

Calculation of average molecular parameters, functional groups, and a surrogate molecule for heavy fuel oils using ^1H and ^{13}C NMR spectroscopy

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26 **Abstract:**
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30 Heavy fuel oil (HFO) is primarily used as fuel in marine engines and in boilers to generate
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32 electricity. Nuclear Magnetic Resonance (NMR) is a powerful analytical tool for structure
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34 elucidation and in this study, ^1H NMR and ^{13}C NMR spectroscopy were used for the structural
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36 characterization of 2 HFO samples. The NMR data was combined with elemental analysis and
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38 average molecular weight to quantify average molecular parameters (AMPs), such as the
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40 number of paraffinic carbons, naphthenic carbons, aromatic hydrogens, olefinic hydrogens, etc.
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42 in the HFO samples. Recent formulae published in the literature were used for calculating
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44 various derived AMPs like aromaticity factor (f_a), C/H ratio, average paraffinic chain length (\bar{n}),
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46 naphthenic ring number (R_N), aromatic ring number (R_A), total ring number (R_T), aromatic
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48 condensation index (φ) and aromatic condensation degree (Ω). These derived AMPs help in
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50 understanding the overall structure of the fuel. A total of 19 functional groups were defined to
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52 represent the HFO samples, and their respective concentrations were calculated by formulating
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3 balance equations that equate the concentration of the functional groups with the
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5 concentration of the AMPs. Heteroatoms like sulfur, nitrogen, and oxygen were also included in
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7 the functional groups. Surrogate molecules were finally constructed to represent the average
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9 structure of the molecules present in the HFO samples. This surrogate molecule can be used for
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11 property estimation of the HFO samples and also serve as a surrogate to represent the
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13 molecular structure for use in kinetic studies.
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19 **1. Introduction**

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22 HFOs have been largely used as fuel in the marine industry since the 1960's. Although
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24 they are viscous and dirty, HFOs have found use in the marine industry and also in power
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26 generation sectors primarily because they are inexpensive. Approximately 240 Mt of HFO is
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28 used by the shipping industry every year¹. High sulfur content (nearly 4.5 % by weight) in HFO²
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30 translates into sulfur dioxide emissions that are primarily due to the sulfur content in the fuel.
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32 HFO combustion also results in release of particulate matter like smoke, cenospheres and ash³.
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34 Due to their harmful effects on the environment and on human health, the international
35
36 Maritime Organization (IMO) has mandated, starting from 2015, that marine fuels should
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38 contain less than 0.1% of sulfur on ships sailing in the North Sea, English Channel and the
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40 Baltics⁴. This has resulted in a worldwide demand of 40 Mt/y of low sulfur fuels. By 2020, there
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42 are plans to extend this regulation to the rest of the world. In 2011, the IMO placed a complete
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44 ban on the use of HFO on ships sailing in the Antarctic waters to preserve the ecosystem from
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46 harm⁵. This means that if HFOs are to be used in the future, then they need to become
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48 "cleaner", or it could mean the end of their use in the marine industry. Therefore, significant
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50 research is required on HFO combustion to reduce its environmental impact. With this ultimate
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3 goal in mind, and as a first step, we find ourselves in need of characterizing HFOs to understand
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5 their molecular structure. The information can subsequently be used to correlate combustion
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7 characteristics and emissions with fuel molecular structure, such that better combustors could
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9 be designed.
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14 Structural characterization of hydrocarbon fractions obtained during the distillation of
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16 crude oils is an important aspect of the refinement process. The combustion chemistry of fuels
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18 is dependent on their structural composition and therefore their chemical characterization is an
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20 important step in understanding the combustion phenomena and also necessary for predictive
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22 studies⁶⁻⁷. HFOs are residues of petroleum refineries that have high molecular weights, high
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24 sulfur and asphaltene content and are highly viscous. Lighter distillates are sometimes added to
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26 reduce the overall viscosity to enable their use as fuel. HFOs are a mixture of thousands of
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28 hydrocarbon molecules with the presence of hetero-atoms like sulfur, nitrogen, oxygen etc.
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30 Identifying all of the individual molecules is neither feasible nor is it useful. Conventional
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32 techniques such as gas chromatography coupled with mass spectroscopy (GC-MS), a widely
33
34 used characterization technique, cannot provide enough information to characterize the
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36 structure of complex hydrocarbon mixtures like HFO⁸. The application of these methods to
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38 characterize HFOs are limited because the molecules present in HFOs have a wide distribution
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40 of chemical classes and prohibitively high molecular weights. Therefore efforts need to be
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42 made to characterize such fuels by other methods.
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52 A suitable technique for studying such complex mixtures is nuclear magnetic resonance
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54 (NMR) spectroscopy, which is a powerful tool that makes use of the magnetic properties of
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56 nuclei. The benefits of NMR methods are that they are accurate, highly predictable, and
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3 require short measurement time. Moreover solution NMR spectra are usually well resolved and
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5 can be used for both identification and quantification of compounds within simple mixture
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7 samples. The different functional groups that appear in HFOs can be easily distinguished using
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9 NMR. Similar functional groups with different neighboring nuclei also give distinct signals that
10
11 helps in their identification. This places NMR spectroscopy as one of the ideal methods to
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13 characterize complex fuels like HFOs. In a recent review⁹, the state of the art techniques to
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15 characterize heavy crude fractions like high performance liquid chromatography (HPLC), thin
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17 layer chromatography, Raman spectroscopy, Infrared spectroscopy (IR) and mass spectrometry
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19 were reviewed, and NMR spectroscopy was identified as the technique of choice.
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27 The purpose of this study is the structural characterization of a complex fuel, namely
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29 HFO, as such information is important for studying the combustion and pyrolysis of HFOs. NMR
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31 data by itself, or in combination with other experimental data, can be processed to derive
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33 useful information that can help us characterize the structure of complex mixtures. Three basic
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35 methods have been developed for this purpose, namely the method of average molecular
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37 parameters (AMPs), functional group analysis and surrogate molecule representation¹⁰. In the
38
39 present work, ¹H NMR and ¹³C NMR experiments were performed and the above methods were
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41 extended to study the detailed structural characterization of 2 samples of Saudi Arabian HFOs.
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43 The samples were collected from two different electrical power plants. These will be
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45 henceforth referred to as HFO A and HFO B. The three methods stated above are used to study
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47 the structural distribution and help formulate surrogate molecules that can represent the
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49 structure of HFO.
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56 57 **2. Experimental Methods** 58 59 60

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3 Deuterated chloroform CDCl_3 was used as a solvent to dissolve 50 μl of HFO in 1 ml of
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5 the solvent. From the mixture 0.6 ml was transferred into 5 mm NMR tubes. A 700 MHz Bruker
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7 AVANCE III spectrometer was used to obtain the spectra at 298 K. The spectrometer was
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9 equipped with a Bruker CP TCI multinuclear CryoProbe (from Brukerbiospin, Rheinstetten,
10
11 Germany). To record the ^1H NMR spectra, 128 scans were collected with a recycle delay time of
12
13 5 seconds. A standard 1D 90° pulse sequence was used with standard zg program from the
14
15 Bruker pulse library. Tetramethylsilane (TMS) was used as the internal chemical shift reference.
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17 A spectral width of 14098 Hz was digitized into 64 K data points to collect the free induction
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19 decay (FID). To record the ^{13}C NMR spectra a 1D sequence was used with power gate
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21 decoupling along with a 30° flip angle . The standard 1D 90° pulse sequence zsig30 program
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23 from the Bruker pulse library was used. A spectral width of 41666.67 Hz was digitized into 64 K
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25 complex data points. Every single spectrum was recorded with a 7 second recycle delay by
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27 collecting 12 k transients. Fourier transformation was applied after applying a line broadening
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29 of 1Hz. The Bruker Topspin 2.1 software was used to process the experimental data. The ^1H
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31 NMR and ^{13}C NMR spectra of HFO A and HFO B are shown in Fig. 1. The spectra used for the
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33 analysis were phase and baseline corrected. Each spectra was processed 5 times and the
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35 average values were used in the calculation.
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49 **3. Calculation Methods**

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52 The NMR spectra are represented in terms of chemical shift's i.e. the resonant
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54 frequency of the nuclei relative to the magnetic field. Different nuclei exhibit different shifts
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56 and the number and position of these shifts are often diagnostic of the molecular structure. ^1H
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3 NMR spectra has a chemical shift range of -4 to +14 parts per million (ppm) and the range
4 typically used is 0 - 12 ppm. ^{13}C NMR has a much larger range (0 - 220 ppm). Tetramethylsilane
5
6 is usually used as the internal standard¹¹ whose chemical shift is 0.0 ppm for both ^1H and ^{13}C
7
8 NMR spectra. Specific regions within the spectra correspond to a particular group of nuclei. For
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10 example hydrogen in aromatic rings usually have shifts in the range of 6 -9 ppm and carbons
11
12 have a shift between 120 – 160 ppm. The intensity of the peaks is proportionate to the number
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14 of nuclei as is in the case of ^1H nuclei. Integrating the peaks between a specific range helps to
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16 quantify the particular nuclei in the mixture. Therefore NMR is ideally suited to study the HFOs
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18 which have a wide distribution of chemical classes.
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25 26 27 3.1. Average molecular parameters (AMPs) 28 29

30 The approach to characterize complex petroleum fractions by the method of AMPs was
31 first developed by Williams¹² and Brown and Ladner¹³ to quantitatively characterize the
32 structure of petroleum fuel fractions. Using this method, the relative amount of various
33 structural fragments such as number of aromatic carbons, olefinic carbons, aromatic
34 hydrogens, naphthenic hydrogens etc. in the fuel can be determined. This method does not
35 reveal the exact structure of the different molecules in the sample or how structural fragments
36 are distributed within the different molecules. However, in such complex samples, there are an
37 enormous number of similar molecules that vary only slightly, so it is more rational to
38 characterize the individual fragments rather than entire molecules. This method makes use of
39 elemental analysis and average molecular weight of the sample along with the data from NMR.
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41 The AMPs of a fuel can also be used for property estimation studies of the mixture. For
42 example, the AMPs can be used in correlations as variables for equation of state parameters¹⁴.
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3.1.1. Definition of AMP

In general an AMP can be described as per the following equation,

$$X_i = \frac{I_i}{I_{total}} \cdot \%X \quad (1)$$

where, X refers to either C or H atom, I refers to ^1H NMR or ^{13}C NMR integral and the index i refers to a particular chemical shift region in the NMR spectra. $\%X$ stands for the weight percent of X from the elemental analysis.

3.1.2. Average molecular formula

The average molecular formula of HFO can be calculated in the form of $\text{C}_c\text{H}_h\text{O}_o\text{N}_n\text{S}_s$, where the subscripts c , h , o , n and s represent the average number of atoms of carbon, hydrogen, oxygen, nitrogen and sulfur respectively in a hypothetical surrogate molecule. For example c , the average number of carbon atoms can be calculated from the following equation,

$$c = MW_{avg} \cdot \%C \cdot \frac{1}{100} \cdot \frac{1}{a_C} \quad (2)$$

where, MW_{avg} is the average molecular weight of HFO, which was measured as 750 g/mol from FT-ICR mass spectrometry experiments¹⁵. $\%C$ is the weight percent of carbon measured from the elemental analysis and a_C is the atomic mass of carbon in g/mol. Eqn (2) can be applied similarly for other atoms. The elemental analysis of HFO A and HFO B are reported in Table 1. The average molecular formula of HFO A and HFO B were calculated as $\text{C}_{53.12}\text{H}_{81.68}\text{O}_{0.01}\text{N}_{0.21}\text{S}_{0.77}$ and $\text{C}_{52.72}\text{H}_{79.88}\text{O}_{1.08}\text{N}_{0.17}\text{S}_{0.54}$, respectively.

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4 This method of characterizing fuels by AMPs has been carried out for lignin pyrolysis
5 oils¹⁶, vacuum residues¹⁷, tar from wood pyrolysis¹⁸, oil sands¹⁹ and asphaltenes²⁰. Table 2 and
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8 Table 3 lists the AMPs that were calculated from ¹H NMR and ¹³C NMR respectively. The
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11 chemical shift assignments and the nomenclature used for denoting the symbols were taken
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14 from Poveda and Molina²¹.
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16 17 3.1.3. Derived AMPs 18

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20 In addition to the AMPs calculated from the basic integrals, a number of derived AMPs
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22 can be calculated i.e the AMPs are re-arranged to give derived AMPs that have no dimensional
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24 unit. These derived AMPs give valuable additional information about the overall structure of
25
26 the sample. The method by Williams¹² and Brown and Ladner¹³ employed ¹H NMR to determine
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28 the AMPs and derived AMPs. Clutter et al.²² combined the data from ¹H NMR with ¹³C NMR
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30 data to determine the same derived AMPs but used ¹³C NMR data wherever possible. This gives
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32 better accuracy compared to when ¹H NMR data alone is used. Many derived AMPs have been
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34 reported in early literature, which are derived by using hypothetical models and usually present
35
36 a simple method of calculation. Recently, more precise and complex models have been
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38 developed²¹ to characterize heavy petroleum fractions, and use of these latest models has been
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40 made in the present work to study the structure of HFOs. Derived AMPs such as aromaticity
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42 factor (f_a), (C/H) ratio, average chain length (\bar{n}), naphthenic ring number (R_N), aromatic ring
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44 number (R_A), aromatic condensation index (φ) and aromatic condensation degree (Ω) have
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46 been calculated in the present work. The formulae used to calculate the above derived AMPs
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48 were taken from Poveda and Molina²¹ and are shown in Table 4.
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3 Aromaticity factor (f_a) was the first derived AMP reported in the literature to denote
4 the aromatic content in the sample. It is usually defined as the ratio of aromatic carbons to the
5 total carbons in the sample. Different formulae have been proposed in the literature to
6 calculate (f_a) by Williams¹², Brown and Ladner¹³ and Lee and Glavincevski²³. A drawback when
7 these formulae are applied to HFOs is that they do not account for the significant quantities of
8 heteroatoms like sulfur, nitrogen and oxygen present in HFOs. This is overcome by the formula
9 used in the present work where a correction is proposed to account for the heteroatoms. The
10 fraction of the heteroatoms that are aromatic are calculated and used in the formula²¹.
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24 (C/H) ratio (or (H/C) ratio) is another important derived AMP which is the ratio of
25 number of carbon to hydrogen atoms in the fuel. The amount of energy released when burning
26 a fuel is related to (C/H) ratio of the fuel i.e. lower the (C/H) ratio more is the energy released
27 during combustion. NMR data can be used to calculate the (C/H) ratio of a fuel. The ASTM D-
28 5291²⁴ technique which is used to calculate the (C/H) ratio cannot be employed for low boiling
29 samples. In these cases, NMR presents as a useful alternative method to calculate the (C/H)
30 ratio. (C/H)_{par} and (C/H)_{Ar} represent the carbon to hydrogen ratio in paraffinic and
31 aromatic content of the fuel respectively and these can also be calculated.
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45 The term average paraffinic chain length (\bar{n}), or the number of carbons in a paraffinic
46 group, was coined by Williams¹². It was calculated by using ¹H NMR data alone without taking
47 into account the carbon structure. Here (\bar{n}) is calculated in 3 ways, (i) the ratio between the
48 total number of paraffinic carbons to the number of paraffinic carbons appearing in terminal
49 methyl groups (\bar{n}_1); (ii) the ratio between the total number of paraffinic carbons to the number
50 of paraffinic carbons appearing in the beginning of the chain (\bar{n}_2); and (iii) by assuming that the
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3 paraffinic chains are connected with aromatic rings ($\overline{n_3}$). This formula²¹ can be derived from
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6 the general formula for paraffins namely, C_nH_{2n+2} . We get
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$$9 \quad (C/H)_{par} = \frac{\overline{n_3}}{2 \overline{n_3} + 2} \quad (3)$$

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12 Since the paraffinic chain is assumed to be connected to an aromatic ring, the formula for
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14 paraffins becomes C_nH_{2n+1} . Eqn (3) can be re-written as
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$$17 \quad (C/H)_{par} = \frac{\overline{n_3}}{2 \overline{n_3} + 1} \quad (4)$$

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19 Eqn (4) can be used to calculate ($\overline{n_3}$).
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23 The naphthenic ring number (R_N) has been calculated by a number of equations developed by
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25 Knight²⁵, Qian et al.²⁶ and Rongbao et al.²⁷. These equations require the knowledge of too many
26
27 variables and become difficult to be used. The following equation gives the relation proposed
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29 by Williams¹²
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$$33 \quad R_N = \frac{C_{Nap}}{3.5} \quad (5)$$

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35 where C_{Nap} is the number of naphthenic carbons in an average molecule. Assuming that the
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37 unsaturated molecules are of benzonaphthenic type, Poveda and Molina²¹ changed the factor
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39 3.5 in eqn (5) to 4 as the number of carbons required for a benzonaphthenic ring structure to
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41 be formed from an aromatic ring is 4. Also an additional naphthenic ring would require 4
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43 carbon atoms. The aromatic ring number (R_A) has been calculated in a number of ways. In the
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45 present work it is calculated by using the following equation,
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$$53 \quad R_A = \frac{C_{Ar} - C_{Ar}^P}{2} + 1 \quad (6)$$

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3 Where C_{Ar} refers to the number of aromatic carbons and C_{Ar}^P to the number of
4 peripheral aromatic carbons in an average molecule. The total ring number R_T is the sum of
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6 naphthenic and aromatic ring numbers.
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11 The aromatic condensation index (ϕ) helps to establish the relationship between the
12 total number of aromatic carbons and those aromatic carbons that form poly-condensed
13 structures. A value of 0 denotes the absence of a condensation center and high values of 0.7
14 point to structures that are highly condensed. Aromatic condensation degree (Ω) was defined
15 by Poveda and Molina²¹ and it is the ratio number of peri-condensed aromatic carbons to the
16 number of cata-condensed aromatic carbons.
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27 3.2. Functional group analysis

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29 The method of characterizing a fuel by the method of functional groups was first
30 introduced by Allen et al.²⁸ to study coal derived liquids. The molecules in hydrocarbon
31 mixtures are made up of a limited number of functional groups and it is these functional groups
32 that mostly determine the chemical properties of the fuel. Quantification of these functional
33 groups provides a useful characterization technique and also allows for comparison between
34 fuels. The functional groups are calculated by combining the data from elemental analysis and
35 NMR spectroscopy after converting them into units of concentration (mol/100g). Another
36 advantage of this method is that, by using these functional group concentrations, we can
37 calculate physical properties like heat of formation, heat capacities²⁹, critical properties and
38 thermodynamic properties.
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3 The first step involved in this procedure is to propose a set of functional groups that can
4 ideally represent the structures in the fuel. Choosing the appropriate functional groups is
5 subjective and the choice is based on experience or experimental data from experiments like
6 Infra-red (IR) and Mass spectrometry (MS). The proposed set must be large enough to make use
7 of the experimental data (elemental and NMR), and at the same time small enough that
8 meaningful concentrations are determined using the available data.
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19 The next step in the procedure is to relate the concentration of the unknown functional
20 groups to sum of the concentrations of the atomic species it is made up of. For example, the
21 concentration of benzene is calculated by summing the concentration of aromatic hydrogens
22 and protonated aromatic carbons and dividing it by 6. This is done by forming a set of balance
23 equations as per eqn (7)
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$$\sum_{j=1}^n A_{ij}y_j = b_i \quad (i = 1, \dots, m) \quad (7)$$

32 where, y_j ($j = 1, \dots, n$) are the unknown functional group concentrations. b_i ($i = 1, \dots, m$) are
33 the atomic species concentration (determined from nmr). A_{ij} , represent the stoichiometric
34 coefficients.
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43 Along with eqn (7), we use the condition from eqn (8) i.e. concentrations of the functional
44 groups cannot be negative
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$$y_j \geq 0 \quad (8)$$

49 For the problem presented by eqns (7) and (8), two solutions are possible. In the first
50 case, the number of balance equations given by eqn (7) are greater than the unknown
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functional group concentrations. Here the equations are over-estimated and the concentrations of the unknown functional groups are estimated using the method of least squares. In the second case, when the number of equations are lesser than the number of unknown functional groups, there can be either no solution or an infinite number of solutions. If there is no solution, then the set of functional groups chosen has to be revised to better describe the available experimental data. If space for a solution exists, a single solution can be selected from the feasible range. The unknown functional group concentrations (y_1, \dots, y_n) in such a case are chosen such that a function $P(y_1, \dots, y_n)$ is minimized, as per the following equation.

$$P = \sum_{i=1}^m \sum_{j=1}^n \left(\frac{b_i}{A_{ij}N_i} - y_j \right)^2 \quad (9)$$

where, N_i is the number of unknown functional groups species i . Eqn (9) is built on the assumption that the probability of distribution of the atoms is same for all the functional groups. Concentrations of the unknown functional groups can then be found by collectively using eqns (7), (8) and (9). Alternately when qualitative data from experiments like high resolution mass spectra is available, the function P to be minimized can also be represented by the following equation,

$$P = \sum_{i=1}^n (y_i - f_i)^2 \quad (10)$$

where, f_i is the concentration of the functional group i , predicted from high resolution mass spectra. This is calculated by assigning a structure to every peak in the mass spectrum. The structures are composed of the pre-defined functional groups. The concentrations of the

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3 functional groups are calculated by adding the contributions from all the peaks. Now the eqns
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6 (7), (8) and (10) are used to calculate the functional group concentrations.
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9 4. Results & Discussion

10 4.1. AMPs

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15 Using eqn (1) the AMPs are calculated directly with unit as weight percentage and by
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17 combining with the result from eqn (2), they are calculated as the number of atoms per average
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19 molecule. The AMPs for the HFOs calculated from ^1H NMR and ^{13}C NMR are reported in Table 2
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21 and 3 respectively. HFO A has 53.12 carbon and 81.68 hydrogen atoms in its average molecule
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23 while HFO B has 52.72 carbon and 78.88 hydrogen atoms along with other heteroatoms.
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25 Functionalities like aldehydes, carboxylic acids and olefins were found to be negligible
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27 compared to the paraffinic and aromatic content in both the samples. Most of the carbon and
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29 hydrogens in the HFOs were found to appear as paraffinic CH_2 groups, some as paraffinic CH_3
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31 groups and naphthenic CH_2 groups. HFO B has a higher naphthenic content compared to that
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33 seen in HFO A. Other AMPs were found to be more or less similar for both the HFOs.
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41 The values of the derived AMPs calculated are reported in Table 4. HFO B was found to
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43 be slightly more aromatic ($f_a = 0.37$) compared to HFO A ($f_a = 0.33$). The high (C/H) values
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45 of 0.65 and 0.66 for HFO A and HFO B indicate the presence of high aromatic content and the
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47 high $(C/H)_{Ar}$ values of around 4 indicate that 4 out of 6 aromatic carbons are non-protonated.
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49 This means that the aromatic rings could be condensed or have multiple side chains connected
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51 to them. The average chain length calculated from the 3 methods was found to vary between 2
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60 to 6. This could indicate the possibility of multiple short chains connected to aromatic rings

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3 rather than longer and fewer chains. These derived AMPs help to give an overall understanding
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5 of the structure of the HFOs. The naphthenic ring number (R_N) of 1.58 for HFO B was higher
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7 than 1.01 for HFO A. This was expected since the sample B had a higher naphthenic content.
8
9 Low values of the aromatic condensation index (φ) for both samples shows that the surrogate
10
11 HFO molecule is only slightly condensed. Also low values (< 0.15) of the aromatic condensation
12
13 degree (Ω) indicates that the condensation type is cata-condensation.
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18 19 4.2. Functional group analysis 20 21

22 The functional groups chosen to represent the HFOs are shown in Fig. 2. The set
23
24 accounts for the major structural features of HFOs namely, aromatics (single and condensed),
25
26 naphthenes, paraffinic chains, alcohols, ketones, aldehydes, carboxylic acid and hetero-atoms
27
28 (S, N, O). Particular attention was given to characterize the presence of sulfur and so functional
29
30 groups that contain sulfur were used. Sulfur was assumed to be present in the HFOs in
31
32 structures like mercaptans (thiophenol), benzo and dibenzothiophenes³⁰. In the present case, a
33
34 total of 19 functional groups have been specified ($n = 19$) and 26 atomic species were used
35
36 ($m = 26$). The values of the concentrations of the atomic species and the stoichiometric
37
38 coefficients (A_{ij}) are reported in Table 5. The values of the functional group concentrations
39
40 were calculated by the method of least squares using eqns (7) and (8). The concentrations of
41
42 the functional groups are reported in Table 6. The functional groups calculated represent 93%
43
44 and 94% of the mass of HFO A and HFO B respectively.
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52 53 4.3. Surrogate molecule representation 54 55 56 57 58 59 60

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4 The idea behind the surrogate molecule representation is to generate a molecule which
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6 has functionalities distributed in a manner similar to that of the real fuel. This surrogate
7
8 molecule also possesses the average molecular weight of the fuel. This method helps obtain a
9
10 clear picture about the types of structures that can be found in the mixture. Another advantage
11
12 of this method is that property estimation of the mixture can be carried out from the surrogate
13
14 molecule using group additivity³¹. This is done by assuming that the properties of the mixture is
15
16 same as the properties of the surrogate molecule. A disadvantage of this method is that only
17
18 integer number of atoms can be used in the surrogate structure. For example when the average
19
20 molecular formula yields, say 0.33 moles of sulfur per molecule, then it becomes impossible to
21
22 generate the surrogate molecule without over-representing it. In such a case, 3 molecules can
23
24 be used to represent the fuel where one molecule alone contains the sulfur atom. This problem
25
26 becomes severe for other hetero-atoms when their percentage is low. For example, HFO A
27
28 contains 0.01 moles of oxygen per surrogate molecule. In this case 100 molecules would be
29
30 needed to represent the fuel, one of which carries an oxygen atom. In such cases when the
31
32 percentage of an atom is low it can be neglected, but the impact of such an approximation on
33
34 property estimation is unknown. When there is high impact, then property estimation can be
35
36 done through the functional groups approach. A non-integer or low value of the concentration
37
38 of a functional group will not make a difference. Another disadvantage of this method is the
39
40 inability to arrive at a surrogate molecule when the molecular weight of the mixture is too low.
41
42 For example, when a fuel with an average molecular weight (e.g, 100) contains distribution of
43
44 groups like paraffin's, naphthenes, olefins, aromatics etc., then it becomes impossible to
45
46 represent all the groups in a single molecule as the surrogate molecule would be a C7 or a C8
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3 molecule. But this is not seen in the case of heavy petroleum fractions (like HFO) that usually
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5 have high molecular weights. The concept of surrogate molecules has been used to draw
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7 average molecules of vacuum residues¹⁷, asphaltenes from tar¹⁸, pyrolytic pitch fractions²⁶ and
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9 solvent refined coal³².
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14 The surrogate molecule for the HFO is assumed to be aromatic connected with
15
16 paraffinic chains. To develop the surrogate molecule data presented in Tables 2, 3 and 4 were
17
18 used. Fig. 3 shows the surrogate molecule for HFO A and HFO B. Carbon and hydrogen atoms
19
20 that appear as aldehydes, carboxylic acid, olefins and alcohols were neglected from the
21
22 surrogate molecule due to their low percentage and also for the sake of simplicity. Carbon,
23
24 hydrogen and sulfur atoms are used in the surrogate molecule of HFO A and hetero-atoms like
25
26 nitrogen and oxygen were neglected as their percentage was less. Table 7 shows the carbon
27
28 type distribution in the surrogate molecules. The surrogate molecule of HFO A is composed of 7
29
30 CH₃ groups (2 in α positions to aromatic ring), 23 CH₂ groups (in 5 chains), 1 CH group, 3
31
32 aromatic rings (1 separate and other 2 condensed) and 1 naphthenic ring with a molecular
33
34 formula of C₅₁H₈₀S. The surrogate molecule for HFO B is composed of 5 CH₃ groups (1 in α
35
36 position to aromatic ring), 21 CH₂ groups (in 4 chains), 3 aromatic rings (1 separate and other 2
37
38 condensed) and 2 naphthenic rings. The molecular formula for the surrogate molecule of HFO B
39
40 is C₅₁H₇₆OS. HFO B has a higher oxygen content compared to HFO A and it was found to appear
41
42 as a carbonyl (keton) group. The primary difference between the HFOs is that the sample B has
43
44 a higher naphthenic content than sample A. HFO B was slightly more aromatic ($f_a = 0.37$) than
45
46 HFO A ($f_a = 0.33$). The structure proposed in Fig. 3 can be drawn in a number of ways such
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48 that it satisfies the AMPs calculated from the data. The surrogate molecule can be used for
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3 property estimation of the fuel or can also function as a surrogate for the fuel which can help in
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5 kinetic modeling studies. Table 8 shows some of the properties calculated³³⁻³⁴ for the surrogate
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7 molecules using Quantitative structure-property relationship (QSPR) approach. The principle
8
9 behind QSPR is the premise that structural formula of a compound contains within itself all the
10
11 required information that determines the physical, chemical and biological properties of the
12
13 compound. The properties are calculated by establishing a mathematical relationship between
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15 the property and one or more molecular descriptors of the structure. Accurate prediction of
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17 properties like standard enthalpy of formation³⁵, standard entropy³⁶, density³⁷, flash point³⁷,
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19 higher heating value³⁷ etc. and many others have been made using this approach. In the
20
21 present study, four physical properties of the HFO surrogates, i.e., density, viscosity, specific
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23 gravity, refractive index and one chemical property, i.e., enthalpy of combustion, were
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25 predicted and experimentally validated. As shown in Table 8, the predicted values match well
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27 with the experimental data, which indicates that the proposed molecules can be used as
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29 surrogates to represent the HFO samples. The predicted values of other properties like critical
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31 pressure, critical temperature, critical volume etc. could not be experimentally verified and
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33 have been presented for the knowledge of the readers.
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44 4.4. Comparison of the methods

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47 The methods presented above help in characterizing complex petroleum fractions like
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49 HFOs. Each method has its advantages and its limitations. These are approximate methods and
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51 their accuracy depends upon the accuracy of the data used. For example, chemical shift
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53 assignments used to denote specific carbon and hydrogen atoms vary among researchers³⁸⁻⁴¹
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55 where different chemical shift ranges were used to denote the same atom types. Characterizing
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3 a fuel by defining functional groups depends on the functional groups chosen. A poor set of
4
5 functional groups will result in a poor characterization of the fuel. The surrogate molecule
6
7 constructed is a hypothetical molecule that may or may not be present in the fuel. It provides
8
9 for a way where the analytical data can be interfaced with property estimation methods.
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11 Comparison of the values calculated from the above 3 methods is reported in Table 9.
12
13 The (C/H) ratio was found to be almost the same for the 3 methods and the value matched the
14
15 experimental (C/H) ratio calculated from the elemental analysis. Major differences are seen
16
17 for the $(C/H)_{Ar}$ ratio calculated from the AMPs and the functional group method. The low
18
19 values reported by the functional group method is expected because the carbons in the
20
21 aromatic functional groups are protonated while most of the aromatic carbons seen from the
22
23 AMPs are non-protonated. These 3 methods represent a useful technique for the structural
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25 characterization of complex petroleum fractions like HFOs.
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34 **4. Conclusion**

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37 The average molecular parameters (AMPs), functional groups and a surrogate molecule
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39 were calculated for 2 samples of Saudi Arabian heavy fuel oils (HFOs) by using NMR
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41 spectroscopy, elemental analysis and average molecular weight. The AMPs were used to
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43 calculate the number and type of carbon and hydrogen atoms present in the HFOs. Derived
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45 AMPs like aromaticity (f_a), C/H ratio, average chain length (\bar{n}), naphthenic ring number (R_N),
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47 aromatic ring number (R_A), total ring number (R_T), aromatic condensation index (φ) and
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49 aromatic condensation degree (Ω) were also calculated by using the recent formulae from
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51 literature. These derived AMPs can help in understanding the overall structure of the HFOs. 19
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53 functional groups were defined to represent the HFOs and their concentrations were calculated
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3 which can be used for property estimation studies. Heteroatoms like sulfur, nitrogen and
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5 oxygen were also used in the functional groups. The HFOs were also represented by a surrogate
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7 molecule by utilizing the data from the AMPs and the derived AMPs. The surrogate molecule
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9 can be used for property estimation studies and a number of useful properties were calculated
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11 for the surrogate molecule using the QSPR approach. The surrogate molecule can also as a
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13 surrogate to represent the molecular structure of the HFOs for kinetic studies.
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24
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28
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31 research program.
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36 **References**

- 37
38
39 1. Vazzoler, Frederic. *The Low Sulfur Fuel Oil Issue on Shipping and Impact on Oil Suppliers*. Paris,
40 France: Total Marine Fuels, 2012. Web. 1 Nov. 2015. OOCL / Total Marine Fuels Presentation For
41 ICC.
42
43 2. Kalli, Juha, Tapio Karvonen, and Teemu Makkonen. *Sulphur Content in Ships Bunker Fuel in 2015.*
44 *A Study on the Impacts of The New IMO Regulations And Transportation Costs*. Ministry of
45 Transport and Communications, 2009. Web. 12 Oct. 2015
46
47 3. Goldstein, H. L.; Siegmund, C. W. *Environ. Sci. Technol.* 1976, 10 (12), 1109–1114.
48
49 4. MEPC, Resolution MEPC.176 (58): Amendments to the annex of the Protocol of 1997 to amend
50 the international convention for the prevention of pollution from ships, 1973, as modified by the
51 protocol of 1978 relating thereto (Revised MARPOL Annex VI) in MEPC 58/23/Add.1
52 International Maritime Organization, Editor; 2008.
53
54 5. [http://www.imo.org/en/MediaCentre/PressBriefings/Pages/44-MARPOL-](http://www.imo.org/en/MediaCentre/PressBriefings/Pages/44-MARPOL-amends.aspx#.VcnYPnGqpBc)
55 [amends.aspx#.VcnYPnGqpBc](http://www.imo.org/en/MediaCentre/PressBriefings/Pages/44-MARPOL-amends.aspx#.VcnYPnGqpBc) (last accessed 14 Oct. 2015)
56
57 6. Schönborn, A.; Ladommatos, N.; Williams, J.; Allan, R.; Rogerson, J. *Combust. Flame* 2009, 156
58 (7), 1396–1412.
59
60

- 1
 - 2
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 - 53
 - 54
 - 55
 - 56
 - 57
 - 58
 - 59
 - 60
7. Calcote, H. F.; Manos, D. M. *Combust. Flame* 1983, 49 (1-3), 289–304.
8. Gough, M. A.; Rowland, S. J. *Nature* 1990, 344 (6267), 648–650.
9. Silva, S. L.; Silva, A. M. S.; Ribeiro, J. C.; Martins, F. G.; Da Silva, F. a.; Silva, C. M. *Anal. Chim. Acta* 2011, 707 (1-2), 18–37.
10. Petrakis, L.; and Allen, D., *NMR for liquid fossil fuels*, Analytical Spectroscopic Library, Vol. 1 (elsevier, New York, 1987).
11. Morcombe, C. R.; Zilm, K. W. *J. Magn. Reson.* 2003, 162 (2), 479–486.
12. R.B. Williams. Symposium on composition of petroleum oils, determination and evaluation ASTM Spec. Tech. Publ. No. 224, 1958, pp. 168–194.
13. Brown, J. K.; Ladner, W. R. *Fuel* 1960, (39), 87–96.
14. Gregory L. Alexander , A. Louise Creagh, J. M. P. *Ind. Eng. Chem. Fundamen* 1985, 24 (3), 301–310.
15. Elbaz, A. M.; Gani, A.; Hourani, N.; Emwas, A.-H.; Sarathy, S. M.; Roberts, W. L. *Energy & Fuels* 2015, 29 (12), 7825–7835.
16. Ben, H.; Ragauskas, A. J. *Energy and Fuels* 2011, 25 (5), 2322–2332.
17. Hauser, A.; AlHumaidan, F.; Al-Rabiah, H.; Halabi, M. A. *Energy & Fuels* 2014, 28 (7), 4321–4332.
18. López, D.; Acelas, N.; Mondragón, F. *Bioresour. Technol.* 2010, 101 (7), 2458–2465.
19. Wang, Q.; Jia, C.; Ge, J.; Guo, W. *Energy & Fuels* 2016, *acs.energyfuels.5b01215*.
20. Poveda, Juan-Carlos; Molina, Daniel-Ricardo; Pantoja-Agreda; Edgar-Francisco. *Ciencia, Tecnología y Futuro.* 2014, 5(4), 49-60.
21. Poveda, J. C.; Molina, D. R. *J. Pet. Sci. Eng.* 2012, 84-85, 1–7.
22. Clutter, D.; Petrakis, L.; Stenger, R.; Jensen, R. *Anal. Chem.* 1972, 44 (8), 1395–1405.
23. Lee, S. W.; Glavincevski, B. *Fuel Process. Technol.* 1999, 60 (1), 81–86.
24. ASTM D5291 – 10(2015) Standard test methods for instrumental determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants.
25. Knight, S. A. *Chem. Ind.* 1967, 1920
26. Rongbao, L.; Zengmin, S.; Bailing, L. *Fuel* 1988, 67 (4), 565–569.
27. Qian, S. *Fuel* 1985, 64 (8), 1085–1091.
28. Alien, D.; Petrakis, L.; Grandy, D.; Gavalas, G.; Gates, B. *Fuel* 1984, 63 (6), 803–809.
29. Thuy, T.; Allen, D. *Fuel* 1985, 64 (12), 1754–1759.
30. Choudhary, T. V. *Ind. Eng. Chem. Res.* 2007, 46, 8363–8370.
31. Ruzicka, V.; Fredenslund, A.; Rasmussen, P. *Ind. Eng. Chem. Process Des. Dev.* 1983, 22 (1), 49–53.
32. Wooton, D. L.; Coleman, W. M.; Taylor, L. T.; Dorn, H. C. *Fuel* 1978, 57 (1), 17–21.
33. Mol-Instincts Realtime Predictor, A Fundamental Property Predictor based on QSPR, Copyright by ChemEssen, Inc. (<http://www.mol-in.com>). ID: OZPSBPYUAZAKOL-UHFFFAOYSA-N, <http://realtime.molinstincts.com/chemical-info.ce?ID=OZPSBPYUAZAKOL-UHFFFAOYSA-N> (retrieved October 14, 2015).
34. Mol-Instincts Realtime Predictor, A Fundamental Property Predictor based on QSPR, Copyright by ChemEssen, Inc. (<http://www.mol-in.com>). ID: KETFHNLNBPVDL-UHFFFAOYSA-N, <http://realtime.molinstincts.com/chemical-info.ce?ID=KETFHNLNBPVDL-UHFFFAOYSA-N> (retrieved October 14, 2015).

- 1
2
3 35. Vatani, A.; Mehrpooya, M.; Gharagheizi, F. *Int. J. Mol. Sci.* 2007, 8 (5), 407–432.
4 36. Duchowicz, P.; Castro, E. a.; Toropov, A. a. *Comput. Chem.* 2002, 26 (4), 327–332.
5 37. Yuan, H.; Yang, B.; Yang, J. J. *Am. Oil Chem. Soc.* 2009, 86 (4), 375–382.
6 38. Rodríguez, J.; Tierney, J. W.; Wender, I. *Fuel* 1994, 73, 1863–1869.
7 39. Winschel, R. A.; Robbins, G. A.; Burke, F. P. *Fuel* 1986, 65, 526–532.
8 40. Yoshida, T.; Maekawa, Y.; Uchino, H.; Yokoyama, S. *Anal. Chem.* 1980, 52, 817–820.
9 41. Delpuech, J. J.; Nicole, D.; Daubenfeld, J. M.; Boudel, J. C. *Fuel* 1985,64, 325-334.
10
11
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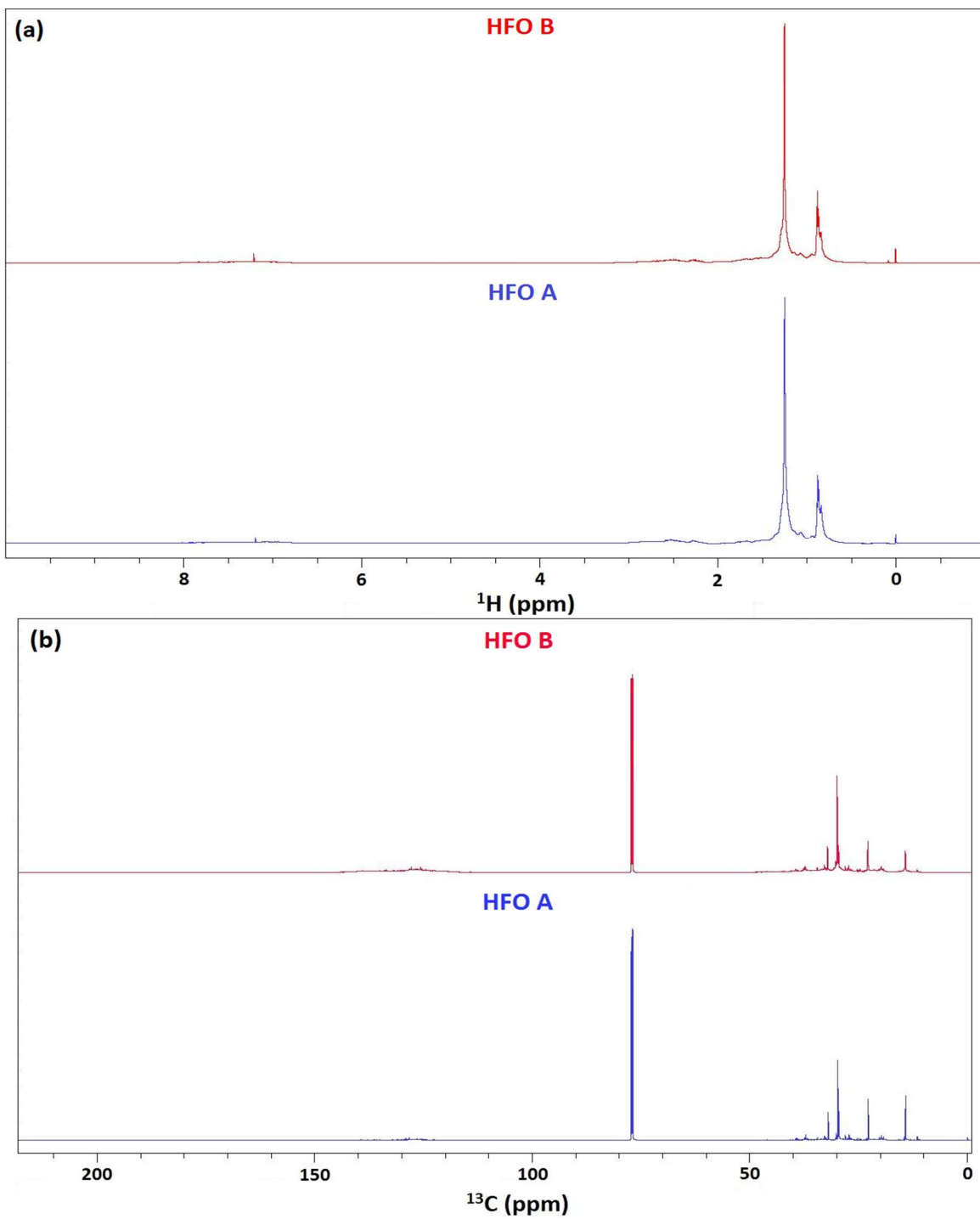


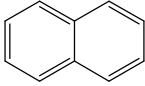

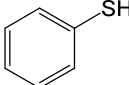
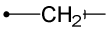
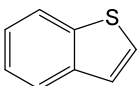
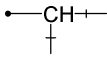
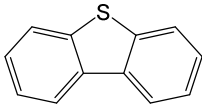
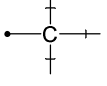
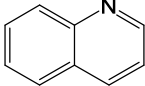


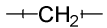

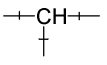

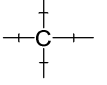
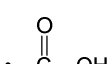
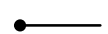


Fig. 1. (a) ^1H NMR spectra of HFO A and HFO B and (b) ^{13}C NMR spectra of HFO A and HFO B

1 Benzene		11 Naphthene	
2 Naphthalene		12 Alpha CH ₃	
3 Thiophenol		13 Apha CH ₂	
4 Benzothiophene		14 Alpha CH	
5 Dibenzothiophene		15 Alpha C	
6 Quinoline		16 Beta and Beta(+) CH ₃	
7 Phenol		17 Beta and Beta(+) CH ₂	
8 Ketone		18 Beta and Beta(+) CH	
9 Aldehyde		19 Beta and Beta(+) C	
10 Carboxylic acid			

Notation:

 Connected directly to an aromatic ring

 Aliphatic C-C bond

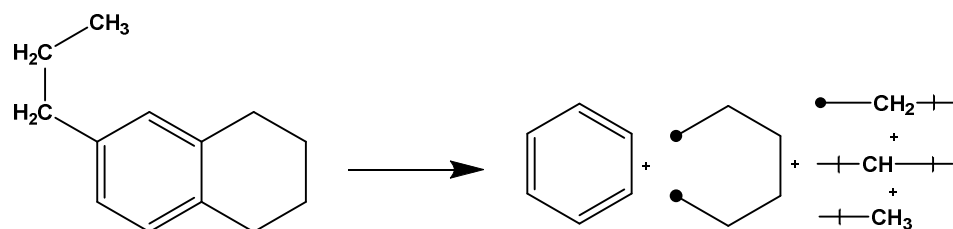
Example:

Fig. 2. List of functional used to represent HFOs

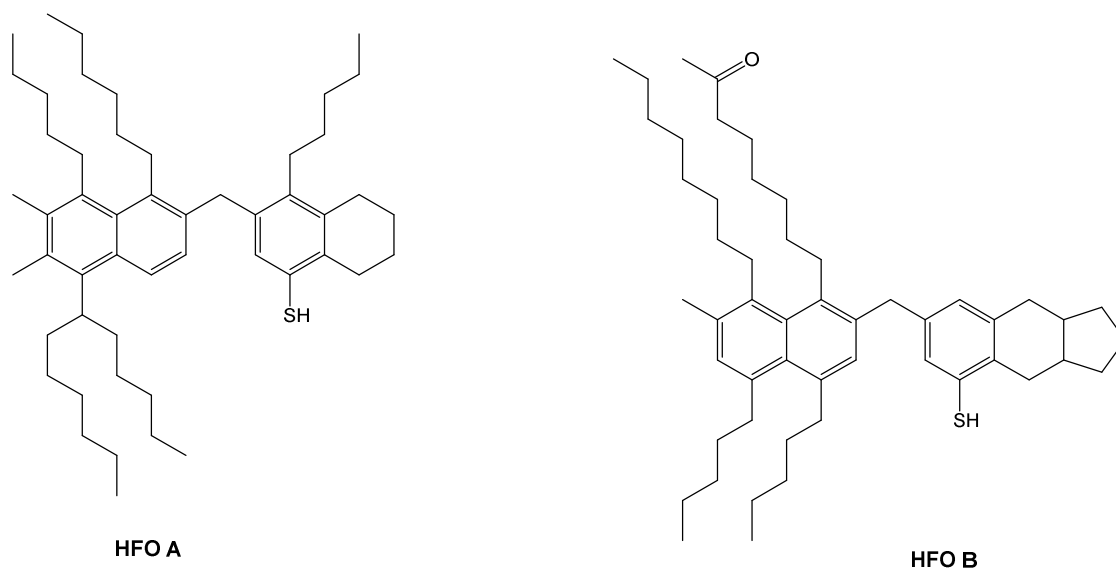


Fig. 3. Surrogate molecule of HFO A and HFO B

Table 1

Elemental analysis

Element	HFO A	HFO B	Method
	(mass %)	(mass %)	
Carbon	85.0	84.35	EPA 440
Hydrogen	10.89	10.65	EPA 440
Oxygen	0.03	2.29	EPA 440
Nitrogen	0.24	0.31	EPA 440
Sulfur	3.29	2.39	ASTM D4294-10

Table 2

AMPs derived from ^1H NMR

Symbol	Description	Chemical shift (ppm)	Number of atoms in surrogate molecule of HFO A	Number of atoms in surrogate molecule of HFO B
$H_{ald} + H_{car}$	Aldehydic and carboxylic hydrogens	9.0 – 12.0	0.44	0.76
H_{ald}	Aldehydic hydrogens		0.12	0.18
H_{car}	Carboxylic hydrogens		0.34	0.58
H_{Ar}^{pa}	Aromatic hydrogens in poly-aromatic rings	7.2 – 9.0	2.15	2.61
H_{Ar}^{ma}	Aromatic hydrogens in mono-aromatic rings	6.0 – 7.2	2.01	1.96
H_{ole}	Olefinic hydrogens	4.5 – 6.0	0.15	0.12
$H_{Par}^{\alpha-Ar} + H_{Nap}^{\alpha-Ar} + H_{OH} + H_{SH}$	Hydrogens in paraffinic and naphthenic groups (CH_3 , CH_2 and CH) in α position to aromatic ring; other groups like OH, SH also appear in this region	2.0 – 4.5	20.55	22.41
$H_{Par}^{\alpha-Ar}$	Hydrogens in paraffinic groups (CH_3 , CH_2 and CH) in α position to aromatic ring		13.4	12.38
$H_{Nap}^{\alpha-Ar}$	Hydrogens in naphthenic groups (CH_2 and CH) in α position to aromatic ring		5.32	8.34
H_{OH}	Hydrogens in OH group in α position to aromatic ring		0.45	1.21
H_{SH}	Hydrogens present in mercaptan groups (SH)		1.38	0.48
$H_{Nap-CH_2}^{\beta-Ar}$	Hydrogens in naphthenic group (CH_2) in β position to aromatic ring	1.5 – 2.0	5.8	6.21
$H_{Par-CH_2}^{\beta-Ar}$	Hydrogens in paraffinic group (CH_2) in β position to aromatic ring	1.0 – 1.5	35.55	32.15
$H_{Par-CH_3}^{\gamma-Ar}$	Hydrogens in paraffinic group (CH_3) in γ position and further, to aromatic ring	0.1 – 1.0	14.74	13.66

Table 3

AMPs derived from ^{13}C NMR

Symbol	Description	Chemical shift (ppm)	Number of atoms in surrogate molecule of HFO A	Number of atoms in surrogate molecule of HFO B
$C_{ald} + C_{ket}$	Aldehydic and ketonic carbons	190.0 – 220.0	0.43	1.16
C_{ald}	Aldehydic carbons		0.11	0.14
C_{ket}	Ketonic carbons		0.32	1.02
C_{qui}	Quinolinic carbons	178.0 – 190.0	0.93	0.68
C_{car}	Carboxylic carbons	160.0 – 178.0	0.31	0.58
C_{Ar-sat}	Quaternary aromatic carbons	137.0 – 160.0	9.16	10.82
$C_{Ar}^{\alpha-S,N}$	Quaternary aromatic carbons (mercaptans, benzo, dibenzothiophene and benzopyridine type structures) in α position to sulfur or nitrogen atom	137.0 – 140.5	1.18	0.88
$C_{Ar}^{\alpha-O}$	Quaternary aromatic carbons (in benzo and dibenzo type structures) in α position to Oxygen atom	154.0 – 157.0	0.08	0.12
$C_{Ar-sat}^{\alpha-CH_3} + C_{Ar}^{AA}$	Aromatic carbons linked to CH_3 group in α position; and carbon bridging 2 aromatic rings together	129.2 – 137.0	3.71	3.13
C_{Ar}^{AA}	Aromatic carbons bridging 2 aromatic rings together	129.7 – 131.7	1.81	2.01
$C_{Ar-sat}^{\alpha-CH_3}$	Aromatic carbons linked to CH_3 group in α position		1.9	1.12
$C_{Ar-H} + C_{Ar}^{AAA} + C_{ole}$	Protonated aromatic carbons; aromatic carbons bridging 3 aromatic rings together; and olefinic carbons	85.0 – 129.2	4.44	5.26
C_{Ar-H}	Protonated aromatic carbons Aromatic carbons bridging 3		4.09	4.89

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	C_{Ar}^{AAA}	Protonated aromatic carbonsAromatic carbons bridging 3		0.21	0.28
	C_{ole}	Olefinic carbons		0.14	0.09
	$C_{Par}^{\alpha-OH}$	Paraffinic carbons in α position to OH	60.0 – 75.0	0.22	1.03
	C_{Par-C}	Quaternary paraffinic carbons	50.0 – 60.0	0.33	0.23
	$C_{Par-CH_2} + C_{Par-CH}$	Paraffinic and naphthenic carbons (CH ₂ and CH)	21.5 – 50.0	26.49	24.61
	$C_{Nap-CH_2} + C_{Nap-CH}$				
	C_{Par-CH}	Paraffinic carbons (CH)	32.9	1.2	0.21
	C_{Par-CH_2}	Paraffinic carbons (CH ₂)		21.48	18.22
	$C_{Nap-CH_2} + C_{Nap-CH}$	Naphthenic carbons (CH ₂ and CH)		3.81	6.18
	$C_{Par-CH_3}^{\alpha-Ar}$	Paraffinic carbons (CH ₃ type) in α position to aromatic ring	18.5 – 21.5	2.1	1.31
	C_{Par-CH_3}	Paraffinic carbons (CH ₃ type)	3.0 – 18.5	4.73	3.91

Table 4

Derived AMPs

Equations	HFO A	HFO B
	(no unit)	(no unit)
$f_a = \frac{C_{Ar-sat} + C_{Ar-sat}^{\alpha-CH_3} + C_{Ar}^{AA} + C_{Ar}^{AAA} + C_{Ar-H} - C_{ole} + \frac{2}{3} C_{Ar}^{\alpha-S,N} \cdot C_{Ar}^{\alpha-O} + C_{qui}}{c + s + n + o}$	0.33	0.37
$(C/H)_{par} = \frac{C_{Par}}{H_{par}} = \frac{C_{Par-CH_3} + C_{Par-CH_2} + C_{Par-CH} + C_{Par-C}}{H_{Par-CH_3}^{\gamma-Ar} + H_{Par-CH_2}^{\beta-Ar} + H_{Par}^{\alpha-Ar}}$	0.43	0.39
$(C/H)_{Ar} = \frac{C_{Ar}}{H_{Ar}} = \frac{C_{Ar-sat} + C_{Ar-sat}^{\alpha-CH_3} + C_{Ar}^{AA} + C_{Ar}^{AAA} + C_{Ar-H}}{H_{Ar}^{ma} + H_{Ar}^{pa}}$	4.13	4.18
$(C/H) = \frac{C_{Par} + C_{Ar} + C_{ald} + C_{Ket} + C_{qui} + C_{car} + C_{ole} + C_{Par}^{\alpha-OH} + C_{Nap-CH_2} + C_{Nap-CH} + C_{Par-CH_3}^{\alpha-Ar}}{H_{par} + H_{Ar} + H_{ald} + H_{car} + H_{ole} + H_{Nap}^{\alpha-Ar} + H_{OH} + H_{SH} + H_{Nap-CH_2}^{\beta-Ar}}$	0.65	0.66
$\bar{n}_1 = \frac{C_{Par-CH_3} + C_{Par-CH_2} + C_{Par-CH} + C_{Par-C}}{C_{Par-CH_3}}$	5.86	5.77
$\bar{n}_2 = \frac{C_{Par-CH_3} + C_{Par-CH_2} + C_{Par-CH} + C_{Par-C}}{C_{Ar-sat} - C_{Ar}^{\alpha-O} - C_{Ar}^{\alpha-S,N}}$	3.52	2.30
$\bar{n}_3 = \frac{C_{Par}}{H_{par} - 2 \cdot C_{Par}}$	3.38	3.07
$R_N = \frac{C_{Nap-CH_2} + C_{Nap-CH} + C_{ole}}{4}$	1.01	1.58
$R_A = \frac{C_{Ar-sat}^{\alpha-CH_3} + C_{Ar}^{AA} + C_{Ar}^{AAA}}{2} + 1$	2.96	2.71
$R_T = R_A + R_N$	3.97	4.29
$\varphi = \frac{C_{Ar}^{AA} + C_{Ar}^{AAA}}{C_{Ar-sat} + C_{Ar-sat}^{\alpha-CH_3} + C_{Ar}^{AA} + C_{Ar}^{AAA} + C_{Ar-H}}$	0.11	0.12
$\Omega = \frac{C_{Ar}^{AAA}}{C_{Ar}^{AA}}$	0.12	0.14

Table 5

Stoichiometric Coefficients (A_{ij})

Constraint (b_i)	Concentration (mol/100g)		Stoichiometric Coefficients (A_{ij})																		
	HFO A	HFO B	Functional group (j)																		
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
H_{ald1}	0.016	0.024	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
H_{car2}	0.045	0.077	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
H_{Ar3}^{pa}	0.284	0.345	0	8	0	0	8	7	-1	-1	-1	-1	-2	-1	-1	-1	-1	0	0	0	0
H_{Ar4}^{ma}	0.266	0.259	6	0	5	6	0	0	-1	-1	-1	-1	-2	-1	-1	-1	-1	0	0	0	0
$H_{Par5}^{\alpha-Ar}$	1.772	1.637	0	0	0	0	0	0	0	0	0	0	0	0	3	2	1	0	0	0	0
$H_{Nap6}^{\alpha-Ar}$	0.704	1.103	0	0	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0
H_{OH7}	0.060	0.160	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
H_{SH8}	0.183	0.063	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$H_{Nap-CH_29}^{\beta-Ar}$	0.767	0.821	0	0	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0
$H_{Par-CH_210}^{\beta-Ar}$	4.702	4.252	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0
$H_{Par-CH_311}^{\gamma-Ar}$	1.950	1.807	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0	0	0
C_{ald12}	0.015	0.019	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
C_{ket13}	0.043	0.136	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0

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2																					
3																					
4	$C_{qui_{14}}$	0.124	0.091	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0
5	$C_{car_{15}}$	0.041	0.077	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
6	$C_{Ar-sat_{16}}$	1.220	1.441	0	2	0	2	4	2	0	0	0	0	0	0	0	0	0	0	0	0
7	$C_{Ar-H_{17}}$	0.545	0.651	6	8	5	6	8	7	0	0	0	0	0	0	0	0	0	0	0	0
8	$C_{Par}^{\alpha-OH}_{18}$	0.029	0.137	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
9	C_{Par-C}_{19}	0.044	0.031	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1
10	C_{Par-CH}_{20}	0.160	0.028	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0
11	$C_{Par-CH_2}_{21}$	2.862	2.427	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0
12	C_{Nap-CH_2}	0.508	0.823	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0
13	+ $C_{Nap-CH_2}_{22}$																				
14	C_{Par-CH_3}	0.910	0.695	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0
15	+ $C_{Par-CH_3}^{\alpha-Ar}_{23}$																				
16	N_{24}	0.017	0.022	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
17	O_{25}	0.002	0.143	0	0	0	0	0	0	1	1	1	2	0	0	0	0	0	0	0	0
18	S_{26}	0.102	0.075	0	0	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0

Functional groups (j) are defined in Fig.2

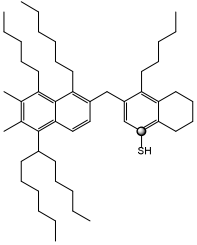
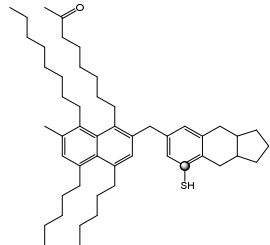
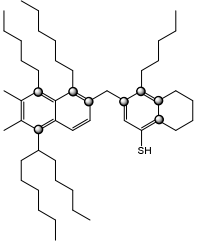
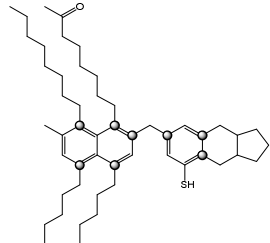
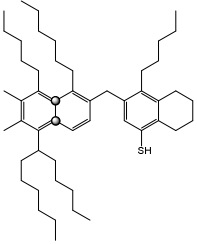
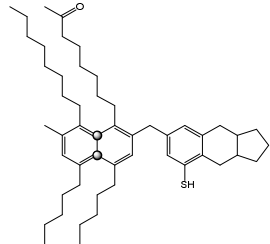
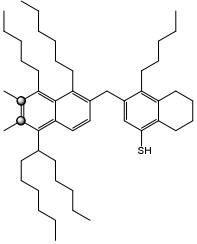
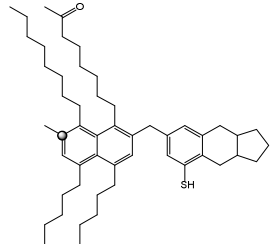
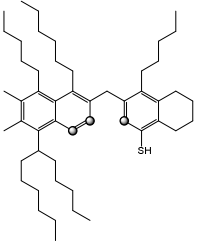
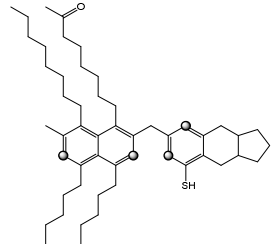
Table 6

Concentration of the functional groups

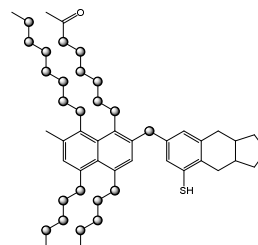
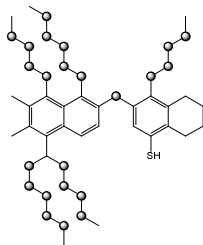
Functional group	Concentration (mol/100g)	
	HFO A	HFO B
Benzene	0.081	0.092
Naphthalene	0.075	0.071
Thiophenol	0.048	0.047
Benzothiophene	0.045	0.051
Dibenzothiophene	0.030	0.034
Quinoline	0.026	0.029
Alcohol	0.004	0.007
Ketone	0.006	0.011
Aldehyde	0.003	0.005
Carboxylic acid	0.006	0.018
Naphthene	0.165	0.204
α CH ₃	0.260	0.142
α CH ₂	0.511	0.482
α CH	0.030	0.020
α C-C	0.063	0.052
β and β + CH ₃	0.210	0.159
β and β + CH ₂	2.280	2.120
β and β + CH	0.110	0.078
β and β + C-C	0.061	0.058

Table 7

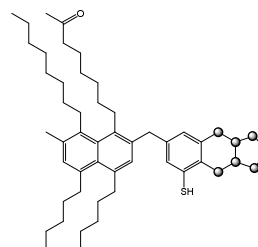
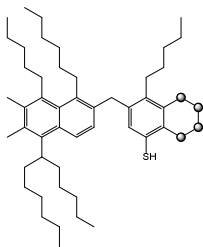
Carbon type distribution in the surrogate molecules

Carbon type	Number of atoms in surrogate molecule		Position of the carbon atom in the surrogate molecule	
	HFO A	HFO B	HFO A	HFO A
$C_{Ar}^{\alpha-S,N}$	1.18	0.88		
$C_{Ar-sat} - C_{Ar}^{\alpha-S,N}$	7.98	9.94		
C_{Ar}^{AA}	1.81	2.01		
$C_{Ar-sat}^{\alpha-CH_3}$	1.9	1.12		
C_{Ar-H}	4.09	4.89		

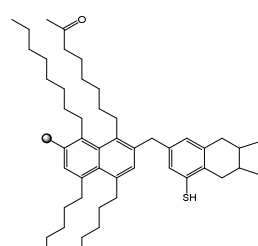
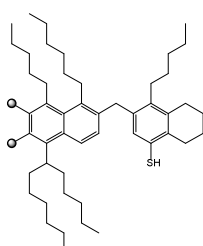
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3 C_{Par-CH_2} 21.48 18.22



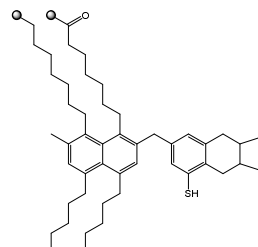
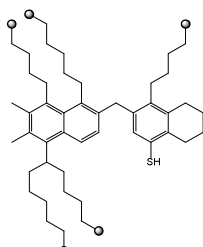
12 $C_{Nap-CH_2} +$
13 C_{Nap-CH} 3.81 6.18



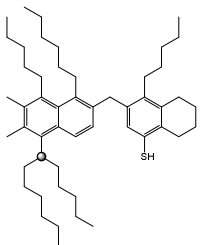
21 $C_{Par-CH_3}^{\alpha-Ar}$ 2.1 1.31



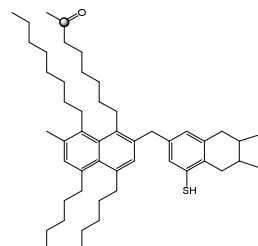
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31 C_{Par-CH_3} 4.73 3.91



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41 C_{Par-CH} 1.2 0.21



49 C_{ket} 0.32 1.02



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Table 8

Predicted properties of the surrogate molecule using QSPR

Property	Unit	HFO A		HFO B	
		Predicted	Measured	Predicted	Measured
density (@ 288 K)	kg/m ³	956.5	970.5	954.2	968
specific gravity (@ 288 K)	-	0.9561	0.9711	0.954	0.9677
kinematic viscosity (@ 313 K)	cSt	658.2	617.7	712.5	746.5
critical pressure	atm	22.81	-	23.20	-
critical temperature	K	1088	-	1156	-
critical volume	m ³ /mol	0.027	-	0.027	-
normal boiling point	K	924	-	942	-
melting point	K	334	-	342	-
refractive index	-	1.63	1.58	1.64	1.62
absolute entropy (@ 298 K and 1 bar)	J/mol/K	997.4	-	953.5	-
enthalpy of formation (@ 298 K and 1 bar)	kJ/mol	-793.7	-	-902.1	-
enthalpy of combustion (@ 298 K)	MJ/mol	-29.26	-30.81	-28.67	-31.35
Heat of vaporization (@ 298 K)	kJ/mol	245.6	-	253.9	-

Table 9

Comparison of the methods

Parameter	Elemental analysis		AMPs		Functional group		Surrogate molecule	
	HFO A	HFO B	HFO A	HFO B	HFO A	HFO B	HFO A	HFO B
(C/H)	0.65	0.66	0.65	0.66	0.63	0.66	0.64	0.67
$(C/H)_{par}$	-	-	0.43	0.39	0.49	0.50	0.45	0.45
$(C/H)_{Ar}$	-	-	4.13	4.18	1.20	1.21	6	4.5
Paraffinic C/Total C	-	-	0.54	0.45	0.53	0.47	0.61	0.52
Naphthenic C/Total C	-	-	0.07	0.12	0.09	0.12	0.07	0.13
Aromatic C/Total C	-	-	0.32	0.36	0.37	0.39	0.31	0.31
Average chain length (\bar{n}_3)	-	-	3.38	3.07	-	-	3.87	4.5
R_N	-	-	1.01	1.58	-	-	1	2
R_A	-	-	2.96	2.71	-	-	3	3
R_T	-	-	3.97	4.29	-	-	4	5