Factors Affecting Cenosphere Morphology in HFO Single Droplet Combustion

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Abstract

To better understand cenosphere formation and differences between two types of cenosphere morphologies in HFO combustion. Falling droplet combustion inside a preheated furnace was done under a series of conditions and particulate matters are collected from the cooled exhaust gas. By using SEM, morphology of cenosphere samples can be characterized. Results show that air co-flow rate and entrance zone temperature inside furnace are the two main factors that affect the morphology of cenospheres. The morphology changes from porous shell to skeleton-membrane if air co-flow rate decreases from 150 lpm to 30 lpm or if entrance zone temperature decreases from 600 C to 250 C. Relatively high entrance zone temperature and high air co-flow rate are both required to generate cenospheres with porous shell structure.

Keywords: HFO, Cenosphere, Morphology, SEM

1 Introduction

Heavy fuel oil (HFO), as a byproduct of crude oil refining process, has the advantages of low price, wide availability and greater abundance compared to conventional light oil. It has been used in shipping and electric power plants for many years. A significant portion of the energy requirements in many parts of the world is met by combustion of heavy fuel oil (HFO)[1]. However the emission of particulate matters as well as exhaust gases during combustion of heavy fuel oil still remains a concern.
The cenosphere in particular, causes not only environmental problems, but also operational issues such as fouling and erosion of equipment[2]. In size it ranges from several to hundreds of micrometers, larger than soot and accounts for the majority of particle mass generated by HFO combustion.

Based on former researches [3-6], burning of HFO could be distinguished between two phases: first a liquid phase, vaporizing volatile components; and later a solid phase, oxidizing a coke particle formed during the liquid phase. The pyrolysis of fuel components inside the droplet leads to disruptive burning and causes a cenosphere particle to form at the end of the liquid burning phase[7].

Two typical types of cenosphere morphologies could be found in earlier research. The traditional morphology, which is widely observed [8-15], has a carbonaceous and porous shell. A common explanation [8, 13, 16, 17] for how this kind of structure is formed is that volatile components of HFO at the droplet surface evaporate and form a vapor layer surrounding the droplet. As a result, the more viscous components remaining at the surface begin to form a shell, which prevents the emission of vapor formed by the volatile inner components. With a diffusion flame formed outside the vapor layer, droplet temperature increases, accelerating vaporization and vapor accumulation inside the shell. Eventually, the inside vapor ejects out through the weak points of the shell, forming the porous structure.

In the work of Kwack[13], the other type of morphology is mentioned as globules, which can reach a maximum diameter of 600 micrometers, much larger than that of traditional cenosphere. The globules are hollow and contain many bubbles. Seen from outside, the cenosphere is a skeletal structure, attached by a membrane among those frames. This structure was also observed by Wornat[18], from single droplet combustion of pine oil and by Gay [15], during fluidized-bed combustion of bituminous coals.

However, few studies are found which explain this phenomenon, nor has any investigation of the
factors that contribute to these different morphologies. In this paper, focuses are put on finding out those main factors and comparing between two different types of cenospheres. To reach this purpose, cenospheres were collected from the combustion of a stream of uniform HFO single droplets, surrounded by a preheated air co-flow inside a controllable furnace. Scanning Electron Microscope (SEM) was implemented to investigate the physical characteristics of cenospheres.

2 Experimental setup

![Figure 1 Schematic map of experimental apparatus](image)

Figure 1 shows the experimental setup for combustion of falling droplets. For easier piping and ignition, the feeding line of HFO from the pressurized HFO tank to the droplet generator was heated up to 150°C. A stream of uniform droplets is generated at the top of furnace and then goes vertically into furnace. By using different orifices and HFO flow rates, the droplet generator (TSI MDG100 Monodisperse
droplet generator) can generate three different droplet diameters (422 ±23 µm, 365±22 µm, 291±15 µm).

Surrounding the central droplet entrance hole, four holes are uniformly distributed and connected to air, which is heated by an inline heater (Sylvania heater, F074719, 8000 Watt). Before flowing into the vertically positioned quartz tube (134 mm inner diameter and 150 cm length) inside a hinged tube furnace (Lindberg/blue, HTF55000 series), the co-flow air first goes through a ceramic honeycomb; after that, the flow proceeds to the furnace is assumed to be uniform as a result. The tube furnace includes three separate heating zones and individual temperature controllers. With this feature of the furnace, we can adjust the temperature profile inside the quartz tube. Cenospheres are collected from water cooled exhaust gas by paper filter (retention diameter 20 microns) placed on a wire mesh at the end of the exhaust tube and the exhaust gas is sucked away by a vacuum pump.

3 Results

Heavy fuel oil was collected from Shoaiba Power Plant in Saudi Arabia. Asphaltene content of HFO used in Saudi Arabia mostly ranges between 7 wt% to 15 wt% and has sulfur content of 4 wt%[1]. Physical and chemical properties of HFO used in our experiment are shown in Table 1[1]. As it is a byproduct from distillation process of crude oil, it contains nonvolatile components, metals, ashes etc. and has a very high viscosity, which makes it more difficult to pipe HFO compared with other light fuels. In our experiment, uniform heating was applied to keep the HFO feeding line at a stable temperature of 150 C, thus to decrease the viscosity to an acceptable level but without causing decomposition problems before generating droplets.

Table 1 Physical and chemical properties of HFO sample[1]

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Method</th>
<th>Units</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 288 K</td>
<td>ASTM D4052-11</td>
<td>Kg/m³</td>
<td>970.5</td>
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<tr>
<td>Property</td>
<td>Method</td>
<td>Unit</td>
<td>Value</td>
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<tr>
<td>--------------------------------</td>
<td>---------------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>Specific gravity (60/60°F)</td>
<td>ASTM D4052-11</td>
<td></td>
<td>0.9711</td>
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<tr>
<td>Kinematic viscosity at 40°C</td>
<td>ASTM D445-12</td>
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<td>617.740</td>
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### Compositional data

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<th>Substance</th>
<th>Method</th>
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<th>Value</th>
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</thead>
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<tr>
<td>Sulfur</td>
<td>ASTM D4294-10</td>
<td>mass%</td>
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<td>Asphaltenes content</td>
<td>IP 143</td>
<td>Wt%</td>
<td>8.2%</td>
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<tr>
<td>Vanadium</td>
<td>IP 501-05</td>
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</tr>
<tr>
<td>Nickel</td>
<td>IP 501-05</td>
<td>mg/Kg</td>
<td>11.0</td>
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<tr>
<td>Sodium</td>
<td>IP 501-05</td>
<td>mg/Kg</td>
<td>3.4</td>
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<td>Zinc</td>
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<td>mg/Kg</td>
<td>&lt;1.0</td>
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<td>Lead</td>
<td>IP 501-05M</td>
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<td>0.4</td>
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<tr>
<td>Potassium</td>
<td>IP 501-05M</td>
<td>mg/Kg</td>
<td>0.1</td>
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<tr>
<td>Carbon</td>
<td>EPA 440.0</td>
<td>mass%</td>
<td>85.0%</td>
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<tr>
<td>Hydrogen</td>
<td>EPA 440.0</td>
<td>mass%</td>
<td>10.89%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>EPA 440.0</td>
<td>mass%</td>
<td>0.030%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>EPA 440.0</td>
<td>mass%</td>
<td>0.239%</td>
</tr>
</tbody>
</table>

### Heating Values

<table>
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<tr>
<th>Heating Value</th>
<th>Method</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
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<td>Higher heating value</td>
<td>ASTM D4868</td>
<td>BTU/IB</td>
<td>18258</td>
</tr>
<tr>
<td>Lower heating value</td>
<td>ASTM D4868</td>
<td>BTU/IB</td>
<td>17255</td>
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</table>

3.1 SEM analysis

To better understand how the cenosphere looks like and how it forms, SEM (Quanta 600F) was done to give a clear knowledge on cenosphere morphology and its microstructure. From a series of cenosphere samples collected under various conditions, two different types of large particles were
observed, shown in Figure 2. The left cenosphere has many small holes and several large holes on the thick shell, called porous-shell structure. This kind of structure is widely observed in earlier researches. While totally different from the left one, the right cenosphere has a skeletal structure with membrane spreading and connecting between those frames, called skeleton-membrane structure. Some of this type of cenosphere has only one outside membrane layer and hollow inside, while some contain several layers formed by lots of cells, which are also enclosed by membrane and hollow inside. Cenospheres with traditional structure (50~200 micron) are always smaller than initial droplets, while those with skeleton-membrane structure (300~1100 micon) are much larger. Obviously, the mechanisms of forming these two cenosphere types are different. According to our experiment, two main factors, air co-flow rate and initial temperature profile inside furnace, were found to be relating with this morphological difference.

![Figure 2 Two typical morphologies of cenosphere (left: porous shell; right: skeleton-membrane)](image)

1) Effect of air co-flow rate on cenosphere morphology

By adjusting the temperature set point of 3-zone furnace and inline heater, temperature profile along the centerline of furnace was kept consistent with different air co-flow rates changing from 30 lpm to 150 lpm. Temperature profiles were presented in Figure 3 for all these cases. The maximum temperature along centerline can reach about 700C. Initial droplet sizes were also kept the same in these 5 cases with diameter of 291±15 µm. HFO droplets burn inside furnace and smoke was sucked away by a vacuum pump. Cenospheres were collected by filtration of the cooled exhaust gas from
From the SEM results, we found that with increasing air co-flow rate, cenosphere average size and morphology changes gradually. When air co-flow rate is relatively low, like 30, 50, 90 lpm, in each case, cenospheres have uniform size (larger than initial droplets) and have a skeleton-membrane structure, a typical example (291 micron droplet and 30 lpm air co-flow) is shown in the right of Figure 2. Besides, the average size of these cenospheres decreases with increasing air co-flow rate, shown as blue triangles in Figure 8.

However, when air co-flow rate goes up to 130 lpm, the other type of cenosphere (porous shell) begins to appear together with the skeleton-membrane cenosphere (not fully developed), shown in Figure 4. Difference is that those porous-shell cenospheres (less than 200 micron) has a shell structure and are smaller than the initial droplet. The left particle is more like a skeleton-membrane cenosphere but has some difference. From its magnified image, we can see that on the surface, there are lots of wrinkle and not fully developed small bubbles, different from that morphology in cases shown in Figure 8. It is more proper to regard it as a transition product between skeleton-membrane and porous shell. In this case, as more than one type of structures coexist, the size of cenosphere is not uniform. The same goes for the case with 150 lpm air co-flow. At the same time, with increasing air co-flow rate, more ash was observed in the sample.
2) Effect of temperature profile inside furnace on cenosphere morphology

The other factor that found to be affecting cenosphere morphology is the temperature profile inside furnace, especially the temperature at the droplet entrance zone. Shown in Figure 5 are the temperature profiles along the droplet path. In the case that has a high temperature entrance zone (above 600 C), quartz tube outside furnace was removed and droplet generator was moved close to furnace so that droplet goes into a high temperature zone directly without being heated gradually like the other two cases. Cases with moderate (around 360 C) and low (around 250 C) entrance temperature zone were conducted by including the outside quartz tube. Due to heat loss in the outside furnace part and decreased set points of inline heater and furnace, temperature profiles are controlled to be relatively lower in these two cases. Initial droplet diameter was kept consistent at 291±15 µm and air co-flow
rate was kept at 130 lpm.

From SEM results, it is found that with high entrance temperature (presented in Figure 7), cenospheres collected are all with porous shell structure and have uniform size (smaller than initial droplets). With moderate temperature profile (shown before in Figure 4), there is transition particles coexist with porous shell ones. While with low entrance zone temperature (Figure 6), skeleton-membrane structure coexist with porous shell cenosphere. Worth to mention is that porous shell cenosphere always appears with a lot of ash collected on paper filter.

![Temperature profiles inside furnace with different entrance temperatures](image)

**Figure 5** Temperature profiles inside furnace with different entrance temperatures

![Two types of cenosphere collected with low entrance temperature profile](image)

**Figure 6.** Two types of cenosphere collected with low entrance temperature profile
3.2 Factors affecting skeleton-membrane cenosphere size

As observed from SEM images, size of skeleton-membrane cenosphere varies a lot with different conditions, especially air co-flow rate and initial droplet size. Three average initial droplet diameters and three air co-flow rates are investigated. The temperature profiles inside furnace are kept consistent, already shown in Figure 3. The cenosphere diameters of seven cases are plotted in Figure 8. It could be found that average cenosphere diameter decreases with decreasing initial droplet size and increasing air co-flow rate. What’s more, average sizes of skeleton-membrane cenosphere are always larger than the corresponding initial droplet size, regardless of air co-flow rate and initial droplet diameter.
4 Discussions

Based on the previously described experimental results, it is possible to determine that with the same source of HFO, the air co-flow rate and the entrance temperature profile are the main factors affecting cenosphere morphology.

When a droplet enters a high temperature zone, it undergoes several stages before becoming a cenosphere, volatile component evaporation, droplet swelling, and vapor burning surrounding the droplet. Variations in these stages cause different morphology. When the air co-flow rate is high, the oxygen surrounding a droplet is sufficient; this helps to form a diffusion flame in the vapor layer surrounding the droplet (if the surrounding temperature is high enough). This, in turn, leads to formation of a shell, a sudden increase of temperature inside the droplet and acceleration of internal vaporization. Due to the high temperature caused by flame, viscosity decreases greatly and surface tension is insufficient to balance the suddenly increased internal pressure. When pressure inside the droplet reaches a critical value, internal vapor will eject out through weak points on the shell to form a porous-shell structure. The ejected vapor also enhances the surrounding flame. The same occurs
when the entrance temperature is high. Evaporation rate on the surface is fast, which leads to a rapid accumulation of volatile vapor surrounding the droplet at this high temperature zone. And if the oxygen is sufficient, a diffusion flame will quickly occur, helping to form the porous shell structure.

On the other hand, if the air co-flow rate is low (low oxygen concentration), or the entrance temperature is low (low evaporation rate), formation of a diffusion flame will be delayed; which will allow sufficient time for volatile components to evaporate gradually and form many small bubbles inside. But the vapor does not eject out because of a relatively slow temperature increase caused by furnace radiation and convection, rather than a flame. As the droplet goes from a low temperature zone to a relatively high temperature zone, droplet temperature gradually increases and the bubbles become larger. This process is seen as droplet swelling; and the resulting cenosphere is recognized as having a skeleton-membrane structure.

During the formation of cenosphere with a porous shell structure, the ejections of internally vaporized volatile components (micro-explosion) cause many very fine droplets to break up and escape from the main droplet. Fine droplets and ejected vapor burn around the main droplet and form those ashes observed with porous-shell cenospheres. For those conditions that only form skeleton-membrane cenosphere, the sample seems cleaner, containing only cenospheres without much ash.

5 Conclusions
This study focused on the two different cenosphere morphologies, skeleton-membrane structure and porous shell structure, observed in falling HFO droplet combustion experiments. By comparing the cenospheres collected under various conditions with SEM, air co-flow rate and temperature profile inside furnace are decided to be the main factors that affect cenosphere formation. For same temperature profile and initial droplet size, cenosphere morphology changes from skeleton-membrane
to porous shell when air co-flow rate increases from 30 lpm to 150 lpm and skeleton-membrane cenosphere size decreases with increasing air co-flow rate. For same air co-flow rate and initial droplet size, cenosphere morphology changes from porous shell to skeleton-membrane when entrance temperature becomes lower. From these comparisons, it is shown that relatively high entrance temperature and high air co-flow rate are required to be fulfilled at the same time to generate porous shell cenosphere, otherwise it will be possible to find cenospheres with skeleton-membrane structure.

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References