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PM FROM THE COMBUSTION OF HEAVY FUEL OILS

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Abstract

This work presents an experimental study investigating the formation and oxidation of particulate matter from the combustion of heavy fuel oil, HFO, droplets. The study includes results from both a falling droplet in a drop tube furnace and a suspended droplet in a heated convective flow. The falling droplets in a heated coflow air with variable temperature path and velocity were combusted and the resulting particles, cenospheres, were collected. To characterize the microstructure of these particles, scanning electron microscopy (SEM), and energy dispersive X-Ray (EDX) analysis were used. The particles were found to have either a porous or a skeleton/membrane morphology. The percentage of particles of either type appears to be related to the thermal history, which was controlled by the heated co-flow velocity. In the suspended droplet experiments, by suspending the droplet on a thermocouple, the temperature inside the droplet was measured while simultaneously imaging the various burning phases. A number of specific phases were identified, from liquid to solid phase combustion are presented and discussed. The droplet ignition temperature was seen to be independent of the droplet size. However, the liquid phase ignition delay time and the droplet lifetime were directly proportional to the initial droplet diameter.

Keywords: *heavy fuel oil, PM, cenospheres*

Nomenclature

D_{cen} : Cenosphere diameter.
 D_d : Droplet diameter.
 D_f : Flame size diameter.
 D_i : Initial droplet diameter.
 DPI: Dots per inch.
 EDX: Energy dispersive X- Ray.
 f : Excitation frequency.
 HFO: Heavy fuel oils.
 IDT: Ignition delay time.
 Nu: Nusselt number.
 PM: Particulate matter.
 Pr: Prandtl number.
 Q: HFO flow rate.
 Re: Reynolds number.
 SEM: Scanning electron microscopy.
 slpm: Standard liter per minute air flow rate.

1. Introduction

The combustion of low-grade fuels as a source of energy has received growing attention again due to the favorable economics. In Saudi Arabia, for example, a significant portion of the energy demand for electricity generation is met through the combustion of heavy fuel oil (HFO) [1]. The reason behind burning HFO rather than conventional light oil is due to its lower production cost and higher availability. The 2015 HFO price and the 2025 predicted price are projected by the change in crude oil prices. The comparison of crude oil prices versus the HFO over the past five years shows that the HFO is approximately 30% cheaper. In 2025, the crude oil projected price is nearly \$83 per barrel, and therefore the HFO is estimated to be \$58 [2]. By the gasification process, the heavy fuel oil is converted mainly into CO and H₂ (syngas). The generated syngas can be used as the inlet feedstock of solid oxide fuel cell or other power generation systems [3]. In addition, the syngas can be used either for enrichment of traditional combustors, or for the generation of electricity by direct combustion [4]. Thus, the gasification process of the heavy fuel oil is

considered one of the solutions to reduce the emission production in the power generation systems [5, 6]. In oil field steam injection boilers, oxy-fuel combustion of heavy fuel oil can be utilized, which allows the usage of both heavy fuel oil and CO₂ resources [7]. The oxy-fuel combustion of heavy fuel oil technology, not only improves the CO₂ capturing but also enhances the utilization of HFO resources. Therefore, this clearly indicates the promising use of heavy fuel oil resources for power generation via different methodologies.

However, the use of HFO as source of energy has been declining since reaching its peak in the late 1970s due to its adverse environmental effects. The formation of particulate matter from the combustion of heavy fuel oils does not only have negative impact on the environment but also may result in fouling and corrosion of heat transfer surfaces inside the boilers and furnaces. Thus, introducing difficulties and high cost of maintenance. Marrone *et al.* [1] believed that this problem is related to the high amount of sulfur and heavy metal impurities into HFO. The solid particulates associated with the HFO exhaust gases result in harmful effects on the environment and human health. Consequently, the International Maritime Organization (IMO) has prohibited heavy fuel oils which contain more than 0.1% of sulfur to be used on ships sailing in the Baltics, English Channel, and the North Sea [8, 9]. Therefore, understanding the HFO combustion characteristics is crucial for marine transportation and power plant equipment such as boilers, furnaces, and gas turbines.

Spray combustion of liquid fuel through a burner nozzle is very commonly employed in practical applications. However, studying the behavior of burning droplet in sprays is challenging due to the difficulty in identifying the thermal histories of various sizes of droplets along the multitude of paths the droplets may take during the burning process [10, 11]. To simplify the process, a variety of single droplet combustion techniques have been used successfully to measure

a range of combustion parameters [12]. Reports relevant to studying HFO combustion go back to the 1950s. These studies can be classified into three main areas: characteristics of general combustion behavior, cenosphere formation, and reduction of pollutant emissions. Most of these studies were conducted primarily through two methods of single droplet techniques as it can be seen by the literature review summarized in Table 1. In particular, the first method was the single falling droplet experiment which was more oriented toward studying cenosphere characteristics and formation [1, 10, 13-18]. The second method was based on a suspended droplet which had an advantage in studying the area of general combustion characteristics covering the burning of the volatile constituents to the solid residue [19-23].

The burning phases of HFO droplets can be divided to a liquid and a solid phase [24, 25]. The liquid phase is more complicated than the solid phase and can be subdivided into two consecutive steps as suggested by Hottel *et al.* [26], namely: a pre-heat sub-phase and flammable combustion sub-phase. Associated with the combustion of heavy fuel oil droplets or sprays, a large number of spheroidal carbonaceous solid particles, with diameters between one and a few hundred of microns, are formed, known as cenospheres [14]. It is known that these cenospheres are formed during the HFO liquid-phase thermal decomposition process, where volatile components at the droplet surface evaporate and form a vapor layer surrounding the droplet [15]. The more viscous, higher molecular weight components remaining at the surface begin to form a shell. With a diffusion flame formed outside the vapor layer, droplet temperature increases, accelerating vaporization, and vapor accumulation inside the shell. Eventually, the vapors inside the forming shell are ejected out through the weakest point on the surface due to the growing pressure, forming the porous structure.

Table 1: Summary of the main findings of the related studies on HFO falling and suspended droplet.

Authors (Year)	Method	Application	Gas temperature	Findings
Falling droplet				
Urban et al. (1992) ^[15] Urban et al. (1991) ^[14]	Free falling droplets through a vertical quartz tube, droplet diameter (200 - 700 μ m).	A stream of isolated heavy fuel droplets was directed through a hole in the center of premixed flat flame burner and the droplets ignited by the burner combustion gases.	1200 - 1700K	The coke formation index for residual oil has been identified. ^[15] The cenospheres formation has been investigated. ^[14]
Moszkowicz et al. (1996) ^[16] Bomo et al. (1984) ^[17]	Free falling droplets through a vertical crystal glass tube placed in an oven, droplet diameter (140 - 200 μ m) ^[16] – (320 - 460 μ m) ^[17] .	A stream of single droplets is obtained using a vibrating membrane to cut the incoming jet stream into an inert environment.	1223 - 1373K	The formation of heavy fuel droplets cenospheres produced by very fast pyrolysis have been studied. ^[16] ^[17]
Marrone et al. (1984) ^[1]	Free droplets generated by mechanically chopping a capillary fuel jet, droplet diameter (260 – 800 μ m).	A stream of single droplets was projected through the center of a premixed flat flame burner, parallel to the flow of the hot post combustion gases.	800 - 1400K	The combustion and coking of isolated free droplets of a residual oil have been studied.
Suspended droplet review				

Ikegami et al. (2003) ^[20]	Suspended droplet on a thermocouple wire with diameter of 0.025mm, droplet diameter (0.9 – 1.52mm).	A single droplet in a microgravity environment suspended (approximately 1–2mm) above electrical igniter.	3.5A current passing through the igniter for 1.6s.	The combustion of single droplets comprised of heavy oil residual have been investigated.
Xu et al. (2002) ^[22] Kobayasi et al. (1955) ^[24]	Suspended droplet on a quartz fiber, droplet diameter (0.6 – 1.8mm) ^[22] - (0.7 – 1.7) ^[24] .	A single droplet suspended inside an electric moving oven generated an atmospheric hot air chamber.	993 - 1183K	The entire process of burning a heavy oil droplet was investigated ^[22] . The combustion of fuel droplets was investigated experimentally by means of motion pictures ^[24] .
Villasenor et al. (1999) ^[19]	Suspended droplet on a filament, droplet diameter (750 μ m).	A single droplet suspended in a highly radiative oxidizing environment where a 1000W tungsten filament lamp is positioned into a hollow furnace displaced 15 mm from the sphere's center.	Maximum heating rate of 1273K/s.	The influence of asphaltene concentration on droplet combustion was assessed using the captive droplet technique.
Marrone et al. (1984) ^[1]	Suspended droplet on a quartz filament, droplet diameter (1 – 1.15mm).	A single droplet suspended (10-15mm) above premixed flat flame burner.	1500K	The combustion and coking of isolated suspended droplets of a residual oil have been studied.
Michael et al. (1967) ^[25]	Suspended droplet on thermocouple beads, droplet diameter (0.7 – 1.5mm).	A single suspended droplet subjected to air streams at atmospheric pressure and high temperatures.	1255K	The mechanism of vaporization and self-ignition of residual fuel droplets was investigated.

Most of the previous investigations were carried out on industrial combustion facilities [10, 11] and concluded that the cenosphere are produced by pyrolysis of the liquid phase with a subsequent carbonization inside the droplets which results in a porous structure of the cenospheres. This was concluded without investigating other parameters related to the thermal path (*i.e.*, time-temperature history) of the droplet, as determined by the velocity of the droplet and oxidizer. The specific focus of this work was aimed at gaining insight into the effects of both co-flow air around the droplets and the thermal profiles along the droplet domain on the cenosphere characteristics, e.g., particle size and morphology, and surface composition. To the authors' knowledge and according to the previous droplet studies listed in Table 1, there is no information in the existing literature in this regard, which is crucial for analytical modeling of the cenosphere formation process in practical applications. Although, worthwhile information has been through the aforementioned studies on droplet combustion (Table 1), there still remain many questions related to the thermal path into which the droplet is admitted. Such information is very important for understanding the emission and particulate matter formation mechanism. In this investigation, two single droplet experiments were performed: a falling droplet combustion through a drop tube furnace and a suspended droplet in a heated convective air stream. In the falling droplet experiments, a string of monodisperse droplets of HFO is released down in a heated air environment, which has its own convective velocity. Two sets of experiments were conducted in this drop tube furnace. In the first set, we kept the flow rate of the co-flow air constant at 130 slpm, while the thermal histories along the path of the droplets was varied by changing the axial temperature profile along the droplet path. In second set, the temperature profile was held constant, but the co-flow air flow rate was varied, altering the residence time in the furnace. The influence of air coflow temperature profiles are discussed in the section 3. Details of the structure and

composition of the collected cenospheres are acquired via scanning electron microscope (SEM), and energy dispersive X-Ray (EDX). In the second experimental setup, the droplet was suspended on the bead of thermocouple and both the temperature and in-situ video imaging of the droplet burning stages were recorded to investigate the droplet burning process.

2. Experimental method.

The droplet combustion experiments were conducted on a sample of Saudi Arabia heavy fuel oil (HFO). The physical properties and elemental composition of the HFO used in this work are listed in Table 2, and more details about the oil physical and chemical properties can be found in the work of Elbaz *et al.*[27], and the quantified average molecular parameters are presented in [9]. For more information, the pyrolysis and combustion of the same HFO sample in nitrogen and air using thermo-gravimetric analysis (TGA) coupled with a Fourier-transfer infrared (FTIR) are presented in [28].

2.1. Falling droplet experiment.

A schematic of the falling droplet setup is shown in Fig. 1a. Preheated HFO was pressurized and fed into the droplet generator, where a string of monodisperse droplets of HFO was generated through a squeezing piezo-electric droplet generator (TSI-MDG100) fixed at the top of a vertical quartz tube of 150 cm length and 13.4 cm inner diameter. The inner tube of the droplet generator terminated in a stainless-steel orifice. High-frequency oscillations of the inner tube, triggered by two piezo-ceramic parts, generated uniform droplets from the fuel orifice. The HFO feed line from the tank to the droplet generator was uniformly heated to 150°C to decrease HFO viscosity. For better control on the temperature profile of the air surrounding the droplets, the air was preheated using an inline heater (Sylvania heater, 8000 Watt), which then flowed through a ceramic honeycomb, eliminating large scale motions before entering the quartz tube. The first 30 cm length

of the quartz tube was insulated, while the rest of the length was positioned inside a hinged tube furnace (Lindberg/blue, HTF55000 series) with three separate heating zones. Air is heated by convection from the wall of the cylindrical quartz tube inside the furnace to well above the auto-ignition temperature of the HFO. The exhaust gases were pumped out at the bottom of the furnace and filtered through a paper filter (20 μm) placed on water-cooled wire mesh to trap the PM.

Table 2: HFO physical properties and elemental composition.

Physical properties	Units	Results
Density at 288 K	kg/m ³	970.5
Specific gravity (60/60°F)	-----	0.9711
Kinematic viscosity at 40°C	cSt	617.740
Compositional data	Units	Results
Sulfur	mass%	3.292%
Asphaltenes content	wt%	8.2%
Vanadium	mg/kg	18.0
Nickel	mg/kg	11.0
Sodium	mg/kg	3.4
Zinc	mg/kg	<1.0
Lead	mg/kg	0.4
Potassium	mg/kg	0.1
Carbon	mass%	85.0%
Hydrogen	mass%	10.89%
Oxygen	mass%	0.030%
Nitrogen	mass%	0.239%
Heating Values	Units	Results
Higher heating value	BTU/lb	18258
Lower heating value	BTU/lb	17255

The HFO droplet diameters were formed and controlled by forcing HFO jet through a small orifice (140 to 200 μm) at the end of the droplet generator. The jet is naturally unstable and will breakup to form drops with a range of sizes. However, with a disturbance in the form of a square wave at the appropriate frequency supplied to the droplet generator reservoir, the jet will breakup into uniform droplets. Because the drop formation rate is equal to the excitation frequency, the drop volume could be estimated as $D_i = [6Q/\pi f]^{1/3}$, where Q is the HFO flow rate, and f is the excitation frequency. The aforementioned equation is accurate for low viscous liquids, thus the

actual droplet size was measured via imaging the actual droplet size downstream the droplet generator. Particularly, by adjusting the HFO flow rate and the excitation frequency of the droplet generator, three initial droplet diameters could be generated: 422, 365, and 291 μm . These diameters were measured based on the average of 1000 droplets diameters measured using a backlight high-speed imaging technique. The magnified high definition video of the droplet was captured at 3000 frames per second, the image in 8-bit grayscale with 300 DPI resolution was processed using a Matlab code to calculate the droplet diameter. Schneider *et al.* [29] showed that the diameter of the liquid jet from the droplet generator and its rupture excitation frequency must be manipulated to avoid the formation of satellite droplets. In these experiments, the range of excitation frequency was between 2.5 and 3 kHz. Due to this restriction, the droplet generator was limited in producing droplets only between 291 and 422 μm . The droplets ignited and burned as they flowed down in the quartz tube. At the exit of the quartz tube, the gas and the solid material were cooled with air and water. The collected particle morphology and surface composition were then determined by SEM and EDX techniques.

Figure 1.

2.2. Suspended droplet experiment

A schematic of the suspended droplet setup is shown in Fig. 1b. A convective air stream is preheated by flowing inside an inline heater (Sylvania heater, F074719, 8000 Watt). To reach the desired convective air temperature, the preheated air flowed vertically upwards through a ceramic honeycomb fixed at the bottom of a quartz tube (of 13.4 cm inner diameter, and 75 cm length) installed inside tube furnace. The air flow rate during the experiments was kept constant at 20 slpm, yielding a velocity of 0.082 m/s based on the air mass flux at the droplet location.

Once the temperature inside the electrical furnace reached the set point, a droplet of HFO suspended on a thermocouple bead was inserted to the centerline of the heated air stream. To form the droplet around the thermocouple bead, the thermocouple stem is attached to a programmed 2-D translation mechanism. The droplet is hung on the thermocouple bead outside the furnace using a micro syringe containing HFO and positioned vertically above the bead of the thermocouple. The syringe contains the required HFO quantity for one droplet, however, due to thermocouple bead effect on the droplet size and HFO traces which may be left inside the syringe, the droplet size was also measured by averaging the high speed droplet images. With the 2-D translation mechanism, the thermocouple and droplet is admitted from a side hole in the quartz tube to the furnace. This arrangement is capable of keeping the droplet at a fixed position inside the furnace, where the droplet imaging inside the furnace does not show a change in the droplet position. In addition, the vertical and radial temperature measurements within 40 mm around the droplet insertion central position, which is large relative to the droplet size, show only ± 2 °C change in temperature profile.

To prevent preheating of the oil droplet during droplet insertion, the thermocouple carrying the droplet was surrounded by an air-cooled shield until reaching the centerline where it was retracted, exposing the droplet to the heated air. A type S thermocouple with a wire diameter of 75 μm supported the droplet and measured the inner droplet temperature throughout the entire combustion process. A NI-114 data acquisition card recorded the droplet temperature data at a 1000 Hz sampling rate. Simultaneously, the droplet was imaged using a high-speed camera (Imager HS) with a backlight view at a repetition rate of 1000 frame/s capturing all phases of combustion. The droplet temperature history and the measurements of the droplet diameter were repeated ten times to ensure repeatability of the thermal histories and minimizing uncertainty.

3. Results and discussion

3.1. Falling droplet results

Two sets of experimental conditions were investigated in the falling droplet experiments. In the first set, the temperature profile of the co-flow air through which the droplets fall is varied. At an air co-flow rate of 130 slpm, three temperature profiles were specified down the centerline of the quartz tube. These are designated as high, moderate, and low temperature profiles, and are shown in Fig. 2a. The initial co-flow temperatures, at the beginning of the insulated section, were measured to be 585 °C, 350 °C and 245 °C for the high, moderate, and low profiles respectively. The profiles were measured along the centerline with a nickel/chromium alloy thermocouple. Droplets, with an average diameter of 291 μm , were released and fell with the heated air, the residence time was around 18 ms. The residence time of a droplet inside the drop tube furnace depends on the initial drop velocity, the gravity, and drag forces between the droplet and air. The droplet velocity at the furnace inlet was calculated from the high speed droplet imaging. Particularly, for the droplet of 291 μm diameter, the droplet initial velocity was around 15 m/s. At these temperature profiles, shown in Fig. 2a and a flow rate of 130 slpm, the air velocity based on the mass flux varied between 0.483 m/s at 585 °C, 0.35 m/s at 350 °C and 0.291 m/s at 245 °C. This indicates that the air velocity is too small relative to the droplet velocity, thus, from the classical computation described in [30], the residence time was estimated. Since the air velocities for all three temperature profiles has a negligible effect on the estimated droplet residence time, the three cases residence times were estimated to be constant around 18 ms.

The residual particulate matter was collected on the paper filter at the bottom of the quartz tube. Particle morphology was determined using a scanning electron microscope (SEM), operating at 5 kV. The different axial air temperature profiles resulted in different particles morphologies as

shown in Fig. 2b. The high-temperature profile led to the formation of shell type cenospheres (top left of Fig. 2b), this cenosphere morphology has been observed before in [10, 14], while bead cenospheres with cellular structure (bottom of Fig. 2b) were formed in the low-temperature profile case. A transition between these two cenospheres morphologies was obtained at the moderate temperature profile (top right of Fig. 2b). It is obvious that the thermal path into which the droplet is admitted is crucial for the burning of the droplet and hence the collected particle morphology. The temperature history affects the heat transfer to the droplet. For simplification, the convective heat transfer analysis to the droplet in the regime of forced convection to a sphere is considered and governed by Nusselt number, Nu . Nusselt number is related to the flow Reynolds number, Re , and Prandtl number, Pr , by the following equation [31]: $Nu = 2 + 0.6 Re^{1/2} Pr^{1/3}$. Considering the air properties and velocity at the initial temperature at the top of the drop tube furnace of the three temperature profiles, Fig. 2a, and at the droplet diameter of $291\mu m$, the heat transfer to the droplet was estimated. Normalizing the heat transfer to the droplet at moderate and low temperature profiles by the heat transfer at the high profile, values of 47% and 22 % are shown, respectively. This indicates that the heat transfer to the droplet is the main factor affecting the rate of thermal decomposition. This may lead to the sudden increase of the droplet temperature; influencing the PM morphology.

Figure 2.

For the high temperature profile, with the high heat transfer to the droplet, the volatile components at the droplet surface and those that diffuse from inside to the droplet surface initially evaporate and form a diffusion flame. The initial rate of the temperature rise of the droplet surrounded by the flame leads to cracking reactions and local formation of solids which accumulate on the droplet surfaces. The loss of the lighter species leads to an increase in the

viscosity and formation of an outer shell. This shell then inhibits the diffusion of the volatile components from the interior. However, with increasing temperature from the surrounding diffusion flame, additional volatile components are vaporized and this results in an increase of the interior pressure. This elevated pressure helps the vaporized components escape through the weakest points within the shell. Ejection of the vaporized lighter components will continue to create more holes and fissures at the surface until all of the volatile components are gone, resulting in the formation of a tarry coke particle. Thermal decomposition of this tarry coke liberates lighter volatiles and resulting in the formation of carbonaceous residues. After all the volatile components have burned and the residue has formed, later the surface tension causes contraction of the shell, this is noticed in the suspended droplet investigation. This indicates that the rate, at which the droplet temperature increases, is the significant factor affecting the cenosphere formation. It was noticed that, when a fuel produces cenospheres, each droplet gives one cenosphere along with an occasional formation of carbon soot particles of less than 1 μm size.

The detailed structures of the collected particles are shown in Fig. 3, where a length scale and magnification are given at the bottom of the figure. Figure 3 shows the typical cenosphere morphologies collected at the bottom of the falling drop facility. The same morphologies have been observed in previous works [1, 13, 14, 18], as well as the modeling work presented in [32]. The cenospheres collected are of a uniform size, as illustrated in Fig. 3a, the particles have a smaller diameter relative to the initial droplet diameter. Most of the particles contain only large blowhole from two sides with several smaller holes on the shell surface. The observed porosity of the particles (Figs. 3b –c) is due to opening voids and pores, as burn out progresses and the lighter constituents of the oil abruptly flow out from inside the droplet. In Fig. 3b, the shell appears to be smooth but pitted with many small pores on the order of a view micrometers in diameters (see the

enlarged image to the right of Fig. 3b). Cenospheres with more porosity are shown in Fig. 3c, and one can notice a sponge-like foam structure. With microscopic examination (image to the right of Fig. 3c) one can see that a somewhat rough, flaky, and layered surface is formed with cavities and holes. The internal surface of a shell and the structure of the shell walls visible through a broken cenosphere is shown in Fig. 3d, where the shell thickness is nearly 12 μm . The ratio of the outer to the inner diameter of the shell appears to be in the order of 1.2-1.3. It is clear that within the shell thickness, it has small cavities and they do not necessarily penetrate to the surface; this may be due to internal evaporation within the shell or it could just be the tip of a larger void. The images in Fig. 3 illustrate the complexity of the formed shell structure.

The effect of the asphaltene content on the ratio of the cenosphere shell diameter, D_{cen} , to the initial droplet diameter, D_i , is shown in Fig. 4. In this plot the ratio of D_{cen}/D_i from the current experiment (where the asphaltene content is 8.2 % by weight (as shown in Table 2), as well as the previous data from the literature [1, 11, 13] are presented. There is no data available in the literature for asphaltene content in the range of 5.2 to 10%, and our results help fill in this gap. All the data show approximately linear correlation between the asphaltene content and D_{cen}/D_i , which shows $D_{\text{cen}}/D_i = 0.15$ at zero asphaltene content.

Figure 3.

Figure 4.

In the second set of experiments, the temperature profile was kept constant at the above described moderate profile (Fig. 2a), and the air flow velocities were varied as 0.08, 0.134, and 0.243 m/s, with a droplet initial diameter of 291 μm . The collected particles illustrate the foam morphology as shown in Fig. 5. As indicated, these particles are significantly larger than the initial droplet diameter, and larger than the shell cenospheres type. The morphology of these foam

particles show no blowholes, as seen in the shell cenospheres; however, many bubbles are observed, indicating the existence of vapor pockets. These vapor pockets blow out the viscous liquid fuel at the surface leading, to the formation of bubbles with very thin membranes. These bubbles stick to each other forming the skeleton bounding the bubbles (the dark lines in the SEM images).

These results indicate that the temperature history (and consequently the initial heat transfer to the droplet) around the droplet plays a significant role during the evolution of the particle morphology. The lower the temperature history of the droplet, the higher the probability of the bead formation morphology. The foam structure of these particles is similar to those observed in the burning of char particles [33]. Moreover, similar to skeleton/membrane morphology was observed the combustion of biomass (oak) oil [34]. Also, a local gradient in the surface tension may lead to the formation of these cellular structure, where the multi-component nature of the heavy fuel oil may lead to the formation of such local gradients.

To gain more knowledge about this foam structure, rarely investigated before, EDX was applied to determine the local chemical composition of different features of this morphology. EDX elemental composition of the foam particles (formed from a droplet with an initial diameter of 422 μm and air flow velocity of 0.134 m/s) surface contains information to about 1 μm depth. As Fig. 5d indicates, there is significant variation in the sulfur content between the skeleton feature and the membrane feature. It is clearly shown that the material is primarily a lightly oxidized frozen carbon liquid with an enrichment of sulfur. Also, there is a negative gradient in sulfur from the cell to the darker regions bordering the cells. On the other hand, as shown in Figs. 5a-c, increasing the air flow velocity leads to a decrease the foam particle diameter. This is attributed to the shorter

residence time and the higher shear rate at the droplet surface (it was noticed more soot particles are formed at the high air flow velocity, shown in Fig. 5c).

The effect of the flow velocity on the foam particle size is shown in Fig. 6 for different initial droplet diameters. As seen in this figure, a linear decrease in the bead diameter with increasing air flow velocity is evident. Also, it is obvious that at the same air flow rate of 90 slpm, the larger the initial droplet diameter, the larger the formed bead diameter. These results provide a more heuristic approach of well-defined boundary conditions single droplet HFO combustion. The current observed two PM morphologies were found in the exhaust of spray combustion facility [11]. However, it was not possible in spray combustion to isolate and track the myriad of the individual droplet path, thus, it was difficult to interrupt their results.

Figure 5.

Figure 6.

3.2. Suspended droplet results

3.2.1 Burning steps

A droplet of HFO, with initial diameter of 950 μm , was suspended on the thermocouple bead, and inserted into the furnace where the air flow temperature and velocity was set to 680 $^{\circ}\text{C}$ and 0.082 m/s (20 slpm air flow rate), respectively. Figure 7 illustrates the recorded droplet temperature history starting from the instant of the droplet insertion inside the furnace until coke extinction. The corresponding high-speed images during the droplet burning process are presented in Fig. 8. Based on the droplet temperature history and the high speed imaging, the droplet burning illustrates two different consecutive combustion phases. The first phase is the liquid burning phase, while the second phase is the solid (residue) combustion phase. The liquid phase begins when the droplet is first subjected to the heated air flow (as shown in Fig. 8a), and ends with the formation of the

carbon residue where the solid combustion phase starts (Fig. 8c). The liquid burning phase is composed of two sequential stages, a pre-ignition heating period and a flaming period, shown in Fig. 7. During the pre-ignition period, the droplet temperature increases gradually, where the volatile components diffuse to the drop surface, evaporate, and diffuse out and mix with the surrounding hot flowing air. When the air/vapor mixture within the flammability range reaches the auto-ignition temperature, it ignites, quickly consuming the flammable premixed reactants and leading to a diffusion flame. Due to the flow around the droplet, the diffusion flame is pushed to the downstream side of the droplet, see Fig. 8b.

The droplet ignition is identified by the first sudden increase in droplet temperature, identified by the vertical arrow in Fig. 7. The time between the droplet insertion to droplet ignition defines the ignition delay time of the liquid phase, IDT. The ignition delay time includes the time required for volatilization and transport time of the vaporized fuel to the flammability radius. It can be longer with more viscous fuel due to the difficulty of fractionation process of lighter species from the heavier components in the droplet [22]. Due to the large temperature difference between the flame and the droplet, the heat transfer from the flame to the droplet is increased, thus, the observed steep temperature increase of the droplet after ignition. Later, the temperature profile shows a plateau for a period of 200 ms, and this is associated with bubbling from inside the droplet as shown in Figs 8b-b₁. As a result, the internal heavier components move to the surface and form a viscous shell. Ikegami et al [18] found similar plateau period for a residual oil droplet but in a microgravity environment, and that for a suspended droplet approximately 1–2mm above electrical igniter. Increasing the droplet temperature accelerates the thermal decomposition processes. Due to fractionation, viscosity increases, making transport more difficult, and causing trapped lighter

components to undergo a phase change, resulting in a micro-explosion and resulting in the evolution of more volatile gases for combustion, as shown in Fig. 8b₂.

At the end of the thermal decomposition phase, Fig. 8b₃, the droplet experienced a rapid solidification process which ends with flame extinction, shown in Fig. 8c associated with a decrease in particle temperature. As indicated in Fig. 7, the solid phase can be subdivided into two steps namely: oxidation and smoldering, which ends with extinction of chemical reactions. During the oxidation step, the surrounding air will diffuse to the surface and react heterogeneously with the high temperature solid particle surface. Thus, a significant amount of energy is released and a peak temperature within the solid phase combustion is observed, see Fig. 7. This is followed by the smoldering stage of the particles, as indicated in Fig. 8d, where burning the remaining coke particle continues until the heat losses to the surrounding air exceeds the heat generation, leading to extinction of the solid combustion phase. The residual mass remaining after extinction, composed of unburned carbon and inorganics, is the cenosphere.

Figure 7.

Figure 8.

Figure 9 shows the HFO droplet and flame size histories during the burning phases, *i.e.*, both liquid and solid phases. Both the droplet diameter, D_d , and the flame size diameter, D_f , defined in Fig. 9 were normalized by the initial droplet diameter D_i . As shown during the pre-ignition period, before ignition, the droplet experiences an initial swelling followed by a contraction. At the start the droplet shows a limited amount of swelling and it is believed to be due to the formation of volatiles inside the droplet at a rate faster than they can diffuse to the droplet surface. Due to the large differences in volatility between the wide ranges of molecular weight species in the HFO, with increasing temperature, as these lighter species diffuse away from the surface, leaving higher

molecular weight species, the surface tension on the droplet increases, leading to a contraction of the droplet diameter. This process of swelling and contraction repeats itself during the ignition delay time. At the ignition point, the droplet diameter (D_d) was approximately equal to the initial droplet diameter (D_i). After ignition, heat expansion swelled the droplet sharply because of the greater vapor pressure, and the flame size is seen to follow the droplet size after the ignition. Thus, the droplet size reaches a maximum just before the micro-explosions start to occur. With the steep temperature increase during flame stage, leading to higher rates of vaporization and transport away from the surface of the lighter species, the droplet surface becomes more viscous and exhibits less splashing but more micro-explosive behavior. This leads to a contraction of the droplet size associated with the depletion of the vaporized gaseous. This helps in understanding the previously observed shell porous particle morphology at the high temperature profile in the falling droplet, Fig 3.

Figure 9.

3.2.2. Parametric dependence

To investigate the effect of the air flow temperature on HFO droplet burning, at an air flow velocity of 0.082 m/s, the droplet was subjected to four different air flow temperatures, starting from 600°C and ranging up to 680°C. The initial droplet diameter was approximately 500 μm in each case. This temperature range was carefully chosen after many trials such that auto-ignition temperature is founded. Figure 10 shows the temperature history of HFO droplets exposed to the different air flow temperatures. At the higher air temperatures (*i.e.*, 680°C and 650°C), the droplet temperature history is quite different compared to that of at lower air temperatures (*i.e.*, 630°C and 600°C). One can notice that increasing the air flow temperature increases the recorded peak flame

temperature, and increases the rate of vaporization during the liquid pre-ignition period which facilitates the formation of flammable mixture around the droplet. For the suspended experiment, the temperature field around the droplet is uniform and does not show this axial temperature variation noticed along the axial axis in the falling droplet experiments, Fig. 2a. Clearly the results of the suspended droplet experiment, indicates that the higher air temperature around the droplet, the higher the flame peak temperature, and the steeper temperature increases. Thus leads to a faster thermal decomposition and hence increasing the viscosity of the formed shell layer. This can explain the observed shell cenosphere morphology at the high temperature profile in the falling droplet experiment. Increasing the air temperature increases the flame peak temperature, thus, quicker shell formation and consequently high probability of micro-explosion and the formation of porous.

Figure 10.

On the other hand, the droplet does not ignite at air flow temperatures below 650°C . This implies, in order of ignition to occur both the evaporation rate and the heat transfer rate should be high enough to reach the critical ignition conditions of mixture concentration and temperature. The droplet size affects the ignition delay time of the burning droplet as shown in Fig. 11. This figure depicts the droplet temperature histories of three different droplets with initial diameters of $500\text{ }\mu\text{m}$, $750\text{ }\mu\text{m}$, and $950\text{ }\mu\text{m}$. The air flow temperature was maintained at 680°C , above the auto-ignition temperature found in Fig. 10. The results show qualitatively similar burning characteristics as previously indicated in Fig. 7. One can notice that increasing the initial droplet diameters increases the liquid phase ignition time, IDT, while the ignition temperature is very similar for the three droplet sizes. The plateau in the temperature profile after ignition due to the inner droplet bubbling was remarkable in the large droplet diameter of $950\text{ }\mu\text{m}$. Also, it is obvious that the

increase in the oxidation step time and the smoldering period with increasing the HFO droplet size from 500 μm to 950 μm . This implies that the ignition delay is therefore a function of the time required to heat the droplets to form a combustible mixture around the droplet which is a function in the droplet size.

Figure 12 shows a typical plot of the ignition delay time versus the droplet diameter for 50 repetitive experiments. It shows a linear correlation between the droplet size and the ignition delay time, IDT. Related to the droplet diameter range covered in this work, it was observed that, if the suspended droplet diameter is too small, it may fail to ignite and it may increase the effect of the thermocouple bead on the burning of the droplet. While the very large droplets would fall without ignition, this puts a limitation on the suspended droplet experiment droplet size range. However, the covered droplet diameter range in both falling and suspended studies provide useful information, since the current work is considered a first step for an integrated work which will end by the spray, PM and emission characterization of HFO swirling flames. The covered range of the droplet diameters fits well with the spray droplet distribution of the planned spray air atomized nozzle for the swirling HFO flame. In particular, the distribution of droplet sizes for HFO spray is shown in Fig. 13 with changing the atomization air flow rates. The droplet distribution was measured using a Malvern Spraytec aerosol and spray droplet size analyzer. The droplet distribution at different air atomized flow rate are bimodal with high peaks around centered 750 μm . These high peaks are attenuated with increasing the air atomization flow rates. This indicates that the covered droplet diameters in the current study in both the falling and the suspended experiments represent a reasonable range of the droplet spray size distribution of a practical spray nozzle.

Figure 11.

Figure 12.

Figure 13.

4. Conclusions

Two experimental methods were used to understand the factors governing the morphology of PM resulting from the combustion of Heavy Fuel Oil droplets, namely a free-falling droplet method and a suspended droplet method. In the falling droplet experiments, a string of monodisperse droplets of HFO, ranging between 290 and 422 μm in diameter, was generated and injected vertically in a heated air flowing over a range of velocities to vary the residence time in the tube furnace. The droplets temperature history was varied by changing the temperature of the furnace, resulting in a high, moderate, and low temperature history. Consequently, the particles collected from the bottom of the furnace were exposed to a variety of thermal and reacting environments. Depending on the thermal history and the heat transfer rate to the droplet at the start of the evaporation, the burning droplets result in two different particulate matter morphologies: porous shell morphology and foam-like morphology. To our knowledge, this foam-like and the factor behind its formation was not reported before from the combustion of single droplet HFO combustion. For the shell morphology, the ratio between the cenosphere diameters to the initial droplet diameter was smaller than one, and a linear increase in size with the percentage of asphaltene content. On the contrary, the structure of the foam-like morphology has a skeleton and membrane structure. There was a reduction in the sulfur content in the membrane structure as compared to the skeleton structure, which may contribute to the local gradient in the surface tension and hence the formation of the foam like particles. The foam-like particle had a larger size

relative to the initial droplet diameter, and this size decreased with increasing the heated air flow velocity. In the suspended droplet experiments, a single droplet of HFO was suspended on a thermocouple bead and exposed to a flow of heated air. High-speed images sequences during the combustion process along with inner droplet temperature, droplet size and flame histories were recorded. The results revealed two combustion phases of the HFO droplet: liquid and solid with two separate steps in each phase. The steps are pre-ignition heating, flaming, oxidation, and smoldering. The droplet ignition can only occur if critical conditions are met by the ambient air temperature and the droplet volatile components. The ignition delay time is seen to be a function of the droplet size, where increasing droplet size leads to a longer ignition delay time.

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Figure 1. (a) Schematic of the falling droplet experiment including the fuel line, droplet generator and the drop tube furnace, and (b) schematic of the suspended droplet experiment showing the droplet imaging method as well as the heated flow arrangement.

Figure 2. (a) Three temperature profiles at a flow rate of 130 slpm inside the drop tube furnace, and (b) different particles morphology at each temperature profile for an initial droplet diameter of 291 μm.

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Figure 4. Cenosphere to initial droplet diameters ratio (shell type) versus HFO asphaltene content.

Figure 5. SEM of globules particles with initial droplet diameter 291 μm collected at different air flow rate (a) at air flow rates of 30 slpm corresponds to air flow velocity of 0.08 m/s, (b) at 50 slpm air flow rate corresponds to air flow velocity of 0.134 m/s, (c) at 90 slpm air flow rate corresponds to air flow velocity of 0.243 m/s, and (d) EDX analysis of the bead cenosphere morphology.

Figure 6. The effect of the air flow rate on the bead morphology diameters.

Figure 7. HFO suspended droplet temperature history showing the combustion steps. The droplet initial diameter is 950 μm , and air flow temperature and velocity was set to 680 $^{\circ}\text{C}$ and 0.082 m/s, respectively.

Figure 8. Transient images for the HFO suspended droplet and flames, corresponding to the temperature profile shown in Fig. 7, where the initial droplet diameter was 950 μm .

Figure 9. HFO droplet and flame size histories normalized by the initial droplet diameter. The initial suspended droplet diameter, D_i , of 950 μm . D_d is the droplet diameter and D_f is diameter of the flame surrounding the droplet.

Figure 10. Temperature-time history of HFO droplet with different ambient air temperature, the droplet initial diameter of 500 μm.

Figure 11. Temperature history of the HFO droplets with different initial droplet size, at air temperature of 680°C.

Figure 12. Liquid ignition delay time for different HFO droplet size.

Figure 13. Droplet size and distributions for HFO spray issued from air-atomized nozzle, where T_{air} is the temperature of the atomization air, T_{f} is the temperature of the HFO jet.

Highlights

- We examined the morphology of the particles collected after burning HFO droplets.
- The temperature history has a significant effect on the morphology of the collected particles.
- The droplet ignition temperature was seen to be independent of the droplet size.
- Ignition delay time is directly proportional to the initial droplet diameter.