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Heavy fuel oil pyrolysis and combustion: kinetics and evolved gases investigated by TGA-FTIR

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Highlights

- Pollutant gases evolved during heavy fuel oil combustion analyzed
- Functional groups evolved during heavy fuel oil pyrolysis analyzed
- Kinetics of heavy fuel oils pyrolysis and combustion modeled using distributed activation energy model
- Pyrolysis and combustion characteristics of heavy fuel oil analyzed with respect to fuel chemistry

Abstract:

Heavy fuel oil (HFO) obtained from crude oil distillation is a widely used fuel in marine engines and power generation technologies. In the present study, the pyrolysis and combustion of a Saudi Arabian HFO in nitrogen and in air, respectively, were investigated using non-isothermal thermo-gravimetric analysis (TGA) coupled with a Fourier-transform infrared (FTIR) spectrometer. TG and DTG (differential thermo-gravimetry) were used for the kinetic analysis and to study the mass loss characteristics due to the thermal degradation of HFO at temperatures up to 1000 °C and at various heating rates of 5, 10 and 20 °C/min, in air and N₂ atmospheres. FTIR analysis was then performed to study the composition of the evolved gases. The TG/DTG curves during HFO combustion show the presence of three distinct stages: the low temperature oxidation (LTO); fuel decomposition (FD); and high temperature oxidation (HTO) stages. The

TG/DTG curves obtained during HFO pyrolysis show the presence of two devolatilization stages similar to that seen in the LTO stage of HFO combustion. Apart from this, the TG/DTG curves obtained during HFO combustion and pyrolysis differ significantly. Kinetic analysis was also performed using the distributed activation energy model, and the kinetic parameter (E) was determined for the different stages of HFO combustion and pyrolysis processes, yielding a good agreement with the measured TG profiles. FTIR analysis showed the signal of CO_2 as approximately 50 times more compared to the other pollutant gases under combustion conditions. Under pyrolytic conditions, the signal intensity of alkane functional groups was the highest followed by alkenes. The TGA-FTIR results provide new insights into the overall HFO combustion processes, which can be used to improve combustor designs and control emissions.

Keywords: heavy fuel oil; TGA-FTIR; pyrolysis; combustion;

1. INTRODUCTION

Heavy fuel oil (HFO) or residual fuel oil is the portion of the crude oil remaining after lighter hydrocarbons like gasoline and distillate fuel oils have been removed via distillation. It is usually the product from the visbreaking unit in a refinery, which is mixed with light distillates (cutter stock) to meet required fuel specifications. It is characterized by its high viscosity, tar-like nature and high asphaltene (n-heptane insolubles) content that makes it difficult to burn. HFOs are also characterized by high sulfur contents of up to 4.5 mass % [1], which leads to SO_2 emissions. Combustion of HFO in boiler furnaces leads to the emission of particulate matter comprised of cenospheres, smoke and ash residues, soot, sulfuric acid and organic materials [2–4]. In addition, HFO has various amounts of trace heavy metals like vanadium, nickel, lead, copper *etc.* that pose additional problems including high temperature corrosion and fouling that

require additives to mitigate these issues [5]. In spite of all these drawbacks, HFOs have been largely used by the marine industry for more than five decades as a fuel to propel marine engines due to their relative low cost. HFOs are also used in boilers in many countries to generate electricity for the same reason. The market price of HFO is estimated to be half the price of light oil [6]. Despite recent regulations [1] limiting the use of HFO, it can be seen from present trends that HFOs are here to stay for the foreseeable future. Therefore, there is a need to gain better understanding of HFO combustion due to their complex nature, so as to obtain improve combustion efficiency and emissions control.

HFOs have been characterized by various techniques like thermogravimetry [7,8], nuclear magnetic resonance (NMR) spectroscopy [1,7] and Fourier transform-ion cyclotron resonance (FT-ICR) mass spectroscopy [7] to gain insights into their complex molecular structure, because most of the conventional chromatographic techniques like GC-MS [9] are unable to handle such heavy fuels. However, these techniques cannot explain the real time evolution of gaseous pollutants or other hydrocarbon functional groups during their pyrolysis or combustion, *i.e.*, information that could help understand and control their combustion characteristics. To the authors' knowledge, techniques such as thermo-gravimetric analysis (TGA) coupled with a Fourier-transform infrared (FTIR) spectrometer (TGA-FTIR) have not been applied on HFOs. The TGA-FTIR technique can provide useful information on the composition of the evolved gases. These techniques are advantageous due to their high accuracy, repeatability, high sensitivity, small sample size requirements and their ability for real time measurements. They have been applied to study a number of different substances including lignite [10], oil shale [11,12], bio-oil from rice husk [13], coal [14], agricultural residues [15], wheat straw [16–18], cottonseed [19],

alkali lignin [20], co-polymers [21], biodiesel [22], palm kernel [23], tobacco-glycerol mixtures [24], tobacco-diammonium hydrogen phosphate mixtures [25], blends of carbonized oil palm biomass and coal[26], petroleum ether extracts [27], coal tar residue [27], waste materials [16], tannery effluents [28] and petroleum hydrocarbons [29].

The aim of the present work is to investigate heavy fuel oil combustion and pyrolysis using TGA-FTIR. A kinetic analysis of the combustion and pyrolysis is performed using the distributed activation energy model. A comprehensive study of the composition of the evolved gases as a function of temperature change from 50 to 1000 °C and at different heating rates is presented and discussed.

2. EXPERIMENTAL

A typical Saudi Arabian heavy fuel oil was used in pyrolysis and combustion experiments, the properties of which are shown in Table 1. The TG analysis was performed on a Mettler Toledo TGA/DSC (thermal gravimetric analysis/differential scanning calorimetry) instrument equipped with a GC 200 Gas Controller and an auto-sampler. For each test, approximately 10 mg of sample was weighed and placed in the alumina crucible. The sample was first subjected to isothermal treatment of 50 °C for 30 minutes under flowing N₂ (99.9999 % purity) or air (ZERO AIR GAS) with a flow rate of 50 ml/min in order to remove atmospheric CO₂ and H₂O, which were introduced into the TGA furnace during sample insertion. The samples were subsequently subjected to heating rates of 5, 10 and 20 °C/min up to 1000 °C. Prior to each experiment, a blank test was performed with the same alumina crucibles used during TG analysis in order to correct for buoyancy effects.

Evolved gases from the TG furnace were carried by means of a heated line (Thermo Scientific TGAFTIR Interface Nicolet iZ10) maintained at 190 °C and equipped with a swagelok 15 μm filter. It was connected to an IR cell, which was kept at a temperature of 200 °C in order to avoid condensation of volatiles and for analysis of the evolved gases during the pyrolysis and combustion experiments. The FT-IR spectra was acquired with a Thermo Scientific Nicolet iS10 connected to iZ10 interface, equipped with a deuterated triglycine sulfate (DTGS) detector and KBr beamsplitter. Prior to collecting the FTIR spectra, the FTIR was aligned and the background data was amassed with a resolution of 4 cm^{-1} . A total of 16 spectral lines within the region of 4000 to 400 cm^{-1} were acquired. During the TGA ramp, FTIR spectra were collected at 25 seconds interval. Thermo Scientific OMNIC software was utilized for spectral analysis. The experiments were repeated twice to ensure repeatability. The characteristics IR bands selected in this study and their assignments are shown in Table 2.

3. RESULTS & DISCUSSION

3.1 Fuel Characteristics

The properties of heavy fuel oil (HFO) depend on the composition of the parent crude and the conditions in which the crude was processed. If necessary, lighter cuts, based on refinery availability, may be added to reduce its viscosity. The present HFO sample was sourced from a refinery in Saudi Arabia and its physical and chemical properties were studied in previous works [1,7] and are briefly presented in Table 1. HFO has a high viscosity of 746.5 ($10^{-6} \text{ m}^2/\text{s}$) at 313 K, more than a thousand times the viscosity of water at the same temperature. HFO is usually pre-heated to reduce its viscosity before being atomized and burned in boilers or in marine engines.

The sample contains 2.39 mass % of sulfur which acts as a potential source of SO₂ emissions when burned. It also contains some nitrogen (0.31 mass %) and oxygen (2.29 mass %). The proximate analysis of HFO was performed using the thermo-gravimetric method by Karetepe et al. [30]. The sample contains low (< 1 mass %) moisture and ash content and has a high (84.79 mass %) volatile matter content. HFO contains asphaltenes, which are high molecular weight aromatics with largely unknown chemical identity. They are defined as the content of the fuel insoluble in n-heptane and usually range between 2.6 to 12 mass % [7]. They are generally considered as precursors to the formation of cenospheres [31–33] and are difficult to burn. Unlike fly ash, cenospheres are mostly hollow spheres, light in weight and carbonaceous, which are formed during droplet combustion at temperatures lower than that of soot formation [34]. Their formation is known to depend more on the asphaltene chemistry than the asphaltene quantity in the HFO [34]. Abdul Jameel and coworkers [1] presented the composition of this HFO sample in terms of the average molecular fragments, the concentration of different functional groups present, and a surrogate molecule that represents the average structure of the entire fuel. The fuel has a high aromatic content of nearly 37 mass% including multiple fused aromatic and naphthenic rings. The results from hetero nuclear multiple bond correlation (HMBC) NMR spectroscopy [7] indicate the presence of multiple short alkyl chains of an average length of 5.77 connected to the aromatic rings. The fuel has low percentages of alkenes, aldehydes, and alcohols. The oxygen content in the fuel was mostly found to be concentrated in ketonic groups. FTICR-MS studies revealed the average molecular weight of the fuel to be 750 g/mol [7].

3.2 TG and DTG results

3.2.1 Pyrolysis of HFO

Fig. 1 shows the TG and DTG curves of HFO pyrolysis in N_2 atmosphere at the different heating rates. Due to the absence of oxygen, the HFO molecules decompose and release different hydrocarbon species at different temperatures. Fig. 1, shows that as the temperature increases the rate of mass loss increases due to devolatilization and reaches a peak (referred to as d_1 in Fig. 1) at 210, 232 and 243 °C for heating rates of 5, 10 and 20 °C /min, respectively. Devolatilization of the fuel during pyrolysis occurs in 2 separate steps. This peak (d_1) corresponds to the rate of maximum mass loss of '*step 1*' of the devolatilization process where the low boiling volatiles (alkane and alkene groups) are released due to the scission of the alkyl side chains [7] of the heavy compounds in HFO. With further increase of temperature, the rate of mass loss decreases briefly because the bulk of the low boiling volatiles are depleted and then there is a steep increase peaking (d_2) at a temperature of 450, 459 and 470 °C for heating rates of 5, 10 and 20 °C /min, respectively. This represents '*step 2*' of the devolatilization where the high boiling volatiles (aromatics) are released. As the temperature of the fuel is further increased, the rate of mass loss decreases due to depleting volatile content and reaches a minimum value beyond which there is no mass loss in the fuel. This marks the end of '*step 2*' of the devolatilization and the pyrolysis of the sample. No further apparent thermal degradation of the fuel is seen beyond this point, where the fuel is purely carbonaceous in nature and is approximately 13% of the initial mass. These two devolatilization steps in the DTG curves match with the two devolatilization stages observed during the combustion of HFO. However the peaks (d_1 & d_2) are seen at a higher temperature during pyrolysis and the rate of mass loss recorded at these points is also higher.

3.2.2 Combustion of HFO

The combustion of HFOs is a complex process that involves a large number of parallel reactions that occur at a given time due to the highly distributed and multicomponent nature of the fuel [35]. Fig. 2 shows the TG/DTG curves obtained during the combustion of HFO at the different heating rates. Studying the curves, three distinct stages can be identified in the DTG curves: the low temperature oxidation (LTO), fuel decomposition (FD) and high temperature oxidation (HTO) stages. As the HFO is heated, the fuel undergoes devolatilization [7], which includes processes like evaporation, distillation and visbreaking. These processes together constitute the LTO stage, after which the evolved volatile gases (called tar) undergo oxidation in the gas phase. Here the devolatilization of the fuel also occurs in 2 separate stages as observed during pyrolysis which extends up to 394, 405 and 421 °C for heating rates of 5, 10 and 20 °C /min respectively. The first appreciable mass loss due to devolatilization begins at a temperature of 145, 135 and 122 °C for heating rates of 5, 10 and 20 °C /min, respectively. Subsequently, the rate of mass loss exceeds 1 %/min and reaches a peak value (referred to as d_1 in Fig. 2) at a temperature of 196, 211 and 236 °C for heating rates of 5, 10 and 20 °C /min respectively. This represents '*step 1*' of devolatilization where the low boiling volatile gases evolve from the fuel. As the temperature of the fuel is increased further, the rate of devolatilization falls and '*step 2*' of the devolatilization begins at a temperature of 314, 330 and 351 °C for heating rates of 5, 10 and 20 °C /min, respectively. This is where the rate of mass loss begins to increase due to the evolution of the high boiling volatiles as a consequence of higher temperatures necessary for their release. The peaks (d_2) at this step are seen at a temperature of 373, 385 and 408 °C for heating rates of 5, 10 and 20 °C /min respectively, after which the rate of devolatilization decreases and reaches a minimum value marking the end of '*step 2*' and the LTO stage. When

the heating rate is increased, the position of the peaks are shifted towards higher temperatures. This is because at higher heating rates, thermal hysteresis increases and the sample does not reach thermal equilibrium until a higher temperature is reached compared to when the sample was exposed to a lower heating rate. The TG/DTG curves also shift towards the higher temperature when the heating rate is ramped up. The heating rate, however does not affect the shapes of the TG/DTG curves.

The next stage is the FD stage, where the homogenous gas phase oxidation of the evolved volatiles in the LTO continues. In this stage the observed weight loss is due to the liquid phase oxidation of hydrocarbons. The higher temperatures necessary are now attained and the presence of heavy metals like Vanadium, Nickel, Copper etc. catalyze liquid phase oxidation reactions [36,37]. Also, oxidative desulfurization (ODS) method used to reduce the sulfur content in HFO is carried out in the liquid phase in the presence of metal catalysts [38]. The volatile fractions break up the 'skin like' form [7] of the fuel that is formed during the LTO, and the highest rate of mass loss is achieved in the FD stage. The FD stage extends up to a temperature of 490, 505 and 530 °C for heating rates of 5, 10 and 20 °C/min respectively. The rate of mass loss then decreases due to the mass transfer resistance offered by the formation of a non-volatile carbonaceous fuel particles, which is analogous with the 'cenospheres' formed during HFO droplet combustion [32,33,39,40]. The end of the FD stage leaves a fuel with a very high C/H ratio that possesses cracks and pores throughout the volume of the fuel [32,33].

The third and final part of the HFO combustion is the HTO stage which ranges from 490 – 589 °C, 505 – 620 °C and 530 – 655 °C for heating rates of 5, 10 and 20 °C /min, respectively, at the end of which the rate of mass loss falls below 1 %/min. This is the phase where the

heterogeneous surface reactions referred to as char oxidation begins accompanied with a high mass loss (> 30%). The abundance of cracks on the surface and pores in the interior of the fuel allows for O₂ diffusion and oxidation of the '*cenosphere char*' which is primarily composed of asphaltenes [32,33,41]. At the end of the HTO stage, nearly 99.4% of the initial mass of the fuel is lost, leaving behind an ash residue that mostly contains the heavy metals.

Combustion parameters like initial decomposition temperature (T_{in}), peak temperature (T_{max}), and burnout temperature (T_b) help in identifying the important stages associated with the combustion of a fuel and aid in combustor design. T_{in} represents the initiation of weight loss and is defined as the temperature at which the rate of weight loss reaches 1 %/min [42]. T_{max} is the temperature at which the rate of reaction (rate of mass loss) is maximum. T_b represents the temperature at which the fuel oxidation is completed, and it is taken as the point when the rate of mass loss falls to 1 %/min after T_{max} is crossed. The values of these combustion parameters discussed above for HFO combustion are presented in Table 3 along with the temperature ranges associated with the LTO, FD and HTO stages.

3.3 Kinetic Analysis

In this work, the distributed activation energy model developed by Miura and Maki [43,44] was used to determine the kinetic parameters of HFO oxidation and decomposition. This model was chosen over other widely used models by Friedman [45], Kissinger-Akahira-Sunose (KAS) [46] and Ozawa-Flynn-Wall [47] as these 'model free methods' do not require the assumption of any kinetic model and can only provide the activation energy. In contrast, the Miura and Maki model can provide both the kinetic parameters, i.e. activation energy and pre-exponential factor, with

which the TG profiles can be re-plotted and compared with the experimental data. Also the pyrolysis and combustion of HFO is a complex phenomenon occurring in many stages, as shown by the TG/DTG plots, and the activation energy cannot be expected to be constant. The Miura and Maki model can be used to obtain variable kinetic parameters with changes in the reaction degree. For these reasons this method has gained wide acceptance due to its simplicity and has been successfully applied to analyze heavy oils [48]. The model assumes that the overall reaction rate is approximated by a single first order reaction, given by,

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

where α is the degree of conversion, T is temperature, β is heating rate, E is activation energy and A is pre-exponential factor. The degree of conversion α , is defined by,

$$\alpha = \frac{m_t - m_f}{m_i - m_f} \quad (2)$$

Where m_i , m_t , and m_f are the initial, in process and final mass weight of the sample oxidation or decomposition process.

Taking the logarithm of Eq. (1) gives,

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln[A(1 - \alpha)] - \frac{E}{RT} \quad (3)$$

The plot of $\ln(\beta d\alpha/dT)$ as a function of $1/RT$ at the same α gives the apparent value of E and A for $\beta = 5, 10$ and 20 °C/min. The values are sensitive to the linearity relation of $\ln(\beta/T^2)$ versus $1/T$, and in ideal conditions the regression coefficient, R^2 is 1. In most cases of experimental data, R^2 is less than unity and therefore only the values with $R^2 > 0.96$ were utilized.

Figs. 3 and 4 show the apparent value of E as a function of conversion degree for HFO combustion in air and pyrolysis in nitrogen, and the TG curve at $\beta = 10\text{ }^{\circ}\text{C}/\text{min}$ is used as the reference temperature range to make clear comparison. It is seen that the apparent activation energy for HFO combustion have three distinct values that are corresponding to the three periods in the DTG curve. At the end of the LTO stage, the conversion degree is about 0.42, and E grows slowly to reach a peak value of 275 kJ/mol. In the FD stage, the conversion degree range is from 0.42 to 0.7, and E grows rapidly to reach a peak value of 380 kJ/mol. In the last HTO stage, the values of E changes to about 100 kJ/mol with certain fluctuations. The difference of the apparent activation energies between these three stages indicates the presence of three characteristic reactions in the combustion processes. The E values in Fig. 4 for HFO pyrolysis shows two characteristic stages. In the first stage, the conversion degree is about 0.4, and E grows gradually from 50 to 110 kJ/mol. In the second stage, E grows to a plateau of 240 kJ/mol. In particular, the E values close to $\alpha = 1$ jumps rapidly to about 350 kJ/mol because for these points $R^2 < 0.98$ and the kinetic values are sensitive to the linearity relation.

Using the kinetic parameters obtained above, the TG profiles were reproduced by Eq. (1) and the results are compared with the experimental data, as shown in Figs. 5 and 6 for HFO combustion and pyrolysis, respectively. It is seen that the model prediction are in good agreement with experimental results for all heating rates. This confirms the validity of the adopted modeling in describing HFO combustion and pyrolysis.

3.4 FTIR results

When the FTIR technique is complemented with a TG apparatus, useful information can be obtained about the composition of the evolved gases. A number of typical compounds can be identified by their characteristic absorbance bands. As a result, this technique was used to identify and measure gaseous compounds present during HFO pyrolysis and combustion. Fig. 7 shows a three-dimensional (3D) FTIR spectra of the gases evolved during the combustion of HFO at a temperature range of 50 – 1000 °C at the different heating rates. The temperature range discussed is the temperature of the TG furnace from where the gases are swept to the IR cell by a carrier gas. The spectra is represented in terms of absorbance corresponding to the vibrational modes of the various functional groups and bonds present in the gases obtained at different temperatures versus the wavenumbers. Observing the 3D plot parallel to the temperature axis allows the analysis of the IR peaks obtained for fixed wavenumbers, and inspecting the plot parallel to the wavenumber axis allows the analysis of the IR peaks corresponding to the evolved gases at different temperatures. Fig. 7 shows that as the temperature increases, the intensity of the absorption peaks (at various wavenumbers) increases due to an increase in the total amount of evolved gases. It reaches a maximum at a temperature of 531, 565 and 610 °C for heating rates of 5, 10 and 20 °C/min, respectively. At higher temperatures (> 700 °C) the intensity of the absorption peaks decreases steadily because most of the fuel is consumed, as evident from the TG/DTG curves. Fig. 8 shows the 3D plot of the FTIR spectra of the gases obtained during the pyrolysis of HFO. As the temperature increases, the intensity of the peaks increases and reaches a maxima at 460, 473 and 482 °C at heating rates of 5, 10 and 20 °C/min, respectively

Analyzing the FTIR spectra in Figs. 7 and 8 parallel to the wavenumber axes shows the presence of peaks at different wavenumber regions, each corresponding to specific chemical

bonds. The characteristics IR bands selected in this study and their assignments are shown in Table 2. The assignments were made after evaluating the spectra from the NIST database [49] and other works [13–17,22–24,26,27]. Fig. 9a shows the FTIR spectra of the gases obtained during combustion of HFO at 565 °C where the maximum intensity was observed. Peaks in the band of 4000 – 3500 cm^{-1} corresponding to stretching of O-H bonds clearly denote the presence of water vapor (H_2O). Peaks in the region of 2400 – 2224 cm^{-1} and 2180 – 2108 cm^{-1} shows the presence of asymmetric and symmetric stretching of C=O bonds, respectively. This confirms the presence of CO_2 and CO in the evolved gases. Pollutant gases such as NO and SO_2 were also assigned in the spectra, which are formed due to the oxidation of nitrogen and sulfur content in HFO. Fig. 9b shows the FTIR spectra of the gases obtained during the pyrolysis of HFO at 473 °C at a heating rate of 10 °C/min and the different peak assignments. Due to the absence of an oxidizing environment, HFO degrades into various hydrocarbon species (or functional groups). For example, this clearly shown by the presence of peaks in the region of 3050 – 2850 cm^{-1} , corresponding to vibrations due to C-H stretching, and in the region 1700 – 1500 cm^{-1} due to C=C stretching.

The intensity of the absorption peaks, which is a measure of total evolved gases detected by the IR spectrometer, varies with the temperature of the TGA furnace and usually corresponds with the weight loss stages seen in the thermo-gram. Gram-Schmidt (GS) curves provide additional information through the plots of the total evolved gases at different temperatures, as shown in Fig. 10. As expected, the GS curves are consistent with the weight loss shapes seen in the DTG curves (see Figs. 1 and 2). Fig. 10a shows the presence of three peaks at 379 °C, 455 °C and 569 °C at a heating rate of 10°C/min and three peaks at 406 °C, 481 °C and 612 °C at a heating

rate of 20 °C/min. These three peaks correspond to the LTO, FD and HTO stages discussed above. The peaks seen in the GS curves are slightly shifted towards higher temperature because of the delay arising from transferring gases from the TGA furnace and detection in the IR cell. In addition, some low volatility gases may condense inside the transfer line only to vaporize at a later time when the temperature of the furnace is higher than when the gases were originally sampled. Fig. 10b shows the GS curves recorded during the pyrolysis of HFO at heating rates of 10 and 20 °C/min. The GS curves are consistent with the DTG curves in capturing the two devolatilization stages. Peaks corresponding to the point d_1 in the GS curves at 248 °C and 269 °C for heating rates of 10 and 20 °C/min, respectively, are readily observed. Point d_2 is seen at a temperature of 468 °C and 491 °C or heating rates of 10 and 20 °C/min, respectively. Point's d_1 and d_2 are seen at slightly higher temperatures (nearly 15 to 20 °C) in the GS curve because delay in transferring the gases from the furnace to the cell. At higher temperatures (>800°C), some gases are detected because condensed gases continue to re-evaporate as a consequence of the flow of the carrier gas.

3.4.1 Analysis of pollutant gases

The emission of gaseous pollutants like CO₂, CO, SO₂, NO and H₂O at different temperatures during the combustion of HFO at the heating rates of 5, 10 and 20 °C/min was studied. The emissions data gathered from the combustion of a fuel provides valuable information in designing a combustor and also help in conforming to regulations. For example NO emissions are temperature dependent whereas the final SO₂ emissions from a combustor are not influenced by temperature [45]. At high temperatures, NO emissions increase while reducing the combustor temperature tends to decrease the fuel burnout and hence overall efficiency.

Therefore, information relating the dependence of emissions on temperature, as provided in the present work, help establish operating conditions that can reduce emissions without compromising on efficiency. An HFO fired furnace shows significantly higher pollutant emissions of CO₂, SO₂, SO₃, NO and soot when compared with a furnace co-fired with natural gas/heavy fuel oil or natural gas alone [50].

3.4.1.1 CO₂

The absorbance peak corresponding to 2361 cm⁻¹ was selected to represent CO₂. Fig. 11a shows the emission of CO₂ during the combustion of HFO at different TGA furnace temperatures. The magnitude of the absorbance peaks are represented in terms of relative absorbance (*i.e.*, absorbance/mg of HFO). At 10 °C/min, the emission of CO₂ rises gradually and at a temperature of 190 °C the intensity increases more rapidly corresponding to the 'step 1' of the devolatilization in the LTO stage. This is probably due to the breakage of the alkyl side chains of the molecules in HFO. At 388 °C, corresponding to the point d₂, a CO₂ peak is observed indicating the maximum de-volatilization rate. The intensity then falls and reaches another minor peak at 458 °C. This is when the FD stage ceases and the HTO stage begins, peaking at a temperature of 575 °C. The peak in the HTO stage, which is dominated by char burning, is more prominent than others. This is because some of the evolved gases at LTO and FD may get oxidized in the HTO stage or there could be a lapse in CO₂ detection in the IR cell. The intensity of CO₂ absorbance falls rapidly indicating the end of combustion as nearly 95% of the mass of the fuel is burnt by the time it reaches 600 °C. When the heating rate is 20 °C/min, three peaks are observed (at 410 °C, 485 °C and 615 °C) and that correspond with the LTO, FD and HTO stages. The absorbance values for CO₂ were significantly higher, more than 50 times when compared with the other gases analyzed

in the present work. In both the cases, a very small amount of CO₂ is detected by the IR cell even after 800 °C when almost 99 % of the fuel is burnt. This is most likely due to the condensed gases inside the transfer line evaporating to the IR cell.

3.4.1.2 CO

Fig. 11b shows the CO emission profile of HFO combustion at the different furnace temperatures. The spectra shows a distinct peak at 2119 cm⁻¹ representing C=O stretching that was assigned for CO. The initial formation of CO is not seen until the fuel reaches a temperature of 275 °C when the alkyl side chains containing carbonyl groups (-CHO) undergo decarboxylation reactions. Minor CO peaks at 335, 354 and 375 °C corresponding to the LTO stage are observed when the heating rate is at 5, 10 and 20 °C/min, respectively. The CO absorbance slightly dips and begins to increase beyond 400 °C, which could be attributed to secondary reactions like thermal cracking of the tar released from the fuel. The CO absorbance reaches a peak value at 530, 565 and 610 °C for heating rates of 5, 10 and 20 °C/min respectively, when the rate of char burning is at its maximum in the HTO stage. The CO emission then reduces drastically until there is no CO present in the gases. There is no CO detected in the IR cell beyond 750 °C for all heating rates. The concentration of CO present in the evolved gases is approximately 50 times lower than that of CO₂ at all times.

3.4.1.3 SO₂

Our previous work [7] showed that 52% of the molecules present in HFO occur as S₁ class species (one sulfur atom containing hydrocarbons) and 21.4 % of the molecules are of S₂ class. Sulfur containing oxygenated hydrocarbons (OS₁ and OS₂) of up to 4% were also found in the HFO

sample. This shows that the sulfur present in the fuel is well distributed throughout the volume of the fuel. Nearly 95% of the sulfur in the fuel is oxidized to SO_2 and the remaining to SO_3 , both of which are harmful pollutants [51]. The presence of heavy metals like vanadium which are abundant in HFO tend to act as a catalyst for sulfur oxidation [2,5]. Fig. 11c shows the emission of SO_2 gas during the combustion of HFO at the different temperatures. The FTIR spectra showed a single peak for SO_2 at 1342 cm^{-1} . The SO_2 emission is first seen at $300\text{ }^\circ\text{C}$ after ‘step 1’ of the devolatilization is over. This is because sulfur in the fuel is usually released as H_2S around $270\text{ }^\circ\text{C}$, as shown by Levy *et al.* [52]. The SO_2 emission continues to increase with the increase in temperature peaking at 550 , 575 and $620\text{ }^\circ\text{C}$ for heating rates of 5 , 10 and $20\text{ }^\circ\text{C/min}$, respectively. The peaks for SO_2 disappear at a temperature of $800\text{ }^\circ\text{C}$ and above.

3.4.1.4 NO

The peak at 1762 cm^{-1} was assigned for NO and the emission of NO during the HFO combustion at different temperatures is shown in Fig. 11d. The HFO sample contains 0.31 mass % of nitrogen that acts as a source for fuel bound NO [53]. Studies have shown that fuel nitrogen in heavy fuel oils is mostly present in the form of hetero-cycles similar to the components of coal. During devolatilization, the organically bound nitrogen is released as intermediate species, which thermally decompose into radicals like HCN or NH_3 [54]. These radicals react with other free radical species (like OH and O) to form NO. Fig. 11d shows that NO formation starts around $250\text{ }^\circ\text{C}$ and increases steadily. NO formation peaks at 555 , 580 and $610\text{ }^\circ\text{C}$, which corresponds to the peak points of DTG curves in HTO stage for heating rates of 5 , 10 and $20\text{ }^\circ\text{C/min}$, respectively. NO formation is observed well into the HTO stage, showing that some of the nitrogen is char-bound that does not evolve during devolatilization. NO formation reduces significantly after the peaks,

and further increase in temperature does not result in any thermal NO formation which is relevant only at much higher temperatures [55].

3.4.1.5 H₂O

Fig. 11e shows the release of water vapor during HFO combustion at 3566 cm⁻¹ which has been assigned to represent H₂O. No peaks are observed around 75-125 °C, indicating the absence of moisture in the HFO sample. The formation of water vapor is first observed around 160 °C when the devolatilization reactions corresponding to 'step 1' are midway and the volatile gases oxidize to form H₂O and CO₂ gases. The H₂O absorbance increases in magnitude as the temperature rises and a local maximum associated with the LTO stage is observed at a temperature of 360, 384 and 410°C for heating rates of 5, 10 and 20 °C/min respectively. H₂O release increases with increasing temperature due to char burning and peaks at 550, 570 and 620 °C for heating rates of 5, 10 and 20 °C/min, respectively, and then falls steadily.

3.4.2 Analysis of functional groups

The composition of the gaseous products released during the pyrolysis (in N₂ atmosphere) of HFO was analyzed in terms of functional groups like aromatics, alkenes (=CH₂), alkanes and carbonyl groups (aldehydes and ketones). Analysis of the formation of different functional groups is necessary for the comprehensive understanding of the thermal degradation pathways. During gasification it is desirable to increase the yield of certain gases due to their higher heating values or other favorable properties. At certain fixed temperatures, some gases are released more than others and such information could be used to increase the yield of desirable gases or reduce those with high affinities for pollutant formation. For example, some compounds such as

1,3-butadiene (an alkene) and benzene (an aromatic) act as soot precursors [56]. Also, some functional groups, such as polycyclic aromatic hydrocarbons (PAHs), are released during the incomplete combustion or pyrolysis of hydrocarbon fuels, have been proven to be carcinogenic in nature [57]. Detecting and understanding their release is of enormous importance to limit their emission into the atmosphere.

3.4.2.1 Aromatics

Fig. 12a shows the evolution of the aromatic groups during the pyrolysis of HFO at the various heating rates; the IR peak at 3076 cm^{-1} were assigned for the aromatics. A significant portion of HFO is aromatic in nature as shown in previous work [1,7]. Most of the aromatic carbons are non-protonated emphasizing the presence of fused rings or a high degree of alkylation. The surrogate molecule of HFO is a 53 C molecule, containing 3 aromatic rings, in which 2 of them are fused together and the other ring is fused with a naphthenic ring. Aromatic groups are less reactive compared with the other functional groups [58]. The absorbance peak for aromatic C=C stretching (benzene skeleton) is first detected around $265\text{ }^{\circ}\text{C}$ showing that a small amount of the aromatic groups maybe released even during devolatilization. As the temperature increases, their magnitude increases reaching the peak at a temperature of 458, 473 and $482\text{ }^{\circ}\text{C}$ for heating rates of 5, 10 and $20\text{ }^{\circ}\text{C/min}$, respectively. Further increase in temperature reduces the release of aromatics, and after $750\text{ }^{\circ}\text{C}$ there is minimal signal detected. However, a small value is still detected even after $750\text{ }^{\circ}\text{C}$, which could be the condensed aromatics in the transfer line re-evaporating due to the flow of the carrier gas.

3.4.2.2 Alkenes

HFO contains a small fraction of alkene groups ($=CH_2$). Alkenes detected during combustion and pyrolysis are likely formed by the scission of the bond between the alpha carbon and the aromatic ring as demonstrated by Hillier et al. [11,12]. Fig. 12b shows the evolution of alkenes during the pyrolysis of HFO. The IR absorbance peak at 3018 cm^{-1} was assigned for the alkene functional group. Alkenes are detected as early as $125\text{ }^\circ\text{C}$ due to the breakage of the alkyl chains from the aromatic rings during the devolatilization. The alkene formation reaches a peak at 454 , 475 and $485\text{ }^\circ\text{C}$ with heating rates of 5 , 10 and $20\text{ }^\circ\text{C/min}$, respectively, corresponding with 'step 2' of the devolatilization process. The alkene signal then decreases with further increase in temperature. The absorbance values recorded for alkenes are 4 – 5 times higher compared to the aromatic groups released during pyrolysis.

3.4.2.3 Alkanes

Alkanes ($H-C-H$) can be formed during pyrolysis of HFO by subsequent hydrogenation of the alkenes formed by the elimination of the alpha bond. They can also be formed directly by scission of the bond between the alpha and the beta carbon [11,12]. Fig. 12c shows the evolution of the alkanes ($H-C-H$) during the pyrolysis of HFO at the various heating rates. The peak of formation is noticed at 460 , 473 and 484°C for the heating rates of 5 , 10 and $20\text{ }^\circ\text{C/min}$, respectively, after which their evolution decreases. However, some alkanes are continuously detected at the IR cell even after the furnace reaches $800\text{ }^\circ\text{C}$ and this is due to condensed gases on the transfer line.

3.4.2.4 Carbonyl groups

Ketonic groups (RC(=O)R') that are formed due to the thermal degradation of HFO isomerize into aldehyde groups (H-C=O) and usually are not detected [22] in the IR spectra. These groups together comprise the carbonyl group and are assigned the IR absorbance peak at 1705 cm^{-1} . Fig. 12d shows the evolution of the carbonyl group from the pyrolysis of HFO. The peak formation of the carbonyl group is seen at a temperature of 450, 461 and $468\text{ }^{\circ}\text{C}$ for heating rates of 5, 10 and $20\text{ }^{\circ}\text{C/min}$, respectively, which corresponds well with 'step 2' of the devolatilization process.

4. Conclusion

This paper presented a TGA-FTIR study of the pyrolysis and combustion of heavy fuel oil at heating rates of 5, 10 and $20\text{ }^{\circ}\text{C/min}$. For the combustion case, the TGA results showed the presence of three stages namely the low temperature oxidation (LTO), fuel decomposition (FD) and high temperature oxidation (HTO). Two devolatilization stages 1 and 2, (associated with peaks d_1 and d_2) were identified during the LTO stage. In 'step 1', low boiling volatiles like alkanes and alkenes were evolved and high boiling volatiles comprising the aromatics evolved during 'step 2'. Peak d_1 was found at 196, 211 and $236\text{ }^{\circ}\text{C}$ for heating rates of 5, 10 and $20\text{ }^{\circ}\text{C/min}$, respectively and the peak d_2 was seen at temperatures of 373, 385 and $408\text{ }^{\circ}\text{C}$ for heating rates of 5, 10 and $20\text{ }^{\circ}\text{C/min}$, respectively. During the pyrolysis of the fuel, two devolatilization stages were observed, but the peaks (d_1 and d_2) moved towards higher temperature. A kinetic analysis was performed and the TG profiles of HFO combustion and pyrolysis were reproduced from the kinetic parameters calculated from the distributed activation energy model. Evolved gaseous products were analyzed in an IR cell to study the composition of the gases. Pollutant gases (*e.g.*, CO_2 , CO , SO_2 , NO and H_2O) were observed during the combustion of HFO, and the peak emission

values were recorded at furnace temperatures of 530, 565 and 610 °C with heating rates 5, 10 and 20 °C/min respectively, for most of the pollutant gases. The absorbance values of CO₂ was the highest and were 50 times higher than the other gases recorded. During the pyrolysis of HFO, the formation of functional groups such as aromatics, alkenes (=CH₂), alkanes (H-C-H) and carbonyl groups (R-C=O) at different temperatures was also analyzed. The HFO pyrolysis gases were mostly found to contain alkanes/alkenes, and their peak formation was noticed at a temperature of 460, 473 and 482 °C for heating rates of 5, 10 and 20 °C/min, respectively. The information presented here via TGA-FTIR can be useful to understand the role of HFO fuel composition on the combustion process. Furthermore, the valuable information on pollutant emissions can be used to develop chemical kinetic models for HFO surrogates.

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Table 1

Physical and chemical properties of HFO

Property	unit	value	method
density (at 288 K)	Kg/m ³	968	ASTM D4052-11
specific gravity (at 288 K)	no units	0.967	ASTM D4052-11
kinematic viscosity (at 313 K)	10 ⁻⁶ m ² /s	746.5	ASTM D445-12
enthalpy of combustion (at 298 K)	MJ/mol	31.35	ASTM D4868
asphaltene content	mass %	8.2	IP 143
Ultimate analysis			
carbon	mass %	84.35	EPA 440
hydrogen	mass %	10.65	EPA 440
oxygen	mass %	2.29	EPA 440
nitrogen	mass %	0.31	EPA 440
sulfur	mass %	2.39	ASTM D4294-10
Proximate analysis			
moisture	mass %	0.81	[30]

ash content	mass %	0.55	[30]
volatile matter	mass %	84.79	[30]
fixed carbon	mass %	13.85	[30]

Table 2

IR bands assignment

Wavenumber range (cm ⁻¹)	Selected (cm ⁻¹)	Origin	Assignment	References
3500 - 4000	3556	O-H stretching	H ₂ O	[23,24]
3130 - 3070 1600 – 1500	3079	Aromatic C-H bending Aromatic C=C stretching	Aromatics	[13,23,24]
3040 - 3010 1600 - 1680	3018	Alkene C-H stretching Alkene C=C stretching	Alkenes	[12,22,24]
2970 – 2950 2880 – 2860 1470 – 1430 1380 – 1370 2935 – 2915 2865 – 2845 1485 - 1445	2968, 2920	Methyl C-H asymmetric stretching Methyl C-H symmetric stretching Methyl C-H asymmetric bending Methyl C-H symmetric bending Methylene C-H asymmetric stretching Methylene C-H symmetric stretching Methylene C-H bending	Alkanes or alkyl substituents	[11– 13,23,24]
1750 - 1680	1705	Carbonyl group	Ketones & aldehydes	[12,13,23,24]
2400 – 2224	2361	O=C=O asymmetric stretching	CO ₂	[13,17,22– 24,26,27]
2180 – 2108	2119	C=O stretching	CO	[16,24,26]

1762	NO	[26]
1342	SO ₂	[26]

Table 3

Combustion characteristics of HFOs

Characteristic	Heating rate		
	5 °C/min	10 °C/min	20 °C/min
LTO stage	145 – 394 °C	135 – 405 °C	122 – 426 °C
FD stage	394 – 490 °C	405 – 505 °C	426 – 530 °C
HTO stage	490 – 589 °C	505 – 620 °C	530 – 655 °C
Initial decomposition temperature (T_{in})	145 °C	135 °C	122 °C
Peak temperature (T_{max})	541 °C	580 °C	467 °C
Burnout temperature (T_b)	589 °C	620 °C	655 °C

Fig. 1. TG/DTG curves of pyrolysis of HFO at heating rates of 5, 10 and 20 $^{\circ}C/min$. The various stages of mass loss are denoted in the figure and discussed in the main text.

Fig. 2. TG/DTG curves of combustion of HFO at heating rates of 5, 10 and 20 °C/min. The various stages of mass loss are denoted in the figure and discussed in the main text.

Fig. 3. Apparent activation energy vs. (a) conversion degree and (b) temperature relationship determined for HFO combustion

Fig. 4. Apparent activation energy vs. (a) conversion degree and (b) temperature relationship determined for HFO pyrolysis

Fig. 5. Experimental (black) and calculated (red) TG curves at $\beta = 5, 10, 20$ °C /min for HFO combustion

Fig. 6. Experimental (black) and calculated (red) TG curves at $\beta = 5, 10, 20$ $^{\circ}\text{C}/\text{min}$ for HFO pyrolysis

Fig. 7. Three dimensional (3D) FTIR spectral plot of the gases evolved during the combustion of HFO in air at a heating rate of (a) 5 $^{\circ}\text{C}/\text{min}$ (b) 10 $^{\circ}\text{C}/\text{min}$ and (c) 20 $^{\circ}\text{C}/\text{min}$

Fig. 8. Three dimensional (3D) FTIR spectral plot of the gases evolved during the pyrolysis of HFO in N_2 at a heating rate of (a) 5 $^{\circ}C/min$ (b) 10 $^{\circ}C/min$ and (c) 20 $^{\circ}C/min$

Fig. 9. FTIR spectra of the evolved gases obtained at a heating rate of 10 °C/min showing the various assignments during (a) combustion of HFO at 565 °C and (b) pyrolysis of HFO at 473 °C

Fig. 10. Gram-Schmidt (GS) curves of (a) combustion of HFO in air and (b) pyrolysis of HFO in N₂

Fig. 11. Evolution of pollutant gases during the combustion of HFO in air at heating rates of 5, 10 and 20 °C/min. (a) CO₂, (b) CO, (c) SO₂, (d) NO and (e) H₂O

Fig. 12. Evolution of various functional groups during the pyrolysis of HFO in N₂ at heating rates of 5, 10 and 20°C/min. (a) aromatics, (b) alkenes, (c) alkanes and (d) carbonyl groups