Preferential Vaporization Potential of Crude Oils and its Impact on Flame Flashback Behaviors

Ayuob Al wahaibi

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Preferential Vaporization Potential of Crude Oils and its Impact on Flame Flashback Behaviors

by

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ABSTRACT

As combined cycle gas turbines for power generation operating on light distillate fuels provide a sufficient energy, there is a global trend in using heavy liquids (e.g. HFO, crude oils) for direct-firing in gas turbine. However, using these heavy fuels imposes many challenges due to their wide range of physical/chemical properties, which control near-limit combustion behaviors, such lean blow-out and flashback. In addition, the ignition propensity of these heavy fuels is not reported in crude assays, and utilizing a simple, with small sample, and quick methodology to characterize the ignition propensity is important in determining the fuel quality.

In this work, the derived cetane number (DCN) of whole crudes and their distillation cuts are measured. Four crudes were distilled into four fractions as reported in crude assays: light naphtha, heavy naphtha, kerosene, and light gas oil. The DCN of each fraction was measured and compared using an ignition quality tester (IQT), where the DCN values for all the crude cuts increase from 23-35 for lighter fractions to 50-60 for heavier one. This variation of DCN values over their distillation curves was observed before (for distillate fuels, e.g. Petroleum-derived fuels) to be linked to strongly influence near limit combustion behaviors (e.g. LBO) through preferential vaporization, which suggests that preferential vaporization will play a significant role when using whole crudes in gas turbine applications. To further analyze such a behavior, $^1$H and $^{13}$C NMR spectra were acquired to characterize the chemical functional groups controlling
the DCN and their distinctive influence. Based on a chemical functional groups approach, a QSPR regression model was developed indicating that the n-paraffinic CH\textsubscript{2} group has the most influence in determining the global ignition propensity of crude oils. The analysis also suggests that chemical reactivity (DCN) of crude oils can be roughly estimated based on key-functional groups determined from \textsuperscript{1}H and \textsuperscript{13}C NMR analysis.

Finally, to investigate the impact of preferential vaporization on flame flashback, a spray burner was developed which has the ability to control the extent of fuel vaporization. Experiment was first conducted at burner temperature of 700 K with various n-alkanes and iso-alkanes, where two distinct flame flashback behaviors were observed, propagation and ignition-driven flashback. Two binary mixture were formulated that have identical chemical reactivity for fully vaporized fuel/air mixture but exhibit a drastic difference of ignition propensity under partially vaporized conditions. To observe the role of preferential vaporization effectively, the experiment was conducted at 450 K using those two mixtures. One of the Crude oils was used to investigate crude oil flashback behaviors in the spray burner.
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LIST OF SYMBOLS

H/C ........................................................................... Hydrogen to Carbon Ratio
E ................................................................................. Activation Energy
atm .............................................................................. Atmosphere
T_b ................................................................................ Boiling Temperature
°C ................................................................................ Degree Celsius
K ...................................................................................... Degree Kelvin
$^{1}$H .............................................................. Proton NMR Spectrum
$^{13}$C ............................................................. Carbon NMR Spectrum
d$_{30}$ ........................................................................... Volume-averaged Diameter
$\tau_{flow}$ ........................................................................ Flow Residence Time
$\delta$ ................................................................................ Chemical Shift
ppm ........................................................................... Parts Per Million
$U_{FB}$ ........................................................................ Flashback Jet Velocity
$u'_{FB}$ ......................................................................... Local Flow Fluctuation
$S_l$ ................................................................................ Laminar Flame Speed
LIST OF ABBREVIATIONS

API .................................................................................................................. American Petroleum

ASL .................................................................................................................. Arabian Super Light

ASTM ................................................... American Society for Testing and Materials

CFR ............................................................ Cooperative Fuel Research

CN .................................................................................................................. Cetane Number

CO₂ ............................................................................................................ Carbon Dioxide

DCN ............................................................................................................. Derived Cetane Number

GE ................................................................................................................. General Electric

H₂S ............................................................................................................... Hydrogen Sulfide

HFO .............................................................................................................. Heavy Fuel Oils

IC ................................................................................................................. Internal Combustion

IDT ............................................................................................................... Ignition Delay Time

IQT ................................................................................................................. Ignition Quality Tester

LBO .............................................................................................................. Lean Blow-out

MFC ............................................................................................................. Mass Flow Controller
MW .................................................................................................................. Molecular Weight

NMR ............................................................................................................ Nuclear Magnetic Resonance

NO_\text{x} ......................................................................................................... Nitro oxides

O_2 .................................................................................................................. Oxygen

PDPA ............................................................................................................. Phase Doppler Particle Analyzer

PMTs ............................................................................................................. Photomultiplier Tubes

QOOH ............................................................................................................ Alkylhydroperoxy Radicals

QSPR ........................................................................................................... Quantitative Structure Property Relationships

R ..................................................................................................................... Fuel Radicals

RO_2 .............................................................................................................. Alkylperoxy Radical

SO_\text{x} ......................................................................................................... Sulfur Oxides

TGA .............................................................................................................. Thermogravimetric Analyzer
CHAPTER 1

INTRODUCTION

1.1 Global Energy Sources

Pursuing the reduction of greenhouse emissions as well as providing the energy needed in our daily life have been a topic of interest for a long time. At a global scale, one of the key greenhouse gases emitted by human activities is Carbon Dioxide. About 65% of Carbon Dioxide is emitted by using fossil fuels (e.g. coal, oil, natural gas, etc.) and industrial processes. Looking at the global emission by economic sector, electricity and heat generation are the dominant sectors leading to the production of those gases [1]. In order to lower the emission of greenhouse gases and to combat climate changes and their impacts, governments around the world have spent a substantial time and efforts.

Starting with the Paris agreements, long term temperature goal to hold the global average temperature increase (below 2°C pre-industrial level), that all countries collaborate to lower greenhouse gas emission to zero within the second half of the 21 century [2]. Moving on with the aviation [3] and marine [4] transportation, by having long term pathway to achieve 50% reduction of CO₂ emission by the year of 2050.

In addition, some countries are highly investing in renewable (solar, water, wind, and geothermal) energies technologies aiming to utilize abundance of renewable sources in lowering greenhouse gaseous emission [5]. Since renewable energy are still the lowest
energy sources for some countries comparing with fossil fuels, it’s very important for these countries to find another source that would support the power need as well as to keep the greenhouse gases emission within an accepted range. To cope with this issue and to lower the dependency on fossil fuels, nuclear energy generation was adopted as it doesn’t produce air pollution or greenhouse gases while operating. Although nuclear power generation provide efficient and clean source of energy, it raises a major environmental concern; a creation of radioactive waste such as: uranium, spent reactor fuel, and radioactive waste. These radioactive wastes can remain radioactive for thousands of years and requires special handling.

Despite all global efforts to lower the dependency on fossil fuel in power generation, it's expected that fossil fuels to stay a dominant source of energy in some countries for decades (figure 1.1). A lot of this energy is being produced as electricity for either residential or industrial sector and mainly generated by burning fossil fuels. In 2019, the U.S. Energy information administration has estimated that about 62.7% of the
US electricity generation comes from burning fossil fuels, and natural gas is the highest fuel contributing in electricity generation comparing with other fuels [6]. In addition to that, about 80% of the total energy consumed in the US during the same year was primarily fossil fuels sources. Figure 1.2 below shows a breakdown of the US primary energy consumption by energy source in 2019 [6].

![Figure 1.2 EIA estimate of the U.S. primary energy consumption breakdown by energy source in the year of 2019.](image)

To generate electricity in power plants, many technologies have been used and gas turbines have been one of the dominant used technologies for power generations. Gas turbines are considered an internal combustion (IC) engine type as the air and the fuel are mixed and burned inside a unit called “combustion chamber”. Natural gas is typically used in many power plants, as it produces the least of greenhouse gases, compared to coal, and combined cycle has been developed to increase the efficiency of power plants. As natural gas combined cycle power plants provide high efficiency and clean energy, there will be increasing demand to provide natural gas in higher quantity. In addition,
some regions, where natural gas prices is rising and the quantity needed may not be available, are looking for other alternatives such as liquid fuels (e.g. distilled fuel, bio-liquids) in order to secure energy stability. In other regions, refined liquid fuels may not be available in economical quantities. thus, an increase interest in using crude oils as a fuel in gas turbines for power generation have been in intense inters. In this regard, manufactures [7,8] have addressed their gas turbine fuel flexibility and capability of burning liquid fuels while operating reliably and continuously. In fact, due to the growing demand for power generations, some rich-oil countries are using crude oil utilizing crude-fired Rankine cycle system for electricity generation and desalination [9].

Gas turbine operating on crude oil and residual oils, also known as Heavy fuel oil (HFO), as opposed to distillate/refined fuel not only avoid costly refinery processes, but also achieves higher energy conversion efficiency. However, the nature of these oils adds additional complexity over refined liquid fuels and imposes numerous technical challenges as a results of their wide range of physical and chemical properties (density, viscosity, Va/Al/Si formation, sulfur content, carbon residue) [10]. Unlike simple hydrocarbons fuels (natural gas and refined distilled fuels), using crude oils as a whole has many challenges as they require special treatments before being introduced into the combustor, to meet industrial gas turbine limits on contaminates and metallic as well as sustaining the operation of the turbine.

Crude oils contain high amount of metals and ash forming compounds that could severally damage gas turbine parts by causing corrosion, erosion, and fouling. For example, some crude oils contain high amount of corrosive elements such as vanadium, sodium, potassium that can lead to accelerated corrosion of the turbine nozzles and
buckets and deposit formation in hot gas path components. Moreover, Ash forming crude oils are undesirable because the accumulation and deposit of ash, which increase over time, restricts the throat area of the nozzle leading to forced outage. This leads to impacting the performance of the gas turbine, and therefore requires frequent maintenance, meaning shorter lifetime of some parts and high service cost [7,11].

1.2 Crude Oil Characterizations by API and Sulfur Content

When evaluating liquid fuels, there are many key parameters to be considered in order to approve that fuel to be used in gas turbine, which reflect its market value and quality characteristics. One key parameter is the sulfur content (by mass), as different crudes contain a widely different sulfur content (figure 1.3), varying from less than 0.05 to more than 10 % Wt, and is measured by different standard techniques [12,13]. Sulfur, which is one of the main contaminants in crude oils, is considered an undesirable contaminant in crude oil, or petroleum refined product, because when it combust, it could produce some toxic gases such as Sulfur oxides (SOx) emissions to the atmosphere, which reacts in the presence of moisture resulting in acidic products (acid rain) [14]. Another example of undesirable contaminant is Hydrogen Sulfide (H2S), which is highly toxic, corrosive, and flammable, and poses real challenges to operators as well as the operation of gas turbine.

Another key parameter is density. Density may vary from very light to very heavy depending on the oil relative density. Therefore, the American Petroleum institute (API) has developed a density scale that reflect how light and heavy the crude compared to water. If the crude’s API gravity is high, it means its lighter than water, has lower
density, and will float on it. On the other hand, if the crude’s API gravity is low, this means that the crude is heavier than water, has higher density, and will sink in the water. In other words, API gravity is the inverse of the crude’s density [15].

In the petroleum industry, there is no clear definition of light vs heavy in density and sweet vs sour in sulfur content, due to the variation of the crude’s quality, market value, and geographic location. Therefore, some petroleum agencies, such as the National Energy Board of Canada and the New York Mercantile Exchange, defines light crude oils at API gravity of 30.1 and higher, and sweet crude oils at sulfur content of 0.5 %wt and lower, respectively. Figure 1.3 summarizes the API gravity and sulfur content for large number of crude oils, but not all crudes, in which refinery assays are reported.
and available [16-19]. Table 1.1 summarizes some of the properties of the four crudes used in this work (including ASL).

Light crude oil with sulfur content < 0.5% mass are more preferable as they contain exponentially large fractions that are directly processed into gasoline, kerosene, and diesel, and produce less emissions. In addition, this grade of crude oil can be directly used in stationary gas turbine for power generation. Recently, gas turbine manufacturers [7,8] have pursued direct firing of selected crudes, such as Arabian Super light (ASL), a very sweet and light crude. ASL is a unique crude with some properties that are similar to distillate oils, such as hydrogen to carbon (H/C) ratio, low vanadium content, and specific density similar to those distilled oils [20]. ASL still requires pre-treatments to remove some undesirable contaminants. By developing some advanced sulfur and ash/metallics removal technologies [20,21] that could mitigate combustion-related fouling/erosion/corrosion characteristics of other crudes, there are potentials of improving petroleum refining and cost effective power generation.

Table 1.1 : Summary of the studied four crude oils properties (including ASL).

<table>
<thead>
<tr>
<th>Crude oil</th>
<th>API</th>
<th>Density at 15 °C [kg/L]</th>
<th>Vanadium [ppm wt.]</th>
<th>Sulfur [% wt.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASL</td>
<td>48.8</td>
<td>0.785</td>
<td>&lt; 1</td>
<td>0.036</td>
</tr>
<tr>
<td>Crude 1</td>
<td>41.3</td>
<td>0.819</td>
<td>1</td>
<td>0.762</td>
</tr>
<tr>
<td>Crude 2</td>
<td>44.3</td>
<td>0.805</td>
<td>2</td>
<td>0.184</td>
</tr>
<tr>
<td>Crude 3</td>
<td>39.1</td>
<td>0.829</td>
<td>1.9</td>
<td>0.208</td>
</tr>
<tr>
<td>Crude 4</td>
<td>34.9</td>
<td>0.850</td>
<td>0.8</td>
<td>0.170</td>
</tr>
</tbody>
</table>
1.3 Crude Oil Combustion Characteristics in Literature Review

Based upon literature review, there has not been any work that have characterized the ignition propensity of crude oils nor they proposed a simple analysis of the ignition propensity of crude oil as a whole or distilled cut. There have been many studies that have characterized crude oil for specific economic and environmental purposes. For instance, some recent studies have demonstrated the possibility of creating a kinetic model for crude oils by identifying some important parameters (e.g. Activation energy (E) and pre-exponential factor), which are important for numerical modeling. In this study, three heavy crude oils (API < 30) were investigated either in their original form (as a whole crude) or mixed with a clay (e.g. sand or crushed carbonate). The experiments were conducted at atmospheric pressure, and used a thermogravimetric (TGA) analyzer, which provides thermal analysis where the mass of a sample is measured over time as the temperature changes. Thus, this study is not meant to be a comprehensive, but to evaluate the basic kinetics constants of crude oils such as activation energy, rate constant, etc. many observations were made based on a general understating of physics and chemistry of combustion. For instance, it was found that there is no observed trend of the API value of crude on combustion kinetics. Also, increasing oxygen partial pressure (out of the total air pressure used in the analyzer) results in lower front temperature and more complete reactions [23].

Other works have studies combustion characteristics of crude oils to assess in oil-spill or fire hazardous of crude oils in storage facilities. For instance, Y.Iwata et al. have conducted a small-scale free burning pool fire testes in a cone calorimeter to obtain some basic characteristics of combusted crude oils. 14 different crude oils (most of them are
light) and kerosene (as benchmark) were used as test samples. It was concluded that some parameters, such as heat release rate, mass loss rate, smoke yield, etc., are a function of the crude type. In addition to this observation, it was observed that some of those parameters correlates well with crude oil density, thus the possibility of predicting combustion characteristics of crude oil based on simple physical properties of the fuel. It's worth noting that this experiment was conducted as a method for fire protection and suppression of crude oil tank fires [24]. In addition, there have been many studies that thermally characterized crude oils for in-situ combustion processes [25-27].

Gas turbine manufacturers and industrial companies have also studied and demonstrated their gas turbine burning experience with some crude oils. General electric (GE), for example, have been using crude oil in heavy duty gas turbine for power generation for years. They, in fact, have more 190 gas turbine (E-class) that have operated on heavy fuel oil and crude oils as primary fuel [7]. Other than GE, Mitsubishi Hitachi Power systems (MHPS) has evaluated the potentials of using crude oils in gas turbine and the risks associated with it. MHPS have shown that the improved design of the combustor can handle gases fuels as well as some crude oils (e.g. ASL) at the same time. They have evaluated some basic physical and chemical properties that are associated with combustion phenomena (e.g. flashback, flame stability), gas emissions (e.g. NOx), and hardware risks (e.g. coke/ash deposit, nozzle clogging) [8].

1.4 Hydrocarbon Fuel Studies Relevant to Gas Turbine Combustor

Liquid hydrocarbon fuels consist of various chemical organic species and are sorted into different categories, such as n-paraffin, iso-paraffin, cyclo-paraffin, olefins
and aromatics. Each one of those species has different properties, and fuels with multi-components have a wide range of chemical and physical properties. Therefore, when using multi-component liquid fuels in gas turbine applications, it involves a multiphase combustion behavior coupled with fuel chemical and physical properties. The variation of those properties with different types of fuels have an effect on the operational limit of gas turbine applications and extending near limit combustion phenomena (e.g. lean blow-out (LBO), flashback, flame stability) have been a subject of intense interests.

Utilizing a rapid, with small sample, and simple characterization tool to predict the global combustion behaviors of different hydrocarbons have been recently demonstrated. Won et al. had demonstrated that the derive cetane number (DCN), which represents the chemical reactivity of fuel, can be used a chemical potential indicator for near limit combustion behaviors [28]. It was observed that DCN values of different fuels, such as alternative and petroleum-derived fuels, can represent the ignition propensity and flame propagation characteristics.

Since most liquid fuels are introduced into the gas turbine combustors as liquid, it’s important to observe the coupling between the chemical (e.g. DCN) and physical (e.g. preferential vaporization) properties on combustion behaviors. researcher suggest that some near limit combustion phenomena (such as LBO), are governed by preferential vaporization [24]. Preferential vaporization occurs when multi-components fuels are injected into the combustor and due to the different vapor pressure of each components, volatile components vaporize faster causing a variation in the global combustion behaviors. To elaborate on that, in a recent study of jet fuels, which have narrower distillation properties than crude oil, it was shown that preferential vaporization has an
influence on near limit combustion behaviors (e.g. Lean blow-out (LBO), flame stability), resulting from the derived cetane number (DCN) variation over their distillation fraction[29]. Unfortunately, this ignition propensity parameter is only available and utilized for distillate fuels, including heavy fuel oils (HFO), and not reported in crude oil assays [31].

Another simple method in characterizing the ignition propensity and quantifying the composition of complex real fuels is the chemical functional groups approach. Since real fuels consist of complex molecular composition as a result of numerous structural variations, the combustion behaviors cannot be characterized based on each specific molecular composition. Therefore, the functional groups approach can define the reaction kinetic characteristics related to combustion behaviors and describes the fuel in terms of its specific groups of atoms within molecules, which is known as constituent atom types or molecular fragments, rather than by its specific molecules [31]. Previous works have shown that the chemical functional groups approach can be used to construct regression models that are capable of predicting references indicators that describes that ignition propensity of fuels such as Octane number (ON), Cetane number (CN), and Derived cetane number (DCN) [30, 32-33] as well as physical properties [34].

The chemical functional groups also permit the construction of a regression model, known as quantitative structure-property relation (QSPR), which can relate each distinctive functional groups to combustion behaviors. The QSPR proposed in [33] was to predict the DCN values utilizing six functional groups descriptors, which are: 1)CH$_2$, 2) (CH$_2$)$_n$, 3) CH$_3$, 4) C, 5) CH, and 6) benzyl-type groups. Those groups represent the n-alkyl, iso-alkyl, and aromatic functionalities, which represents most of the chemical
functionalties in hydrocarbon fuels. Recently, (CH$_2$)-cyclo representing cyclo-alkanes functionality, has been evaluated to see the impact of cyclic ring structure functionality with other chemical functionalities on ignition propensity, which is the extension of prior QSPR [35]. Chemical functional group distributions can be experimentally determined by nuclear magnetic resonance (NMR) spectroscopy. Further details of NMR spectra interpretation can be found elsewhere [31, 36-37].

Since crude oils and/or heavy fuel oils are a mixture of complex molecular structure molecules, it’s difficult to apply a detailed and comprehensive analysis to evaluate combustion behaviors, especially when looking at every single type of species that are presented in the crude. Although manufacturers have evaluated possibility of using crude oils in different classes of gas turbine, their focus is mainly to modify their gas turbine based on the customers’ requirements and the available crudes to be used. Therefore, considering a simple and direct method to evaluate the ignition propensity of any crudes or their distillates will be valuable to be added in crudes assays that are available online.

While operating gas turbine engines in a fuel-lean premixed mode is favored for low emissions and higher efficiency, it comes with unfavorable costs as it creates some operationality issues due to the fuel’s compositions variations. To overcome those issues and sustain the operation of the combustor in more safe and reliable manner, it’s important to address the influence of fuel variability to the combustor performance. Fuel variation, composition, has a significant influence to four known combustor operational phenomena: flashback, autoignition, blowout, and flame stability, and sustaining the combustor above the limit of those phenomena is at high interest [38]. Flame flashback,
as opposed to blowout, imposes a lot of risks to the combustor internal elements and requires a careful consideration. Figure 1.4 shows a burner assembly damaged by flame flashback, which cannot withstand high temperature.

[Figure 1.4 Damaged burner assembly (left) and new burner assembly (right) [39]]

Flashback occurs when flame propagation speed is faster than local flame speed, which leads the flame to physically propagates upstream inside the combustor into the premixing section. Many studies have been conducted over the years to understand flame flashback behaviors. One study has characterized flashback mechanisms by autoignition, boundary layers, turbulence, instability, and flashback induced by vortex [40]. Others have tried to mitigate flashback limit by changing fuel composition, combustion instability, confinement, turbulence and vortex of the flow [38, 41-44]. However, these studies were conducted under pre-vaporized premixed conditions, and multi-phase combustion was not explained, leading to the question: what would happen if the fuel-air mixture was in partially vaporized conditions?
Understanding the evaporation mechanism of multi-component fuel droplet and spray was carefully studied. The variation of droplet evaporation over time due to fuel specific physical properties has a significant influence on the combustion processes [45-49]. When the relevant properties are similar, Yn Cheng liu et al. concluded that there is no significant preferential vaporization impact from droplet evaporation [50]. Once would suspect that if the fuel has a wide range of physical and chemical properties and partially vaporized, the global combustion behaviors will depend on the extent of fuel evaporation (preferential vaporization) as the composition of the partially vaporized fuel changes over time. Many studies have been conducted on multi-phase spray and droplets evaporation and their related combustion behaviors, such as flame propagation [51], lean blow-out [52], and stability of spray combustion [53]. Based upon literature review, no study has been conducted to characterize the impact of preferential vaporization on flame flashback.

In this regard, the objective of this work is to investigate preferential vaporization potential of crude oil and its impact on flame flashback behaviors. The chemical reactivity potential of four crude oils are characterized based on their reported assays and the measured DCN of the distillation fractions of each cut along their boiling temperatures. This involve preparing distillation cuts, for each sample, through a distillation device. The DCN results of four distilled fractions of each crude are then compared. To further analyze the distilled factions of the tested crudes, $^1$H and $^{13}$C NMR spectral results are interpreted to characterize the chemical functional group characteristics controlling the change in DCN values. To investigate the role of preferential vaporization impact on flashback effectively, a spray burner was developed.
which have the ability of controlling the extent of fuel vaporization. Four n-alkanes and two iso-alkanes, representing a wide range of physical/chemical properties, were first evaluated at fully vaporized conditions to observe flashback behaviors. Then, two binary mixtures were formulated that have the same global chemical reactivity but exhibit a drastic difference when preferential vaporization plays a role. Crude 1 was used to observe flashback behaviors in the spray burner.
CHAPTER 2

EXPERIENTAL METHODOLOGY

Due to the limited availability of acquiring crude oil samples, only four light crude oil samples were acquired and tested, and their representing properties are summarized in table 1.1 (labeled as crude 1,2,3, and 4) along with ASL. The API gravity and sulfur content of each crude were obtained from the reported assays and shown in figure 3. As shown in figure 1 and table 1.1, all the crude oil samples have sulfur content less than 0.5% except for Crude 1 and all are light crudes (API < 30.1)

To characterize the chemical reactivity potential of those crude samples over their distillation curves, five distillation cuts of each crude sample were prepared using a distillation device following the ASTM D86 distillation procedure [54]. Then, the distilled cuts were tested to get the their DCN values in ignition quality tester (IQT) according to the ASTM D6980 standard [55].

2.1 Distillation Apparatus

The ASTM D86 distillation method utilizes a heating a glass container ( ~ 1 L) off liquid fuel with electric heater to vaporize the liquid sample while measuring the vaporization temperature at the top exit of the container. Then, the vapor is introduced to a heat exchanger tube, which is located in a chilled water bath continuously cooled by a circulating bath flow (using Cole-Parmer, Polystat UX-12122-62). The chilled water is
Figure 2.1 Current Distillation Device used to distill crude oil sample (following ASTM D86).

maintained at 273 K and ensures a complete condensation of the vaporized samples by the time it reaches a collection glass container. Five distillation cuts were prepared for each crude sample with specific ranges of fuel boiling temperature \( T_b \), representing those temperatures that are typically reported, in crude assays, to characterize refinery distillation parameters [18]. These temperature ranges are: light naphtha at \( T_b < 95 \degree C \), heavy naphtha at \( 95 < T_b < 175 \degree C \), kerosene at \( 175 < T_b < 232 \degree C \), and light gas oil at \( 232 < T_b < 343 \degree C \). For the last cut, \( T_b > 343 \degree C \), thermal cracking of the crude samples was observed during the distillation process (at atmospheric pressure) and defined in this work as “residual” cut. About 1 L of the crude samples were distilled and enough volume of each cut was obtained for the IQT measurement. Figure 2.2 compares the current distillation measurements for Crude 1 along with the reported data in the associated crude assay. Considering the current ASTM D86 procedure has unpredictable uncertainty associated with the liquid volume measurements and the configuration, there
is a close agreement with current measurements, which assures that the distillation procedure and the laboratory equipment are producing sufficiently similar data to those reported in the crude assay.

Figure 2.2 Distillation measurements comparison of Crude 1 with the previous measurements provided by Siemens AG.

2.2 Ignition Quality Tester (IQT)

The chemical reactivity potential of the distilled cuts of each crude sample were characterized by the DCN measurements performed using the IQT (Figure 2.3) in accordance with the ASTM standard D6890. The DCN can be viewed as a global measure of the fuel autoignition propensity, an alternative measurement of the commonly used metric Cetane number (CN), measured by the IQT. An advantage of using the IQT
is it requires lower fuel volume to measure the DCN than the Cooperative fuel research (CFR) engine which measures the CN, the experimental time needed for the measurements and the lower errors. The IQT has a controlled heated (830 K) constant volume pressurized chamber (~20 atm). It measures the ignition delay time (IDT), which is the time between the start of the injection of liquid fuel and the recovery of the combustion chamber pressure (recorded by pressure transducer), then converts it to DCN value. The overall ignition delay measured by the IQT is affected by both spray physics and fuel chemistry, in other words, fuel chemical and physical properties [29]. However, it was demonstrated previously [28] that the conversion of DCN from IDT following ASTM D6890 standard with n-heptane as a calibration fuel allows a sufficient evaluation of fuel’s chemical properties, supporting prior literature in indicating that the DCN is a strong indicator of chemical structure effects on ignition behaviors [56, 57].

It’s worth noting that the IQT is used to quickly and relatively accurately measures the DCN of wide range of hydrocarbons (e.g. diesel fuel, alternative fuel, etc.) within the a measurable range of ignition delay time. Thus, prior to measure the DCN of crude’s distillation cuts, the ability of the IQT to measure the DCN of whole crudes was investigated using Crude 1 in the facility of the IQT manufacturer (Advanced Engine Technology Ltd), since the reactivity potentials (DCN) of crude oils or crude oil fractions were never measured before and the nature of crude oil as a whole (vary viscous liquid) may causes some issues for the IQT hardware. The DCN of whole Crude 1 was successfully determined to be 52.6 at AET facility, which is comparable to the DCN’s of petroleum derived jet fuels recently reported [58, 59].
2.3 Nuclear Magnetic Resonance (NMR)

To further understand the variation of the measured DCN, $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were obtained for each distillation cut. The NMR utilized in this study is a Bruker Avance III-HD 400 MHz NMR facility. The NMR spectra is an analytical chemistry technique the provides information about the content of
a sample as well as the molecular structure. It’s a simple way of determining the presents of distinct functional groups (described previously) that are present in fuels. The NMR machines uses a liquid sample that is exposed to electromagnetic field. When the magnetic field is applied to the samples, the nucleus in the molecules resonates at characteristic frequency, where different nucleus resonates at different frequencies. Atoms in similar bonding environments have similar resonant frequencies, and atoms from the same classes of atom types are treated as molecular fragments, which defines a single functional group. This reaction of different nucleus at different frequencies is then detected by the NMR device and recorded, which later analyzed to determine different functional groups.

The NMR samples were prepared by dissolving the distilled cut (~ 0.1 g) into a mixture of deuterated chloroform (CDCl$_3$, ~ 3 cm$^3$) as a solvent, and Chromium (III) acetylacetone (Cr(C$_5$H$_7$O$_2$)$_3$, ~ 0.15 cm$^3$) as the relaxation agent. The NMR measurements were all taken at ~ 298k, therefore, thermal decomposition of the samples was relatively negligible, and sufficient delay time (30 s for $^1$H, 40 s for $^{13}$C NMR) was applied in order to quantitively acquire $^1$H and $^{13}$C NMR spectra.

2.4 Phase Doppler Particle Analyzer (PDPA)

Phase doppler particle analyzer (PDPA) was used to characterize and measure droplet/spray size and data rate, thus, to estimate the extent of fuel vaporization. The system used in this work is provided by TSI, which includes Powersight laser (TR-SS-1D-532) and a receiver (450300). A single laser beam, with wavelength of 532 nm, is emitted from the laser source and then split into two laser beams by a Bragg cell. Those
Figure 2.4 Schematic of the PDPA setup

two laser beams then intersect at a specific focal length and creates a fringe pattern (a series of light and dark fringes) and a sample volume where all the measurements takes place. The PDPA receiver has two internal optics with a specified focal length (~300 mm and 200 mm). the scattered light is then collected by the receiver optics and fed into a photodetector module (PDM 1000) and converted to electrical signals by Photomultiplier Tubes (PMTs). The frequency of the measured signal is then displayed using a software (FlowSizer64) and the size and velocity are calculated.

A schematic of the PDPA setup is shown in in figure 2.4. The principal of the PDPA system used to measure the velocity of droplets is light scattering. As the laser beam intersect at a specific point, this results in a fringe pattern of light and dark fringes. As a particle is moving through this pattern, it scatters light when crossing the bright fringe, and does not scatter any light when crossing the dark fringe, resulting in
fluctuation in scattered light intensity, where the frequency detected is proportional to the velocity of the particle. Since the frequency of the laser beam, and the distance from the laser lens are known, the distance of the between the light and dark patterns are calculated. Using the distance between the fringes and the frequency of the scattered light, the detected frequency is then converted to velocity. Since PDPA has two receiving optics with known distance, the frequency of the scattered light detected by the receiver would have a phase shift. Using the phase shift and the detected frequency, the droplet diameter is calculated.

2.5 Spray Burner

Figure 2.5 shows the overall schematics of the spray burner, which is designed to control the extent of fuel vaporization. The extent of fuel vaporization is controlled by adjusting atomizer location along with the burner temperature. The burner exit diameter is 20 mm and 75mm converging section. The vaporization section, which controls the fuel vaporization inside the burner, is a 610mm long with inner diameter of 50 mm. Electric heaters, as shown in the figure, and temperature controller were used to control the burner surface temperature, main air inlet temperature, as well as the fuel vaporization in a controlled manner. To control liquid fuel flow rate, a high-pressure syringe pump (Harvard Apparatus, PHD 2000) was used. The air flow rate was controlled with sonic nozzles and mas flow controller (MFC) as sown in the figure, where both calibrated using DryCal 800 (Mesa Labs) at room temperature. The actual volumetric flow rates were converted and obtained by the change of gas density with temperature. The spray injector injects the liquid fuel in the vaporization section through an orifice (diameter of 254 μm) and airflow (0.6 L/min). The spray injector is movable along
When the fuel is injected inside the burner, it was noticed that there is a significant velocity fluctuation and non-uniformity in the velocity profile at the burner exit. This fluctuation is a result of the injected liquid fuel droplets having mean velocities much faster than the surrounding air flow speed. To suppress this fluctuation and homogenize the velocity profile, a converging-diverging tube with throat diameter of 20 mm was placed on top of the injector, where the injected liquid spray passes through it. It was also noticed a fuel gasification of liquid fuel inside the injector before the fuel is
sprayed due to the excessive increase of nozzle temperature. To cope with this issue, a water-cooling system was installed to keep the injected liquid fuel temperature lower than the boiling point of the fuel.

To examine the capability of the spray burner in controlling the extent of fuel vaporization, the droplet size at the exit of the burner were fully evaluated with two n-alkane fuels, n-heptane and n-dodecane, at 300 K and 400 K, respectively and at unit equivalence ratio. Figure 2.6 (a) and (d) shows the results of PDPA measurements of the volume averaged droplet size ($d_{30}$) as a function of flow residence time. Although the boiling temperature of both n-heptane and n-dodecane are higher than the burner temperature, the partial pressure at this temperature allows for continuous evaporation in the air depending on the residence time. Using the partial pressure calculated by the Antoine equation, the initial diameter for both fuels was estimated. In case of a single

![Figure 2.6 Results of PDPA measurements. (a) Volume-averaged diameter ($d_{30}$), (b) application of the D² law, (c) vaporized liquid volume fraction for n-heptane at 300 K, (d) Volume-averaged diameter ($d_{30}$), (e) application of the D² law, (f) vaporized liquid volume fraction for n-dodecane at 400 K.](image-url)
droplet, its known that the droplet evaporates following the D^2 law. Although the injected spray may not be directly following the D^2 law because the burner temperature lower than the boiling temperature of the tested fuels, it was used here to estimate the initial diameter. The measured diameter (d_{30}) was then normalized by the calculated initial diameter, which decreases monotonically with increasing the flow residence time as shown in figure 2.6 (b) and (e).

To estimate the extent of fuel vaporization, the droplet size and data acquisition obtained by PDPA were used. Then, vaporized fraction of fuel (F_{vaporized}) can be estimated from the following equation:

\[
F_{vaporized} = 1 - \frac{\pi d_{30}^3}{6Q_{fuel} A_{exit}} A_f f \quad \text{(Eq.1)}
\]

Where A_{exit} and A_f are the area of the burner nozzle exit and the cross-sectional area of the measuring volume of PDPA, respectively. The diameter d_{30} was used as it represents the droplets volumetric liquid information. Q_{fuel} is the total fuel flow rate into the spray burner. f is the data acquisition rate, where the PDPA detects the number of droplets in unit time through cross-sectional area of the measuring volume. Figure 2.6 (c) and (f) clearly show that extent of fuel vaporization, or the vaporized fraction defined as F_{vaporized}, increases with residence time, where the fully vaporized conditions are achieved around 2.3 s. In case of n-dodecane, identical measurements were obtained, conforming that spray burner has the ability to control the extent of fuel vaporization by adjusting the burner temperature and flow residence time.
CHAPTER 3
RESULTS AND DISCUSSION

3.1. Characterizing Preferential Vaporization Potential of Crude Oil

After verifying the distillation measurements of Crude 1 (figure 2.2) and the applicability of the current distillation procedure (following ASTM D86) and lab equipment, the other crudes were distilled into five distillation cuts. As previously mentioned, the crudes were distilled into five fractions based on specific ranges of fuel boiling temperatures, which are typically reported in crude essays. These distilled fractions are: light naphtha, heavy naphtha, kerosene, light gas oil, and the remaining cut is defined in this study as “Residue.” Figure 8 summarizes the liquid volume fraction of each distilled crude’s cuts with respect to the specified range of boiling temperature ($T_b$).

Light crudes are expected to have more liquid fraction of the lighter cuts (light and heavy naphtha), while heavy crudes are expected to have more liquid fractions of the heavier cuts (e.g. light gas oil, residue). From figure 3.1 Crude 2, the lightest crude, exhibit larger fractions in light and heavy naphtha ranges compared to the other crudes. Whereas Crude 4, the heaviest crude, contains relatively less light naphtha fraction and more light gas fraction. The data from figure 3.1 are consistent with the API values listed in Table 1.1 (also shown in figure 1.3) in terms of “Light” vs “Heavy” crudes. Figure 3.2 compares the measured DCN values for all the distilled cuts of the four crude’s studied in this work. Generally, the DCN values for each distilled cut for all the crudes increases...
from the lighter cuts to the heavier cuts, but with different initial DCN values for the lighter cuts. Crude 1 lightest cut, for instance, has a DCN value of 34.5 and it increases by about 23 units for the heaviest cut. A smaller difference in DCN values of previously characterized petroleum derived jet fuels (e.g. Jet-A, JP-5), where the DCN increases substantially from light to heavy cuts over their distillation curve [29]. The variance of DCN values over distillation cuts, especially for lighter cuts (more volatile fractions) was found to be linked to some near-limit combustion behaviors (e.g. LBO) through preferential vaporization.

Chemical functional groups approach is a low-dimensional descriptor that is capable of describing fuel reaction kinetics and combustion phenomena. Since its
difficult to describe a fuel by its detailed species analysis of molecules, due to the complexity of real fuels, the chemical functional groups describe the fuel in terms of its atom types (molecular fragment). Previous work [33, 60, 61] has shown that the overall chemical structure of real fuels can be characterized through chemical functional group distribution, where key functional groups are identified by appropriately interpreting $^1$H and $^{13}$C NMR. To further interpret the DCN variation of crudes over their distillation cuts, a quantitative $^1$H and $^{13}$C NMR spectra was acquired, and interpreted using the procedure similar to described in [36,37]. Considering the complexity of Crude’s compositions, a simple approach was used to correlate the chemical shift range to each atomic structure in this work.

Figure 3.2 The measured DCN values for four distilled crude samples (except for residual cuts)
Figure 3.3 $^1$H NMR spectra for whole Crude 1 and its distillation cuts
Figure 3.3 shows the $^1$H NMR spectra for whole Crude 1 and its distillation cuts. The $^1$H NMR spectra of whole Crude 1 shows that its compositions is mainly composed of paraffinic and aromatic species, where the peaks of paraffinic structure are dominant over aromatics. By comparing the spectra of whole Crude and its distillation cuts, we can clearly (as indicated in figure 3.3) see that the two chemical functional groups that qualitatively have the major impact on the chemical potential are paraffinic CH$_2$ and CH$_3$ groups. Those key functional groups are observed in the NMR spectral chemical shift of $0.2 < \delta < 1.02$ and $1.02 < \delta < 2.0$ respectively. For the lightest distillation cuts (light naphtha), the CH$_3$ functional groups have higher peak intensity than CH$_2$ functional groups, in other words, qualitatively more dominant. As we move to heavier distillation cuts, the intensity of CH$_3$ becomes less dominant, while CH$_2$’s functional groups exhibit stronger peaks, which indicates that the n-alkyl chain (represented by (CH$_2$)$_n$ group) is increasing from lighter to heavier cuts.

This tendency was demonstrated by Won, et al. where it was shown that the ignition propensity associated with low temperature (and intermediate) kinetics is strongly influenced by the abundance of CH$_2$ over CH$_3$ groups in fuels [62]. It was also proposed that the ratio of CH$_2$/CH$_3$ (by the metric $[CH_2/CH_3] \times ([CH_2]+[CH_3])$) as a potential governing parameter controlling low temperature reactivity (auto-ignition) kinetics of paraffinic fuels. This behavior was clarified based on low temperature kinetics chemistry. It was well established that at low temperature conditions (less 950 K), the fuel molecules (RH) is oxidized through atomic hydrogen (H) abstraction reactions involving OH and HO$_2$, which then forms fuel alkyl radical (R). The fuel radicals (R) is then react with oxygen producing alkylperoxy radicals (R + O$_2$ = RO$_2$). The
isomerization of alkylperoxy by hydrogen forms alkylhydroperoxy (QOOH), which is considered the key species for low temperature chain mechanism that strongly influences auto-ignition [63]. Since the ratio of paraffinic CH$_2$ to CH$_3$ was proposed [62] to define the reactivity of n-paraffinic fuels, it was concluded that this ratio also governs ignition delay time, where fuels with higher paraffinic CH$_2$/CH$_3$ ratio exhibit lower ignition delay (higher DCN), consistent with the DCN tendency in figure 3.2 and the NMR data in figure 3.3.

Table 3.1 Chemical shifts of Proton (H) spectral regions adopted from [36]

<table>
<thead>
<tr>
<th>Proton Type</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 paraffinic CH$_3$</td>
<td>0.2 &lt; $\delta$ &lt; 1.02</td>
</tr>
<tr>
<td>2 paraffinic CH$_2$</td>
<td>1.02 &lt; $\delta$ &lt; 2.0</td>
</tr>
<tr>
<td>3 $\alpha$-to-aromatic CH$_3$</td>
<td>2.1 &lt; $\delta$ &lt; 2.4</td>
</tr>
<tr>
<td>4 $\alpha$-to-aromatic CH$_2$</td>
<td>2.4 &lt; $\delta$ &lt; 4.3</td>
</tr>
<tr>
<td>5 alkenic CH$_2$</td>
<td>4.3 &lt; $\delta$ &lt; 5.1</td>
</tr>
<tr>
<td>6 alkenic CH</td>
<td>5.1 &lt; $\delta$ &lt; 6.2</td>
</tr>
<tr>
<td>7 monoaromatic CH</td>
<td>6.2 &lt; $\delta$ &lt; 7.4</td>
</tr>
<tr>
<td>8 polyaromatic CH</td>
<td>7.4 &lt; $\delta$ &lt; 10.7</td>
</tr>
</tbody>
</table>

Table 3.2 Chemical shifts of Carbon (C) spectral regions adopted from [36]

<table>
<thead>
<tr>
<th>Carbon Type</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 chain $\beta$-CH$_2$, $\alpha$ to ring CH$_3$</td>
<td>21.9 &lt; $\delta$ &lt; 25.0</td>
</tr>
<tr>
<td>2 cycloparaffin CH$_2$</td>
<td>25.0 &lt; $\delta$ &lt; 28.5</td>
</tr>
<tr>
<td>3 chain $\delta$-CH$_2$, $\alpha$ to aromatic napthenes, aromatic attached ethyl CH$_2$</td>
<td>28.5 &lt; $\delta$ &lt; 30.8</td>
</tr>
<tr>
<td>4 chain $\gamma$-CH$_2$, $\beta$ to aromatic CH$_2$</td>
<td>30.8 &lt; $\delta$ &lt; 32.7</td>
</tr>
<tr>
<td>5 paraffinic CH and CH$_2$</td>
<td>32.7 &lt; $\delta$ &lt; 45.0</td>
</tr>
</tbody>
</table>
Based on previous studies, and the procedure described in [36,37], the $^1$H NMR spectra were integrated over a specific range of chemical shift, as listed in table 3.1, to identify eight atom types. The assignment of these ranges was based on extensive studies of hydrocarbons with known molecular structure (composition). To further analyze the functional groups abundance in more details, $^{13}$C NMR spectra of the crude samples and their distillation cuts was acquired. In addition, since $^1$H NMR spectra do not differentiate between cycloparaffin CH$_2$ and n-paraffinic CH$_2$, $^{13}$C NMR spectra analysis were utilized for this reason, and integrated over chemical shifts as listed in table 3.2.

![Graph showing 13C NMR spectra](image)

Figure 3.4 $^{13}$C NMR spectra for whole Crude 1.

Figure 3.4 shows the $^{13}$C NMR spectra for whole Crude 1, where the insert figure shows a full spectrum, where some carbon atoms are detectable at high chemical shift (e.g. quaternary aromatic, aromatic CH). At a relatively low dimensional chemical
complexity of some fuels, it is possible to produce a fully quantitative $^{13}$C NMR (and $^1$H NMR) spectra when accounting for the correct NMR parameters (e.g. pulse width, acquisition time, sweep width, etc) [36,37]. However, when considering a high dimensional complex fuel samples, many things need to be accounted for, such as the NMR characteristics and the acquisition approach, in order to achieve a reasonably fully quantitative C NMR spectrum. Therefore, for the purpose of simplicity, the $^{13}$C NMR was utilized to determine the fraction of cycloparaffin CH$_2$ as a fraction of the total CH$_2$.

The abundance of CH$_2$, cyclo and n-paraffin, was estimated by integrating the $^{13}$C NMR spectra over specific ranges as shown in Table 3.2. Although the chemical shift ranges listed in table 3.2 are primarily known as a result of CH$_2$ groups, there are some contributions from other types of functional groups such as α to ring CH$_3$, α to aromatic naphthene’s, etc. Therefore, accounting for these functional groups that exist in the range of CH$_2$ functional group helps lower the uncertainty in the estimation of the CH$_2$ abundance. The fraction of cycloparaffin CH2 was determined by the ratio of two integrals, ratio of cycloparaffin, in the chemical shift of $25.0 < \delta < 28.5$, over the total CH$_2$ ratio, in the chemical shift of $21 < \delta < 45$. The approach used in the estimation of the mole fraction of CH$_2$ groups was then verified by comparing the values estimated from both the $^1$H and the $^{13}$C NMR. The total CH$_2$ estimated from the $^1$H NMR spectra was found to be 0.64, while the one from $^{13}$C NMR spectra was 0.62, which demonstrate a relatively consistent evaluation of NMR spectra following [36,37].

Analyzing the $^1$H and the $^{13}$C NMR spectra concurrently for whole crude samples and their distillation cuts have identified the amole fraction of seven functional groups that mainly make up have the most effect on the ignition propensity of the studied crudes.
in this work. These functional groups were quantitatively estimated and are: paraffin CH$_2$, $\alpha$ to aromatic CH$_2$, cyclo-paraffin CH$_2$, monoaromatic CH, $\alpha$ to aromatic CH$_3$, paraffin CH$_3$, and polyaromatic CH. Figure 3.5 shows the differences in mole fraction of three key functional groups for crude sample (as whole sample) and their distillation cuts. The whole sample is identified from the figure as cut (0), and the distillation cuts are: light naphtha (1), heavy naphtha (2), kerosene (3), light gas oil (4), and residue (5), respectively. As previously discussed and shown in figure 10 (in the case of Crude 1), the mole fraction of n-paraffin CH$_2$ increases from light to heavy distilled cuts, while paraffin CH$_3$ decreases for all the other distilled crude samples, which demonstrates consistency of DCN values shown in figure 3.2.

![Figure 3.5 The mole fraction of key functional groups.](image-url)
Regarding the monotonic tendency of the fraction of cyclo-paraffinic CH$_2$, it is important to establish a fundamental understanding of the role(s) of cyclo-paraffinic on combustion behaviors especially when the fuel needed to be used in gas turbine applications has a substantial amount of cyclo-paraffinic as they have unique combustion behaviors. This behavior unfortunately was never characterized for crude oils as a whole or distillate oils and will not be fully characterized in this work as well. Instead, since its fraction substantially increases in some jet fuels, the role of cyclo-alkanes was characterized recently [35]. It was concluded that cyclo-alkanes have a unique chemical kinetics, which depends on the molecular structure. In case of the saturated cyclo-alkanes (hydrocarbons consisting of hydrogen and carbon atoms arranged in a single ring structure), it was found that ignition propensity is strongly affected by the steric structure. The isomerization of fuel peroxy-radicals (QOOH), of this type of cyclo-alkanes is mainly controlled by the number of axial hydrogen atoms in each structural confirmation, which influences low-temperature auto-ignition. In the case of alkylated cyclo-alkanes (ring structure hydrocarbon with alkyl CH$_2$ side chain), the ignition propensity is strongly influenced by the alky-CH$_2$ side chain length rather than by the number of carbon atoms that make the ring structure. Since this tendency was not comprehensively quantified in this work and only used to differentiate between the n- and cyclo-paraffinic CH$_2$, it is still important to pay attention to the unique and monatomic behaviors of cyclo-paraffinic CH$_2$ as they have different ignition propensity as shown in figure 3.5.

Using the seven functional groups identified above, a simple analysis was performed to construct a quantitative structure-property relation (QSPR). The purpose of the QSPR analysis is to roughly estimate the role of each key functional groups in
determining the DCN. Previous studies have demonstrated a comprehensive QSPR analysis, and well predicted the DCN, of different surrogate mixtures and real fuels using a chemical functional group approach [33, 60, 61]. The QSPR used in [33,61] utilizes a Scheffe simplex polynomial (using the first and second order of the equation) to roughly predict the DCN values, and interoperate the relationship between the predict and measured DCN. However, due to the limited experimental data/results on whole crudes and their distilled samples, only the first order terms (linear term) of the equation were considered in the regression analysis [64] and shown below:

\[ DCN = \sum_{i} a_i X_i \quad \text{(Eq. 2)} \]

Where \( a_i \) is the regression coefficients and \( X_i \) is the mole fraction of each

![Figure 3.6](image-url)  
Figure 3.6 The predicted values (using the regression equation) versus the measured values (using the IQT) of the DCN measurements.
functional group. Using the equation above as the model equation for the regression analysis, the DCN predicted values were estimated. Figure 3.6 shows the predicted values (using the regression equation) versus the measured values (using the IQT) of the DCN showing a reasonable linear prediction of DCN values. After utilizing the QSPR regression model to estimates the DCN values, a features sensitivity analysis (figure 3.7) based on the regression model was performed to evaluate the role of each functional groups identified above in determining the DCN values.

![Figure 3.7 Sensitivity analysis for each functional groups based on QSPR analysis](image)

The sensitivity analysis shows that paraffin CH₂ functional groups has the greatest impact on the ignition propensity characterized as DCN. This confirms what has been studied and demonstrated before of the dependency of DCN on paraffin CH₂ functional groups [28,62]. Previous analysis of the QSPR regression model for the DCN value of
multi-components mixtures (of hydrocarbons) shows that the DCN values is primarily sensitive to the abundance of paraffin CH$_2$ groups, and moderately sensitive to paraffin CH$_3$ and benzyl types functional groups. Considering the IQT’s temperature and pressure where the DCN is measured, a strong sensitivity of the paraffin CH$_2$ functional groups can be attributed to low temperature chemical kinetics potential which promotes and enhances low temperature chain branching reaction following the addition of oxygen to fuel radicals (e.g. $R + O_2 = RO_2$) [33]. Its worth noting that the abundance of paraffin CH$_2$ groups contribution reflects the ignition propensity of thermal decompositions of fuel and fuel radicals at high temperatures as well. In addition, CH$_2$ groups can be presents (attached) in other atom types (e.g. aromatics), which promotes a moderate role in determining the DCN. Following the analysis of the contribution of CH$_2$ groups in determining the ignition propensity of the distilled crude samples, its noticed that some functional groups (e.g. Polyaromatic CH, paraffinic CH$_3$, and α-to-aromatic CH$_3$) consumes the active radicals species in the oxidation of the species, which contributes negatively to the DCN values as shown in figure 3.7.

From figure 3.3 and 3.7, its suggested that the ignition propensity of crude oil samples and their distillation cuts can be roughly estimated by considering the ratio of paraffin CH$_2$ and paraffin CH$_3$ functional groups. Although previous studies [30,32,33] have shown that the aromatics functional groups plays an important role in the ignition propensities of real fuels, their abundance in the samples studied in this work is relatively lower (< 10%) than paraffin CH$_2$ and CH$_3$. Therefore, figure 3.8 shows the both measured (closed symbols) and predicted (open symbols, estimated from the QSPR regression model) DCN values of four crudes and their distilled cuts as a function of
paraffin CH$_2$ to paraffin CH$_3$ molar ratio. In addition, its suggested that the ignition propensities of whole crudes and their distillation cuts are primarily controlled by the presence of paraffin CH$_2$ and CH$_3$ functionalities. As noted, there is a slight deviation of the estimated DCN values for some samples (e.g. Crude 4 heavy naphtha) in the figure, which is possibly originates for some reasons, such as: preparations of NMR samples, NMR spectral peaks overlaps, and the uncertainties in differentiating between paraffin and cyclo-paraffin CH$_2$.

![Figure 3.8. DCN estimation for measured (closed dots) and predicted (open dots, from QSPR) of four crudes and their distillation cuts as function of paraffinic CH2/CH3 ratio.](image)

Figure 3.8. DCN estimation for measured (closed dots) and predicted (open dots, from QSPR) of four crudes and their distillation cuts as function of paraffinic CH2/CH3 ratio.
3.2. Impact of Preferential Vaporization on Flame Flashback

As noted from figure 3.2, preferential vaporization potential was observed as chemical reactivity of crude oil increase from lighter to heaver cuts, indicating the relative effects of fuel specific properties on the global combustion behaviors are critical. Similar preferential vaporization potentials was observed in jet fuels with relatively lower DCN values [29]. It was concluded that the difference in ignition propensity and/or global reactivity has a significant influence to near limit combustion behaviors (e.g. LBO, flashback, stability) through preferential vaporization. From literature review, the impact of preferential vaporization on flame flashback characteristics is no where to be found as most studies are conducted under fully pre-vaporized conditions. Therefore, a small-scale experiment to verify the effect of fuel properties on global combustion behaviors (e.g. flame flashback) under partially vaporized fuel/air mixture is conducted.

A small-scale spray burner was developed and designed to have the ability to investigate a partially vaporized premixed fuel/air mixture in a controlled manner. The spray burner was designed to have the capability of controlling the extent of fuel vaporization by adjusting the axial injector location and burner temperature. Figure 2.5 shows the spray burner setup along with flow control system.

After conforming that the spray burner is capable of controlling the extent of fuel vaporization (figure 2.6), the flame stability under partially vaporized conditions was characterized. Figure 3.9 below shows the flame stability map for n-heptane (nC7) at stoichiomteric conditions and burner temperature of 300K. The flame stability map is defined by varying flow residence time and jet velocity. The measurements were taken by
either having the jet velocity fixed and moving the spray injector axial positions, or by changing the jet velocity at fixed injector location.

From the flame stability measurements, four distinct flame behaviors were observed as indicated in the figure. As expected, flashback happens at low jet velocity, where propagation flame speed is faster than flame speed. As jet velocity increases, flashback still occurs at lower residence time, where there exits significant fraction of non-vaporized droplets. This occurs due to the local droplet evaporation near flame reaction zone, which induces flow fluctuations and increase the overall burning velocity and burning area. By increasing the flow residence time, two different flame behaviors were observed, wither unstable or attached flame. The unstable flame occur at short residence time, where the flame cannot sustain its stability due to the random evaporation
of droplets resulting in random fluctuation as shown in the inserted photo. On the other hand, as residence time increases and the fuel/air mixture reaches fully-vaporized conditions, resulting in more premixed, stable, Bunsen-type, flame. Finally, when the jet velocity reaches around 190 cm/s, the flame can no longer be sustained and becomes detached flame resulting in blowout.

Since real fuels consists of many components having a wide range of physical and chemical properties, its expected that they would exhibit various behaviors when preferential vaporization play a role. From the flame stability measurements above, its obvious that the extent of fuel vaporization plays a role affecting the flame stability. While the extent of fuel vaporization plays a role, its also important to investigate the role of chemical reactivity potential of the fuel on flame flashback. From the previously characterized ignitions propensity of crude oils, it was observed that the DCN varies from lighter to heavier cuts suggesting that the ignition propensity would play an important role on flame flashback. Therefore, flame flashback behaviors were investigated with various n-alkanes and iso-alkanes at burner temperature of 700K.

Table 3.3 The DCN values and molecular weight of four n-alkanes [65] and two iso-alkanes [66] tested in this work.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Chemical formula</th>
<th>MW [g/mol]</th>
<th>DCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-heptane (nC7)</td>
<td>C₇H₁₆</td>
<td>100.2</td>
<td>53.8</td>
</tr>
<tr>
<td>n-octane (nC8)</td>
<td>C₈H₁₈</td>
<td>114.2</td>
<td>58.2</td>
</tr>
<tr>
<td>n-dodecane (nC12)</td>
<td>C₁₂H₂₆</td>
<td>170.3</td>
<td>74.0</td>
</tr>
<tr>
<td>n-hexadecane (nC16)</td>
<td>C₁₆H₃₄</td>
<td>226.4</td>
<td>100.5</td>
</tr>
<tr>
<td>iso-octane (iC₈, 2,2,4-trimethylpentane)</td>
<td>C₈H₁₈</td>
<td>114.2</td>
<td>18.9</td>
</tr>
<tr>
<td>iso-cetane (iC₁₆, 2,2,4,4,6,8,8-heptamethylnonane)</td>
<td>C₁₆H₃₄</td>
<td>226.4</td>
<td>14.2</td>
</tr>
</tbody>
</table>
Figure 3.10 shows the measured flow speed at flashback ($U_{FB}$) as a function of equivalence ratio for four n-alkanes and two iso-alkanes fuels. The chosen fuels here span a wide range of physical (Molecular weight) and chemical (DCN) properties and are summarized in Table 3.3. From figure 3.10, there are two distinct flame flashback regimes for n-alkane fuels, propagation-driven flashback relatively at lower equivalence ratio, and ignition-driven flashback at higher equivalence ratio. The transition that distinguish the two regimes occur with n-heptane at equivalence ration of 1.5. As the molecular weight of the fuel increases, the transitioning equivalence ratio tends to be

![Figure 3.10 The measured jet velocity at flashback ($U_{FB}$) as a function of equivalence ratio for (a) n-alkanes and (b) iso-alkanes at 700 K.](image-url)
lower towards linear equivalence ratio, 1.4 for n-octane, 1.3 for n-dodecane, and 1.2 for n-hexadecane. From table 3.3 for n-alkane fuels, the chemical reactivity (DCN) increase with increasing the molecular weight, indicating that heavier n-alkanes have higher ignition propensity as a results of their \((CH_2)_n\) chain length. As the \((CH_2)_n\) chain gets longer, there are higher chances for the atomic H in \((CH_2)_n\) chain to be replaced with O\(_2\) resulting in growing a pool of active radicals through the formation of RO\(_2\) and the subsequent isomerization processes \([33,62,66]\). Although this work was conducted in laminar flow regime, Similar transition from propagation to ignition-driven flashback was observed previously in turbulent flow conditions \([67,68]\). Compared to n-alkanes where two regimes were observed, iso-alkanes exhibit only propagation-driven flashback as they tend to have longer ignition delay time \([62,66]\).

In the regime of propagation-driven flashback, the measured jet velocity at flashback shows the well-known trend of laminar flamen speeds as a function of equivalence ratio. Although laminar flame speed for either n-alkanes or iso-alkanes are known to be similar to each other, the measured flashback velocities of lighter fuels tends to have higher peak values. In case of iso-alkanes, which has less negative temperature coefficient compared to n-alkanes, the dominated methyl CH\(_3\) groups substantially suppress the reaction gateway for the formation of RO\(_2\) and subsequent isomerization. Thus, slowing the growth of pool of active radicals and therefore, exhibiting longer residence time.

In the ignition-driven flashback regime, the transitional equivalence ratio moves towards linear conditions as the molecular wight and ignition propensity of the n-alkane fuel increase as shown in figure 3.10. At low temperature, its known that ignition delay
time decreases with increasing n-alkanes molecular weight, more specifically number of 
(CH$_2$)$_n$ chain length, increasing equivalence ratio, and increasing pressure [62, 69]. Its 
worth noting that the current measurements were conducted at atmospheric pressure 
conditions, and since the ignition delay time is directly affected by pressure, its expected 
that the transition from propagation to ignition-driven flashback regime may occur in lean 
condition at higher pressure system relevant to gas turbine engine applications.

Figure 3.11 (a) Flow residence time as a function of equivalence ratio for n-octane, n-
dodecane, and n-hexadecane. (b) Flow residence time normalized by the ratio of CH$_2$ 
over CH$_3$ with equivalence ratio.
In order to demonstrate the role of ignition propensity on the regime of ignition-driven flashback, the measured flow residence time is plotted as a function of equivalence ratio for n-octane, n-dodecane, and n-hexadecane as shown in figure 3.11 (a). N-heptane measurements are not included due to the deviated tendency comparing with other n-alkanes fuels. This deviation comes from heat loss caused by the temperature of the burner, making the ignition-driven flashback of heptane more sensitive. Though the measurements of n-heptane are not included, they show similar tendency but with small deviation.

Based on the theory of low temperature chemical kinetics that was well-established previously [63] and briefly described in chapter 3.1, the ignition delay time of n-alkanes, iso-alkanes, and their mixtures is most sensitive to the abundance of CH₂ and CH₃. Thus, figure 3.11 (b) shows the flow residence time (ignition delay time) well characterized and scaled by the ratio of CH₂ to CH₃, confirming that flame flashback in the ignition-driven flashback is controlled by low-temperature chemical reactivity.

After confirming that the spray burner is capable of controlling the extent of fuel vaporization, the distinct impact of ignition propensity of fuel variation on flashback was demonstrated. In addition, the role of preferential vaporization on the stability of flame, including its role on flashback, was investigated as well. In the case of partially vaporized pre-mixed fuel/air mixture, it was noted that due to the incomplete droplet evaporation before reaction zone, the flame structure and stability was influenced and the possible chemical property variations, although the global chemical properties of each fuel are known. The fuels used to emphasize the flashback behaviors in this study so far under partially vaporized conditions are rather small molecules, which leads to the assumption;
liquid fuels, including crude oils, contain higher order molecular structure and a broad range of physical/chemical properties, which results in a pronounced low-temperature reactivity.

As discussed previously, the DCN represents the chemical reactivity potential and has a direct correlation with low temperature reactivity as well as high temperature kinetics due its sensitivity to functional groups \((\text{CH}_2)_n\) and \(\text{CH}_3\). Thus, once would expect that fuels having same global DCN values are expected to have similar flashback behaviors under fully vaporized conditions. Therefore, to investigate the role of preferential vaporization on flame flashback behaviors effectively, two binary mixtures were formulated having identical chemical reactivity for fully vaporized conditions but will exhibit a drastic change of ignition propensity under partially vaporized conditions. Table 3.4 summarizes the compositions of the two binary mixtures. These two binary mixtures were formulated based on the previously developed QSPR regression model that aims to formulate fuels based on the chemical functional groups approach, where the DCN was estimated to be the same \([33]\).

Table 3.4 The predicted DCN and \((\text{CH}_2)_n/\text{CH}_3\) ratio of the two formulated mixtures

<table>
<thead>
<tr>
<th></th>
<th>DCN</th>
<th>Boiling Temperature (°C)</th>
<th>Mixture 1 (nC8/iC16)</th>
<th>Mixture 2 (iC8/nC16)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Octane (nC8)</td>
<td>58.2</td>
<td>125</td>
<td>0.74</td>
<td>0</td>
</tr>
<tr>
<td>iso-Octane (iC8)</td>
<td>18.9</td>
<td>99.3</td>
<td>0</td>
<td>0.67</td>
</tr>
<tr>
<td>n-Hexadecane (nC16)</td>
<td>98.5</td>
<td>286.8</td>
<td>0</td>
<td>0.33</td>
</tr>
<tr>
<td>iso-Cetane (iC16)</td>
<td>14.2</td>
<td>240</td>
<td>0.26</td>
<td>0</td>
</tr>
<tr>
<td>Calculated DCN</td>
<td>-</td>
<td>-</td>
<td><strong>53.4</strong></td>
<td><strong>53.6</strong></td>
</tr>
<tr>
<td>((\text{CH}_2)_n/\text{CH}_3) ratio</td>
<td>-</td>
<td>-</td>
<td><strong>1.16</strong></td>
<td><strong>1.15</strong></td>
</tr>
</tbody>
</table>
Figure 3.12 (a) The boiling temperature of the two mixtures as a function of distilled molar fraction. (b) Gas-phase mole fraction compositions of mixture 1 as a function of distilled molar fraction. (c) Gas-phase mole fraction compositions of mixture 2 as a function of distilled molar fraction.
As indicated in table 3.4, the mixtures formulated in this work consists of two components each having a different physical (boiling temperature) and chemical (DCN) properties. When the two mixtures are injected inside the burner, they will have similar global combustion behaviors under fully vaporized conditions. However, they will exhibit different behaviors when preferential vaporization plays a role. Figure 3.12 shows the calculated fuel boiling temperatures as a function of distilled molar fraction. The difference in the boiling temperature between n-octane and iso-octane leads to higher initial boiling temperature for mixture 1 due to its large content in mixture 1. Identically, due to the lower boiling temperature of iso-cetane than n-hexadecane, the final boiling temperature of 1 is lower than mixture 2. To demonstrate the difference in the boiling temperature for the two mixture, the distilled mole fraction of each components for the two mixture is plotted as a function of distilled molar fraction. Clearly from figure 3.12 (b) and (c), the lighter components in mixture 1, n-octane, evaporate earlier than heavier components, iso-cetane, thus producing more reactive components in the earlier evaporation stages. On the other hand, lighter components in mixture 2, iso-cetane, evaporates earlier than heavier components, n-hexadecane, producing less reactive components in earlier evaporation stage. From the difference in the chemical reactivity of earlier evaporated components, it is expected that mixture 1 would have more significant reactivity than mixture 2 when preferential vaporization plays a role.

To investigate the effect of preferential vaporization impact on the flame flashback, first the ignition propensity of the two mixtures needs to be investigated at fully vaporized conditions. From the early experiment of single component fuels at fully vaporized conditions, two distinct flame flashback behaviors were identified: propagation
and ignition-driven flashback. Figure 3.13 shows flashback jet velocity as a function of equivalence ratio for the two formulated binary mixture at 700K. From the figure, the identical behaviors in terms of their flashback characteristics confirms the previously proposed assumption that they will exhibit similar behaviors at fully vaporized conditions. The results also show the identical transition from propagation to ignition-driven flashback, consistent with attributed match of key chemical functional groups and DCN values based the QSPR regression model.

![Figure 3.13 Flashback jet velocity as a function of equivalence ratio of the two mixtures at 700 K.](image)

When the fuel/air mixture are at fully vaporized conditions, the global combustion behaviors are shown to be identical (figure 3.13). However, when the binary mixtures are not at fully vaporized conditions, the DCN values are expected to be different, resulting
in different combustion behaviors, thus different flashback behaviors. As previously mentioned, the spray burner has the ability to control the extent of fuel vaporization by changing residence time. Therefore, when the injected spray has shorter residence time, the impact of preferential vaporization will appear differently for the two mixtures due to the DCN difference caused by the distinct evaporation characteristics of each mixture as shown in figure 3.12. Before evaluating the flame flashback behaviors at partially vaporized conditions, it's important to evaluate the spray characteristics first measured by PDPA at 450K. As previously discussed in chapter 2.5, two key parameters were used to evaluate the spray characteristics, volume mean diameter (d30) and data acquisition rate (f). Thus, both of these parameters are plotted as a function of flow residence time as shown in figure 3.14 (a).

As illustrated earlier (figure 3.12), the final boiling temperature of mixture 1 is lower than mixture 2, therefore, the measured volume-averaged diameter of mixture 1 decrease as flow residence time increases. On the other hand, the volume-averaged diameter of mixture 2 remains relatively constant as residence time increase possibly because of higher final boiling temperature. In addition to the volume-averaged diameter, figure 3.14 (a) also shows the data acquisition frequency detected by PDPA for both mixtures. It's obvious that both frequencies decrease as residence time increases indicating the extent of fuel evaporation over time history. The two parameters measured by the PDPA enables estimating the extent of fuel vaporization using Eq. 1. From figure 3.14 (b), the vaporized fraction, or extent of fuel vaporization increase over residence time, confirming that the spray burner can control the extent of fuel vaporization for both mixtures.
Figure 3.14 (a) The measured averaged-volume diameter ($d_{30}$) and data acquisition rate ($f$), (b) The estimated vaporized fraction measured by PDPA at 450 as a function of residence time.

Figure 3.15 shows the flashback jet velocity of the two mixtures as a function of residence time at stoichiometric conditions. The measured flashback jet velocity of both mixtures decrease with increasing residence time. However, flashback jet velocity of
mixture 1 is slightly higher than mixture 2 in earlier stage of evaporation due to preferential vaporization of more reactive components (n-octane) in mixture 1. As residence time increases approaching fully vaporized conditions, the flashback jet velocity exhibit identical values, consistent with the conditions of fully pre-vaporized pre-mixed conditions. The results also show that the DCN difference at partially vaporized conditions influences flame flashback behaviors.

Figure 3.15 Flashback Jet velocity ($U_{FB}$) for the two mixtures as a function of flow residence time at 450 K

Although figure 3.15 clearly shows the impact of preferential vaporization on determining flame flashback, it's important to evaluate the physics involved in the combustion of partially vaporized mixture. First, the random local fuel droplet evaporation prior to the reaction zone premixed Bunsen flame induces local velocity
fluctuation, resulting in perturbing the flame structure, which results in increasing the effective burning area similar to previously studied premixed flame [67,68,70]. Second, it is important to consider the composition in the fuel/air mixture and the correspondent effective equivalence ratio, which is influenced by the accelerated evaporation rate, as they determine laminar flame speed and the global burning characteristics of pre-mixed flame, especially when preferential vaporization controls the global burning characteristics, thus flame flashback behaviors.

To demonstrate the contribution from the local velocity fluctuation and laminar flame speed to flame flashback due to preferential vaporization, the flashback jet velocity is plotted as a function of vaporized liquid fraction of the mixtures measured by PDPA in figure 3.16 (a). Again, as the fuel/air mixture reaches fully vaporized conditions by increasing residence time, the difference in flashback jet velocity for both mixtures exhibit similar values. In figure 3.16 (b), the decrease difference in flashback jet velocity is correlated by decrease in the local flow fluctuation, which is the standard deviation of droplet speed measured by PDPA. The increase flow fluctuation at lower vaporized liquid fraction, or lower residence time, can be attributed to random local fuel droplet evaporation, which therefore induces volumetric expansion through phase change as well as flow perturbation by the fuel spray mechanism. Figure 3.16 (c) shows the laminar flame speed of the two mixtures, based upon a previously developed QSPR regression model for laminar flame speed by employing chemical functional group approach [71]. The estimated laminar flame speed clearly shows mixture 1 exhibit higher values than mixture 2 at lower vaporized fraction due to the higher reactive components in mixture 1.
Figure 3.16 (a) Flashback jet velocity ($U_{FB}$), (b) flow fluctuation ($u'_{FB}$) determined from PDPA, (c) laminar flame speed ($S_L$) as a function of vaporized liquid fraction.

\[
\begin{align*}
U_{FB} \quad [\text{cm/s}] \\
0.6 & \quad 0.7 & \quad 0.8 & \quad 0.9 & \quad 1 \\
170 \quad 210 \quad 230 \quad 250 & \\
\text{Mixture 1 (nC8/iC16)} & \quad \text{Mixture 2 (iC8/nC16)}
\end{align*}
\]

\[
\begin{align*}
u'_{FB} \quad [\text{cm/s}] \\
0.6 & \quad 0.7 & \quad 0.8 & \quad 0.9 & \quad 1 \\
0 & \quad 20 & \quad 40 & \quad 60 & \\
\text{Mixture 1 (nC8/iC16)} & \quad \text{Mixture 2 (iC8/nC16)}
\end{align*}
\]

\[
\begin{align*}
S_L \quad [\text{cm/s}] \\
0.6 & \quad 0.7 & \quad 0.8 & \quad 0.9 & \quad 1 \\
30 & \quad 50 & \quad 60 & \quad 70 & \\
\text{Mixture 1 (nC8/iC16)} & \quad \text{Mixture 2 (iC8/nC16)}
\end{align*}
\]
The overall burning velocity of turbulent premixed flame, derived from the hypothesis of Damkohler equation, is mainly influenced by the effective burning area, in which the turbulent flame speed is normalized by laminar flame speed as follows:

\[
\frac{U_{FB}}{S_L} \sim \left( \frac{u'}{S_L l_f} \right)^{1/2} 
\]

(Eq. 3)

Here, the normalized flame speed is a function of normalized turbulent intensity \((\frac{u'}{S_L})\) multiplied by the integral length scale ratio \((\frac{l}{l_f})\). The parameters are laminar flame speed \((S_L)\), local velocity fluctuation \((u')\), turbulent length scale \((l)\), and flame thickness. The volume-averaged diameter \((d_{30})\) measured by PDPA was used as a turbulent length scale assuming that the velocity fluctuations are induced by the random droplet evaporation. Laminar flame thickness can be estimated from the thermal diffusivity normalized by laminar flame speed of the fuel/air mixture. From figure 3.17 (a), the normalized flashback jet velocity by laminar flame speed as a function of vaporized liquid fraction shows similar tendency for both mixtures, indicating the role of preferential vaporization in differentiating between \(U_{FB}\) for the two mixtures. In addition, since the scaling quantity \((\frac{u'}{S_L l_f})\) is directly proportional to the droplet size and the flow fluctuation, it decrease by increasing residence time, thus more vaporized liquid fuel and less flow fluctuation induced by the random droplets evaporation as shown in figure 3.17 (b). Therefore, flow fluctuation induced by the random droplet evaporation may compensate to flashback behaviors, but the significant different in the measured flashback jet velocity is mainly due to preferential vaporization.
Figure 3.17 Flashback jet velocity ($U_{FB}$) normalized by laminar flame speed ($S_L$) as a function of (a) vaporized liquid fraction, (b) ($u'/S_L l_f$)$^{0.5}$

From the previous experiment with single and multi-components fuels, it was concluded that flame flashback behaviors under partially vaporized conditions, e.g. multiphase combustion, are controlled by the coupling between fuel physical (e.g. evaporation and spray characteristics) and chemical (fuel reactivity) properties. More specifically, the ignition propensity of the fuel cannot be ignored. At elevated temperature relative to gas turbine combustor temperature, it was illustrated that
Flashback exhibit two distinct regimes, propagation and ignition-driven flashback. From the previous chapter, the crude oils and their distillation cuts tested in this work exhibit a wide range of chemical reactivity (DCN), thus it's important to evaluate if the variation of ignition propensity would play a role in controlling flame flashback.

![Bar chart showing DCN values of distillation cuts of Crude 1 compared with whole crude.]

Figure 3.18 The DCN values of the five distillation cuts of Crude 1 compared with whole crude.

To evaluate whether the ignition propensity through preferential vaporization would play a role in governing flashback behaviors, Crude 1 was utilized for this experiment. A large volume of Crude 1 was distilled into five distillation cuts: light naphtha ($T_b < 95 ^\circ C$), heavy naphtha ($95 ^\circ C < T_b < 175 ^\circ C$), kerosene ($175 ^\circ C < T_b < 232 ^\circ C$), light gas oil ($232 ^\circ C < T_b < 342 ^\circ C$), and residue ($T_b > 342 ^\circ C$). The residue was not used in this experiment, particularly was not used in the spray burner due to its high boiling temperature and viscosity, which most likely would lead to clogging in the system and liquid phase cracking during droplet spray heating and evaporation. Figure 3.18 above
shows the measured DCN values of the distilled cuts of Crude 1 compared to Whole Crude. The variation of DCN values over boiling temperature suggest that flashback behaviors are expected to be observed similar to those observed with different n-alkane fuels shown in figure 3.10.

Figure 3.19 Flashback jet velocity ($U_{FB}$) of Crude 1 as a function of fuel/air ratio at 700 K

Figure 3.19 shows the flow speed at flashback ($U_{FB}$) for the four distilled fractions of Crude 1 as a function of fuel/air ratio at fully vaporized conditions (700K). As expected, lighter cut, light naphtha, exhibit the highest flashback jet velocity ($U_{FB}$) near stoichiometric conditions, and deceases with increasing boiling temperature and ignition propensity. In additions, light naphtha exhibits the highest fuel/air ratio for transitioning from propagation to ignition-driven flashback regimes, whereas heavier cuts tend to shift to leaner conditions, similar to what was observed with single components fuels. The
results here are self-explanatory in terms flashback behaviors based on the ignition propensity of each cut, and the composition of each cut based on functional groups obtained from the NMR, however, when preferential vaporization plays a role at partially vaporized conditions, one would expect similar behaviors to the noted behaviors of the binary mixtures tested in this work.
CHAPTER 4

CONCLUSION

The chemical reactivity potential of four light crude oils have been investigated in this work. Four crude samples were distilled (based on ASTM D86) into four-light end distillation factions typically reported in crude assays. Then, the ignition propensities crude samples and their distilled fraction were evaluated and measured in ignition quality tester (Following ASTM D6890). The residual fraction’s DCN ($T_b > 343 \, ^\circ C$) were not measured due thermal cracking observed during the distillation process and possible clogging in the IQT hardware’s. It was observed that all the light fractions have initial DCN values in the range of 23-35 and this value increase for heavier cuts to 50-60 along with an increase in the boiling temperature. This variations of DCN over their distillation curve is relevant to some near-limit combustion behaviors (e.g. LBO, flashback) through preferential vaporization.

To further understand the reason for the general DCN increase tendency, $^1H$ and $^{13}C$ NMR spectra of whole crudes and their distillation cuts were analyzed. The NMR analysis shows that the key functional groups that dominant the ignition propensity are mainly paraffinic. For lighter cuts, n-paraffinic CH$_3$ is dominant, and as boiling temperature increase for heavier cuts, n-paraffinic CH$_2$ becomes dominant. The correlation of paraffinic CH$_2$ and CH$_3$ rations are consistent with the general trends of DCN changes. The functional groups approach used in this study permits to construct a
simple QSPR regression model to roughly predict the DCN values. A logarithmic sensitivity analysis was preformed based on the constructed QSPR and shows that the n-paraffinic CH$_2$ has the significant influence in determining the global ignition propensity of crude oils, consistent with previously characterized distilled fuels. In addition, based on the previous analysis, its suggested that the overall ignition propensities of whole crudes or their distillation cuts are controlled by the metric ratio of paraffinic CH$_2$ and CH$_3$ functional groups.

Finally, to investigate the role of preferential vaporization impact on flame flashback, a spray burner was developed and designed to have the ability to control the extent of fuel vaporization. First, the experiment was conducted with various single components fuels which have a wide range of chemical/physical properties at burner temperature of 700, where two distinct flame flashback behaviors were observed, propagation and ignition-driven flashback. Then, two binary mixtures were purposely formulated with the same global chemical reactivity potential at fully vaporized conditions but will exhibit a drastic difference when preferential vaporization plays a role at partially vaporized conditions. To observe the role of preferential vaporization effectively, the experiment was conducted at partially vaporized conditions (450 K) using those two mixtures. Crude 1 was utilized to investigate flashback behaviors of crude oils.

It is worthwhile to mention that the analysis employed in this work is not meant to be comprehensive, but to provide a quick methodology in charactering the ignition propensity and to investigate preferential vaporization potential of crude oils. A more comprehensive analysis can be used, such as using more complicated QSPR approach, which utilizes more functional groups, that would quantitively describes the combustion
behaviors of crudes in more details. Also, the current experiment was conducted at atmospheric pressure, thus one would speculate the potential difference at elevated pressure on the observation.
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