Chapter: Fundamental aspects and applications of ultrasonically induced cavitation in heavy fuel oil (HFO)
with a focus on deasphalting, emulsions, and oxidative desulfurization

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The combustion of hydrocarbons will continue to feed the planet’s growing demand for mobility and power generation over the next several decades, shifting to lower value, more difficult-to-burn fuels while at the same time meeting more stringent emissions regulations. These lower-value fuels include heavy fuel oils and vacuum residuals, which are difficult to burn cleanly due to the presence of asphaltenes, the exceptionally high molecular weight insoluble fractions found in high concentrations in crude oils. In particular, heavy fuel oils (HFO) are widely used fuels in marine and power-generation sectors, and International Maritime Organization’s (IMO2020) promulgation has redistributed the HFO demand and pushed the world’s economy into a new paradigm. We seek solutions for such a complex oil industry paradigm utilizing some state-of-the-art technologies like ultrasonically induced (UIC) cavitation. In the current chapter, we have discussed a roadmap for use of “bottom-of-barrel fuel” with high asphaltene content via UIC-based fuel upgrading, desulfurization, and direct use (emulsions). We expect that a strategy of using UIC for asphaltene modification and water-in-HFO-enabled micro-explosions will significantly impact the combustion of HFO. Furthermore, ultrasonic-assisted oxidative desulfurization (UAOD) can be utilized to remove undesired sulfur to meet marine or power sector requirements. Applications of deasphalting, emulsions, and desulfurization solutions could be for a multiplicity of combustion-driven energy conversion platforms, including compression ignition engines, gas turbines, and boilers.

1. Introduction

1.1. Overview

Despite impressive annual growth rates for renewables and hydrogen as energy vectors, a transition period spanning through 2050 and longer will be needed for the complete transformation of the primary energy mix. Fossil-based resources may continue to dominate energy production needs even as the world shifts to cleaner and low-carbon sources1. Thus, the most crucial aspect of reducing global carbon- and combustion-generated air-pollutant emissions will be to improve the carbon utilization efficiency of fossil fuel applications, from resource recovery to end-use. However, the availability of "easily extractable" and "low-carbon intensity"2 light and sweet crude oil is expected to decrease drastically3,4 as rampant exploitation to meet burgeoning global petroleum demands has led to progressively depleted oil wells worldwide. Therefore, heavy or sour crude oil and the "bottom of the barrel" products--like heavy
fuel oils (HFO), vacuum residue oils (VRO), pitch, asphalts, and petcoke could be increasingly utilized in combustion applications due to their copious availability and low cost. These so-called "opportunity fuels" in petroleum industry parlance are very difficult to burn and produce heavy pollution in the aftermath of the burning. Several strategies have been proposed in the past to use heavy fuels as a source of energy. The most direct usage consists of burning fuels in suitable combustion devices. Another option is to perform gasification to obtain syngas, which is a high-value, cleanly combustible, and multi-industry chemical feedstock. The so-called brown and blue hydrogens are important products of heavy fuel and vacuum residue gasification.

The combustion or gasification of the HFOs and the subsequent particulate matter (soot, cenosphere, and ash) formation processes are mostly driven by the asphaltenic content (up to 15% wt.)\(^6\). In industrial burners, asphaltenes in spray droplets are slow to react until the late combustion stages. Much of the energetic content of asphaltenes is wasted in the formation of carbonaceous cenospheres and their inefficient burnout. The delayed reaction affects the heat release distribution and the heat transfer profile within the combustion zone and subsequent heat transfer events, significantly limiting energy conversion efficiencies for useful power generation. Asphaltenes are defined as the fraction of petroleum that is insoluble in non-polar aliphatic hydrocarbon solvents (e.g., n-pentane and n-heptane). They make up the heaviest category among the SARA (saturates, aromatics, resins, and asphaltenes) fractions. They have highly refractory heteroatoms of sulfur and nitrogen and organometallic porphyrins that are laden with trace metals like vanadium and nickel. In countries where very heavy crude, oil sands, and shale-derived oils are in abundance, asphaltenes are considered untapped fuels. If asphaltenes could be burned more effectively, a quantum leap in combustion efficiency gain would be possible.

Asphaltene breakup, heteroatom removal, and viscosity reduction are critical areas for upgrading and utilization of HFOs\(^5\). Asphaltene can be efficiently burned in water-in-fuel emulsions that offer tremendous benefits of fuel savings and clean-burning during combustion processes. There is evidence that the problematic structure of asphaltenes can be modified by the intense temperatures and pressures associated with the collapse of microbubbles during cavitation\(^12\). This acoustically generated cavitation is both a physical and chemical effect; the enhancement or alteration of chemical reactions using ultrasound, in particular, is known as sonochemistry\(^13\). A few recent review articles have summarized the previous studies on heavy oil upgrading using cavitation methods\(^16\) and industrial developments\(^18\). Our fundamental understanding of cavitation and its impact on asphaltene/fuel upgrading, desulfurization, and emulsification processes has not yet been sufficiently developed. This chapter describes the potential role played by ultrasonically induced cavitation during selected aspects of fuel treatment and direct usage. HFO has been studied here as the representative "opportunity fuel" since it is heavily utilized in the marine and power generation sectors. A brief overview of the economic drivers and industrial advancements in the study of cavitation is provided. Based on our research at KAUST and a review of the literature, we endeavor to provide a path forward for heavy fuel oil upgrading through water-in-HFO emulsions, oxidative desulfurization, and combustion. To that end, we discuss salient aspects of ultrasonic cavitation with a focus on the following themes or applications:

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- Detailed characterization of heavy fuel oil (HFO) and asphaltenes
- Water-in HFO emulsions from ultrasonically induced cavitation (UIC)
- Oxidative desulfurization (ODS) of HFO

To achieve some of the stated goals of the study, we utilized state-of-the-art analytical (Fourier-transform ion cyclotron resonance mass spectrometry, FT-ICR-MS; Nuclear magnetic resonance, NMR), imaging (Cryogenic electron microscopy) and high-speed camera visualization techniques.

1.2. **Environmental and economic drivers**

SOx emissions from ships have been recognized as a significant threat to the global environment because they are highly destabilizing to many extremely vulnerable ecosystems such as the polar region and near-Arctic sea, leading to the International Maritime Organization's IMO2020 mandate of a sulfur cap on marine fuels. HFO (S>3.5%) is now restricted in marine transport since the IMO2020 regulations came into effect on January 1, 2020. Stringent regulations have been imposed on Emission Controlled Areas (ECA). Consequently, HFO demand is plummeting globally, bringing down its price substantially. Diesel or marine fuel oil (MGO) or other low-sulfur fuel alternatives can meet the displaced demand for HFO in the near term. But these fuels are highly processed, creating a significant carbon footprint, and they will lead to a net loss of export revenue for oil-exporting nations like Saudi Arabia. With the current price differential between low-sulfur fuel oil (LSHFO) and HFO reaching $200 per ton, the price of marine transport could skyrocket globally and severely affect international trade. Alternatives like Liquefied Natural Gas (LNG) are seen as future marine fuels but with a decade or more to wait due to a lack of a sufficient bunkering infrastructure. IMO's 2050 strategy to reduce CO₂ emissions by 50% by 2050 (the base year 2008) adds further strategic challenges to marine transport fuel options. LNG's supply chain and current engine technologies are prone to fugitive methane emissions. An ARAMCO-led study estimates that LNG is non-competitive for climate impact in marine applications based on a 20-year global warming potential. Hence, an HFO with sufficiently reduced sulfur content meeting IMO2020 specifications (S<0.5% for Non-Emission Controlled Area (non-ECA); and S<0.1% for ECA) can potentially play a dominant role in marine transport for decades to come. It is important to note, however, that even low-sulfur HFO operations will require onboard carbon capture to be fully compliant with IMO2050.

There are projections of an up to 3 million barrels per day (b/d; 50%) drop in demand for high sulfur HFO in 2020. The displaced HFO from the marine industry is likely to be absorbed by the power generation sector in countries like Saudi Arabia, United Arab Emirates, Iraq, Lebanon, Bangladesh, Sri Lanka, South Korea, Cuba, and Pakistan. Currently, 132 GW of HFO-fired power plants are operational worldwide. Out of these, only 11 GW have
any kind of scrubber to control SOx emissions. With an 88 GW total generating capacity, Saudi Arabia is perhaps the biggest consumer of HFO in the power and desalination sector. The country's energy mix includes HFO, crude oil, and diesel-fired in respective shares of 16.5%, 24.2 %, and 8.6%. In the aftermath of IMO2020, crude and HFO may displace diesel as preferred fuels for power generation. An estimated 10 GW of new HFO fired capacity is slated to be online in 2020 alone. One of the most critical challenges in burning HFO in boilers is its sulfur content. Current CAPEX and OPEX intensive Flue Gas Desulfurization (FGD) units are insufficient in controlling SOx emissions to the levels prescribed by global regulatory bodies. A power plant's overall efficiency is also affected due to cold-end corrosion issues caused by condensation of sulfuric acid in its exhaust systems. Considering the developments mentioned above, desulfurization and clean burning of HFO in steam boilers are essential developments. Indeed, using bottom-of-the-barrel or opportunity fuels like HFO with upgrading and pre-treatments like emulsification and desulfurization will make the sustainable utilization of petroleum resources possible in hard-to-abate sectors like power and marine transport.

1.3. Cavitation-based HFO emulsions

Cavitation-based processes have been used in many engineering applications in the petroleum industry since the 1950s. The earliest application was related to enhanced oil recovery (EOR), which used the ultrasonic wave-powered sono-capillary effect for improved oil percolation in capillaries and in debris destruction by sound-induced mechanical vibrations inside a well. The extraction of oil from oil shale and tar-sands is currently enabled by major installations of cavitation-based units. Several other processes that heavily utilize cavitation-based methods in downstream refineries, such as desulfurization, removal of trace metals, and breaking the naturally formed emulsions of crude oils, have been used.

Cavitation involves the creation, growth, and eventual collapse of microbubbles. The underlying physics of cavitation is as follows. When the bubbles collapse under the influence of external parameters like varying pressure, they produce violent implosions. These implosions create shock waves and very high temperatures (~5000 K) and pressures (~100s of bar) in the vicinity of the site of the microbubbles. Cavitation can lead to the formation of hydroxyl and hydroperoxyl radicals by the splitting of water molecules under some conditions. These implosions are the foundation of sonochemistry or of the physiochemical transformations that are observed during a cavitation phenomenon. Cavitation can be produced either by ultrasonic or hydrodynamic methods. In the ultrasonic method, a high-intensity sound wave is irradiated on the liquid and microbubbles form and grow to an unstable size and then collapse to produce implosions. In the hydrodynamic technique, the passage of a liquid through a constriction such as an orifice plate throttling valve, or venturi, is responsible for the creation of microbubbles based on Bernoulli’s principle. These bubbles later collapse, leading to similar sonochemical effects as
observed by ultrasonic means. Both methods are used in the petroleum industry for selected applications, and each they have distinct advantages and drawbacks.

Several combustion strategies have been proposed to improve HFO combustion, including combustion enhancing additives, staged combustion with natural gas re-burning, oxy-combustion, gasification, chemical looping, and water-in-HFO emulsions. Among these, the emulsification of HFO with a certain amount of water has been one of the most researched methods. Spray combustion involves fuel droplet breakup, vaporization, mixing with air, and subsequent burning. The advantage of burning HFO emulsion consists in the occurrence of micro-explosions. The high volatility differential between water and HFOs triggers the formation of water bubbles within the fuel droplets when these are exposed to high temperature. The bubbles eventually overcome the surface tension of the droplet resulting in multiple ejection which create secondary smaller droplets resulting in the so-called, “micro-explosion” phenomenon. Water-in-liquid fuel emulsions provide therefore a dramatic improvement in the droplet-break stage. The surface area of smaller droplets thus formed is several orders of magnitude larger than what is possible to achieve using traditional atomizers. Subsequent mixing with air is intense and uniform, enabling efficient burning, lower temperatures and less NOx and particulate matter formation.

Emulsion formation by cavitation also leads to breaking of the large asphaltene clusters, which may speed up the burning of these difficult-to-burn fuel components. In addition, the emulsions so produced will also aid in oxidative desulfurization (ODS) of HFO. Application of water-in-liquid emulsions could be in multiple combustion platforms such as compression ignition engines, gas turbines, and boilers.

1.4. Industrial advancements in cavitation-based emulsification and oxidative desulfurization

Until a few years ago, emulsions were not an industrially preferred solution for HFO burning. Some of the reasons included the high cost of emulsifiers or surfactants and the huge water storage and desalting (removal of hot corrosion-causing sodium and potassium trace metals) infrastructure and expenses. However, in recent years, commercially available emulsion technologies have seen exponential growth due to the development of cavitation-based devices, which can enable in-situ or inline-prepared emulsions without the need for long-term storage. There has been a great focus on scaling up cavitation technologies to make water-in-fuel emulsions using cavitation techniques. This industrial focus is driven by the need to improve spray combustion in practical combustors, involving hard-to-atomize viscous fuels like heavy distillates, crude oils, biofuels, and HFOs. Another important application is oxidative desulfurization (ODS), which tailgates on the micro-emulsions from cavitation- and sonochemistry-induced oxidation of organosulfur species.

In 2000, Arisdyne Systems Inc. (USA) patented a large-scale hydrodynamic cavitation-based device (called a Controlled Cavitation Device, CCD™) for emulsion preparation. This device has no moving parts. It harnesses cavitation by using a liquid that moves via a flow-through compartment with an upstream portion and a downstream
portion, where the cross-sectional area of the flow-through space increases incrementally in the direction of the fluid flow. The arrangement of several baffles creates a cavitation phenomenon and fuel-water mixing. The manufacturers claimed that their hydrodynamic cavitation is superior to the ultrasonic method, which is violent and hard to control. Alternative Petroleum Technologies (APT, USA) uses a proprietary shear-based mixing of fuel and water with surfactants to create stable emulsions of HFO and other fuels. At the heart of APT's emulsion technology is a mixing device with a constant flow area and includes a high shearing apparatus for creating uniformly distributed water in fuel droplets. APT's emulsion units come with ~18000 GPH flow capacity, and they claim that they can produce highly reduced NOx and particulate matter (PM) emissions. NoNox LTD. (USA) has a patented hydrodynamic cavitation-based surfactant-free water-in-HFO emulsion preparation method. In a boiler operation with water-in-HFO inline-prepared emulsion, they claim a reduction of 5-15% in fuel consumption, 25-50% in NOx, 5-15% in CO2, and 60-90% in PM. NoNox units are available in 25-50 gallon per hour (GPH) flow rates.

Several other companies are working on ultrasonics-based cavitation methods to manufacture industry-scale emulsifying and oxidative desulfurization (ODS) units. Powerful shearing and mixing from the cavitation effects allow for effective oxygen transfer from the oxidant to sulfur-containing and other fuel compounds. The process is claimed to bring about the rupture of complex asphaltic structures and breaking of bonds of complex hydrocarbons, leading to overall upgrading of the fuel oil. Technoveritas (Portugal) makes commercial units by the name ENEREMULSION for inline ultrasound emulsification systems. Technoveritas has conducted large-scale testing of their commercial units with Sulzer/Wartzfall 12ZAV40 marine engines with diesel and HFO as fuels, claiming PM reductions up to 80%. Extensive literature suggests that ultrasonic water decomposition leads to various compounds like peroxides. These compounds and derived free radicals, like H2O2, act as strong oxidizers and aid in combustion and oxidative desulfurization (ODS).

The manufacturers of hydrodynamic cavitation-based devices claim that these devices have a better chance of scaling up to industrial scale and cost compared with ultrasonic-based devices. However, several advancements in high-power ultrasonic transducer designs have made ultrasonic-based devices more cost-competitive. Germany's Hielscher company successfully produced and operated a high-power cylindrical transducer in 2007. China developed first-generation piezoelectric ceramic material-based transducers in 2006, which were modified to give rise to the second generation of such transducers in 2013. This technology was later utilized in oil fields in China for enhanced oil recovery applications. Some other recent advances include developing new lithium-niobate crystals that have a 10^5 times greater mechanical quality factor than conventional piezoelectric transducers. These lithium niobate-based ultrasonic methods are being used in mainstream industrial applications and are bringing highly upgraded ultrasonic-based cavitation technologies to the fore. Hielscher's industrial ultrasound processor, UIP16000, is claimed to be the world's most powerful, designed to work in a cluster of several of these units. Four of these...
units can process up to 13000 GPM of liquid. If we consider a typical 400 MW boiler-based power plant, the mass flow rate of HFO could be in the vicinity of 75,000-100,000 GPH. As is evident, the Hielscher unit is closing the gap for direct application on a large scale power-plant. The above list of companies is not exhaustive, and this brief overview was intended only as a glance at the latest developments in cavitation-based emulsification from the industrial world. The challenge with all the above-mentioned industrial units for emulsification is that the exact scientific details are either obscure due to the Edisonian approach of the development or protected as trade secrets.

2. Heavy fuel oil (HFO) deasphalting

2.1. Physiochemical properties

Although ultrasonically induced cavitation can effectively reduce the size of asphaltene aggregates, it can not substantially cut the presence of asphaltene molecules. However, the process of completely deasphalting HFOs is a commercially viable solution to improve the performance of the fuel.

HFO accounts for a significant portion of extracted petroleum, also known as residual fuel oil or bunker fuel in the marine industry. HFO is generally commercialized as products from blending of vacuum residues and diesel or other lighter cuts. HFO has a tar-like appearance characterized by high viscosity and dark color. Because of the extremely variable composition of HFOs, they are distinguished by their viscosity, which has to be a maximum of 700 cSt at 50 °C according to the ISO 8217 standard or they have a maximum density of 1010 kg/m³ according to the ISO 8217 standard. A specification of sulfur content is provided to standardize the use of HFOs. As described below, their chemical composition is incredibly complex. The boiling range of HFO spans from 180 to 1000 °C (data obtained from extrapolated normal boiling point curves). HFO has comparable energy content to distillate fuels, but its high viscosity necessitates heating before spray combustion inside a boiler or internal combustion engine.

HFOs are traditionally separated into four fractions: Saturates, Aromatics, Resins, and Asphaltenes. The SARA approach is based on differences in the solubility and polarity of these chemical classes. The saturate fraction mostly contains aliphatic compounds, while the aromatic one consists of aromatic groups with aliphatic side chains. Resin is a class characterized by heavier and more polar molecules than saturates and aromatics. Asphaltenes are hard-to-burn heavy polycyclic aromatic compounds with embedded heteroatoms, which lead to the formation of large cenospheres during inefficient burning. Asphaltenes are insoluble in alkyl solvents and are the most complex fraction. Sulfur is present mainly in thiophene and sulfidic structures. The most abundant form in which nitrogen is found are derivatives of pyrrole and pyridine. Organometallic porphyrins are also present in significant quantities. Oxygen is individuated in carboxylic, phenolic, and ester functional groups. HFO can contain asphaltenes (up to 15 % weight), carbon residue, trace metals like vanadium, and fuel-bound nitrogen and sulfur. The sulfur content (2-5%) leads to the formation of harmful SOx emissions. With the use of increasingly lower grades of HFO, the problems engendered by higher asphaltene and sulfur contents are expected to grow in intensity.
2.2. Deasphalting HFO

We evaluated and quantified the impact of asphaltene content on the physical properties of HFO in several studies. The properties of HFO samples, as received from Saudi Arabian power plants, can vary significantly in terms of heteroatoms and trace metals. In a previous study by our group\(^{70}\), an HFO sample (named HFO\(^a\)) was deasphalted resulting in deasphalted oil (DAO\(^a\)). The deasphalted oil is the portion of the HFO remaining after the asphaltenes are removed by precipitation.

The elemental analysis of DAO\(^a\) is compared with that of pure HFO\(^a\) in Table 1\(^70\). All measurements were conducted at KAUST in accordance with standard methods for HFO samples from Saudi Arabian origin. The elemental analysis was conducted using a CHNS/O analyzer (Flash 200 Thermo Scientific, USA), whereas the trace metal analysis was conducted using inductively coupled plasma atomic emission spectroscopy (ICP-OES, Agilent 5110). The viscosity of HFO emulsions at different temperatures was determined by an electromagnetically spinning viscometer (EMS-1000, KEM Kyoto Electronic Manufacturing CO., LTD, Japan). The density of HFO was measured by an electronic densitometer (JN-300S/E, Shanghai Jenner Industrial Co., Ltd, China). The heating values of HFO and DAO were determined by a Parr Instrument 6400 Automatic Isoperibol Calorimeter.

![Figure 1: Overview of solvent deasphalting of HFO. Adapted with permission from \(^70\). Copyright 2019 Elsevier.](image1)

![Figure 2: Extracted asphaltenes](image2)

**Table 1:** Physio-chemical properties of HFO\(^a\) and DAO\(^a\) of Saudi Arabian origin. Reproduced with permission from\(^70\). Copyright 2019 Elsevier.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Method</th>
<th>Units</th>
<th>HFO(^a)</th>
<th>DAO(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density @ 288 K</td>
<td>ASTM D4052-11</td>
<td>kg/m(^3)</td>
<td>970.5</td>
<td>930.4</td>
</tr>
<tr>
<td>Specific gravity @ 288 K</td>
<td>ASTM D4052-11</td>
<td>-----</td>
<td>0.971</td>
<td>0.931</td>
</tr>
</tbody>
</table>
The asphaltene separation process followed the ASTM – D3279 standard. We used a three-step process, beginning with the transfer of approximately 1 – 1.3 g of HFO into a 250 ml flask. This was followed by adding 100 ml of the solvent n-Heptane per 1g of HFO that was originally added to the flask. The mixture was heated for 30 min using a reflux condenser. Next, the contents were allowed to pass through double filter pads and then into a filter flask. The filtered asphaltene particles were then kept inside a furnace maintained at a constant temperature of 110 °C for 30 mins to remove any solvent impurities. The formed precipitate was then extracted by pouring toluene on the filter pads. The toluene was then evaporated from the asphaltene sample by the use of a rotary evaporator device. Figure 1 provides a pictorial representation of solvent deasphalting of HFO. An image of solid asphaltene appearing as hard lumps extracted from the HFO sample is provided in Figure 2.

A different sample called HFOb was deasphalted more recently, using the same ASTM-D3279 method, and used for more detailed analysis. Table 2 reports the elemental composition of HFOb and DAOb. The table also reports compositional data (CHNSO, trace metals) of HFOb and DAOb when the asphaltenes content of these samples are varied. The HFOb sample differs from the HFOa described in Table 1 in its sulfur and trace metals content. We quantified the effect of asphaltenes in HFOb of Saudi Arabian origin on the elemental composition, viscosity, and density. We used ICP-OES to further analyze the composition of the asphaltene. In comparison to HFOa, the asphaltenes in HFOb have lower hydrogen content (8%) and a higher content of sulfur, nitrogen, nickel, vanadium,
and magnesium. The elemental analysis of DAO\textsuperscript{b} and extracted asphaltene is compared with that of pure HFO\textsuperscript{b}. The extracted asphaltene was used to prepare the HFO\textsuperscript{b} samples with wt% 4 and 16 asphaltene quantity.

Table 2: Effect of asphaltene content on elemental composition and trace metals of HFO\textsuperscript{b}

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Net Asphaltene content in sample, %</th>
<th>N, wt%</th>
<th>C, wt%</th>
<th>H, wt%</th>
<th>S, wt%</th>
<th>O, wt%</th>
<th>K, ppm</th>
<th>Na, ppm</th>
<th>Ni, ppm</th>
<th>V, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(DAO\textsuperscript{b})</td>
<td></td>
<td>0</td>
<td>0.21</td>
<td>83.22</td>
<td>10.81</td>
<td>3.14</td>
<td>2.62</td>
<td>20.8</td>
<td>65.2</td>
<td>17.5</td>
</tr>
<tr>
<td>DAO\textsuperscript{b} + additional asphaltene</td>
<td></td>
<td>4</td>
<td>0.23</td>
<td>83.19</td>
<td>10.58</td>
<td>3.32</td>
<td>2.68</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HFO\textsuperscript{b}</td>
<td></td>
<td>8</td>
<td>0.28</td>
<td>84.86</td>
<td>10.65</td>
<td>3.53</td>
<td>0.69</td>
<td>10.7</td>
<td>29.5</td>
<td>24.5</td>
</tr>
<tr>
<td>HFO\textsuperscript{b} + additional asphaltene</td>
<td></td>
<td>16</td>
<td>0.28</td>
<td>84.75</td>
<td>10.31</td>
<td>3.88</td>
<td>0.78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Asphaltene</td>
<td></td>
<td>100</td>
<td>0.88</td>
<td>82.77</td>
<td>6.53</td>
<td>7.76</td>
<td>2.05</td>
<td>133.1</td>
<td>450.3</td>
<td>254.4</td>
</tr>
</tbody>
</table>

Table 3: Comparison of density and viscosity of HFO\textsuperscript{b} and DAO\textsuperscript{b} at selected temperatures

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Density @ 25°C, gm/ml</th>
<th>Dynamic viscosity @ 25°C, mPa.s</th>
<th>Dynamic viscosity @ 40°C, mPa.s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure HFO\textsuperscript{b}</td>
<td>0.9668</td>
<td>2194</td>
<td>648.2</td>
</tr>
<tr>
<td>DAO\textsuperscript{b}</td>
<td>0.929</td>
<td>231</td>
<td>95.9</td>
</tr>
<tr>
<td>Asphaltene</td>
<td>1.771</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Asphaltenes have high concentrations of sulfur, nitrogen, and trace metals. The net quantity of asphaltene in pure HFO\textsuperscript{b} is nearly 8%; as a consequence, deasphalting only partially removed the refractory sulfur and trace metals from the HFO\textsuperscript{b}. Table 3 reports the physical properties of HFO\textsuperscript{b} and DAO\textsuperscript{b}. The viscosity of DAO\textsuperscript{b} is nearly 10 and 8 times lower than the pure fuel at 25 and 40 °C, respectively (see Table 3). The variation in viscosity for HFO\textsuperscript{b} samples with 0, 4, 8, 16, and 100% asphaltenes is plotted in Figure . As is evident, asphaltenes impart high viscosities to heavy fuels, enabling tremendous transport and flow processes. At low temperatures, the viscosity rise is almost asymptotic. The transport problems related to high viscosity can be overcome either by operating at temperatures higher than the ambient temperature, by removing asphaltenes or by modifying their structure. Hence, either the asphaltenes needs to be broken down (i.e., upgraded) or removed. Asphaltenes extracted from heavy oils like HFO can be used as asphalt...
for construction of roads, production of carbon black \(^{71}\), as surfactants \(^{5}\) and can also be used in gasifiers as fuel for syngas production.

\[\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Variation of the viscosity of HFO\(^{\text{p}}\) with the asphaltene content}
\end{figure}\]

2.3. Molecular-level characterization

Many experimental techniques, such as nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and X-ray absorption near edge structure (XANES), have been widely employed as powerful characterization tools for the identification and quantification of elemental composition and the chemical state of the elements present in HFO and asphaltenes. State-of-the-art analytical techniques like NMR spectroscopy and FT-ICR mass spectrometry are the preferred techniques when analyzing residual petroleum fuels like HFO or vacuum residues as these complex fuels possess millions of individual molecules of varying sizes and functional groups with the presence of hetero atoms like O, N, and S \(^{72}\). Gas chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC), and other conventional analytical techniques are not suitable for the characterization of petroleum residual fuels like HFO and asphaltenes. Molecular characterization of HFO by our group at KAUST \(^{66, 73, 74}\) has revealed valuable information on the molecular structure and complexity of asphaltenes.

2.3.1. FT-ICR mass spectrometry

FT-ICR mass spectrometry has the ability to assign unique elemental formulas to resolved ions, even those ions that have very minor differences in mass at the order of an electron \(^{75}\). First, the sample has to be ionized with a suitable
technique that is determined based on the chemical characteristics of the sample. In the present work, HFO, asphaltenes and DAO samples were ionized by two known techniques; namely positive ion atmospheric pressure photoionization (APPI) and electrospray ionization (ESI). Both these ionization techniques have been successfully demonstrated to ionize a number of heavy petroleum fuels. ESI is usually applied for ionizing heteroatom-containing polar molecules (N,O,S species), which are notorious for causing catalyst fouling, corrosion, and deposit formation. APPI is efficient in ionizing the bulk non-polar aromatic species present in HFO, like benzo and dibenzothiophenes, polyaromatic hydrocarbons, cycloalkanes, etc. and it is therefore suitable for analyzing the composition of petroleum samples. Many researchers have used APPI along with FT-ICR MS to study the molecular characteristics of several asphaltene samples. The FT-ICR MS technique, in fact, gives an important, although hardly quantitative, insight into the structure of hydrocarbon mixtures. Marshall’s group studied a number of crude oil samples using APPI. FT-ICR mass spectrometry has been used to analyze a number of other samples, like base oils, HFO, fuel oil derived DAO, vacuum residue derived DAO, vacuum residues, furnace oil, coal liquefaction products, lubricants, tyre pyrolysis oils, biomass besides crude oils and asphaltenes.
Figure 4: APPI and ESI FTICR mass spectra of HFO, asphaltenes, and DAO

The experimental procedure used for analyzing samples using APPI and ESI FT-ICR mass spectrometry is discussed in detail elsewhere. A Bruker Daltonics FT ICR mass spectrometer (9.4 T Solarix XR, Bremen, Germany) was used for the analysis. Toluene was used to dilute the fuel samples as it can dissolve the asphaltenes present in the sample and keep them in solution. This was followed by direct injection into the APPI source. For ESI ionization, the samples were dissolved in methanol at a concentration of 100 pm. The aqueous samples were diluted 50 times with toluene APPI and with methanol for ESI. For both APPI and ESI, the ionization was done in the positive mode with a mass range of m/z 154–1200. For APPI, the nitrogen nebulizer gas pressure was 2.5 bar, and the vaporizer...
temperature was set to 400 °C, along with a dry temperature of 280 °C. A krypton light with ionization energy of 10.6 eV was the APPI source. The samples underwent soft ionization into molecular ions, with no fragmentation of the parent molecules. For ESI, a pressure of 0.5 bar was used for the nebulizer, and the dry temperature applied was 180 °C. The ion accumulation time for APPI hexapole was 0.01 s, and for ESI, the time was 0.07 s. The spectra for both the ionization methods were acquired with 300 scans, transient length 4.47, and time-domain size of 8 mega-point.

Figure 5: Carbon number vs DBE plot for S1 and S2 species present in HFO<sup>a</sup>, asphaltenes, and DAO<sup>a</sup>

The FTICR mass spectra obtained using APPI and ESI ionization for HFO<sup>a</sup>, asphaltenes, and DAO<sup>a</sup> samples from one of our previous studies<sup>70</sup> are presented in Figure 4. The mass-to-charge ratio (m/z) for all three samples ranged
from 154 to 1200. The average molecular weight (AMW) of HFOa was reduced from 565 m/z to 531 m/z on account of asphaltene removal. This suggests that the asphaltene content of HFOa has a higher percentage of molecules that are bigger in size as compared to HFOa, which resulted in a lower AMW for the DAOa sample. As discussed before, the present HFOa sample had an asphaltene content of 8%. The AMW of all three samples was calculated by multiplying the masses of the ions with their corresponding signal intensity, followed by the summation of the products. The obtained number was then divided by the total intensity of the observed ions.

The distribution of S1 and S2 species in HFOa and DAOa as a function of the double bond equivalent (DBE) and the carbon number are presented in Figure 5. The size of the bubbles indicates the abundance of the resolved species. The degree of unsaturation (aromaticity) present in the sample with the variation in molecular size can be understood from the DBE vs. carbon number plots. Paraffins with a zero DBE and carbon numbers less than 15 are not observed in any of the three samples because they are not present in the samples or they could not be ionized. The latter possibility could be higher due to the stabilized paraffin ions that are difficult to ionize. The DBE plots of S1 and S2 species are presented as these classes are the most prevalent in sulfur-laden residual fuels like HFOa, asphaltenes, and DAOa. The S1 class indicates that the core structure of these fuels can be in the form of thiophenic functional groups or thiolic groups; the former seems to be more probable based on NMR results of petroleum fuels discussed in the literature. The DBE of the polycyclic aromatic sulfur heterocycles (PASH) species in the samples falls in the vicinity of 7-12 for molecules having carbon numbers between 30 and 50. These molecules are more likely to be benzothiophenes (DBE 6), dibenzothiophenes (DBE 9) and benzonaphthothiophenes (DBE 12) with either short or long paraffinic chains. The DBE plots also indicate the prevalence of tetra and penta aromatics in HFOa, asphaltenes and DAOa due to the presence of molecules with high carbon numbers (around 80) and large DBE values of around 20.
The molecular species in HFO\textsuperscript{a}, asphaltene, and DAO\textsuperscript{a} can be disassembled into their underlying classes based on the presence of S, N, and O heteroatoms. They are shown in Figure 6. HC stands for pure hydrocarbon molecules present in the sample. Hydrocarbon molecules containing one, two and three sulfur atoms are indicated as S\textsubscript{1}, S\textsubscript{2} and S\textsubscript{3}, respectively. Similarly, N, O and NS stand for hydrocarbon species with one nitrogen atom, one oxygen atom and one nitrogen and sulfur atom each, respectively. The ions presented in Figure 6 are a sum of both protonated ions and radical cations, which are both observed in the APPI ionization mode. The species distribution in HFO\textsuperscript{a} and DAO\textsuperscript{a} are similar with minor differences between the HC, S\textsubscript{1} and S\textsubscript{2} classes. HFO\textsuperscript{a} has a higher percentage of molecules with sulfur atoms at 62.3\% compared with DAO\textsuperscript{a}, which has sulfur atoms in 60.8\% of its molecules. This suggests that the asphaltenes removed from HFO\textsuperscript{a} have a slightly higher sulfur distribution than HFO\textsuperscript{a}. The molecular classes observed from APPI indicates the abundance of sulfur atoms distributed in the volumes of HFO\textsuperscript{a} and DAO\textsuperscript{a}, which suggests that desulfurization techniques applied on these fuels will lead to significant structural modifications. Asphaltenes on the other hand have slightly lower HC species than HFO whereas the S\textsubscript{1} and S\textsubscript{2} class species are higher in asphaltenes compared to both HFO\textsuperscript{a} and DAO\textsuperscript{a}. The distribution of the species discussed in Figure 6 is with respect to abundance % (in terms of number of species resolved) whereas the elemental analysis in tables 1 and 2 is terms of mass %. The number of N species observed in DAO (5.4\%) and asphaltenes (5\%) are both greater than HFO (4.6\%) which may appear to be slightly analogous. This is mostly due to the uneven APPI ionization of the sample that may not accurately reflect the species distribution actually present in the sample. Also, the data reported in Figure 6 corresponds to only

Figure 6: Molecular distribution of species present in HFO\textsuperscript{a} and DAO\textsuperscript{a}
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the resolved ions whose signal to noise (S/N) ratio is greater than 5. However the errors are minor and the FT-ICR data is fairly accurate and gives a good overview of the molecular diversity present in the sample.

2.3.2. 1H NMR spectroscopy

High-resolution NMR spectroscopy has the inherent ability to provide qualitative and even quantitative structural information such as the various hydrocarbon functional groups present in fuels. The molecular structure is identified by studying the NMR spectra, which is presented in the form of chemical shifts, which in turn are diagnostic of the molecular structure. NMR spectroscopy is ideal for analyzing hydrogen and carbon functional groups, as each of these groups appears distinctly on the spectra. For example, aromatic groups are always observed around 6.7 -8 ppm on a 1H NMR spectra. Spectral processing techniques can also remove the overlap seen in some functional groups (like naphthenic CH₂ and paraffinic CH groups) and make NMR convenient for quantifying the groups present. One of the advantages of 1H NMR spectroscopy is that the measurement can be performed in a few minutes, making it ideal for high-throughput operations. Also, the spectra are reproducible almost every time, provided the experimental conditions are the same. The structural information obtained from 1H and 13C NMR can also be used to predict combustion properties and sooting propensities of hydrocarbon fuels. NMR-derived functional groups have been widely used to predict the combustion properties fuels, such as octane and cetane numbers. NMR spectroscopy has been applied to study the molecular structure of various fuels like gasoline, diesel, shale oils, HFO, coal-derived liquids, base oils, tyre pyrolysis oils, vacuum residues, asphalts, and crude oil.

HFO, asphaltenes, and DAO samples were analyzed by 1H NMR spectroscopy using a Bruker 700 AVANAC III spectrometer. In preparation, 6100 µl of each of the three samples were transferred to 5 mm NMR tubes and then 1600 µl of CDCl₃ were added to the NMR tubes. The 1H NMR spectra were recorded with a recycle delay time of 5 s at a temperature of 298 K. A total of 128 scans were collected using a standard one-dimensional (1D) 90° pulse sequence. The detailed measurement procedure and the experimental conditions used were described previously. The spectra were collected and analyzed using the Bruker Topspin 2.1 software (and MestreNova NMR software was used for processing the results). The 1H NMR spectra of HFO, asphaltene, and DAO samples are presented in Figure 7.

Comparisons of various 1H types in the samples are presented in Figure 8. The paraffinic CH₃ and CH₂ groups are slightly higher in DAO (73.4 mol %) compared to HFO (65.5 mol %) as the hydrogen content in DAO is also slightly higher as observed from the elemental analysis of the samples. The aromaticity (number of aromatic carbons divided by total number of carbons) of HFO and DAO is 0.38 and 0.33 respectively, which indicates the remaining carbon atoms are present mostly as substituted alkyl side chains. Also, the average aromatic ring number of HFO and DAO is 3.2 and 2.9 respectively, which indicate possibility of poly-condensed aromatic rings. This is the reason for the low content of aromatic hydrogen atoms in HFO and DAO. Asphaltenes have lower paraffinic content compared to
both HFO and DAO. The aromatic content in asphaltenes is, however, greater than that observed in HFO. Since asphaltenes have been shown to possess a higher PASH content than the parent source fuel, the polyaromatic content in HFO at 4.5% is greater than that in DAO at 2.9%. The other species distribution in HFO and DAO are comparatively similar to each other, with only minor variations, whereas olefin species are absent in both fuels.

Combining the data from $^1$H NMR spectra with data from other analytical techniques like FT-ICR MS and elemental analysis (CHNSO), enables us to calculate the average molecular parameters (AMP) of the fuel sample. The AMP method is based on quantifying various functional groups present in the fuel by imagining a hypothetical average molecule designed from the elemental distribution and AMW obtained from mass spectrometric methods like FT-ICR. An example of an AMP is the number of paraffinic hydrogens (or carbons) present in the average molecule. The advantage of this method is that it can help us to visualize the structure of a complex fuel like HFO or DAO and also to estimate the fuel properties by using various quantitative structure-property relationship (QSPR) techniques. The average molecular formula of HFO and DAO calculated using the CHNS and AMW data are $\text{C}_{40}\text{H}_{60.5}\text{O}_{0.01}\text{N}_{0.1}\text{S}_{0.58}$ and $\text{C}_{37.4}\text{H}_{60}\text{O}_{0.01}\text{N}_{0.1}\text{S}_{0.52}$, respectively. The AMPs calculated for HFO, asphaltenes, and DAO are presented in Figure 9. The numbers of hydrogen and carbon atoms in HFO are 61.5 and 40, respectively. HFO has 4.7 paraffinic CH$_3$ groups and 15.3 paraffinic CH$_2$ groups in its average molecule, whereas DAO has 4.3 paraffinic CH$_3$ groups and 14.1 paraffinic CH$_2$ groups. Asphaltenes have a slightly lower content of paraffinic CH$_2$ and CH$_3$ groups compared to both HFO and DAO; whereas the proportion of monoaromatic and polyaromatic groups in asphaltene is higher. The number of aromatic atoms is higher in HFO compared to DAO, whereas the heteroatoms, namely S, N, and O, are present in a negligible amount in both HFO and DAO.
Figure 7: $^1\text{H}$ NMR spectra of HFO, asphaltenes and DAO. Reproduced with permission from 70. Copyright 2019 Elsevier.
Figure 8: $^1$H types present in HFO, asphaltene and $^{20}$DAO.
3. Ultrasonically induced cavitation (UIC) and water-in HFO emulsions

3.1. Fundamental aspects

Ultrasonically induced cavitation is a phenomenon whereby vapor-filled cavities are formed by the application of a fluctuating pressure field within a liquid medium. This is expected to occur in areas of the liquid domain where the pressure drops below the liquid's vapor pressure. However, recent studies\textsuperscript{109-111} demonstrated that a pressure below the saturation pressure is not enough to trigger the formation of bubbles. In fact, very high stress is required to pull the liquid apart and finally generate a cavity. Classical Nucleation Theory (CNT) does not hold true in the case of homogeneous nucleation induced by pressure gradients. The controlling mechanism of bubble formation in still liquids is expected to be heterogeneous nucleation, with the bubbles nucleating on the sonotrode surface and eventually migrating to the bulk following the velocity streamlines generated by the sonotrode motion\textsuperscript{112}.

However, nucleation can also be favored by solid particles dispersed in the bulk liquid that may lower the energy required for the bubbles to nucleate. It is worth noting that asphaltene clusters may serve this purpose if sonication takes place in HFOs. After nucleation, the bubbles' lifetime will be affected by the interaction with the oscillating pressure field. At high-pressure amplitudes, bubble motion is strongly non-linear.
When the acoustic pressure wave enters the rarefaction phase, the bubble's volume grows. Subsequently, the acoustic pressure wave enters its compression phase, and the drop will continue the expansion phase. However, this system configuration is energetically unfavorable; indeed, bubble growth is quickly arrested. The bubble now begins a rapid collapse. The velocity of this collapse in its last stages can be enormous and, in some cases, can be several times the speed of sound in gas at ambient temperature and pressure. The violent implosion of an acoustically driven bubble leads to the generation of high intra-cavity temperatures and pressures. In these hot spots, temperatures of thousands of kelvin are expected with strains of up to 100 bar.

The dynamics of such bubbles is usually modeled by adopting the Rayleigh-Plesset (RP) equation (see Equation 1). The RP equation directly derives from the continuity equation applied to a bubble immersed in an incompressible, viscous Newtonian fluid:

$$\begin{align*}
\frac{d^2 R}{dt^2} + \frac{3}{2} \left( \frac{dR}{dt} \right)^2 + \frac{4 \nu_L \Delta R}{R} + \frac{2 \sigma R}{\rho L R} + \frac{\Delta P(t)}{\rho_L} &= 0,
\end{align*}$$

where $R$ is the radius of the bubble, $\nu_L$ is the kinematic viscosity, $\Delta P$ is the pressure difference between the external and internal pressure, and $\sigma$ is the surface tension coefficient. No mass transfer between the bubble and the bulk is considered in this analysis. Contributions of viscosity and surface tension to the RP equation are usually neglected. However, this assumption becomes incorrect when dealing with heavy fuels. The assumption of polytropic transformation leads to the following relation for temperature:

$$T_b(t) = \frac{T_{b0}}{R_0} R(t)^{\gamma(1-\gamma)} \left( \frac{2 \sigma}{\gamma R_0 P_0} + 1 \right),$$

where $\gamma$ is the polytropic exponent and the 0 index indicates the initial conditions. Figure report the result of the numerical solution of Equation 1 and Equation 2 using the physical properties of HFO at 50 °C and the pressure profile reported in Equation 3.
Figure 10: Heavy Fuel Oil bubble oscillations under an oscillating pressure field. The frequency of the oscillating field is 20 kHz. The vaporizing bubble is supposed to have the same thermodynamic properties of diesel fuel.

Figure 11: Temperature profile of the oscillating bubble. The temperature fluctuates with the radius of the droplet.

Equation 3: $p = p_a \sin(\omega t),$

where $p_a$ is the pressure amplitude and $\omega$ is the oscillation frequency.

Although the results were obtained from a simplistic analysis, they are representative of the physics which takes place in UIC driven phenomena. Heavy Fuel Oils are generally a blending of diesel and vacuum residue in a proportion of 40:60 by mass. Diesel will eventually be the fraction that will evaporate once negative pressure is established in the liquid.

Figure , in particular, depicts the radius fluctuations of a bubble immersed in a pressure field generated by oscillations of the sonotrode. The sonotrode vibrates at 20 kHz, and the derived pressure field is supposed to have the same periodicity. Collapse occurs when the pressure peaks as the expansion step and short oscillations occur when the pressure moves to negative values. When the bubble collapses, the droplet's temperature increases dramatically, reaching values above 2000 K (see Figure ), which makes the occurrence of radical formation possible in the hotspot region also with the eventual migration of the radicals to the liquid phase.

The consequences of these extreme conditions are chemical reactions (Sonochemistry) and intense physical forces that can be used for various processing applications and for promoting chemical reactions. These effects include radical generation, light emission-sonoluminescence, shock waves, micro-jets, shear forces, and turbulence.
3.2. Direct upgrade of HFOs through breakage of asphaltene clusters and cracking of hydrocarbons

As described above, ultrasonically induced cavitation induces local hot spots and, in general, increases the temperature of the mixture. When an ultrasonic source is applied to water, decomposition takes place (Figure 113, 114). The water decomposition results in the formation of H· and OH· upon collapse. However, when water is not present in the mixture, some authors suggested other mechanisms to take place such as the Rice mechanism in case of presence of hydrocarbons.

Two effects play a role in changing the structure of the liquid. The first effect is a physical effect: jet formation, which follows bubble collapse and may cause breakage of the asphaltene clusters. The sizes of asphaltene clusters and bubbles are on the same order of magnitude. The second is a chemical effect. A series of reactions takes place as a consequence of radical formation in the local hotspot and because of the increased temperature. These reactions can eventually occur in the gas or liquid phase. Gas-phase reactions take advantage of the high number of radicals made available by extremely high temperatures as well as of the large pressure gradients generated by bubble oscillations. Liquid-phase reactions occur at lower temperatures because the intense mixing of the strong temperature gradients is promptly distributed within the bulk phase. Typical temperatures range from 60 to 150 °C.

By looking at the system from a macroscopic perspective, a straightforward energy balance allows us to estimate how much fuel can potentially be converted into smaller molecules in a UIC system. We are supposed to break a C-C bond per molecule to form a smaller component using a 400 W sonotrode to process 1 kg of fuel for 1 min. Assuming that all the energy is involved for the conversion of hydrocarbons, the size of 14 g of a 200 g/mol diesel could be reduced to create smaller molecules. Therefore, a notable chemical effect is plausible, especially considering the large size of HFO molecules, which have an average molecular weight of 750 g/mol. Hydrocarbon
cracking starts through C-C bond cleavage and proceeds by propagation, followed by termination reactions. The production of lighter hydrocarbons, however, is not the only chemical pathway that sonicated fuels follow. Following the Rice mechanism\textsuperscript{115} as suggested by Suslick et al.\textsuperscript{13,116}, the initiation step is described as given below where R refers to an alkyl group:

\begin{verbatim}
    RR'→R•+R'•
\end{verbatim}

The propagation step reactions proceed through the following:

\begin{verbatim}
    R•+R″H→RR″H•  
    H•+R″H→HR″H•  
    HO•+R″H→HOR″H•
\end{verbatim}

While the termination step eventually ends up with a recombination or formation of lighter species.

\begin{verbatim}
    R•+R•→R-R  
    R•+H•→RH  
    H•+H•→H₂
\end{verbatim}

Eventual recombination of free alkyl radicals may lead to polymerization and polycondensation reactions that create a counterproductive effect and to formation of a high viscosity and tar-like material in the reactor. This tendency is one of the main limitations, and major challenges of the ODS process are described later. Several studies demonstrated the ability of ultrasonically induced cavitation can either reduce the viscosity of hydrocarbons\textsuperscript{117} or increase that\textsuperscript{118}. The reduction of the asphaltene clusters size is one of the key drivers of such behavior.
Figure 13: Hydrocarbon species distribution as a function of DBE and the number of carbon atoms at different sonication times.

Figure 14: Sulfur species distribution as a function of DBE and the number of carbon atoms at different sonication times.

The device used in this work was an ultra-sonic homogenizer UP400s Hielscher (Germany). Different sonotrodes are available for this device, and in this work, the sonotrode H14, Hielscher, was used, as it has a high
an acoustic power density of 105 W² cm⁻¹ and a maximum amplitude of 125 µm. The device operates at a frequency of 24 kHz and is controlled by two parameters:

- Amplitude, which consists of the displacement of the sonotrode with respect to its equilibrium position. The operative range, which can be chosen, varies from 0 to 100%, where 100% corresponds to the maximum power generated.

- Pulse, which consists of the repetition rate of the sonotrode activation.

The study was conducted on HFO by sonicating 300 g of fuel for 5/10/60 min. The temperature was kept constant at 50 °C using a water bath. The vibration of the sonotrode was set at 20000 Hz, while the periodicity was 0.3. APPI FT-ICR MS analysis was performed on the sonicated HFO to identify the changes to the fuel structure due to sonication. A plot of carbon number vs DBE is shown in Figure 13 for the hydrocarbon species whereas Figure 14 presents the carbon number vs DBE plot for sulfur species. The black dots represent molecules that have a high molecular weight after 5 min of sonication and eventually were broken after 10 min. After one h, recombination occurred, resulting in a higher fraction of molecules having larger DBE. This was mainly observed with pure hydrocarbons while less evident with sulfurized molecules.

We measured the viscosities at various temperatures (see Figure) and found very little change. The reason for the viscosities remaining nearly the same could be the breakdown of heavier molecules followed by some kind of recombination. Such a breakdown and recombination has been reported in several previous studies. However, evidence of it at the molecular level is scant. The observations reported here therefore provide vital clues to the extent of modification of heavy structures like asphaltenes with ultrasonic treatment.
3.3. Water-in-fuel emulsions

Form emulsions from HFOs serves two important purposes in combustion applications:

- Enhancing secondary atomization thereby increasing carbon efficiency.
- Reducing the production of pollutants, such as NO\textsubscript{x}, SO\textsubscript{x}, and PM through the presence of water in the combustion chamber.

The quality of the emulsion is mainly a function of three parameters: water content, the size distribution of droplets, and the stability of the emulsion. Whereas the water content and size distribution of the droplets directly influence the combustion behavior, the emulsion's stability is relevant only when long-term storage is required. In in-line emulsions, the emulsion's desired stability is necessary only for a short time (on the order of hours or days). Some stability-related concerns can, therefore, be relaxed when emulsions are prepared for immediate burning. However, some stability in emulsions, even those prepared for immediate burning, is essential for maintaining the physical properties of the emulsified fuel until burning. Advanced techniques like sonication can provide small enough size distributions of droplets for required stability without addition of any surfactants. Therefore, the goal for characterization involves determining the optimal water content and droplet size distribution for the emulsions under study.

Figure 15: Measured viscosities of sonicated HFO samples at 5, 10, and 60 minutes.
The formation of stable water-in-HFO emulsions without surfactants is possible because of two factors. First is the high asphaltene and resin content of HFO. As noted above, asphaltenes are a class of hydrocarbons with heteroatoms like S, N, and O defined only by their precipitation in non-polar solvents like pentane, hexane, or heptane. They are also natural emulsifiers. The resins in HFO are smaller in size (as indicated by the number of carbon atoms) than asphaltenes, but they have a similar structure. Both are polar compounds as characterized by their solubility criteria. In crude and derived fuel oils, asphaltenes are suspended as micelles stabilized in the solution by resins. Variations in pressure, temperature, and composition of the oils can cause the asphaltene molecules to form aggregates of different mean molecular weights, which can result in precipitation, deposition, and filter clogging. The dominant molecular and colloidal structure of asphaltenes has been categorized in the Yen-Mullins model. Asphaltenes migrate to the oil-water interface and self-assemble to form a rugged but elastic and stable film around the oil droplet. Resins act as solvents to asphaltenes and provide added stability. In this study, we evaluated the role played by asphaltenes in the stability of water-in-HFO emulsions. Figure shows the typical structures of asphaltenes and resins.

The second factor is the small droplet size distribution: Emulsions with small droplets are usually more stable than those with large droplets because smaller droplets can resist flocculation, creaming, and coalescence. Droplet breakup is an important process that determines the size distribution of droplets in an emulsion. Droplets can be broken by applying energy to overcome the pressure difference between the convex and concave sides of the
interface, known as Laplace pressure. This can be accomplished by using high shearing forces or fluctuating velocities and pressures. Typical methods include mechanical homogenization at high rotational speeds or ultrasonics. Interfacial tension can be lowered by adding surfactants, which reduces the energy needed to break the droplets. Ultrasonic homogenization has the potential to produce very tiny droplets in common oil-water mixtures.

We have characterized emulsions as created by UIC with two modern techniques: Cryogenic microscopy and high-speed visualization.

### 3.3.1. Cryogenic Electron Microscopy (Cryo-EM)

We have utilized highly sophisticated imaging techniques such as Cryogenic-Scanning Electron Microscopy (Cryo-SEM) and Cryogenic Transmission Electron Microscopy (Cryo-TEM) for emulsion characterization\textsuperscript{125}. A deeper understanding of the role of asphaltenes in the emulsification phenomenon has thereby evolved. The capability of determining the exact droplet size distribution can be critical in testing the emulsified fuel combustion characteristics since earlier work\textsuperscript{42, 126, 127} suggests it is a crucial parameter for optimizing combustion performance.

We have demonstrated accurate measurements of emulsion size distribution via Cryo-EM imaging as explained below.

The specimen preparation for both cryo-SEM and cryo-TEM was described previously by our group\textsuperscript{125}. In Figure , we present images of UIC-created water-in-HFO emulsions by both optical and cryo-electron microscopy. The image shown in Figure (C) was acquired with an optical microscope with a large field-of-view (FOV). It shows the dispersion of water droplets in a water-oil (W/O) emulsion droplet. The size of the water droplets is found to be in the range of a few microns or less. Figure (B) was acquired using the cryo-SEM technique. Before cryo-SEM analysis, W/O emulsion droplets were frozen and then transferred to the SEM chamber held at cryo-conditions. Before cryo-SEM imaging, the samples were warmed up to -139 °C to sublime the water from the W/O emulsion droplets. This step is essential to have successful cryo-SEM imaging because the presence of water in the specimens degrades the quality of the acquired images. Otherwise, the interpretation of images becomes difficult if not impossible. In this way, the image shown in Figure (B) is a result of sublimation. The volumes that were once the water droplets within the emulsified sample are observed as void volumes from which information about the water droplet size distribution in the original W/O emulsion can be obtained.
Figure 17: Water in HFO emulsions analyzed with cryoSEM and cryoTEM

Nevertheless, the image shows the droplets' W/O droplet size and the interconnectivity of oil and water. The size of W/O droplets is similar to that at direct optical microscopic resolution. Even so, this type of analysis gives improved contrast over direct optical microscopic observations while permitting resolution of water droplet sizes (void sizes) to 100 nm, far smaller than allowed by direct optical microscopy. The image shown in Figure (A) is a cryo-TEM image of the W/O specimen. The specimen for cryo-TEM is very different compared to that for cryo-SEM. For cryo-SEM, the W/O emulsion was dissolved into the oil, while for cryo-TEM analysis, the W/O emulsion was dissolved into water. This is necessary because oil is too viscous to produce a specimen that can be conducive to cryo-TEM analysis. The image in Figure (A) shows the presence of the W/O emulsion in water. Lighter regions in the emulsion droplets are actually water that was trapped by the oil network. The cryo-TEM results confirm the cryo-SEM observations and show the presence of water in the W/O emulsion droplets in the native state. One disadvantage of cryo-TEM observations is that they capture only small size droplets, i.e., 100 nm to 500 nm.

On the contrary, we achieved greater success in characterizing water-in-HFO with cryo-SEM than with cryo-TEM. Much of our emulsion study was therefore based on the Cryo-SEM technique. The emulsions produced with UIC were visualized using the Cryo-SEM technique (see Figure (A)), which allows us to image details at a scale of a few nm, which is comparable to the size of asphaltene clusters. The asphaltenes in HFOs are a natural surfactant and they tend to form a solid shell around the water droplets, which stabilizes the emulsions. No surfactant is therefore required to form commercially viable emulsions. Ultrasonically produced emulsions contain smaller water droplets that are more uniformly distributed and very stable. The oil matrix presents holes and bumps, which we suppose are a residue of the water droplets present in the mixture in the form of eutectic ice. The Energy Dispersive X-Ray Analysis (EDS)
technique was used to identify the elements in the obtained images. Figure (B) and Figure 18 (C) show carbon and oxygen, respectively.

The presence of oxygen confirmed that eutectic ice remained after desublimation. The bumps on the other side correspond to the droplet, which maintained an intact shell surrounding the water. We suppose that the shell that surrounds the water droplets is mainly formed by asphaltenes since no surfactant was added. The asphaltenes have been found to be able to stabilize W/O mixtures\textsuperscript{38, 124, 127-130}.

\textbf{Figure 18: Cryo-SEM results from the emulsified fuel. A raw image is presented in (a). (b) and (c) show carbon and oxygen EDS analysis, respectively.}
Figure 19: Asphaltenes covering the skeleton of a sublimated water droplet: the hollow sublimated water droplet (void) with oil remnants shows the scaffolding of an asphaltene layer.

Figure 20: Asphaltene scaffolding as seen from an angled view; the void is more evident in this image.

Figure shows a zoomed view of a void from a single sublimated droplet from a UIC water-in-HFO emulsion. Figure presents another view of the void, where the hollowness is clearly evident. Figure and Figure provide images of water droplets obtained through UIC and mechanical mixing. The size of the emulsified droplets was calculated from the SEM images using an in-house algorithm consisting of circle detection coupled with color gradient detection and inspired by the well-known Hugh-Transform algorithm\(^\text{131}\). Multiple pictures were analyzed, and the sum of the voids was validated against the mass fraction of water used in the emulsion resulting in a small error. The UIC droplets are much smaller, falling in the nano-scale. Two reasons are proposed to explain this observation. First, UIC guarantees better mixing than mechanical mixing because of the activity of the bubbles, which collapses water emulsions acting in the nano-scale. The second reason for the smaller size may be found in the presence of smaller asphaltene aggregates.
As mentioned above, asphalteneic aggregates are disrupted by UIC; from the images, the size of the asphalteneic aggregates can be approximately measured (the uncertainty is the resolution of the machine at 2 nm). The size of the layer for mechanically produced samples is between 5 and 10 nm (Figure 2), while the size of the layer for ultrasonically produced samples is about 2-3 nm. A smaller water droplet size is also obtained with less water in the mixture. This can be caused by the fact that the amount of asphaltenes per unit volume becomes larger and therefore more droplets can be covered on a statistical basis. Figure compares the droplet size distribution of mechanical stirring vs. ultrasonically produced emulsions. The implication of this difference in practical applications is enormous. Asphaltenes are the main constituent of cenospheres, and they are responsible for the low carbon efficiency and difficult combustion of HFOs. Asphaltenes will be disrupted when secondary atomization occurs during spray formation leading to cleaner combustion. This mechanism was described in the past and extensive results are reported in the following sections. We have also estimated the droplet size distribution of UIC water-in-HFO emulsions with varied water content (see Figure ). We believe that with optimized UIC conditions and water content, water-in-HFO emulsions can be designed for various performance criteria.
3.3.2. High-speed visualization

We used high-speed visualization to fundamentally discern how ultrasonically induced cavitation affects the chemical and physical properties of fuel. We characterized the water-fuel emulsification process through sonication. A significant challenge in high-speed imaging of emulsion formation during ultrasonic cavitation is the opaqueness of HFO. This opaqueness is due to the high concentration of asphaltenes and other solidified components in the fuel. A similar problem was noted in our earlier work on imaging of water emulsion droplets inside crude oil samples. Our imaging approach is based on using relevantly thin channels with glass walls, in which the sample is observed, e.g., square profile capillaries that have 0.5 × 0.5 mm inner cross-sections and on using Near-Infra-Red (NIR) laser illumination, which has a stronger penetration through the oil phase than white light illumination has\(^\text{133}\).

We ran several tests to evaluate the extent of these limitations. In these tests, we used a NIR laser diode of 980 nm, a high-speed monochrome camera (Photron SA-5) with attached micro-objectives that can give up to 30× magnification (\(\sim 1.5 \mu m/pixel\)), and a thin channel microfluidic cell with internal channel dimensions of 0.1 mm thickness, 8 mm length and 38 mm width\(^\text{134}\).
Figure 25: High-speed camera video snapshots of water in a heavy fuel oil (HFO) emulsion inside a microfluidic cell channel of 0.1 mm thickness. (A) Coarse emulsion of 2 wt % water content filmed using NIR illumination and (B) the same sample filmed using white light illumination. (C) NIR illumination of a 20 wt. % fine water droplet emulsion film spreading on a glass slide showing the edge of the film. (D) Lower water content < 2 wt % of fine water droplet emulsion film filmed using NIR illumination.
Figure 26: Snapshots from high-speed camera videos showing cavitation bubbles near the sonotrode tip in pure water. Ultrasonication is at 20 kHz. Filming rate of 4000 fps, shutter speed 1/40000 (40 kHz). As marked with the arrows, individual bubbles can be discerned.

Figure shows some representative examples of an HFO emulsion imaged inside a microfluidic cell. Figure (A) is a snapshot of a 2 % wt coarse water droplet emulsion filmed using NIR laser illumination, and Figure (B) shows the same sample using regular white-light illumination. The comparison demonstrates the better visibility achieved using NIR illumination. Figure (C) shows a thin liquid film with a high water concentration of 20 % wt in HFO with fine water droplets mixed by ultrasonication. At the edge of the film, single water droplets can be discerned. However, once the film is slightly thicker (> several microns), the very high concentration of the water droplets makes the sample opaque (milk effect) to the NIR light, which is absorbed by the water phase. Once the sample is further diluted with HFO to bring the water concentration to below 2 % wt, the droplets' movements inside the thin film are readily observed, as shown in Figure (D).

The high-speed camera is capable of imaging sonication bubbles produced by the sonication device (UP400S, Hielscher). As clarified above, visualization inside bulk HFO emulsions is possible only for very thin layers. We used pure water, transparent diesel fuel oil, and diesel fuel with water droplet emulsions as model systems to capture the cavitation bubbles. The sonication frequency was 20 kHz, while the acoustic power density was 105 W/cm². Figure shows several high-speed video snapshots of sonication in pure water, demonstrating that imaging under these sonication parameters of individual bubble growth is possible. In the example given, the frame rate is 4000 fps and shutter speed 1/40000 sec (40 kHz), which is comparable with the sonication frequency.
Figure 27: Snapshots from ultra-high-speed camera video showing cavitation bubbles near the sonotrode tip in pure water. Ultrasonication is at 20 kHz. Filming rate of 500,000 fps, shutter speed 160 ns. As marked with the arrows, individual bubbles pulsate and occasionally burst (D) during the sonication cycle (50 µs) can be tracked.

Figure 28: Snapshots from high-speed camera video showing the cavitation bubble structure under the sonotrode tip: (a) General view of the bubble structure in the case of pure diesel fuel and (b) diesel fuel with water droplet emulsion. High magnification images near the tip shortly after the sonication impulse is stopped for (c) pure diesel or (d) diesel with water droplets emulsion.

Figure demonstrates the capability of our ultra-high-speed Kirana video camera to capture 180 images at up to 5 million images/second at full resolution (924 x 768 px / 180 frames / 5,000,000 FPS). The example shows the sonication of pure water. The high filming rates allow for detailed tracking of cavitated bubble progression during the sonic cycle, even capturing bubble burst events (red arrow Figure (D)). Figure shows a cavitation bubble plume at the sonotrode during sonication in pure diesel (Figure (A)) or in a diesel–water emulsion (Figure (B)). Figure (C & D) shows higher magnification images of the area below the sonotrode tip shortly after the sonication is terminated for the respective cases of pure diesel (Figure (C)) and diesel–water emulsion (Figure (D)) in which finer details can be resolved. In all cases, we can observe the bubble cloud progressing during the application of the ultrasonic pulses with the imaging quality matching literature examples. These videos were filmed using a filming rate of 1000 frames per second (fps). The individual cavitation bubble size is expected to be several microns below sonication conditions.
Although the above are preliminary experimental results, they do provide us with valuable information on UIC-based water-in-fuel emulsions. The imaging information can fill a vast gap in the validation of computational models for UIC water-in-fuel emulsions.

4. Oxidative Desulfurization (ODS)

4.1. A brief overview of ODS

Oxidative desulfurization (ODS)\(^{136-140}\) is a technology for removing sulfur in fuel by oxidizing it to polar sulfoxides or sulfones. The polarity of the formed sulfoxides/sulfones is different from that of the parent sulfur in the fuel, and this enables the extraction of the formed sulfones using a suitable extractant. This technique includes two processes: oxidation and the following extraction and separation\(^{50, 141, 142}\).

Hydrodesulfurization (HDS) is a widely used mature commercial method integrated into crude oil refinery processing to remove sulfur compounds from fuel oil and to avoid downstream catalyst poisoning. In HDS, the sulfur compounds are converted into gaseous \(\text{H}_2\text{S}\) with the aid of hydrogen and a catalyst under extreme reaction temperature (300–340 °C) and pressure (20–100 bar). HDS effectively eliminates sulfides/disulfides and thiols but is ineffective on refractory sulfur compounds like thiophenes due to ineffective adsorption of these heterocyclic sulfur compounds on the catalyst’s surface\(^{143}\). After the commercial HDS process, the sulfur content in the fuel oil ranges from several dozens to hundreds ppm beyond which the sulfur content does not reduce further and does not meet the sulfur standards. Most of the remaining sulfur compounds are refractory heterocyclic sulfur compounds. If these were to be removed using the HDS technique, then the reactor size would need to be enlarged by 5–15 fold under much severer reaction temperature and pressure with more active catalysts. These steps would also result in undesired side reactions, including saturation of olefins and loss of octane number\(^{143}\). Thus, HDS is not economically and technically feasible for total sulfur removal, and alternative methods are necessary.

In recent years, one of the most promising techniques, namely ODS, has been widely studied for deep or ultra-deep desulfurization of fuels such as gasoline and diesel\(^{141}\) to meet sulfur emission regulations. Compared with HDS, ODS offers several advantages: (i) ODS is effective against refractory thiophenes and their derivatives under very mild reaction conditions (25–90 °C and ambient pressure); (ii) there is no need for expensive hydrogen; and (iii) the capital requirement for the ODS process is significantly low.

In recent decades a number of oxidative systems have been utilized in the ODS process, such as a biphasic hydrogen peroxide system of \(\text{H}_2\text{O}_2/\text{organic (formic/acetic) acids}\)\(^{144-147}\), \(\text{H}_2\text{O}_2/\text{heteropolyacid}\)\(^{148-150}\), \(\text{H}_2\text{O}_2/\text{Transition metal salts}\)\(^{151-153}\), as well as single-phasic non-hydrogen peroxide systems, \(\text{O}_2\), \(\text{O}_3\), \(\text{N}_2\text{O}\)\(^{154-157}\). Among all of these oxidative systems, the hydrogen peroxide system, especially \(\text{H}_2\text{O}_2/\text{organic (formic/acetic) acids}\), is the most well-
studied and has been demonstrated as the most promising oxidative system because the oxidant, hydrogen peroxide, has the highest percentage of active oxygen (47%). In addition, this system is also commercially available, cost-efficient, non-polluting and produces an environmentally friendly byproduct, namely water. In this system, the peracids, which have a more powerful oxidation ability and stronger selectivity than H$_2$O$_2$, are generated in situ by carboxylic acids reacting with hydrogen peroxide to increase the oxidation ability and selectivity of the process. The main challenge of the hydrogen peroxide system using the ODS process is excessive consumption of the oxidant and the mass transfer restriction in the biphasic system leading to a slow reaction rate. To overcome mass transfer limitations in the biphasic system, enhanced mass transfer measures, such as mechanical stirring and sonication, should be adopted, causing extra energy consumption.

Oxidative desulfurization takes advantage of a liquid phase reaction where sulfur becomes oxidized by an oxygen donor. A variety of oxidants was used in the past for this purpose, such as H$_2$O$_2$, molecular oxygen, peracids, ozone, and also air. Three categories of oxidants can be identified depending on the state of reagent and reactant:

- Liquid-Liquid reactions, where the oxidizer is water-soluble.
- Single phase reactions when the oxidizer is oil soluble.
- Gas-Liquid reactions when the oxidizer is present as a gas in the mixture.

### 4.2. Oxidative desulfurization of heavy fuel oils (HFO)

Currently, many published ODS studies focus on deep-desulfurization of gasoline, diesel, and model fuels. Compared with the number of studies on ODS of gasoline and diesel, studies on ODS of HFO are fewer, and they highlight the complexity of the process. Table 4 summarizes some of the HFO ODS applications. The results in the table indicate that the sulfur removal efficiency of HFO is generally lower than that of gasoline and diesel. This is due to the high viscosity of HFO, which significantly impedes the biphasic mass transfer resulting in low oxidation efficiency of sulfur compounds. Several recently developed techniques, however, are suitable for ODS of HFO. Among these techniques, sonication is one of the most promising and will eventually be explored to improve the HFO ODS process.

<table>
<thead>
<tr>
<th>Fuel with temperature (°C)</th>
<th>Oxidant</th>
<th>Catalyst</th>
<th>O/S molar%</th>
<th>S content (wt%)</th>
<th>S removal (wt%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFO</td>
<td>H$_2$O$_2$</td>
<td>Formic acid</td>
<td>~10</td>
<td>2.75</td>
<td>58.5</td>
<td>159</td>
</tr>
<tr>
<td>HFO</td>
<td>H$_2$O$_2$</td>
<td>FeCl$_3$</td>
<td>-</td>
<td>3.85</td>
<td>39</td>
<td>160</td>
</tr>
<tr>
<td>Vacuum gas oil (VGO)</td>
<td>H$_2$O$_2$</td>
<td>Acetic acid</td>
<td>100</td>
<td>1.99</td>
<td>&gt;89</td>
<td>161</td>
</tr>
</tbody>
</table>

Table 4: Summary of ODS application for HFO
In ODS, the reactivity of organosulfur compounds is increased with the increase of electron density on the sulfur atom\textsuperscript{166}. The reactivities of dibenzothiophene (DBT) derivatives are influenced by the electron donation of substituted alkyl groups. Thus, the reactivity decrease in the order of 4,6-DMeDBT > 4-MeDBT > DBT, reversing the order of reactivities for HDS (see Figure)\textsuperscript{166}. ODS has demonstrated the ability to desulfurize HFO effectively\textsuperscript{141}. However, the above process encounters many difficulties, primarily due to complications imposed by the very high viscosity and molecular structures (asphaltenes) in the fuel. There has consequently not been significant deployment of this technology.
Figure 29: Order of reactivity in HDS and ODS for the different classes of organosulfur compounds. Modified version of the illustration from\textsuperscript{166}

According to our previous study,\textsuperscript{79} results from FT-ICR MS of HFO indicate that hydrocarbon compounds containing one sulfur atom (S1 class) are the most abundant at 52\%, followed by 21.4\% hydrocarbon compounds that contain two sulfur atoms (S2 class) (see Figure ). Most of the sulfur species are refractory heterocyclic sulfur compounds, such as benzo thiophenes (BT, DBE of 6), dibenzo thiophenes (DBT, DBE of 9), and benzonaphthothiophene (BNT, DBE of 12), and their naphthenic derivatives at DBE of 7–8, 10–11, and 13–15, respectively (see Figure ). HDS is therefore not suitable for heavy fuels like HFO, whereas ODS has high oxidation efficiency with these refractory thiophenes and their derivatives under very mild reaction conditions and is potentially the most suitable technique for HFO desulfurization.
4.3. Oxidative desulfurization without using ultrasound cavitation

4.3.1. Experimental procedure

Our HFO ODS experiment was conducted in a magnetic stirring water/oil bath reactor. The reaction temperature was precisely controlled up to 400 °C corresponding to water and silicone oil heating, respectively, with the variation within ±0.5 °C. The magnetic stir speed was up to 2600 round/min. Here, we adopted a widely used and cost-efficient H$_2$O$_2$/organic acid oxidative system for HFO ODS. Considering the fast decomposition of H$_2$O$_2$ under a higher temperature, the temperature of ODS using H$_2$O$_2$ oxidant is normally lower than 100 °C$^{142, 167}$. Thus, the water bath temperature was high enough for the current ODS of HFO.

The detailed experimental procedure was as follows: 100 ±0.5 g of HFO (with a sulfur content of 3.5 wt%) was put into a 500 mL beaker. H$_2$O$_2$ oxidant with a specific ratio of H$_2$O$_2$/S and organic acid (formic or acetic acid) catalyst with a specific ratio of catalyst/H$_2$O$_2$ were separately added into the beaker. A specific amount of extractant (such as water, methanol, acetonitrile, etc.) was also added to the beaker. When the water bath reactor was heated up to the desired temperature, the beaker containing HFO, oxidative solution, and extractant was put into the bath reactor and magnetically stirred for a specific reaction time for ODS and extraction. After the end of the reaction, the mixture solution was poured into a separation funnel and kept at least for 12 h to ensure the separation of oil in the aqueous phase. The desulfurized HFO was then separately analyzed by ICP-OES and CHNS analyzer (Thermo Scientific™ Flash 2000) to obtain sulfur and other elemental composition. Then the ODS efficiency was calculated.

For sulfur measurement using the ICP-OES method, it should be noted that the HFO sample was first digested by a microwave digester. Then the ICP-OES instrument was used to accurately determine HFO sulfur content. The HFO
For copyeditor
digestion procedure was as follows: an accurately weighed HFO sample (less than 200 mg) was added into 8 ml nitric acid (70 wt% of concentration) and digested by ETHOS-E microwave digester (Italy Milestone Corporation). The digestion Teflon ware was heated from room temperature to 220 °C for 20 min and then kept at 220 °C for 15 min. After cooling down to room temperature, it was diluted to 25 mL by distilled water for the ICP-OES analysis.

4.3.2. Results and Discussion

Factors such as reaction temperature, reaction time, oxidant/S ratio, oxidant/catalyst ratio, oxidant catalyst type, extractant type, extraction time influence ODS efficiency. In the current preliminary study, we studied the most important factors, such as oxidant/S ratio, oxidant/catalyst ratio, and extractant type affecting ODS efficiency. The reaction temperature and time were selected as 60 °C and 60 min, respectively, and the extractant to HFO ratio was 1:1 based on the results reported in the literature. Based on previous studies, the presence of sulfur-extracting agents like acetonitrile in the ODS process has been proved to enhance ODS efficiency. Thus, we combined the processes of sulfur oxidation and extraction by combining HFO, oxidant/catalyst, and extractant reagents together.

The sulfur and CHN/O contents of the raw and desulfurized HFO are listed in Table 5. To determine the quantity of polar sulfur compounds existing in the raw HFO that can be directly removed by the extractant, HFO was exposed to the extractants, namely, acetonitrile and methanol, without the oxidation process. After extraction by acetonitrile and methanol, the sulfur content in HFO changed from 3.53 to 3.36 and 3.31, respectively. This result indicates that at least 6.2 wt% of the polar sulfur component exists in the raw HFO, and the extraction performance of methanol is better than that of acetonitrile. Then the effect of the O/S ratio and extractant on sulfur removal was investigated. First, the influence of the O/S ratio was studied by varying the catalyst content and keeping the experimental conditions constant. The O/S ratios tested were 1.5, 3, 5, 10 mol/mol. The quantities used are reported in Table 5. It can be noticed from the atomic composition that no linear correlation is present among the results of the different samples. This is mainly due to the presence of water and acetonitrile residue at the end of the process. This problem indicates that the CHNS analysis is useful to estimate the quality of the separation process but not the efficiency of the ODS reaction in case of incomplete separation. Comparing the different extractants, namely acetonitrile and methanol, sulfur removal using acetonitrile was better than that using methanol. The sulfur removal efficiency using methanol was 15.0 and 14.4 wt% while that using acetonitrile was 22.1 and 21.0 wt% at an H₂O₂/S ratio of 5:1 and 3:1, respectively.

<table>
<thead>
<tr>
<th>No.</th>
<th>H₂O₂/S (mole ratio)</th>
<th>H₂O₂/Acid (mole ratio)</th>
<th>Extractant</th>
<th>N (wt %)</th>
<th>C (wt %)</th>
<th>H (wt %)</th>
<th>O (wt %)</th>
<th>S (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw HFO</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.36</td>
<td>85.50</td>
<td>10.84</td>
<td>&lt;0.1</td>
<td>3.53</td>
</tr>
<tr>
<td>#1</td>
<td>0</td>
<td>0</td>
<td>Acetonitrile</td>
<td>1.01</td>
<td>82.60</td>
<td>10.76</td>
<td>2.27</td>
<td>3.36</td>
</tr>
</tbody>
</table>
4.3.3. Molecular-level characterization

Raw HFO and desulfurized HFO samples were ionized by atmospheric pressure photoionization (APPI) and electrospray ionization (ESI) coupled with FT-ICR MS, as these have been used extensively to study residual fuel samples. ESI is efficient for ionizing polar molecules (heteroatom-containing N, O, S species) which are notorious for causing catalyst fouling, corrosion, and deposit formation, whereas APPI is efficient in ionizing species that are not observed by ESI, like benzo and dibenzothiophenes, polyaromatic hydrocarbons, cycloalkanes, etc., and it is, therefore, suitable for analyzing the overall composition of petroleum samples.

The mass spectra of HFO and the desulfurized HFO obtained from various O/S ratios using APPI and ESI FT-ICR mass spectrometry are presented in Figure 32 and Figure 33. ESI FT-ICR MS was employed because it is effective in ionizing heteroatom-containing (N, O, S) species. The mass spectra show the weight distribution of various species in the fuel, which have a significant effect on their physical properties. They also show how the fuel changes on account of the oxidative desulfurization processes. The AMW of HFO calculated from APPI FTICR MS was found to be 549 Da. The AMWs of the desulfurized HFO samples obtained using O/S ratios 1.5, 3, 5, and 10 were calculated as 555, 561, 562, and 566 Da, respectively. The increase in AMW of the desulfurized HFO is due to the addition of the oxygen atoms to the sulfur to form sulfones and sulfoxides.
Figure 32: APPI FT-ICR mass spectra of desulfurized HFO samples with varying O/S ratios
The abundance of various molecular species in the samples obtained from APPI and ESI FT-ICR MS is shown in Figure 33 and Figure , respectively. HC indicates pure hydrocarbon species. Hydrocarbon molecules containing one, two, and three sulfur atoms are represented with the following notation: $S_1$, $S_2$, and $S_3$, respectively. Similarly, the notations N, O, and NS indicate hydrocarbon species with one nitrogen atom, one oxygen atom, and one nitrogen and...
sulfur atom each, respectively. Since ODS resulted in the oxidation of S compounds to form sulfones (SO$_2$) and sulfoxides (SO) and other species (OS$_2$), all oxygen and sulfur-containing heteroatoms are collectively indicated by OS species. This also includes NOS (species containing all three heteroatoms). The quantity (in relative %) of each class is evaluated from the knowledge of the intensity of the specific class divided by the sum total of all measured ion intensities. The S1, S2, and S3 classes in the desulfurized HFO samples reduced continuously when the O/S ratio was increased as the excess oxidant converted the S species in HFO to sulfones/sulfoxides. The abundance of OS species in HFO is 1.1% as determined using APPI, whereas the abundance of the OS species in the desulfurized HFO sample increased from 8.8% to 18.8% when the O/S ratio was increased from 1.5 to 10. From the ESI FTICR MS, the OS species in HFO increased from 6.7% to 85.3% in the desulfurized sample when the O/S ratio was 10. Similarly, the abundance of the OS species increased in the aqueous phase when the O/S ratio was increased.

Figure 34: APPI FTICR MS: Relative abundance of molecular classes present in HFO and desulfurized HFO
The different compound classes and their distributions were then visualized based on their DBE, carbon number (CN), and relative abundance. The molecular class distribution of OS species as a function of DBE and carbon number is presented in Figure 35 and Figure 36. The bubble size indicates the magnitude of the recorded mass peaks. DBE values allow us to understand the molecular structure of the species based on their degree of unsaturation. The APPI and ESI FTICR MS show that there are very few OS species present in the HFO sample and that the oxidant increases as the OS species increase.
Figure 36: APPI FTICR iso-abundance plot (carbon number vs DBE) of HFO and desulfurized HFO of hydrocarbon molecules containing OS heteroatoms
The ODS experiments presented several challenges, the most important of which was emulsion formation between HFO and the aqueous-phase $\text{H}_2\text{O}_2$/catalyst solution. This was observed after the ODS process due to the presence of the emulsifier component (asphaltene) naturally present in HFO. When a high stirring speed (high shear force) was used to enhance the interaction of the sulfur compounds with the oxidant, HFO was well emulsified and the aqueous-phase $\text{H}_2\text{O}_2$/catalyst solution became separated from the oil phase, resulting in a decrease in the carbon content of the mixture whereas the O content increased markedly. Even at lower stirring speed, a small amount of aqueous-phase $\text{H}_2\text{O}_2$/catalyst solution was still not completely separated from HFO. These results show that the carbon contents of the desulfurized sample decreased by around 10 wt% after the ODS process, indicating the presence of the aqueous phase in the desulfurized oil. Another challenge was that the HFO became sticky after the ODS process, and its...
viscosity increased, which is in accordance with the results of some previous studies\textsuperscript{141, 159}. A reduction in the residence time was expected to be the correct solution to solve problems related to recombination and emulsion formation. A continuous stirring process was the logical solution to obtain better separation and a less viscous product.

We also combined the continuous stirring process with ultrasonically induced cavitation to speed up the oxidation process and achieve good conversion with lower residence time.

### 4.4. Ultrasonically assisted oxidative desulfurization (UAOD)

ODS assisted by ultrasonic cavitation has significant efficacy and performance advantages\textsuperscript{50, 164, 165, 172}. Acoustic cavitation introduced by ultrasonic waves (within 20 to 50kHz for industrial applications) generates extreme temperatures and pressures via the collapse of microbubbles. This phenomenon has been known to cause sonochemical changes leading to the formation of hydroxyl radicals via homolytic cleavage of a water molecule. They are highly reactive with other molecules in the system. A typical product from this system is in-situ hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}). A further advantage of sonication is a reduction in viscosity, achieved by cracking of asphaltenes into smaller, low-boiling-temperature molecules. The sulfur is catalytically oxidized into sulfones, which are easily separated.

The increase in surface area from ultrasonic treatment enhances both the kinetics and the mass-transfer in the ODS process as follows. Oxidative desulfurization occurs in a biphasic system that has an organic and an aqueous phase. The aqueous phase forms the dispersed phase, and oil as the continuous phase is separated by a layer of asphaltenes and resins in the case of HFO. Upon reaction with a catalyst, the oxidant creates an in-situ, highly diffusive oxidative species that diffuses out of the aqueous-phase surface layer of the droplet into the organic phase. This in-situ species oxidizes the sulfurous compounds inside the organic phase to their corresponding sulfones. The sulfones, once formed, tend to cover the layer (droplet surface) that is separating the phases and accumulate there. After a while, when this sulfone accumulation is high, further diffusion of the oxidative species from the aqueous phase to the organic phase is hampered, slowing down the ODS process. Thus, mass-transfer limitations are imposed unless sufficiently small droplet sizes are achieved while preparing bi-phasic emulsions. Therefore, the oxidative desulfurization of liquid fuels can be considerably accelerated by ultrasound treatment, which renders very small-sized (nano-scale) droplets.

The most widely used oxidizing agent in the literature was hydrogen peroxide. Hydrogen peroxide is soluble in oil and commercially available as diluted in water. It contributes to oxidation in a liquid-liquid reaction, Oxidation is expected to take place at the interface between hydrogen peroxide/water and oil. The reaction rate is proportional to the surface area between the two liquids. This makes clear the importance of good mixing to improve the surface area available for the reaction. As discussed in the previous sections, ultrasonically induced cavitation is an effective way to form very fine emulsions. A direct comparison between mechanical and ultrasonically induced cavitation as a
mixing method highlights a difference in the obtainable surface area of more than 100 times, which results from the ratio between the surface exposed to an equivalent volume of water in the oil.

Another relevant aspect that makes UIC particularly suitable to improve the efficiency of ODS consists of bubble formation. The bubbles formed by the pressure oscillations of the sonotrode are largely formed by the most volatile species, which in an H₂O₂/HFO/Acetic Acid system are acetic acid and H₂O₂. The occurrence of cavitation bubbles results in the contribution of another mechanism to the reactivity of the system, the gas-liquid reactions.

4.4.1. UAOD experiments and results

UIC-enhanced ODS experiments were performed in a pre-pilot-scale continuous system at KAUST. The UAOD rig commissioning is described in detail in an upcoming publication from our group. The reactor consisted of a cylindrical vessel in which a sonotrode vibrates at a frequency of 20000 Hz. The power input of the sonotrode was 2000 W. The fuel flows parallel to the sonotrode. Both oxidizing agent (H₂O₂) and catalyst (CH₃) were mixed before injection to the reactor chamber. The fraction of hydrogen peroxide was kept 3:1 the stoichiometry of oxidation reaction, while the amount of acetic acid was kept in a 1:1 molar ratio with the sulfur molecules.

The fuel tested in the facility was a blend of Arabian Extra Light (AXL) and HFO. The choice to dilute HFO in the initial tests was driven by difficulties in operating a continuous process with a highly viscous fuel. The first test consisted of running with AXL. AXL is a relatively low-sulfur fuel (0.7 % by mass) compared to HFO, for which the sulfur ranges from 2.7 to 4 % by weight. AXL also presents lower viscosity than HFO, which simplifies the operation of the rig. We proceeded by gradually adding HFO to AXL and modifying the process where needed. It is important to note that AXL includes the entire spectrum of organo-sulfur compounds, and only the heaviest of those are amenable to ODS. In contrast, HFO include predominantly heavy sulurous compounds. Intuitively, we expected to see more sulfur reduction in HFO than AXL from the ODS treatment.

The detailed discussion on the UAOD experiments conducted on the KAUST UAOD rig is presented in a separate publication. Here, we briefly summarize some key results. We explored three combinations: a) Pure AXL; b) AXL 10% and HFO 90% by mass; and c) AXL 50% and HFO 50% by mass. The 50% HFO run with AXL dilution was a sufficient demonstration of the ODS rig’s operation capability in handling highly viscous fuels. We managed to run the process smoothly for more than three hours with no significant problems while achieving a steady operation after approximately 10 minutes.

The reactor temperature increased with time during the test and reached 75 °C because of the action of the sonotrode. The reactor was operated for two hours with recirculation. Given the size of the reactor, 0.005 m³, and the flow rate of 10 kg/h, the residence time was about half of the total time spent in the loop. The mixture of AXL/HFO,
acetic acid, and hydrogen peroxide was extracted after 30 min, 1 h, and 2 h. The mixture was also washed with an equivalent amount of acetonitrile, and then the sulfones were separated through centrifugation (5 min). The elemental composition of the aqueous and organic phase was measured through ICP-OES to determine the sulfur content and the eventual dilution through mass balance.

The results reported in Figure 38 clearly demonstrate the substantial reduction in sulfur and confirm that ODS preferentially oxidizes heavy molecules, validating literature reports\textsuperscript{166}. In the DBE vs. carbon number plot (see Figure 38), the raw fuel includes a wide spectrum of molecules containing sulfur. The carbon atom range goes from 10 to 80 mainly because of the contribution of the vacuum residue fraction of HFO. A large proportion of the sulfurized molecules was removed through the ODS reaction and the following separation that was performed with acetonitrile. The black dots indicate the normalized fraction of sulfurized molecules. It is possible to see that the range of carbon atoms drastically decreased to between 10 and 40 and that the maximum DBE was reduced compared to the raw fuel. The data confirm the tendency of peroxides to preferentially oxidize large molecules in general and tiophenic groups in particular. This strengthens our premise that HDS and ODS are complementary. As expected, the reduction in sulfur increased by increasing the amount of HFO in the mixture, as more molecules became available for the oxidation process. Figure reports the results in terms of sulfur percentage reduction by mass. A reduction in the sulfur by nearly 40% by weight was achieved.

The separation step was expected to be the limiting step of the ODS process. It is likely that by increasing the amount of HFO, the removal of sulfur will become more substantial because of the higher availability of sulfur species suitable for ODS. The ODS process still requires further optimization with addition of deasphalting and mild-HDS.
Figure 38: Distribution of sulfur molecules in AXL before and after sonication. The range of sulfurized molecules substantially reduces after the ODS. The test was performed in the KAUST ODS rig on AXL. Results shown are from FTICR-MS performed on the samples. The size of the points reflects the relative amount of the species. DBE stands for double bond equivalent, a measure of aromaticity.
Figure 39: Sulfur reduction by mass % for three samples tested in the KAUST ODS rig facility. The reduction was measured through elemental composition with the ICP-OE technique and cross-validated with the EDX technique. Mass balance was accurately calculated to account for dilution, although it was negligible.

5. Conclusions

The combustion of hydrocarbons will continue to feed the planet’s growing demand for mobility and power generation over the next several decades, shifting to lower value, more difficult-to-burn fuels while at the same time meeting more stringent emissions regulations. These lower-value fuels include heavy fuel oils and vacuum residuals, which are difficult to burn cleanly due to the presence of asphaltenes, the exceptionally high molecular weight insoluble fractions found in high concentrations in crude oils. In particular, HFOs are widely used fuels in marine and power-generation sectors, and IMO2020 promulgation has redistributed the HFO demand and pushed the world’s economy into a new paradigm. We seek solutions for such a complex oil industry paradigm utilizing some state-of-the-art technologies like ultrasonically induced (UIC) cavitation. In the current chapter, we have discussed a roadmap for use of “bottom-of-barrel fuel” with high asphalten content via UIC-based fuel upgrading, desulfurization, and direct use (emulsions). We expect that a strategy of using UIC for asphalten modification and water-in-HFO-enabled micro-explosions will significantly impact the combustion of HFO. Furthermore, ultrasonic-assisted oxidative desulfurization (UAOD) can be utilized to remove undesired sulfur to meet marine or power sector requirements. Applications of deasphalting, emulsions, and desulfurization solutions could be for a multiplicity of combustion-driven energy conversion platforms, including compression ignition engines, gas turbines, and boilers. Some salient points need reiteration are as follows:
1. We conducted a detailed characterization of the physicochemical properties and molecular-level structural information of HFO, deasphalted oil, and asphaltenes. FTICR-MS and $^1$H NMR analytical methodologies are sufficient to decipher relevant molecular-level information for heavy viscous fractions of crude oils. Deasphalting of HFO imparts great advantages in terms of transport properties like viscosity and corrosion propensity and induces trace metal removal. However, the reduction of heteroatoms like sulfur and nitrogen is marginal. The proportion of light/lesser aromatic structural classes increases with deasphalting, which should improve combustion efficiency and reduce particulate matter formation.

2. Sonication is expected to act mostly on the structure of the asphaltenes and, therefore, to influence the physical properties of the mixture. But the fundamental understanding of how the average molecular weight of the asphaltenes changes in time as a result of the sonication process is yet unknown. We delved into the fundamentals of UIC and how it may impact asphaltenes structures. The dependence on molecular structure modification on sonication time was explored by extracting samples from the irradiated batch sample at different times. The asphaltene break up is followed by free-radical recombination reactions to form larger aggregates, and hence could be counter-productive. FTCIR-MS data acquired from HFO-sonication experiments confirmed this point and highlighted the need for an optimized irradiation time.

3. We characterized UIC-based water-in HFO emulsions using two techniques high-speed camera visualization and cryo-EM. Capturing the cavitation phenomenon at time-scales of cavitation offered unique information that could be utilized to validate computation models. Cryo-EM imaging provided insights into droplet size distribution and asphaltene’s role in emulsion stability. Engineering of optimized emulsions for various combustion applications can be based on information achieved from such characterization techniques.

4. We reported oxidative desulfurization (ODS) experiments without and with ultrasound (UAOD). ODS is ineffective for lighter sulfur species, easily removed by conventional hydro-desulfurization (HDS). ODS assisted by ultrasonic cavitation has significant efficacy and performance advantages. Our most recent results convey a 40% reduction of sulfur from AXL/HFO blends following UAOD using the KAUST rig.

5. The biggest identified challenge in UAOD or ODS is the asphaltene content of the HFO. It is responsible for high-viscosity, which impedes flow processes, leads to catalyst poisoning, and an assortment of undesired heavy particulate-matter (sludge-like) formations when oxidized during the ODS process. Hence, deasphalting as a pretreatment of HFO before desulfurization could improve the process by reducing these obstacles and overall cost.
6. The ODS and HDS processes have mutually reverse reactivity characteristics for the spectrum of organosulfur compounds found in petroleum products. The molecular-level characterization of ODS HFO reveals the extent and kind of structural classes in HFO that are amenable to ODS. A much higher reduction is achievable if mild-HDS is used prior to the ODS step. Hence, the ODS and the HDS must be utilized as complementary processes for maximum effectiveness, completeness of sulfur reduction, and overall process optimization.

7. Overall, we recommend: (a) Deasphalting, (b) UAOD with mild HDS, and (c) UIC-based water-in-HFO emulsions as some potential solutions for HFO utilization as a fuel in the marine and power-generation sectors.

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