AN EXPERIMENTALLY VERIFIED APPROACH TO DESIGN EFFICIENT GASOLINE AND DIESEL FUEL SURROGATES

A Thesis

by

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Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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May 2016

Major Subject: Chemical Engineering

ABSTRACT

Gasoline or diesel fuel sourced from crude oil source is a complex mixture of hundreds of hydrocarbons. It is extremely difficult to simulate for better understanding of the fuel flow and combustion behaviors which are essential to enhance fuel quality and to improve engine performance. To overcome this difficulty, a surrogate fuel, that has fewer compounds and that emulates certain important physical properties of a target fuel, can be utilized.

The surrogate mixtures for both gasoline and diesel are designed through a computer aided model based technique by our collaborator at Technical University of Denmark (DTU), and their relevant target properties are predicted. Following the preparation of surrogate blends, target physical properties of both fuel surrogates are measured according to American Society of Testing and Materials (ASTM) methods using advanced analytical equipment in the Fuel Characterization Laboratory.

For both gasoline and diesel surrogates, the model predictions are found to be in good agreement with the experimental results except for a few reported cases such as the Reid Vapor Pressure (*RVP*) of gasoline. For such cases, modifications are made to the model in order to improve the predicted results. Therefore, the experimental investigations are found to be extremely essential for improving the assumptions used to define interactions of the hydrocarbons in the mixtures, which in turn enables enhanced predictability of the model.

The developed model, which leads to a property driven product, can be further investigated to prepare new fuel blends and identify suitable renewable additives in a known amount that can aid in designing of future generation of fuels obtained from either conventional crude oil sources or non-conventional sources. Even though this model provides an excellent, fast and reliable opportunity for screening large number of fuel surrogates and optimization of the same, it is extremely important to experimentally verify the final blends and fine-tune them if necessary before their utilization in engine. Also, the measured property values help to improve the accuracy of the property models as well as the assumptions used to develop them.

ACKNOWLEDGEMENTS

I would like to express my gratitude towards my thesis advisor, Dr. Nimir Elbashir and my thesis committee, Dr. Ahmed Abdul-Wahab and Dr. Haitham Abu-Rub for their continuous guidance and support throughout the course of this research. This project has been an outstanding learning curve in my academic life and I am extremely grateful to my committee members especially to Dr. Nimir for imparting his vast array of knowledge and experience onto me and guiding me in difficult situations.

I want to thank all my group members in Gas and Fuel Research Center for the help in accomplishing this work, in particular Dr. Hanif Choudhury who despite being very busy, always took out time to provide me with valuable ideas, Muhammad Nasr for his tremendous support in the experiments and Salima Mamakova for providing me the training on all the equipment in the Fuel Characterization Laboratory. I would like to acknowledge Sawitree Kalakul and Professor Rafiqul Gani from Technical University of Denmark for helping me in the research work. The faculty members in Texas A&M University at Qatar are also acknowledged for helping me to learn the fundamentals in Chemical Engineering which were very useful in the research work. The financial support in this project by Qatar Science and Technology Park (QSTP) and Qatar National Research Fund is heartily acknowledged.

Finally, I would like to thank my parents for their encouragement and to my wife for her patience and love.

NOMENCLATURE

ASTM	American Standard Testing Methods
TAMUQ	Texas A&M University at Qatar
FCL	Fuel Characterization Laboratory
GTL	Gas-to-Liquid
DTU	Technical University of Denmark
n-	*normal*-paraffins
iso-	*iso*-paraffins
cyclo-	*cyclo*-paraffins
GC-DHA	Gas Chromatography-Detailed Hydrocarbon Analysis
RON	Research Octane Number
RVP	Reid Vapor Pressure
VP	Vapor Pressure
wt%	Weight Percent
vol%	Volume Percent
SI	Spark Ignition
MINLP	Mixed Integer Non-Linear Programming
NIGP	National Industrial Gas Plant
CP	Cloud Point
PP	Pour Point
PSA	Project/Process Safety Analysis
PM	Particulate Matter

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1. INTRODUCTION

With the increase in population, changes in lifestyle and rapid growth of global markets the demand for energy has seen a sharp increase. This trend has led to an increase in consumption of fuels that is further expected to rise during the next two decades [1]. Fossil Fuels will continue to play a significant role in meeting the increase in energy demand [2]–[4]. There has been a growing share of transportation in the world's total fossil fuel consumption amongst which gasoline and diesel accounts for a significant proportion [5]. Depletion of fossil fuels means that the availability of crude oil supply is one of the issues related to gasoline and diesel fuel. The reserves of oil have been estimated to be about ~ 1.47 trillion barrels. Keeping in mind the total consumption of oil which is approximately ~ 84 million barrels per day and the increase in energy consumption (around 1.4% per year), the proven reserves are sufficient for roughly half a century [6]. Also, the search for cleaner fuels with less impact on environment become of the focus of research in oil and fuel research centers. This has led to an increasing interest of scientists in the alternative energy sources for powering vehicles such as fuel derived from Gas-To-Liquid (GTL) technology, bio-based fuel sources such as bioethanol, etc. Alternatively, one can also develop noble fuel blends comprising of the conventional fuel and additives from renewable sources. The goal is not only to lower petroleum usage but also to generate a fuel that is benign, have a good fuel performance and have low environmental impacts [7], [8].

The fuels coming from conventional (petroleum) or non-conventional sources (e.g. from natural gas via gas-to-liquid (GTL), coal via coal-to-liquid (CTL) or biofuels) are a complex mixture of hundreds of hydrocarbons that frequently vary with time and location [5], [9]. This complexity makes it extremely difficult to study the underlying fundamental processes such as the effects of fuel composition on combustion, emission and other physical properties. Moreover, efficient optimization of engine performance requires a combination of detailed chemical kinetics and computational fluid dynamics (CFD).

Currently, it is not possible to model the conventional fuels in a detailed kinetic model since kinetics of all compounds in conventional gasoline, and their interaction has not been fully understood [10], [11]. As a result, a favorable approach to overcoming these problems would be the development of surrogate fuels that meets the required standards as prescribed by the American Society of Testing and Materials (ASTM). In general, a surrogate fuel is one which comprises of a small and diverse number of compounds that mimic certain target characteristics of the original fuel [9]. Since simulations are now frequently performed during modern engine and combustion development, a simpler composition of surrogate fuels will allow more efficient simulations [12]. Surrogate fuels will not only be able to provide a better understanding of the effects of the composition on different properties but also have value as time-invariant reference fuels for experimental studies [10].

2. PROBLEM

2.1 Background

There have been several published articles on developing surrogates for gasoline, diesel and jet fuel. Mehl et al. [13] formulated a gasoline surrogate consisting of *n*-heptane, *iso*-octane, toluene and 2-pentene using the intrinsic qualities of the chemical behavior of the original fuel. They attempted to formulate surrogate that match the real non-oxygenated gasoline. They achieved a reduction in detailed kinetic mechanism without compromising the real ignition delay times and flame speeds in a broad range of operating conditions. Mueller et al. [10] developed a methodology to predict the composition for diesel surrogate using a regression model based on the composition, Cetane number, and volatility characteristics. Based on the model, two surrogates comprising of eight compounds were prepared by blending to represent two different diesel fuels from a refinery. The surrogates were then investigated experimentally for Cetane number and volatility characteristics and compared with the results predicted by the model and target fuels. Reiter et al. [12] also formulated surrogates for four different types of diesel fuels by simultaneously fitting the liquid density at 15 °C, true boiling point (TBP) curve, and the Cetane number. The formulation was later followed by a laboratory examination of two of the surrogates that involved measuring of both the fitted properties and additional properties (not used for fitting). This approach helped firstly to validate the model and secondly to obtain a comparison of the surrogate with the target fuel in terms of a wide range of properties. This approach is similar to the method used in the present study. A recent study using computational methodology was done by Ahmed et al. [5] which involved formulation of surrogates for two different types of FACE (fuels for advanced combustion engines) gasoline. The following target properties were chosen for this study - Carbon bond types, ignition delay, H/C ratio, density, and distillation characteristics and a regression-based optimization was used to mimic these properties. This study also involved experiments in engine operating at controlled auto-ignition (CAI) mode to compare the global reactivity of surrogates with FACE gasolines at different regimes corresponding to low-temperature combustion (LTC), negative temperature coefficient (NTC), and high temperature combustion (HTC).

Pitz et al. [11] reviewed surrogate gasoline mixtures that represent the combustion behavior of conventional gasoline. The group identified candidate compound species for gasoline surrogate and discussed the chemical kinetic models for these compounds and their interactions. Mehl et al. [14] analyzed the combustion behavior of several compounds related to gasoline surrogate formulation giving particular attention to Primary Reference Fuels (PRF) mixtures (*iso*-octane and *n*-Heptane), 1-hexene (olefin) and toluene (aromatic). This analysis was done over a broad range of pressures and temperatures to be consistent with the conditions inside the engine.

The focus has been to not only formulate a surrogate mixture that mimics a target fuel, but also to understand how the different hydrocarbon classes can affect the fuel properties, combustion behavior and emissions. A previous study by Elmalik et al. [1] was focused on understanding the role of hydrocarbon building blocks (*normal*, *iso* and *cyclo* paraffins) on Gas-to-Liquid (GTL) derived jet fuel on the different properties of critical importance to jet fuel certification. These properties are: density, freezing point, flash point and heat content. They prepared 35 (surrogates) blends were using decane (*n*-paraffin), decalin (*cyclo*-paraffin) and Shell-Sol T (*iso*-paraffin) as the building blocks of surrogate jet fuel at different compositions. They have also identified an optimum composition that meets the ASTM-D 1655 that define the properties of jet fuels (Jet A and Jet A-1). This enabled the development of a visualization technique for the relationship between jet fuel derived from GTL and their building blocks (i.e. paraffinic hydrocarbons).

Several studies have also been done to identify renewable additives for gasoline. Canakci et al. [7] investigated effects of alcohol blended with gasoline on the exhaust emission of a Spark Ignition (SI) engine experimentally. Similarly, Masum et al. [8] attempted to optimize the blends of alcohol and gasoline to enhance fuel properties, engine performance and emission characteristics of an SI engine. There have been other studies (summarized in Table 1) as well related to the testing of different fuels in the engine to measure engine performance, Brake Specific Fuel Consumption (BSFC), Brake Thermal Efficiency (BTE) and emission properties. These studies signify the importance of carrying an engine test to observe the real time performance while trying to formulate fuels for future generations.

2.2 Research Problem

Development of detailed kinetic models and computational fluid dynamics (CFD) is very important for automotive researchers since it helps them to simulate the combustion behavior of the transportation fuels like diesel and gasoline and to design efficient engine parts for fuel atomization and emission control. This simulation will enable them to improve engine performance and efficiency in order to cope up with the increase in demand for energy. Conventional diesel and gasoline comprises of hundreds to thousands of compounds, which makes their representation in a detailed kinetic model extremely difficult. Therefore, a practical approach is required to develop a surrogate mixture that meet ASTM standards [9].

Table 1: Literature review of engine studies

Article Reviewed	Description of Work	Comments
1) Sajjad et al. [15]	This review focuses on the impact of GTL and its blends with diesel and bio-diesel on engine performance and emission characteristics on the basis of the of the previous research works. It also explains the feasibility of GTL fuel in context of comparative fuel properties with conventional diesel and bio diesel.	• Fuel properties analysis helped list down the different properties such as Cetane number (CN) and density, and their impact on certain characteristics essential for the overall performance of diesel fuel. • Engine performance features and emission features for both GTL and GTL blended fuels were discussed.
2) Hewu et al. [16]	This paper discusses the effect of GTL diesel fuel on the engine performances (such as power, efficiency and emission) carried out on one Euro III common rail (CR) heavy duty (HD) diesel engine without any modification.	• The engine performance and emission characteristics of both GTL diesel fuel and conventional diesel have been compared on a diesel engine without any modification. • The use of GTL on engine can achieve significant reductions of NO_x, CO, THC, and PM emissions however the max torque and power are slightly lower than for conventional diesel.
3) Masum et al. [8]	The paper discussed the effect of alcohol-gasoline blends optimization on fuel properties, performance and emissions of a Spark Ignition engine. Multiple alcohols (C_2 to C_6) at different ratios were used and three optimum blend ratios were selected (MaxH, MaxR and MaxD). The blends prepared were used for testing in a four cylinder gasoline engine at the wide open throttle condition with varying speeds (1000 to 6000 rpm). The obtained outcomes were compared with that of E15 as well as gasoline	• The engine performance is evaluated on torque, BSFC and BTE. • Optimized blends improved engine torque and BTE than gasoline and E15. BSFC value for optimized blends was lower than that of gasoline but higher than that of E15. • All alcohol gasoline blends emitted lower CO and HC emissions. However NO_x emissions were higher than gasoline and but lower than E15. • Overall outcomes demonstrate that optimized blends have improved fuel properties and indicates better performance and emission in gasoline engines without any modification.

Table 1: Continued

Article Reviewed	Description of Work	Comments
4) Sanjid et al. [3]	This paper presents experimental results of the research carried out to evaluate the BSFC, engine power and noise emission characteristics of a combined palm biodiesel and jatropha biodiesel blend (PBJB5, PBJB10) in a single-cylinder diesel engine (without modification) at different engine speeds ranging from 1400 to 2200 rpm. The results are then compared with diesel fuel (B0), palm biodiesel blend and jatropha biodiesel blend.	• Seven test fuels were prepared for conducting the research. • The properties tested were density, kinematic viscosity, flash point, cloud point, pour point and calorific value. • Engine performance was evaluated in terms of BSFC and engine brake power output. • The maximum brake power output was lower for PBJB5 and PBJB10 than B0. • At the expense of a slight increase in BSFC and NO emissions, the PBJB blends slowed better emission (HC, CO, CO_2, noise) characteristics.
5) Bergthorson and Thomson [17]	The fundamental combustion and emission properties of advanced biofuels are reviewed, and their impact on engine performance is discussed.	• Gasoline fuels, and other fuels used in SI engines, are specified by their octane ratings. Octane rating are a measure of the inclination of the fuel to auto-ignite. Fuels that ignite easily have a lower octane rating. • Engine knock is an unfavorable engine operating condition, which can lead to significant engine damage. It can be inhibited by using a higher octane, or less ignitable, fuel. • Higher octane fuels such as highly branched alkanes are less reactive at low temperatures than straight chain hydrocarbons, which exhibit higher levels of low-temperature chemistry and thus have lower octane numbers. • Diesel fuels traditionally fuel Compression-ignition (CI) engines. • The Cetane number is a diesel-fuel property that measures the ignition propensity of a fuel sprayed into a standard engine-test apparatus. Higher Cetane values indicate that a fuel will ignite more readily.

Table 1: Continued

Article Reviewed	**Description of Work**	**Comments**
6) Fernadez et al. [18]	In this work, the performance of a direct-injection diesel engine, without any modification, fueled with 1-pentanol/diesel fuel blends has been evaluated. Blends with 10% pentanol/90% diesel fuel, 15% pentanol/85% diesel fuel, 20% pentanol/80% diesel fuel and 25% pentanol/75% diesel fuel were tested and engine performance results were compared with those provided by neat diesel fuel. Properties measured were kinematic viscosity, flash point, density and HHV.	• Experimental results showed insignificant engine power, BTE and BSFC variations when the engine was fueled with the majority of the blends instead of straight diesel fuel. • Existence of oxygen in the molecular structure of 1-pentanol offsets its reduced LHV, showing better combustion and BTE than diesel fuel. • During engine starting, no difficulties were experienced and the engine performed satisfactorily on the blends throughout the entire test. • Based on this study 25% pentanol/75% diesel fuel can be recommended as a diesel fuel substitute if long-term diesel engine provide satisfactory results.
7) Yang and Chou [19]	In this study the performance and emission formation of a direct injection engine fueled with gasoline/diesel blend fuel are investigated numerically. Simulations are conducted on pure diesel and its blend fuels with 10%, 20%, 30% and 40% gasoline under 10%, 50% and 100% loads at a fixed engine speed of 2500 rpm.	• It could be implied that for a conventional diesel engine, pure diesel should be fueled at low load. With the increase of engine load, better performance could be achieved by blending gasoline. • KIVA4-CHEMKIN was used to examine the effect of gasoline and diesel fuel on combustion and emission characteristics in a conventional diesel engine.
8) Armas et al. [20]	This study investigates the effect of alternative fuels on exhaust emissions during diesel engine operation with matched combustion phasing. The study was carried out using a 2.5L direct injection common-rail turbodiesel engine operated at 2400 rpm and 64 Nm torque.	• The study had two main objectives. The first objective was to investigate the impact of the start of injection (SOI) on performance and emissions of each fuel. The second objective was to the isolated impacts of the test fuels on pollutant emissions by adjusting the injection parameters (SOI and fuel rail pressure) for each fuel, while producing practically the same combustion phasing. • FT fuel can reduce all regulated diesel emissions.

Table 1: Continued

Article Reviewed	Description of Work	Comments
9) Yehliu et al. [21]	In this paper, both composition of the fuel and fuel injection process are considered by comparing conventional, synthetic and vegetable oil-derived diesel fuels and by comparing a single pulse injection and a split (pilot and main) injection process. This study was carried out in a direct injection 2.5 L common-rail turbodiesel engine working at four engine operation modes. In all modes engine was tested with single and split injection.	• Paper focused on characterization of the combustion process and emissions produced by three substantially different diesel fuels; an ultra-low sulfur diesel fuel, a pure soybean methyl ester, and FT fuel from gas-to-liquid process. • This study confirms that ignition character of the fuel affects the start of the combustion process. • FT fuel can reduce both NOx and PM specific emissions in all modes under both single and split injection modes. • This work also confirms that biodiesel can reduce particle concentration. However in some cases and increase of PM mass has been observed.

While trial-and-error experiment based design methods are still used for the design and verification of the blended surrogate products, these methods are both costly and time consuming. Therefore, an experimentally verified approach is required to design efficient gasoline and diesel fuel surrogates via computation and property integration methods. To be more specific an integrated methodology needs to be developed for solving the mixture/blend design problems dealing with single component and multi-component surrogate mixtures. The significance of chemical blends can be summarized as following:

1. Reduce the consumption of critical raw materials such as fossil fuel, so that the life-span of fossil fuel can be extended.
2. Add value to the non-conventional fuels and chemicals obtained from bio-renewable sources or from other fossil fuel sources such as natural gas and coal.
3. Reduce the pollutants by replacing the most harmful chemicals with the environmentally friendly chemicals.
4. Increase the safety level of chemical products by substituting the hazardous chemicals with the safer chemicals, especially in contact with human.
5. The blends will help determine how the composition affects the different fuel properties.
6. Have value as reference fuels in experimental and computational studies.

Figure 1 describes the research problem of this study in the form of a flowchart.

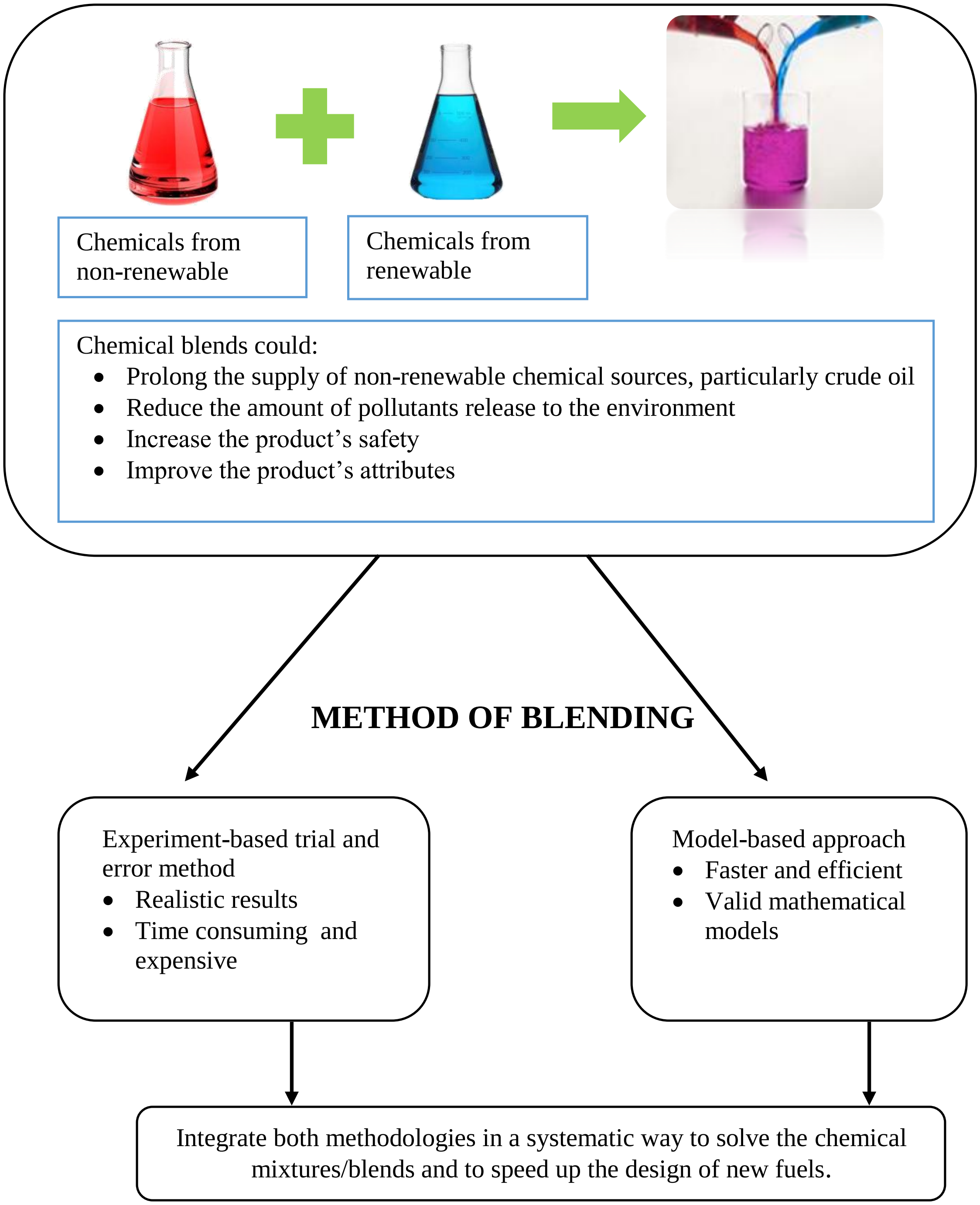

Figure 1: Research problem

2.3 Research Objective

This objective of this study is to formulate and analyze surrogate mixtures for both gasoline and diesel. The candidates for surrogates are determined through a computer aided model approach developed at the Technical University of Denmark (DTU). Subsequently, target physical properties of these fuel surrogates are measured using advanced analytical equipment and experimental techniques developed at Texas A&M University at Qatar (TAMUQ). Our role at TAMUQ is to experimentally validate the models developed at DTU to design surrogate fuels. Moreover, some additional properties that were not determined through the model were also measured for the surrogate blends in order to analyze the mixtures more comprehensively. The results of this study provide a basis to further improving the computer aided models used to design the surrogates and for designing of future generations of efficient fuels of different composition obtained from both conventional sources (petroleum) and non-conventional sources (e.g. from natural gas via gas-to-liquid (GTL), coal via coal-to-liquid (CTL) or biofuels). Also, the outcome of this study will be used in optimizing the design of fuel blends obtained from the aforementioned sources.

3. RESEARCH METHODOLOGY

3.1 Designing of Surrogates

As mentioned earlier, the designing of the surrogate fuels is done by our collaborator in DTU. The surrogate fuels are designed through a computer aided model based technique “Mixed Integer Non-Linear Programming” (MINLP). The main architecture in MINLP has four structures viz.

(i) problem definition,
(ii) property model identification,
(iii) mixture blend design,
(iv) Model-based verification.

Supporting tools, namely, a chemical database, composition optimizer and a property model library have also been developed for this work [22]. The product design stage starts from identifying the target properties that need to be considered. The target properties calculated for gasoline surrogate were high heating value (*HHV*), research octane number (*RON*), Reid vapor pressure (*RVP*), flash point (T_f), density (ρ), lethal concentration (LC_{50}) and dynamic viscosity (η). Target properties calculated for diesel surrogate were *HHV*, kinematic viscosity (v), lethal concentration (LC_{50}), weight percent of oxygen (Wt_{O2}), ρ and vapor pressure (*VP*). All the above properties are quantitative in nature that can be modeled. A mixture/blend design algorithm is applied to obtain the mixtures/blends that match the set of target properties. This algorithm employs a decomposition base solution strategy, where, in each step, the search space is reduced by screening out alternatives by considering property constraints according to a pre-determined hierarchy. The algorithm results in a surrogate mixture that matches its constraints with known composition of the chemicals present in the blend and known values of the target properties.

3.2 Surrogate Blend Preparation and Sampling

The experimental analysis of this study were conducted at a well- established Fuel Characterization Laboratory (FCL) of Gas and Fuel Research Center within Texas A&M University at Qatar. The FCL has an efficient Quality Management System (QMS) and Data Management System (DMS) in place to maintain quality of experimental results. The lab recently went through a rigorous International Organization for Standardization (ISO) 9001:2008 certification process and as a result of the quality of its management system, it successfully received the ISO 9001:2008 certification. The high quality management system means that it has a very well-known reputation of testing facility both domestically and internationally. In addition, this laboratory follows strict safety protocols having safety as their number one value. Figure 2 and Figure 3 illustrate the main tasks which QMS and DMS rely on.

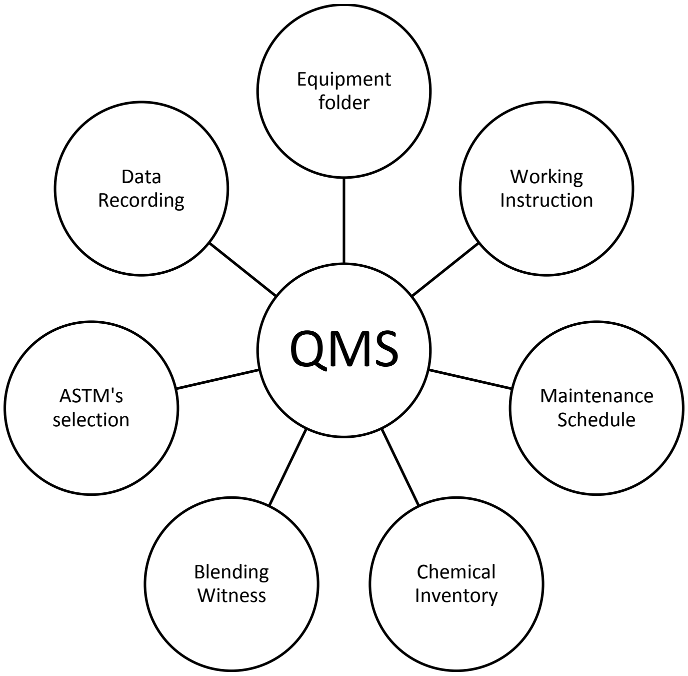

Figure 2: Quality management system features

Figure 3: Data management system features

An important point to highlight is the safety culture that is promoted in the FCL of Gas and Fuel Research Center. A strong emphasis is given on wearing the necessary Personal Protective Equipment (PPE) while carrying out any task in the FCL whether it is blending or testing of the blends. The PPE that were worn at all times during the experimental investigations are safety goggles, fuel non-absorptive lab coat type and powder- free nitrile gloves. The blending and testing of both gasoline and diesel surrogates were carried, keeping in mind the quality management system and safety regulations in the lab.

The gasoline surrogates formulated in this study has a high butane concentration (approximately 5%). Butane, having a very high vapor pressure of 244 kPa at 25 ^{O}C, has the tendency to escape on exposure to ambient conditions. Moreover, 1-pentene, which also has a high vapor pressure of 80.4 kPa at 25 ^{O}C, is highly volatile in nature. Therefore, the blend composition is prone to change on its exposure to ambient conditions due to escaping nature of butane and 1-pentene. The conventional blending and sampling techniques as well as testing methods were found to be incompetent for the highly volatile mixtures used in this study. Therefore, to minimize changes in composition of the gasoline surrogate blends, an advanced blending technique and a unique sampling methodology was developed. This is extremely important because in order to verify the model-based simulated results, the composition during testing of the properties must not differ from the proposed composition using model-based simulation.

The blends of gasoline are prepared in collaboration with the National Industrial Gas Plant (NIGP), Doha, Qatar with an accuracy of ±2%. The method of preparation is unconventional as it required blending of a gas with liquids. The blends are prepared in 2 liters (2L) high pressure Aluminum gas cylinders termed as stock cylinders which are equipped with dip tubes and a regulator to control the gas-liquid flow. The stock cylinders have two dedicated inlet ports: one for liquids that is connected to a dip tube and the other for gases. The blend preparation is done in three stages. In the first stage, measured quantity of all liquid compounds (approx. 750 milliliters (mL)) are introduced into the stock cylinders through the liquid inlet port. Subsequently, a mass flow controller (MFC) is used to introduce butane into the stock cylinder through the liquid port. Butane flow rate is controlled at 1 mL/min on the Proportional Integral Derivative (PID) controller of the MFC. In the second stage, electrically controlled horizontal cylinder rollers are used to spin the stock cylinder in order to prepare a consistent mixture. Spinning of the stock cylinders is done at 50 rpm for 2 hours at ambient conditions. In the final stage, stock cylinders are pressurized with a Helium gas at approximately 17 barg (gauge pressure) to prevent escape of butane and 1-pentene from the liquid mixture. The Helium gas is introduced into the stock cylinder through the gas port from a Helium cylinder via double stage gas regulator to cover the head space of the stock cylinder. Helium gas over pressure is maintained in the stock cylinders throughout the transportation, storage and even after sample withdrawal. The samples have a shelf life of 36 months as denoted by the NIGP, however; all the sampling is done within fifteen days of preparation of samples. The three stages of sample preparation are shown in the Figure 4.

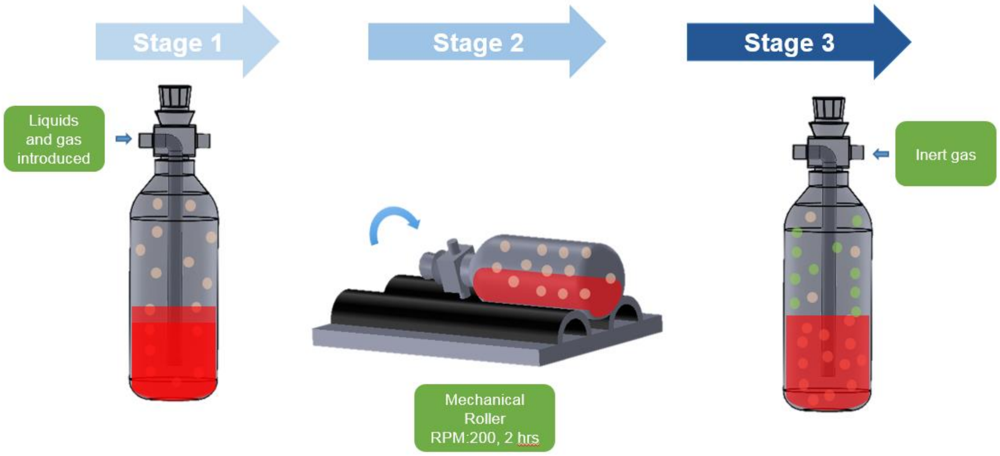

Figure 4: Blend preparation

In order to test target physical properties, different sample sizes are required for different analytical equipment. For e.g. DHA analysis requires few microliters (1-10µL) of sample volume whereas for RVP and density approximately 5-10mL of sample is needed. It is difficult to withdraw a small quantity of sample with precision from stock cylinders. Moreover, the stock cylinders are kept at a very high pressure (approx.17 barg) whereas ambient condition is desired for the analytical equipment used in this study. Therefore, a sampling device which can be used to efficiently withdraw sample from the pressurized stock cylinder and deliver precise sample has been designed. The sampling device consists of a 300 mL double ended gas cylinder made of stainless steel (SS316) procured from Swagelok (TM) having a design pressure of 128 bar. A pressure gauge is connected to one end of the cylinder to monitor pressure inside the cylinder. Downstream to the pressure gauge a 3-way valve (1) is installed to control gas flow into the cylinder and the other end of the 3-way valve (1) is sealed with a metal plug. On the other end of the cylinder another 3-way valve (2) is connected. On one end of the 3-way valve (2), a small SS316 tube of OD ¼” is connected that can fill 10 mL of sample. End of this tubing is sealed with a GC septum from where sample of desired volume is withdrawn. The other end of the 3-way valve (2) is left open to fill the gas-liquid sample from stock cylinders.

In a typical sample withdrawal session, gas-liquid mixtures are introduced from the stock cylinders through the 3-way valve (2) while turning the other 3-way valve (1) towards its open position. As soon as trickling of liquid is observed from the 3-way valve (1), both the 3-way valves (1 & 2) are immediately closed and the stock cylinder is disconnected. Subsequently Helium gas pressure of 3 barg is applied from 3-way valve (1) using a Helium gas cylinder. Helium gas cylinder is then disconnected from the 3-way valve (1) and subsequently the valve is turned towards closed position again. Now the 3-way valve (2) is turned towards the SS316 tube to fill the liquid in it due to gravitational force and then the valve (2) is closed again. At this stage the sampling device is ready for extracting sample of desired sizes. The sample is withdrawn from the SS316 tube in the required amount using the syringe intended for injection into analytical equipment. The sampling methodology is shown in Figure 5.

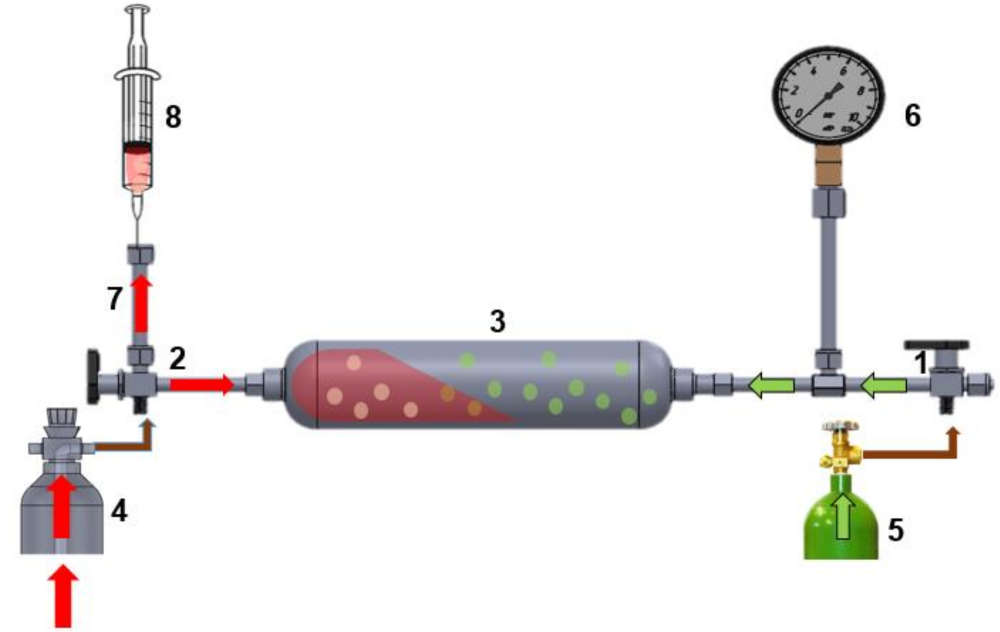

Figure 5: Sampling methodology

(1) 3-way valve 1; (2) 3-way valve 2; (3) 300 ml double ended gas cylinder; (4) Sample injection; (5) Helium gas pressure applied; (6) Pressure gauge (PG); (7) SS316 tube of OD 1/4"; (8) Sample withdrawn in syringe

On the other hand, diesel surrogate blending and testing is straightforward as the mixture comprised of liquids at room temperature. Cleaned pipettes (separate for each compound) are used to put the chemical compound in desired volume from the stock bottles into a 1 liter glass bottle prepared for the blend. The bottle is closed and shook vigorously in horizontal motion to ensure proper mixing of the blend.

3.3 Composition of Surrogate Blends

The composition of fuel has a major impact on the combustion of the fuel [23]. The composition varies from place to place due to a difference in source of crude as well as the refinery processes utilize [11]. The varying composition can affect the vaporization of fuel, ignition delay, reactivity of pollutants, heat release, etc. [5]. The classes of hydrocarbons, generally found in commercial U.S. gasoline are shown in Figure 6 below [11].

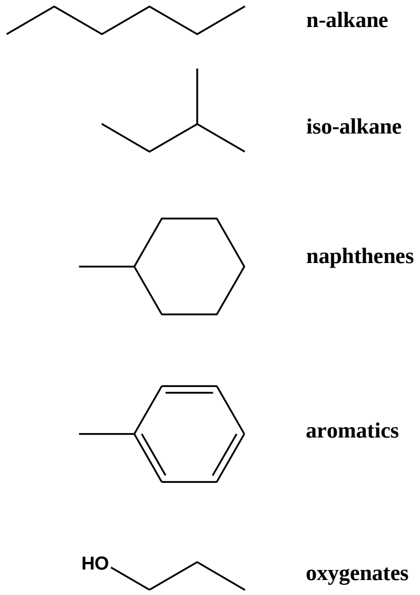

Figure 6: Molecular structures of hydrocarbons

Detailed Hydrocarbon Analysis (DHA) for all the gasoline surrogate blends is carried out by Gas Chromatography (GC) according to ASTM D6730. As the composition of the blends is already known, the major purpose of carrying out this analysis is to confirm that the composition was not changing during the experiments. Moreover, using this analysis the efficacy of blend preparation and sampling technique was also determined. The sample is injected into a GC which comprises of an open tubular (capillary) column coated with a methyl silicone liquid phase, modified with a capillary pre-column. The vaporized sample gets transported through the column by helium carrier gas. In the column it gets partitioned into individual compound which, after they elute from the end of the column, are detected by the flame ionization detector. Analyzing reference standards or samples are used to identify each eluting compound by comparison of their retention time under identical conditions. This process helps in determining the concentration of each compound in mass % after correction with detector response factors and normalization of the peak areas. GC operating conditions are given in Table 2.

Table 2: GC operating conditions

Column Temperature Program	
Initial temperature	5°C
Initial time	10 min.
First program rate	5.0°/min
First hold temperature	50°C
First hold time	to the elution of ethylbenzene (~50 min)
Second program rate	1.5°/min
Final temperature	200°C
Final hold time	5 min
Injector	
Temperature	250°C
Split ratio	150:1
Sample size	0.1 - 0.2 µL
Detector	
Type	flame Ionization
Temperature	250°C

Moreover, the hydrocarbon classes found in conventional diesel fuel are given in Figure 7 in the form of a pie-chart.

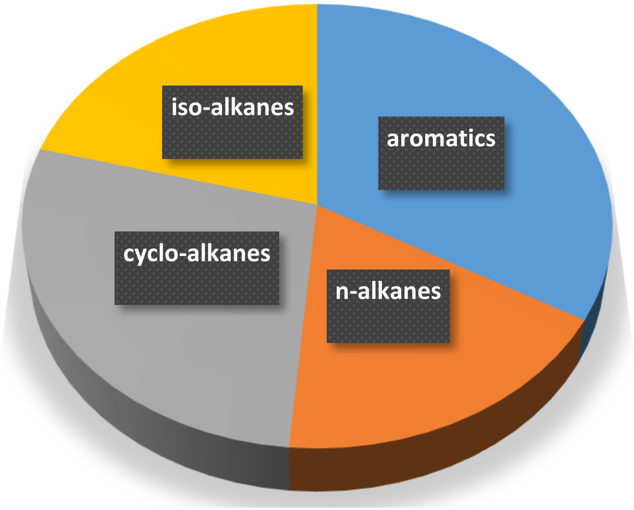

Figure 7: Relative amounts of various chemical classes in diesel fuel. Adapted from Pitz and Mueller 2011 [9]

Density exhibits a linear trend with respect to the volume percent (vol %) of the individual compounds and therefore it is a good approach to verify the blends formulated [1]. In order to confirm that the blending of diesel was done accurately to achieve target composition, the theoretical and measured densities are compared.

3.4 Properties Measured

In this section, fuel properties measured are discussed and details are given of their significance with respect to the fuel. Table 3 below lists down some of the properties that were measured in the experimental campaign with their respective ASTM standards and equipment used.

Table 3: Properties measured with ASTM standards and equipment

Property	**ASTM Method**	**Equipment Name & Model**	**Manufacturer**
Density (ρ)	ASTM D4052	DMA 4100	Anton Paar
Composition by GC	ASTM D6730	Clarus 500	PerkinElmer
Kinematic Viscosity (v)	ASTM D7042	Stabinger viscometer	Anton Paar
Dynamic Viscosity (η)	ASTM D7042	Stabinger viscometer	Anton Paar
Pour point (*PP*)	ASTM D5949	Cold flow properties analyzer 70Xi	Phase Technologies
Cloud point (*CP*)	ASTM D5773		
Flash point (T_f)	ASTM D93	PM 93	Stanhope-Seta
Vapor pressure (*VP*)	ASTM D6378	MiniVapXpert	Grabner inst.
High Heating Value (HHV)	ASTM D240	Bomb calorimeter	Parr Instrument
Distillation	ASTM D86	Distillation unit	Petrotest Co.
Cetane number (*CN*)	ASTM D613	-	-
Research Octane Number (*RON*)	-	Clarus 500	PerkinElmer

3.4.1 Vapor Pressure (*VP*)

A fuel's volatility is expressed by a number of physical properties viz. vapor pressure, vaporization enthalpy, distillation characteristics and sometimes also by the vapor/liquid ratio.

Vapor pressure of gasoline fuel plays a significant role in the combustion process particularly in starting the spark ignition (SI) engine on cold days and in continuous operation on hot days. Vapor pressure of gasoline fuel at 37.8 ^{o}C is also known as Reid vapor pressure (RVP) [24]. When gasoline RVP is lower than 45kPa, an engine may have to be cranked a long time before it starts and may not start at all if it is extremely low. To ensure easy engine starting RVP of fuel must be higher than 45kPa, but it must not exceed 103kPa as it may cause vapor lock or excessive evaporative emissions [25]. A gasoline that has RVP between 45-103 kPa tend to have lower evaporative emissions and is more desirable for gasoline engines.

Vapor pressure is not the most important property for diesel fuels as it is not mentioned in the standard specification for diesel fuel. However, the vapor pressure of conventional diesel fuel is normally found to be as low as 0.2 kPa (for typical conventional diesel fuel obtained from WOQOD in Qatar).

3.4.2 Density (ρ)

Density is defined by the mass of fuel per unit volume. A fuel with a high density will have a higher energy concentration which will in turn minimize the chance of fuel leakage. A much higher density will lead to a very high viscosity which will negatively impact the fuel as it will cause poor spray atomization efficiency resulting in poor combustion with more emissions [15]. Density exhibits a linear trend with respect to its composition and therefore, it is a good approach to verify the blends formulated.

Typically for gasoline fuel, the value of density at 20^{o}C lies between 0.720 g/cm^3 and 0.775 g/cm^3 [26]. According to US Navy military specification, density of diesel fuel should be less than 0.876 g/cm^3 [27].

3.4.3 Viscosity

The viscosity of the fluid is defined as the measure of the resistance to gradual deformation by shear stress or tensile stress. The consistency of fuel flow given by viscosity is an important parameter in determining how the fuel flows inside the engine.

In diesel fuel, it affects the fuel injection as well as spray atomization. A high value of kinematic viscosity (v) will increase fuel pump requirement, will yield poor spray and atomization. It will also lead to an increase in the fuel consumption [15]. According to ASTM D975, the specification of viscosity of diesel is given in Table 4.

Table 4: Viscosity specification for diesel

Kinematic Viscosity (mm^2/s)			
Grade	**No-1D**	**No-2D**	**No-4D**
Minimum	1.3	1.9	5.5
Maximum	2.4	4.1	24.0

In gasoline fuel, although the ASTM D4814 does not provide any specification for the value of density and viscosity, the gasoline refiners and sometimes even the automobile refiners may set some additional internal specifications. Typically, for gasoline fuel dynamic viscosity (η) at 20^{o}C lies between 0.3 mPa.s and 0.6 mPa.s [26].

3.4.4 Heat Content

Heat content or heating value is the amount of heat produced by the complete combustion of fuel. It is measured in energy per unit mass or volume of a substance. Higher value of heat content of a fuel is desired. This is because during combustion, it favors the heat released and hence improves engine performance [15]. It is known to have a direct impact on the torque and power of the engine. Moreover higher heat content also means lower Brake Specific Fuel Consumption (BSFC).

Gross heat of combustion (Qg) also known as higher heating value (HHV) is measured by burning fuel in constant volume enclosure in oxygen rich bomb, without water in liquid state. Net heat of combustion (Qn) also known as lower heating value (LHV) is the quantity of energy released when unit of fuel mass is burned at constant pressure, with all of the products including water. Gross heat value is obtained from the instrument and net heat value calculated by following formula.

$$Q_n = 10.025 + (0.7195)Q_g \tag{1}$$

3.4.5 Cloud Point (CP) / Pour Point (PP)

These properties are essential to investigate engine performance of diesel fuel in cold atmosphere. Blockage of the fuel system such as filters, fuel lines etc. may occur in case of a partial or complete solidification of fuel. This will lead to an interruption of fuel supply to the engine coupled with inadequate lubrication and may lead to problems in driving or even engine damage. Cold flow characteristics of the fuel are determined by CP and PP [15]. CP is the temperature below which a cloudy appearance is observed. PP is the temperature at which fuel becomes semisolid and loses its flow characteristics. Both CP and PP help give an indication of how the diesel fuel will operate in low-temperatures. It is seen that a high composition of *iso*-paraffinic compounds are expected to lower the cloud point and pour point significantly. Hence, the cold-flow performance of the fuel is improved by the presence of *iso*-paraffinic compounds [28][9]. The value specification of cloud point and pour point vary from region to region and in a cold country like Canada, the specification can be more stringent as very low values ($\leq$ - 40^{o} C) of both CP and PP are required.

3.4.6 Flash Point (T_f)

The flash point is the lowest temperature at which the vapor above the liquid can be ignited in air. The flash point of a diesel fuel has no relation to its performance in an engine nor to its auto ignition qualities. It is more related to transportation and storage of the fuel. Only flash point of diesel surrogate fuel is measured in this study. According to ASTM D975, the specification of flash point of diesel is given in Table 5 below.

Table 5: Flash point specification for diesel

Flash Point (°C)			
Grade	**No-1D**	**No-2D**	**No-4D**
Minimum	38	52	55
Maximum	-	-	-

3.4.7 Cetane Number (CN)

Cetane number indicates the ignition quality of diesel fuel. It is an important factor in determining the quality of diesel fuel. A low value of CN will cause ignition delay which will lead to startup problems. Moreover, other problems like unstable engine operation, poor fuel economy, noise and exhaust smoke may also result. This is why a value of CN greater than 40 is desired and specified in ASTM D975 for all grades of diesel fuel oil except grade 4-D for which the value cannot be less than 30. Higher CN helps in shortening ignition delay. This in turn leads to a lesser pre-mixed charge resulting in lower combustion temperature as a result of which NO_x formation is reduced [16]. A higher *n*-paraffinic content in the fuel leads to a higher CN. Higher *n*-paraffinic composition in GTL produces more reactive radicals compared to conventional diesel and as a result GTL fuels have a higher CN [15].

CN is calculated using ASTM D4737 by using the four variable equation. This method uses a correlation that has been established between the ASTM CN and the density and 10%, 50% and 90% distillation recovery temperatures of the fuel. Equation 2 shows the correlation that has been established in this specification.

$$CCI = 45.2 + (0.0892)(T_{10N}) + [0.131 + (0.901)(B)][T_{50N}] + [0.0523 - (0.420)(B)][T_{90N}] + [0.00049][(T_{10N})^2 - (T_{90N})^2] + (107)(B) + (60)(B)^2 \qquad (2)$$

where,

CCI = Calculated Cetane Index by Four Variable Equation,

D = Density at 15^{o}C, g/mL determined by Test Methods D1298 or D4052,

DN = D – 0.85,

B = $[e^{(-3.5)(DN)}] - 1$,

T_{10}= 10% recovery temperature, ^{o}C, determined by Test Method D86 and corrected to standard barometric pressure,

T_{10N}= T_{10} – 215,

T_{50}= 50% recovery temperature, ^{o}C, determined by Test Method D86 and corrected to standard barometric pressure,

T_{50N}= T_{50} – 260,

T_{90}= 90% recovery temperature, ^{o}C, determined by Test Method D86 and corrected to standard barometric pressure,

T_{90N}= T_{90} – 310,

This test method (D4737) is a supplementary tool for estimating Cetane number when it is not possible to obtain result from ASTM D613. Please note that this test method is not an optional method for expressing ASTM Cetane number and if possible the result should be verified with ASTM D613.

3.4.8 Distillation

Distillation is also carried out to measure fuel's volatility and has a significant effect on the engine behavior. This effect explains why the fuel regulations have many parameters to control the distillation curve [29]. A distillation profile, or distillation curve, is the set of increasing temperatures at which fuel evaporates for a fixed series of increasing volume percentages (10 percent (T10), 50 percent (T50), and 90 percent (T90)). Various ranges of a distillation profile correlate with specific aspects of gasoline performance. Front-end volatility is adjusted to provide:

- Easy cold starting
- Easy hot starting
- Freedom from vapor lock or other hot fuel handling problems

- Low evaporation and running-loss emissions

Midrange volatility is adjusted to provide:

- Rapid warm-up and smooth running
- Good short-trip fuel economy
- Good power and acceleration
- Protection against carburetor icing and hot-stalling

Tail-end volatility is adjusted to provide:

- Good fuel economy after engine warm-up
- Freedom from engine deposits
- Minimal fuel dilution of crankcase oil
- Minimal volatile organic compound (VOC) exhaust emissions

Distillation for gasoline surrogates (that contain butane) developed is measured using GC-DHA technique. This is due to the safety concerns associated owing to presence of butane in the blends. According to ASTM D4814, the specification of distillation of gasoline is given in Table 6.

Table 6: Distillation specification for gasoline

	Distillation Class					
Distillation Temperature (°C)	**AA**	**A**	**B**	**C**	**D**	**E**
10 volume % max	70	70	65	60	55	50
50 volume % min	77	77	77	77	77	77
50 volume % max	121	121	118	116	113	110
90 volume % max	190	190	190	185	185	185
End Point max	225	225	225	225	225	225

For diesel surrogate blends, ASTM D86 is used as shown in Table 3. Lowering distillation characteristics helps improve atomization and dispersion of fuel spray. It also helps ensure that the fuel is easily evaporated which accelerates the fuel mixing with air leading to a more combustible air-fuel mixture. Moreover, lowering distillation characteristics also helps to reduce smoke and PM emissions. Lower end point, during operation at low loads and frequent idle periods, is desired to reduce smoke and combustion deposits. These characteristics were observed when GTL diesel fuel was tested [15]. According to ASTM D975, the specification of distillation (90% volume) of diesel is given in Table 7 below.

Table 7: Distillation specification for diesel

Distillation Temperature 90% volume (^{o}C)			
Grade	**No-1D**	**No-2D**	**No-4D**
Minimum	-	282	-
Maximum	288	338	-

3.4.9 Research Octane Number (*RON*)

This property is important for gasoline. Knocking in spark ignition (SI) engines is an abnormal combustion phenomenon that takes place when the fuel air mixture explode in the ignition chamber in an uncontrolled fashion. Knocking can damage the engine if it is not prevented or controlled. Knocking is caused by pre-ignition or unwanted chemical reactions in the combustion chamber, resulting in a loud noise inside the engine. Anti-knock quality of the fuel is determined by a parameter called octane number which is indicated by research octane number (RON) and motor octane number (MON) [30]. RON indicates fuel antiknock performance in engines at wide-open throttle and low-to-medium engine speeds whereas MON indicates fuel antiknock performance in engines operating at wide-open throttle and high engine speeds. A higher value of RON (≥ 92) is desired which allows a higher compression ratio to achieve increased engine performance. Typically, RON of gasoline is found to vary between 88 and 98 across the globe [31].

4. RESULTS AND DISCUSSION

4.1 Gasoline Fuel

The surrogate designed using the computer aided model for gasoline is given in Table 8 below which is termed as Main Ingredient (MI).

Table 8: Gasoline surrogate (MI) composition provided by DTU

Chemical	Composition (wt %)
n-Butane	6.58
n-Heptane	12.6
Iso-octane	53.99
1-Pentene	3.63
Methylcyclopentane	8.47
Toluene	14.73

Based on the MI composition in Table 8, an observation can be made regarding the feasibility of testing this mixture in the Fuel Characterization Lab (FCL) of Texas A&M University at Qatar. MI in Table 8 contains butane which is a gas at room temperature; however, the FCL is currently not equipped for blending gas-liquid mixtures. Therefore, it is proposed that the butane be replaced by *n*-pentane, as this is the closest chemical in terms of carbon number and chemical structure that can be feasibly blended, and is also readily available in the FCL.

In order to convert the weight percentage (wt %) compositions in Table 8 to volume percentage (vol %) for blending purposes, the densities of the different chemicals are needed. These are measured experimentally in the lab and also looked up from the literature (using an online search) to verify the experimental data. The results of this testing are shown in Table 9. As the results show, the measured densities match well with the literature values, except for 1-Pentene. The discrepancy for 1-Pentene may be attributed to the fact that it is extremely volatile at room temperature, causing bubbles to form in the sample holder; thus, for our purposes the literature value may be used. The calculated composition, in vol % of the model gasoline to be tested in the FCL is shown in Table 10.

Table 9: Measured and literature densities (referred to as lit) for model gasoline compounds

Chemical	**Density at 20 °C, measured (g/ml)**	**Density at 20 °C, from lit (g/ml)**
n-Pentane	0.6263	0.626
n-Heptane	0.6834	0.6838
Iso-octane	0.6918	0.6918
1-Pentene	0.6285	0.64
Methylcyclopentane	0.7476	0.74
Toluene	0.8667	0.866

Table 10: Composition of MI to be prepared in the FCL

Chemical	**Composition (vol %)**
n-Pentane	7.5
n-Heptane	13.1
Iso-octane	55.3
1-Pentene	4.0
Methylcyclopentane	8.1
Toluene	12.0

The blend of gasoline (MI) was prepared in the FCL and tested for various properties as described in Section 3.4. The results of the analysis are listed in Table 11 below.

Table 11: Results of MI with n-pentane

Property	**Result**	**Target Values**
ρ at 20˚C (g/cm^3)	0.7097	0.720 – 0.775
η at 20˚C (cP)	0.5106	0.3 – 0.6
RVP at 37.8˚C (kPa)	28.1	45 – 60
HHV (MJ/kg)	44.2752	≥ 35
Distillation (˚C)		
10 %vol	81.40	≤ 70
50 %vol	95.90	77 – 121
90 %vol	99.00	≤ 190
EBP	105.70	≤ 225

The volatility characteristics i.e. vapor pressure and distillation (10 %vol) of MI when replacing n-butane with n-pentane do not meet the gasoline ASTM specification defined in the Section 3.4 and are well outside the target values shown in Table 11. Moreover, density of the MI also lies outside the target values defined for density. Replacement of *n*-butane with *n*-pentane does not work well for the fuel as described and therefore, the original composition defined for gasoline MI in Table 8 is considered. Moreover, DTU also described more blends that involved MI blended with different renewable additives. Table 12 shows the different blends that are prepared along with the MI.

Table 12: Blend composition of MI with renewable additives

Blend	Composition (vol%)
Blend 1	MI (69), Tetrahydrofuran (11), 2-Methyl Tetrahydrofuran (20)
Blend 2	MI (67), Acetone (13), 2-Methyl Tetrahydrofuran (20)
Blend 3	MI (72), Acetone (10), 2-Butanone (18)
Blend 4	MI (75), 2-Butanone (13), 2-Methyl Tetrahydrofuran (12)
Blend 5	MI (77), Ethanol (12), 2-Methyl Tetrahydrofuran (11)

4.1.1 Composition

An advanced blending technique and a unique sampling methodology (discussed in Section 3.2) was developed to minimize loss of butane and 1-pentene. Detailed Hydrocarbon Analysis (DHA) for gasoline surrogate was carried out by Gas Chromatography (GC) according to ASTM D6730 to verify the efficacy of both blending technique and sampling method. The chromatograms of all the surrogate blends of gasoline can be found in Appendix A. Concentration of each compound present in the blends as obtained by DHA study were compared with prepared blend concentration and variation is presented in terms of the Relative Standard Deviation (RSD). RSD is a standardized measure of variation in data that is given by the ratio of standard deviation (σ) and the mean (μ). RSD is expressed in percentage and can be calculated by Equation 3 given below:

$$RSD = \frac{\sigma}{\mu} \times 100 \tag{3}$$

Table 13 lists the composition of all the blends and their respective RSD values. RSD value did not exceed 6.24% for any of the compounds in all the blends which suggests that the prepared blend compositions did not change significantly. Relatively larger RSD values for 1-pentene and *n*-butane in comparison with other blend compounds are observed due to highly volatile nature of 1-pentene and *n*-butane which renders subtle losses during sampling. Moreover, the blends are prepared with an accuracy of ±2%, and there is a possibility that this might have also contributed to the difference. The small deviations in results of blend compositions as denoted by their RSD values confirms the efficacy of the blend preparation and sampling techniques used in this study.

Table 13: Composition verification of all blends using DHA

	MI			Blend 1			Blend 2			Blend 3			Blend 4			Blend 5		
	X	**Y**	**RSD (%)**	**X**	**Y**	**RSD (%)**	**X**	**Y**	**RSD (%)**	**X**	**Y**	**RSD (%)**	**X**	**Y**	**RSD (%)**	**X**	**Y**	**RSD (%)**
***n*-butane**	6.58	6.06	5.82	4.24	3.94	5.19	4.17	4.00	2.94	4.57	4.26	4.96	4.73	4.33	6.24	4.89	4.48	6.19
1-pentene	3.63	3.46	3.39	2.34	2.24	3.09	2.30	2.20	3.14	2.52	2.41	3.16	2.61	2.44	4.76	2.70	2.53	4.60
Methylcyclopentane	8.47	8.31	1.35	5.46	5.34	1.57	5.37	5.24	1.73	5.88	5.77	1.34	6.09	5.90	2.24	6.29	6.08	2.40
***Iso*-octane**	53.99	54.33	0.44	34.81	34.82	0.02	34.21	34.07	0.29	37.48	38.09	1.14	38.81	38.96	0.27	40.09	39.67	0.74
***n*-heptane**	12.60	12.85	1.39	8.12	8.24	1.04	7.98	8.06	0.71	8.75	9.01	2.07	9.05	9.23	1.39	9.36	9.41	0.38
Toluene	14.73	14.97	1.14	9.50	9.59	0.67	9.33	9.38	0.38	10.23	10.59	2.45	10.59	10.82	1.52	10.94	11.00	0.39
Tetrahydrofuran (THF)	-	-	-	12.94	12.08	4.86	-	-	-	-	-	-	-	-	-	-	-	-
2-Methyltetrahydrofuran	-	-	-	22.60	23.77	3.57	22.87	24.07	3.62	-	-	-	13.91	14.40	2.45	12.83	13.39	3.02
Acetone	-	-	-	-	-	-	13.77	12.97	4.23	10.80	10.22	3.90	-	-	-	-	-	-
2-Butanone	-	-	-	-	-	-	-	-	-	19.78	19.65	0.47	14.20	13.92	1.41	-	-	-
Ethanol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	12.93	13.44	2.74

Where,

X = Blend Composition (wt%)

Y = DHA Composition (wt%)

4.1.2 Reid Vapor Pressure

RVP for all the gasoline blends are determined according to ASTM D323 and given in the Table 14, which also lists the predicted values by the property model along with their RSD.

Table 14: RVP for gasoline blends

Sample	$RVP\ (kPa)$		
	Experimental	**Model**	**RSD(%)**
MI	51.0	55.16	5.54
Blend 1	46.2	46	0.31
Blend 2	60.4	46	19.14
Blend 3	58.9	49	12.98
Blend 4	50.1	45	7.58
Blend 5	55.1	45	14.27

The RVP values predicted by the model are found to be lower for blend 2-5 and higher for MI as compared to results obtained from experiment. Only for blend 1, the model prediction is in good agreement with the experimental result. Modified Rault's law is used for calculation of RVP which is a function of mole fraction (x_i), activity coefficient (γ_i) and saturated vapor pressure (P_i) as shown in Equation 4 below.

$$RVP = \sum_{i=1}^{n} x_i \gamma_i P_i^{sat} \tag{4}$$

Assuming ideal solution behavior, activity coefficients for all the molecules present in the surrogates are assumed to be unity for the sake of simplicity of calculations. This assumption inevitably means that there is negligible interaction between the molecules of the different compounds in blends. However, results given in Table 14 suggest that this assumption is not consistent. To improve the model prediction on RVP, interactions between the molecules is considered (non-ideality) i.e. activity coefficient for all the compounds is incorporated in Equation 4. The activity coefficient of the compounds is determined using Universal Functional-group Activity Coefficients (UNIFAC) equation of state. UNIFAC is a model that can be, in principle used for all types of phase behavior calculations. UNIFAC is one of the most widely used Group-contribution (GC) models which is important in process and product design especially in predicting the liquid phase activity coefficients of mixtures [32]. UNIFAC is preferred because it does not require experimental binary parameters since interaction parameters evaluated by chemical group contribution may be obtained from a database [33]. Table 15 shows much improved results of RVP obtained from model in comparison with the experimental results.

Table 15: Improved RVP for gasoline blends

Sample	$\boldsymbol{RVP}\ (\boldsymbol{kPa})$		
	Experimental	**Model**	**RSD (%)**
MI	51.0	54.0	4.04
Blend 1	46.2	50.8	6.71
Blend 2	60.4	64.5	4.64
Blend 3	58.9	63.7	5.54
Blend 4	50.1	53.5	4.64
Blend 5	55.1	58.9	4.71

RSD values in Table 15 are smaller than the RSD values of Table 14 and this could be attributed to the incorporation of activity coefficient in Equation 4 determined through UNIFAC. Similar results were reported by Asher and Pankow [34] for vapor pressure calculations for alkenoic and aromatic organic compounds where authors made prediction with UNIFAC with great degree of accuracy. The experimental results show that RVP values for all the blends are within the acceptable defined range (45-100 kPa) in ASTM D4814 and also within the specified target values defined by Yunus et al. [22] (45 – 60 kPa) for gasoline used at average ambient temperature of 27^{o}C.

4.1.3 Research Octane Number (*RON*)

RON can be approximated by Equation 5 given below [35].

$$RON = \sum_{i=1}^{n} (a_i c_i) \tag{5}$$

where, c_i is the composition of compound *i* and a_i is octane number of the compound *i*.

In this study, the *RON* value is measured by GC-DHA technique where c_i (wt%) values of each compound is determined by normalization of the peak areas after correction with detector response factor. *RON* for all the gasoline blends is measured using the same equipment used for verification of composition (Perkin-Elmer Clarus-500). The octane number of each compound is already present in the inbuilt library supplied with the equipment. Table 16 gives concentration (wt%) of *n*-paraffins, *iso*-paraffins, olefins–naphthenes, oxygenates and aromatics and their respective contribution to the total RON.

Table 16: RON of surrogates and their individual compounds

Research Octane Number (RON)												
	MI		Blend 1		Blend 2		Blend 3		Blend 4		Blend 5	
	wt(%)	RON	wt (%)	RON	wt (%)	RON	wt(%)	RON	wt (%)	RON	wt(%)	RON
Paraffins	18.92	6.85	12.17	4.45	12.06	4.53	13.27	4.81	13.56	4.9	13.89	5.06
***Iso*-paraffins**	54.33	54.3	34.81	34.8	34.07	34.1	38.09	38.1	38.96	39	39.67	39.7
Olefins	3.46	4.09	2.24	2.64	2.2	2.6	2.41	13.1	2.44	2.88	2.53	2.99
Naphtenes	8.32	7.4	5.34	4.75	5.24	4.66	5.77	5.13	5.89	5.25	6.08	5.41
Aromatics	14.97	18.6	45.44	-	33.45	32.3	10.59	2.85	25.23	25.8	24.39	25.2
Oxygenates	0	0	0	0	12.98	13	29.87	-	13.92	-	13.44	13.4
Total		91.24		-		91.19		-		-		91.76

Equation 5 inevitably exhibits linear combination of the octane number and the composition of each compound. However, octane number of the blend is not a linearly mixed property as interactions are present between the different chemicals (oxygenates, paraffins, aromatics, naphthenes and olefins) [35]. Therefore, RON values reported in this study needs further investigation through ASTM D2699.

Nevertheless, RON measurement done using GC-DHA technique is an excellent method for approximation only. Lugo et al. [35] reported octane number calculation using linear mixing rule and ASTM method and reported a difference of ± 2.8 RON. Table 17 provides list of the results of RON measurement in comparison with the model predicted values.

Table 17: RON of gasoline blends

Sample	**Research Octane Number (RON)**		
	GC-DHA (calculated)	**Model**	**RSD (%)**
MI	91	92	0.77
Blend 1	-	-	-
Blend 2	91	-	-
Blend 3	-	-	-
Blend 4	-	-	-
Blend 5	92	96	3.01

The RON values obtained using GC-DHA for MI and blend 5 are slightly lower than the model prediction. The difference in results can be attributed to the change in composition that occurs while injecting the sample in the GC. For blends other than MI and Blend 5, RON values are not calculated since individual RON contribution for Tetrahydrofuran and 2-butanone are not available in the open literature. The results of RON are found to be in the typical range of RON desired for gasoline (88-98).

4.1.4 Density (ρ) and Dynamic Viscosity (η)

Density (ρ) and Dynamic Viscosity (η) for all the blends are measured according to ASTM 7042. Table 18 shows the experimental results of density and dynamic viscosity of gasoline surrogates in comparison with the results derived from the model.

Table 18: Density and viscosity of the gasoline surrogates

Sample	**ρ at 15°C** $(\frac{g}{cm^3})$			**η at 20.0°C** $(mPa.s)$		
	Experimental	**Model**	**RSD (%)**	**Experimental**	**Model**	**RSD (%)**
MI	0.7113	0.7260	1.45	0.50	0.51	1.40
Blend 1	0.7596	0.7709	1.04	0.54	0.48	8.32
Blend 2	0.7482	0.7618	1.27	0.46	0.47	1.52
Blend 3	0.7333	0.7480	1.40	0.45	0.48	4.56
Blend 4	0.7395	0.7528	1.26	0.46	0.50	5.89
Blend 5	0.7357	0.7487	1.24	0.61	0.57	4.79

The experimental values of density are in close agreement with model prediction which can be observed from their RSD values in Table 18. However, when experimental results of dynamic viscosity were compared with model prediction a small difference in results is observed. This difference may be attributed to the assumption of ideal solution behavior (γ=1) made in the calculation of dynamic viscosity in the model. Further, we have compared experimental results with model prediction on dynamic viscosity using Group Contribution UNIFAC based method reported by Cao et al. [36] as shown in the Table 19.

Table 19: Viscosity of gasoline surrogates using GC-UNIFAC (Model)

Sample	**Dynamic Viscosity (η)** $(mPa.s)$		
	Experimental	**Model**	**RSD (%)**
MI	0.50	0.51	1.40
Blend 1	0.54	0.46	11.31
Blend 2	0.46	0.43	4.77
Blend 3	0.45	0.43	3.21
Blend 4	0.46	0.45	1.55
Blend 5	0.61	0.58	3.57

It is evident from the Table 19 that there is no significant improvement in RSD values from Table 18 of MI and Blend 3 – 5 whereas for Blend 1 and Blend 2 the RSD values have even deteriorated. This inevitably means that the linear mixing rule has similar accuracy compared to the GC-UNIFAC based method and can be used for viscosity calculations. All the blends comply with the target values of density and dynamic viscosity defined in model except slight difference in density of MI and viscosity of blend 5. Further, mixing of renewable additives in MI significantly improved the density for all the blends. Moreover, presence of ethanol in blend 5 increased the dynamic viscosity from the rest of the blends due to higher viscosity of ethanol (1.095mPa.s).

4.1.5 Distillation Temperatures

Normally, the distillation curve is determined experimentally using ASTM D86, however; we could not determine the distillation curve using ASTM D86 for any blends due to safety concerns associated owing to presence of butane in the blends. In view of this distillation temperatures are determined by GC-DHA technique for all the six blends. The GC-DHA technique uses simulated distillation (SD) by a gas chromatography (GC) in which hydrocarbon compounds of the sample are eluted in order of increasing boiling points in a nonpolar capillary column (methyl silicone phase) as described elsewhere [37]. Petroff et al. [37] has compared the GC-DHA method with true boiling point (TBP) distillation and ASTM D86. Boiling range obtained by their study revealed that GC-DHA technique is essentially equivalent to TBP distillation, however, a small difference in distillation temperature is observed with ASTM D86. The distillation temperatures T10, T50 and T90 for all the blends are given in Table 20.

Table 20: Distillation temperatures of surrogates and ASTM limit for gasoline

	T10		**T50**		**T90**	
MI (^{0} C)	72	ASTM D4814 Max. 70	99	ASTM D4814 Min. 77 & Max. 121	111	ASTM D4814 Max. 190
Blend 1 (^{0} C)	66		98		99	
Blend 2 (^{0} C)	56		98		99	
Blend 3 (^{0} C)	56		98		99	
Blend 4 (^{0} C)	72		99		99	
Blend 5 (^{0} C)	72		99		99	

T10 values for MI, blend 4 and blend 5 are slightly higher than ASTM D4814 maximum limit of 70 ^{O}C. T50 and T90 values of all the blends are found to be within the acceptable limit of ASTM D4814. Although, distillation curve is not used in the model to define surrogates, it is an important parameter for gasoline fuel’s volatility and needs to be determined for such fuels.

4.2 Diesel Fuel

In diesel fuel, different compositions are recommended using the computer aided model. As many as nine blends of diesel surrogate are formulated and their compositions are given in the Table 21. The changes in the composition are made in conjunction with the experimental feedback. This enabled the development of a surrogate that is a good representative of the diesel fuel, satisfies ASTM requirements for physical properties and is benign for an engine application. Overall process diagram of diesel surrogate formulation is shown in Figure 8. This approach is an example of integration of both computation and experiments to reach the desired results as demonstrated in Figure 1 in Section 2.2. This approach not only helped in developing a promising surrogate composition but also enabled a thorough validation of the model results which can be useful for development of future fuel surrogate mixtures. Since different surrogates are prepared with different compositions, they assisted in understanding the influence of hydrocarbon classes on the physical properties of the fuel.

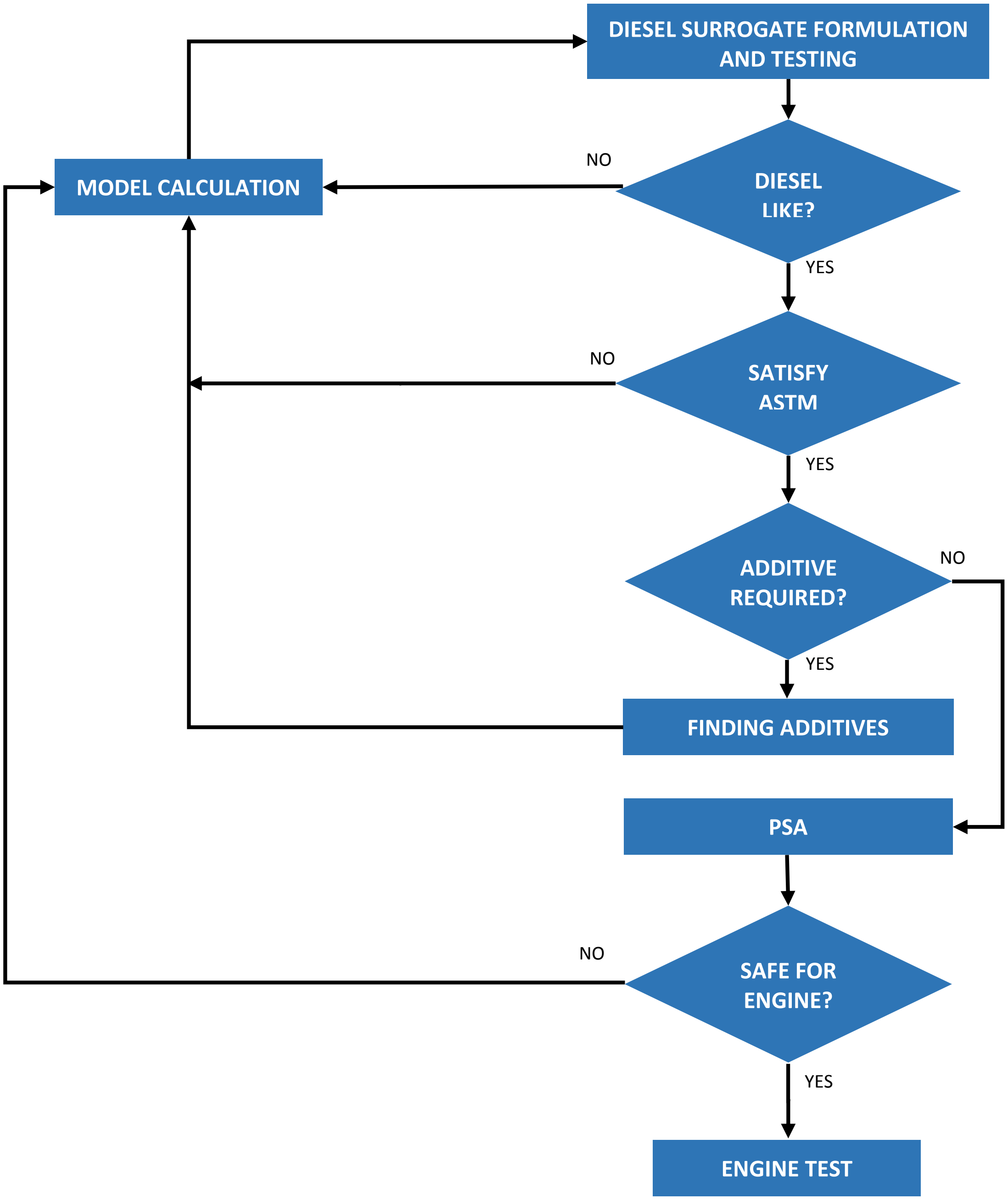

Figure 8: Process flowchart for diesel surrogate formulation

Table 21: Diesel surrogate blend compositions

Compounds	**MI Model 1**	**MI Model 2**	**MI Model 3**	**MI Model 4**	**Blend 1**	**Blend 2**	**Blend 3**	**Blend 4**	**Blend 5**
n-Decane	11.6	-	-	-	-	-	-	-	14.2
n-Undecane	11.6	-	-	-	-	-	-	-	-
n-Dodecane	14.7	35.0	35.0	15.0	23.0	25.6	31.9	32.2	12.9
n-Tetradecane	15.8	20.0	20.0	31.0	13.2	14.6	18.2	18.4	26.6
n-Hexadecane	24.2	-	-	-	-	-	-	-	-
n-Octadecane	10.5	-	-	-	-	-	-	-	-
n-Eicosane	11.6	-	-	-	-	-	-	-	-
Iso-octane	-	5.0	-	-	3.3	3.7	4.6	4.6	-
Cyclo-octane	-	20.0	20.0	44.0	13.2	14.6	18.2	18.4	37.8
Tetralin	-	20.0	20.0	-	13.2	14.6	18.2	18.4	-
Cyclohexylacetate	-	-	-	-	34.2	-	8.9	-	-
Cyclohexanone	-	-	-	-	-	26.9	-	8.0	-
Iso-Cetane	-	-	5.0	9.0	-	-	-	-	7.7
Toluene	-	-	-	1.0	-	-	-	-	0.9

Investigations on fuel properties for GTL Diesel (from ORYX GTL) and conventional diesel (from WOQOD, Qatar) are also carried out and presented in the Table 22. The results shown in Table 22 are compared with all the different surrogate fuels prepared in this study to have a fair comparison of the surrogates with conventional and GTL diesel.

Table 22: GTL and conventional diesel results

Properties	**GTL Diesel**	**Conventional Diesel**
ρ at 15°C (g/cm^3)	0.7675	0.8295
v at 40°C (mm^2/s)	2.0089	3.1033
VP at 37.8°C (kPa)	0.5	0.2
CP (°C)	-2.5	-1.5
PP (°C)	-12	-9
T_f (°C)	57.0	76.0
HHV (MJ/kg)	47.3710	46.0721
CN	78.2	58.7
Distillation (°C)		
IBP	163.1	193.8
10 %vol	185.3	234.5
50 %vol	246.3	275.7
90 %vol	324.5	335.4
EBP (°C)	346.8	368.2

The results of all the nine surrogates are given in two Tables (Table 23 and Table 24) in comparison with the predicted results from the model.

Table 23: Results of MI Model 1, MI Model 2, MI Model 3, MI Model 4

Properties	**MI Model 1**			**MI Model 2**			**MI Model 3**			**MI Model 4**		
	Mod.	Exp.	RSD (%)	Mod.	Exp.	RSD (%)	Mod.	Exp.	RSD (%)	Mod.	Exp.	RSD (%)
ρ at 15^{o}C (g/cm^3)	0.7672	0.7665	0.06	0.8330	0.8131	1.71	0.8260	0.8174	0.74	0.7975	0.7989	0.12
v at 40^{o}C (mm^2/s)	2.1302	2.1246	0.19	1.71	1.50	9.10	1.86	1.61	10.11	1.822	2.14	11.36
VP at 37.8^{o}C (kPa)	0.14	0.13	6.59	1.1	1.3	11.79	0.47	0.50	4.37	1.10	0.39	67.39
CP (^{o}C)	-	7.5	-	-	-28.2	-	-	-30.3	-	-18.0	-	-
PP (^{o}C)	-	6	-	-	-33	-	-	-33	-	-19.0	-	-
T_f (^{o}C)	77.9	77.5	0.32	40.0	38.5	2.70	49.6	54.5	6.66	40.5	60.8	28.34
HHV (MJ/kg)	47.31	47.21	1.15	43.08	45.78	4.29	43.16	46.10	4.66	47.01	47.00	0.02
CN	-	88.0	-	-	41.9	-	-	41.5	-	-	-	-
Distillation (^{o}C)												
IBP	-	191.23	-	-	134.7	-	-	171.7	-	-	-	-
10 %vol	-	204.7	-	-	172.1	-	-	183.6	-	-	-	-
50 %vol	-	253.57	-	-	206.4	-	-	209.4	-	-	-	-
90 %vol	-	307.1	-	-	231.7	-	-	232.6	-	-	-	-
EBP (^{o}C)	-	323.57	-	-	249.2	-	-	247.9	-	-	-	-

Table 24: Results of blend 1-5

Properties	**Blend 1**			**Blend 2**			**Blend 3**			**Blend 4**			**Blend 5**		
	Mod.	Exp.	RSD (%)	Mod.	Exp.	RSD (%)	Mod.	Exp.	RSD (%)	Mod.	Exp.	RSD (%)	Mod.	Exp.	RSD (%)
ρ at 15°C (g/cm^3)	0.8776	0.8655	0.98	0.8695	0.8466	1.88	0.8741	0.8264	3.97	0.8418	0.8231	1.59	0.7903	0.7848	0.49
v at 40°C (mm^2/s)	1.68	1.47	9.43	1.68	1.48	8.95	1.07	1.48	22.74	2.73	1.48	41.99	1.91	1.64	10.70
VP at 37.8°C (kPa)	0.7	1.8	62.2	0.7	2.0	68.87	1.0	1.3	22.14	1.0	1.7	35.90	1.02	0.90	8.84
CP (°C)	-	-29.8	-	-	-27.7	-	-	-29.8	-	-	-28.2	-	-	-21.0	-
PP (°C)	-	-33	-	-	-30	-	-	-33	-	-	-33	-	-	-22.1	-
T_f (°C)	46.4	42.5	6.20	43.5	34.5	16.35	42.1	39.0	5.34	41.1	35.0	11.37	38.3	41.5	5.74
HHV (MJ/kg)	29.02	40.66	2.91	40.34	42.37	3.47	41.76	44.62	4.68	42.19	45.06	4.65	47.10	47.17	0.11
CN	-	-	-	-	24.1	-	-	-	-	-	36.3		-	48.5	-
Distillation (°C)															
IBP	-	142.5	-	-	135.4	-	-	136.7	-	-	131.2		-	154.0	-
10 %vol	-	169.5	-	-	154.6	-	-	171.0	-	-	161.2		-	161.9	-
50 %vol	-	-	-	-	178.7	-	-	-	-	-	202.5		-	186.7	-
90 %vol	-	-	-	-	227.0	-	-	-	-	-	230.0		-	242.6	-
EBP (°C)	-	-	-	-	248.5	-	-	-	-	-	248.4		-	250.7	-

MI Model 1 comprises of only *n*-paraffinic hydrocarbons as shown in Table 20. Most of the properties of the MI Model 1 comply with the ASTM D975 standards defined for diesel fuel grade 2. Moreover, the model predictions are also found in close agreement with experimental results for all the properties viz. density, kinematic viscosity, vapor pressure, flash point and HHV with RSD values of 0.06%, 0.19%, 6.59%, 0.32% and 1.15% respectively. MI Model 1, being highly paraffinic in nature, has low density as compared to conventional diesel from WOQOD Qatar (0.8295 g/cm^3). This is the major reason why the density of MI Model 1 is highly comparable with that of GTL Diesel from ORYX (0.7675 g/cm^3) which is also highly paraffinic. MI Model 1 also has very poor cold flow properties i.e. cloud point and pour point are very high and operation in low ambient temperatures might cause solidification of the fuel which may incur blockage of fuel system such as filters, fuel lines etcetera. From literature survey it is observed that cold flow properties would improve with the induction of *iso* and *cyclo* paraffinic compounds [28]. Lack of *iso* and *cyclo* paraffinic compounds in MI Model 1 could explain the poor cold flow properties. The heat content and Cetane index of MI Model 1 have high values as the high *n*-paraffinic content exhibits much higher values [28,15].

Although, most of the results except cold flow properties and density are found to be promising, the composition did not represent either conventional diesel or GTL diesel. A different composition is suggested by model calculations as given in Table 21 and this composition is termed as MI Model 2 for future reference. The results of MI Model 2 are given in Table 23. The properties of MI Model 2 comply well with the ASTM standards defined for Grade 1 diesel fuel oil. Moreover, the model predictions are also found in close agreement with experimental results for all the properties viz. density, kinematic viscosity, vapor pressure, flash point and HHV with RSD values of 1.71%, 9.10%, 11.79%, 2.70% and 4.29% respectively. It is important to note that MI Model 2 contains all the hydrocarbon classes present in conventional diesel fuel as shown in Figure 7 in section 3.3, making it a good representation of diesel fuel. Density of MI Model 2 is higher than density of MI Model 1 due to the induction of the aromatic compound, tetralin which has a high density of 0.967 g/cm^3. The cold flow properties have improved significantly from

MI Model 1 owing to the presence of *iso* and *cyclo* paraffinic compounds like *iso*-octane and *cyclo*-octane respectively. Properties like flash point have decreased significantly, however, the flash point value does comply with ASTM D 975 Grade 1 diesel fuel specifications. The decrease in flash point can be attributed to the presence of *iso*-octane which has a flash point of -12 ^{o}C. The decrease in *n*-paraffinic content has also hugely reduced the calculated Cetane index of MI Model 2.

Further attempts are made to improve MI Model 2 results by introduction of renewable additives that could enhance the flash point. This is done using the computational model and the new blends proposed (Blend 1, Blend 2, Blend 3, Blend 4) are given in Table 21. The results of these blends are given in Table 24. The results for the blends 1-4 (Table 24) were found to be extremely poor and did not satisfy the model predictions at all especially for vapor pressure. This can be attributed to the fact that the model could not predict the interactions that result with the addition of cyclohexyl acetate and cyclohexanone. The additives, cyclohexyl acetate and cyclohexanone did not improve any of the properties of MI Model 2. They help in increasing the density, however, the HHV decreases significantly. Moreover, for the blends containing cyclohexyl acetate (Blend 1, Blend 3), distillation according to ASTM D86 could not proceed after a particular time period and only IBP and distillation temperature at 10%vol is known. This also means that Cetane index which is calculated based on the distillation temperatures is not determined for Blend 1 and Blend 3. The Cetane index and flash point reported for blend 2 and blend 4 are also found to be below the ASTM limits defined. Hence, all these four blends are rejected as potential candidates for diesel surrogate as ASTM requirements were not met.

A slight alteration is suggested in MI Model 2 based on literature study as *iso*-octane in MI Model 2 did not represent the carbon range for diesel fuel (C10-C22) [9]. Therefore, *iso*-octane which has a very low flash point of -12^{o}C is replaced with *iso*-Cetane which not only has a much higher flash point of 96^{o}C but also is readily available in high purity at a relatively low cost. It also lies in the middle of the carbon range for diesel fuel (C10-C22) which helps in improving the match of the distillation curve of diesel [9]. The new composition containing *iso*-cetane is termed as MI Model 3 and is given in Table 21. The results of MI Model 3 are given in Table 23. The physical properties measured for MI Model 3 comply well with ASTM D975 Grade 1 Diesel fuel specifications. Moreover, the results predicted by the model are in good agreement with the experimental results for all the properties viz. density, kinematic viscosity, vapor pressure, flash point and *HHV* with RSD values of 0.74%, 10.11%, 4.37%, 6.66% and 4.66% respectively. The density of MI Model 3 lies in between GTL and conventional diesel fuel. There is significant improvement in flash point of the fuel with the induction of *iso*-cetane. The cold flow properties of MI Model 3 are very good as evident from Table 23, therefore, this fuel could be suitable for very cold ambient condition applications. No improvement in Cetane Index (calculated) is observed, however, Cetane Index of MI Model 3 is complying with the ASTM specification. MI Model 3 is found to be a very strong potential candidate for further investigations viz. engine test and emission studies. In view of this, a detailed risk assessment, given in Appendix B, according to TAMUQ regulations is carried out for MI Model 3 in order to analyze the safety concerns associated with MI Model 3 inside the engine. Tetralin present in MI Model 3 has been reported in Safety Data Sheets (SDS) to produce peroxide on aerial oxidation at high temperatures. It is identified as a major hazard after reviewing the Safety Data Sheets (SDS) available online. Although, tetralin has been utilized in engine before to understand the oxidation chemistry of cyclic hydrocarbons in a motored engine by Yang and Boehman [38], MI Model 3 is rejected for further studies due to safety concerns and therefore, finding an alternate chemical compound is considered to alleviate the risk.

In view of the above mentioned difficulties, tetralin is replaced with toluene in the surrogate composition and calculations are repeated using the model. The new composition is termed as MI Model 4 and is given in Table 21. The results of MI Model 4 are given in Table 23. The model predictions are not in agreement with the experimental results for MI Model 4 and huge RSD values of 11.36%, 67.39% and 28.34% are reported for kinematic viscosity, vapor pressure and flash point respectively except for density and *HHV* which have RSD values are 0.12% and 0.02% respectively. The experimental results enabled improvements in calculation using the model. Non-ideal interaction between the chemical constituents are considered in the new assumption in the model and the mixture properties are re-calculated using the model. The new results are demonstrated in the Table 25 in comparison with the experimental results.

Table 25: Revised computational results for MI Model 4 in comparison with experimental results

Properties	**MI Model 4**		
	Experimental	**Computational**	**RSD (%)**
ρ at 15°C (g/cm^3)	0.7975	0.7989	0.12
v at 40°C (mm^2/s)	1.822	2.09	9.70
VP at 37.8°C (kPa)	1.10	1.09	0.65
CP (°C)	-18.0	-	-
PP (°C)	-19.0	-	-
T_f (°C)	40.5	37.2	5.95
HHV (MJ/kg)	47.01	47.00	0.02
CN	-	-	-

The new computation results show a significant improvement as can be seen from their low RSD values of 9.70%, 0.65% and 5.95% for kinematic viscosity, vapor pressure and flash point respectively. The results of MI Model 4 comply with the ASTM D975 specification for grade 1 diesel fuel oil. MI Model 4 has a higher paraffinic content like is the case in GTL Diesel which is also seen from the experimental analysis. The flash point of MI Model 4 decreases on replacing tetralin with toluene, however, it complies with the ASTM D975 specification for grade 1 diesel fuel. A subtle increase in kinematic viscosity is observed from MI Model 3 due to the higher paraffinic nature of MI Model 4. Moreover, the cold flow characteristics of MI Model 4 are good as evident from its low cloud point and pour point values which makes it even suitable for diesel engines operating in low temperature regions.

Further, *n*-decane was proposed as an additive using the model to improve fuel properties viz. flash point, Cetane Index and heat content. The new blend of MI Model 4 and the additive (*n*-decane) is termed as Blend 5 and its composition is given in Table 21. The results of Blend 5 are shown in Table 24. The results predicted via computer aided model are in good agreement with the experimental results as evident from their RSD values of 0.49%, 10.70%, 8.84%, 5.74% and 0.11% for density, kinematic viscosity, vapor pressure, flash point and *HHV* respectively. Blend 5 meets ASTM D975 specification for grade 1 diesel fuel oil for the measured properties. Blend 5 shown in Table 20 has an even higher *n*-paraffinic content as the additive *n*-decane is also an *n*-paraffinic compound. This high paraffinic nature resulted in a decrease in density of Blend 5 which is similar to the density of GTL Diesel. GTL diesel is almost entirely paraffinic in nature causing it to have a higher hydrogen-carbon ratio which leads to a low value of density as compared with the conventional diesel [15]. The low density also means that GTL diesel has a lower kinematic viscosity as compared with kinematic viscosity of conventional diesel which is also observed in the previous cited literature [15]. The higher paraffinic content of GTL fuel also leads to a higher *HHV* and Cetane index [15]. The slightly higher *n*-paraffinic content in Blend 5 improves the cold flow characteristics and *HHV* of the fuel as compared to MI Model 4. In addition, Blend 5 also shows an improvement from MI Model 3 in terms of Cetane Index which can again be attributed to the high *n*-paraffinic content. Blend 5 satisfies all the ASTM D975 specifications and therefore is being considered for further investigations. A detailed PSA is conducted and part of it is reported in Appendix C. No significant risk is identified for blend 5 after the review of the PSA. In view of this, Blend 5 has been recommended for further studies viz. engine test and emission studies. Distillation profiles for all the prepared surrogate mixtures, conventional diesel and GTL diesel are presented in Figure 9.

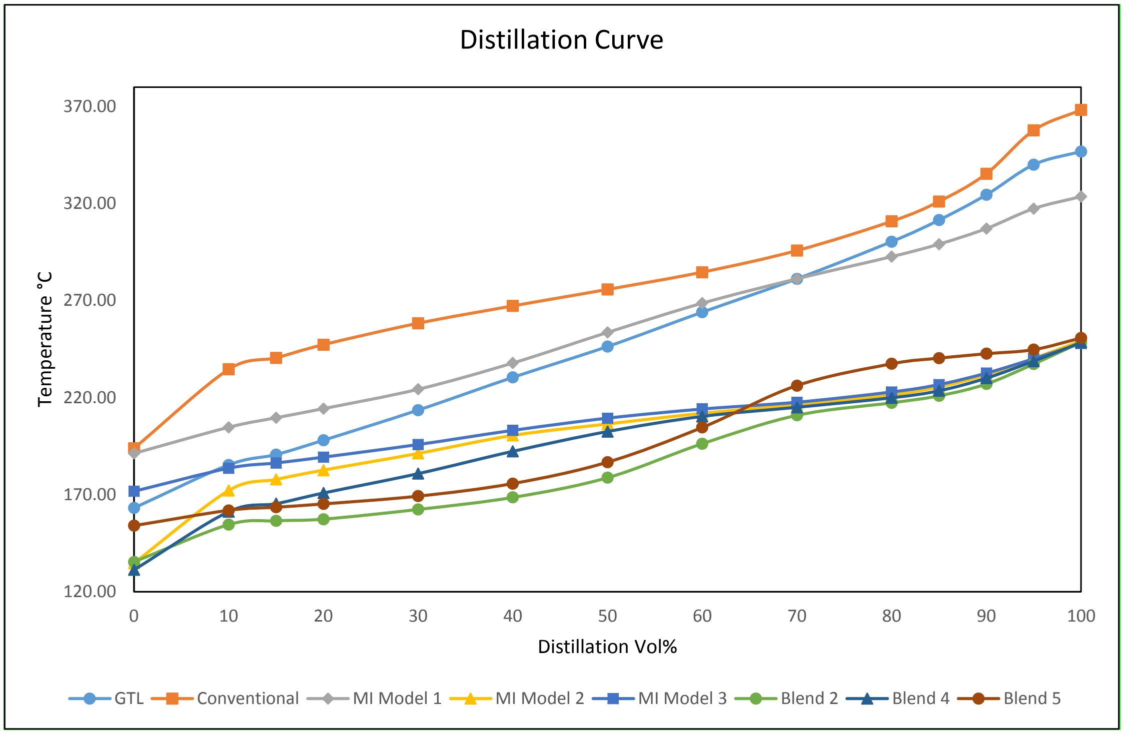

Figure 9: Distillation profile of surrogate blends

Table 26: Average chain length of surrogates

Blend	**MI Model1**	**MI Model2**	**MI Model3**	**MI Model4**	**Blend 1**	**Blend 2**	**Blend 3**	**Blend 4**	**Blend 5**
Avg. Chain Length	14.5	11.0	11.4	11.2	10.0	9.7	10.7	10.6	11.0

All the prepared surrogate blends show a distillation trend similar to conventional and GTL diesel. IBP for all the surrogates are lower than the conventional diesel except for MI Model 1. MI Model 3 has slightly higher IBP than that of GTL diesel. The IBP of

MI Model 1 and MI Model 3 suggested that these two fuels will have easy hot and cold starting.

All the surrogate fuel blends except MI Model 1 have very low match with the middle and tail end of the distillation profile of both conventional and GTL diesel. This shortcoming can be attributed to the shorter carbon chain length compounds present in all the surrogate blends except MI Model 1 which also comprises of C18 and C20 compounds. Average chain length is calculated according to the method described by Jeng, 2006 [39]. The average molecular chain length of all the surrogate blends are given in Table 26. As average molecular chain length of MI Model 1 is 14.5 and much higher than the rest of the blends, therefore its distillation temperatures are also found to be higher than all other surrogate blends as shown in Figure 9. In addition to this, the distillation temperatures of MI Model 1 are closer to both conventional and GTL diesel. Therefore, incorporation of higher chain length compounds in the range of C15-C16 will enable a better matching of the distillation curve of any surrogate fuel.

Blend 5 is more volatile as compared to MI Model 1 and therefore, the distillation temperatures are also much lower. The distillation curves indicate that Blend 5 has much lower distillation characteristics as compared to both GTL and conventional diesel which may improve atomization and dispersion of fuel spray. It also may lead to a more combustible air-fuel mixture as lower distillation characteristics ensures ease of evaporation. Moreover, reduced smoke and Particulate Matter (PM) emissions are also expected.

5. CONCLUSION AND FUTURE WORK

5.1 Conclusion

The model developed by Yunus et al. [22] can be used to prepare new fuel blends and identify suitable renewable additives in a known amount that can aid in designing of future generation of fuels obtained from either conventional crude oil sources or non-conventional sources (e.g. from natural gas via. Gas-To-Liquid (GTL), coal via. Coal-To-Liquid (CTL) or biofuels). Even though these models provide an excellent and affordable way for screening large number of fuel surrogates and optimization of the same, it is extremely important to experimentally verify the final blends and fine tune them if necessary. Also, the measured property values help to improve the accuracy of the property models as well as the assumptions used to develop them. The main focus of this study is to integrate both computation and experiments in the development of surrogate fuels. In order to achieve this, model developed by Yunus et al. [22] is used to conduct two case studies on gasoline surrogate and diesel surrogate. Model results on targeted gasoline surrogates' properties (e.g. *RON*, *RVP*, dynamic viscosity and density) and targeted diesel surrogates' properties (density, kinematic viscosity, Vapor Pressure, flash point and *HHV*) are experimentally verified.

Six blends of gasoline were prepared and characterized using unique preparation and sampling techniques. The following conclusions can be drawn from the experimental analysis of gasoline surrogates:

- The blending and sampling methodology developed for this study was capable of ensuring minimal composition variation during the analysis despite the fact that the blend is composed of both gas and liquid compounds. The effectiveness of the blending and sampling methodologies was verified using GC-DHA. Smaller RSD values for the blends composition confirmed the efficacy of our blending and sampling techniques.

- The model predictability of *RVP* data for all blends is initially found to significantly differ from the experimental measurements with a maximum RSD value close to 20% for blend 2. This was attributed to the fact that Yunus et al. [22] model assumed ideality of the blend mixtures. The experimental verification of the *RVP* data has led to the improvement in the property model by considering the non-ideality of blend mixture. Non-ideality is accounted for by means of the activity co-efficient for all chemical constituents in the blend using UNIFAC Equation of State. Approximately 3-fold reduction in RSD values is obtained after this correction.
- The model prediction on *RON* for MI and blend 5 is in good agreement with GC-DHA results.
- Densities of all the blends are also in close agreement with model prediction evident from their small RSD values.
- Experimentally determined dynamic viscosities are found to have small difference compared to their model predictions with a maximum RSD of 8.32% for blend 1. To account for this difference, Group Contribution UNIFAC based method is also used to determine viscosity; however, no significant improvement was observed. Linear mixing rule was found to have a similar accuracy compared to the Group Contribution UNIFAC based method and therefore linear mixing rule can be used to calculate viscosity for other blend formulations.
- The distillation temperatures are not considered during designing of blend; however, it is an important characteristic of gasoline fuel and routinely determined using ASTM D86 for the determination of the volatility of the fuel.
- The model developed by Yunus et al. performs well except for a few reported cases. Improvements have been made where the model predictions were not good especially in the case for *RVP*.
- The developed gasoline surrogate blends comply well with volatility specifications (*RVP* and distillation temperatures) of gasoline in ASTM D4814 except for T10 values for MI, Blend 4 and Blend 5 which do not comply with the

specification. At this stage we are unable to give any rationale behind this, however, the deviation in these cases was very small and could be due to error in peak integration in GC.

- Further, inclusion of distillation profile in the model would add another constraint that would lead to improvement in determination of right candidates for fuel blends.

Likewise, nine blends of diesel surrogate were prepared and analyzed for the physical properties. The developed surrogates were all compared with diesel fuel utilized in the market coming from both crude oil source and GTL source. The following conclusions can be drawn from this detailed study of diesel surrogates:

- The surrogate composition of Blend 5 is found to be a good representative of the diesel fuel and satisfy ASTM D975 specifications for grade 1 diesel fuels for all physical properties measured. Moreover, after a detailed PSA, it is also considered safe for testing in engine to determine engine performance and emission characteristics.
- The computer aided model results were also verified for Blend 5 and are found to be in good agreement with the experimental results. RSD values of 0.49%, 10.70%, 8.84%, 5.74% and 0.11% were reported for density, kinematic viscosity, vapor pressure, flash point and *HHV* respectively.
- For MI Model 4, the results predicted via computational means are not in agreement with the experimental results for few properties and relatively high RSD values of 11.36%, 67.39% and 28.34% are reported for kinematic viscosity, vapor pressure and flash point respectively. As a result, non-ideal mixture assumption was used and the new computation results show an improvement as can be seen with the low RSD values of 9.70%, 0.65% and 5.95% for kinematic viscosity, vapor pressure and flash point respectively.

- The measured properties of MI Model 3 comply well with ASTM D975 Grade 1 Diesel fuel specifications. MI Model 3 is not found to be safe for engine test due to the presence of potentially hazardous chemical (Tetralin).
- MI Model 1 comprises of only *n*-paraffinic compounds making it very paraffinic in nature and is highly comparable with GTL Diesel which is also paraffinic in nature. Although, MI Model 1 complies with all the tested fuel properties but due to the lack of *iso* and *cyclo* paraffinic compounds, poor cold flow characteristics are observed for MI Model 1.
- Replacing tetralin with toluene in the surrogate caused a significant decrease in flash point of surrogate mixture due to low flash point of toluene. In order to compensate flash point, relatively low concentration (1 vol%) of toluene is utilized in the surrogate mixture.
- From the distillation study of diesel surrogates, it is observed that average chain length has a significant influence on the distillation temperatures of the surrogate. A higher average molecular chain length is preferred to match the distillation profile with the diesel fuel in the market. An average chain length of approximately higher than 14 of the surrogate will have matching distillation temperatures to that of conventional and GTL diesel.

5.2 Future Work

The work presented in this thesis is part of a research project conducted at Texas A&M University at Qatar in collaboration with DTU. The ultimate goal of this research work is to develop surrogates for gasoline and diesel via experimental and modeling activities. The gasoline surrogate developed in this study is not feasible for real time application owing to the risk factor associated with its handling as well as the high cost of the hydrocarbons used. This study comprises of individual compounds of the different hydrocarbon classes and to prepare new feasible fuel blends mixtures of hydrocarbons that are easily available at a lower cost should be studied. This will lead to development of more realistic gasoline that has real time application. In diesel surrogate, hydrocarbons with higher chain lengths are required to match distillation profile and other physical properties to that of conventional diesel.

Emissions of toxic gases like Carbon Monoxide (CO), NOx and hydrocarbons are associated with incomplete combustion of the fuel in the internal combustion engine. This could happen due to the presence of large quantity of aromatics in conventional diesel as well as poor air and fuel mixtures. GTL diesel was reported to have significantly lower emissions compared to conventional diesel since GTL diesel do not have any aromatics while at the same time having a higher Cetane index [15]. The surrogate diesel in our study has an optimized quantity of aromatic, though it has a lower Cetane index. Moreover, it has a lower distillation temperature profile which could induce rapid vaporization of the fuel and reduce the flame quenching and improve ignition. Moreover, its high paraffinic nature leading to a high H/C ratio and its low aromatic content can help facilitate combustion and improve CO reduction.

Distillation temperature of the surrogate diesel was found to be lesser than that of GTL that could favor proper mixing of the fuel with air to constitute more combustible mixture that could result in lower HC emission [15]. The surrogate diesel could produce more NOx on combustion since it has lower Cetane index than both GTL and conventional diesel. However, lower distillation temperature of model diesel in this study could favor lesser NOx emission due to better combustion in engine. These are few questions that remained unanswered and could be determined by conducting engine test. An engine test of the diesel surrogate would also help in developing a correlation between the hydrocarbon classes, different physical properties, and engine performance and emission characteristics.

In summary, it is observed in the open literature that some groups have prepared a surrogate fuel through modelling while others have used other criteria such as cost and availability to decide compounds of surrogate fuel. And most of them have even tried to validate their models by measuring the properties of their surrogate. Some of the groups have even gone further so as to test ignition delay and combustion properties. But none of the groups, according to the author’s knowledge, have done a comprehensive study that comprises modeling, physical property measurement and real time engine testing to design a fuel. In addition to this, results obtained from this study will be communicated to our collaborators in DTU to incorporate the data to add engine performance and emission characteristics while designing surrogates.

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APPENDIX A

GAS CHROMATOGRAMS OF GASOLINE SURROGATE BLENDS

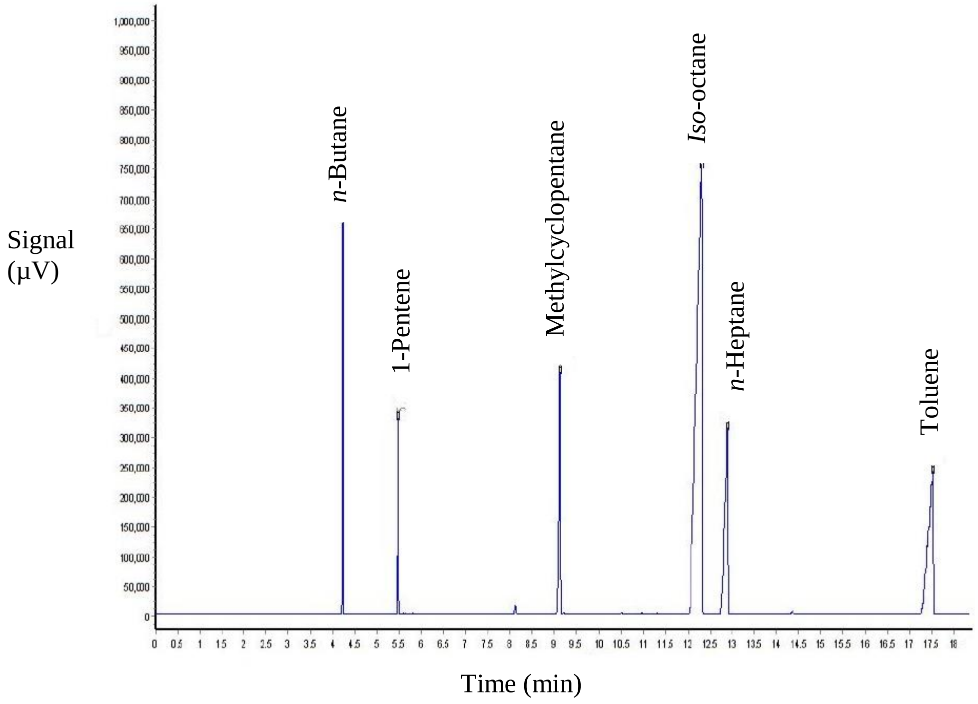


Figure A- 1: Gas chromatogram of MI

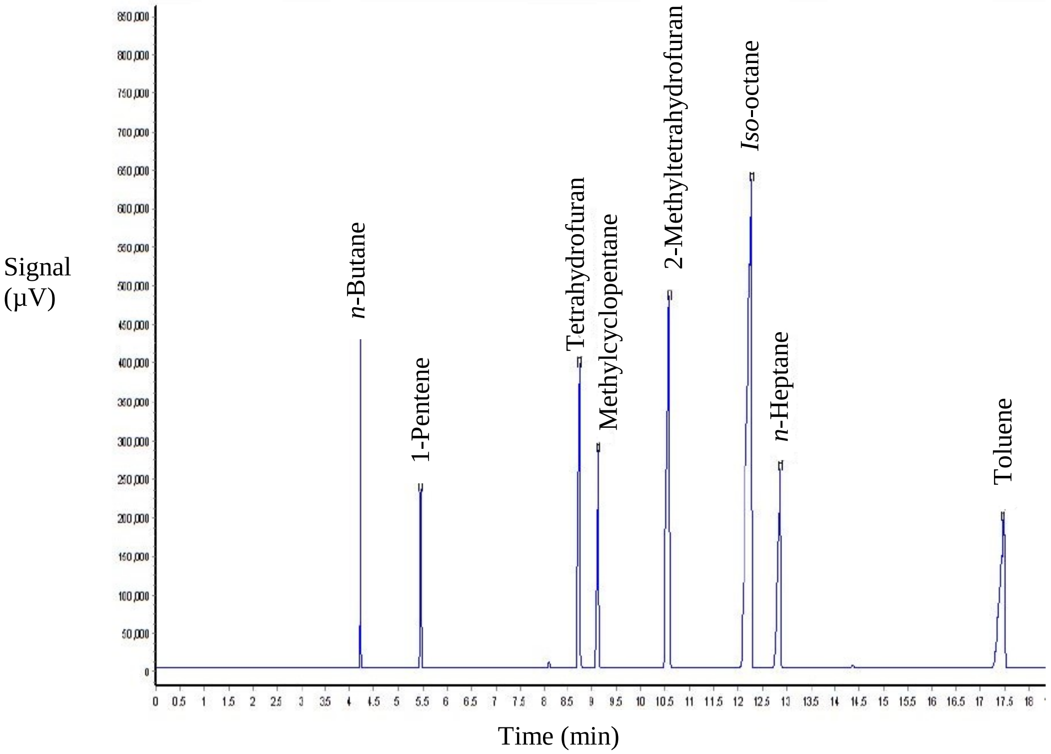


Figure A- 2: Gas chromatogram of Blend 1

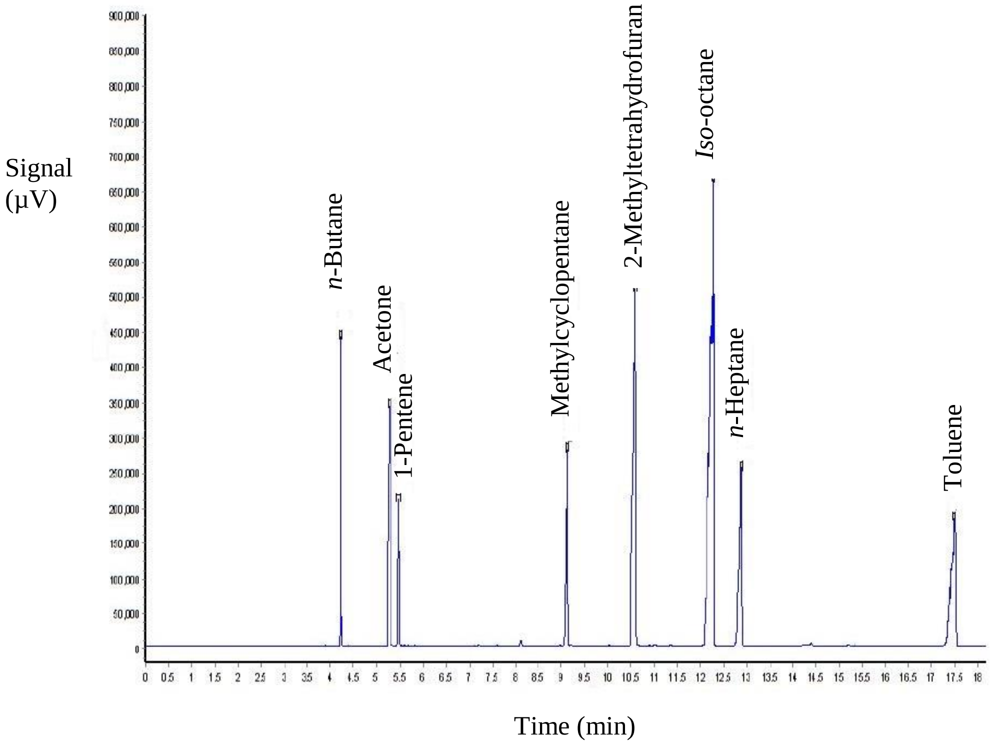


Figure A- 3: Gas chromatogram of Blend 2

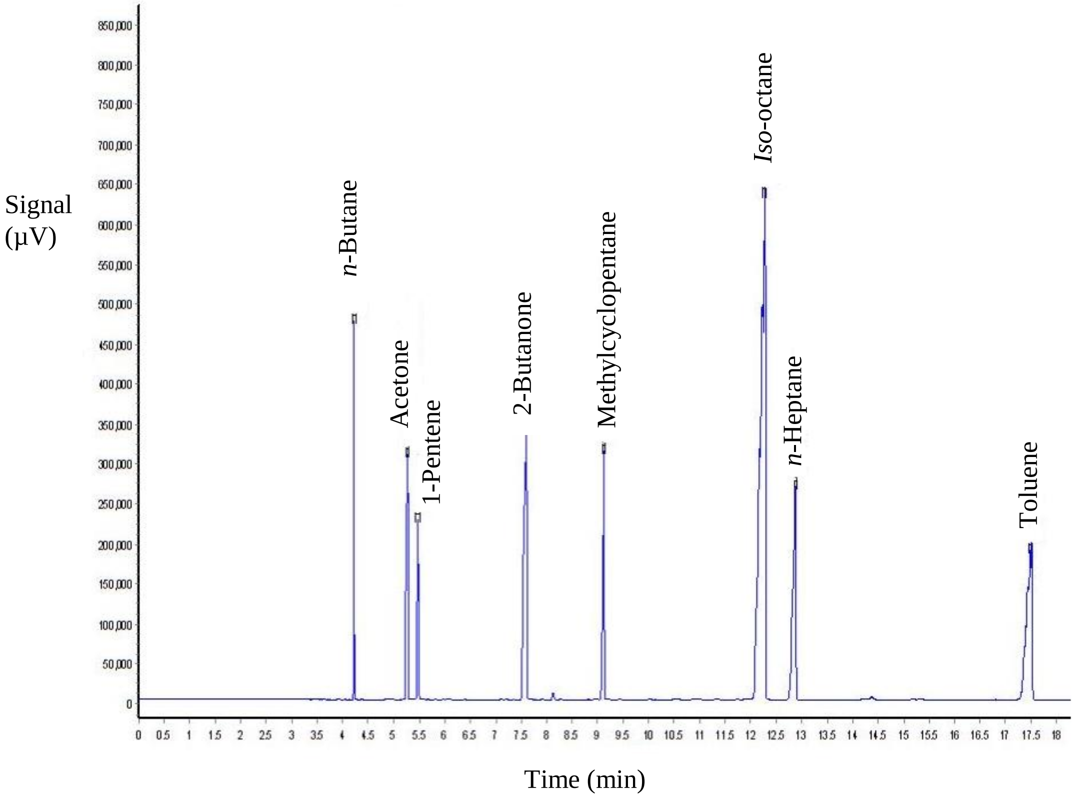


Figure A- 4: Gas chromatogram of Blend 3

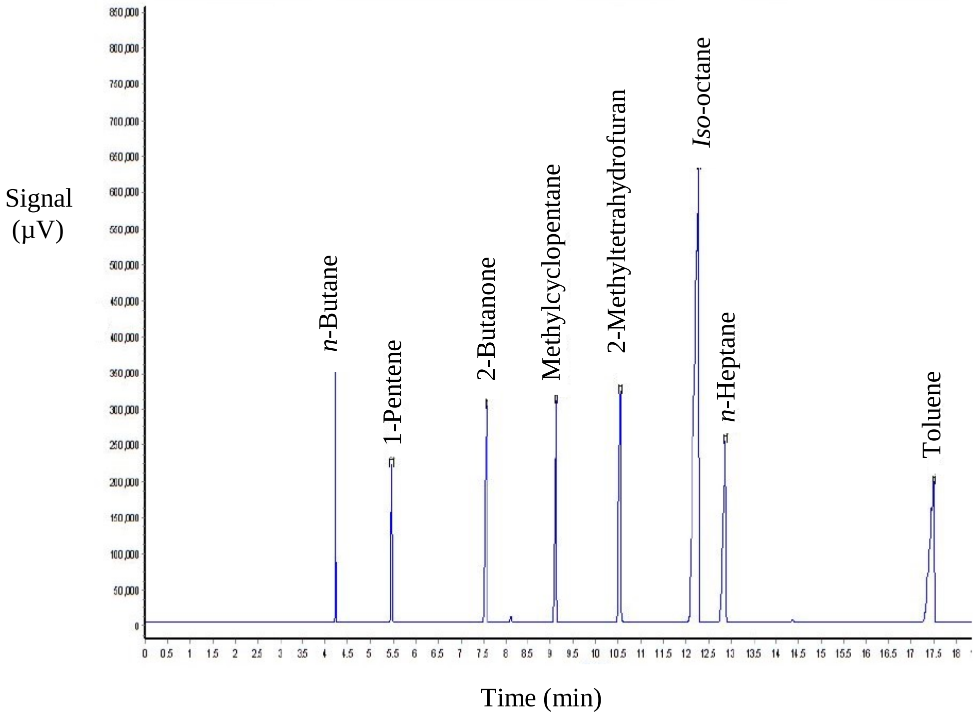


Figure A- 5: Gas chromatogram of Blend 4

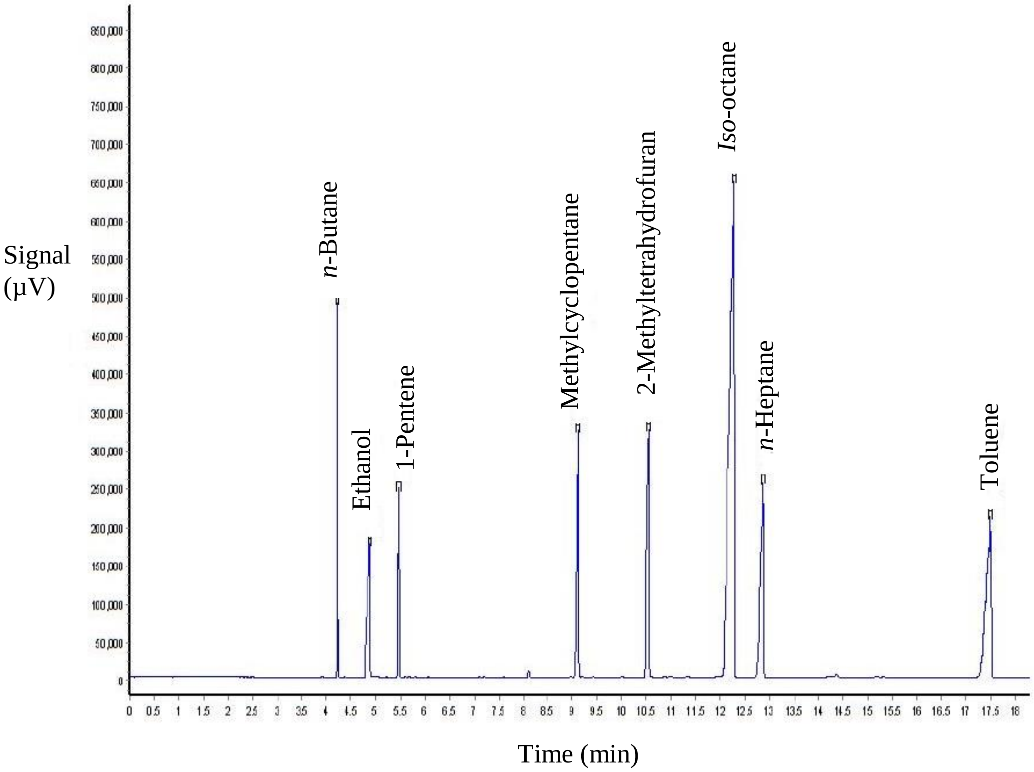


Figure A- 6: Gas chromatogram of Blend 5

APPENDIX B

DETAILED RISK ASSESSMENT FOR MI MODEL 3

Case	Consequence	Effective Safeguards	Safeguard Category	Before Risk Reduction			Recommendation	Recommendation category	After Risk Reduction			Comments
Flammable Hazard												
1. leak from engine or pipe from fuel tank and can come in contact with hot moving part of engine or spark from electrical devices causing fire 2. Ignited fuel due to spark from static discharge 3. Spill while filling fuel tank 4. Other hot surfaces in general	1. First to third degree burns 2. Permanent equipment damage 3. Vapors of hydrocarbon will be present in the lab which may cause suffocation due to scarcity of oxygen 4. Death from burn injuries	1. Engine is designed for flammable fuels 2.Hydrocarbon detector installed in lab 3. Fire alarms 4. Hot surfaces covered in insulation 5. Fire extinguishers 6. Flame blankets 7. Adequate signs for flammable, combustible and possible hazardous materials 8. Funnel is always used to fill the tank 9. Always a small volume of fule is filled from the stock to prevent spill 10. Laboratory room ventilation system designed for 6-8 air exchanges per hour	1.Inherent safer design 2. Administrative control 3. Administrative control 4.Engineering control 5. Administrative control 6. Administrative control 7. Administrative control 8. Administrative control 9. Administrative control 10. Engineering control	**1**	**D**	**1D**	1. High quality pipe fittings are installed to prevent any leakage 2. Keep sufficient quantity of spill mats in lab 3. Ensure proper grounding of the equipment 4. Do not run unattended operation 5. Stay away from equipment when running 6. Allow adequate time for equipment to cool down before re-rerunning 7. Use appropriate PPE	1. Engineering control 2. Administrative control 3. Engineering control 4. Administrative control 5. Administrative control 6. Administrative control 7. PPE	**2**	**E**	**2E**	

Case	Consequence	Effective Safeguards	Safeguard Category	Before Risk Reduction			Recommendation	Recommendation category	After Risk Reduction			Comments
Explosion												
1.Reactive chemicals present in the fuel 2. High pressure due to fuel pump malfunctioning rising pressure in the combustion chamber 3. Pyrophoric chemical present in the fuel	1. Sharp debris launched into the air causing severe injury 2. Equipment damage 3. Explosion could be a fire hazard if it comes into contact with other reactive materials	1. Face shields are to be worn at all time when the experiment is running 2. All moving parts are covered and hot surfaces covered in insulation 3. No reactive chemicals are used in the engine 4. No pyrophoric materials are used in fuel mixture 5. Always check the equipment temperature and pressure of the equipment are within safe limits	1. PPE 2. Engineering control 3. Administrative control 4. Administrative control 5. Administrative control	**2**	**C**	**2C**						
Chemical Hazard												
CO and CO2 Hazards associated to leak from equipment or from calibration cylinders	1. Reduce oxygen-carrying capacity of the blood 2. fatal consequences to people with heart diseases 3. High CO and CO2 concentrations cause suffocation or death	1.Firmly secure all engine openings with air -tight screws 2. Secure all gas cylinders and turn off the regulators after use 3. Gas alarms installed that will go off on the slightest increase of CO and CO2 levels 4. Portable gas monitors for lab personnel also present 5. Laboratory room ventilation system designed for 6-8 air exchanges per hour	1. Engineering control 2. Administrative control 3. Administrative control 4. Administrative control 5. Engineering control	**1**	**D**	**1D**	Consider shut off engine on the event of alarm goes off stopping any more production of toxic CO gas.	Engineering control	**3**	**D**	**3D**	

Case	Consequence	Effective Safeguards	Safeguard Category	Before Risk Reduction			Recommendation	Recommendation category	After Risk Reduction			Comments
Chemical Hazard												
NOx Hazards associated to leak from equipment or from calibration cylinders	1.Severe respiratory effects 2. Asthma, emphysema, and bronchitis	1.Firmly secure all engine openings with air -tight screws 2. Secure all gas cylinders and turn off the regulators after use 3 Portable gas alarms help to detect if any increase in NOx level 4. Laboratory room ventilation system designed for 6-8 air exchanges per hour	1. Engineering control 2. Administrative control 3. Administrative control 4. Engineering control	**3**	**D**	**3D**						
***Iso*-cetane** present in the fuel mixture may form vapor and leak in the lab	1.Can cause fire on contact with heated surfaces 2. May cause respiratory effects	1.Must be preheated to form vapor Since it has high boiling point(240 deg C) 2.High flash point (96 deg C) ensures prevents it to form flammable mixture at ambient condition 3. Laboratory room ventilation system designed for 6-8 air exchanges per hour 4. All moving parts are covered and hot surfaces covered in insulation 5. Hydrocarbon detector	1.Inherent safer design 2.Inherent safer design 3. Engineering control 4. Engineering control 5. Administrative control	**4**	**E**	**4E**						

Case	**Consequence**	**Effective Safeguards**	**Safeguard Category**	**Before Risk Reduction**			**Recommendation**	**Recommendation category**	**After Risk Reduction**			**Comments**
Chemical Hazard												
Cyclo octane present in the fuel mixture may form vapor and leak in the lab	1. First to third degree burns due to fire 2. May cause asphyxiation	1. No live fire source present in the vicinity of the engine. 2. Must be preheated to form vapor Since it has high boiling point(99 deg C) 3. Laboratory room ventilation system designed for 6-8 air exchanges per hour 4. All moving parts are covered and hot surfaces covered in insulation 5. Hydrocarbon detector 6. Fire alarms 7. Fire extinguishers 8. Flame blankets	1.Engineering control 2.Inherent safer design 3. Engineering control 4. Engineering control 5. Administrative control 6. Administrative control 7. Administrative control 8. Administrative control	**1**	**E**	**1E**	Consider using fire protective PPE for all lab personal during operation	PPE	**2**	**E**	**2E**	
Tetradecane present in the fuel mixture may form vapor and leak in the lab	1. First to third degree burns due to fire 2. May cause asphyxiation	1.Must be preheated to form vapor Since it has high boiling point(257deg C) 2.High flash point (100 deg C) ensures prevents it to form flammable mixture at ambient condition 3. Laboratory room ventilation system designed for 6-8 air exchanges per hour 4. All moving parts are covered and hot surfaces covered in insulation 5. Hydrocarbon detector	1.Inherent safer design 2.Inherent safer design 3. Engineering control 4. Engineering control 5. Administrative control	**4**	**E**	**4E**						

Case	Consequence	Effective Safeguards	Safeguard Category	Before Risk Reduction			Recommendation	Recommendation category	After Risk Reduction			Comments
Chemical Hazard												
Dodecane present in the fuel mixture may form vapor and leak in the lab	1. First to third degree burns due to fire 2. May cause asphyxiation	1.Must be heated or high ambient temperature to burn Since it has high boiling point(216 deg C) 2.High flash point (71 deg C) ensures prevents it to form flammable mixture at ambient condition 3. Laboratory room ventilation system designed for 6-8 air exchanges per hour 4. All moving parts are covered and hot surfaces covered in insulation 5. Hydrocarbon detector	1.Inherent safer design 2.Inherent safer design 3. Engineering control 4. Engineering control 5. Administrative control	**4**	**E**	**4E**						

Case	Consequence	Effective Safeguards	Safeguard Category	Before Risk Reduction			Recommendation	Recommendation category	After Risk Reduction			Comments
Chemical Hazard												
Tetralin present in the fuel mixture may form vapor and leak in the lab	1. Potentially explosive Peroxides can form on long-term storage in contact with air. Light and heat accelerate peroxide formation 2. First to third degree burns due to fire or explosion due to peroxides leading to fatalities. 3 Can cause temporary health hazard or residual injury. Inhalation of vapor or mist is irritating to the respiratory tract that may produce headache, nausea, vomiting 4. May cause asphyxiation 5. Carbon dioxide and carbon monoxide may form when heated to decomposition 6. Under pyrolysis at 700C yields tars that contain 3,4benzopyrene 7. 1,2-dihydronapthalene, Indene and naphthalene may produce on oxidation at temperature ≤677 deg C	1. Sealed storage tank ensuring no air contact eliminate any peroxide formation. Stored in Flammable cabinets at 25 deg C. 2. Must be heated or high ambient temperature to burn Since it has high boiling point(207 deg C) 3. High flash point (77 deg C) ensures prevents it to form flammable mixture at ambient condition 4. All moving parts are covered and hot surfaces covered in insulation 5. Laboratory room ventilation system designed for 6-8 air exchanges per hour 6. Hydrocarbon detector 7. Engine exhaust is designed for handling emissions of carbon dioxide and carbon monoxide and hooked to emission benches and then released to ventilation duct designed for toxic gases. 8. Engine will be operated at an rpm that do not generate heat more than 650deg C in the ignition chamber 9. PPE	1. Administrative control 2. Inherent safer design 3. Inherent safer design 4.Engineering control 5. Engineering control 6. Administrative control 7. Inherent safer design 8. Administrative control 9.PPE	**1**	**E**	**1E**						1. Tetralin is a major chemical hazard identified by most of the SDS. However, after conducting literature survey we understood that at operational condition of a diesel engine no peroxides are being formed [38]. Although it appears to lie in Tolerable Risk we would still recommend to review the risk with an expert. 2. 1,2-dihydronapthalene, Indene and naphthalene is discussed individually in the next cause

Case	Consequence	Effective Safeguards	Safeguard Category	Before Risk Reduction			Recommendation	Recommendation category	After Risk Reduction			Comments
Chemical Hazard												
1,2-dihydronapthalene may be formed during combustion of Tetralin and released in lab	1.Can cause significant skin irritation on contact 2. Minor burn injuries	1. Engine exhaust is designed for handling emissions and hooked to emission benches and released to ventilation duct designed for toxic gases. 2. Engine is designed for flammable fuels 3.PPE 4. Laboratory room ventilation system designed for 6-8 air exchanges per hour 5. Hydrocarbon detector	1. Inherent safer design 2. Inherent safer design 3.PPE 4.Engineering control 5. Administrative control	**3**	**E**	**3E**						
Naphthalene may be formed during combustion of Tetralin and released in lab	1. Can cause temporary health hazard or residual injury. 2. Minor burn injuries	1. Engine exhaust is designed for handling emissions and hooked to emission benches and released to ventilation duct designed for toxic gases. 2. Engine is designed for flammable fuels 3.PPE 4. Laboratory room ventilation system designed for 6-8 air exchanges per hour 5. Hydrocarbon detector	1. Inherent safer design 2. Inherent safer design 3.PPE 4.Engineering control 5. Administrative control	**3**	**E**	**3E**						

Case	Consequence	Effective Safeguards	Safeguard Category	Before Risk Reduction			Recommendation	Recommendation category	After Risk Reduction			Comments
Chemical Hazard												
Indene may be formed during combustion of Tetralin and released in lab	1. Can cause temporary health hazard or residual injury. 2. Minor burn injuries	1. Engine exhaust is designed for handling emissions and hooked to emission benches and released to ventilation duct designed for toxic gases. 2. Engine is designed for flammable fuels 3.PPE 4. Laboratory room ventilation system designed for 6-8 air exchanges per hour 5. Hydrocarbon detector	1. Inherent safer design 2. Inherent safer design 3.PPE 4.Engineering control 5. Administrative control	**3**	**E**	**3E**						

APPENDIX C

PSA FOR ENGINE TEST OF BLEND 5

Project Identification

Project Name: **Testing of surrogate diesel in Engine lab**

1.1 Project Purpose, Scope and Details (project, equipment, job, task)

The primary objective of this project is to carry out an engine test of the diesel surrogate designed using computation by our collaborator in Technical University of Denmark (DTU). The designed surrogate was tested for different physical properties using advanced experimental techniques and determination of engine performance features and emission characteristics will add value in the field of development of diesel surrogates.

In open literature it is reported that GTL diesel perform poorly in engine than conventional. Properties like torque/Power, Brake Specific Fuel Consumption (BSFC) are always reported to be lower for GTL diesel than conventional diesel since GTL diesel has lower density and LHV [1]. The surrogate diesel developed has higher density and higher heating value than that of GTL and almost comparable to conventional diesel. We have carefully designed our surrogate fuel that comprises only 1% (vol%) of aromatic that meets most of the ASTM requirement under study for a synthetic diesel. Higher concentrations of aromatics (>30%) in conventional diesel renders poor combustible properties [2]. An engine test reporting torque/power and BSFC would be essential to determine the fuel performance of the surrogate fuel as compared to GTL and conventional diesel. Such a surrogate have true resemblance with GTL target diesel.

Emissions of toxic gases like CO, NOx and hydrocarbons are associated with incomplete combustion of the fuel in the internal combustion engine. This could happen due to the presence of large quantity of aromatics in conventional diesels as well as poor air and fuel mixtures. GTL diesel were reported to have significantly lower emission compared to conventional one since they do not have any aromatics as well as of having a higher CN index [1]. The surrogate diesel in our study has an optimized quantity of aromatic, though it has a lower CN index. However, it has lower distillation temperature profile. This could induce rapid vaporization of the fuel and reduce the flame quenching and improve ignition. Moreover, its high paraffinic nature leading to a high H/C ratio and its smaller aromatic content can help facilitate combustion and improve CO reduction. Distillation temperature of the surrogate diesel was found to be lesser than that of GTL that could favor proper mixing of the fuel with air to constitute more combustible mixture that could result in lower HC emission [1]. The surrogate diesel could produce more NOx on combustion since it has lower CN index than both GTL and conventional diesel. However, lower distillation temperature of model diesel in this study could favor lesser NOx emission due to better combustion in engine. These are few questions that remained unanswered and could be determined by conducting engine test. An engine test of the diesel surrogate would also help in developing a correlation between the hydrocarbon classes, different physical properties, and engine performance and emission characteristics.

In summary, it is observed in the open literature that some groups have prepared a surrogate fuel through modelling while others have used other criteria such as cost and availability to decide compounds of surrogate fuel. And most of them have even tried to validate their models by measuring the properties of their surrogate. Some of the groups have even gone further so as to test ignition delay and combustion properties. But none of the groups, according to the author’s knowledge, have done a comprehensive study that comprises modeling, physical property measurement and real time engine testing to design a fuel. In addition to this, results obtained from this study will be communicated to our collaborators in DTU to incorporate the data to add engine performance and emission characteristics while designing surrogates.

Ref: References

[1] H. Sajjad, H. H. Masjuki, M. Varman, M. a. Kalam, M. I. Arbab, S. Imtenan, and S. M. A. Rahman, “Engine combustion, performance and emission characteristics of gas

to liquid (GTL) fuels and its blends with diesel and bio-diesel," Renew. Sustain. Energy Rev., vol. 30, pp. 961–986, 2014.

[2] C. J. Mueller, W. J. Cannella, T. J. Bruno, B. Bunting, H. D. Dettman, J. a. Franz, M. L. Huber, M. Natarajan, W. J. Pitz, M. a. Ratcliff, and K. Wright, "Methodology for formulating diesel surrogate fuels with accurate compositional, ignition-quality, and volatility characteristics," *Energy and Fuels*, vol. 26, no. 6, pp. 3284–3303, 2012.

1.2 Overall process/project description (flow chart if any)

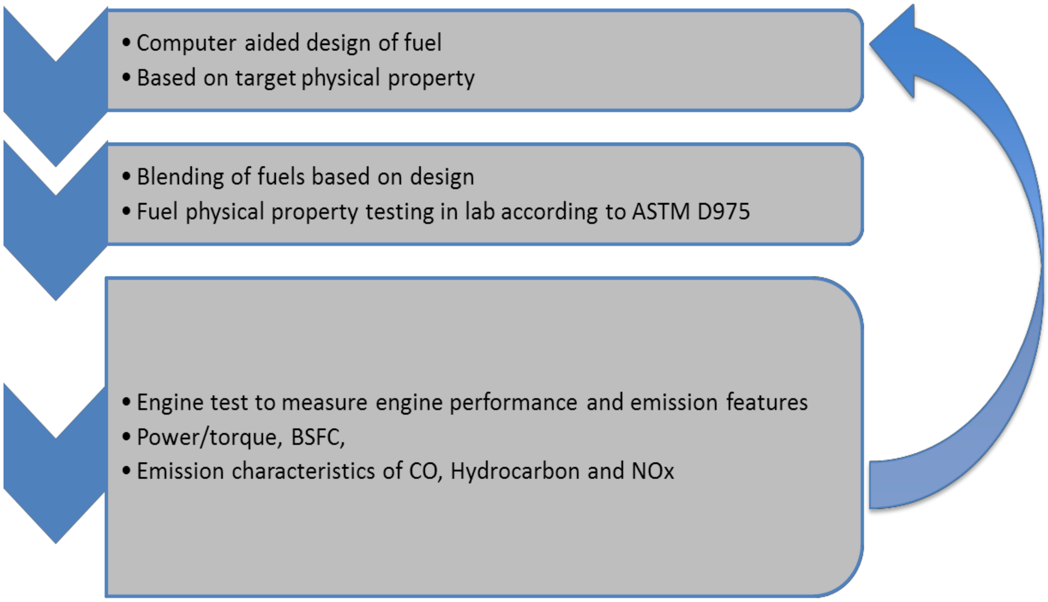


Figure C- 1: Overall process description

2. Detailed Description of all equipment and processes

Not Relevant to Thesis

2.1 Location of each equipment and description/plan of the surroundings

Not Relevant to Thesis

2.2 Utilities needed

Not Relevant to Thesis

2.3 Required facility alterations and preparedness

Not Relevant to Thesis

2.4 Design and methods

Not Relevant to Thesis

2.5 Working policy and plans (eg. Working alone, at night, weekends)

1. No work with any equipment or parts of engine lab setup is allowed unless someone familiar with "Project Procedures" and has signed the PSA.
2. The buddy system of having two people in the lab is also to be enforced which ensures that at the time of the running the experiment more than one individual is present.
3. Unattended operation must not occur.
4. During off hours (weekend, evenings, holidays), lab personnel must check in with the security at time of entering TAMUQ building. At the time of departure check out with security is needed.
5. As the lab has research equipment for other departments, during the running of other research equipment, the engine lab personnel will be barred from entering the vicinity and vice versa unless they have read and agreed to this PSA.
6. The door has to be left unlocked from the inside during the running of the experiment to expedite any evacuation or emergency procedures if the need be.

2.6 Preliminary Precautions

1. All Laboratory power outlets are supplied through an automatic circuit breaker and fuse to protect from over-current and/or short-circuit faults.
2. An emergency switch located on each table where workbench equipment are located.
3. First aid kits and fire blankets are available in the lab.
4. Fire extinguishers are placed inside the lab, and are to be used in case of fire.

5. Laboratory personnel and all attendees present are required to wear safety goggles at times where tools are being used or equipment are in operation.
6. Lab coats, gloves and eye protection is to be worn when experiment is underway.
7. Safety labels are included on laboratory door and equipment.
8. Safety labels are included on laboratory door and equipment.

2.7 Limits of Safe Operation

1. All equipment are to be used in accordance with the work instructions.
2. No researchers or personnel should use any of the equipment without reading and signing the PSA and have undergone proper training.
3. Any malfunction of any of the equipment has to be reported to the facility supervisor, and operation is to be halted.
4. In case of emergency, user has to press the emergency power break switch labelled clearly on the equipment.
5. Daily machine operation is to be recorded in a designated log sheet located beside each equipment.
6. A record for machine maintenance is recorded on a visible label on each equipment. Machines should not be operated in case maintenance date has passed.
7. Only authorized and trained personnel should perform calibration or minor maintenance on any equipment.
8. For the dynamometer and engine, the safe limits of operation are the rotational speed of 2700 RPM under high-load conditions. Exceeding these limits can only cause mechanical failure of the fuel injection pump system.
9. In the unlikely event of a mechanical failure, the fuel supply to the engine has to be cut off immediately by toggling the fuel pump power switch.
10. For the Horiba analytical machine the limit of safe operation would not be hindered due to extensive runs since it is only an analytical tool.
11. The temperature of the apparatus like any other equipment would tend to rise on prolonged use. However, given our proposed time runs this would not be an issue.

3. Internal Emergency Preparedness and response plans

Personnel are trained to proceed with emergency shutdown procedures at any moment they begin to detect an unsafe situation, or feel uncomfortable with the test operation. An emergency shutdown has no negative effects on the laboratory or test equipment. Examples (non-exhaustive) of events that necessitate emergency shutdown procedures may include the following:

1. Observation of a fuel leak.
2. Abnormal noise during operation.
3. Detection of any abnormal smell.
4. Mechanical failure
5. Building power failure
6. Untrained personnel entering the laboratory environment unexpectedly.
7. Excessive rise in temperature of the laboratory or the test equipment.

In order to minimize the risks of unsafe conditions, all personnel are required to undergo standard safety training through the appropriate university mechanisms. Specifically, all lab personnel must complete: Laboratory Safety Training, Machine Shop & Tool Safety Training and Extinguisher Training. In addition to general safety training, each researcher is required to undergo lab-specific training.

Fuel Storage

Fuel (combustible/flammable) will be contained in approved and labeled containers and segregated from potential shock / spark, heat, and oxidizing hazards. All Fuels will be placed inside a special flammable cabinet. Fuel will be stored in a well-ventilated area near fire extinguishers. Fuel in use will be in a marked leak and explosion-proof container.

Emergency response equipment

Fire extinguisher, first aid kit, oil spill kit, fire blanket, fire hose reel (available in the hallway) have been made available and the stocks will be checked bi-weekly to ensure that all necessary emergency apparatus are up and working.

Personal Protective Equipment (PPE)

All lab personnel are required to wear PPE at all times when doing any experimental procedures:

1. Long Pants, Long Sleeved Shirts are to be worn and no shorts, skirts are allowed
2. Closed –toed shoes are to be worn at all times, no slippers are to be allowed.
3. Aprons / lab coats as well as safety glasses / face shields are to be worn when handling chemicals, metal work, and while the engine is operational.
4. Gloves are also to be worn when handling hot components.
5. Hearing protection is also provided in the lab.

4. Operating procedures and conditions (e.g. pressure, temperature, flow, voltage, total volume of utilized chemicals, fuels)

Not Relevant to Thesis

5. Risk Assessment - ALL Processes and Equipment

5.1 List all processes and equipment that you will prepare a risk assessment

A. Physical hazards

Slippery

1. Wet surfaces due to leakage of fuel tank or spill while filling the fuel tank can cause slippery surface which can lead to injuries.
2. Best practices include wearing appropriate shoes and using anti slip floor materials.
3. Ensure using a funnel while filling the fuel tank.

Temperature

1. Hot engine unit parts may cause severe burns to the skin.
2. Best management practices include not touching any hot parts and to insulate hot sections. Sign will be placed when reactor in operation (Don’t Touch Hot Surface).
3. Fire may break out if vapors of fuel comes in contact with the hot surface of the engine. Ensure insulating the hot engine parts/surfaces and make sure all the sealing integrity has not been compromised.

Noise

1. The engine produces a noise due to moving pistons. However, the noise produce by the engine is within OSHA defined safety limits (90 dBA, for 8h.) Engine will not be operated for more than 4 hours at a stretch to protect researchers and the lab personal from over exposure.

B. Electrical Hazards

1. Electrical shocks may lead to heart failure, burns and damage to tissue at relatively low voltages and currents. Electrical sparks may also ignite fire.
2. Best practices management includes the use of electrical safety equipment and monitoring in combination with fast acting circuit breakers and proper grounding. The system has an advanced electrical box with circuit breakers and will be grounded to prevent electrical issues to become life threatening. The electrical ratings have to be checked upon commencement of experimentation and upon addition of new equipment to the rig. It is advisable to have annual electrical testing performed on all electric equipment in the laboratory.

C. Mechanical hazards:

Moving objects

1. Engine comprises of moving parts like piston, crank shaft, cam-shaft and cam valves. Additionally, a cooling fan and a fuel pump is also part of the engine setup. However,

these moving parts are encapsulated within a robust housing that isolate the lab personals from the moving part of the engine.

D. **Chemical Hazards** (toxic exposure, reactive, flammable, radioactive, etc.)

1. Using chemicals in the laboratory leads to risk of exposure to these chemicals. Known routes of exposure are by inhalation and absorption through skin. In addition chemicals may be flammable, toxic, poisonous, reactive, carcinogenic, teratogenic and environmental hazards.

Best management practices include understanding the risk involved with using a particular chemical and understanding its reactivity, and toxicity and knowledge of first aid procedures. An SDS database is readily available at the entrance of the lab and consulted before use of any chemical. Proper monitoring should be in place in case any of the chemicals are particularly hazardous. When handling chemicals proper PPE should be used, including wearing appropriate gloves (nitrile) and safety specs. The anticipated chemicals associated with engine test include common organic solvents listed in the Table C-1.

Table C- 1: NFPA rating table for chemicals and exhaust gasses associated with diesel engine test

Name of Chemical	**CAS No.**	**Health**	**Flammability**	**Instability**
Iso-cetane	4390-04-9	0	1	0
Cyclo octane	292-64-8	0	3	0
Toluene	00108-88-3	2	3	0
Tetradecane	629-59-4	1	1	0
Dodecane	112-40-3	1	2	0
Decane	124-18-5	1	2	0
Surrogate diesel blend	-	2	2	0
Diesel (conv.)	-	1	2	0
GTL	-	0	2	0

5.2 List needed emergency response materials to be on hand in the lab

A) Utility Failure (power, water, air, steam, room ventilation, etc.)

In the event of power, air, cold water, or room ventilation failure, the following standard shut-down procedures must be followed:

A) Hammer Natural gas emergency shutdown mushroom switch
B) Hammer dyno emergency shutdown mushroom switch
C) Turn fuel pump off
D) Shut off the main switch powering the dyno system “Switch 2”
E) Shut off the main power breaker “Switch 1”
F) Power down emissions bench and smoke meter

B) Leaks and Spills

As containment measures, all the possible leaking items, such as fuel and oil will be checked before starting the procedure. In case of identifying any leaks, the area will be cleaned and dried and the material will be safely disposed. SDS, oil spill kit, acid spill kit, and PPE will be available.

Lab will have the capability to properly manage, contain, and dispose of spills less than or equal to 4 liters. For spills more than 4 liters, HSSE at TAMUQ should be notified promptly.

The worst case scenario for a fuel spill or leak is the breakage of a fuel container/cylinder. Prevention is done through

a) Training of personnel,
b) Proper handling equipment such as carts,
c) Proper storage equipment such as explosion proof containers and
d) Proper labeling of fuel level and type.

In the event of fuel spillage, oil / fuel sorbents will be on hand to immediately contain the spill and avoid any seepage into floor drains, holes, trenches, and away from walls and electrical equipment. All work in the laboratory must cease immediately to avoid the introduction of any ignition sources until the fuel spill is properly cleaned up. In the case of a fuel gas leak, the laboratory should be ventilated personnel should be promptly evacuated (see evacuation plan in Appendix 1), and EH&S should be notified. University safe-disposal practices must be followed to ensure proper cleanup and disposal of the chemical (fuel) hazard.

C) Equipment Failure (Procedures attached at the end of the document)

In the event of equipment failure for any piece of lab equipment (engine, dyno, emissions cabinet and smoke meter) procedure described in section 3.2.A should be followed.

D) Fire Prevention

Fire Extinguisher Locations: At doorway location.

E) Building Emergency Evacuation Plan

1. Exit lab 169B, turn left on the hallway, go through the emergency exit door, turn left and continue alongside atrium towards the first exit gate.
2. Exit lab 169B, turn right, go through the emergency door and proceed to the nearest assembly point.

F) Emergency Response Procedure

If emergency medical attention is required, dial Qatar Foundation Security at **4454-0999** (dial 9 first). Notify authorities that you are in TAMUQ laboratory 169B. If non-emergency medical attention is required, take the injured person to the doctor of their choice. For any injury occurring during work, employees must immediately notify their supervisor who must notify EH&S at **4423-0032** or **5574-6657** (dial 9 first) within 24 hours. A report must be filed for each emergency or accident.

G) Incident Reporting and Notification Procedure

For any incident, employees must immediately notify their supervisor who must notify HSSE at **4423-0032** or **5573-2364** within 24 hours. An incident report must be written and filed. Sample reports should be obtained from Environmental Health and Safety Office.

7. Essential Information for External Emergency Services

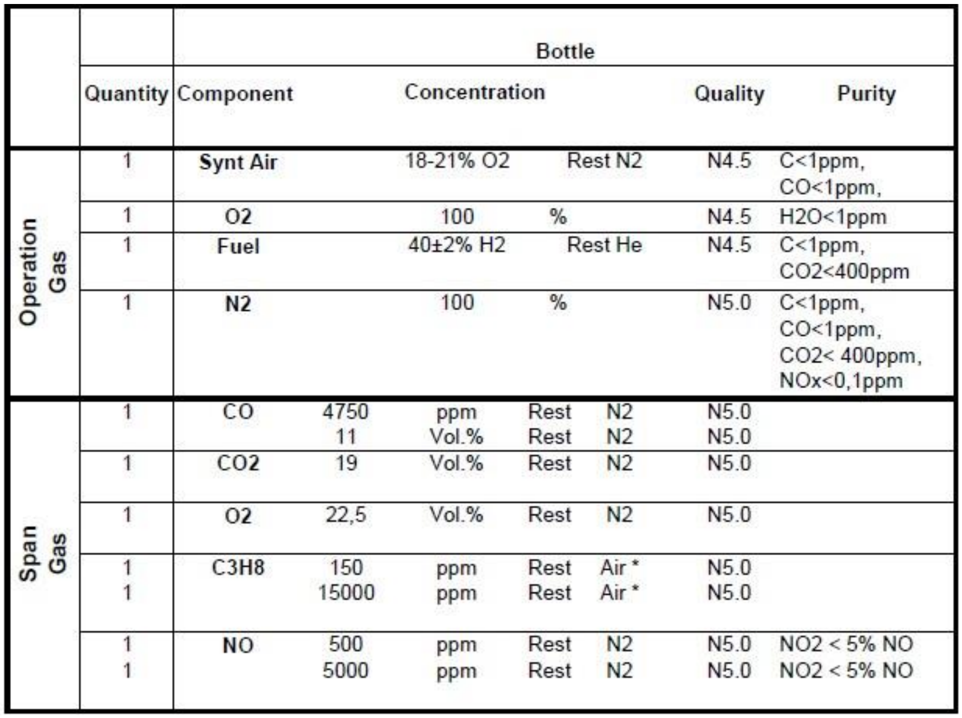
7.1 Completed Emergency Contact List for the lab which also must be posted outside the lab door.

Not Relevant to Thesis

7.2 Chemical and Gas Management

The following Table C-2 entails all gases present in the lab which are required for the calibration of the emissions bench in the TAMUQ engine lab.

Table C- 2: TAMUQ engine lab gas list



			Bottle		
	Quantity	Component	Concentration	Quality	Purity
Operation Gas	1	**Synt Air**	18-21% O_2 Rest N_2	N4.5	C<1ppm, CO<1ppm,
	1	**O_2**	100 %	N4.5	H_2O<1ppm
	1	**Fuel**	40±2% H_2 Rest He	N4.5	C<1ppm, CO_2<400ppm
	1	**N_2**	100 %	N5.0	C<1ppm, CO<1ppm, CO_2< 400ppm, NO_x<0,1ppm
Span Gas	1	**CO**	4750 ppm Rest N_2	N5.0	
			11 Vol.% Rest N_2	N5.0	
	1	**CO_2**	19 Vol.% Rest N_2	N5.0	
	1	**O_2**	22,5 Vol.% Rest N_2	N5.0	
	1	**C_3H_8**	150 ppm Rest Air *	N5.0	
	1		15000 ppm Rest Air *	N5.0	
	1	**NO**	500 ppm Rest N_2	N5.0	NO_2 < 5% NO
	1		5000 ppm Rest N_2	N5.0	NO_2 < 5% NO

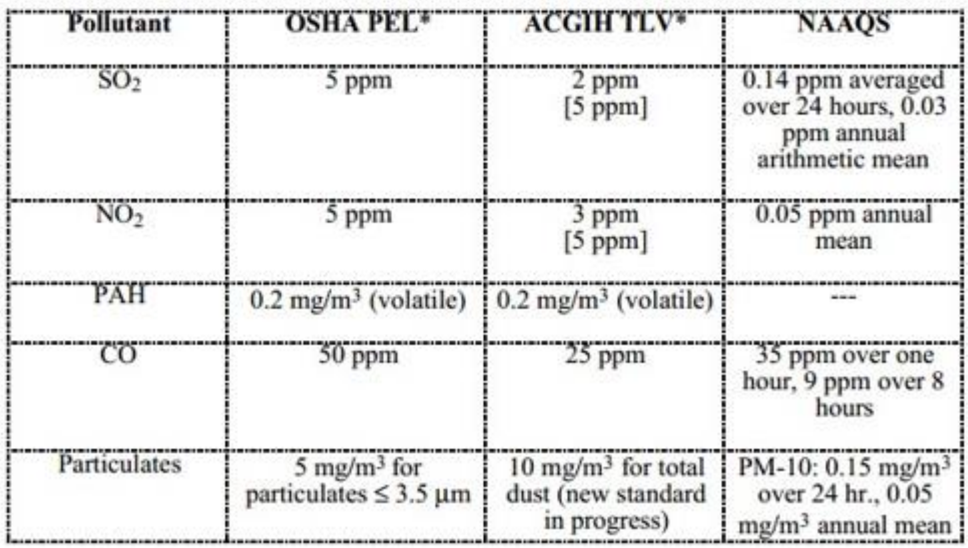
All required SDS information will be posted along with the cylinders. The working pressure required for calibration of the equipment is 1 bar, which is set-up with the help of gas regulators. The regulators shall be removed and the cylinders need to be sealed when not in use.

Any leaks from the exhaust system (ventilation backflow) and leaks from gases will be addressed immediately and OBO and HSSE will be informed.

According to the Agency for Toxic Substances and Disease Registry (ATSDR), the long term exposure to the fumes is dangerous; however, short terms effects are manageable. People who breathed mists of used mineral based engine for a few minutes had slightly irritated noses and throats, and the mists were irritating to the eyes of some people. But the levels we would probably generate would be below event the minimum required levels for adverse health effects.

The chemicals in the engine oil are diverse and includes mostly hydrocarbons. The most common byproduct are carbon dioxide and water, however, small amounts of toxic gases are emitted as well. These include sulfur dioxide, nitrogen dioxide and carbon monoxide. Small amounts of polynuclear aromatic hydrocarbons (PAHs) are also emitted. These gases would be well below the threshold of acceptable norms. This can be seen in Table C-3.

Table C- 3: Pollutant exposure limits



Pollutant	OSHA PEL*	ACGIH TLV*	NAAQS
SO_2	5 ppm	2 ppm [5 ppm]	0.14 ppm averaged over 24 hours, 0.03 ppm annual arithmetic mean
NO_2	5 ppm	3 ppm [5 ppm]	0.05 ppm annual mean
PAH	0.2 mg/m^3 (volatile)	0.2 mg/m^3 (volatile)	---
CO	50 ppm	25 ppm	35 ppm over one hour, 9 ppm over 8 hours
Particulates	5 mg/m^3 for particulates ≤ 3.5 µm	10 mg/m^3 for total dust (new standard in progress)	PM-10: 0.15 mg/m^3 over 24 hr., 0.05 mg/m^3 annual mean

* Occupational Safety and Health Administration (OSHA)

* American Conference of Industrial Hygienists (ACGIH)

* National Ambient Air Quality Standards (NAAQS)

Fuel composition of surrogate diesel to be tested in this project is given in Table C-4.

Table C- 4: Chemical composition of the surrogate diesel

Chemicals	**Vol (%)**
Iso-cetane	7.7
Cyclo-octane	37.8
Toluene	0.9
Tetradecane	26.6
Dodecane	12.9
Decane	14.2

The surrogate diesel contains compounds which are present in the conventional fuel in different ratios, therefore on combustion, it is expected that carbon dioxide, carbon monoxide, NO_X, elemental carbon and particulates will be produced like is the case with conventional diesel.

Three different types of fuel are to be used for the experiment are; Conventional diesel fuel, GTL Diesel and Surrogate diesel. Table C-5 lists the basic properties of these fuels.

Table C- 5: Properties of used fuels

PROPERTY	DIESEL	GTL DIESEL	SURROGATE DIESEL	ASTM D975 (Gr. 1)
Density @ 15^{O} C (Kg/L)	0.829	0.768	0.7848	-
Flash point (°C)	76	57	41.5	38(min.)
Cetane number(cal.)	58	73	48	40(min.)
Kinematic Viscosity @ 40^{O} C (cSt)	3.103	2.008	1.6414	1.3-2.4
Lower heating value (Mj/kg)	43.174	44.109	43.966	-
Total Sulphur(ppm)	199.5	0	0	15ppm (max.)
Total aromatics(Vol%)	22.9	0.88	0.9	35
Cloud Point (°C)	-1.5	-2.5	-22	-
Pour Point (°C)	-9	-12	-21	-
Distillation				
IBP (°C)	193.8	163.1	154.0	-
T10 (°C)	234.3	185.3	161.9	-
T50 (°C)	275.7	246.3	186.7	-
T90 (°C)	335.4	324.5	242.6	288 (max.)
EBP (°C)	368.2	346.8	250.7	-

Definitions:-

- Flash point: described as the lowest temperature at which a volatile material can vaporize to form an ignitable mixture in the presence of air.
- Cetane number: it is an indicator for the speed of combustion of diesel fuel.
- Lower heating value: The property used to define the amount of heat energy released by combusting a specific quantity of fuel at a specific reference temperature and allowing water vapor to leave without being condensed.
- Total Sulfur: Sulfur content in the fuel source
- Cloud Point/Pour Point: These properties are the cold flow properties of the fuel and determine whether the fuel is suitable in cold conditions.

- Distillation Temperature: Distillation curve is also used to describe the volatility of any fuel. A distillation curve/distillation profile, is the set of increasing temperatures at which fuel evaporates for a fixed series of increasing volume percentages (10 percent (T10), 50 percent (T50), 90 percent (T90).

Since diesel fuels flash point is lower to petrol and it is not readily ignitable the risk for fire is low; however, all necessary precautions will be thoroughly followed through.

7.2 Chemical Labelling

All chemical components have been labelled as per OBO & HSSE policies. SDS information is also available as per the hyperlinks below:-

P:\Research and Graduate Studies\Engine Research Laboratory\Inventory\MSDS

P:\Research and Graduate Studies\Engine Research Laboratory\Inventory\F-755-002-A-Chemical Inventory - Engine Research Laboratory.xls