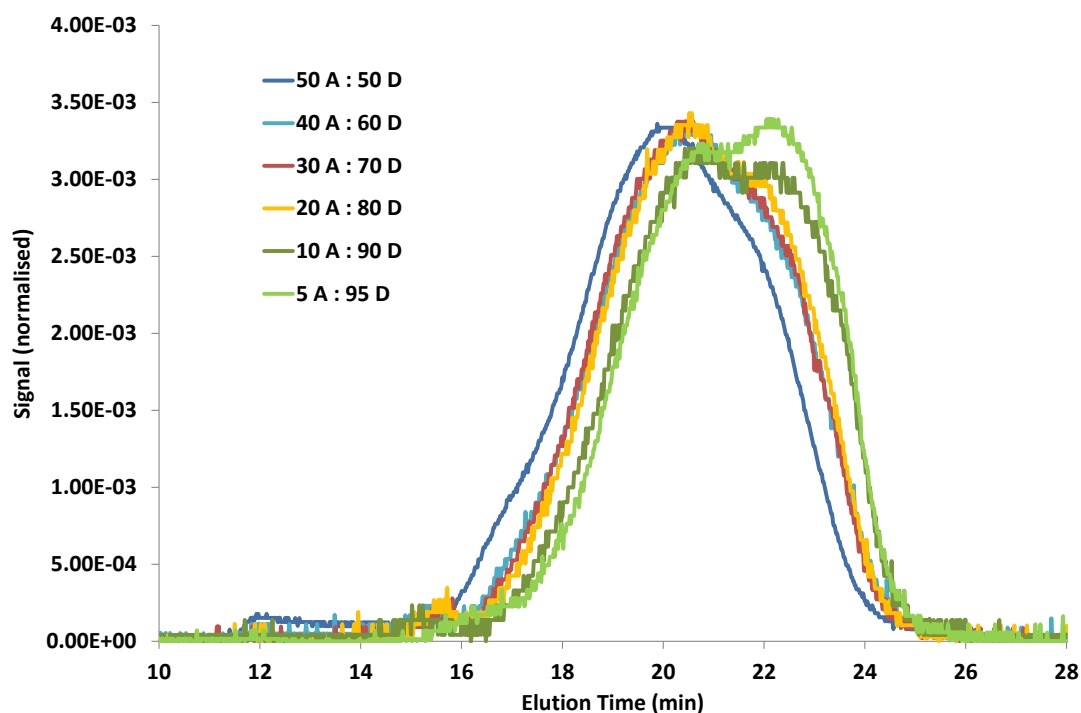


Figure 7.15 Size Exclusion Chromatograms of the deposit samples of Crude A and Crude D blends for active blending action.

Further comparisons were made between the deposits of similar original compositions for both passive and active blending actions. The chromatograms of 50%, 10% and 5% Crude A are shown in Figure 7.16. It was observed that for these three mixtures, the chromatograms of deposits from passive blending showed longer elution times than those of active blends for each of the mixture ratio. This was not the case however for the other ratios where both passive and active deposits generated similar chromatograms. It is worth to mention here that the solubilities of these samples were found to be comparable, hence the chromatograms shown here were of similar level of solubility.

This is an interesting observation as each sample originated from the same blend of crude oils. It would be expected that deposits produced would be of similar nature but they had been proved to be different, at least in terms of molecular weight distributions. It is thought that blending action coming from incompatible region of the blend somehow extracted heavier fraction of the oil that was further turned into heavier deposits on the heated wall. It could also be that agglomerations of heavier asphaltenes were further enhanced through active blending action.

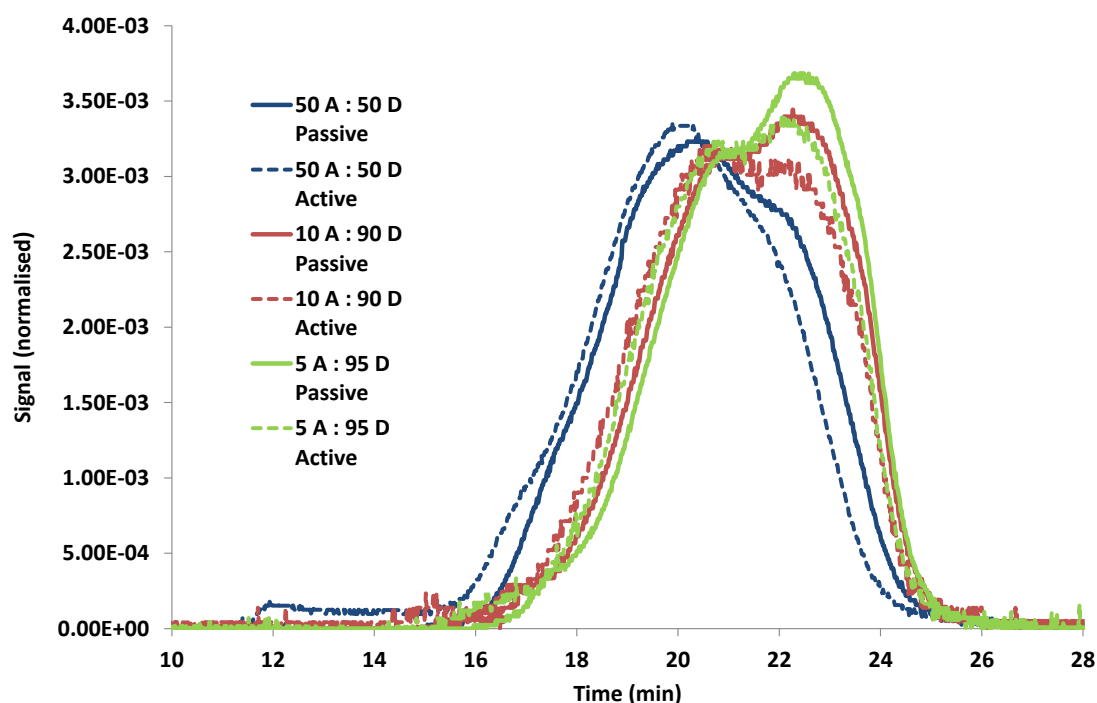


Figure 7.16 Size exclusion chromatograms of deposit samples for 50:50, 10:90 and 5:95 blending ratios of Crude A and Crude D for both active and passive blending actions.

7.3.4. Characterisation by UVF

Figure 7.17 shows the synchronous spectra of deposit samples from Crude A and Crude D blend. Deposits of 50:50 volume ratio gave shift towards the longest wavelength indicating biggest aromatic ring systems amongst the samples. The shorter spectral shift was detected from deposits of 5:95 blend, corresponding to smaller aromatic ring structures. This is in agreement with the results of SEC which showed that bigger aromatic ring structures may be related to components of higher molecular weight distributions. It was also can be seen that spectra containing higher percentages of Crude D, for example at 90 vol% and 95 vol%, produced more peaks especially in the shorter wavelength regions, notably at 310 nm, 350 nm and 380-390 nm. These peaks appeared largely from contributions of smaller components in Crude D as in the spectrum of the original sample in Figure 7.9. On the other hand, the spectrum of deposits from 50 vol% Crude D gave about two peaks at 310 nm and 410 nm associated to more complex molecular structures.

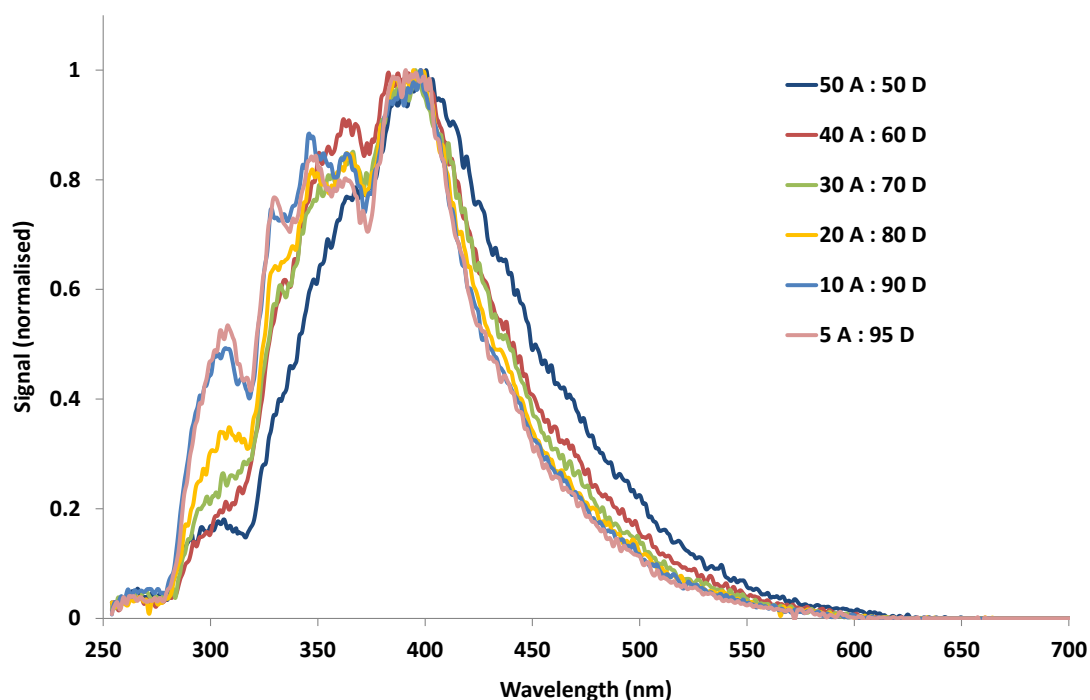


Figure 7.17 Synchronous UVF spectra of deposit products of blends of Crude A and Crude D at various volume ratios in active blending action.

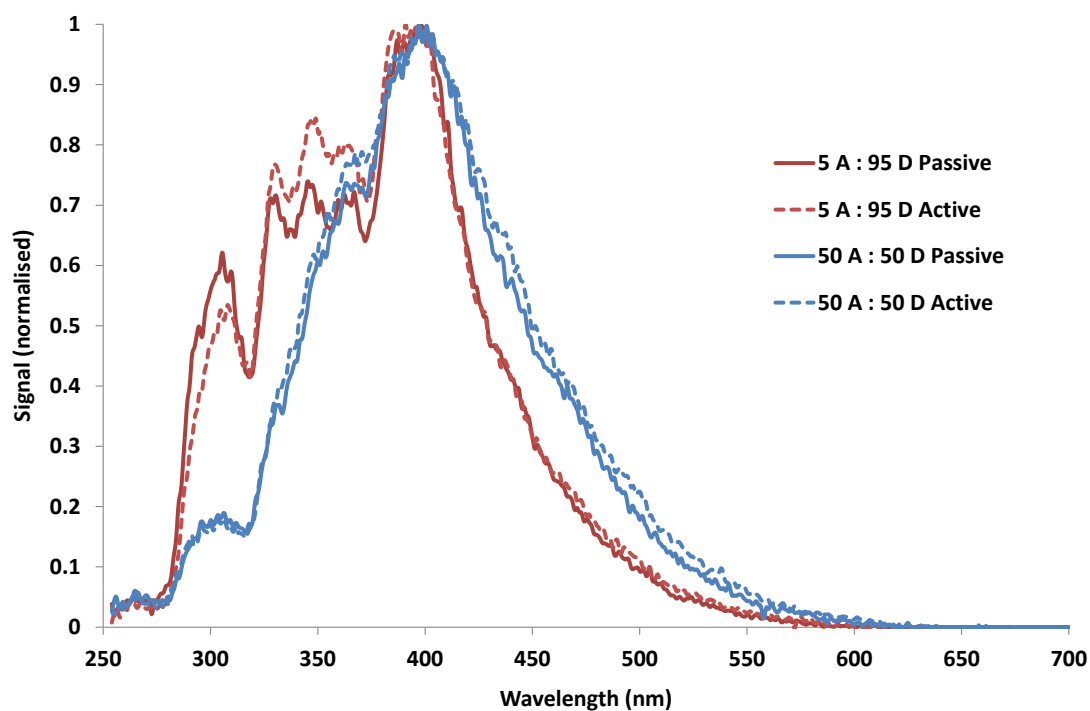


Figure 7.18 Synchronous UVF spectra of the passive and active deposits of 5:95 and 50:50 blends of Crude A and Crude D.

Further comparisons were made between the passive and active deposits as shown in Figure 7.18. The spectra of two samples at each end of the blending ratio range, i.e. at 5:95 and 50:50 ratios, were plotted against each other. There was a shift towards longer wavelength for deposits of active blending in both samples, suggesting bigger aromatic structures compared to deposits from passive blending action. As the SEC chromatograms of these samples eluted at relatively shorter times, deposits from active blended samples proved to be made up of heavier components and more complex molecules.

7.3.5. Characterisation by TGA

TGA analysis was performed for active-blending deposit samples and the results are summarised in Figure 7.19.

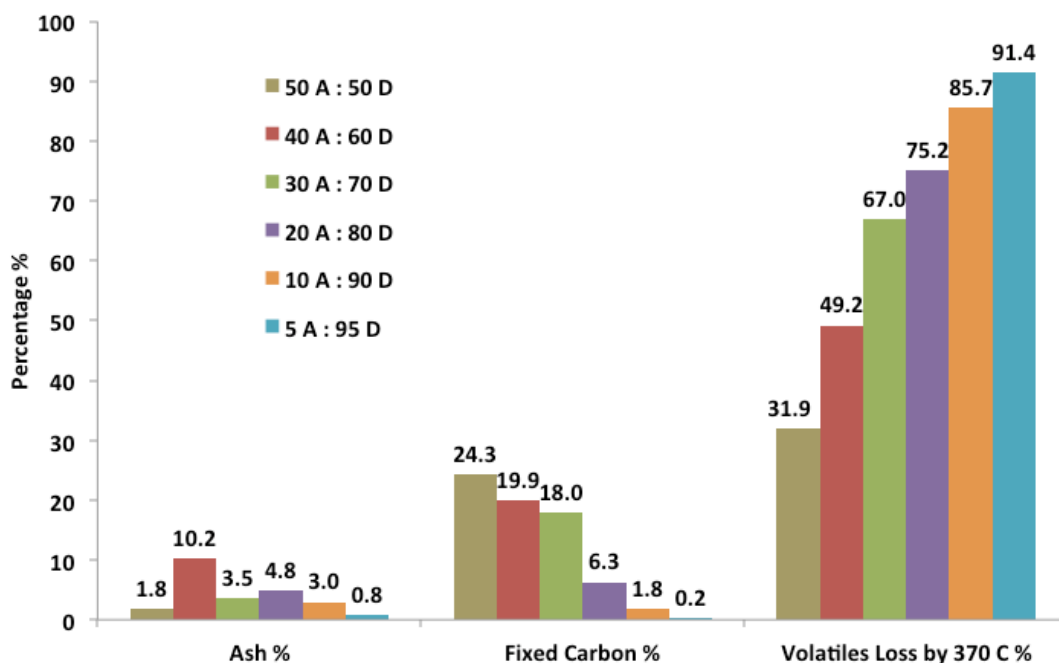


Figure 7.19 Percentages of ash, fixed carbon and volatiles loss at 370 °C in deposits produced from active blending of Crude A and Crude D.

TGA results of active and passive blending are compared. There was a similarity in terms of the increasing amount of volatile loss by 370 °C from the lower volume percentage of Crude D to the higher. The higher percentage of volatile loss was recorded for deposit of 95 vol% of Crude D at 91% and the lower is at 32% for 50 vol% of Crude D. Most of the values in active blending were lower than those of deposits in passive blending. For the fixed carbon content, the reverse was observed, i.e. the higher percentage (24%) was recorded at the lower volume ratio of Crude D at 50 vol%. This trend was expected as this blend contained the highest percentage of heavier Crude A. For 5:95 blending ratio, the deposit product contained only about 0.2% fixed carbon content, which was similar to that of passive blending. As all samples followed the same heating programme, the consistency of fixed carbon amounts among the passive and active blending actions

indicates that each sample underwent similar thermal degradation. The low percentages of ash content show that fouling was mainly due to coke produced during heating with limited contribution from inorganic compounds. This result was also observed in the TGA analysis of passive blending.

7.4.Fouling Behaviour of Crude B and Crude D Blend: Passive Blending

For this particular blend, four samples of blending ratios of 50:50, 30:70, 20:80 and 10:90 Crude B to Crude D were selected. This blend has a bigger range of incompatible region, starting at 67 vol% of Crude D and making the last three blending ratios inside the incompatibility region of this oil mixture. Samples were prepared in similar procedures as in the blend of Crude A and Crude D. Each sample was stirred for 20 minutes with a magnetic stirrer before it was fed into the reactor, heated at 350 °C wall temperature at 10 bar for 48 hour. Since the run of neat Crude B has not been discussed elsewhere in this work, the discussions that follow would include the results of individual run of Crude B.

7.4.1. Solubility of Deposits

The solubility test for each deposit was conducted following the procedure described in Section 7.2.1. The results are presented in Table 7.5.

Table 7.5 Summary of the solubility test in 6:1 NMP/CHCl₃ solution for deposits samples of Crude B and Crude D from passive blending action.

Deposit Sample	Solubility (%)
Crude B	57 ± 3.5
50 B : 50 D	64 ± 3.3
30 B : 70 D	71 ± 3.2
20 B : 80 D	77 ± 2.6
10 B : 90 D	80 ± 2.1

The solubility of deposits increased as the volume of Crude D increased in the original sample. The solubilities of these deposits were also comparable to the deposits of passive blended samples of Crude A and Crude D blend. Deposits from blend of Crude A gave slightly higher degree of solubility but each was recorded within the errors of the experiments.

7.4.2. Amount of Deposit

A summary of the deposit amounts collected at the end of each run is presented in Figure 7.20. Each sample was run twice in the reactor and the values reported here are the average amounts recovered. Crude B is classified as medium heavy oil, contains about 5.4% asphaltenes with API gravity of 24. In the individual run of Crude B, the amount of deposits produced was 0.377 ± 0.017 g, a higher value in comparison to Crude A (0.18 g) and Crude D (no deposit). Since Crude B has a lower asphaltene content than Crude A, the compounds contributing to fouling were most likely coming from other heavy materials and deposition was likely to be further enhanced by a higher amount of sulphur.

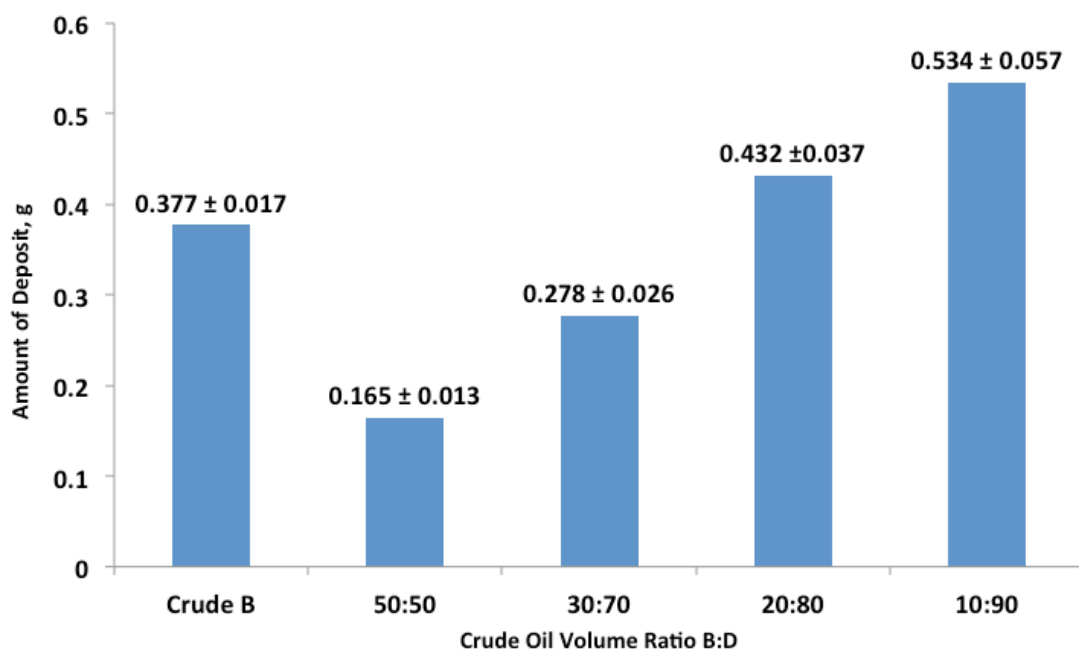


Figure 7.20 Amount of deposit produced for each oil ratio of Crude B and Crude D in passive blending action.

Moving into higher volume of Crude D, at 50:50 blending ratio the amount of deposits recovered was less, recorded here at 0.165 ± 0.013 g. This blend is within the compatible region of the mixture. Similar to Crude A, the presence of lighter Crude D reduces the propensity of fouling to occur as long as the blended oils are within the compatible region. At 30:70 ratio, the blend is just inside its incompatibility region, however the amount of deposit collected was below that of neat Crude B. This result suggests that incompatible oils do not always produce higher amount of deposits compared to its individual values. Once the blend moved deeper into the incompatible region, at 20 vol% and 10 vol% of Crude B the amount of deposits produced increased significantly with the higher recorded for 10 vol% Crude B at 0.534 ± 0.057 g. Both values were higher than the amount produced for individual Crude B indicating the increasing effect of Crude D in precipitating asphaltenes out of the oil solution. These deposits however appeared to be lighter in nature compared to Crude B deposit. Nevertheless, deposition of foulants on the heated wall surface for this particular blend was enhanced in the incompatible region, especially towards higher volume concentration of Crude D. Even though this behaviour was also observed in the blend of Crude A and Crude D, every pair or mixture of crude oils has their own fouling compatibility character and each has to be investigated and studied comprehensively to understand its fouling behaviour.

7.4.3. Characterisation by SEC

Figure 7.21 shows the chromatograms of each deposit sample including deposit of neat Crude B. It was found that the chromatograms of Crude B deposit produced similar elution behaviour with deposit from 50:50 oil blend. Both chromatograms peaked at around 20.5 minutes corresponding to ~ 240 atomic mass unit (amu). Solubility of Crude B deposit in NMP/ CHCl_3 was found to be at 57%, slightly lower than that of the 50:50 blend deposits at 64%. The resultant chromatograms however were identical suggesting that some components dissolved for 50:50 blend deposits were not resolved by the SEC column.

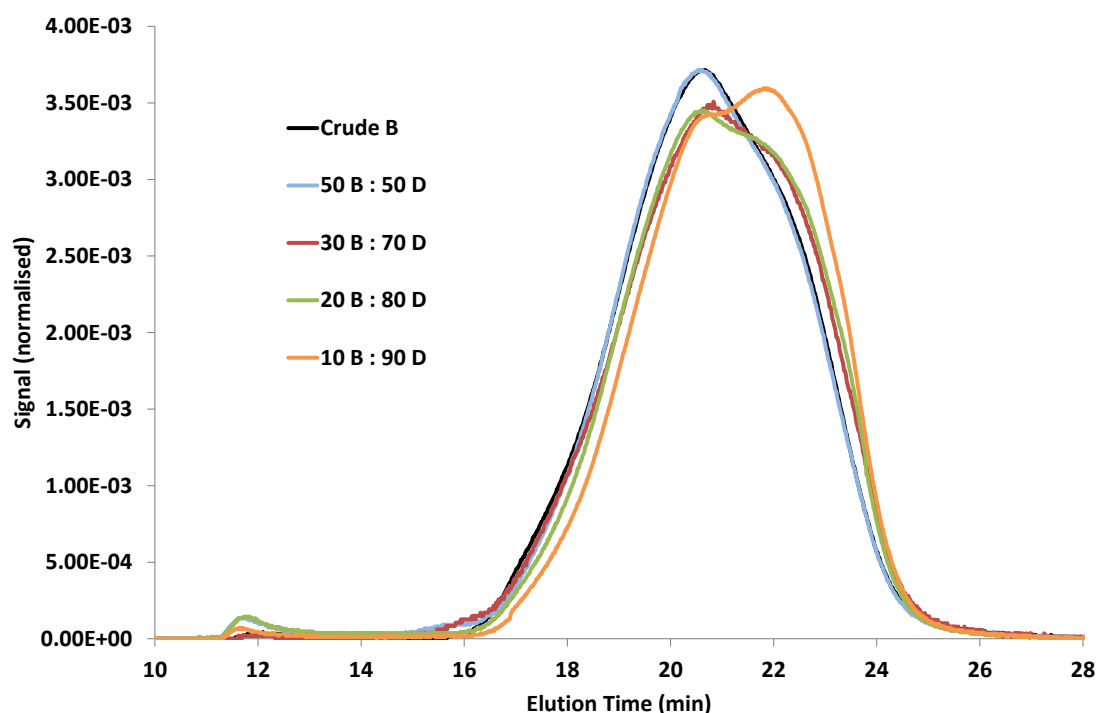


Figure 7.21 Size exclusion chromatograms of the deposit samples of individual Crude B as well as Crude B and Crude D blends for passive blending action.

On the other hand, similar chromatograms were also recorded for deposits of 30:70 and 20:80 mixtures. These showed longer elution times than the previous two chromatograms, even though they peaked at similar elution time. The lower molecular weight distribution was found at deposits from 10:90 blending ratio, which eluted at the longer times. This was anticipated as this blend contained the higher percentage of lighter Crude D. Similar to the blend of Crude A and Crude D, more deposits were collected at the incompatible 10:90 blending ratios, but the deposits produced were lighter in nature and made up of light components.

Comparisons between chromatograms of 50:50 and 10:90 blending ratio of Crude B + Crude D and their counterparts from Crude A + Crude D blend are shown in Figure 7.22. For 50:50 ratio, the retained peak of deposits from Crude A and D eluted at shorter elution times, between 16 to 26 minutes, peaking at 20 minutes. Its equivalent of Crude B and D blend gave a shift towards longer elution time, lifting up at 16.5 minutes, down at 26 minutes, and peaking at 20.5 minute. The results indicate that at this ratio, blend containing Crude A produced deposits at a bigger range of molecular weights. The solubilities of both deposits were of similar degree, recorded at 64% for blend with Crude

B, and at 67% for blend of Crude A. This result suggests that at lower concentration of Crude D (50 vol%), heavier deposits were produced with Crude A, indicates that asphaltenes precipitation of Crude A formed bigger molecular weight components as deposits. As reference, deposits of Crude A and Crude B produced rather identical chromatograms, shown in Figure 7.23. The solubility of Crude B deposits in NMP/CHCl₃ however was lower than that of Crude A's, at 57% compared to 64%, hence a bigger fraction of Crude A deposits was analysed by SEC. This finding somehow implies that upon blending with lighter Crude D, deposits produced from Crude B gave a bigger change in the molecular weight distribution compared to that of Crude A.

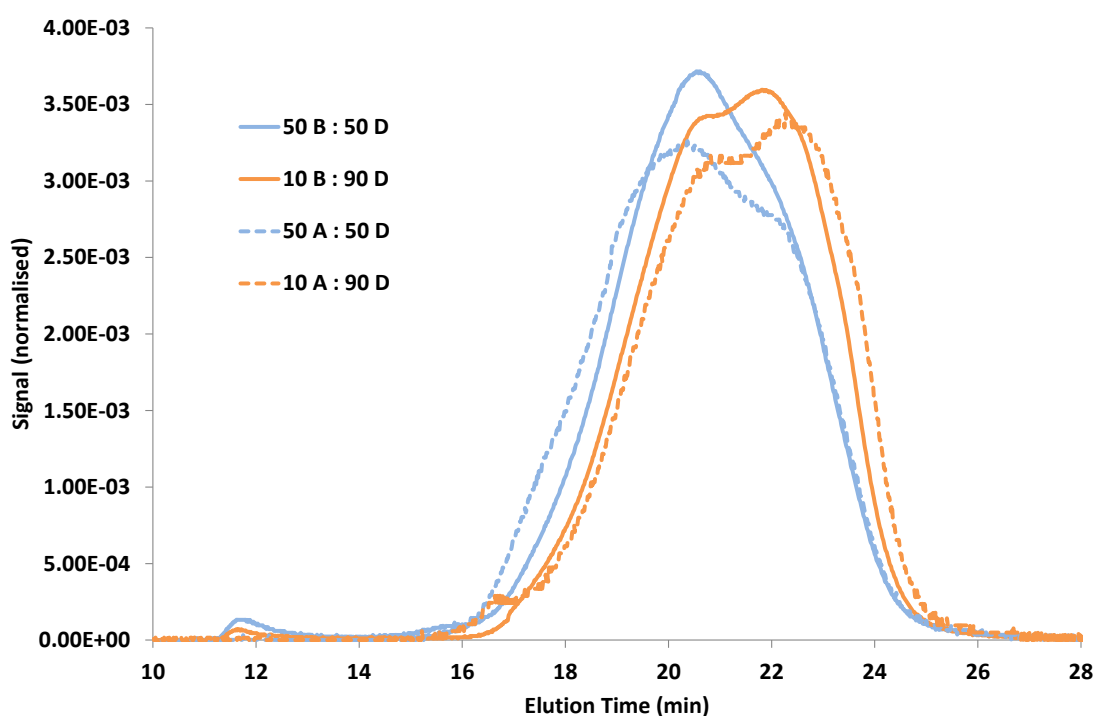


Figure 7.22 Size exclusion chromatograms of the deposit samples of 50:50 and 10:90 blending ratios for Crude A + D and Crude B + D blends for passive blending action.

At the other end of blending ratio i.e. at 10:90 mixture, the longer shift happened for blend of Crude A and D peaking at 23 minutes with its counterparts of blend Crude B and D at 22 minutes. This was the exact opposite to results observed with the 50:50 mixture. Note that the solubility of these deposits were also quite similar, at 80% for blend of Crude B and 82% for blend of Crude A. As the concentration of Crude D was increased i.e. at 90 vol%, lighter components in Crude D comparatively dominate the MW distribution of deposits in the Crude A and D blend. This blend produced more deposits than Crude B + D blend (0.71 g vs 0.53 g), signifying that lighter compounds made up most of the deposits in this particular sample.

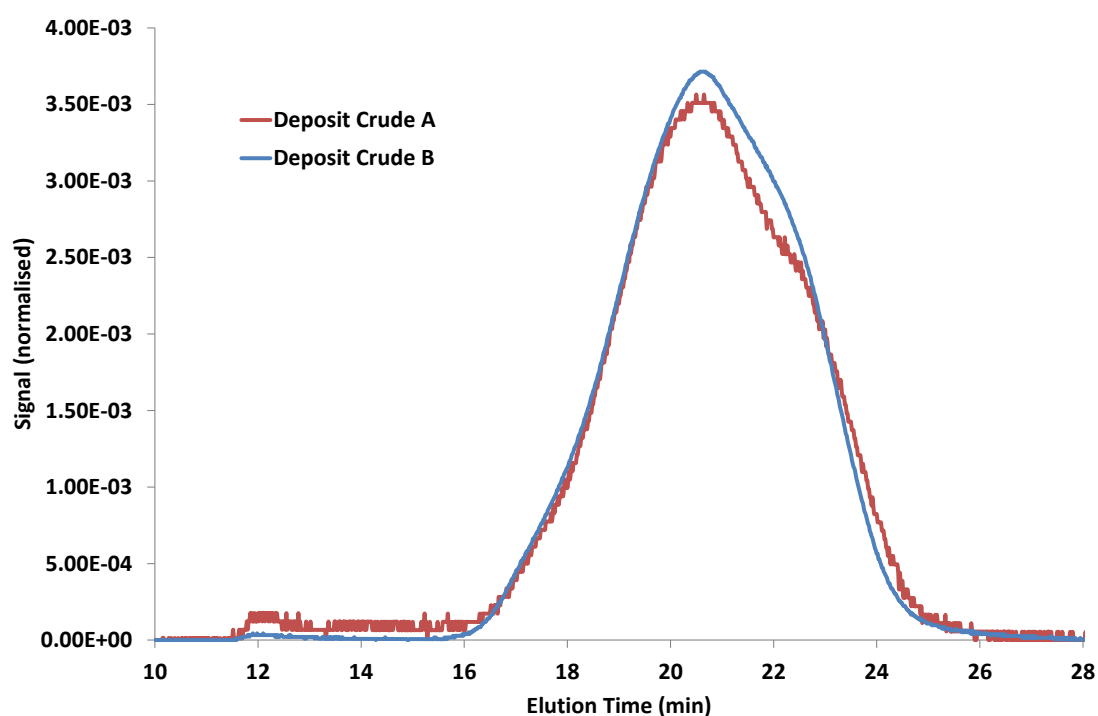


Figure 7.23 Size exclusion chromatograms of Crude A and Crude B deposits.

7.4.4. Characterisation with UVF

The difference in molecular structures amongst the deposits was investigated through UVF spectrometry. Figure 7.24 shows the synchronous spectra of these deposit samples as well as the deposit from individual run of Crude B.

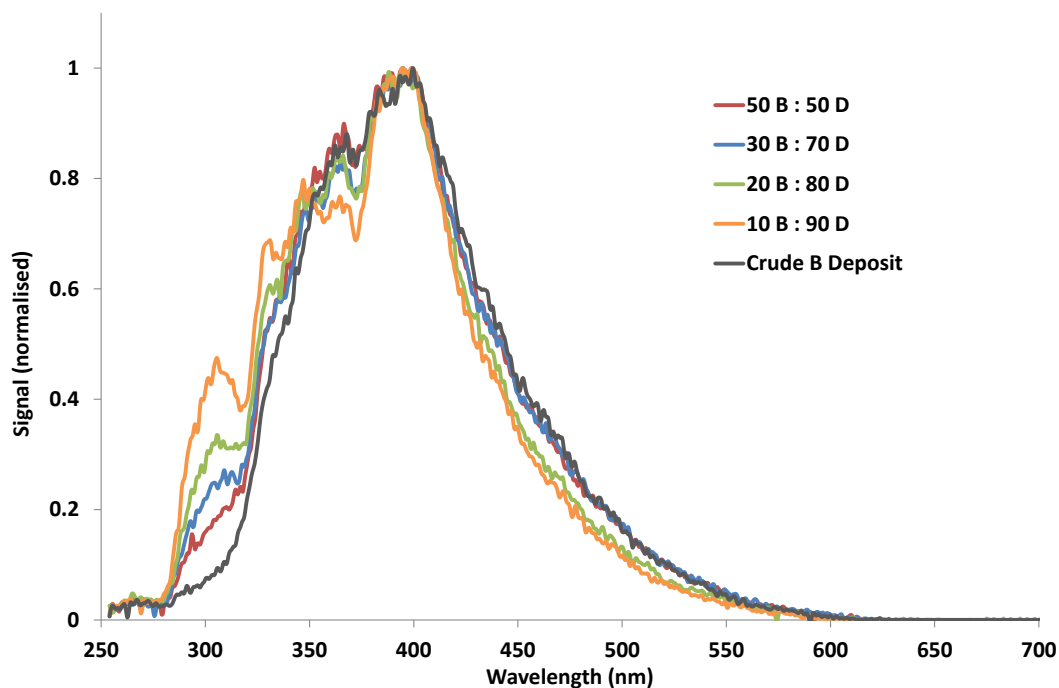


Figure 7.24 Synchronous UVF spectra of deposit samples of Crude B and passive blends of Crude B and Crude D.

Crude B deposits gave shift towards the longer wavelengths amongst all samples, corresponding to bigger conjugated aromatic rings. For deposits from the blends, the 50:50 mixture produced spectra at the longer wavelengths whereas deposits from 10:90 ratio gave the shorter ones. This result agrees with findings from SEC and relates bigger aromatic chromophores to larger molecular weight distribution. In the short wavelength region, i.e. between 275 to 350 nm, the higher intensity was recorded for 10:90 blending ratio, indicating that smaller conjugated aromatic systems showed higher fluorescence for this deposit. Similar to the blend of Crude A and Crude D, deposits originated from the higher percentage of Crude D gave the higher signal at shorter wavelengths, most likely corresponding to components from Crude D. To compare the molecular structure between deposits from these two blends, the spectra of deposits from 10:90 and 50:50 blends are plotted in Figure 7.25.

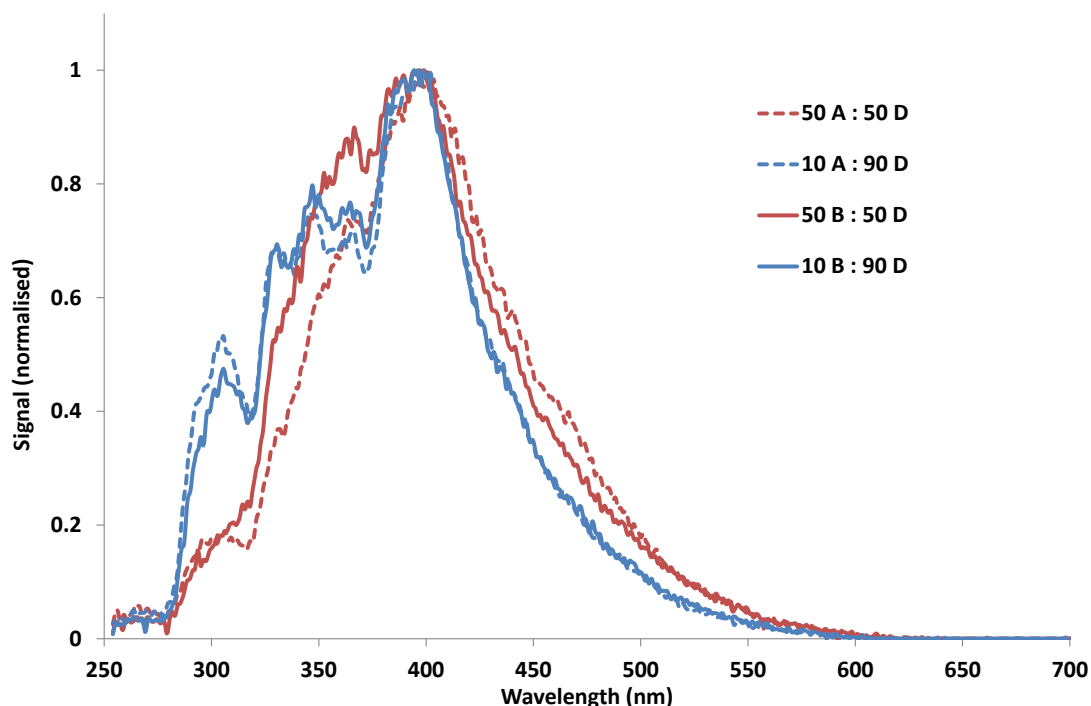


Figure 7.25 Synchronous UVF spectra of deposit samples from passive blends of Crude B + D and Crude A + D for 50:50 and 10:90 blending ratio.

The spectra show that between the two blends, spectra of blend containing Crude A produced spectral shift at the shorter and longer wavelength. This is in agreement to SEC results discussed earlier in which the deposits coming from blend of Crude A + D gave the smaller and larger molecular weight distribution at both ends. Deposits of 10:90 ratio fluoresced at a shorter wavelength compared to that of blend of Crude B + D. The only possible explanation is that deposits from Crude A + D blend consisted of more components from the lighter Crude D and hence showed a much more pronounced spectral shift to shorter wavelengths.

As for the 50:50 blending ratio, deposits from Crude A gave shift towards longer wavelengths compared to blends containing Crude B. This indicates bigger aromatic chromophores in deposits Crude A + D. This may be explained by the spectra of deposits from individual runs of Crude A and Crude B shown in Figure 7.26. The difference in spectral shift between the two samples is quite evident with deposits from Crude A producing a shift towards longer wavelength indicating bigger aromatic ring systems. At 50:50 blending ratio, the effect of heavier crude oil was more pronounced compared to at 10:90. As there were more components from Crude A present in the 50:50 blend, the

effect towards change in molecular structure was more pronounced for this particular deposit. At higher concentration of Crude D however, in this case at 90 vol%, the deposits produced were much more dominated by their lighter components, more so for the blend containing Crude A.

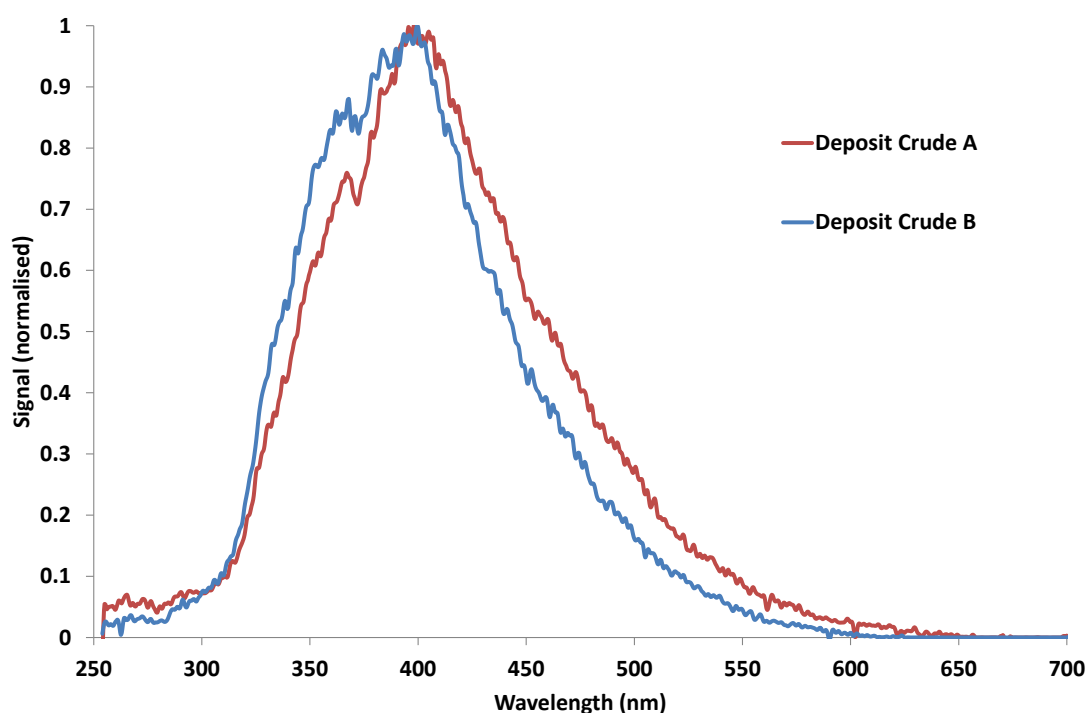


Figure 7.26 Synchronous UVF spectra of deposit samples of Crude A and Crude B

7.4.5. Characterisation by TGA

The approximate compositions and thermal behaviour of the deposits were investigated via TGA analysis. The results are summarised in Figure 7.27. The volatile loss ranged from 43% to 76% with the higher recorded for the 10:90 deposits whilst deposits from Crude B registered the lower percentage. This was expected as concentration of Crude D was the highest in this blend. The opposite was observed for the fixed carbon content, of which the higher percentage was recorded for Crude B deposits at 30.4% and the lower for deposits of 10:90 blending ratio at 5.6%. The results indicate that the carbon compounds were largely originated from the heavier Crude B and ended up at higher concentrations in deposits with higher percentages of Crude B. Similar to the analysis of

Crude A + Crude D deposits, the percentages of ash contents did not show any well-defined trend and were most likely due to the presence of corrosion products.

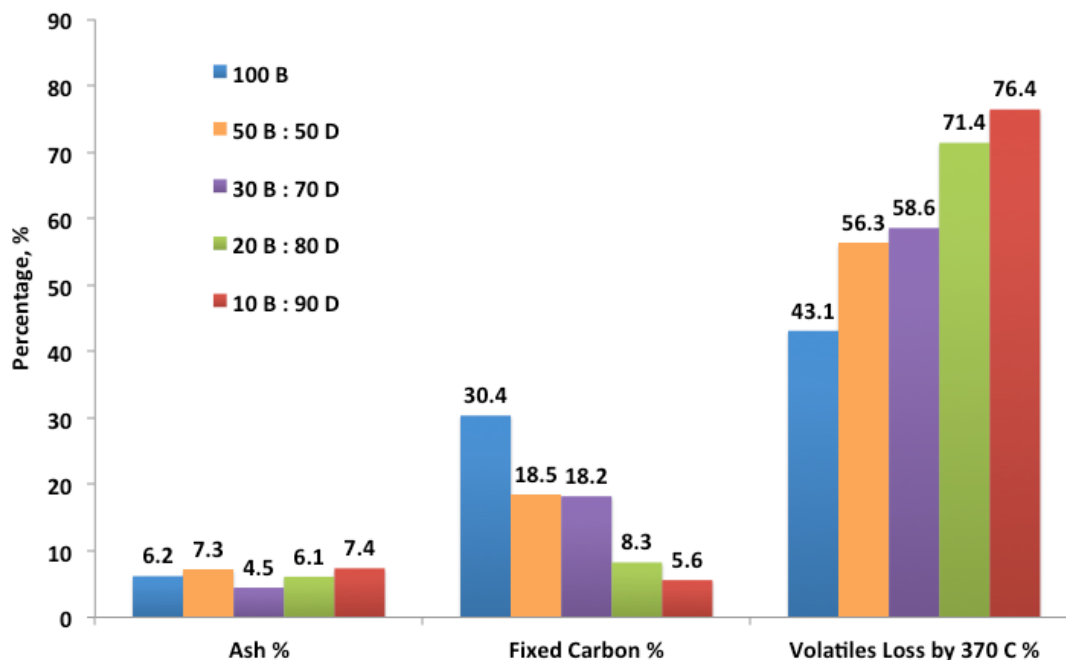


Figure 7.27 Percentages of ash, fixed carbon and volatiles loss by 370 °C in the deposits produced from Crude B and passive blending of Crude B and Crude D.

Comparisons between the analyses of passive blending of blend Crude B + D and Crude A + D for 50:50 and 10:90 ratios were made and are summarised in Table 7.6. For 50:50 blend, the deposits containing Crude A gave lower percentage of volatile loss and higher fixed carbon content. This is in agreement to the results of SEC and UVF indicating bigger and heavier composition in these deposits. For 10:90 blend, it was the deposits containing Crude B that produced lower percentage of volatiles loss and higher fixed carbon content which was also shown by the results of SEC and UVF suggesting heavier composition of this deposit. The analyses of SEC, UVF and TGA seemed to agree with each other showing how different blends of oils produce deposits of various characteristics. These deposits require detail investigation and thorough analysis in order to grasp full understanding of the fouling behaviour.

Table 7.6 Comparison of percentages of fixed carbon and volatiles loss for 50:50 and 10:90 blending ratios for Crude A + D and Crude B + D in passive blending action.

Sample	Blend	Fixed Carbon (%)	Volatiles Lost by 370 oC (%)
Crude A + D	50:50	20.5	27.7
	10:90	0.8	87.4
Crude B + D	50:50	18.5	56.3
	10:90	5.6	76.4

7.5.Fouling Behaviour of Crude B and Crude D Blend: Active Blending

To continue the investigation on fouling behaviour of Crude B and Crude D blend, the order of blending was changed to active blending action. A similar procedure as previously described in this chapter was followed and the deposits produced were analysed for their compositional characteristics.

7.5.1. Solubility of Deposits

Solubility of each deposit in NMP/ CHCl_3 mixture was first measured prior to the analysis of SEC and UVF. The test was conducted following the procedure described in Section 7.2.1 and results are presented in Table 7.7. As observed in the other tests, the degree of solubility increased as the percentage of Crude D in the original sample increased. These values were also similar to those recorded for deposits of the passive blending action providing similar degree of sample evaluation in the SEC and UVF analyses.

Table 7.7 Summary of the solubility test in 6:1 NMP/CHCl₃ solution for deposits samples of Crude B and Crude D from active blending action.

Deposit Sample	Solubility (%)
Crude B	57 ± 3.5
50 B : 50 D	64 ± 2.7
30 B : 70 D	72 ± 2.2
20 B : 80 D	76 ± 1.6
10 B : 90 D	81 ± 1.4

7.5.2. Amount of Deposit

The amount of deposits produced is presented in Figure 7.28, with the amount produced from each ratio counterparts in passive blending also included for comparison purposes. The amounts of deposits produced for blending ratio of 20:80 and 10:90 for both active and passive blended samples were comparable and within the experimental error.

As concentration of Crude B increased, the amount of deposit for active blending decreased. The reduction of quantities however were less paramount compared to those of passive blended samples, especially at 50 vol% of Crude B. This particular mixture is within the compatible region of the blend. For active blending action, the amount of deposit produced from this blend was higher than in the passive. The acts of adding Crude B into Crude D enhanced the formation of deposits through precipitation of asphaltenes and at the same time triggered further the accumulation of other components in the blended oils. These components were deposited as heavier materials on the wall. This was also seen in the blend of 30:70, even though the blend is within the incompatible blending region. The amount produced in passive blending was less than in the active, suggesting the blending order, which was the only parameter changed in these experiments, caused further deposition. This was also observed in the blend of Crude A and Crude D as shown by SEC and UVF analysis, hence it would be expected similar behaviour for Crude B and Crude D blend.

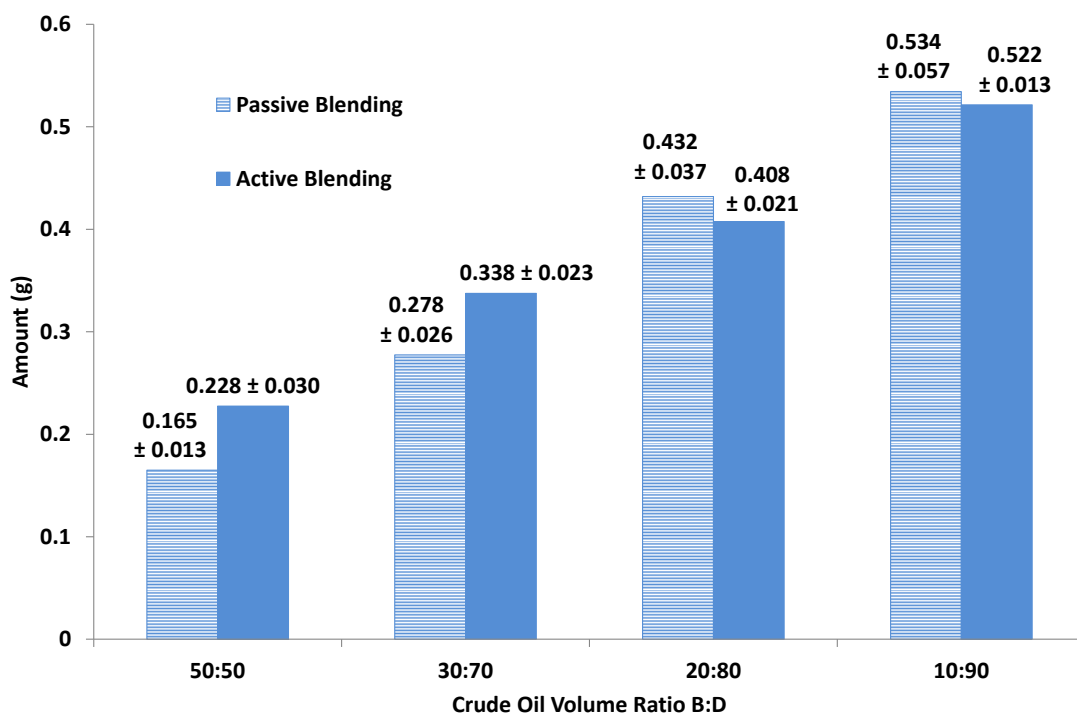


Figure 7.28 Amount of deposit produced for each oil ratio of Crude B and Crude D in both passive and active blending action.

7.5.3. Characterisation by SEC

Figure 7.29 displays the SEC chromatograms of deposits from active blending of Crude B and Crude D. The difference in terms of the elution time between the deposits from 50:50 blending ratio and the other samples is clearly shown. The chromatogram of 50:50 deposits was shifted to earlier retention times with a peak at 20.5 minute. The other three chromatograms seemed to follow similar elution times with the exception of deposit from 90 vol% Crude D. This deposit produced chromatogram that shifted towards longer elution time. Although the three chromatograms peaked at a similar time around 21 minutes, the one of 10:90 blend lifted at a later retention time at 16.5 minutes compared to around 15-16 minutes for the other two. This observation was expected taking into account the results from other blends discussed earlier.

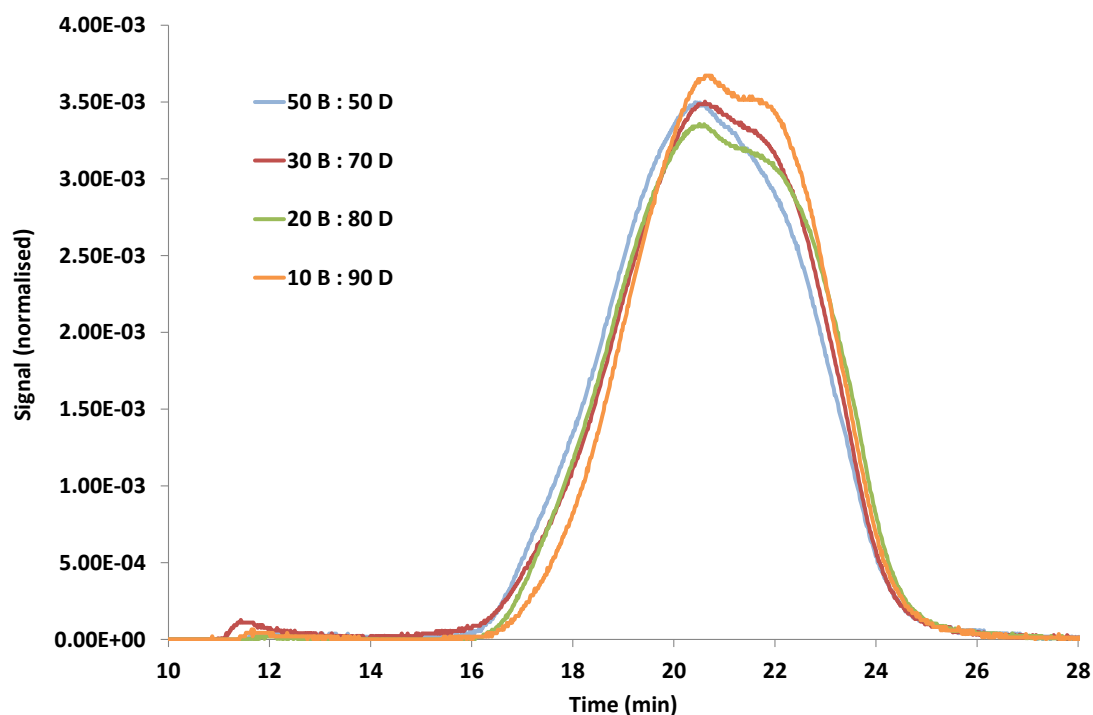


Figure 7.29 Size exclusion chromatograms of the deposit samples of Crude B and Crude D blends for active blending action.

To further investigate the characteristics of these deposits, the chromatograms of passive and active blends were plotted, shown in Figure 7.30 and Figure 7.31. For the case of 50:50 and 10:90 blending ratio, it was apparent that deposits from active blend action produced chromatograms at shorter elution times, corresponding to larger molecular weight distribution. This result is consistent to that of blend Crude A and Crude D confirming the observation that if the heavier crude oil is added into a lighter oil, not only would it enhanced deposition in the compatible region, but it would also produce relatively heavier deposits compared to oils that were blended in passive manner.

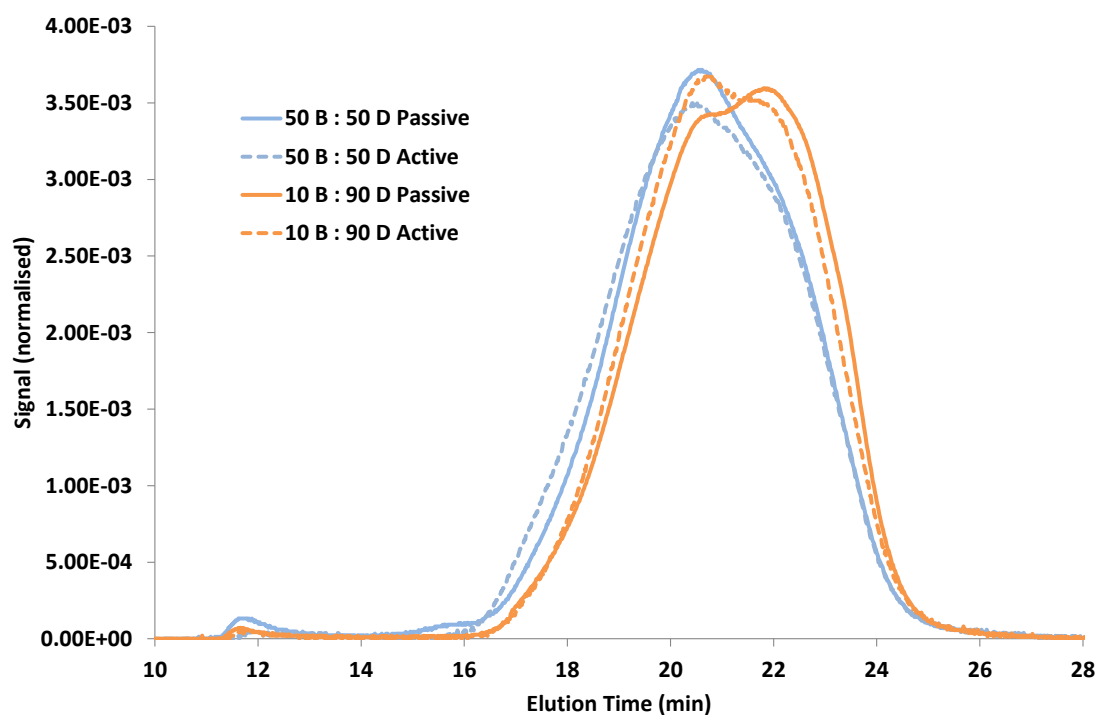


Figure 7.30 Size exclusion chromatograms of the deposit samples of 50:50 and 10:90 blending ratios for passive and active blending actions.

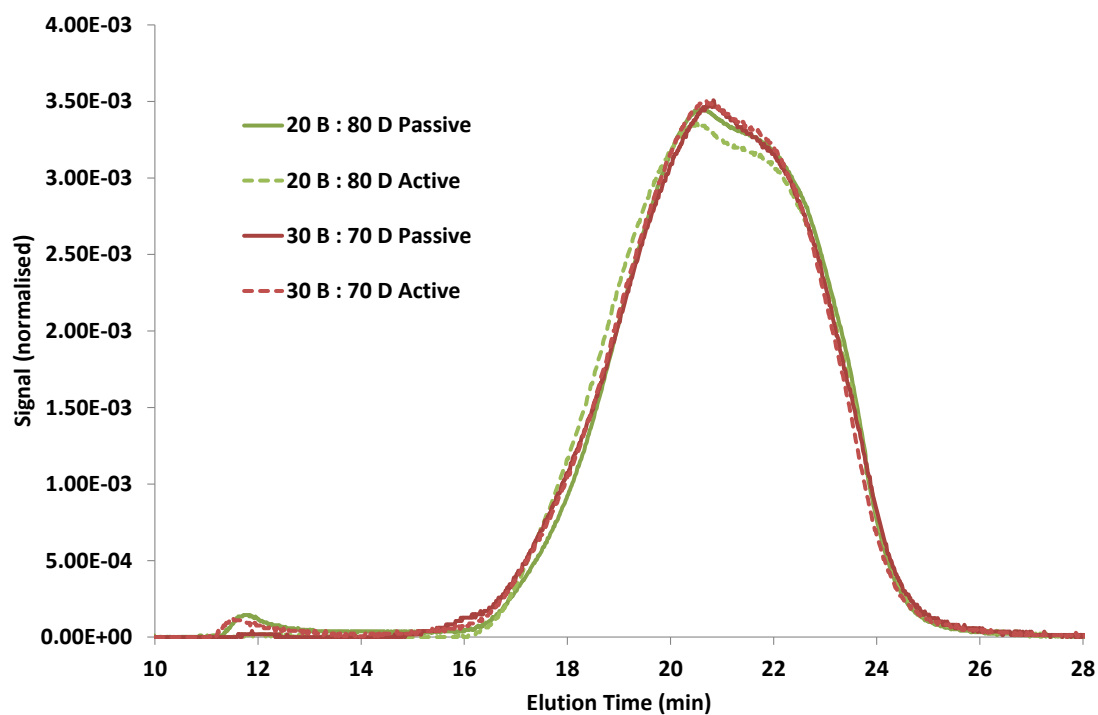


Figure 7.31 Size exclusion chromatograms of the deposit samples of 20:80 and 30:70 blending ratios for passive and active blending actions.

The chromatograms of 20:80 and 30:70 blends also gave similar behaviour, although the difference in elution times was not quite apparent especially in the deposit of 30 vol% Crude B. Nevertheless, the results of SEC suggest that even at similar crude oil composition, if blending was performed in different manner the resulting deposits would be of different characteristics. To investigate if the structures of deposits also behave in similar manner, characterisation by UVF was performed.

7.5.4. Characterisation by UVF

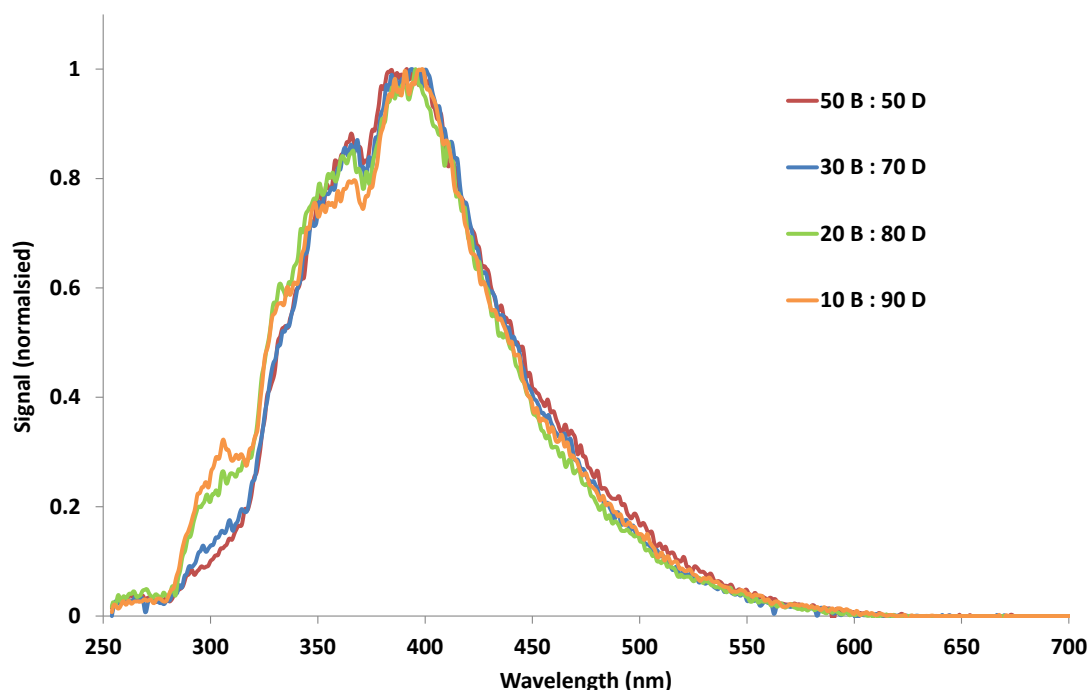


Figure 7.32 Synchronous UVF spectra of deposit samples of active blends of Crude B and Crude D.

The synchronous spectra of deposits from active blending of Crude B and D are presented in Figure 7.32. The shift towards longer wavelength was recorded for deposit from 50:50 blending ratio whereas the shorter was registered for the 10:90 deposits. The same trend was observed for the passive and active blend of Crude A + D as well as for the passive blend of Crude B + D. This result is also consistent with the findings of SEC associating large molecular weight distribution with big aromatic chromophores.

How do these deposits compare with those of passive blend? Figure 7.33 shows the comparison of synchronous spectra for deposit samples from both types of blending. Only deposits for 50 vol% and 90 vol% of Crude D are shown as they produced more distinct differences amongst the blending ratios. Comparing deposits of 10:90 blend, the spectrum of passive blended sample gave a shift towards shorter wavelength suggesting smaller aromatic ring systems. As for deposits from 50:50 blend, it was also observed here that the spectrum from passive blended sample fluoresced at shorter wavelength compared to active blended deposit. Once again, the UVF results are in agreement with SEC in concluding that shorter spectral shift of UV-F i.e. smaller aromatic rings corresponds to longer elution time i.e. smaller molecular weight. This trend was also observed for deposits from Crude A + Crude D blend supporting the argument that by blending crude oils starting from its incompatible region, formation of heavier deposits in terms of bigger aromatic structures and larger molecular weights may be expected.

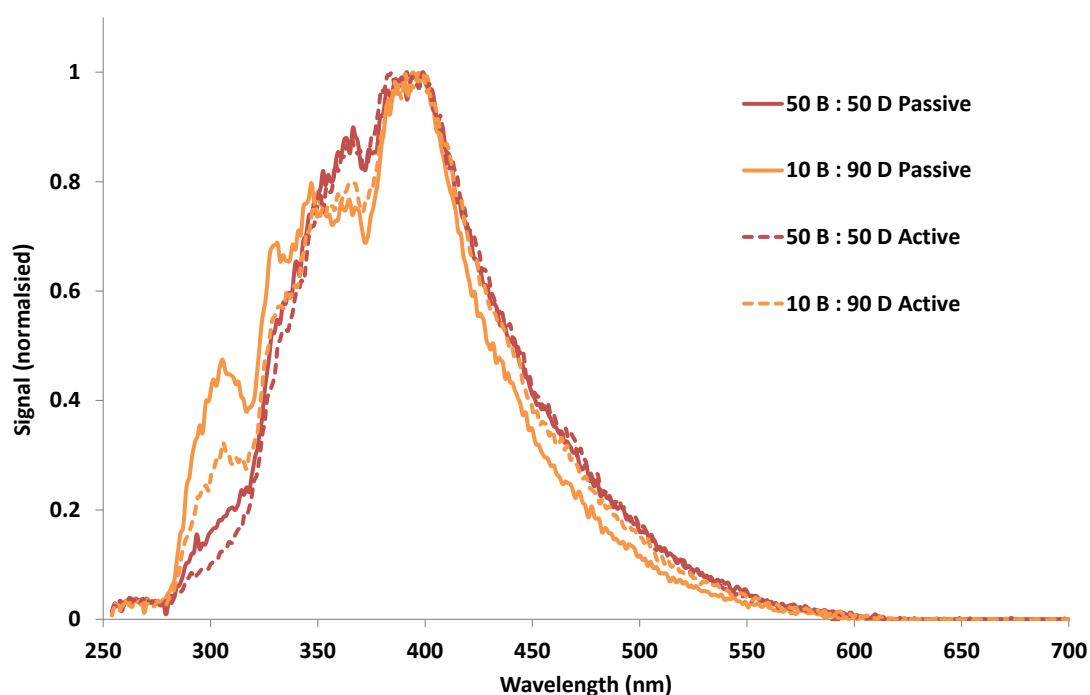


Figure 7.33 Synchronous UVF spectra of deposit samples of active and passive blends of Crude B and Crude D. Deposits are from 10:90 and 50:50 blend volume ratio.

7.5.5. Characterisation by TGA

TGA analysis of active blended deposit samples are summarised in Figure 7.34. As anticipated, the higher volatile loss by 370 °C was recorded for deposit of 10:90 blending ratio and the lower for 50:50 volume ratio. This was also observed in the other deposit samples of passive blend of Crude B + Crude D, as well as passive and active blends Crude A + Crude D. The amounts of volatile loss between the two set were comparable with values ranging between 57% to 85% for the active blended deposits. The amount of fixed carbon content varies from 2.3% to 20.4% with the higher value recorded for 50:50 and 30:70 blending ratios. Similar to the passive blended deposits, the fixed carbon contents for these two ratios were almost identical, suggesting that fouling due to coke was more pronounced in these two blends.

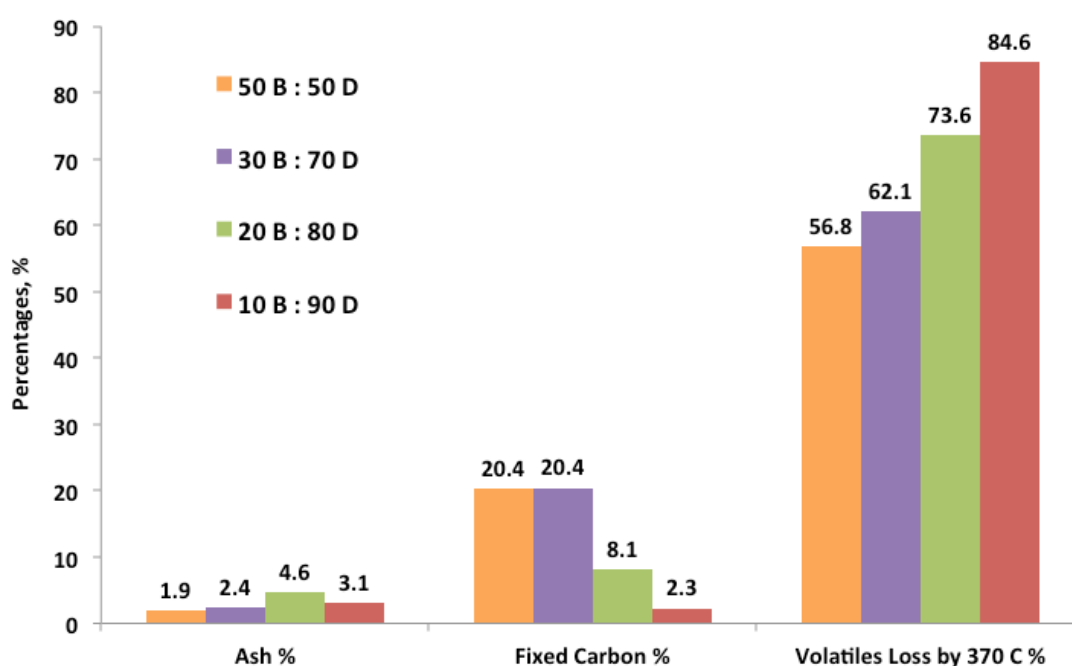


Figure 7.34 Percentages of ash, fixed carbon and volatiles loss by 370 °C in the deposits produced from active blending of Crude B and Crude D.

Comparisons between TGA results of active blends containing Crude A and Crude B are presented in Table 7.8. Deposits containing Crude A showed heavier nature in the 50:50 ratio as it produced lower volatiles loss (31.9% vs. 56.8%) and higher fixed carbon content (24.3% vs. 20.4%). The reverse was observed in the deposits of 10:90 volume

ratio, in which lower volatile loss (84.6% vs. 85.7%) and higher fixed carbon content (2.3% vs. 1.8%) came from deposits comprising Crude B. These results are coherent with TGA results of passive blending (Table 7.6) showing agreements in terms of the compositional changes trend of the two blended samples.

Table 7.8 Comparison of percentages of fixed carbon and volatiles loss for 50:50 and 10:90 blending ratios for Crude A + D and Crude B + D in active blending action.

Sample	Blend	Fixed Carbon (%)	Volatiles Lost by 370 °C (%)
Crude A + D	50:50	24.3	31.9
	10:90	1.8	85.7
Crude B + D	50:50	20.4	56.8
	10:90	2.3	84.6

7.6. Conclusions

A number of conclusions may be made from this study. The qualitative analyses of the deposits were performed to investigate the effect of the act of blending towards the change in the composition of deposits in molecular level. These conclusions are listed below:

1. The fouling compatibilities of Crude A and Crude D as well as Crude B and Crude D blends have been established using the oil compatibility model by Wiehe [42]. The compatibility region is bigger in the blend of Crude A and D with incompatibility region started at 86 vol% of Crude D, whereas for Crude B and D blend, incompatibility is first encountered at 67 vol% of Crude D. The model gave good agreement with the analyses conducted for both blends in terms of the amount of deposit produced in both regions. More deposits were formed at the incompatible part of the blends in both cases. An increase in the amount of deposits was also observed at the near-incompatible region of Crude A and D blend.

2. Active blending action further promotes formation of deposits in both blends of crude oils. This is especially the case in the compatible part of blends whilst within the incompatible region, amount of deposits formed are comparable of each other. If oils are blended from its incompatible region, i.e. by adding heavier crude oil into lighter oil, the agglomeration and precipitation of asphaltenes are immediate. The precipitated asphaltenes act as precursor to fouling, undergo chemical reaction in the bulk and/or on the heat transfer surfaces with other components to form heavy deposits. The instantaneous precipitation of asphaltenes from active blending action most likely trigger further formation of deposits compare to passive blending as shown in this study.
3. Deposits produced in the incompatible region of oil blends are made up of lighter and smaller components. The amounts of deposits produced in the incompatible region are higher but the composition of deposits shows higher volatility and lower molecular weight distribution. Results of SEC and UVF show that for both oil blends, deposits formed inside this region are found to be built up of smaller aromatic ring structures as well as smaller molecular weight distribution. Results from TGA also recorded higher volatile loss by 370 oC for these deposits. It is believed that most of the deposits are made up of lighter components that agglomerate further by the incompatibility behaviour of the blends.
4. Comparisons of the UVF spectra, SEC chromatograms and TGA proximate analysis were made between the passive and active blends of both Crude A + D and Crude B + D blends. Deposits originated from blends containing Crude A give bigger molecular weight distribution and larger aromatic rings structures, but only at the compatible part of the blend. Within the incompatible region, deposits produced are heavier in the blend containing Crude B. It is thought that Crude D solvent power plays a main role of this observation. At different blend volume ratios, Crude D showed different behaviour in precipitating asphaltenes of the heavier crude oils. It is proposed that a study may be performed with a variety of lighter oils to further understand this phenomenon.

8. Conclusions and Recommendations for Future Work

At the beginning of this study, three main objectives were defined; i) to design and develop a lab-scale batch reactor system for production of deposit samples, ii) to study the effect of vanadyl porphyrins towards deposition of foulants and characterise the resultant deposit products, iii) to study the effect of crude oil blending and the blending order towards deposition of foulants and characterise the resultant deposit products.

In Chapter 4, the design of the batch reactor system was presented and discussed. Some modifications on the control and design of the reactor were made and reflected to the operating procedure of the system. Chapter 6 provides the comprehensive analysis of fouling behaviour with the presence of vanadyl porphyrins at various concentrations. Characteristics of deposits produced from this study were presented based on the results of SEC, UVF and ICP-MS. This has provided insights on the impact of processing crude oils with high concentration of Vanadium and the possibility of increased deposits formation on heat exchanger surfaces. Fouling behaviour towards changes in crude oil compositions through blending has been discussed in Chapter 7. Moreover, characterisation of deposits produced from the oils blends based on their compatibility behaviour was performed and discussed. The outcome of this analysis provides a better understanding of the nature of deposits produced in terms of their molecular mass composition and structure as well as the effect of blending action on the manners in which deposits are formed.

This chapter provides the summary and conclusions for each of the studies performed, together with the achievements accomplished in the study. These are followed with recommendations that may be considered for future studies.

8.1. Conclusions

Conclusions of this study can be broken up into three main items:

1. Design and construction of a batch reactor system.

A batch system has been designed and constructed with the aim of producing consistent and repeatable runs of generating deposit samples for characterisation study. The system was designed to overcome limitations posed by a previous system in which an interface between liquid samples and nitrogen gas gave rise to sample loss in experiments conducted [16]. The newly developed system eliminates the two-phase condition by employing a procedure that pushes the sample into the test section. This is done by applying pressure from nitrogen cylinder that directs the sample into the heated section. Deposits were produced at a lower pressure in comparison to the earlier system operating at 80 bar, reducing the effect of sample volatilisation. Each experimental run was conducted at 350 °C at 10 bar for 48 hours. Recoveries of both liquid and deposit products between runs of similar conditions were consistent throughout the study. The reactor has been successfully commissioned with some modifications made against the preliminary design to cater for few setbacks in process control and results inconsistencies encountered during the commissioning period. Repeatability of results and control of the reactor upon modifications has been improved significantly. The modifications and improvements included:

- i) Change of the test section material from stainless steel to carbon steel. Deposition of foulant proved to be difficult when stainless steel was used due to its relatively smoother surface roughness compared to carbon steel.
- ii) Positioning and selection of certain type of valves in the reactor. A check valve was replaced with a needle valve (14) in the test section assembly to provide better control of sample flow during start up hence provided better consistencies between runs. A ball valve was changed to a needle valve (8) in the feeding section to allow better control of nitrogen gas during degassing of crude oil sample. A ball valve was installed (2) in the nitrogen line to isolate the pressure of the system and pressure from the gas cylinder.

- iii) Configuration of the thermocouple assembly in the test section. This configuration had to be changed due to the inconsistencies in the recovery of liquid products thought to be caused by nitrogen gas trapped during sample loading.
- iv) Control of the heating via ring thermocouple attached to the tube outer wall. Initial control and measurement were made by thermocouple at the bulk fluid in the test section. This ensured improved accuracy of the wall temperature measurement and heating control of the system hence better consistencies between repeats.

2. Effect of vanadyl porphyrins on deposition of foulants

Introduction of vanadyl porphyrins on neat crude oil samples increases the likelihood of fouling on heat transfer surfaces. However, the increment on the amount of deposit is only significant at much higher concentrations of vanadyl porphyrins relative to its original amount in the crude oils used in this work. In this particular study, heavier Crude A gave higher amount of deposits than lighter Crude D at similar concentration of added vanadyl porphyrins. The increment of deposit amount between samples without added vanadyl porphyrin and samples at the higher concentration of added vanadyl porphyrin is higher for Crude A. This may be used as an indication that heavier oils are more affected than lighter oils. However a larger variety of samples should be subjected to analysis to further understand the generic behaviour of fouling upon addition of Vanadium.

Vanadium was recorded at much higher concentrations in the deposit fractions than in the liquid for both crude oils. The added porphyrins mostly ended up in the deposits, suggesting its propensity to be associated with heavy components as found in its natural forms as vanadyl porphyrins linked with asphaltenes in most crude oils. At similar concentrations of added vanadyl porphyrin, deposits of Crude D recorded higher concentrations of Vanadium most probably due to lower hydrocarbon contents in these deposits compared to those of Crude A.

As expected, analysis of SEC showed larger molecular weight distribution in the deposits as opposed to the liquid products. This was true for both Crude A and

Crude D. It is worth to mention here that not all of the components in these deposits were analysed by SEC and UV-F due to its partial solubility in CHCl_3/NMP mixtures. Comparison amongst the deposit products showed increments of molecular weight distribution as the concentration of added vanadyl porphyrin in crude oil samples increased. GC results supported observations of SEC of which samples with higher concentration of vanadyl porphyrin produced heavier deposits. At the higher concentration of added vanadyl porphyrin however, particularly in the case of Crude A, the deposits showed smaller molecular mass range compared to the liquid. The solubility of this deposit in chloroform is the lower amongst the deposit products, hence it was likely that species of larger molecular weight were not analysed. The results of GC confirmed this observation, with higher residue fraction recorded for Crude A deposit. It was also confirmed by analysis of UVF with smallest aromatic ring structures observed in this deposit.

The UVF spectra of the other products followed the observation in the SEC analysis. Bigger conjugated aromatic chromophores were found in the deposit samples compared to their liquid counterparts. Deposits produced from samples with higher concentration of vanadyl porphyrin produced spectra corresponding to bigger aromatic ring structures. The results proved that the presence of extra Vanadium in the crude oil increases the complexity of deposits produced in terms of bigger aromatic ring systems as well as larger molecular weight distribution.

3. Effect of crude oil compatibility on deposition of foulants

The likelihood of fouling to occur in process streams is enhanced if incompatible crude oils are blended together. This is especially the case if the blended oils are within the incompatible region and if the blending action was done by adding the heavier crude oil into the lighter oil. This action would trigger immediate precipitation of asphaltenes and hence it increases the possibility of deposition. This was observed in this study for the two sets of crude oil blends studied. The compatibility regions for each set of blends were established. There was a clear distinction between the two regions in terms of the amount of fouling deposits. Blends within the incompatible section produced higher amount of deposits.

Characterisation by SEC and UVF showed that deposits formed within the incompatible region of the blends contain smaller molecular weight distributions with smaller aromatic ring systems. As the ratio of lighter Crude D was higher, it could be that these components were originated from Crude D and formed through combinations of smaller chains of hydrocarbon molecules and later deposited on the wall surfaces. Characterisation through TGA supports this observation in which higher volatiles lost were recorded in deposits from incompatible region.

One of the main findings of this study is the different nature of deposits produced from the two blending actions. The amounts of deposits produced in the incompatible regions from both active and passive blending actions were comparable and within the experimental errors. Having said that, if blending were performed in the active manner, more foulants were deposited at similar crude oil ratios in the compatible region. The characteristics of deposits from oils with similar blending ratios were found to be different, with heavier and more complex structures identified in deposits formed from active blending action. This observation shows that the correct blending action must be applied not only to reduce the formation of deposits, but also to reduce formation of deposits more complex and heavier in nature.

8.2. Recommendations for Future Work

Several recommendations have been identified and may be considered for future work. These are listed as follows:

1. Design and Operability of Fouling Reactor
 - a. Use of a pump may be considered to ensure a better control of sample flow in the filling procedure. Flow of sample from the sampling cylinder can be controlled to allow for improved consistency in introducing samples into the test section.
 - b. Instead of a heating tape, a tube furnace may be used to achieve a uniform temperature profile along the test section. The use of heating tape may have

created hot spots in certain parts of the test section and resulted in inconsistencies between repeats of identical runs.

2. In addition to the work of vanadyl porphyrin, the effect of other trace metals such as Nickel towards deposition may be studied. The presence of Nickel and its derivatives in crude oil are about as frequent as Vanadium as it is also associated to asphaltenes and heavy hydrocarbon components in crude oil. The establishment of the effect of these metals on fouling behaviour may be developed and it may provide better understanding towards the mechanism of crude oil fouling. As various types of metallo-porphyrins exist in crude oils, a different form of vanadyl porphyrin may be used in future studies. In addition, different types of crude oils of various origins, API values or asphaltenes content may also be selected.
3. To complement the experimental work on vanadyl porphyrins, the modelling studies at molecular level of porphyrins contribution towards fouling may be performed. By having this information, a better insight towards the behaviour of foulant deposition with the presence of vanadyl porphyrins may be established. A detail study on the molecular level shall provide a more mechanistic explanation on the formation of heavier hydrocarbon fractions that is influenced by the porphyrin complexes. The study may be conducted starting from a simple model compound of asphaltenes containing porphyrin complexes which may include studies on several factors such as polarity, molecular bond strength of metal porphyrin-asphaltenes components and reactivities of such compounds in hydrocarbon fluids.
4. The establishment of compatibility regions of crude oil blends may be further investigated at molecular level. This can be studied in terms of the stability of asphaltenes molecules in bulk solution either via simulation or experimental work using a model compound. This information again would be beneficial in understanding further the mechanism of which asphaltenes stability in crude oil is unbalanced by oil blending hence provide information on the fouling behaviour of oil mixtures. Consequently, experiments can then be tailored to test the hypotheses of crude oil compatibility from molecular level perspectives.

5. Following the characterisation study of deposits formed from incompatible pair of crude oils, crude oils that are self-compatible and compatible may be subjected to similar analysis to better understand the behaviour of fouling through oil blending. A wider range of crude oils should be included not only limited to a pair of crude oil, but mixtures of several oils should also be studied.
6. Characterisation of deposits and supernatant liquid products can be broadened to more analysis such as MALDI-MS, Elemental analysis and NMR to provide further understanding on the nature of deposits formed. MALDI-MS for example can overcome the limitations of limited solubility for deposit samples, and elemental analysis can provide information on the carbon and hydrogen contents that can be coupled with TGA analysis to measure the relative heaviness between deposits.

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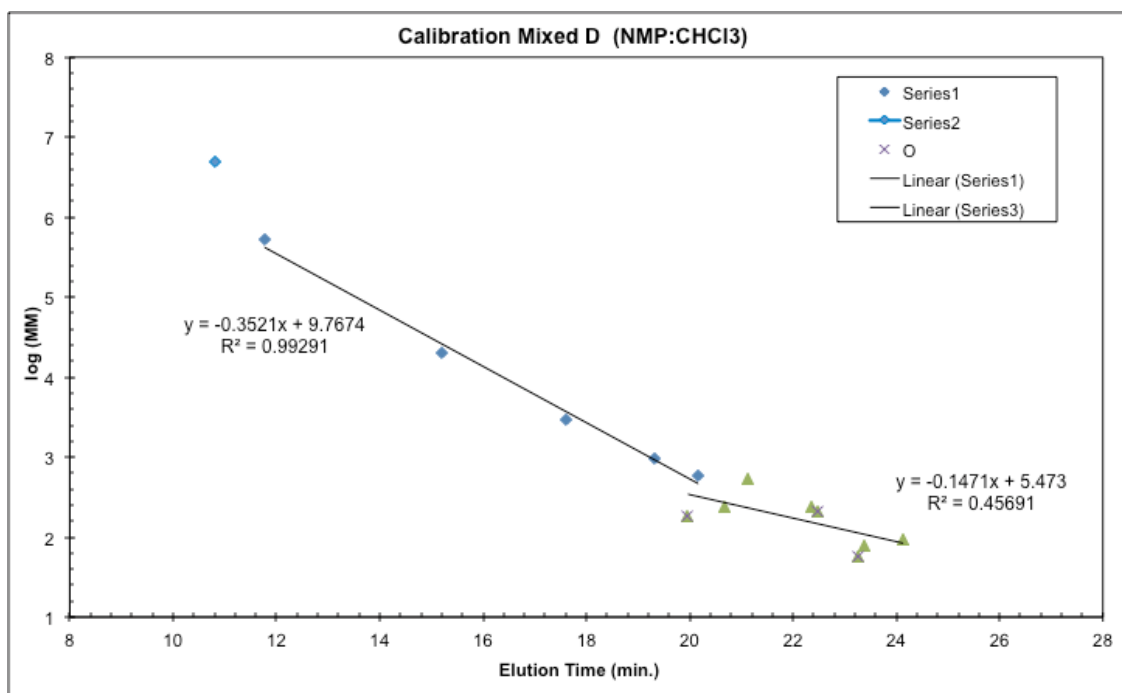
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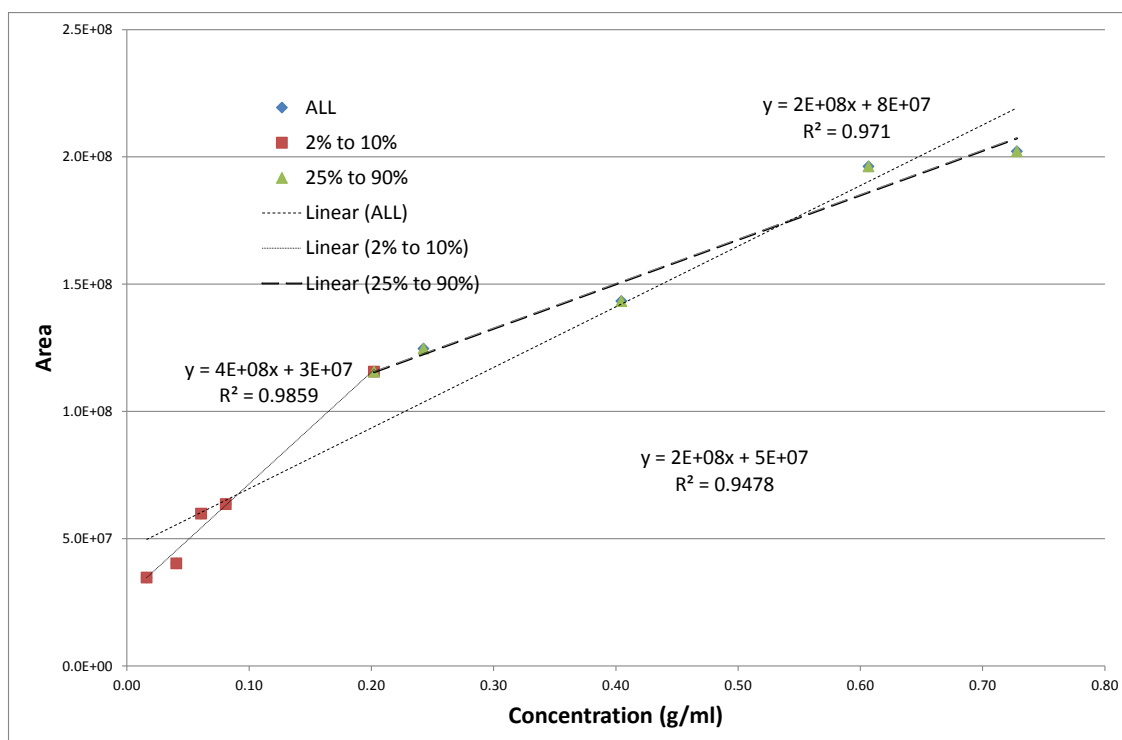
Appendices

Chapter 3

Appendix 3.1: Calibration Curve of SEC Column with polymers



Appendix 3.2 Calibration curve of GC with a standard gas oil



Chapter 5

Appendix 5.1 Blank samples reading of ICP-MS analysis for sample SRM 1635, SRM 1634c and deposits DA and DB.

Sample	Al	V	Cr	Cr	Mn	Co	Ni	63 Cu	65 Cu	66 Zn	68 Zn	75As	Cd	Pb	Pb
Blank 1															
Values ppm	24.62	2.18	23.04	22.38	0.76	0.05	2.96	14.66	14.41	50.94	48.53	0.06	0.08	6.74	6.81
Std.Dev	0.20	0.02	0.13	0.25	0.01	0.00	0.06	0.09	0.13	0.26	0.23	0.01	0.01	0.05	0.05
Blank 2															
Values ppm	5.73	0.12	-1.38	-1.45	0.13	0.01	5.86	1.04	1.03	190.43	179.78	-0.01	0.04	3.56	3.61
Std.Dev	0.39	0.01	0.01	0.02	0.01	0.00	0.17	0.05	0.05	4.37	4.41	0.01	0.00	0.12	0.11
Blank 3															
Values ppm	63.35	0.16	14.20	0.25	0.15	0.02	0.59	2.59	3.25	45.40	42.79	0.02	0.03	1.02	1.01
Std.Dev	1.61	0.01	2.52	0.31	0.01	0.00	0.02	0.06	0.07	1.14	1.01	0.00	0.00	0.03	0.02
Blank 4															
Values ppm	9.44	0.06	30.00	8.14	2.72	0.00	0.25	1.13	1.25	151.18	142.80	0.05	0.02	1.39	1.40
Std.Dev	0.18	0.00	4.59	0.62	0.05	0.00	0.02	0.05	0.05	3.93	3.61	0.03	0.01	0.03	0.03
Blank 5															
Values ppm	307.0	0.27	4.37	1.26	4.08	0.30	4.36	21.62	21.25	71.09	66.88	0.04	1.07	28.28	28.75
Std.Dev	9.50	0.01	0.48	0.12	0.11	0.02	0.14	0.37	0.46	1.01	1.21	0.01	0.07	0.71	0.66

Chapter 6

Appendix 6.1 Concentration of Vanadium and Nickel in Crude A and its fractions (results in ppm) ICP-MS

Element	Neat Crude A	Maltenes Crude A	Asphaltenes Crude A
Vanadium 51	67.5 ± 3.5	30.9 ± 0.4	528 ± 12
Nickel 60	17.8 ± 1.6	7.19 ± 0.25	179 ± 4

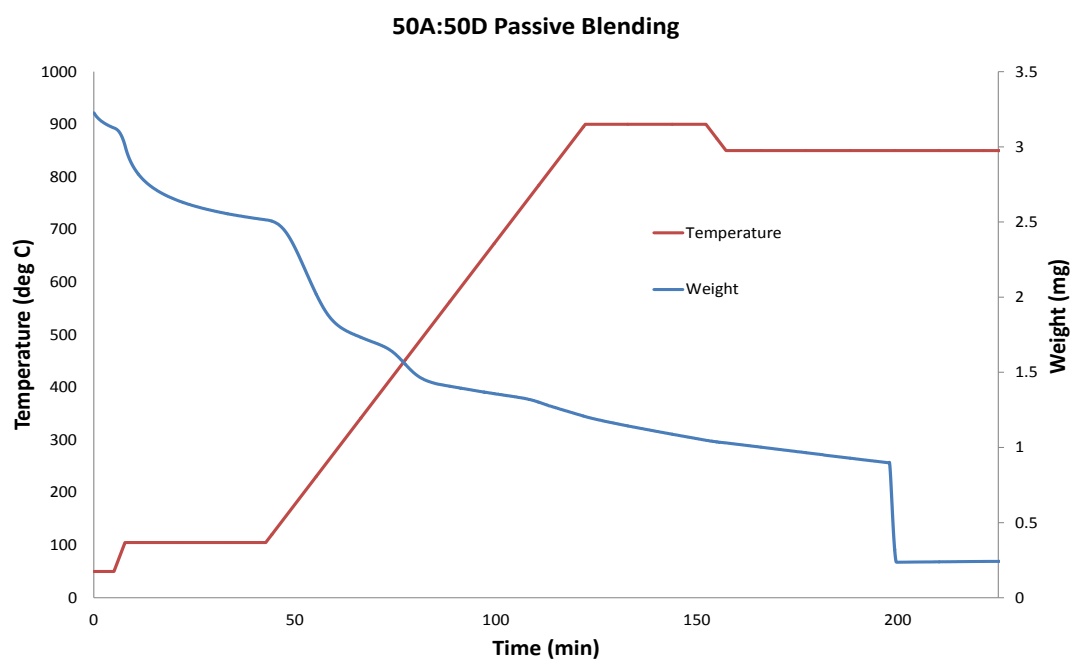
Appendix 6.2 ICP-MS analysis of Crude D and its fractions (results in ppm)

Element	Neat Crude D	Maltenes Crude D	Asphaltenes Crude D
Vanadium 51	<LOD	<LOD	0.5 ± 0.2
Nickel 60	3.2 ± 0.1	4.5 ± 0.8	2.6 ± 0.6

Appendix 6.3 Blank samples reading of ICP-MS analysis for sample SRM 1635, SRM 1634c and deposits of Crude A and Crude D with added Vanadium

	51 V	60 Ni	66 Zn	68 Zn	75 As	77 Se	78 Se	82 Se
Blank 1								
Values (ppm)	0.05	0.11	10.64	9.80	0.04	0.11	0.58	0.16
Std.Dev	0.02	0.01	4.37	4.41	0.05	0.05	0.01	0.17
Blank 2								
Values (ppm)	0.04	0.05	25.94	23.20	0.05	0.11	0.73	0.09
Std.Dev	0.02	0.05	3.61	3.93	0.05	0.03	0.01	0.03
Blank 3								
Values (ppm)	0.02	0.03	6.82	7.13	0.04	0.10	0.93	0.14
Std.Dev	0.14	0.37	0.46	1.01	1.21	0.01	0.07	0.71
Blank 4								
Values (ppm)	0.01	0.09	9.66	9.37	0.03	0.15	0.71	0.13
Std.Dev	0.06	0.09	0.13	0.26	0.23	0.01	0.01	0.05

Chapter 7



Appendix 7.1 Temperature and Pressure profile for Sample 50A:50D in passive blending action.