TG/DTG, FT-ICR mass spectrometry, and NMR spectroscopy study of heavy fuel oil

A.M. Elbaz, Abdul Gani, Nadim Hourani, Abdul-Hamid Emwas, S. Mani Sarathy, and William L. Roberts

Energy Fuels, **Just Accepted Manuscript** • DOI: 10.1021/acs.energyfuels.5b01739 • Publication Date (Web): 12 Nov 2015

Downloaded from <http://pubs.acs.org> on November 13, 2015

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

TG/DTG, FT-ICR mass spectrometry, and NMR spectroscopy study of heavy fuel oil

A.M. Elbaz^{*,§,†}, Abdul Gani[§], Nadim Hourani[§], Abdul-Hamid Emwas^{*}, S. Mani Sarathy[§], W.L. Roberts[§]

^{*} E-mail: ayman.elhagrasy@kaust.edu.sa

[§] *Clean Combustion Research Center, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.*

[†] *Faculty of Engineering-Materia, Helwan University, Cairo-Egypt.*

^{*}*Imaging and Characterization Core Laboratory, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.*

ABSTRACT: There is an increasing interest in comprehensive study of heavy fuel oil (HFO) due to its growing use in furnaces, boilers, marines, and recently in gas turbines. In this work, the thermal combustion characteristics and chemical composition of HFO were investigated using a range of techniques. Thermogravimetric analysis (TGA) was conducted to study the non-isothermal HFO combustion behavior. Chemical characterization of HFO was accomplished using various standard methods in addition to direct infusion atmospheric pressure chemical ionization Fourier transform ion cyclotron resonance mass spectrometry (APCI-FTICR MS), high resolution ¹H nuclear magnetic resonance (NMR), ¹³C NMR, and two dimensional hetero-nuclear multiple bond correlation (HMBC) spectroscopy. By analyzing thermogravimetry and differential thermogravimetry (TG/DTG) results, three different reaction regions were identified in the combustion of HFO with air, specifically, low temperature oxidation region (LTO), fuel deposition (FD) and high temperature oxidation (HTO) region. At the high end of the LTO region, a mass transfer resistance (skin effect) was evident. Kinetic analysis in LTO and HTO regions was conducted using two different kinetic models to calculate the apparent activation energy. In both models, HTO activation energies are higher than those for LTO. The FT-ICR MS technique resolved thousands of aromatic and sulfur containing compounds in the HFO sample and provided compositional details for individual molecules of three major class species. The major classes of compounds included species with one sulfur atom (S₁), with two sulfur atoms

(S₂), and purely hydrocarbons (HC). The DBE (double bond equivalent) abundance plots established for S₁ and HC provided additional information on their distributions in the HFO sample. The ¹H NMR and ¹³C NMR results revealed that nearly 59% of the ¹H nuclei were distributed as paraffinic CH₂ and 5% were in aromatic groups. Nearly 21% of ¹³C nuclei were distributed in aromatic groups indicating that most paraffinic CH₂ groups are attached to aromatic rings. A negligible amount of olefins was present and an appreciable quantity of mono-aromatic and poly-aromatic content were observed. Molecular connectivity between the hydrogen and carbon atoms using HMBC spectra was utilized to propose several plausible skeletal structures in HFO.

▪ INTRODUCTION

Petroleum is presently the most important energy resource for the world. Heavy crude oil fractions are a major economic revenue source because of their greater abundance compared to conventional light oil.¹ However, the increased demand for light distillate products has resulted in refineries producing even heavier fractions for the fuel oil market. A significant portion of the energy requirements in several locations of the world is met by combustion of heavy fuel oil (HFO). It is therefore important to investigate HFO basic oxidation and pyrolysis characteristics, so that the overall combustion process can be understood to aid in combustor design and emissions control. Furthermore, the chemical characterization of HFO can help understand fuel quality effects on combustion characteristics and emissions. The particulate emissions from HFO combustion may be divided into three basic categories; smoke, cenosphere, and ash.² Ash residue and cenosphere correspond for the major part of the emitted particulates from HFO combustion. These types of particulates are mainly dependent on fuel composition. Most of the heavy fuel oils used in Saudi Arabia have asphaltene content in the range of 7-15 wt% with a

high sulphur content of 4 wt%. Nowadays, heavy fuel oil is a suitable alternative to conventional gaseous fuels used in gas turbines because of its availability and lower cost.³ However, the high sulfur content, levels of thermal radiation, ash, other contaminants, as well as the troubles with atomization introduce difficulties in part maintenance and low emissions.

Recently, thermal analysis techniques have been applied to interpret fossil fuel oxidation and the pyrolysis kinetics parameters has gained interest.⁴⁻¹⁰ Thermal analysis methods can be characterized as dynamic (non-isothermal) wherein the temperature is modified at a predefined heating rate, or isothermal wherein temperature is held constant. Thermogravimetry (TG) and differential thermogravimetry (DTG) analysis are the principal thermo-analytical methods developed to continuously investigate the physical and chemical changes occurring as the temperature of a sample is changed.

The first attempt to use thermo-analytical techniques to investigate the crude oil combustion was conducted by Tadema⁴. Additional studies have been conducted applying thermal analysis methods to in situ combustion (ISC) investigations. The oxidation and pyrolysis of heavy fuel oils and their aromatic, paraffinic, polar and asphaltenes fractions were investigated by Ciajolo and Barbella⁵. The thermogravimetric kinetics of individual oil fractions have been studied by several investigators⁶⁻⁸. Kok⁹ characterized the medium and heavy crude oils in limestone matrix by the use of TG/DTG and differential scanning calorimeter (DSC). In the oxidation process of such oils, two major transitions were observed, specifically, low and high-temperature oxidation. Recently, Fan et al.¹⁰ employed thermogravimetric analysis technique to explore the oxidation performance of one sample of Chinese HFO, and obtain the kinetic parameters by using the

distributed activation energy model for non-isothermal kinetics over a temperature range from 30 to 550 °C.

Besides thermogravimetric methods, high-resolution analytical techniques for studying the molecular composition of complex fuels are of interest. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is extensively employed for crude oil analysis.¹¹⁻¹² FT-ICR MS allows resolution of complex elemental compositions for crude oil derived samples. FT-ICR MS can be coupled to different ionization techniques such as ESI, APCI and APPI to characterize different petroleum matrices.¹³⁻¹⁵ Recently APCI FT-ICR MS was used to characterize complex hydrocarbon mixtures containing saturated, aromatic and sulfur containing hydrocarbons without derivatization or adduct chemistry.^{14, 16-17} The information obtained from such MS analyses can be used to develop surrogate fuel mixtures and their chemical kinetic models for such complex hydrocarbon mixtures.¹⁸⁻¹⁹

Nuclear magnetic resonance (NMR) spectroscopy analytical techniques have been well established over the past few decades to study the structure of organic molecules. NMR spectroscopy measures the chemical shift, which depends on the atomic surrounding of the investigated nuclei. A significant advantage of NMR is that accurate results which are also quantitative can be obtained as the intensity of the peaks are directly proportional to the number of nuclei. Methods like ¹H NMR and ¹³C NMR have been used to study complex mixtures like crude oils²⁰, gasoline²¹, heavy oils²², shale oil distillates²³, coal derived liquids²⁴, heavy fuel oils²⁵ and asphaltenes²⁶. NMR spectroscopy is particularly useful for the characterization of fuels with high molecular weights (like heavy fuel oil), which cannot be easily studied by conventional methods like GC-MS (gas chromatography mass spectrometry). The various structural categories in the fuel can be determined with a high degree of resolution, and their

corresponding magnitudes can also be obtained by integrating the peaks in the spectrum. This is usually done by separating the NMR spectrum into several regions based on their chemical shifts (i.e., spectral chemical shift regions can be assigned to paraffins, olefins, aromatics etc.). Understanding these structural categories provides valuable information for predicting combustion characteristics and emissions. For example, NMR data can be used to predict fuel combustion properties by using molecular descriptors, like octane ²⁷and cetane numbers.²⁸ Furthermore, specific structural information provided by NMR spectroscopy can be associated with the physical and chemical properties of the heavy fuel oil.²⁹ In addition, structural features of heavy fuels can be used for the development of chemical kinetic combustion models based on a functional group approach.³⁰

The aim of this research was to determine the thermal combustion behavior and chemical composition of a Saudi Arabian heavy fuel oil. The thermal behavior of HFO will be investigated under non-isothermal conditions. A kinetic model of HFO combustion with Arrhenius and Coats and Redfern approximations will be implemented to calculate the activation energy. Chemical analyses will be conducted using APCI- FT-ICR mass spectroscopy, ¹H NMR, ¹³C NMR and two dimensional hetero-nuclear multiple bond correlation (HMBC) spectroscopy to provide an improved understanding of the chemical characterization of HFO. FT-ICR MS will be used for a comprehensive molecular level characterization for HFO. Additionally, NMR techniques will be used to quantify the structural groups within normal various classes (e.g., normal paraffins, branched paraffin, cyclo-paraffin, mono-aromatics and poly-aromatics.)

▪ EXPERIMENTAL AND METHODS

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1. Thermogravimetric analysis. Samples were analyzed using a Netzsch TG 209 F1Iris thermogravimetric (TG-DTG) analyzer. The TGA instrument is capable of measuring the weight loss the sample with a resolution of 0.1 μg for a temperature range of 20 $^{\circ}\text{C}$ to 1100 $^{\circ}\text{C}$. The heating rate can be modified in the range of 0.001 $^{\circ}\text{C}/\text{min}$ to 200 $^{\circ}\text{C}/\text{min}$. The TG/DTG module is capable of measuring and recording the weight loss in a well-controlled atmosphere, as well as the derivative as a function of time or temperature. For each run, a 10 mg sample was placed in Al_2O_3 crucible. A carrier of high purity air was used for oxidation experiments with a 50 ml/min flow rate and a Nitrogen as a purge gas at 25 ml/min, and then performing the experiments at a heating rate of 5 $^{\circ}\text{C}/\text{min}$. The tests were conducted over the temperature range of 25 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$. The measurements are registered as a function of either time or temperature. With calcium oxalate monohydrate, the TG analyzer was calibrated before conducting the experiments. The experiments were conducted in triplicate to check the repeatability. The aim of these experiments was to determine the thermal oxidation behavior of HFO under non-isothermal thermogravimetric conditions, and to provide data for a kinetic evaluation. An Arrhenius model and a Coats and Redfern model were employed to deal with TG/DTG non-isothermal data to calculate the apparent activation energy of HFO oxidation.

2. FT-ICR Mass Spectrometry. The HFO sample was analyzed using a solariX Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 12 T refrigerated actively shielded superconducting magnet and a new dynamically harmonized analyzer cell. Sample preparation was performed by diluting 1 μl HFO in 5 ml n-heptane. The asphaltenes within HFO will precipitate, as they are insoluble in n-heptane. The diluted HFO sample was directly infused with a flow rate of 50 $\mu\text{L}/\text{min}$ into an

atmospheric pressure chemical ionization (APCI) source coupled with the FTICR MS. The analysis of the HFO sample Mass spectra was acquired in positive APCI mode using nitrogen as sheath gas. External calibration with arginine clusters was applied for HFO spectra and it was acquired with 8 M data points. The transient time was 4.18 s that resulted in a resolution of 1,000,000 at m/z 400 in the magnitude mode. The mass range between m/z 184 and 3000 were recorded. The bias of the cell was set to 0.7 V with front and trapping potentials of 0.95 V. Ion transfer time (TOF) was set to 0.75 ms. The skimmer voltage was set to 45 V to reduce the formation of non-covalent complexes. At least 100 scans were accumulated to reduce the noise effect. For APCI settings vaporizer temperature was set at 400 °C, drying gas temperature at 250 °C, drying gas flow at 4 L/min, nebulizer pressure at 2.5 bar, capillary voltage at -2000 V, end plate voltage at -1500 V and corona needle current at 3000 nA. A mass accuracy better than 0.2 ppm with known homologous series was obtained as mass spectra were internally calibrated.

Based on the elemental compositional data (shown in Table 1), a maximum formula of $C_6H_8N_3O_3S_3$ was applied for the molecular assignment. The molecular formula were obtained as van Krevelen molecular formula to distinguish homologous series with the same heteroatom composition and the same double-bond equivalents (DBE, number of rings plus double bonds) but different degree of alkylation. Protonated and radical cations were distinguished and indicated separately ($M+\bullet$, $M [H]^+$, respectively). Based on previous results protonated compounds $[M + H]^+$ ions was considered to represent the HFO species and to establish the DBE distribution plots. [14]

3. NMR spectroscopy. A 0.6 ml sample from a mixture of 50 μ l HFO in 1 ml of deuterated chloroform CDCl_3 was prepared in 5 mm NMR tubes. NMR spectra were acquired at 298 K using a Bruker 700 AVANAC III spectrometer equipped with Bruker CP TCI multinuclear *CryoProbe* (BrukerBioSpin, Rheinstetten, Germany). The ^1H NMR spectra were recorded by collecting 128 scans with a recycle delay time of 5s, using standard 1D 90° pulse sequence using standard (zg) program from Bruker pulse library. Chemical shifts were adjusted using Tetramethylsilane (TMS) as internal chemical shift reference. The free induction decay (FID) data were collected with spectral width of 14098 Hz digitized into 64k data points. The ^{13}C NMR spectra were recorded using a 1D sequence with power-gate decoupling, a 30-degree flip angle with spectral width of 240 ppm and digitized into 64 K complex data points. Each spectrum was recorded by collecting 12 k transients with 5 s recycle delay. Exponential line broadening of 1 Hz was applied before Fourier Transformation. The 2D ^1H - ^{13}C HMBC spectrum were recorded using pulse sequence (hmbcgp12ndqf) program from Bruker pulse library. The spectra widths were set to 11160 Hz in F2 and 42255 Hz in F1 dimension. HMBC data were collected in the absolute-value mode with 4096 data points in t2 and 512 data point t1 increments (48 scans per increment) and with a recycle delay of 3.0 s. Bruker Topspin 2.1 software (BrukerBioSpin, Rheinstetten, Germany) was used for recording the NMR spectra and for data analysis.

RESULTS AND DISCUSSION

1. General characteristics of heavy fuel oil. The composition of a particular crude oil is unique and it is not possible to define the composition accurately. Heavy oils are products derived from crude oils. Thus, HFO composition varies depending on the crude oil source and the range of methods used for crude oil processing.³¹⁻³² HFOs are composed entirely, or substantially, of the residuals from petroleum refining operations, i.e., materials condensed and

remained after distillation processes. The HFO sample used in this study was collected from Saudi Arabian power generation facility. The oil was characterized in a sequence of standard tests to determine its physical properties and elemental composition, which are listed in Table 1. The Table indicates the corresponding standard test methods that have been used for determination of the physical properties, asphaltenes content, and compositional data. The measured viscosity for the present sample is 617.714 cSt at 40 °C; literature values for HFO range from 245 to 1,000 cSt at 38 °C.³¹

A characteristic aspect of HFO is the presence of high sulphur content. Use of these fuels has often been limited and sometimes discontinued due to stringent regulations on sulphur emissions. The sulphur content in the HFO depends on their geographical origin and it ranges from 0.5 % to 6%³³ by mass; it is 3.292 % by mass in the present sample. Desulphurization of HFO is a difficult task due to the complexity of the fuel and the need for molecular level characterization of sulphur compounds. Though a lot of research³⁴⁻³⁶ has been carried out to study sulphur removal from heavy oils it yet remains elusive. The asphaltenes content is 8.2 wt %, while previous studies showed asphaltenes contents ranging from 2.6 to 12.12 wt %.³⁷⁻³⁹

2. Thermogravimetric analysis. The combustion of HFO is complex because of the multicomponent hydrocarbon mixture (refer to section 3.3. on APCI-FT-ICR MS), and its varying composition as combustion progresses. At a heating rate of 5 °C /min, figure 1 shows TG and DTG data of the HFO sample. From these curves, three distinguished regions are identified in HFO oxidation. The first region identified in the DTG curves for the HFO sample extends to a temperature of 342 °C. This region involves distillation, visbreaking and low-temperature oxidation (LTO), and the maximum rate of decomposition/devolatilisation occurs around 174 °C due to loss of volatile fractions. In the LTO region, a smooth, continuous and

steep descent line corresponding to a rapid mass loss is observed in the TG curve. In the LTO region, the side chains of heavy compounds are split and subject to low-temperature oxidation.⁴⁰ TG and DTG curves level off when the temperature reaches 342 °C, indicating a delay in the degradation process. Such occurrences may be attributed to the mass transfer resistance caused by the generation of “skin-like” products from the polymerization reaction in the LTO region⁴¹, it looks like the cenosphere shell formation. After the LTO reaction, fuel decomposition processes (FD) or middle-temperature oxidation occurs from 342 °C to 469 °C. FD reactions are homogeneous gas phase reactions and this leads to partial oxidation of pyrolysis products. These reactions occur before the third high-temperature oxidation (HTO) region. In the FD region, volatile fractions break up the skin like form and the TG and DTG curves indicate continual fuel degradation. High- temperature oxidation (HTO) occurs in the temperature range of 469 °C to 580 °C, in which the combustion intermediates formed in the FD region are completely oxidized. HTO is considered as the main combustion region. The TG results indicate a residual amount around 6 % at 999.5 °C. The results show that the burn out temperature is 580 °C, which is the point where the rate of weight loss suddenly drops to zero or, in keeping with specific criteria, where the rate of weight loss becomes less than 1 % per minute.⁴² These results are summarized in Table 2.

A global kinetic analysis was performed to obtain activation energies (E) in different temperature regions. During HFO combustion, non-isothermal weight loss kinetics is a complex phenomenon. This is because multiple reactions occur simultaneously; hence, the evaluated kinetic parameters should be regarded as apparent kinetic values representing complex parallel and serial reactions. We assume that the mass transfer constraints have negligible effect on the reaction progress of because the small size of the sample and there is an excess of purge gas

supply around the sample crucible. Therefore, it is reasonable to assume that the first-order rate equation can describe the non-isothermal combustion.⁴³ In this work, two different kinetic models (Arrhenius⁴⁴ and Coats and Redfern⁴⁵, see also¹⁰) were applied to determine the activation energy of HFO. In the Arrhenius model with reaction order of unity, it is assumed that the rate of the sample mass loss is mainly dependent on the rate constant, temperature, and the remaining mass of the sample. Based on that, the Arrhenius Kinetics equation could be take the following final form:

$$\log \left[\left(\frac{dW}{dt} \right) / W \right] = \log A - E / (2.303RT)$$

Where dW/dt is the rate of mass change (gm/s), A is the frequency factor (s^{-1}), E is the activation energy (KJ/mol), R is the universal gas constant (8.314 J/mol K), and T is the temperature (K). Applying this model to the TG/DTG results shown in Fig. 2a, and by plotting the left hand side of the Arrhenius equation against $1/T$, a straight line is obtained for both LTO and HTO regions with a slope equal to $E/2.303R$, wherein the activation energy can be obtained. Activation energies of HFO were determined both in LTO and HTO reaction regions as shown in Fig. 2.

In the Coats and Redfern approach, by defining α as the sample fraction decomposition at any time t , the mass loss due to the thermal process can be addressed by the following rate equation:

$$\frac{d\alpha}{dt} = k (1 - \alpha)^n \quad (1)$$

$$K = A \exp \left(-\frac{E}{RT} \right) \quad (2)$$

Where k is the rate constant, n is the order of reaction, t time (s), A frequency factor (s^{-1}), E activation energy (KJ/mol), R the universal gas constant (J/mol K) and T absolute temperature. For a linear heating rate of, say, β deg. /min: $\beta = dT/dt$ substitute equation (2) in (1), and introducing the linear heating rate β , we get equation (3):

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_0^T e^{-E/RT} dT \quad (3)$$

The right hand side term of equation (3) has no exact solution, but by substituting $u = E/RT$, equation (3) for non-isothermal kinetics becomes:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \quad (4)$$

Assuming $n = 1$ and taking logarithms of equation (4) and, we obtain equation (5)

$$\log_{10} \left[-\log_{10} \frac{(1-\alpha)}{T^2} \right] = \log_{10} \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad (5)$$

By knowing β and TG data, a plot of $\log_{10} \left[-\log_{10} \frac{(1-\alpha)}{T^2} \right]$ versus $1/T$ (as illustrated in Fig. 2b), the activation energy, E , can be obtained from the slope of the straight lines fit for both LTO and HTO regions. The observed activation energies for LTO and HTO reaction regions using both methods are shown in Table 2. As indicated, a higher activation energy value was obtained in HTO regions at higher temperature. The change of the combustion mode in these three distinct regions leads to the different activation energies from one region to another. In the LTO region, the fuel is partially oxidized and pyrolyzed via heterogeneous reactions, and the oxidation rate of asphaltenes is very slow with almost no mass loss.⁴⁶ The LTO region is followed by homogenous (gas phase) reactions in the FD region to form the fuel compounds for the HTO region. The reactions in the third region appear to be in the mode of hydrocarbon/char reactions^{9, 46}. Similar trends of the activation energies were obtained in^{9, 46} with slightly higher values, which is most likely due to the higher asphaltenes content in the current sample. The difference in the activation energy obtained by both methods is due to the different model assumptions and equation parameters.

3. FT-ICR MS results. The positive-ion mode APCI-FT-ICR mass spectrum of HFO is shown in Fig. 3. The average resolution of the full width at half maximum (FWHM) peak height

was almost 600,000 across the mass range of m/z 250 and 1500. However the average resolution between m/z 250 and 700 was almost 1,000,000. More than 3,100 unique masses were recorded (number represents protonated ions of the identified class species). Such massive count of molecular species can only be resolved and assigned by the FT-ICR MS. This is evident in the zoomed mass insets at m/z 761 which shows 17 different elemental compositions were assigned in Fig. S1. About 12000 singly charged ions were recorded considering their isotopic distribution pattern in the HFO mass spectrum (including isotopes and molecular ion peaks). Figure 4 shows the class plot (heteroatom content) of the HFO sample. Relative abundance for each class is calculated by dividing the sum of magnitudes of the species of a particular class over the total sum of magnitudes of all species in the spectrum. . As shown, the major compound classes were hydrocarbon with one sulfur atom (S_1 class) (52%), hydrocarbons with two sulfur atoms (S_2 class) (21.4%), and hydrocarbon class HC (21.1%). Very low levels of oxygenated hydrocarbons with sulfur, such as OS (3.35%) and OS_2 (1.02 %), and mono-nitrogen hydrocarbons N_1 (1%) were detected. This demonstrates the ability of APCI to detect different class species under positive-ion conditions without interference from the asphaltene fraction. It should be noted that different ionization modes may generate different relative abundances of class species present in the HFO, as this depends on the ionization efficiency in the ionization source.

The class distribution profiles of S_1 and HC classes species as a function of DBE (double bond equivalent) and carbon number is presented in Fig. 5, where the bubble size represents the magnitude of the detected species. The DBE values allow us to distinguish molecular structures present in the sample based on their unsaturation degree. The distribution of S_1 class species in the HFO sample indicates that the class species had one main molecular core structure that are

likely thiophenic. The most abundant S_1 class species corresponding to polyaromatic sulfur hydrocarbon (PASH) species had 6-12 DBE and 40-60 carbon numbers. The most abundant PASHs series are benzothiophenes (BT, DBE 6), dibenzothiophenes (DBT, DBE 9) and benzonaphthothiophene (BNT, DBE 12) and their naphthenic derivatives thereof at 7-8, 10-11 and 13-15 DBE respectively. These BT, DBT and BNT with one or more additional naphthenic rings exhibit a wide range of carbon number reaching up to 100 carbon atoms. In contrast to S_1 class, HC class species cover up to 80 carbon atoms as shown in Fig. 5b. The HC distribution plot doesn't show any fully saturated hydrocarbons (DBE 0-3), which explains the aromatic nature of the HC class of the HFO sample. This indicates that fully saturated hydrocarbons are already refined out of the HFO. The most abundant HC class species are alkylated diaromatic (DBE 7) and triaromatics (DBE 10) and their naphthenic derivatives. These abundant aromatic compounds extend to 70 carbon atoms. The presence of tetraaromatics and pentaaromatics including naphthenic rings, with lower abundance, is also evident which shows the high boiling range of this HFO fraction.

4. NMR spectroscopy results. The ^1H NMR and the ^{13}C NMR spectra of the HFO are shown in Fig. S2. The heavy fuel oil consists of a large number of individual molecules and determining the structure of these molecules is not possible. Therefore, the procedure is to identify and quantify different structure categories based on their chemical shifts. Work⁴⁷⁻⁵¹ has been carried out to assign chemical shifts for different structural categories; however, these values differ notably between studies. The reason for these differences can be attributed to many factors. For example, the sample viscosity, temperature and the polarity of the solvent can affect the chemical shift of NMR signals. Moreover, some carbon atoms give no NMR signal because

they are completely substituted and thus go unaccounted for. Correction factors to account for these inherent errors while assigning the chemical shifts have been introduced by some workers.⁵² The range of the chemical shifts used for different structure groups and their corresponding percentage obtained after integrating the baseline corrected spectrum of ^1H NMR and ^{13}C NMR are reported in Table S1 and Table S2, respectively using ⁴⁷⁻⁵¹, while the percentages of these structure groups deduced from ^1H NMR and ^{13}C NMR are presented in Fig. 6. ^1H NMR results indicate that HFO contains a significant quantity of paraffinic H atoms (CH_3 , CH_2), relatively low amount of mono aromatic and polyaromatic H atoms (5%), and a negligible percentage of olefins. This result corroborates the HFO data extracted from FTICR MS results. The high abundance of paraffinic CH_3 and CH_2 units confirms the alkylation degree demonstrated in the DBE vs. carbon number distribution plots for HC and S1 classes (Fig. 5). The high alkylation degree (CH_2 - increments of 59.2 % in ^1H NMR) of the same homologous series explains the high carbon number range present in Figure 5. The ^{13}C NMR spectra showed the presence of many different types of C atoms of varying proportions. 5% of the C atoms were naphthenic in nature. Aldehyde and ketonic C atoms and olefinic C atoms were found to be negligible. It is interesting to see that although 19% of the C atoms occur in aromatic groups only 5% of H atoms are aromatic. This is expected since aromatic groups are mainly CH or quaternary and thus contain fewer protons, whereas CH_3 and CH_2 groups in the aliphatic region are bonded to a greater number of protons. ^{13}C NMR data in Fig. 6 (b) also shows that a significant abundance of CH_2 attached to aromatic (20 %) and cycloparaffin CH_2 (5 %). The presence of higher number of non-protonated C atoms shows that the aromatic rings are either highly substituted or condensed structures. The FT-ICR mass spectrometry shows that the molecules are highly aromatic with large values of DBE present in Fig. 5. Also the presence of

cycloparaffin CH₂ carbon atoms corroborates the DBE series which represent naphthenic derivatives of both PAHs (HC) and PASHs (S1) shown in Fig. 5. Combining the results of FTICR-MS and NMR indicates that the molecules in the HFO are aromatic-based with high degree of alkylation. It is important to mention that ¹³C NMR is less sensitive compared to ¹H NMR because of its lower sensitivity and low natural occurrence of ¹³C nuclei; yet it is widely used for structure elucidation of complex mixtures as it generates a spectra with well resolved features. Furthermore, ¹³C NMR has a larger shift (> 220 ppm) and thus there is greatest error associated with chemical shift assignments to different structural groups.

To understand molecular connectivity between the atoms, two-dimensional NMR methods can help to identify hydrogen atoms attached to carbon atoms several bonds away. Heteronuclear multiple bond correlation (HMBC) is a powerful 2D NMR technique which is used for the structural understanding of complex molecules. It detects the ¹³C – ¹H long range couplings (about 2-4 bonds) from the most sensitive NMR (¹H) nucleus by applying a method of inverse detection, and can provide unique information regarding the skeleton of a molecule. This method has a high sensitivity especially when ¹H signals appear as sharp peaks, such as methyl groups. It is a better technique compared to other two dimensional NMR techniques for assigning side chain structures to aromatic groups. The HMBC spectrum of the heavy fuel oil corresponding to the region ¹H (0 – 3.5 ppm) and ¹³C (0 – 50 ppm) is shown in Fig. 7. The spectrum is represented with ¹H chemical shift in the horizontal axis and the ¹³C chemical shift in the vertical axis. Such spectra can be used to establish C-H_n connectivity among the molecules in different regions. High intensity regions are identified as peaks wherein ¹H and ¹³C axes meet with each other in the spectral region. Fifteen of such high intensity regions were identified and are shown in Fig. 8. Each region has a specific ¹H and ¹³C chemical shift. By combining these two shifts,

various possible skeletal structures of the molecule can be identified. The various plausible structures for different regions assuming a 20-carbon molecule are reported in Table 3 along with their chemical shifts. It is observed that many of the plausible structures include paraffinic groups (CH_3 and CH_2) attached with the aromatic groups as expected. High intensities are seen in regions 4 (^1H 0.5 – 1.09 ppm, ^{13}C 21.9 – 25 ppm), 6 (^1H 1.09 – 2 ppm, ^{13}C 28.5 – 30.8 ppm) and 7 (^1H 1.09 – 2 ppm, ^{13}C 30.8 – 32.7 ppm), which correspond to C-H connectivity near aromatic rings. This indicates the occurrence of many short paraffinic chains attached to aromatic rings rather than longer chains. Region 5 (^1H 1.09 – 2 ppm, ^{13}C 25 – 28.5 ppm) indicates high prevalence of connectivity between naphthenic C atoms to paraffinic H atoms. Similarly other regions identified in Fig. 8 help to establish important C-H connectivity's present in HFO. The results from HMBC unravel the structural connectivity, which is suggested by the FTICR MS data. The connectivity of CH_3 and CH_2 into aromatic and naphthenic rings present in the various DBE series shown in Fig.5 is elucidated. The structures of molecules shown in Table 3 using the data from HMBC NMR helps in understanding the structural distribution of molecules and in generating surrogate molecules that could represent HFO.

▪ CONCLUSIONS

There is limited research published about the analysis of Saudi Arabian heavy fuel oil. Thus, this work combines various analytical techniques, such as thermal gravimetric analysis TG/DTG, positive ion APCI-FTICR mass spectroscopy and ^1H - ^{13}C NMR spectroscopy, to study HFO composition and characterisation. The thermogravimetry analysis reported herein was successful in identifying three regions during non-isothermal decomposition of HFO in air: the low

temperature (LTO) region, a fuel deposition region (FD), and the high temperature (HTO) region. At the high end of the LTO region, a mass transfer resistance (skin effect) was observed and associated with a plateau in the TG/DTG curves. The gathered data and the corresponding analyses enabled a kinetic analysis of the reaction regimes. The apparent activation energy was calculated based on the classical Arrhenius and Coats and Redfern models. The TGA data showed that the activation energy of HTO is higher than that for LTO. Even though the kinetic model used has several limitations, it provides information for comparative purposes.

The detailed compositional analysis of the HFO sample was performed using a high resolution FT-ICR MS with accurate mass measurement. Around 3100 chemical formulae were identified containing S_1 , S_2 , HC, OS, OS_2 and N_1 compound classes and the results show that the major compound class was S_1 .

The DBE maps demonstrate that the most abundant S_1 class species are alkylated BT, DBT and BNT with their naphthenic derivatives, while the abundant HC class species are the diaromatic and triaromatic compounds and their naphthenic derivatives. The enriched aromatic compounds in both S_1 and HC classes reflect the aromatic nature and high boiling range of the HFO fraction.

^1H NMR and ^{13}C NMR data showed that the HFO contains different structural groups. Most of the H atoms were distributed in paraffinic groups (CH_2 , CH_3) and that they are most likely attached to aromatic rings. The quantity of olefins was found to be negligible. HMBC spectra were used to propose several skeletal structures from the high intensity regions and it could be seen that most of the skeletal structures have paraffinic (alkyl) groups attached to aromatic rings. Understanding these structural groups gives valuable insight for predictive combustion studies. The thermal gravimetric and chemical characterization of HFO presented herein provides an improved understanding of the HFO thermal oxidation behavior and molecular structure. This

present work provides a basis of future experimental and modeling work, including HFO single droplet combustion and pyrolysis, HFO swirling flames, and identification of HFO surrogate fuel.

ACKNOWLEDGMENTS

Research reported in this publication was supported by Alstom and by competitive research funding from King Abdullah University of Science and Technology (KAUST). The authors acknowledge support from the Clean Combustion Research Center under the Future Fuels research program. The authors acknowledge FTICR-MS assistance from Dr. Matthias Witt of Bruker Daltonik, Bremen, Germany.

REFERENCES

- (1) Shah, A.; Fishwick, R.; Wood, J.; Leeke, G.; Rigby, S.; Greaves, M. A review of novel techniques for heavy oil and bitumen extraction and upgrading. *Energy & Environmental Science* **2010**, 3, 700–714.
- (2) Goldstein, H.; Siegmund, C. Influence of heavy fuel oil composition and boiler combustion conditions on particulate emissions. *Environmental Science & Technology* **1976**, 10, number 12, 1109–1114.
- (3) Goodger, E.; Najjar, Y.; Heavy-fuel flame radiation in gas turbine combustors-exploratory results. *Fuel* **1977**, 56, 437–440.
- (4) Tadema, H. Mechanism of oil production by underground combustion. *5th world petroleum congress* **1959**, 279–287.
- (5) Ciajolo, A.; Barbella, R. Pyrolysis and oxidation of heavy fuel oils and their fractions in a thermogravimetric apparatus. *Fuel* **1984**, 63, 657–61.
- (6) Freitag, P.; Verkoczy, B. Low-temperature oxidation of oils in terms of SARA fractions: why simple reaction models don't work. *Journal of Canadian petroleum technology* **2005**, 44, 54–61.
- (7) Kok, M. V.; Karacan, O. Kinetic analysis of oxidation behavior of crude oil SARA constituents. *Energy & Fuels* **1998**, 12, 580–588.
- (8) Ranjbar, M. Improvement of heavy and light oil recovery with thermocatalytic in situ combustion. *Journal of Canadian Petroleum Technology* **1995**, 34, 25–30.
- (9) Kok, M. V. Characterization of medium and heavy crude oils using thermal analysis techniques. *Fuel processing Technology* **2011**, 92, 1026–1031.
- (10) Cheng, F.; Cheng, Z.; Qiang, Z.; Desheng, M.; Yue, C.; Hang, J.; Lin, S.; Fei, W. The oxidation of heavy oil: thermogravimetric analysis and non-isothermal kinetics using the distributed activation energy model. *Fuel processing technology* **2014**, 119, 149–153.
- (11) Marshall, A. G.; Rodgers, R. P. Petroleomics: Chemistry of the underworld. *Proc. Nat. Acad. Sci. U. S. A* **2008**, 105(47), 18090–18095.
- (12) Cho, Y.; Witt, M.; Kim, Y. H.; Kim, S. Characterization of Crude Oils at the Molecular Level by Use of Laser Desorption Ionization Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry. *Anal. Chem.* **2012**, 84 (20), 8587–8594.
- (13) Muller, H.; Andersson, J. T.; Schrader, W. Characterization of high-molecular-weight sulfur-containing aromatics in vacuum residues using Fourier transform ion cyclotron resonance mass spectrometry. *Anal. Chem.* **2005**, 77 (8), 2536–2543.
- (14) Hourani, N.; Andersson, J. T.; Moeller, I.; Amad, M.; Witt, M.; Sarathy, S. M. Atmospheric pressure chemical ionization Fourier transform ion cyclotron resonance mass spectrometry for complex thiophenic mixture analysis. *Rapid Commun. Mass Spectrom.* **2013**, 27 (21), 2432–2438.

- (15) Kim, E.; Myoung-han, N.; Koh, J.; Kim, S. Compositional characterization of petroleum heavy oils generated from vacuum distillation and catalytic cracking by positive-mode APPI FT-ICR mass spectrometry. *Mass Spectrom. Lett.* **2011**, 2(2), 41-44.
- (16) Hourani, N.; Kuhnert, N. Development of a novel direct-infusion atmospheric pressure chemical ionization mass spectrometry method for the analysis of heavy hydrocarbons in light shredder waste. *Anal. Methods* **2012**, 4 (3), 730-735.
- (17) Hourani, N.; Kuhnert, N. High molecular weight non-polar hydrocarbons as pure model substances and in motor oil samples can be ionized without fragmentation by atmospheric pressure chemical ionization mass spectrometry. *Rapid Commun. Mass Spectrom.* **2012**, 26 (19), 2365-2371.
- (18) Mueller, C. J.; Cannella, W. J.; Bruno, T. J.; Bunting, B.; Dettman, H. D.; Franz, J. A.; Huber, M. L.; Natarajan, M.; Pitz, W. J.; Ratcliff, M. A.; Wright, K. Methodology for formulating diesel surrogate fuels with accurate compositional, ignition-quality, and volatility characteristics. *Energy Fuels* **2012**, 26, 3284-3303.
- (19) Pitz, W. J.; Mueller, C. J. Recent progress in the development of diesel surrogate fuels. *Progress in Energy and Combustion Science* **2011**, 37, 330.
- (20) Hasan, M.; Ali, M.; Bukhari, A. Structural characterization of Saudi Arabian heavy crude oil by n.m.r. spectroscopy. *Fuel* **1983**, 62, 518-23.
- (21) Burri, J.; Crockett, R.; Hany, R.; Rentsch, D. Gasoline composition determined by ^1H NMR spectroscopy. *Fuel* **2004**, 83, 187-93.
- (22) Yang, Y.; Liu, B.; Xi, H.; Sun, X.; Zhang, T. Study on relationship between the concentration of hydrocarbon groups in heavy oils and their structural parameter from ^1H NMR spectra. *Fuel* **2003**, 82, 721-7.
- (23) Netzel, D. A.; McKay, D. R.; Heppner, R. A.; Guffey, F. D.; Cooke, S. D.; Varie, D. L.; Linn, D. E. ^1H - and ^{13}C -n.m.r. studies on naphtha and light distillate saturate hydrocarbon fractions obtained from in-situ shale oil. *Fuel* **1981**, 60, 307-20.
- (24) Menendez R, Bermejo J, Moinelo SR, Marsh H. Flash chromatography, extrography and ^1H -NMR to characterize coal-derived liquids. *Org Geochem* **1990**, 15, 161-8.
- (25) Nielsen, K. E.; Dittmer, J.; Malmendal, A.; Nielsen, N. C. Quantitative analysis of constituents in heavy fuel oil by ^1H nuclear magnetic resonance (NMR) spectroscopy and multivariate data analysis. *Energy & Fuels* **2008**, 22 (6), 4070-4076.
- (26) Poveda, Juan, C.; Molina; Daniel,R.; Pantoja,A.; Edgar,F. , ^1H - and ^{13}C -nmr structural characterization of asphaltenes from vacuum residua modified by thermal cracking. *CT&F Ciencia, Tecnología y Futuro* **2014**, 49-59.
- (27) Meusinger, R.; Moros, R. Determination of octane numbers of gasoline compounds from their chemical structure by ^{13}C NMR spectroscopy and neural networks. *Fuel* **2001**, 80, 613-21.
- (28) DeFries, T. H.; Kastrup, R. V.; Indritz, D. Prediction of cetane number by group additivity and carbon-13 Nuclear Magnetic Resonance. *Ind Eng Chem Res* **1987**, 26, 188-93.
- (29) Brekke, T.; Kvalheim, O. M.; Sletten, E. Prediction of physical properties of hydrocarbon mixtures by partial-least-squares calibration of carbon-13 nuclear magnetic resonance data. *Anal Chim Acta* **1989**, 223, 123-34.
- (30) Mehl, M.; Pitz, W. J.; Sarathy, S. M.; Westbrook, C. K. Modeling the combustion of high molecular weight fuels by a functional group approach. *International Journal of Chemical Kinetics* **2012**, 44, 257-276.
- (31) Dryer, F. L.; Kerho, S. E. An overview on carbon formation in heavy oil combustion. *Princeton University-Electric Power Technologies Inc report*, **1987**, 1-42.
- (32) Whithead, E. V. Fuel oil chemistry. The Heavy End of the Barrel-Future Trends in Oil Firing. *Institute of Energy Symposium, The Institute of Energy, Portsmouth (England)*, **1981**, 16-43.
- (33) Raimbault, C. Overview heavy fuels. TOTeM11 (Topic Oriented Technical Meeting: Liquid Fuels: Heavy oils, wastes and slurries), *International Flame Research Foundation, Biarritz (France)*, **1995**, 1-22.

- (34) Choudhary, T. V.; Parrott, S.; Johnson, B. Unraveling heavy oil desulfurization chemistry: Targeting clean fuels. *Environ. Sci. Technol.* **2008**, 42 (6), 1944–1947.
- (35) Choudhary, T. V. Structure-reactivity-mechanistic considerations in heavy oil desulfurization. *Ind. Eng. Chem. Res.* **2007**, 46, 8363–8370.
- (36) Wang, M.; Zhao, S.; Chung, K. H.; Xu, C.; Shi, Q. Approach for selective separation of thiophenic and sulfidic sulfur compounds from petroleum by methylation/demethylation. *Anal. Chem.* **2015**, 87 (2), 1083–1088.
- (37) Bartle, K. D.; Jones, J. M.; Lea-Langton, A. R.; Pourkashanian, M.; Ross, A. B.; Thillaimuthu, J. S.; Waller, P. R.; Williams, A. The combustion of droplets of high-asphaltene heavy oils. *Fuel* **2013**, 103, 835–842.
- (38) Bomo, N.; Lahaye, J.; Prado, G.; Claus, G. Formation of cenospheres during pyrolysis of residual fuel oils. *Twentieth symposium (international) on combustion insitute*, **1984**, 903–911.
- (39) Davis, L. U.; Frederick, L. D. New results on coke formation in the combustion of Heavy-Fuel Droplets. *Twenty-Third Symposium (international) on combustion/the combustion institute*, **1990**, 1437–1443.
- (40) Millington, A.; Price, D.; Hughes, R. The use of thermal analysis techniques to obtain information relevant to the situ combustion process for enhanced oil recovery. *J Therm Anal Calorim* **1993**, 40, 225–38.
- (41) Pereira, A. N.; Trevisan, O. V. Thermoanalysis and reaction kinetics of heavy oil combustion. *J Braz. Soc. Mech. Sci. Eng.* **2014**, 36, 393–401.
- (42) Morgan, P. A.; Robertson, S. D.; Unsworth, J. F. Combustion studies by thermogravimetric analysis: 1. Coal oxidation. *Fuel* **1986**, 65, 1546–1551.
- (43) Murugan, p.; Mahinpey, N.; Mani, T.; Freitag, N. pyrolysis and combustion kinetics of Fosterton oil using thermogravimetric analysis. *Fuel* **2009**, 88, 1708–1713.
- (44) Kok, M. V.; Car, A. C. Kinetic of crude oil combustion. *J. Therm Anal Calorim* **2006**, 83, 445–449.
- (45) Coats, A.; Redfern, J. Kinetic parameters from thermogravimetric data, *Nature* **1964**, 201, 68–69.
- (46) Ambalae, A.; Mahinpey, N.; Freitag, N. Thermogravimetric studies on pyrolysis and combustion behavior of a heavy oil and its asphaltenes. *Energy & Fuels* **2006**, 20, 560–565.
- (47) Delpuech, J.J.; Nicole, D.; Daubenfeld, J.; Boubel, J.C. Method to evaluate benzonaphthenic carbons and donatable hydrogens in fossil fuels. *Fuel* **1985**, 64, 325–34.
- (48) Gupta, P. L.; Dogra, P. V.; Kuchhal, R. K.; Kumar, P. Estimation of average structural parameters of petroleum crudes and coal-derived liquids by ^{13}C and ^1H n.m.r. *Fuel* **1986**, 65, 515–9.
- (49) Rodriguez, J.; Tierney, J. W.; Wender, I. Evaluation of a delayed coking process by ^1H and ^{13}C n.m.r. spectroscopy: 1. Material balances. *Fuel* **1994**, 73, 1863–1869.
- (50) Behera, B.; Ray, S. S.; Singh, I. D. Structural characterization of FCC feeds from Indian refineries by NMR spectroscopy. *Fuel* **2008**, 87, 2322–33.
- (51) Poveda, J. C.; Molina, D. R. Average molecular parameters of heavy crude oils and their fractions using NMR spectroscopy. *J Petrol Sci Eng* **2012**, 84, 85:1–7.
- (52) Myers, M. E.; Stollsteimer, J.; Wims, A. M. Determination of hydrocarbon-type distribution and hydrogen/carbon ratio of gasolines by nuclear magnetic resonance spectrometry. *Anal Chem* **1975**, 47, 2010–5.

Figure captions:

Figure 1. TG (—) and DTG (---) non-isothermal curves of a heavy fuel oil sample in air at a heating rate of 5 °C/min.

Figure 2. (a) Arrhenius and (b) Coats and Redfern methods.

Figure 3. Broadband positive-ion mode APCI MS of a HFO sample using heptane as a solvent.

Figure 4. Class distribution plot of the species present in the HFO sample as observed by positive-ion mode APCI-FTICR MS.

Figure 5. DBE versus carbon number distribution plots for (a) S_1 and (b) HC class species observed in an HFO sample using positive-ion APCI FT-ICR MS.

Figure 6. Distribution of structures obtained from (a) ^1H NMR and (b) ^{13}C NMR.

Figure 7. HMBC spectra of a HFO.

Figure 8. High-intensity regions in the HMBC spectrum.

Figure S1. Zoom mass inset at $m/Z = 761$ showing 17 different elemental compositions assigned in a HFO sample.

Figure S2. (a) ^1H NMR spectrum of HFO and (b) ^{13}C NMR spectrum of HFO (* denotes solvent contaminated signal).

Table 1. HFO physical properties and elemental composition

Physical properties	Method	Units	Results
Density at 288 K	ASTM D4052-11	Kg/m ³	970.5
Specific gravity (60/60°F)	ASTM D4052-11	-----	0.9711
Kinematic viscosity at 40°C	ASTM D445-12	cSt	617.740
Compositional data			
Sulfur	ASTM D4294-10	mass%	3.292%
Asphaltenes content	IP 143	Wt%	8.2%
Vanadium	IP 501-05	mg/Kg	18.0
Nickel	IP 501-05	mg/Kg	11.0
Sodium	IP 501-05	mg/Kg	3.4
Zinc	IP 501-05	mg/Kg	<1.0
Lead	IP 501-05M	mg/Kg	0.4
Potassium	IP 501-05M	mg/Kg	0.1
Carbon	EPA 440.0	mass%	85.0%
Hydrogen	EPA 440.0	mass%	10.89%
Oxygen	EPA 440.0	mass%	0.030%
Nitrogen	EPA 440.0	mass%	0.239%
Heating Values			
Higher heating value	ASTM D4868	BTU/IB	18258
Lower heating value	ASTM D4868	BTU/IB	17255

Table 2. Reaction intervals, burnout temperature of HFO (TG-DTG), E (KJ/mol), and A(1/min) of HFO

LTO int. (°C)	FD int. (°C)	HTO int. (°C)	Burn- out (T) (°C)	E (LTO) ^a , Arrhenius	E (HTO) ^a , Arrhenius	A (LTO), Arrhenius	A (HTO), Arrhenius	E (LTO) ^a , (C&R)	E (HTO) ^a , (C&R)	A (LTO), (C&R)	A (HTO), (C&R)
25-342	342-479	497-580	580	18.06 ± 2	218.5 ± 5.1	0.4	3.88X10 ⁻¹¹	24± 3.1	231.6 ± 4.3	2.14	1.11X10 ⁻¹⁵

a Mean (± S.D.) of triple measurements, (C&R) Coats and Redfern method.

Table 3. Possible skeletal structures of molecules in the high-intensity region of the HMBC spectrum

Region	¹ H shift region	¹³ C shift region	Possible skeletal structural groups
1	0.5–1.09	5–12.3
2	1.09–2	12.3–14.7
3	0.5–1.09	14.7–17.6
4	0.5–1.09	21.9–25
5	0.5–1.09	25–28.5
6	1.09–2	28.5–30.8
7	1.09–2	30.8–32.7
8	0.5–1.09	30.8–32.7

9 0.5 –1.09 32.7 – 45

10 2.4 – 4.3 120 –129

11 2.4 –4.3 129 – 155

12 6.2 – 7.4 32.7 – 45

13 7.4 – 10.7 129 – 155

14 7.4 – 10.7 165 – 190

15 4.3 –5.1 165 – 190

● represents a carbon atom, ○ represents a hydrogen atom

Figure 1. TG (—) and DTG (---) non-isothermal curves of a heavy fuel oil sample in air at a heating rate of 5 °C/min.

Figure 2. (a) Arrhenius and (b) Coats and Redfern methods.

Figure 3. Broadband positive-ion mode APCI MS of a HFO sample using heptane as a solvent.

Figure 4. Class distribution plot of the species present in the HFO sample as observed by positive-ion mode APCI-FTICR MS.

Figure 5. DBE versus carbon number distribution plots for (a) S₁ and (b) HC class species observed in an HFO sample using positive-ion APCI FT-ICR MS.

Figure 6. Distribution of structures obtained from (a) ¹H NMR and (b) ¹³C NMR.

Figure 7. HMBC spectra of a HFO in the aliphatic region.

Figure 8. High-intensity regions in the HMBC spectrum.

Supplementary

Table S1. Structural assignments in ^1H NMR and their integrated values

Structural definition	Structure	Chemical shift region (ppm)	Moles (%)
paraffinic CH_3		0.5 – 1.09	27.885
paraffinic CH_2		1.09 – 2	59.202
alpha to aromatic CH_3		2 – 2.4	2.010
alpha to aromatic CH_2		2.4 – 4.3	5.862
olefinic CH_2		4.3 – 5.1	0.062
olefinic CH		5.1 – 6.2	0.020
monoaromatic H		6.2 – 7.4	3.057
polyaromatic H		7.4 – 10.7	2.007

○ represents a hydrogen atom

Table S2. Structural assignments in ¹³C NMR and their integrated values

Structural definition	Structure	Chemical shift region (ppm)	Moles (%)
branched chain CH ₃		5 – 12.3	1.155
chain alpha CH ₃		12.3 – 14.7	6.061
aromatic attached ethyl CH ₃		14.7 – 17.6	1.229
alpha to ring CH ₃		17.6 – 21.9	6.725
chain beta-CH ₂ , alpha to aromatic or isobutyl		21.9 – 25	7.071
cycloparaffin CH ₂		25 – 28.5	5.707
aromatic attached ethyl CH ₂		28.5 – 30.8	20.798
chain gama-CH ₂ or beta to aromatic CH ₂		30.8 – 32.7	5.590
paraffinic CH*CH ₂		32.7 – 45	14.819
paraffinic CH		45 – 55	1.387
R-CH ₂ OH		55 – 65	0.543
R-C---C-R		65 – 70	0.104

		100 – 113	0.147
aromatic CH		113–115	0.251
quaternary aromatic		120 –129	9.534
RCOOH		129 –155	11.817
RCHO		165 –190	5.710
RCOR		190 - 200	0.370
	200 – 220	0.973

Figure S1. Zoom mass inset at m/Z = 761 showing 17 different elemental compositions assigned in a HFO sample.

Figure S2. (a) ^1H NMR spectrum of HFO and (b) ^{13}C NMR spectrum of HFO (* denotes solvent contaminated signal)