Characterization of deasphalted heavy fuel oil using APPI (+) FT-ICR mass spectrometry and NMR spectroscopy

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Abstract:

Asphaltenes are n-alkane insoluble compounds found in crude oils and heavy fuels (high and non-boiling petroleum fractions). Asphaltene molecular structure has not been fully elucidated, and their presence in fuels is a source of concern. They reduce combustion efficiency and are responsible for particulate matter emissions. Removing the asphaltenes, or deasphalting, is a way of upgrading the fuel to improve its quality. This study reports the removal of asphaltenes from heavy fuel oil (HFO) using a solvent extraction method, and the detailed molecular characterization of the deasphalted oil (DAO) using positive ion atmospheric pressure photo ionization Fourier transform-ion cyclotron resonance mass spectrometry (APPI (+) FT-ICR/MS) and ¹H and ¹³C Nuclear magnetic resonance (NMR) spectroscopy. Approximately 8.2 mass % of asphaltenes were removed from HFO using n-heptane as solvent. This resulted in significant improvements in the HFO's physical properties. The resulting DAO was five times less viscous and contained significantly less heavy metals (e.g., Ni and V). There was also a slight reduction in the sulfur content from 3.3 to 3.1 mass %. 52,753 and 46,315 ions with a mass to charge ratio (m/z) ranging from 154 to 1200 were detected in HFO and DAO samples, respectively, using APPI FT-ICR/MS. Amongst them, 6,729 (HFO) and 6,030 (DAO) ions were resolved into their underlying elemental compositions (C, H, O, N and S) and a unique chemical formula was assigned to each mass. The resolved masses were then further classified based on their molecular class and were analyzed as a function of double bond equivalent (DBE) vs carbon number. ¹H and ¹³C NMR analyses of HFO and DAO were performed and the results indicate the total aromatic groups in HFO (¹H 7.7 mol %, ¹³C 37.6 mol %) are more compared to DAO (¹H 4.7 mol %, ¹³C 32.6 mol %). The average molecular parameters (AMPs) of HFO and DAO were also calculated from the ¹H and ¹³C NMR spectra and compared. A surrogate molecule that visualizes the average molecular structure of the entire fuel was developed for both HFO and DAO using the data from the above analytical techniques. Understanding the molecular chemistry of these fuels provides valuable data to develop

better desulfurization techniques for these sulfur laden fuels and help predict fuel properties using structure-property relationships.

Keywords: asphaltenes; heavy fuel oil; APPI (+) FT-ICR mass spectrometry; ^1H and ^{13}C NMR spectroscopy;

1. INTRODUCTION

Asphaltenes[1–4] are compounds found in heavy petroleum fractions that are insoluble in n-alkanes (e.g., n-heptane) and soluble only in aromatic solvents (e.g., quinoline). Their chemical structures are still not understood and they are defined by their solubility class instead of their chemical identity. Asphaltenes in crude oils precipitate and deposit along the reservoir walls thereby plugging the wells and also cause fouling issues in flow lines [5–7]. Asphaltenes have a major effect on the physico-chemical properties of heavy fuels and residuals comprising these compounds. It has been shown that asphaltenes are the most aromatic fraction of heavy fuels like vacuum residues and heavy fuel oils, and thus increase the viscosity of the fuel [8]. This requires the addition of solvents or pre-heating the fuel to improve flow properties. The presence of asphaltenes makes the fuel difficult to burn and they are responsible for the formation of cenospheres i.e. hollow carbonaceous spheres formed during droplet combustion of heavy fuels [9,10]. Khateeb et al.[11] experimentally investigated the influence of asphaltene concentration on combustion of heavy fuel oil droplets and showed that addition of asphaltenes in the fuel resulted in increased burning and ignition delay times. Due to these reasons, asphaltenes have been viewed as detrimental fractions in petroleum fuels [12].

Deasphalting (i.e., removing asphaltenes) is a suitable technique to upgrade petroleum heavy ends as the deasphalted oil (DAO) or maltenes are richer in paraffins and can be used as base oil for lubricants [13]. Deasphalting prevents coke formation and metal buildup (Ni, V) in catalysts when the DAO is used as a feed in fluid catalytic cracking (FCC) or other subsequent refinery processes[14]. Asphaltene removal leads to a significant reduction in viscosity by 2-3 orders [8]. Heavy metals like Ni and V are also reduced as these are concentrated in the asphaltenes [6]. Deasphalting has proven to be economically advantageous with a net realization of 1.1 USD/bbl for heavy oils [15]. This work explores the deasphalting of heavy fuel oil (HFO).

HFO is a residue mostly obtained from the visbreaking unit of a refinery. It is used primarily as fuel to propel marine engines and is therefore termed as ‘marine fuel’ and also as ‘bunker fuel’. Due to the emission of sulfur dioxides, the International Maritime Organization (IMO) has indirectly restricted the use of HFO by imposing a sulfur cap of 0.5 wt% beginning from 1st January 2020. The sulfur cap has been

further tightened to 0.1 wt % in many emission controlled area's (ECA), and, in some cases, the IMO has banned the use of HFO on ships sailing in the Antarctic region [16] due to the deleterious effect of particulate matter emissions on the ecosystem. Deasphalting HFO can significantly reduce particulate matter emissions such as cenospheres, ash and smoke. It can also result in slightly lower sulfur dioxide emissions as the asphaltene fraction of heavy fuels possesses slightly higher sulfur content [6,17]. Understanding the molecular chemistry of these fuels is the first step to establishing a fundamental relationship between emissions and molecular structure. Desulfurization techniques [18–20] like oxidative desulfurization (ODS), hydrodesulfurization (HDS), and extractive desulfurization are dependent on fuel molecular chemistry. A better understanding of HFO and DAO molecular composition can help devise and optimize desulfurization techniques as different sulfur containing compounds behave differently to desulfurization processes [21].

High resolution analytical techniques like FT-ICR mass spectrometry and NMR spectroscopy are ideally suited to characterize heavy petroleum ends which are complex fuels that possess tens of thousands of individual molecules along with the presence of hetero atoms like O, N and S [22]. Conventional techniques like gas chromatography coupled with mass spectrometry (GC-MS) or high performance liquid chromatography (HPLC) are unable to analyze such heavy complex fuels [23]. FT-ICR mass spectrometry can resolve ions at the molecular level by assigning unique elemental compositions to each, and also detect extremely low mass differences at the order of an electron [24]. The sample is volatilized and then ionized by a number of different techniques before being detected by FT-ICR mass spectrometry. In the present work, HFO and DAO samples were ionized by positive ion APPI which has been used to ionize various petroleum samples and their derivatives. Chacon Patino et al. [3], Giraldo-Davila et al. [25], Pereira et al. [12] have used positive ion APPI method to ionize different asphaltene samples. Marshalls group [1,4,22,26] have also used APPI to ionize a number of crude oil samples. Cho et al. [27] have also used APPI as an ionization source to study crude oils. Pereira et al. [28] performed a study analyzing 5 different methods for ionizing asphaltenes and concluded that APPI and APCI (atmospheric pressure chemical ionization) to be more suitable to obtain sample composition. Panda et al. [29] ionized PAH and PASH fractions of Saudi Arabian crude oil using APPI. Lozano et al. [30] analyzed Colombian crude oils and vacuum residuals using APPI ionization methods. FT-ICR mass spectrometry has been used to analyze a number of other samples like base oils [31], HFO [32], fuel oil derived DAO [33], vacuum residue derived DAO [34], vacuum residues [35], furnace oil [36], coal liquefaction products [37], lubricants [38], biomass [39,40] besides crude oils [25,26,41–43] and asphaltenes [12,44–46]. High resolution ^1H and ^{13}C NMR spectroscopy can also reveal rich qualitative and quantitative information

about the molecular distribution of heavy fuels [47]. NMR spectra are represented in terms of chemical shifts which indicate the molecular structure. Using NMR, fuels can be characterized in terms of molecular fractions or functional groups that make up all the constituent molecules. Each functional group gives rise to peaks in the NMR spectra in their characteristic regions which make NMR spectroscopy ideal to study complex hydrocarbon fuels. Functional groups that are similar in structure produce distinct signals, which aid their identification and quantification. For example, ^1H nuclei in paraffinic CH_3 groups usually appear between 0.25 – 0.94 ppm in the ^1H NMR spectra, whereas the peaks corresponding to the ^{13}C nuclei appear between 3 – 18.5 ppm in the ^{13}C NMR spectra. The relative quantity of each nuclei type in the mixture can be calculated by the integral intensity of the particular peaks divided by the sum of integral intensities of all peaks. NMR derived functional groups have been used as molecular descriptors to predict combustion properties like cetane number [48], octane number [49] and also to formulate fuel surrogates [50–52]. NMR spectroscopy has been applied to study the molecular structure of various fuels like gasoline [48,53], diesel [51], shale oils [54,55], HFO [16,32], coal derived liquids [56], base oils [47], vacuum residues [57], asphalts [58] and crude oil [59].

2. EXPERIMENTAL METHODS

2.1 Deasphalting

Solvent deasphalting is a technique where a suitable solvent is used to precipitate the asphaltenes. The HFO sample used in the present study was obtained from a refinery in Saudi Arabia. The process of separating asphaltenes from HFO was completed in three steps, as described in ASTM D3279 [60]. First, 1 – 1.3 g of HFO was transferred into a 250 ml flask. Then, 100 ml of n-heptane was added per gram of HFO sample to the flask and heated for 30 min under a reflux condenser. Second, the mixture was poured through double filter pads into a Büchner flask (i.e., filter flask). Afterwards, the filters, now containing asphaltene particles, were placed in an oven at 110 °C for 30 min. Third, the precipitate was extracted from the filter pads by adding toluene. The toluene solvent was then separated from the asphaltene using a rotary evaporator device. An overview of the entire process is presented in the supplementary material.

2.2 APPI (+) FT-ICR mass spectrometry

Samples were analyzed on a Bruker Daltonics FT-ICR mass spectrometer (9.4 T Solarix XR, Bremen, Germany). The samples were diluted in pure toluene and directly injected into the atmospheric pressure photo ionization (APPI) source. The FT-ICR mass spectra of samples were acquired using the positive APPI ionization mode with a mass range of m/z 154–1200. The following APPI (+) conditions were used:

nitrogen nebulizer gas pressure, 2.5 bar; vaporizer temperature 400 °C and dry temperature 280 °C. The APPI source utilizes a krypton light, which provides 10.6 eV of ionization energy for the analytes and only singly charged ions were observed. Thus, the sample molecules were mainly ionized into molecular ions without fragmentation. The ion accumulation time in the hexapole was 0.01 s, and each spectrum was acquired by accumulating 300 scans with a time domain size of 8 *mega-points*, transient length of 4.4739 s. All mass spectra were externally calibrated using 0.05 mg mL⁻¹ of a polystyrene solution (*m/z* from 100 to 1200). The raw data was further internal recalibrated using a set of homologous alkylated compounds for each sample. The mass list with signal to noise ratio > 5 of each mass spectrum was generated by DataAnalysis V4.4 and imported into the *Composer* software (Sierra Analytics, Pasadena, CA, USA) for chemical formulas assignment[61]. Giving an error range of 0.5ppm, the most probable elemental composition of each monoisotopic mass peak was calculated according to the determined accurate mass within the range of C₁₋₁₀₀H₁₋₂₀₀N₀₋₃O₀₋₃S₀₋₃. Then, in order to get an overview of the compound distributions, all the assigned chemical formulas were divided into different subgroups (HC, S1, S2, etc.) according to the heteroatom numbers. The abundance of each molecular class is calculated by the total intensity of the particular class divided by the intensity of all assigned peaks. The resulting chemical formulas were further sorted into different compound classes and their distributions were visualized based on their double bond equivalent (DBE)[27], carbon number (CN)[12], and relative abundance.

2.3 ¹H and ¹³C NMR spectroscopy

Samples were prepared by transferring about 100 µl of sample to 5 mm NMR tubes, and then 600 µl of deuterated chloroform CDCl₃ were added to the NMR tubes. NMR spectra were recorded using Bruker 700 AVANAC III spectrometer equipped with Bruker CP TCI multinuclear *CryoProbe* (BrukerBioSpin, Rheinstetten, Germany). The NMR spectra were recorded at 298 K 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 [62]. Before Fourier transform, the free induction decay (FID) values were multiplied by an exponential function equivalent to a 1 Hz line broadening factor, spectra were then visually phased, base lines were adjusted using abs command, and the spectra were referenced to 0.0 ppm using Tetramethylsilane (TMS) as internal chemical shift reference. To ensure complete relaxation of carbon magnetizations, ¹³C NMR spectra were recorded using a 1D sequence with power-gate decoupling, a 30° flip angle with a recycle delay time of 20 seconds.. Bruker Topspin 2.1 software (Bruker BioSpin, Rheinstetten, Germany) was used in all experiments to collect and analyze the data. Each spectra was

processed 5 times and the average values are reported. The ^1H and ^{13}C NMR spectra of HFO and the DAO are shown in figures 1 and 2, respectively.

3. RESULTS & DISCUSSION

The physical and chemical properties of HFO and DAO are reported in Table 1. HFO has a very high kinematic viscosity of 617 ($10^{-6}\text{m}^2/\text{s}$ or cSt) at 313 K which is approximately 1000 times the viscosity of water at 313 K. There is a good correlation between viscosity of heavy oils and the relative content, molecular structure and the physico-chemical properties of its constituent asphaltenes [63]. Deasphalting has a significant improvement in the physical properties of HFO. Its kinematic viscosity is reduced by more than a factor of five after the asphaltenes are removed. The density of DAO was also lower than HFO because asphaltenes possess a higher density due to the large molecular sizes and higher aromatic content [5,64]. The DAO has a slightly lower C content and a slightly higher H content. There is also a slight reduction in sulfur content (from 3.3 to 3.1 mass %) on account of the deasphalting process. The concentration of heavy metals, Ni and V, on the other hand were reduced by more than 50 % in the DAO as these are more concentrated around asphaltenes. The gravimetric higher heating value of the DAO is slightly more than that of HFO mostly due to the nominal increase in the H content of the sample.

3.1 APPI (+) FT-ICR/MS results

The mass spectra of HFO and DAO are presented in Figure 3 and show a mass to charge ratio (m/z) ranging from 154 to 1200. The average resolution of the peaks was 1,147,000 across the recorded mass range. Due to the ultrahigh resolution and mass accuracy of FT-ICR/MS, around 6,700 different mass peaks were resolved and a unique chemical formula was assigned to each mass peak. The precipitation and subsequent removal of asphaltenes from HFO resulted in a drop in the average molecular weight from 565 m/z to 531 m/z as recorded from the mass spectra. This shows that the 8 mass % asphaltene fraction in HFO removed via solvent deasphalting has a higher molecular size distribution compared to the remaining fraction of the fuel. The average molecular weight of the fuel sample was calculated by summing the product of mass to charge (m/z) ratio and signal intensity of each recorded ion and dividing by the total intensity of all the recorded ions. The ions recorded by FT-ICR/MS are dependent on the efficiency of the ionization source employed. Different ionization modes may produce a varying distribution of species, and choosing the appropriate ionization source depends on the nature of the sample. Here the APPI mode was chosen as it is more effective in ionizing higher aromatic and sulfur containing molecules [31,65].

The assigned chemical formulae of the species can be separated into different molecular classes based on the heteroatom content. The relative abundance of different molecular classes in HFO and DAO are shown in Figure 4. HC refers to hydrocarbons with no heteroatoms present. S_1 , S_2 and S_3 species refer to hydrocarbon molecules with one sulfur, two sulfur and three sulfur atoms respectively. N refers to the class of hydrocarbons with one nitrogen atom, NS to hydrocarbons with one nitrogen and sulfur atom and O to oxygenated hydrocarbons. Positive mode APPI ionization also produces protonated ions $[M+H]^+$ along with the radical cations $[M\cdot]^+$ [22,28,41] and in the present study $HC[H]$ and $S_1[H]$ protonated ions were also recorded. The HC and S_1 molecular classes presented in Figure 4 are a sum of both $[M\cdot]^+$ and $[M+H]^+$ ions. This was done in-order to reduce the complexity of the molecular distribution and ease of comparison. DAO has slightly more hydrocarbons (29.2 %) compared to HFO (28.6 %) as determined using APPI FT-ICR/MS. The relative abundance of hydrocarbons with sulfur (S_1 , S_2 and S_3) atoms is the most abundant class and is slightly more in HFO (62.3 %) compared to DAO (60.8 %). This shows that the sulfur atoms in the fuel are distributed evenly throughout the fuel, which poses a challenge for desulfurization techniques.

The molecular class distribution of HC, S_1 , S_2 , and N class species as a function of DBE and carbon number are presented in Figures 5, 6, 7 and 8, respectively, where the bubble size denotes the magnitude of the recorded mass peaks. DBE values allow us to understand the molecular structure of the species based on their unsaturation degree. The HC molecular distribution plot (figure 5) for HFO and DAO show no saturated molecules (DBE < 1) which were most likely stripped during refinery operations or may also be due to the inability of alkanes to form stabilized ions efficiently [66]. The S_1 class of species is the most abundant sulfur class in both HFO and DAO. The S_1 class indicates that the core skeletal structure of the molecules is either thiophenic or thiolic in nature (which is corroborated by the ^{13}C NMR results below). The S_1 class distribution plot (Figure 6) shows that the most abundant polycyclic aromatic sulfur heterocycles (PASH) species in HFO and DAO have DBE between 7-12 and carbon numbers in the range of 30-50. This indicates that benzothiophenes (DBE 6), dibenzothiophenes (DBE 9) and benzonaphthothiophenes (DBE 12) and their derivatives with alkyl side chains may be the most abundant PASH species [31] in both HFO and DAO. These PASH species exhibit carbon numbers up to 80, which shows the presence of long or multiple short alkyl chains connected to the rings [58,67–69]. The high boiling range of these fuels is evident due to the presence of large DBE values (>20) which indicate the presence of tetra and penta aromatics[31,70]. The S_2 and N class plots show clear apparent differences between HFO and DAO. S_2 class species with DBE (15 -25) in the carbon range of (72-78) are not present in DAO, while N class species with DBE (12-22) with carbon numbers (62-70) are also absent. This shows

that the asphaltenes in HFO may possess more heteroatoms and have higher carbon numbers than the remaining portion of the fuel.

Planar limits [71] defined as lines connecting maximum DBE values at given carbon numbers can be used for interpreting molecular structure of crude compounds [25,34,46]. The planar limit slope indicates the condensation degree of cyclic molecules present and mixtures containing rich aromatic structures yield higher planar limit slopes. Linear addition of benzene rings to aromatic cores (cata-condensation) results in planar limit slope of 0.75, whereas non-linear addition (peri-condensation) gives a value of 0.9. Addition of naphthenic rings to a starting core results in values around 0.25. Planar limit slopes, calculated by Cho et al. [71] for saturates, aromatics, resins and asphaltenes of a heavy oil yielded values of 0.28, 0.73, 0.68 and 0.9 respectively. The planar limit slopes calculated for HC, S_1 , S_2 and N class species in HFO are 0.68, 0.64, 0.66 and 0.55 respectively whereas the values for HC, S_1 , S_2 and N class species in DAO are 0.66, 0.62, 0.61 and 0.50. The lower planar limit slope values corresponding to DAO indicates that its aromaticity may be lower than that of HFO.

3.2 ^1H and ^{13}C NMR results

The characteristic ^1H and ^{13}C chemical shifts used to identify and quantify various nuclei are reported in Tables 2 and 3, respectively. The chemical shift assignments for the various functional groups were taken from Poveda et al. [59] and Abdul Jameel et al. [50]. Comparisons of various ^1H and ^{13}C types in HFO and DAO are also presented in Tables 2 and 3. DAO has more paraffinic CH_3 and CH_2 groups (^1H 73.4 mol %, ^{13}C 54.4 mol %) compared to HFO (^1H 65.5 mol %, ^{13}C 48.2 mol %) whereas the total aromatic groups in HFO (^1H 7.7 mol %, ^{13}C 37.6 mol %) are more compared to DAO (^1H 4.7 mol %, ^{13}C 32.6 mol %). There are more aromatic carbon atoms than aromatic hydrogen atoms in both HFO and DAO, which shows that a majority of aromatic carbon atoms are non-protonated. This could be because the aromatic rings are fused or due to the presence of multiple alkyl side chains. HFO also has slightly more naphthenic groups compared to DAO, while the olefinic content is negligible in both. The ^{13}C NMR spectra for HFO and DAO show peaks in the region between 137.0 – 140.5 ppm which indicates the presence of quaternary carbon atoms in alpha position to sulfur atoms. This shows that the sulfur atoms in HFO and DAO may be present in the form of thiophenes or even as thiols.

3.2.1 Average molecular parameters (AMPs)

Combining the data from ^1H and ^{13}C NMR spectra, elemental analysis and average molecular weight (from APPI FT-ICR/MS) enables the characterization of complex hydrocarbon fuels in the form of AMPs. This

method provides the total distribution of atoms in a fictitious average molecule of the fuel (i.e., number of paraffinic, naphthenic, olefinic, aromatic etc. carbon and hydrogen atoms). This method was first applied to analyze petroleum fractions by Williams [72]. The AMPs can also be used for property estimation of complex mixtures.

An AMP denoted by A_i is defined as per equation 1.

$$A_i = \frac{I_i}{I_{total}} \cdot \%A \quad (1)$$

where, A refers either to H or C atom and I is the ^1H NMR or ^{13}C NMR integral. The subscript i indicates a particular interval in the chemical shift corresponding to a characteristic atom type. $\%A$ is the mass % of A measured from elemental analysis.

The first step is to calculate the average molecular formula of HFO and DAO in the form of $\text{C}_c\text{H}_h\text{O}_o\text{N}_n\text{S}_s$. The subscripts c , h , o , n and s are the average number of carbon, hydrogen, oxygen, nitrogen and sulfur atoms in the average molecule. These can be calculated from elemental analysis and average molecular weight. For example, the average number of H atoms (h) is calculated by using Equation 2.

$$h = MW_{avg} \cdot \%H \cdot \frac{1}{100} \cdot \frac{1}{a_H} \quad (2)$$

where, MW_{avg} is the average molecular weight. $\%H$ is the mass% of hydrogen measured from elemental analysis and a_H is the atomic mass of hydrogen in g/mol. Similarly, other atoms are also calculated. The average molecular formula of HFO and DAO are $\text{C}_{40}\text{H}_{60.5}\text{O}_{0.01}\text{N}_{0.1}\text{S}_{0.58}$ and $\text{C}_{37.4}\text{H}_{60}\text{O}_{0.01}\text{N}_{0.1}\text{S}_{0.52}$, respectively. Using equations 1 and 2, the AMPs are calculated as number of atoms per average molecule. The AMPs calculated for HFO and DAO using ^1H NMR and ^{13}C NMR are presented in Figure 9. HFO has 40 C and 61.5 H atoms, whereas DAO has 37.3 C and 60.5 H atoms in its average molecule on account of its lower molecular weight. The AMPs dictate that there should be 4.7 paraffinic CH_3 groups, 15.3 paraffinic CH_2 groups in an average HFO molecule while DAO must possess 4.3 paraffinic CH_3 groups and 14.1 paraffinic CH_2 groups in its average molecule. HFO has a higher number of aromatic quaternary C atoms (7.7) compared to DAO (6.1) in their average molecules. The number of aromatic carbon atoms bridging 2 rings in HFO and DAO are 2.5 and 2 respectively, whereas there are 0.6 and 0.2 aromatic carbon atoms in HFO and DAO respectively that bridge three rings. These results complement the planar limit slope values calculated from the DBE vs carbon number plots which indicate a higher aromaticity of HFO compared to DAO. The heteroatoms, N and O are negligible while there is only 0.58 and 0.52 S atoms in HFO and DAO, respectively.

By re-arranging the AMPs, a number of dimensionless numbers termed as derived AMPs can be calculated. Some of these derived AMPs combine the data from ^1H NMR and ^{13}C NMR and provide valuable information regarding the overall molecular structure of the mixture. The derived AMPs calculated in the present work are reported in Table 4 along with their description. The formulae utilized to calculate these derived AMPs along with their derivations were obtained from Poveda and Molina [59]. HFO has a higher aromaticity factor (0.38) than DAO (0.33), whereas DAO has a higher paraffinic chain length (4.5) than HFO (4.2). HFO has more rings (aromatic and naphthenic combined) per average molecules (4.1) compared to DAO (3.65).

3.2.2 Surrogate molecule

The surrogate molecule is a hypothetical representation of the average structure of the fuel. It has a similar distribution of chemical functionalities, average molecular weight and atom types observed in the fuel. It helps us evaluate the overall structure of the fuel by condensing all the information into a single fictitious molecule, which may or may not be actually present in the real fuel. The surrogate molecule can also help to evaluate fuel properties like density, viscosity etc. using quantitative structure property relationships (QSPR [73]), especially when experimentation is not possible. It can also serve as a surrogate for chemical kinetic modeling studies of the fuel. The surrogate molecules for HFO and DAO (shown in Figure 10) were developed manually by combining the data from all the above analytical techniques. These molecules can be drawn in a number of ways such that they satisfy the calculated AMPs and the derived AMPs; the reported structures are one of many such possible structures. Average molecular structures reported in the literature for fuels like vacuum residues [57], asphaltenes from wood tar [74], coal tar pitch [75], solvent refined coal [76] etc. have been developed manually due to ease and simplicity; however, complex automated methods exist [77,78], but they are not easily accessible. The surrogate molecules are assumed to be aromatic with alkyl side chains [16,32]. Carbon, hydrogen and sulfur atoms were included while N and O were neglected due to their low percentages. One atom of sulfur was included in the surrogate molecule, although the average molecular formula allows for 0.58 and 0.52 atoms in HFO and DAO, respectively. The surrogate molecule of HFO ($\text{C}_{40}\text{H}_{58}\text{S}$) contains 5 paraffinic CH_3 groups (1 CH_3 group in α position to an aromatic ring), 14 paraffinic CH_2 groups (3 in α position to aromatic rings) and 1 paraffinic CH group. DAO contains ($\text{C}_{38}\text{H}_{58}\text{S}$) contains 5 paraffinic CH_3 groups (2 CH_3 groups in α position to an aromatic ring), 16 paraffinic CH_2 groups (2 in α position to aromatic rings) and 1 paraffinic CH groups in its surrogate molecule. HFO surrogate has 3 aromatic rings, 2 of which are condensed and the other ring is thiopenolic with a fused cyclohexane ring. DAO surrogate has an aromatic ring fused with

a cyclopentane ring and the sulfur atom is present in a thiophenic group. The sulfur atom in the surrogate molecule of HFO and DAO was drawn as thiolic and thiophenic respectively, as this design resulted in better matching of the AMPs and derived AMPs.

A few physical and thermochemical properties of the surrogate molecules of HFO and DAO predicted using QSPR [79] are reported in Table 5. The fundamental principle underlying QSPR prediction is that the molecular structure of a compound contains coded within it the required information to predict its properties. Mathematical relationships can be established between molecular descriptors and various properties of interest. Properties like critical temperature, critical pressure, critical volume etc. that cannot be easily measured for heavy fuels can now be predicted by using the surrogate molecule and QSPR approaches. Physical properties like kinematic viscosity, density, specific gravity and one thermochemical property namely enthalpy of combustion of the surrogate molecules calculated using QSPR were compared with the experimental measurement of the fuels and a good comparison between the two can be observed.

3.3 Comparison of the methods

Physical and chemical properties can be evaluated by a number of techniques and comparing values provides a way for validating various techniques and also provides more information about the sample analyzed. A comparison of various properties determined using the above methods for HFO and DAO is presented in Table 6. The C/H ratio is an important fuel property that dictates the oxidizer requirements and the energy released during combustion. HFO has a slightly higher C/H ratio than DAO as determined by all the methods. This shows that the carbon fraction in asphaltenes is higher than the remaining fraction of HFO. As asphaltenes are also highly aromatic (from the results above), this indicates that a majority of the aromatic C atoms in asphaltenes may occur as non-protonated poly condensed structures, as shown by a number of studies [3,44,46,67,68]. The C/H ratio was calculated from APPI FT-ICR/MS from knowledge of the chemical formulae of all the resolved masses and their abundance values. Sum of the product of C/H ratio of each unique mass and its abundance was divided by the total abundance of all resolved masses to yield the average C/H ratio of the sample. Similarly the average DBE and carbon number of the samples were also calculated. The reported C/H ratio from APPI FT-ICR/MS is approximately 10 % higher than those reported by other techniques which are consistent with each other. This may be because MS is inherently non-quantitative in nature. Another underlying reason could be due the APPI ionization source used in the present work, which is effective in ionizing non-polar hydrocarbon molecules (like benzo and dibenzothiophenes, polycyclic aromatic hydrocarbons (PAHs), cyclo-alkanes

etc.) which comprise bulk of the fuel. However it is not effective in ionizing heteroatom (N, O, S) containing molecules which are highly polar in nature. A good comparison is seen between the average chain length ($\bar{n}$) and ring numbers of the surrogate molecule and the AMPs as the former were drawn from the calculated AMPs as reference. The DBE of HFO (11.5) is higher than that of DAO (10.3) as calculated from the AMPs which is consistent with the higher aromaticity value of HFO. The average DBE values of HFO (13.8) and DAO (13) as reported by APPI FT-ICR/MS are higher than the values from the AMPs. HFO has a slightly higher carbon number than DAO and the values reported by the techniques are consistent with each other. The surrogate molecule for HFO and DAO was designed such that it conforms to these calculated values.

4. Conclusion

This study reported the deasphalting of HFO using n-heptane as solvent and the molecular characterization of the acquired DAO using APPI (+) FT-ICR mass spectrometry and ^1H and ^{13}C NMR spectroscopy. Deasphalting had a significant improvement in reducing the kinematic viscosity of HFO by more than five times and also significantly reduced the heavy metals Ni and V, by more than 50 %. There was also a slight reduction in sulfur content (5.5 mass %) in the resulting DAO. The APPI FT-ICR/MS of HFO and DAO recorded ions with a mass to charge ratio (m/z) ranging from 150 to 1200. The HC class species were slightly more in DAO (29.2 %) compared to HFO (28.6) while the S_1 class species were more in HFO as determined using APPI FT-ICR/MS. The S_1 class of species is the most abundant molecular class in both HFO (42.5 %) and DAO (41.8 %) which may indicate the presence of a core thiophenic skeletal structure as corroborated by ^{13}C NMR results. The average DBE of HFO (13.8) is higher than that of DAO (13.0) which indicates that HFO has a higher fraction of cyclic molecules. Large DBE values (> 20) of PASH species in HFO and DAO indicate the presence of tetra and penta aromatics along with naphthenic rings. The ^1H and ^{13}C NMR results show that DAO has more paraffinic CH_3 and CH_2 groups compared to HFO, whereas the total aromatic groups in HFO are greater. The derived AMPs show that the aromaticity factor for HFO (0.38) is higher than that for DAO (0.33), whereas DAO has a higher average paraffinic chain length (4.5) than HFO (4.2). The surrogate molecule of HFO ($\text{C}_{40}\text{H}_{60}\text{S}$) contains 5 paraffinic CH_3 groups, 14 paraffinic CH_2 groups and 1 paraffinic CH group. DAO surrogate ($\text{C}_{38}\text{H}_{58}\text{S}$) contains 5 paraffinic CH_3 groups, 16 paraffinic CH_2 groups and 1 paraffinic CH groups in its surrogate molecule. The sulfur atom in the HFO surrogate molecule is thiolic while in DAO it is thiophenic. The molecular information of these fuels obtained from the above analytical techniques provides valuable information to design better

combustors, predict properties using QSPR methods and to develop better chemical desulfurization techniques.

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References

- [1] Groenzin H, Mullins OC. *Asphaltenes, Heavy Oils, and Petroleomics*. New York, NY: Springer New York; 2007. doi:10.1007/0-387-68903-6.
- [2] Schuler B, Fatayer S, Meyer G, Rogel E, Moir M, Zhang Y, et al. Heavy Oil Based Mixtures of Different Origins and Treatments Studied by Atomic Force Microscopy. *Energy & Fuels* 2017;31:6856–61. doi:10.1021/acs.energyfuels.7b00805.
- [3] Chacón-Patiño ML, Rowland SM, Rodgers RP. Advances in Asphaltene Petroleomics. Part 1: Asphaltenes Are Composed of Abundant Island and Archipelago Structural Motifs. *Energy & Fuels* 2017;31:13509–18. doi:10.1021/acs.energyfuels.7b02873.
- [4] McKenna AM, Marshall AG, Rodgers RP. Heavy Petroleum Composition. 4. Asphaltene Compositional Space. *Energy & Fuels* 2013;27:1257–67. doi:10.1021/ef301747d.
- [5] Wang X, Gu Y. Characterization of precipitated asphaltenes and deasphalted oils of the medium crude oil-CO₂ and medium crude oil-n-pentane systems. *Energy and Fuels* 2011;25:5232–41. doi:10.1021/ef201131n.
- [6] Sámano V, Guerrero F, Ancheyta J, Trejo F, Díaz JAI. A batch reactor study of the effect of deasphalting on hydrotreating of heavy oil. *Catal Today* 2010;150:264–71. doi:10.1016/j.cattod.2009.09.004.
- [7] Wei B, Zou P, Zhang X, Xu X, Wood C, Li Y. Investigations of Structure-Property-Thermal Degradation Kinetics Alterations of Tahe Asphaltenes Caused by Low Temperature Oxidation. *Energy and Fuels* 2018;32:1506–14. doi:10.1021/acs.energyfuels.7b03565.
- [8] Ilyin S, Arinina M, Polyakova M, Bondarenko G, Konstantinov I, Kulichikhin V, et al. Asphaltenes in heavy crude oil: Designation, precipitation, solutions, and effects on viscosity. *J Pet Sci Eng* 2016;147:211–7. doi:10.1016/j.petrol.2016.06.020.

- [9] Abdul Jameel AG, Han Y, Brignoli O, Telalović S, Elbaz AM, Im HG, et al. Heavy fuel oil pyrolysis and combustion: Kinetics and evolved gases investigated by TGA-FTIR. *J Anal Appl Pyrolysis* 2017;127:183–95. doi:10.1016/j.jaap.2017.08.008.
- [10] Elbaz AM, Khateeb AA, Roberts WL. PM from the combustion of heavy fuel oils. *Energy* 2018;152:455–65. doi:10.1016/j.energy.2018.03.163.
- [11] Khateeb AA, Elbaz AM, Guida P, Roberts WL. Influence of Asphaltene Concentration on the Combustion of a Heavy Fuel Oil Droplet. *Energy & Fuels* 2018;acs.energyfuels.8b03260. doi:10.1021/acs.energyfuels.8b03260.
- [12] Pereira TMC, Vanini G, Oliveira ECS, Cardoso FMR, Fleming FP, Neto AC, et al. An evaluation of the aromaticity of asphaltenes using atmospheric pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry – APPI(±)FT-ICR MS. *Fuel* 2014;118:348–57. doi:10.1016/j.fuel.2013.10.062.
- [13] Shin S, Lee JM, Hwang JW, Jung HW, Nho NS, Lee KB. Physical and rheological properties of deasphalted oil produced from solvent deasphalting. *Chem Eng J* 2014;257:242–7. doi:10.1016/j.cej.2014.07.037.
- [14] Abdul Jameel AG, Alkhateeb A, Telalović S, Elbaz AM, Roberts WL, Sarathy SM. Environmental Challenges and Opportunities in Marine Engine Heavy Fuel Oil Combustion. *Proc. Fourth Int. Conf. Ocean Eng., Springer; 2019, p. 1047–55. doi:10.1007/978-981-13-3119-0_72.*
- [15] Díaz-Boffelli G, Ancheyta J, Muñoz JAD, Centeno G. Experimental Study and Economic Analysis of Heavy Oil Partial Upgrading by Solvent Deasphalting–Hydrotreating. *Energy & Fuels* 2018;32:55–9. doi:10.1021/acs.energyfuels.7b02442.
- [16] Abdul Jameel AG, Elbaz AM, Emwas A-H, Roberts WL, Sarathy SM. Calculation of Average Molecular Parameters, Functional Groups, and a Surrogate Molecule for Heavy Fuel Oils Using ¹H and ¹³C Nuclear Magnetic Resonance Spectroscopy. *Energy & Fuels* 2016;30:3894–905. doi:10.1021/acs.energyfuels.6b00303.
- [17] Papayannakos N. Kinetics of catalytic hydrodesulphurization of a deasphalted oil and of the asphaltenic and non-asphaltenic fractions of a petroleum residue. *Appl Catal* 1986;24:99–107. doi:10.1016/S0166-9834(00)81260-9.
- [18] Farshi A, Shiralizadeh P. Sulfur reduction of heavy fuel oil by oxidative desulfurization (ODS) method. *Pet Coal* 2015;57:295–302.
- [19] Javadli R, de Klerk A. Desulfurization of heavy oil. *Appl Petrochemical Res* 2012;1:3–19. doi:10.1007/s13203-012-0006-6.
- [20] De Filippis P, Scarsella M. Oxidative Desulfurization: Oxidation Reactivity of Sulfur Compounds in Different Organic Matrixes. *Energy & Fuels* 2003;17:1452–5. doi:10.1021/ef0202539.
- [21] Han Y, Zhang Y, Xu C, Hsu CS. Molecular characterization of sulfur-containing compounds in petroleum. *Fuel* 2018;221:144–58. doi:10.1016/j.fuel.2018.02.110.
- [22] Marshall AG, Rodgers RP. Petroleomics: Chemistry of the underworld. *Proc Natl Acad Sci* 2008;105:18090–5. doi:10.1073/pnas.0805069105.
- [23] Silva SL, Silva AMS, Ribeiro JC, Martins FG, Da Silva F a., Silva CM. Chromatographic and

- spectroscopic analysis of heavy crude oil mixtures with emphasis in nuclear magnetic resonance spectroscopy: A review. *Anal Chim Acta* 2011;707:18–37. doi:10.1016/j.aca.2011.09.010.
- [24] Xian F, Hendrickson CL, Marshall AG. High Resolution Mass Spectrometry. *Anal Chem* 2012;84:708–19. doi:10.1021/ac203191t.
- [25] Giraldo-Dávila D, Chacón-Patiño ML, Orrego-Ruiz JA, Blanco-Tirado C, Combariza MY. Improving compositional space accessibility in (+) APPI FT-ICR mass spectrometric analysis of crude oils by extrography and column chromatography fractionation. *Fuel* 2016;185:45–58. doi:10.1016/j.fuel.2016.07.096.
- [26] Hur M, Ware RL, Park J, McKenna AM, Rodgers RP, Nikolau BJ, et al. Statistically Significant Differences in Composition of Petroleum Crude Oils Revealed by Volcano Plots Generated from Ultrahigh Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectra. *Energy & Fuels* 2018;32:1206–12. doi:10.1021/acs.energyfuels.7b03061.
- [27] Cho E, Witt M, Hur M, Jung M-J, Kim S. Application of FT-ICR MS Equipped with Quadrupole Detection for Analysis of Crude Oil. *Anal Chem* 2017;89:12101–7. doi:10.1021/acs.analchem.7b02644.
- [28] Pereira TMC, Vanini G, Tose L V, Cardoso FMR, Fleming FP, Rosa PT V, et al. FT-ICR MS analysis of asphaltenes : Asphaltenes go in , fullerenes come out. *FUEL* 2014;131:49–58. doi:10.1016/j.fuel.2014.04.049.
- [29] Lababidi S, Panda SK, Andersson JT, Schrader W. Direct coupling of normal-phase high-performance liquid chromatography to atmospheric pressure laser ionization fourier transform ion cyclotron resonance mass spectrometry for the characterization of crude oil. *Anal Chem* 2013;85:9478–85. doi:10.1021/ac400670s.
- [30] Catalina D, Lozano P, Orrego-ruiz JA, Cabanzo R, Enrique J, Mejía-ospino E. APPI (+) -FTICR mass spectrometry coupled to partial least squares with genetic algorithm variable selection for prediction of API gravity and CCR of crude oil and vacuum residues. *Fuel* 2017;193:39–44. doi:10.1016/j.fuel.2016.12.029.
- [31] Hourani N, Muller H, Adam FM, Panda SK, Witt M, Al-Hajji AA, et al. Structural Level Characterization of Base Oils Using Advanced Analytical Techniques. *Energy & Fuels* 2015;29:2962–70. doi:10.1021/acs.energyfuels.5b00038.
- [32] Elbaz AM, Gani A, Hourani N, Emwas A-H, Sarathy SM, Roberts WL. TG/DTG, FT-ICR Mass Spectrometry, and NMR Spectroscopy Study of Heavy Fuel Oil. *Energy & Fuels* 2015;29:7825–35. doi:10.1021/acs.energyfuels.5b01739.
- [33] Miyabayashi K, Naito Y, Yamada M, Miyake M, Ushio M, Fuchigami J, et al. Compositional analysis of deasphalted oil before and after hydrocracking over zeolite catalyst by Fourier transform ion cyclotron resonance mass spectrometry. *Fuel Process Technol* 2008;89:397–405. doi:10.1016/j.fuproc.2007.11.009.
- [34] Zhang T, Zhang L, Zhou Y, Wei Q, Chung KH, Zhao S, et al. Transformation of Nitrogen Compounds in Deasphalted Oil Hydrotreating: Characterized by Electrospray Ionization Fourier Transform-Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* 2013;27:2952–9. doi:10.1021/ef400154u.
- [35] Qian K, Fredriksen TR, Mennito AS, Zhang Y, Harper MR, Merchant S, et al. Evidence of naturally-

- occurring vanadyl porphyrins containing multiple S and O atoms. *Fuel* 2019;239:1258–64. doi:10.1016/j.fuel.2018.09.115.
- [36] Chen H, Nelson RK, Swarthout RF, Shigenaka G, de Oliveira AHB, Reddy CM, et al. Detailed Compositional Characterization of the 2014 Bangladesh Furnace Oil Released into the World's Largest Mangrove Forest. *Energy & Fuels* 2018;32:3232–42. doi:10.1021/acs.energyfuels.7b03944.
- [37] Wu Z, Rodgers RP, Marshall AG. ESI FT-ICR mass spectral analysis of coal liquefaction products 2005;84:1790–7. doi:10.1016/j.fuel.2005.03.025.
- [38] Kuti OA, Yang SY, Hourani N, Naser N, Roberts WL, Chung SH, et al. A fundamental investigation into the relationship between lubricant composition and fuel ignition quality. *Fuel* 2015;160:605–13. doi:10.1016/j.fuel.2015.08.026.
- [39] Hartman BE, Hatcher PG. Hydrothermal liquefaction of isolated cuticle of *Agave americana* and *Capsicum annuum* : Chemical characterization of petroleum-like products. *FUEL* 2015;156:225–33. doi:10.1016/j.fuel.2015.04.044.
- [40] Matayeva A, Bianchi D, Chiaberge S, Cavani F, Basile F. Elucidation of reaction pathways of nitrogenous species by hydrothermal liquefaction process of model compounds. *Fuel* 2019;240:169–78. doi:10.1016/j.fuel.2018.11.136.
- [41] Cho Y, Witt M, Kim YH, 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;84:8587–94. doi:10.1021/ac301615m.
- [42] Valencia-dávila JA, Witt M, Blanco-tirado C, Combariza MY. Molecular characterization of naphthenic acids from heavy crude oils using MALDI FT-ICR mass spectrometry. *Fuel* 2018;231:126–33. doi:10.1016/j.fuel.2018.05.061.
- [43] Palani R, AbdulGani A, Balasubramanian N. Treatment of Tannery Effluent Using a Rotating Disc Electrochemical Reactor. *Water Environ Res* 2017;89:77–85. doi:10.2175/106143016X14609975746046.
- [44] Klein GC, Kim S, Rodgers RP, Marshall AG, Yen A, Asomaning S. Mass spectral analysis of asphaltenes. I. Compositional differences between pressure-drop and solvent-drop asphaltenes determined by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy and Fuels* 2006;20:1965–72. doi:10.1021/ef0600199.
- [45] Klein GC, Kim S, Rodgers RP, Marshall AG, Yen A. Mass Spectral Analysis of Asphaltenes. II. Detailed Compositional Comparison of Asphaltenes Deposit to Its Crude Oil Counterpart for Two Geographically Different Crude Oils by ESI FT-ICR MS. *Energy & Fuels* 2006;20:1973–9. doi:10.1021/ef0600208.
- [46] Gaspar A, Zellermann E, Lababidi S, Reece J, Schrader W. Characterization of Saturates, Aromatics, Resins, and Asphaltenes Heavy Crude Oil Fractions by Atmospheric Pressure Laser Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* 2012;26:3481–7. doi:10.1021/ef3001407.
- [47] Abdul Jameel AG, Sarathy SM. Lube Products: Molecular Characterization of Base Oils. *Encycl. Anal. Chem.*, Chichester, UK: John Wiley & Sons, Ltd; 2018, p. 1–14. doi:10.1002/9780470027318.a1824.pub2.

- [48] Abdul Jameel AG, Naser N, Emwas A-H, Dooley S, Sarathy SM. Predicting Fuel Ignition Quality Using ¹H NMR Spectroscopy and Multiple Linear Regression. *Energy & Fuels* 2016;30:9819–35. doi:10.1021/acs.energyfuels.6b01690.
- [49] Abdul Jameel AG, Van Oudenhoven V, Emwas A-H, Sarathy SM. Predicting Octane Number Using Nuclear Magnetic Resonance Spectroscopy and Artificial Neural Networks. *Energy & Fuels* 2018;32:6309–29. doi:10.1021/acs.energyfuels.8b00556.
- [50] Abdul Jameel AG, Naser N, Issayev G, Touitou J, Ghosh MK, Emwas A, et al. A minimalist functional group (MFG) approach for surrogate fuel formulation. *Combust Flame* 2018;192:250–71. doi:10.1016/j.combustflame.2018.01.036.
- [51] Gani A, Jameel A, Naser N, Emwas A, Sarathy SM. Surrogate formulation for diesel and jet fuels using the minimalist functional group (MFG) approach. *Proc Combust Inst* 2019;37:4663–71. doi:10.1016/j.proci.2018.09.035.
- [52] Abdul Jameel AG. A functional group approach for predicting fuel properties. King Abdullah University of Science and Technology, 2019. doi:10.25781/KAUST-ZBB21.
- [53] Abdul Jameel AG, Sarathy SM. Prediction of RON and MON of gasoline-ethanol using ¹H NMR spectroscopy. *Proc. Eur. Combust. Meet.*, 2017.
- [54] Hillier JL, Fletcher TH, Solum MS, Pugmire RJ. Characterization of Macromolecular Structure of Pyrolysis Products from a Colorado Green River Oil Shale. *Ind Eng Chem Res* 2013;52:15522–32. doi:10.1021/ie402070s.
- [55] Fletcher TH, Gillis R, Adams J, Hall T, Mayne CL, Solum MS, et al. Characterization of Macromolecular Structure Elements from a Green River Oil Shale, II. Characterization of Pyrolysis Products by ¹³C NMR, GC/MS, and FTIR. *Energy & Fuels* 2014;28:2959–70. doi:10.1021/ef500095j.
- [56] Marsh H. Flash chromatography, extrography and IH-NMR to characterize coal-derived liquids 1990;15:161–8.
- [57] Hauser A, AlHumaidan F, Al-Rabiah H, Halabi MA. Study on Thermal Cracking of Kuwaiti Heavy Oil (Vacuum Residue) and Its SARA Fractions by NMR Spectroscopy. *Energy & Fuels* 2014;28:4321–32. doi:10.1021/ef401476j.
- [58] Betancourt Cardozo F, Avella Moreno E, Trujillo CA. Structural Characterization of Unfractionated Asphalts by ¹H NMR and ¹³C NMR. *Energy & Fuels* 2016;30:2729–40. doi:10.1021/acs.energyfuels.5b02941.
- [59] Poveda JC, Molina DR. Average molecular parameters of heavy crude oils and their fractions using NMR spectroscopy. *J Pet Sci Eng* 2012;84–85:1–7. doi:10.1016/j.petrol.2012.01.005.
- [60] ASTM D3279-12. Standard Test Method for n-Heptane Insolubles. vol. i. 2016. doi:10.1520/D3279-12.2.
- [61] Koch BP, Dittmar T, Witt M, Kattner G. Fundamentals of Molecular Formula Assignment to Ultrahigh Resolution Mass Data of Natural Organic Matter. *Anal Chem* 2007;79:1758–63. doi:10.1021/ac061949s.
- [62] Bruker Ltd. TopSpin Acquisition Commands & Parameters. 2016.

- [63] Luo P, Gu Y. Effects of asphaltene content on the heavy oil viscosity at different temperatures. *Fuel* 2007;86:1069–78. doi:10.1016/j.fuel.2006.10.017.
- [64] Azinfar B, Haddadnia A, Zirrahi M, Hassanzadeh H, Abedi J. Effect of Asphaltene on Phase Behavior and Thermophysical Properties of Solvent/Bitumen Systems. *J Chem Eng Data* 2017;62:547–57. doi:10.1021/acs.jced.6b00836.
- [65] Muller H, Adam FM, Panda SK, Al-Jawad HH, Al-Hajji AA. Evaluation of Quantitative Sulfur Speciation in Gas Oils by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: Validation by Comprehensive Two-Dimensional Gas Chromatography. *J Am Soc Mass Spectrom* 2012;23:806–15. doi:10.1007/s13361-011-0321-7.
- [66] Bell SE, Ewing RG, Eiceman GA, Karpas Z. Atmospheric pressure chemical ionization of alkanes, alkenes, and cycloalkanes. *J Am Soc Mass Spectrom* 1994;5:177–85. doi:10.1016/1044-0305(94)85031-3.
- [67] Castext H. Analysis of asphaltenes by carbon and proton nuclear magnetic resonance spectroscopy 1978;57:435–41.
- [68] Calemme V, Iwanski P, Nali M, Scotti R, Montanari L. Structural Characterization of Asphaltenes of Different Origins. *Energy & Fuels* 1995;9:225–30. doi:10.1021/ef00050a004.
- [69] Elbaz AM, Gani A, Hourani N, Emwas A-H, Sarathy SM, Roberts WL. TG/DTG, FT-ICR Mass Spectrometry, and NMR Spectroscopy Study of Heavy Fuel Oil. *Energy and Fuels* 2015;29. doi:10.1021/acs.energyfuels.5b01739.
- [70] Rongbao L, Zengmin S, Bailing L. Structural analysis of polycyclic aromatic hydrocarbons derived from petroleum and coal by ¹³C and ¹H-n.m.r. spectroscopy. *Fuel* 1988;67:565–9. doi:10.1016/0016-2361(88)90355-9.
- [71] Cho Y, Kim YH, Kim S. Planar Limit-Assisted Structural Interpretation of Saturates/Aromatics/Resins/Asphaltenes Fractionated Crude Oil Compounds Observed by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Anal Chem* 2011;83:6068–73. doi:10.1021/ac2011685.
- [72] Williams RB. Symposium on Composition of Petroleum Oils , Determination and Evaluation. *ASTM Spec Tech Publ* 224 1957:168–94.
- [73] Kapur GS, Ecker A, Meusinger R. Establishing Quantitative Structure–Property Relationships (QSPR) of Diesel Samples by Proton-NMR & Multiple Linear Regression (MLR) Analysis. *Energy & Fuels* 2001;15:943–8. doi:10.1021/ef010021u.
- [74] López D, Acelas N, Mondragón F. Average structural analysis of tar obtained from pyrolysis of wood. *Bioresour Technol* 2010;101:2458–65. doi:10.1016/j.biortech.2009.11.036.
- [75] Díaz C, Blanco CG. NMR: A Powerful Tool in the Characterization of Coal Tar Pitch. *Energy & Fuels* 2003;17:907–13. doi:10.1021/ef020114r.
- [76] Wooton DL, Coleman WM, Taylor LT, Dorn HC. Characterization of organic fractions in solvent-refined coal by quantitative n.m.r. spectroscopy. *Fuel* 1978;57:17–21. doi:10.1016/0016-2361(78)90084-4.
- [77] Verstraete JJ, Schnongs P, Dulot H, Hudebine D, Carlo M. Molecular reconstruction of heavy

- petroleum residue fractions. Chem Eng Sci 2010;65:304–12. doi:10.1016/j.ces.2009.08.033.
- [78] Ren Y, Liao Z, Sun J, Jiang B, Wang J, Yang Y, et al. Molecular reconstruction : Recent progress toward composition modeling of petroleum fractions. Chem Eng J 2019;357:761–75. doi:10.1016/j.cej.2018.09.083.
- [79] Chemical Real- Time Predictor for Extensive Chemical Properties n.d. <http://www.chemrtp.com/> (accessed April 22, 2018).

Table 1

Physical and chemical properties of HFO and DAO

Properties	Method	Units	HFO	DAO
Physical				
density (at 288 K)	ASTM D4052-11	kg/m ³	970.5	930.4
specific gravity (at 288 K)	ASTM D4052-11	-----	0.971	0.931
kinematic viscosity (at 313 K)	ASTM D445-12	10 ⁻⁶ m ² /s	617.7	113.1
Compositional				
carbon	EPA 440.0	mass%	85.0	84.5
hydrogen	EPA 440.0	mass%	10.8	11.3
sulfur	ASTM D4294-10	mass%	3.3	3.1
nitrogen	EPA 440.0	mass%	0.24	0.26
oxygen	EPA 440.0	mass%	0.03	0.05
asphaltenes content	IP 143	mass%	8.2	0*
vanadium	IP 501-05	mg/kg	18.0	9.8
nickel	IP 501-05	mg/kg	11.0	2.0
sodium	IP 501-05	mg/kg	33.4	23.6
zinc	IP 501-05	mg/kg	<1.0	<1.0
lead	IP 501-05M	mg/kg	<1.0	<1.0
potassium	IP 501-05M	mg/kg	<1.0	<1.0
Heating Values				
higher heating value	ASTM D4868	MJ/kg	42.5	43.4
lower heating value	ASTM D4868	MJ/kg	40.2	41.1

* when using n-heptane as solvent

Table 2¹H NMR chemical shift assignments

Symbol	H type	Chemical shift (ppm)	HFO (mol %)	DAO (mol %)
H_{Ar}^{pa}	polyaromatic H	7.20 – 8.99	4.9	3.2
H_{Ar}^{ma}	monoaromatic H	6.20 – 7.20	2.8	1.5
H_{ole}	olefinic CH and CH ₂ groups	4.50 – 6.42	0.3	0.3
H_{CH}^{α}	CH group α to aromatic ring	2.88 – 3.40	2.0	1.8
$H_{CH_2}^{\alpha}$	CH ₂ group α to aromatic ring	2.64 – 2.88	8.8	6.2
$H_{CH_3}^{\alpha}$	CH ₃ group α to aromatic ring	2.04 – 2.64	2.3	2.1
H_{Naph}	naphthenic CH and CH ₂ groups	1.57 – 1.96	11.8	9.8
H_{Par-CH}	paraffinic CH groups	1.39 – 1.57	1.6	1.7
H_{Par-CH_2}	paraffinic CH ₂ groups	0.94 – 1.39	46.1	50.1
H_{Par-CH_3}	paraffinic CH ₃ groups	0.25 – 0.94	19.4	23.3

Table 3¹³C NMR chemical shift assignments

Symbol	C type	Chemical shift (ppm)	HFO (mol %)	DAO (mol %)
C_{Ar}	aromatic quaternary C	140.5 – 160.0	17.0	15.1
$C_{Ar}^{\alpha-S}$	aromatic quaternary C α to S atom	137.0 – 140.5	1.5	1.3
$C_{Ar}^{\alpha-CH_3}$	aromatic C α to position CH ₃ group	131.7 – 137.0	2.5	2.6
C_{Ar}^{AA}	aromatic carbons bridging 2 aromatic rings together	129.2 – 131.7	6.3	5.3
$C_{Ar-H} + C_{Ar}^{AAA} + C_{ole}$	aromatic protonated C; aromatic C bridging 3 rings; and olefinic CH and CH ₂	85.0 – 129.2		
C_{Ar}^{AAA}	aromatic C bridging 3 rings		1.5	0.8
C_{Ar-H}	aromatic protonated C		8.8	7.5
C_{ole}	olefinic CH and CH ₂		0.3	0.3
C_{Par-C}	paraffinic quaternary C	50.0 – 60.0	0.9	1.1
C_{Naph}	naphthenic CH and CH ₂	40.5 – 50.0	7	5.6
C_{Par-CH}	paraffinic CH	35.0 – 40.5	3	3.2
C_{Par-CH_2}	paraffinic CH ₂	21.5 – 35.0	39.1	43.3
$C_{Par-CH_3}^{\alpha-Ar}$	paraffinic CH ₃ α to aromatic ring	18.5 – 21.5	3.0	2.8
C_{Par-CH_3}	paraffinic CH ₃	3.0 – 18.5	9.1	11.1

Table 4

Derived AMPs

Parameter	Description	HFO (no unit)	DAO (no unit)
aromaticity factor (f_a)	ratio of number of aromatic C atoms to total number of C atoms in the sample	0.38	0.33
$(C/H)_{par}$	ratio of number of C atoms to H atoms in the paraffinic content of the sample	0.50	0.48
$(C/H)_{Ar}$	ratio of number of C atoms to H atoms in the aromatic content of the sample	3.3	4.3
(C/H)	ratio of number of C atoms to H atoms in the sample	0.66	0.62
average paraffinic chain length ($\overline{n}$)	average number of C atoms in paraffinic chains connected with aromatic rings	4.2	4.5
naphthenic ring number (R_N)	total number of naphthenic rings in an average molecule	0.9	0.75
aromatic ring number (R_A)	total number of aromatic rings in an average molecule	3.2	2.9
total ring number (R_T)	total number of rings in an average molecule	4.1	3.65
aromatic condensation index (φ)	ratio of total number of aromatic C in poly-condensed structures to number of aromatic C atoms	0.08	0.06
aromatic condensation degree (Ω)	ratio of number of peri-condensed aromatic C atoms to number of cata-condensed C atoms	0.23	0.15

Table 5

Predicted properties of the surrogate molecules of HFO and DAO using QSPR

Property	unit	HFO		DAO	
		Predicted	Measured	Predicted	Measured
density (@ 288 K)	kg/m ³	990.1	970.5	961.2	930.4
specific gravity (@ 288 K)	-	0.956	0.971	0.959	0.931
kinematic viscosity (@ 313 K)	cSt	548.4	617.7	181.2	113.1
critical pressure	atm	15.8	-	16.1	-
critical temperature	K	1077	-	915	-
critical volume	m ³ /mol	0.020	-	0.019	-
normal boiling point	K	878	-	838	-
melting point	K	331	-	303	-
refractive index	-	1.65	-	1.54	-
absolute entropy (@ 298 K and 1 bar)	J/mol/K	823.6	-	744.2	-
enthalpy of formation (@ 298 K and 1 bar)	kJ/mol	501.8	-	288.2	-
enthalpy of combustion (@ 298 K)	MJ/mol	25.1	23.8	24.3	23.1
heat of vaporization (@ 298 K)	kJ/mol	200	-	193.1	-

Table 6

Comparison of the methods

Parameter	Elemental analysis		APPI FT-ICR/MS		AMPs		Surrogate molecule	
	HFO	DAO	HFO	DAO	HFO	DAO	HFO	DAO
(C/H)	0.65	0.62	0.73	0.70	0.66	0.62	0.69	0.65
$(C/H)_{par}$	-	-	-	-	0.49	0.47	0.45	0.46
$(C/H)_{Ar}$	-	-	-	-	3.3	4.3	3.2	4
Paraffinic C/Total C	-	-	-	-	0.55	0.61	0.55	0.61
Naphthenic C/Total C	-	-	-	-	0.07	0.06	0.1	0.1
Aromatic C/Total C	-	-	-	-	0.38	0.33	0.4	0.32
Average chain length ($\bar{n}$)	-	-	-	-	4.2	4.5	3.8	4.2
R_N	-	-	-	-	0.9	0.75	1	1
R_A	-	-	-	-	3.2	2.9	3	2
R_T	-	-	-	-	4.1	3.65	4	4
DBE			13.8	13.0	11.5	10.3	11	10
Carbon number			41.5	39.4	40	37.4	40	38

Figure 1. ^1H NMR spectra of a) HFO and b) DAO

Figure 2. ^{13}C NMR spectra of a) HFO and b) DAO. * represents solvent signal.

Figure 3. APPI (+) FT-ICR mass spectra of a) HFO and b) DAO

Figure 4. Distribution of various molecular classes found in HFO and DAO determined from APPI (+) FT-ICR mass spectra

Figure 5. Relative abundance of HC class species expressed as a function of DBE vs carbon number in a) HFO and b) DAO

Figure 6. Relative abundance of S₁ class species expressed as a function of DBE vs carbon number in a) HFO and b) DAO

Figure 7. Relative abundance of S_2 class species expressed as a function of DBE vs carbon number in a) HFO and b) DAO

Figure 8. Relative abundance of N class species expressed as a function of DBE vs carbon number in a) HFO and b) DAO

Figure 9. Distribution of various AMPs expressed as number of atoms per average molecule in HFO and DAO obtained from a) ^1H NMR and b) ^{13}C NMR

Figure 10. Surrogate molecule of HFO and DAO

Supplementary material

Figure S1. Overview of the solvent deasphalting of HFO