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Extensive chemical characterization of a heavy fuel oil

Extensive Chemical Characterization of a Heavy Fuel Oil

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ABSTRACT: This paper presents procedures for determining the fractions, chemical compositions and combustion characteristics of Heavy Fuel Oil (HFO). This chemical characterization is requisite for better prediction of thermodynamics behavior of multicomponent fuel such as HFO which consist of thousands of different components. Detailed chemical and physical compositions, molecular weight range and mean molecular weight of individual fractions of fuel enable to use more advanced approaches such as continuous thermodynamics for simulation and modelling. Sequential elution solvent chromatography was used to separate HFO into Saturates, Aromatics, Resins and Asphaltenes (SARA) as gas chromatographic analysis was unsatisfactory to reveal the overall composition of HFO, due to the insufficient

volatility in most of the heavy compounds. Subsequent mass spectrometric and elemental analysis showed a wide range of molecular weight distributions for the fractions. The results also indicate that the saturates fraction contains cyclic structures with aliphatic side chains while the aromatics fraction contains tetracyclic aromatic rings with aliphatic side chains. The degree of difference between the Thermo-Gravimetric Analysis (TGA) scans of the fractions in inert and oxidizing atmospheres observed at high temperatures also increases with the degree of functionality of the fractions due to the presumably greater extent of free radical chemistry occurring in an oxidizing environment. The Infrared spectra of the fractions are consistent with what would be expected from a consideration of the solvents used to elute them in column chromatography and supported the classification of the fractions.

1. INTRODUCTION

Maritime transport is the dominant form of transport because it is economical, energy efficient, emits fewer pollutants per tonne-km of goods displacement and is regarded as the safest means of transport. It uses Heavy Fuel Oil (HFO) as the primary source of fuel, which is a blended mixture of the residue from vacuum distillation and a more volatile fuel (cutter stock) [1]. The residue has a high viscosity and before it can be used as fuel, cutter stock is blended with it to lower the viscosity, and to aid the combustion in marine compression ignition engines. Cutter stock may also have a high aromatic content but it has lower molecular weight than the residue [1]. Heavy fuel oil is highly aromatic and has a high carbon to hydrogen ratio. In the industry, HFO is also known as Bunker Fuel Oil (BFO) or Residual Fuel Oil (RFO) while some lighter forms are known as Intermediate Fuel oil (IFO).

Current global environmental legislation and the steady increase in emission regulations have forced the transport industry to develop higher performing and more efficient engines [2-4]. The demand of modern on road transport has forced oil refineries to produce more lighter oil fractions (gasoline, diesel, etc.) and this greater demand together with advancements in petroleum refinery operations has had a direct impact on the quality of HFO. Subsequently, large marine engines are receiving more and more carbon-rich and higher aromatic content HFO. As a result of this poor quality fuel, engine problems are occurring [5] because aromatics are very stable and difficult to ignite. Some of the major issues are piston ring wear, cylinder liner scuffing and exhaust valve sticking [6]. The combustion process of this poor quality fuel in engines is very complex; it involves not only burning of volatile components but also burnout of coke residue. Although HFO is the most important source of fuel, because of difficulties in combined modelling of preferential evaporation and pyrolysis mathematically, to date very little efforts have been made to model the behavior of such multicomponent fuels [7]. Limited research work has been found in the literature on evaporation of multicomponent fuels and most of this work is based on binary component mixtures or up to ten discrete components. This discrete component approach is inadequate in representing fuels such as HFO, which contains thousands of different components. An alternative approach is required to treat a multi-component fuel such as the continuous thermodynamics technique, which represents the fuel components as a series of multi-distribution Probability Density Functions rather than a series of discrete components. Hence it reduces computational simulation load compared to discrete component modelling without degradation of the prediction quality of the complex combustion. The present paper outlines a method of determining the chemical composition of HFO by separating the HFO into fractions that differ in their chemical composition and physical properties, and by analyzing each

fraction. The chemical findings obtained from the separated fractions can be used in HFO combustion modelling including continuous thermodynamics.

The physical and chemical properties of fuels differ according to their location of origin, depth, and age of source. Chemical characterization of a multi-component fuel is an essential tool for understanding its behavior during combustion, as its combustion characteristics are directly related to its composition [8]. Heavy fuel oil is chemically very complex consisting of many different compounds. A complete characterization of HFO is impractical if not impossible [9]. However, there are methods by which the overall composition can be determined by analysing and grouping similar components. Rahimi & Gentzis [9] have reported methods for separating HFO into different fractions based on solubility and adsorption properties. A commonly employed method of fractionating HFO into smaller fractions involves separation by column chromatography, firstly used by Jewell et al [10], and a compound class characterization [11] commonly known as SARA, where SARA stands for Saturates, Aromatics, Resins and Asphaltenes (SARA) fractions. The saturates and the aromatics classes contain non-polar hydrocarbons. The resins fraction is the second least volatile fraction of HFO after the asphaltenes, while the asphaltenes have the highest molecular weight and polarity. The asphaltenes and resins fractions contain Sulphur, nitrogen and oxygen in addition to carbon and hydrogen and are the polar components of the HFO. This polarity of the resins and asphaltenes is mainly responsible for their low volatility.

Often the asphaltenes fraction is initially precipitated from the HFO by treatment with a non-polar hydrocarbon solvent. The remaining fractions (saturates, aromatics and resins) commonly known as maltenes, are then separated by sequential elution solvent chromatography (SESC). In this technique, progressively more powerful solvents are employed to elute progressively more

polar fractions from an adsorbent. A column filled with adsorbent media is employed, and a sample of maltenes is introduced at the top of the column. Different fractions of the maltenes are removed by passing different solvents through the column and collecting the eluent as it emerges from the column. Clearly, both the choice of solvents and adsorbent are important. Most researchers prefer to remove asphaltenes from the samples prior to chromatography because asphaltenes contain very polar compounds which are likely to be irreversibly adsorbed by the adsorbent. Once the fractions are separated, they can be analysed by various methods as outlined later in this paper. Many researchers such as Yasar et al.[12], Vazquez & Mansoori [13], and Farcasiu [14] have used silica gel as the adsorbent media for sequential elution solvent chromatography of petroleum. Liu et al.[15], Schiller & Mathlason [16] and Marquez et al.[17] used alumina while Burke et al.[18] have used glass beads. In addition to different adsorbent media, many different solvents have been used for the elution of the fractions. Summaries of the solvents used by various researchers for precipitation of asphaltenes from HFO and of the solvents and adsorbents used for SESC chromatography are given in Garaniya [7].

Elemental Analysis (EA) provides the molecular composition and estimates the heteroatom content of each separated fraction of HFO components [19]. With aid of this extensively used technique, intricate multi-component fuels such as crude oil and HFO can be characterized [20-21]. The structure of organic molecules [19], physical and chemical properties [22] of multi-component fuels can be investigated using Nuclear Magnetic Resonance (NMR) technique. Despite methods such as gas chromatography and mass spectrometry, this technique enables to characterize high molecular weight components of HFO [23]. The results of NMR analysis enhance our knowledge about properties of heavy components which are playing a key role in the combustion process and subsequently the formation of emissions [24-25].
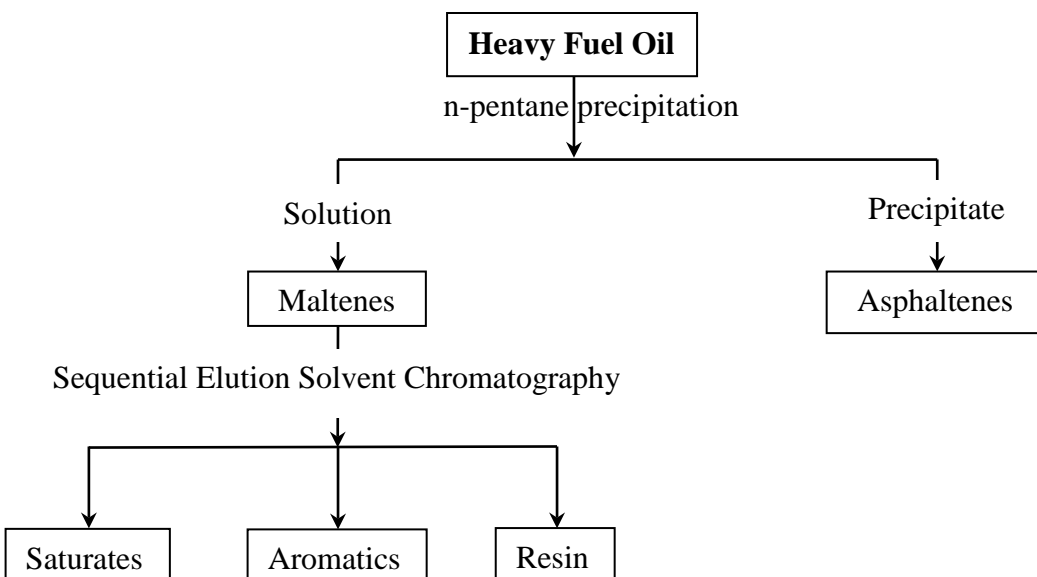
Moreover, in order to characterize the combustion features of HFO, Thermo-Gravimetric Analysis (TGA) can be conducted as the principal thermos-analytical technique [26-29] where the continuous physical and chemical changes of a sample are obtained and investigated. Pioneer study by Tadema [30] showed how TGA could reveal the thermodynamic behaviors of HFOs. Later on, a combined application of Differential Scanning Calorimetry (DSC) and TGA became a conventional approach for researchers [19, 31]. Most recently, Fan et al [32] and Elbaz et al [19] carried out TGA to investigate the oxidation behaviour and kinetics parameters of heavy fuel oil. Elbaz et al's results showed that the activation energy of high-temperature region (497−580 $^{\circ}$C) is higher than that for low-temperature region (25−342 $^{\circ}$C).

2. EXPERIMENTAL ANALYSES

A sample of marine HFO was collected from the port of Sydney and New South Wales, Australia. All other chemicals used were standard laboratory chemicals and all solvents were purified by fractional distillation prior to their use. This precaution was taken to avoid contamination of the original sample by high boiling point impurities in the solvent, which could be concentrated on evaporation of the solvents after fractions were collected. Gas chromatography was used to check the quality of the solvents before and after fractional distillation.

2.1 Procedure

A flowchart of the experimental procedure used for HFO separation is shown in Figure 1.

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                        ┌──────────────────┐
                        │  Heavy Fuel Oil  │
                        └──────────────────┘
                          n-pentane precipitation
                                  │
              ┌───────────────────┴───────────────────┐
              │                                        │
           Solution                               Precipitate
              │                                        │
        ┌───────────┐                           ┌───────────────┐
        │  Maltenes │                           │  Asphaltenes  │
        └───────────┘                           └───────────────┘
   Sequential Elution Solvent Chromatography
              │
      ┌───────┼───────┐
      │       │       │
 ┌──────────┐ ┌──────────┐ ┌────────┐
 │ Saturates│ │ Aromatics│ │ Resin  │
 └──────────┘ └──────────┘ └────────┘
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Figure 1. Experimental procedure for the separation of HFO into different fractions.

2.2 Precipitation of Asphaltenes

The asphaltenes fraction was initially separated from the HFO because it can cause adverse effects on the adsorbent by becoming irreversibly adsorbed. Asphaltenes are also known as 'bad actors' in refineries as they promote coke and sludge formation as well as causing catalyst deactivation during the processes. As described in the literature [14, 33], a 40:1 ratio of solvent to sample was used. An accurately weighed sample (2.557 g) of HFO was mixed with 100 mL of purified n-pentane. This mixture (HFO + n-pentane) was stirred for 24 hours at room temperature and allowed to settle for approximately 3 hours. The precipitated asphaltenes fraction was separated by vacuum filtration through a 0.2 micron Nylon filter. The solvent was allowed to evaporate from the filter at room temperature in a vacuum desiccator for approximately 24 hours and the weight of asphaltenes determined.

2.3 Separation of Maltenes into Saturates, Aromatics and Resins

The maltenes in pentane solution was isolated from asphaltenes by vacuum filtration and collected as a filtrate as described above. During vacuum filtration, some solvent loss occurred and n-pentane was added to make up the volume of the solution of maltenes to 50 mL. 10 mL (20% by volume) from this solution was mixed with 15-20 g silica gel, which had been previously activated by heating for 24 hours at 115 °C. Precautions were taken to ensure uniform mixing of the solution of maltenes with the silica gel by using a vacuum rotary evaporator to remove the solvent during the mixing of silica gel and maltenes over a period of approximately 3 hours.

A glass column with an internal diameter of 2 cm and a height of 35 cm was used for the sequential elution solvent chromatography (SESC). The column was filled with a slurry of pre-activated silica gel (grade 1) in pentane up to 23 cm, while the top 5 cm of the column was filled with the mixture of maltenes and silica gel mixture. The saturates fraction was eluted by passing 125 mL of n-pentane through the column and the eluate was collected in 10 mL test tubes. All test tubes were later examined by gas chromatography to ensure the elution of saturates was complete. Afterwards, only those test tubes which contained significant amounts of saturates were mixed to form a composite solution of saturates in n-pentane. As expected, it was found that only the middle set of test tubes in the sequence contained appreciable amounts of saturates. Some initial and final tubes were free from saturates showing that the amount of solvent used was sufficient to elute all saturates from the maltenes.

Aromatics were eluted similarly to saturates, using 125 mL of toluene as eluent with the eluted fractions were collected in 10 mL test tubes. The presence of aromatics in all test tubes was detected by gas chromatographic analysis. Thereafter, a composite sample of aromatics in toluene was prepared. It proved a difficult task to remove the entire resins fraction from the

column due to their polar characteristics. Initially, a mixture of 110 mL of toluene and 15 mL (12% by volume) of methanol was used to elute the resins fraction, but this was not found to be completely effective. Hence, the second volume of 40 mL of toluene and 10 mL (20% by volume) of methanol mixture was applied, which eluted most of the resins from the column. Finally, a 25 mL toluene and 25 mL (50% by volume) methanol mixture was applied to ensure that all the resins had been eluted and a composite sample was prepared. Thus, all three fractions of maltenes (saturates, aromatics and resins) were separated by the sequential elution solvent chromatography and collected.

The solvents were removed from the three fractions by employing a rotary evaporator. However, this was found to be incapable of removing all the toluene from the aromatics and resins fractions. Consequently, a vacuum oven was used to remove the last traces of toluene. Finally, the dried saturates, aromatics and resin were collected and weighed accurately. The amounts and yields of these fractions are discussed in a later section.

3. RESULTS AND DISCUSSION

3.1 SARA

A large number of solvent and adsorbent media combinations were considered before making the final selection of solvents and adsorbents for this procedure. Ali Mansoori et al. [34] states that the properties of the saturates and aromatics fractions are independent of the solvent used for their elution, whereas the same statement is not true for the composition and properties of asphaltenes and resins which generally vary according to the solvent used for their separation. The authors also mentioned that some resin is always mixed with asphaltenes, while some high molecular weight paraffin wax may also precipitate with the resins and asphaltenes. The results of

fractionation of the current sample showed that HFO contained Saturates 24.08%, Aromatics 55.81%, Resins 6.66%, Asphaltenes 7.86% and Unknowns + Loss 5.59% by weight. Furthermore, some preliminary observations of samples were made by visual inspection. The original HFO sample was dark black in color but that of the fractions were found to vary from a transparent light color to a dark color. Saturates contained viscous compounds of a whitish color. Aromatics contained yellowish viscous hydrocarbons, while the resins fraction had a reddish color, and as expected, asphaltenes contained black solids.

3.2 Elemental Analysis

Elemental analysis of this complex mixture and its separated fractions provided a useful method to estimate the heteroatom content of the components. The results of elemental analyses of the HFO sample and the SARA fractions are given in Table 1. This showed that the resins and asphaltenes fractions contain the majority of heteroatoms (S and N) and are the polar components of HFO, whereas the saturates contain the least.

Table 1. SARA analysis and elemental analysis of HFO and its fractions.

SARA analysis		Elemental analysis					
Components	Weight %	C%	H%	S%	N%	Total	H/C
Saturates	24.08	85.32	13.17	0.48	0.05	99.02	1.852
Aromatics	55.81	83.83	9.92	4.28	0.20	98.23	1.420
Resins	6.66	80.03	10.55	2.78	0.82	94.18	1.581
Asphaltenes	7.86	83.49	8.03	7.07	0.75	99.34	1.154
Loss & unknowns	5.59	85.17	9.16	4.42	0.24	98.99	1.290

As expected the saturates fraction contains mainly carbon and hydrogen (98.5%) although the H/C ratio is less than 2 which might be expected if it is mainly comprised of linear and branched chain alkanes, and indicates that condensed cyclic structures might be important.

The saturates and aromatics fractions contain small amounts of nitrogen and some Sulphur. The significant Sulphur content in the aromatics fraction could be due to thiophenic aromatics as stated by McKay et al.[35], while the oxygen could be present as methoxyl substitutes or involved in furon rings. The H/C ratio indicates the presence of alkyl substitution on the aromatic rings as the ratios for naphthalene and anthracene are much lower at 0.8 and 0.71 respectively. A naphthalene ring required a total of ten alkyl carbons in substituents to reach a H/C ratio of 1.40. The higher percentage of hydrogen in saturates confirms that this fraction is relatively free from aromatics. The hydrogen to carbon ratios (H/C) obtained from this analysis are 1.852 and 1.420 for the saturates and aromatics respectively. This result concurs with Baert [36] that nafteno-paraffins and nafteno-aromatics contain only carbon and hydrogen have very little or no polarity.

Resin contains the majority of the oxygen in HFO and is responsible for the polarity of this fraction, and also contain a significant amount of Sulphur and nitrogen. Asphaltenes contain the most heteroatoms (S, N and O) and have the lowest H/C ratio indicating a high degree of aromaticity. The Sulphur would be expected to be involved in thiophene-based ring systems. The low H/C ratio for asphaltenes (1.154) indicates that it has high aromaticity and condensed ring aromatic structures. The H/C ratio of saturates (1.852%) is less than 2 indicating the presence of cyclic structures, while the relatively large amount of unaccounted material in the resins fractions (5.82%) indicates a significant oxygen content which is consistent with their higher polarity. The total amount of C, H, S and N in the original sample is found to be equal to the summation of all individual fractions with minor errors.

3.3 Gas Chromatography and Mass Spectrometry

Gas Chromatography (GC) of both volatile fractions (saturates and aromatics) were conducted as described in Garaniya et al. [37]. The GC analysis of the resin fraction was not possible due to its

high degree of polarity, while the size, complexity and polarity of the asphaltenes components also mitigate against the GC analysis of this fraction. The GC analysis of saturates fraction showed the presence of a series of n-alkanes ranging from C11 to C29 with a distribution corresponding to a distillation fraction, with the maximum abundance occurring at C15. This presumably represents the cutter stock which has been added to the heavy oil residue and amounts to 10.3% the HFO fraction. The rest of the saturates fraction which amounts 13.78% of HFO is comprised of heavy molecular weight hydrocarbons (greater than 400) which appears from the elemental analysis of this fraction to contain condensed cyclic structures. The aromatic fraction contained less volatile materials which correspond to 5.9% of HFO with a mean molecular weight around naphthalene and phenanthrene. The remaining aromatic fraction (49.91%) of the HFO is high molecular weight materials.

As described in Garaniya et al. [37] the mass spectrum of the saturates fraction was difficult to interpret due to the high instability of the molecular ions of linear alkanes, and the extensive fragmentation as evidenced by the predominance of odd molecular weight ions detected below 400. The GC analysis of the saturates fraction showed the presence of alkanes with molecular weights less than 394 (C_{30}), but corresponding to only 43% of the total saturates fraction. The remaining 57% of this fraction is thought to contain very long chain alkanes and cycloalkanes with molecular weights well in excess of 394. There is some evidence of molecular ions in the range 200-1100 in the mass spectrum, but it is very difficult to accurately estimate the mean molecular weight of these longer chain alkanes. Molecular ions are observed in a regular sequence separated by 14, due to a -CH_2- unit, and are indicative of a homologous series. The first molecular ion shown is 456.4 and consideration of this mass, together with the H/C ratio

obtained for this fraction, suggests a parent structure based on a steroid residue;
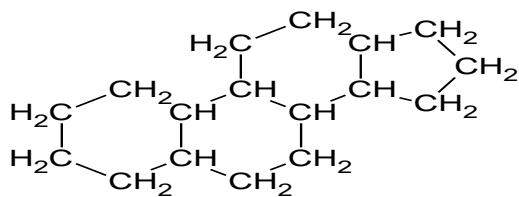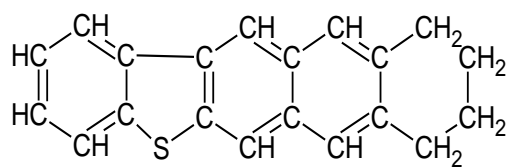
 with an additional 16 -CH$_2$- units attached.

The hydrogen to carbon ratio for this representative structure is 1.818, which is very close to the experimental result (1.852). These 16 -CH$_2$- units could be attached randomly to the structure. Moreover, the remaining molecular ions may contain the same cyclic structure but with additional -CH$_2$- units attached. These tetracyclic molecules with many -CH$_2$- side chains would be expected to form more stable molecular ions than linear alkanes as fission of a carbon-carbon bond in the ring does not result in fragmentation. However, it is possible that these results may not be really representative of the heavy alkane components as the long linear alkanes are not likely to be detected and the situation is further complicated by the molecular ions of the linear alkanes of the cutter stock. The mean molecular weight estimated for the saturates is 580, as shown in Table 2.

Mass Spectra (MS) obtained for the separated aromatics fractions showed the lighter peaks in the beginning of the spectrum are mainly odd weight ions resulting from fragmentation, while the even weight ions are due to the molecular ions of aromatics, which are more stable and likely to persist. A zoom portion of this mass spectrum also shows the presence of a homologous series separated by -CH$_2$- units. Consideration of one of the peaks of mass 582.5, together with the elemental composition of this fraction suggests a structure containing fused aromatics, thiophenic and naphthenic rings;

with an additional 21 -CH$_2$- units as side chain

attachments.

The hydrogen to carbon ratio obtained for this structure is 1.415, which is very close to the

analytical result (1.42) and the S content of 5.5% is relatively close to the analytical result (4.28).

Mean molecular weight calculated from the MS data for aromatics shown in Table 2 is 545.

The mass spectra of resin and asphaltenes fractions are complex and difficult to interpret. This

statistical measure of the obtained masses with time for the aromatics, resins and asphaltenes

fraction displayed two broad humps. In the case of the resins and asphaltenes, the second hump

could be due to decomposition of very polar high molecular weight and relatively non-volatile

compounds on heating. However, it could be an artefact of the instrument due to temperature

variation in different regions of the probe. By normalization of the available data, the mean

molecular weights were estimated as shown in Table 2. Further details about all analysis and

results can be found in Garaniya [7].

Table 2. Mean molecular weights of the SARA fractions.

Sample Name	Mean Molecular weight
Saturates	580
Aromatics	545
Resins	573
Asphaltenes	542

3.4 Infrared Spectroscopy

Infrared (IR) spectra were recorded on a Bruker Vertex 70 using a Diamond single ATR and

DLaTGS detector with spectral range 130-4600 cm^{-1} and spectral resolution 4 cm^{-1}.The IR

spectra of the four HFO fractions are shown in Figure 2. The atomic ratios relative to carbon calculated from their elemental composition are given in Table 3, where oxygen has been determined by difference and will be subject to the greatest error. In view of the relatively low abundance of the heteroatoms and the low polarity of some of carbon to heteroatom bonds, they would be expected to make only very minor contributions to the spectra with the possible exception of carbon to oxygen bonds.
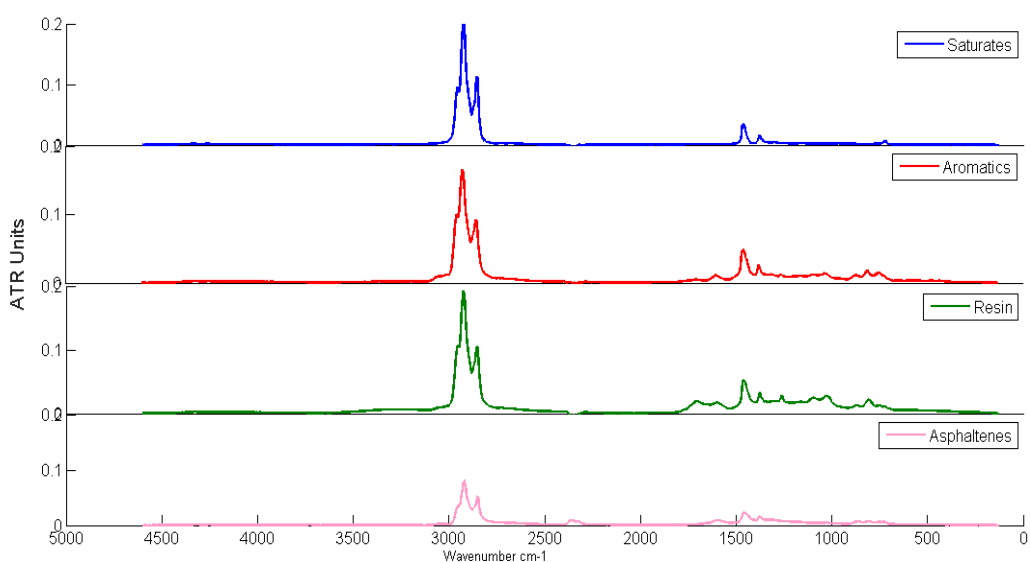
Figure 2. IR spectra of the four HFO fractions.

Table 3. Atomic ratios relative to carbon.

	C	H	S	N	O
Saturates	100.0	183.9	0.2	0.1	0.9
Aromatics	100.0	141.0	1.9	0.2	1.6
Resins	100.0	157.1	1.3	0.9	5.5
Asphaltenes	100.0	114.6	3.2	0.8	0.6

The IR spectrum of the saturates fraction is consistent with a mixture of long-chain alkanes, while the small peaks in the region 900-1300 cm^{-1} indicate the presence of cyclic structures.

These were also detected by mass spectrometry, where the long linear alkanes are much harder to detect. The aromatic fraction spectrum reveals a mixture of heavily alkyl substituted aromatic rings, while the peaks in the region 1300-1000 cm^{-1} indicate the presence of cyclic and furan type structures. The IR of the resins fraction is more complex but also shows a predominance of alkylated aromatic structures. As expected it shows some evidence of oxygen-containing groups, for example at 1703 cm^{-1} which is indicative of a conjugated carbonyl group, and the bands in the region 1260-1000 cm^{-1} are consistent with carbon-oxygen ether bonds. The asphaltene fraction IR is relatively uninformative, with again alkylated aromatic structures predominating. However, the complexity of this fraction and the resulting broadness of the peaks preclude identification of the functional groups.

Overall the Infrared spectra of the fractions are consistent with what would be expected from a consideration of the solvents used to elute them in column chromatography and supports the classification of the fractions.

3.5 Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR) data were acquired using a 4-channel Bruker AVANCE III HD spectrometer with a triple-resonance cryogenically cooled probe with Z-axis gradient coil at spectrometer frequencies of 600.07 MHz and 150.89 MHz for ^{1}H and ^{13}C respectively. All data acquisition and processing were performed using Topspin 3.2 software (Bruker Biospin 2012). Samples were dissolved in deuterated chloroform (CDCl3 – Cambridge Isotope Labs. MA USA) and sample temperature maintained at 27 °C. ^{13}C-1D, ^{1}H-1D, 2D COSY, 2D ^{1}H-^{13}C-HSQC and 2D ^{1}H-^{13}C-HMBC spectra were acquired using the standard Bruker standard pulse program. ^{13}C and ^{1}H NMR spectras for all four fractions are shown in Figure 3 and Figure 4 respectively.
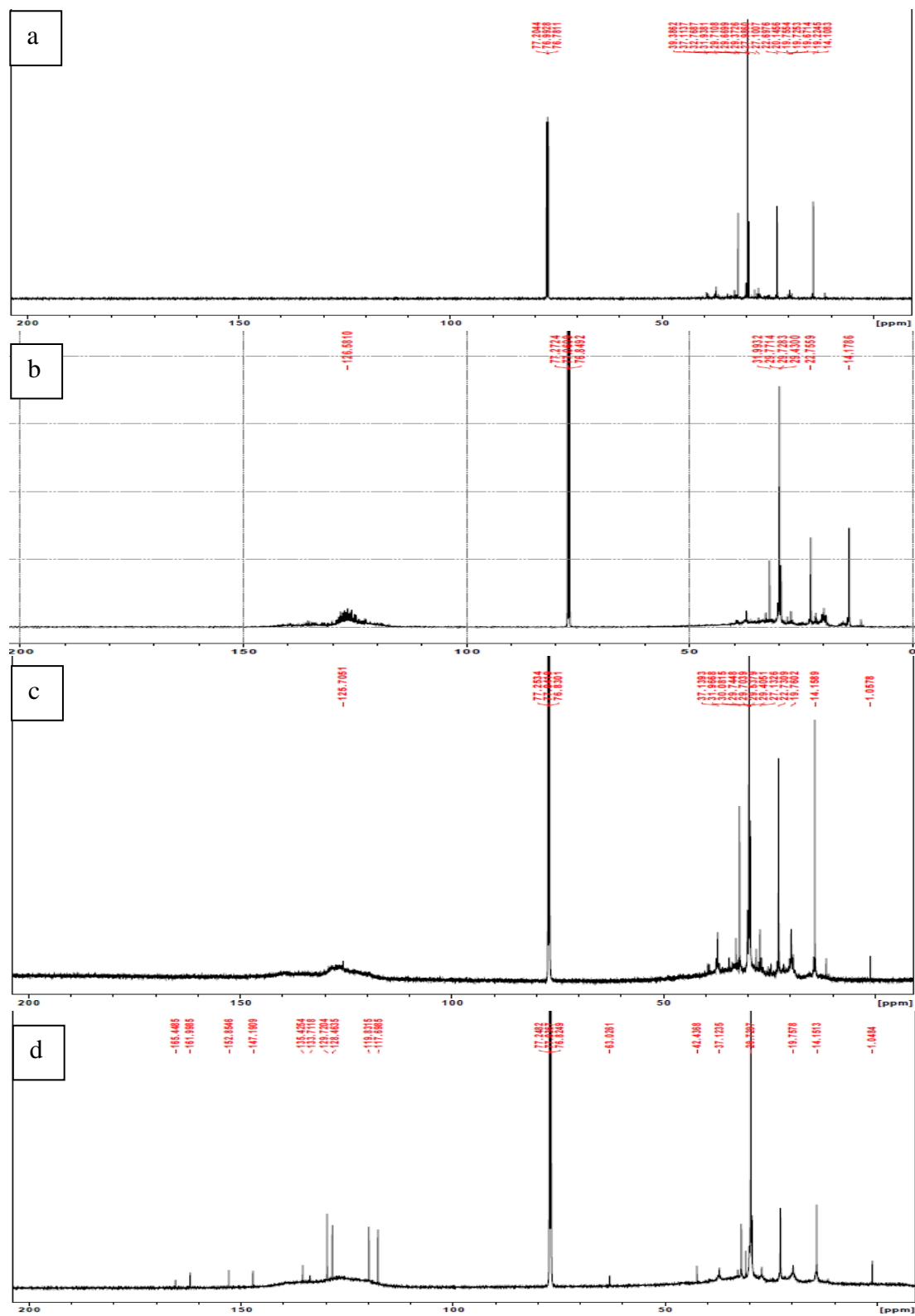
Figure 3. ^{13}C-1D spectra for all four fractions (a) Saturates (b) Aromatics (c) Resin and (d) Asphaltenes. x axis represents ppm, y axis represents intensity.
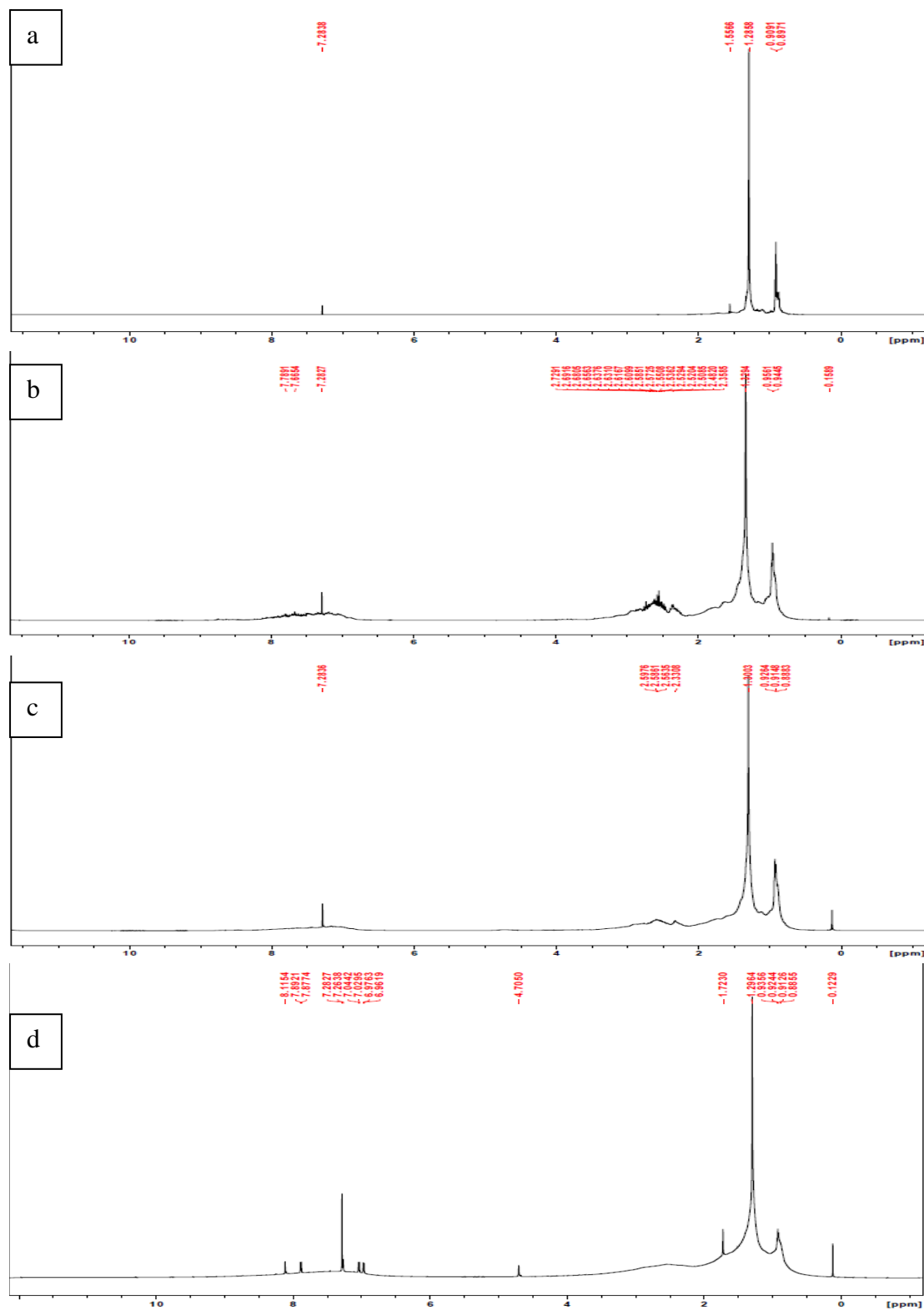
Figure 4. ^{1}H-1D for all four fractions (a) Saturates (b) Aromatics (c) Resin and (d) Asphaltenes.

x axis represents ppm, y axis represents intensity.

Although the NMR spectra of the fractions are of complex mixtures, careful and detailed consideration of the ^{1}H, ^{13}C, COSY, HSQC and HBMC spectra provided the following assignments which are consistent with the observed data. As expected from the GC and IR results, the spectra of the alkane fraction are consistent with a combination of linear and branched alkanes. Branches appear to be mainly methyl groups situated at both the ends of the chain and more centrally. They may also be evidence of small amounts of the cyclic structures which appeared to predominate in the MS. Long linear alkanes fragment in the MS are difficult to detect while cyclic structures often exhibit a molecular ion.

The aromatic fraction appears to be comprised of a mixture of linear and branched alkyl substituted naphthalene, anthracene and phenanthrene ring systems. The amount of alkyl substitution is substantial and in agreement with the IR results. Only a small amount of the resin fraction was available for spectral analysis and consequently, the ^{13}C spectra obtained exhibited a relatively high noise level which limited interpretation. Linear and branched alkyl substituents are present on aromatic ring systems, while the aromatic ^{1}H and ^{13}C chemical shifts indicate the presence of aryl ether bonds in the parent structure similar to that below as well as ketone groups conjugated with the aromatic ring. Carbonyl peaks are not evident in the ^{13}C NMR but perhaps this is not surprising given the low signal to noise ratio of the spectrum.
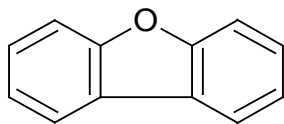

The ^{1}H and ^{13}C NMR spectra of the asphaltenes show the very broad aliphatic and aromatic resonances which would be expected of the most complex fraction. These are consistent with linear and branched alkyl substituted aromatic systems. However also present in the aliphatic and

aromatic regions of both spectra are a number of sharp resonances, which are indicative of simpler structures which have probably been occluded in the asphaltene fraction during precipitation with pentane. As they are relatively intense their sharpness tends to overemphasize their abundance relative to the very broad resonances. The aromatic regions of both spectra are shown in more detail below.

Consideration of the HSQC spectrum shows that the sharp resonances in the region 135-165 ppm of the ^{13}C spectrum do not have attached hydrogen atoms and are possibly due to alkyl substituted aromatic carbons in condensed and fused aromatic ring systems.

The sharp aromatic responses in the aromatic region of the ^{1}H NMR spectrum contain two AB patterns, H(a) H(c) and H(b) H(d) both with a coupling constant of 8.8Hz indicative of ortho coupling. These protons are attached to carbons associated with the sharp aromatic resonances in the 120-130 ppm region of the ^{13}C spectrum as indicated: 1-b, 2-a, 3-c, 4-d. The AB systems are probably due to ortho hydrogens in condensed and substituted aromatic rings with the simple and identifiable components illustrated below.

H 7.88   7.03
C 129.7 117.7

7.27   7.0
128.4   119.8
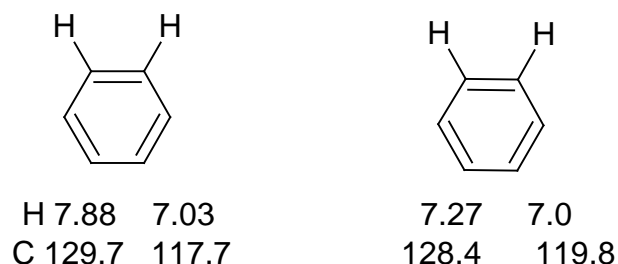
3.6   Thermo-Gravimetric Analysis and Differential Scanning Calorimetry

Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) scans were conducted employing a Netzsch 449 °C Jupiter DSC-TGA. This has an operating temperature range from ambient to 1650°C and incorporates a thermo-balance with exceptional resolution

(10-7 g). Its vacuum-tight construction enables scans to be conducted in a range of controlled atmospheres. Analyses were conducted on the Saturates, Aromatics, Resins and Asphaltenes fractions, as well as the original heavy fuel oil in order to probe the nature of the reactions occurring in and between these components at elevated temperatures. The TGA and DSC scans of the four fractions and heavy fuel oil in both inert and oxidizing atmospheres are shown in Figure 5 to Figure 9.

In inert atmosphere saturates initially undergo endothermic evaporation of the cutter stock and larger alkanes (up to 420 C - 86% mass loss) followed by two small decomposition steps (presumably cracking reactions) between 420- 440 °C and 450-470 °C representing 10% and 4% of the initial mass respectively. The entire sample is converted to gas by 500 °C.
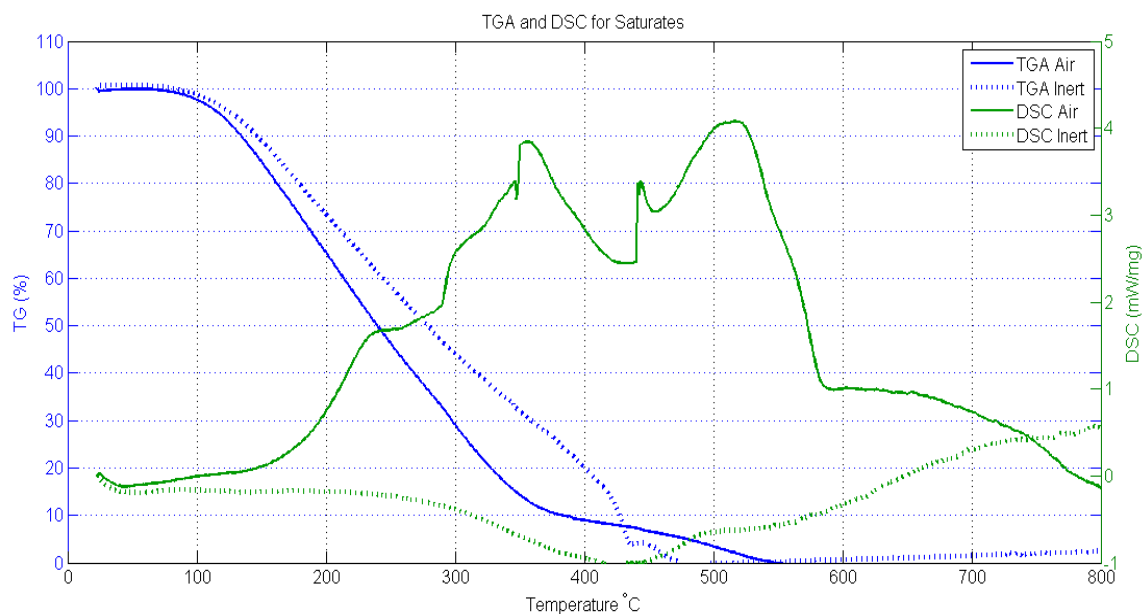

Figure 5. TGA and DSC for Saturates fraction.

In air the saturates show a similar pattern of mass loss up to 380 °C, which is exothermic due to combustion of the cutter stock and long alkanes (90% mass loss). Loss of the final 10% occurs

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between 380 to 560 °C and follows a different pattern to that observed in an inert atmosphere indicative of different chemistry, probably involving cracking and polymerisation, and is strongly exothermic. The relatively greater exothermicity of the later 10% mass loss probably reflects inefficient combustion of some of the lower boiling alkanes at low temperatures (less than 300 °C).

The TGA scan of aromatics an inert environment (Figure 6) shows a relatively smooth and even loss of mass between 160 – 520 °C and the DSC a broad endothermic peak around 460 °C; both indicative of a simple evaporation process. However, 8% of the sample remains up to 800 °C, having been converted to high molecular weight material or coke.
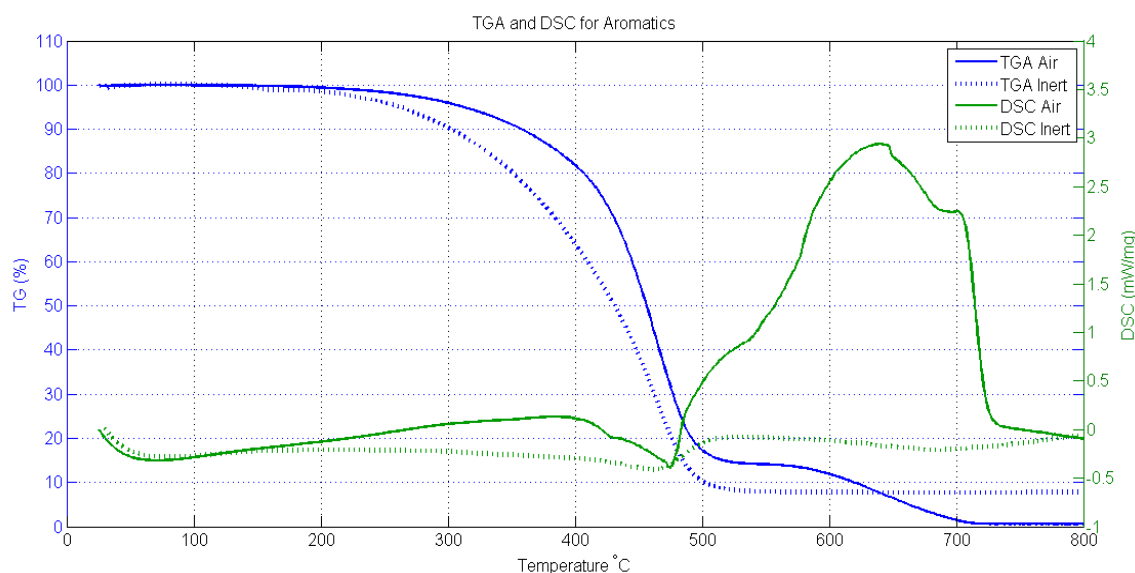

Figure 6. TGA and DSC for Aromatics fraction.

The TGA scan in air shows a similar mass loss between 200-500 °C which is only mildly exothermic in the DSC up to 470 °C again probably reflecting mainly evaporation with only limited combustion at lower temperatures. The 13% mass loss evident in the TGA from 540-700 °C is accompanied by a very strongly exothermic peak from 470-720 °C. The behavior on

heating in the air is somewhat different from that in the inert atmosphere as 15% remains still at 500°C compared to 8%.This indicates that a higher level of decomposition of the aromatic fraction is occurring at higher temperatures in the presence of air, that some coke is formed in this process, and is burned at a subsequent higher temperature.

As shown in Figure 7, in an inert atmosphere the TGA of the resin fraction shows a slight loss up to 250 °C followed by a gradually increasing loss from 250-520 °C, accompanied by an endothermic DSC trace. Due to the increased polarity of this fraction, this is likely to be due to a combination of decomposition and cracking reactions. At 520 °C, about 18% of the original mass remains, presumably as coke.
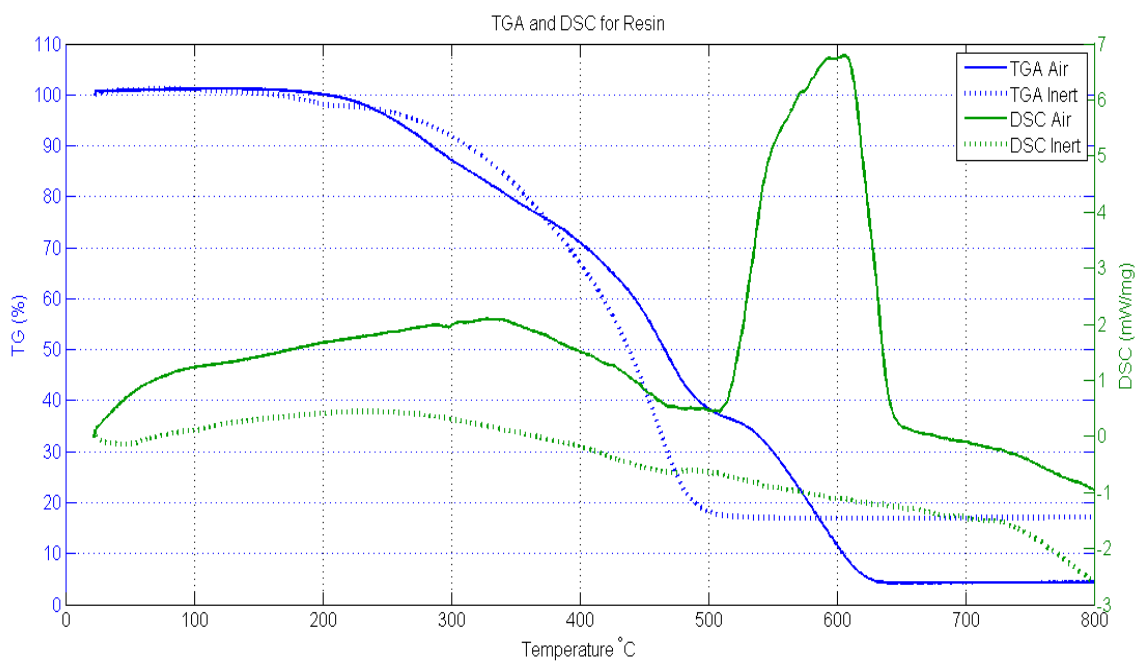

Figure 7. TGA and DSC for Resin fraction.

The TGA trace obtained for the resin fraction in air is more complex, with three stages evident. The first two mass loss stages, from 240-380 °C (24%) and 380-480 °C (38%) are accompanied

by a broad exothermic peak in the DSC trace, and probably represent cracking and combustion reactions of the volatile products. The decrease observed in the TGA from 510-660 °C has an associated strongly exothermic peak in the DSC trace which is presumably due to combustion of coke formed by decomposition. Interestingly the mass loss in this region (36%) is considerably greater than that remaining at 520 °C when heated under inert atmosphere (18%) and that the chemistry in air is again more complex. As shown in Figure 8, the asphaltenes fraction is stable in an inert atmosphere until 420 °C when it then undergoes a rapid mass loss of 40% by 500 °C. This is followed by a more gradual loss of 5% by 600 °C and another rapid loss of 5% from 600-620 °C. 50% of the material remains as a carbonaceous residue. The reactions in this, the most complex fraction, are probably decomposition, cracking and carbonization. The DSC trace shows a moderate endothermic peak at about 460 °C corresponding to the first and major mass loss and a more strongly endothermic peak at 600 °C for the last small mass loss.
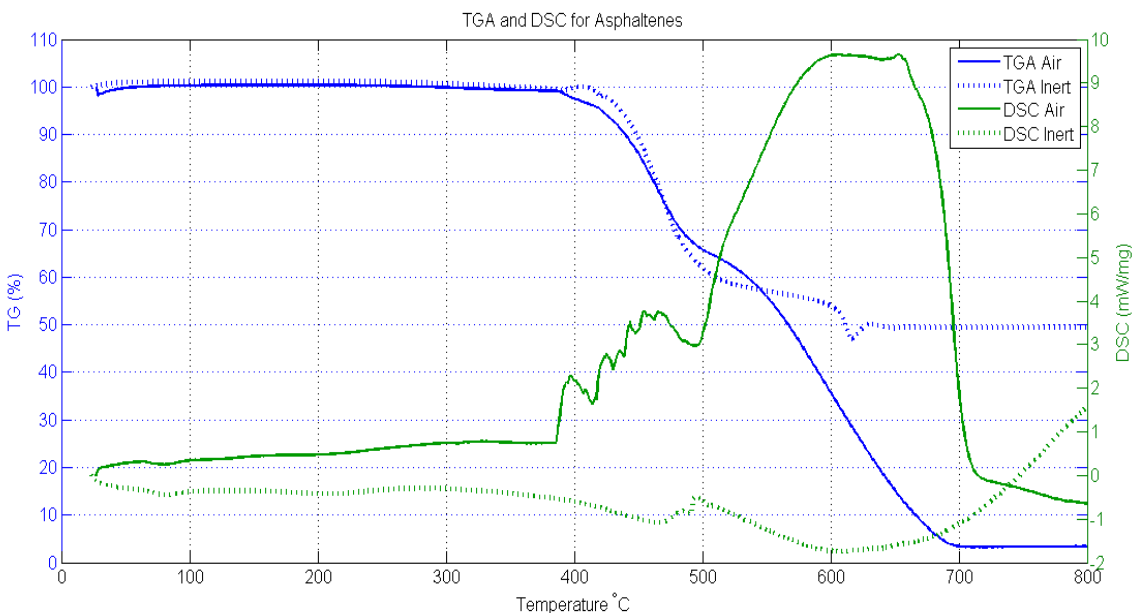
Figure 8. TGA and DSC for Asphaltenes fraction.

The TGA trace for this fraction in air shows a 33% mass loss occurring in the range 400-480 °C, which is accompanied by a moderately exothermic peak in the DSC in the same temperature range. This is followed by a more gradual mass loss between 480-530 °C (7%) while the bulk of the mass is lost between 530-700 °C (60%) and is accompanied very strongly exothermic peak in the DSC in the same temperature range.
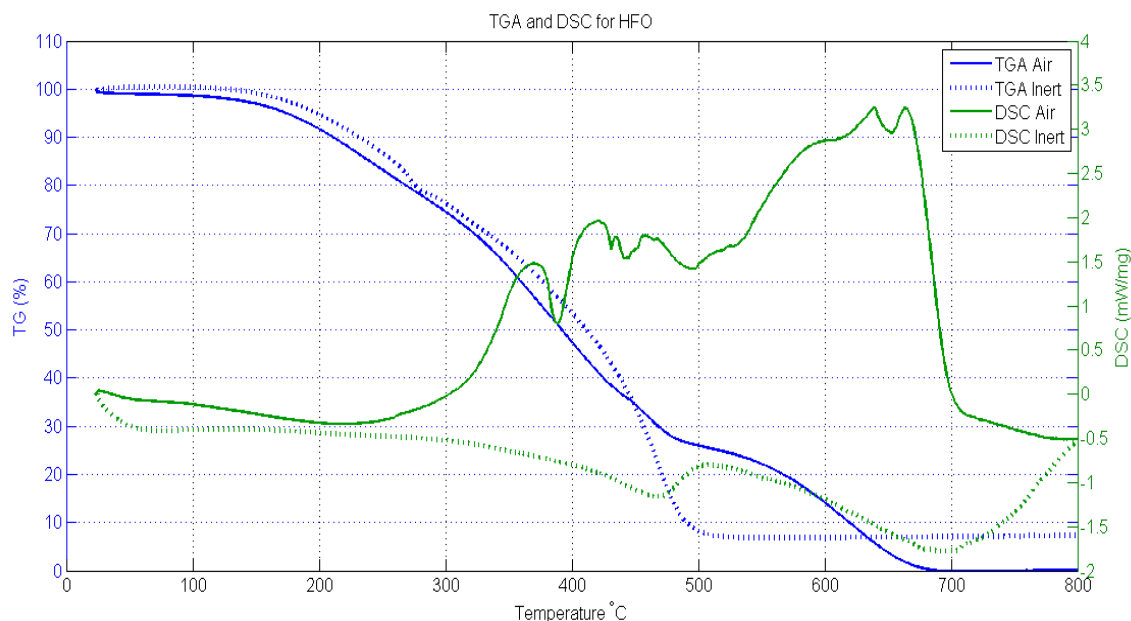
Figure 9. TGA and DSC for HFO.

The relative abundance of the fractions in HFO is saturated 24.1%, aromatics 55.8%, resins 6.7% and asphaltenes 7.9 %. In the absence of chemical reactions occurring between the fractions on heating, the TGA and DSC traces would be expected to closely resemble the sum of the individual traces for the various fractions, after taking into account their relative abundance. On heating HFO in an inert atmosphere, the initial mass loss up to 300 °C is due to evaporation of the cutter stock. This is then followed by progressive loss of the aromatic, resin and apshaltene fractions up to 500 °C. The secondary carbonization observed for the asphaltene fraction is not

clearly evident here as this represents less than 1% of the total sample. The amount remaining as coke after 600 °C (approx. 8%) is in reasonable agreement with that predicted by adding the expected contributions of the fractions (approx. 9%).The DSC of HFO in an inert atmosphere reveals two broad endothermic envelopes around 470 °C and 680 °C, which would appear to be due simply to the independent contributions of the various fractions.

The TGA of HFO in air shows a smooth mass loss up to about 350 °C which is mainly due to evaporation and combustion of the cutter stock, with around 75% of the mass loss occurring by 520 °C. This agrees well with the figure of 78% obtained by combining the estimated mass loss of all fractions by this temperature. The remaining mass loss by 700 °C is due to the combustion of the high molecular weight material and coke formed by thermal decomposition of the aromatic, resin and asphaltene fractions. In the DSC trace for HFO in air in Figure 6, the exothermic peak at 380C can be attributed mainly to saturates and also to aromatics. The large complex series of peaks between 520 to 720 °C can be accounted for progressive contributions from the saturates, resins, aromatics and asphaltene fractions with increasing temperature. As the exothermic peaks for the resins and asphaltene fractions are approximately twice that of the aromatics in this region, their contributions to this peak are greater than expected simply on the basis of their relative abundance. The peak at 470 °C could be due to the asphaltenes, but the peak at 430 °C is not observed in any of the fractions and is probably be due to thermally induced reactions between the fractions. This would most likely involve the more complex and functionally substituted resin and asphaltene fractions.

4. CONCLUSION

The outlined procedure describes the separation of HFO fractions by sequential elution solvent chromatography (SESC) based on chemical functionality groups using a silica gel column. It also provides detailed information on the amounts and chemical characteristics of the separated fractions. The extended study including gas chromatography, mass spectrometry and elemental analysis provided a further chemical characterization of HFO. The SARA analysis provided compositional analysis of saturates, aromatics, resins and asphaltenes in the heavy fuel oil. Estimations of the mean molecular weight and molecular weight range of each separated fraction were obtained by gas chromatography and mass spectrometry. Based on the results it is clear that gas chromatographic analysis alone is not sufficient to determine the overall composition of HFO, because only the medium molecular weight compounds (light compounds) were able to be analysed and most of the heavy compounds were not sufficiently volatile to pass through the column and be detected. The mass spectrometric analysis provided more detail of all separated fractions with mean molecular weight, molecular weight range and possible representative structures of some of the SARA fractions obtained. When the mass spectra of all separated fractions were compared with each other significant differences were noted, though they were difficult to interpret. The results showed that the saturates fraction includes cyclic structures with attached aliphatic hydrocarbons, whereas the aromatics fraction contains tetracyclic aromatics rings along with aliphatic side chains. The separated fractions of HFO possess very broad molecular weight distributions with differing volatility.

The polarity of the components is an important factor for the separation of complex structure multicomponent fuels. The composition information obtained by separating the fractions of HFO is highly important for use in continuous thermodynamics modelling. Continuous

thermodynamics modelling of multicomponent fuel requires the composition, molecular weight range and mean molecular weight of individual fractions. In addition, this paper outlines the criteria for choosing the condition and sequence of solvents to characterize HFO and other analytical methods to obtain the required information for modelling.

The degree of complexity and functionality of the fractions increases in order from saturates, aromatics, resins to asphaltenes. In line with this trend the relative amount of material remaining in TGAs in inert atmospheres at high temperatures increases from 0% saturates, 8% aromatics, 18% resins and 50% asphaltenes, presumably due to the increasing importance of polymerisation and carbonization reactions occurring in these complex fractions at high temperatures. The degree of difference between the TGA scans of the fractions in inert and oxidizing atmospheres observed at high temperatures also increases with the degree of functionality of the fractions. All fractions produce more high-molecular weight and carbonaceous material in air at high temperatures as could be expected due to the presumably greater extent of free radical chemistry occurring in an oxidizing environment.

It is difficult to compare the relative exothermicites of the DSCs of the various fractions in air, as it appears that some of the saturates fraction (and perhaps the aromatics) is simply volatilized before a temperature high enough to initiate combustion is reached, and that consequently the contribution of those components is underestimated. However, the DSC temperature of saturates (around 520 °C) is significantly lower than those of aromatics (640 °C), resin (600 °C), and asphaltene (640 °C).

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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