MASTER THESIS

Characterization of fuel chemical and physical properties and evaluation of property impacts on gasoline engine application

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ABSTRACT

The future advancement of petroleum-derived, petroleum-alternative-derived fuels and advanced propulsion technologies indicate an increasing pretension to understand physical and chemical kinetic fuel property effects on multi-phase, internal combustion engine performance, and their emissions. Surrogate fuel concepts ensure an efficient approach for characterizing the physical and chemical features of real fuels that independently of its geographically, seasonally origin and that include hundreds of individual species. Provided that surrogate fuel formulations for such mixtures can imitate the fuel's combustion behaviors, if they can be simple enough, it can be used in engineering design tools to forecast fuel effects on new combustion technologies, inclusive the compatibility of certain non-petroleum derived alternative fuels measured by conventional equipment. The chemical function group approach combined with quantitative structure-property relationship (QSPR) regression analysis as a low dimensional descriptor has been utilized to predict DCN (Derived Cetane Number), RON (Research Octane Number) and MON (Motor Octane Number) of complex multi-component homogenous fuel/air mixtures, revealing that they have strong constraining capability to define the quantity of linear $(CH_2)_n$ functional group. Further perception, though the molecular compositions of the surrogate mixtures were different, each was found to have nearly the same distribution of key $((CH_2)_n, CH_3, benzyl)$ chemical functional groups. The impact of other group distributions (CH_2, CH, C) are negligible in terms of prediction and was of only secondary importance in determining the global combustion behavior of the mixture.

Furthermore, a new expression was constructed based on quantitative property-property relationship (QPPR) to predict the RON and MON based on DCN. From the correlation between DCN - RON and DCN - MON it can be deduced that RON and DCN measurements have a tight relationship, however, DCN and MON does not correlate well. According to our assumption, this issue may be solved, once DCN measurements contain NO (Nitrogen Oxide) during the combustion of fuel blends. To certify our hypothesis, a new gas supply system for the existing IQT (Ignition Quality Tester) was set up in order to add NO concentrated air to the combustion in the future investigations.

In summary, this paper argued that both QSPR and QPPR regression model is able to provide the understanding of fuel chemical property contributions on different combustion behaviors, and therefore it would be reasonable to further evolve this type of low-dimensional descriptor to be applied not only as a fuel monitoring tool but for directly developing for simple fuel-specific chemical kinetic models for real liquid fuels.

Keywords: Derived Cetane Number, Research Octane Number, Motor Octane Number, Combustion, Autoignition, Ignition Quality Tester, Chemical Functional Groups.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
AET	Advanced Engine Technology
AKI	Anti-Knock Index
BV	Ball-Valves
CFD	Computer Fluid Dynamics
CFR	Cooperative Fuel Research
CI	Compression Ignition
CN	Cetane Number
CO	Carbon-Monoxide
CPT	Combustion Property Target
CSQ	Complete Scheffé Quadratic
CV	Coefficient of Variation
CVCC	Constant Volume Combustion Chamber
DCN	Derived Cetane Number
DIPE	Diisopropyl Ether
EGR	Exhaust Gas Recirculation
ETBE	Ethyl Tert-Butyl Ether
FACE	Fuels for Advanced Combustion Engines
FS	Flame Speed
H/C	Hydrogen/Carbon
HCCI	Homogeneous Charge Compression Ignition
IC	Internal Combustion
ID	Ignition Delay
IDT	Ignition Delay Time
IQT	Ignition Quality Tester
LHV	Low Heating Value
LSPI	Low-Speed Pre-Ignition
LTC	Low Temperature Combustion
MON	Motor Octane Number
MPI	Micropyrolysis index
MTBE	Methyl Tert-Butyl Ether
MW	Molecular Weight
NMR	Nuclear Magnetic Resonance
NO	Nitrogen Oxide
NTC	Negative Temperature Coefficient
NV	Needle-Valve
OI	Octane Index
ON	Octane Number

OS	Octane Sensitivity
PIONA	Paraffins, Isoparaffins, Olefins, Naphthenes and Aromatics
PG	Pressure Gauge
PM	Particulate Matter
PON	Pump Octane Number
PRF	Primary Reference Fuels
QSPR	Quantitative Structure-Property Relationship
QPPR	Quantitative Property-Property Relationship
RCM	Rapid Compression Machine
RON	Research Octane Number
SI	Spark Ignition
SKI	Standard Knock Intensity
SP	Smoke Point
TAME	Tamyl Methyl Ether
TEL	tetra-ethyl lead
TPRF	toluene/n-heptane/iso-octane/ethanol
TSI	Threshold Sooting Index
TWV	Three-Ways-Valve
UPS	Uninterruptible Power Supply
YSI	Yield Sooting Index

1 INTRODUCTION

Crude oil or petroleum is a combustible liquid compound consisting of a complex mixture of hydrocarbons of different molecular weights. Yet this fossil fuel is essential to sustaining our society and our industry. Petroleum is a non-renewable resource and so it will not last forever. It is estimated that the Earth`s oil supplies will run dry towards the end of the century. (1) When that time comes, mankind will be forced to resort to a new source of energy such as solar or geothermal or use other resources. But for now, at least petroleum-derived fuels are essentially what makes the human world go around.

Currently, the global annual primary energy demand by oil is about 100.7 m/b (million barrels). Energy consumption is expected to increase to 111.1 m/b of petroleum-derived oil products by 2040. The transportation sector uses more energy than any other sector, and currently, it consumes more than half of the world's total delivered energy. Worldwide, transportation energy consumption by liquid fuel is expected to grow by 10.3 m/b from 2020 to 2040, while industrial by about 5.1 m/b and other energy consumption by about 0.4 m/b during the same time period. (2)

The increasingly growing energy consumption is the consequence of the rapid rise of the world population and the standard of living. The transportation sector has been growing significantly in parallel to the human population growth in North America and Western Europe since the industrial time. However, the transportation sector growth including the automobile population, aviation, rail and waterways shipping, is becoming almost exponential in the developing world, due to the impact of faster economic growth. With the increase in the number of vehicles, especially passenger cars with internal combustion (IC) engines, liquid fuel demand has gone up significantly. This has been causing a deleterious effect on the environment. (1)

A large part of oil energy consumption is utilized in the form of engine fuels like jet/kerosene, gasoline, light, and heavy diesel. Fuels for IC engines are produced from primary sources, which are composed of combustible molecules. Heat energy can be derived by the fuel's oxidation, which is transformed into kinetic energy. During the combustion of fossil fuels is formed different concentrations of CO_2, CO, NO_x, SO_x, unburned hydrocarbons, soot, and particulate matter as well. (1) As a result of burning these fuel oil, the atmospheric carbon dioxide concentrations have increased from 320 ppm (parts-per-million) in 1965 to 414.7 ppm today. World carbon dioxide emissions by oil type fuel are estimated at 19.8×10^9 metric tons in 2019 and expected to rise to 24.9×10^9 metric tons by 2040. (3) (4) Based on climate change regulations, the energy sector is required to keep the long-term concentration of greenhouse gases to 450 ppm (mg/kg) of carbon dioxide equivalent in the atmosphere so that the global temperature rise can be contained to about 2 degrees centigrade by the end of the century. (1)

The only way to reduce air pollution and consequently the greenhouse effect is to reduce the consumption of hydrocarbon fuels, to produce cleaner-burning fuel or completely alternate fuel combined with their ability to use them to power existing vehicles and to improve the energy efficiency of advanced combustion engines and equipment that are using hydrocarbons.

The future advancement of petroleum-derived, alternative-derived fuels and advanced propulsion technologies require an increasing pretension to understand the effect of physical and chemical kinetic fuel property on the IC engine performance and their emission. The background of this assumption is, that many industries indicated, it is difficult to define what predictive accuracy is desirable for improving IC engine designs tools to advance engine performance. (5)

As the computational consideration is becoming more complex, the need to contain complicated, larger dimensional sub-model descriptions of the fuel becomes essential in terms of utility, especially for engineering design. Developing a well-engineered product is getting more efficient using such a designing tool like Computational Fluid Dynamics (CFD), that can equip designers with detailed and useful information and using its capabilities, engineers can imagine and examine the moving parts geometry and its impact on fluid flows and the complex interactions that occur within an engine. However, the description of fluid flow is not good enough if the CFD analysis includes only fundamental equation of thermodynamics and fluid mechanics. The chemical processes during combustion must be equally considered as emulation targets, which is a difficult challenge for multi-dimensional CFD simulation, because using a high dimensionality by detailed chemical kinetics of complex mixtures is impossible. Consequently, it is important to design a compact enough chemical kinetic model that can be utilized in multi-dimensional CFD simulations for up-to-date engine design and optimization. The complexity of multi-phase combustion requires simplifying approaches in models that can be used to construe the physical and chemical kinetic properties of real fuels and their application on computational software. (5)

Surrogate fuel mixture concepts may be an answer to this problem, which gives a realistic approach for modeling the physical and chemical properties of real fuels, whether it contains hundreds of individual species and geographically located in different areas in the world. This surrogate fuel can be developed by small scale experiments in laboratory circumstances to identify the relative importance of fuel chemical and physical properties in terms of specific global behavioral characteristics. As long as the surrogate fuel formulations can imitate real fuel combustion behaviors and the models derived for numerous mixtures, can be used in engineering design tools to make a good forecast of the fuel effected on new combustion technologies, as well as it can help for various industrial sectors for screening the compatibility of candidate non-petroleum derived alternative fuels with existing equipment. (5)

However, the implementation of this approach is not near so easy as might think. Defining the necessary number of surrogate components and their mixture composition is difficult that obliged to simultaneously model both physical and chemical kinetic characteristics. The chemical kinetic property emulation looks to be more restrictive aspect because the complexity of defining chemical kinetics grows logarithmically proportional to the number of separate molecular classes that are necessary to model a real fuel. Respectively, there is an additional challenge to predict where the simplifying hypotheses in the models for physical and chemical kinetic properties of real fuels will cause the least impact on the interested combustion system parameters. (5)

Some researchers continue to doubt the importance of physical or chemical kinetic fuel properties regarding the combustion process, and the real importance to which physical and chemical behaviors need to be reproduced is shadowy yet. In order to avoid any doubt, experimental studies will be required addressing these particular issues until it verifies the intrinsic need of this hypothesis regarding engineering tool development and applications.

Dr. Sang Hee Won of the Department of Mechanical Engineering at University of South Carolina and his research group has already developed a promising formulation and published significant recent studies characterizing the combustion kinetics of surrogate and real transportation fuel especially focused diesel and jet fuels. In the experiments, the supplied air for the combustion was in every case a homogeneous mixture of pure oxygen and nitrogen. Nevertheless, this does not completely represent the real combustion conditions, since the combustion chambers of an IC engine are never completely purged during the exhaust phase, but also contain remained burned gases, like nitrogen oxides (NO_x). (1) The Ignition Quality Tester (IQT) has the potential to provide an alternative approach, when suitably modified, for characterizing the chemical kinetics of liquid fuels in other circumstances. (6) The main object of this specific research is to develop a new approach to characterize the fuel ignition propensity expeditiously but effectively.

Motivations for this research are the following: to build a new system to get information from the fuel mixture behavior if the condition of their combustion is changed; further investigation of the surrogate formulation method that can be adapted to consider both physical and chemical effects that are important to multi-phase combustion in the future; to improve modeling tools that are useful for parametric computational engineering design; and, in addition, to develop a new method to credibly evaluate the properties of several fuel mixture. (which is the main over-arching subject of this research project).

This specific research project will pursue the following guideline. Firstly, modify the combustion circumstance of IQT equipment by using NO_x concentrated air instead of scientific charge air, that contains just oxygen and nitrogen. An IQT available in the combustion laboratory at the University of South Carolina and it will be provided to measure the ignition propensity of fuels various gasolines and surrogate mixtures. A second objective of this research is to analyze the data by Quantitative Structure-Property Relationship (QSPR) regression models based on the existing characterization approach. The following step is the verification of the reliable operation of QSPR regression model and to draw various conclusions between DCN (Derived Cetane Number), RON (Research Octane Number) and MON (Motor Octane Number) measurements. In case of significant division between predicted DCN and experimental DCN, the coefficients of regression equation must change to provide an acceptable margin of error. Lastly, the QSPR regression model will be cross correlated with the existing RON and MON metrics.

2 BACKGROUND OF SURROGATE FUEL

Today, computational combustion modeling is an indispensable, important tool for engine design. The collaboration of CFD and detailed chemical kinetics brings the possibility to efficiently optimize the performance of the IC engine. For this to happen, computational chemistry models are required to describe the combustion of gasoline in experimental apparatus such as homogeneous charge compression ignition (HCCI) engines and spark ignition engines. At present, it is not possible to create a description of the complex chemistry of full blend gasoline in a detailed chemical kinetic model because the chemical kinetic model contains extremely massive and energy consumer equations. And the issue is not just the barely determined kinetics of all the components, but the chemical kinetic interactions among them are also not fully understood. Furthermore, the large number of components would lead to an unknown number of reactions, species, and thermochemical parameters. Numerous teams of scientists and engineers from industry, universities, and laboratories from the entire world came up together to develop coherence to surrogate fuel and its compositions for gasoline, diesel and jet fuels. (7) Much of the important scientists, who were calling for the need to develop a surrogate fuel composition for numerical modeling was first by Violi et al. (8) and Ranzi et al. (9)

A generally accepted definition of a surrogate fuel is: A mixture, that has a bounded number of discrete molecules that imitate some specific and/or general physical and chemical behaviors of the target real fuel. (5)

Accordingly, a surrogate fuel is a mixture of chemical composition that comprise some important properties from the characteristics and complexities of the real fuel. The most widely accepted utility for a surrogate is to hold some characteristics that affect various combustion behaviors and can be tested experimentally and/or modelled in numerical simulations. The modeling applications can expand for both fully pre-vaporized and/or multi-phase conditions under homogenous, one and/or multi-dimensional conditions. Surrogate mixtures containing only a few components seem to be able to represent real fuel behaviors. Because of how it was mentioned before, using them in complex CFD simulations describing energy conversion systems remains to need considerable reduction of the resulting detailed chemical kinetic model. Consequently, the driving principle for this application is that the surrogate should be made as simple as possible, and only so sophisticated as is necessary to describe the combustion behaviors. The surrogate fuel intention also gives a parallel advantage in the form to be able to observe, quantify, and study the effect of different fuel composition on combustion devices in basic and applied experimental studies as well. (5)

Many prior research projects have tried to create surrogate fuels to emulate real fuel combustion kinetics and physical properties too, including those of petroleum-derived and alternative gasoline, jet, and diesel transportation fuels. Several methods and status of works for jet fuels have been well summarized by Edwards and Maurice at the turn of the second

millennium. (10) The assumptions that they highlighted are basically applicable to all types of fuel. Edwards and Maurice's studies emphasized the necessity to develop surrogates that can describe both the fuel important properties regarding the physical and chemical kinetic processes of a real fuel. They thought that the fuel composition and properties can influence performance and emissions of engines and may be of higher importance in new combustion systems that use fuel properties as an additional control parameter. For physical properties, they had chosen the real fuel distillation curve and phase behavior as key characteristics to describe the vaporization-injection-mixing processes of multi-phase combustion. Other physical features like density and viscosity are also usually identified to be important to spray atomization phenomena. Edwards and Maurice stated that they would prescribe the chemical composition of the surrogate, according to molecular class identity and fraction of the real fuel. (10)

A second significant initial proposal in developing surrogates was that both physical and chemical kinetic property descriptions be integrated into a single surrogate fuel mixture. (10) These theories were executed in the early time by Wood et al. and Schulz, who also recommended surrogates formulated with the purpose of emulating these chemical and physical attributions of the real fuel at the same time. (11) (12) After the evaluation of the merged emulation of real fuel physical and chemical characteristics, both studies suggest more complex mixtures to imitate distillation properties. They suggested using twelve or more individual components. These basic purposes and the concept of modeling the molecular class composition of the real fuel has been generally followed by the researcher, who works in this professional field. The interested reader can find more details of efforts to progress surrogate formulation science for gasoline, which are summarized by Sarathy et al., for kerosene fuels by Dagaut and Cathonnet, and for diesel fuels by Pitz and Mueller. (13) (14) (15) Several important basic concepts of surrogate fuel formulation are written down by Violi et al., and Ranzi et al. (16) (17) Additional generally followed approaches are described by Pitz et al., for gasoline, Colket et al., for jet fuel, Farrell et al., for diesel fuels. (18) (19) (20)

In the literatures, a surrogate formulation approach has received considerable attention, based on describing the molecular class structure of the target real fuel by combining of one or more species. However, its application was not completely successful. The reason is behind it, that the descriptive nature of the assumption was insufficient, both qualitatively and quantitatively. (21) The concept of the molecular class description is restricted to define the chemical kinetic structure of the fuel components. For example, the concept of the molecular class definition is not able to determine neither the degree of isomerization of the isomerized paraffin nor the degree of alkylation and side-chain isomerization of the alkyl aromatic molecular classes, etc. This means an issue because these molecular structures have an effect a fuel's global combustion properties, especially autoignition. (22) Consequently, it is apparent that the molecular class composition concept is inexact and impractical. Since then, these concepts have evolved and new approaches have been developed, that will be discussed later.

Surrogate fuel formulation methods followed a seemingly endless multiplicity of real fuel property. A general object is to design somehow the molecular composition of the surrogate fuel to within the pale of reason. The followed methods are generally similar, but can be distinguished in approach by several factors: (5)

- The selection of fuel properties, that have to be replicated in the surrogate and real fuels, for example, energy density, mass density, octane/cetane number, hydrogen-carbon elemental composition, vaporization property, etc.

- Many approaches select properties of real fuels both physical and chemical without a clear reason, what kind of significance has imparted in the surrogate fuel composition.

- Some studies recognized, that numerous fuel-to-fuel variability may mean that the specific surrogate should be considered for each target fuel.

The formulation of surrogate fuel should focus on the following requisite challenge: What constrains the fuel property to the fundamental law's physics and chemistry? Furthermore, for surrogate fuel evaluation, "What is the significance of the measurement in a certain application?" (5)

How it was stated before, many suggestions and combinations of surrogate fuel formulation specifications have been made for gasoline, jet, and diesel types of fuel. The challenge by each fuel is basically alike, though it may be differentiated by the increasing importance of the liquid-to-vapor transformation. The relative influence of the liquid-to-vapor conversion and gas-phase processes persists a subject of discussion and uncertainty in aviation applications. It is generally believed that liquid-to-vapor transformations are irrelevant for gasoline surrogate fuels, but it is important to diesel surrogate fuels and jet fuels. This phenomenon can be traced back to the collaboration of parts in the fuel-engine, so how engines are typically designed to operate each of these fuels. (12) (14)

The scaling of the vaporization character of fuel from smaller to bigger is gasoline < jet fuel < diesel. (1)

The major spine of science on "surrogates" is most well-formed for the case of kerosene fuels and their applications, the extension of similar concepts to other transportation fuels is feasible. (5)

This section will provide an insight into the process workflow of surrogate fuel development. An overall schematic roadmap of this study is shown in *Figure 1*. Even though other researchers use a slightly different approach and methodology to develop their own surrogate fuel, the basic concept is always the same and the stated roadmap provides basically a good overview for all workflow.

Though it is an order number next to the steps, the sequence is not fixed, many of these actions can be executed in parallel. Mechanism development should follow a hierarchical approach from pure component to the surrogate, with validation at each step by comparison to proper experimental data. Key target aspects can cause significant constraints in the

selection of surrogates. Generally, it is assumed that all kinetically events occurring within the internal combustion apparatus are important. If these constraints were loose, the composition of the surrogate fuel and its model might be more simplified. Furthermore, the selection of a low number of pure compounds may never simultaneously provide all of the target parameters for transportation fuel. Therefore, probably a small modification of a surrogate model may be necessary. (23) The roadmap can be used to review the assistance of the present work.
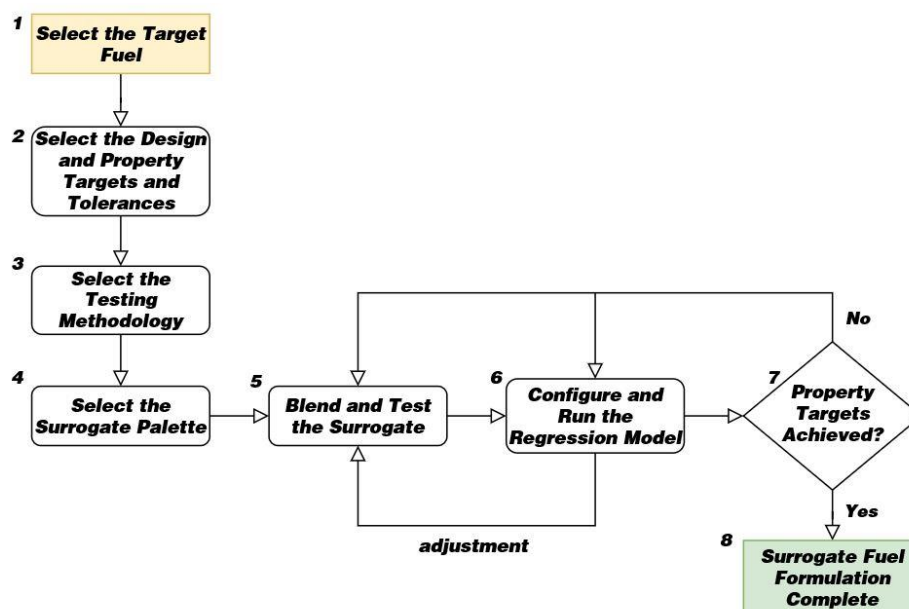
Figure 1: Overview of the process followed to create the surrogate fuels in this study.

The sequence for the approach used in developing a surrogate fuel is outlined in **Figure 1**. The first step is to identify one or more target fuels. Second, the design properties, property targets, and acceptable tolerance rate on meeting the property targets are determined. The selected design properties can be for instance fuel composition, ignition quality, volatility, and density with being aware of the fact that there is no guarantee that imitating these design properties will produce identical engine emissions or performance. Besides many further potential design properties exist, such as surrogate expense, mean molecular weight, hydrogen/carbon (H/C) ratio, lower heating value, and threshold sooting index. However, the cost minimization is usually not explicitly pursued because palette compound costs can differ significantly with order quantity, and it is desired to avoid potentially risking the research precise value of the surrogates based on this variability. After the design properties are selected, the methodology going to be selected. If the apparatus has to be modified to measure the chosen fuel properties correctly, it has to be considered in this step. In the fourth step, the surrogate palette is chosen. A surrogate palette means the collection of pure compounds that can be blended together in limited proportions to create a surrogate fuel mixture. Each pure compound is called a palette compound in a surrogate palette. In an ideal case, each palette compound can represent a class of compounds found in the target fuel, and each has a chemical-kinetic oxidation mechanism disposable so that its combustion

kinetics can be computationally simulated. The next step is to blend pure palette compounds together to produce the surrogates. Once each surrogate composition is determined, each surrogate mixture has to be tested by the chosen methodology. Just a high-quality mixture can construct the regression model. Note that a smaller number of pure components can produce an infinite number of blends that would be impossible to evaluate due to limited resources. Thus, the proportion of the components in the compound must be chosen wisely. (24)

Therefore, the present step and the next step must collaborate simultaneously. It is advisable to start the test with ten-twenty different compounds and then re-construct the ratio of the mixtures based on the evaluation of the results obtained. The next step is to run an optimization code to analyze the mixture for the surrogate, whether the property targets are achieved within their desired tolerances. The preferred optimization code depends on different institutions and universities. (24) This study uses a unique regression model developed at the University of South Carolina.

And last, but not least after each surrogate is tested and evaluated and it is identified that the property targets are not met, the property targets respectively tolerance rates, the regression model applications, and/or the surrogate palette could be re-thought and the process could be checked over and over again until the property targets are matched within their specified tolerances. (24)

In this section, the reader could get basic information about the surrogate model formulation. After that the generally definition, some historical background and description of process workflow was clarified, it is required to discuss about the different formulation mythology of the surrogate model. Before to do this, this section requires contextualizing certain theories of combustion kinetics as they would apply to complex mixtures which represent real fuels. It is important that this information be general, grounded in basic theories and as quantitative as it can be possible.

2.1 Hydrocarbon groups of gasoline-blending compounds

Gasoline is a complex mixture of volatile, flammable liquid of hundreds of hydrocarbons derived from petroleum. Commercial gasoline is a complex mixture, which is distilled from crude oil and it consists several hundred individual species from that raw material.

The chemical composition is one important property of gasoline, which determines all subsequent chemical properties (octane numbers (ONs), H/C ratio, Low Heating Value (LHV), etc.) and physical properties (distillation curve, density, etc.). The Paraffins, Isoparaffins, Olefins, Naphthenes and Aromatics (PIONA) range of typical gasoline fuels is shown in **Figure 2.** and bellow representative molecular structures for each PIONA class. (13)
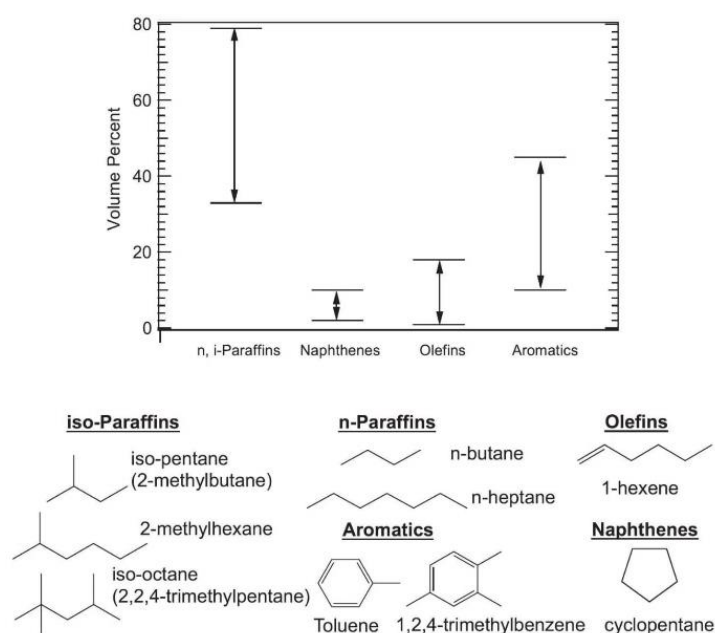
Figure 2: Typical PIONA range of gasoline fuels. (Bottom) Representative molecular structures in gasoline fuels. (13)

Table 1: Main characteristics of hydrocarbon groups as gasoline-blending compounds (1)

Properties	n-Paraffins	Isoparaffins	Naphthenes	Aromatics	Olefins
Density of liquid	Low	Low	Medium	High	Low
Research octane number (RON)	Very low (-19)	High enough (89)	Low (80)	Very high (>100)	High enough (90)
Motor octane number (MON)	Very low (-19)	High enough (86)	Low (77)	High (>95)	Low (75)
Sensibility (RON-MON)	Very low (0)	Low (<+3)	Medium (+3)	High (>+12)	Very high (+15)

Gasoline is distilled from crude oil, and the first cut contains C_4 to C_{10} n-paraffins, isoparaffins, naphthenes (cycloparaffins), and aromatics. Several refinery processes are applied to improve crude distillation products into fuels that meet gasoline requirement specifications; these processes include catalytic condensation, isomerization, alkylation and catalytic reforming (1), all of which are addressed at producing high octane quality molecules in the gasoline molecular weight range. The major properties of the products are presented in **Table 1**.

Paraffins range in carbon numbers from C_4 to C_8. Of all gasoline hydrocarbons, normal paraffins have the lowest octane quality and are not typically found in large amounts in market fuels. Iso-paraffins are just the opposite. Due to their higher octane numbers they are generally found in larger quantities in gasoline. To meet front-end distillation requirements of gasoline, low molecular weight paraffins, for example n-butanes and isobutanes, are blended into petrol, and mostly utilized for cold-start under winter conditions. Further common kinds of paraffin include n- and isopentane and different isomers of heptane, hexane, and octane with multiple methyl substitutions. Octane number increases with the increased degree of methyl substitutions, so higher molecular weight paraffins (C_7-C_8) have one to three methyl substitutions in typical gasoline fuel. The mixture of n- and iso-paraffins is very variable, and because of the huge amount of possible isomeric species, the specific paraffinic structure is presented at only a very limited percentage. For instance, the widely used primary reference fuel surrogates, n-heptane, and isooctane are only present in small quantities in real gasoline fuels (less than 1%).

Typical naphthenes found in gasoline are in the C_5 to C_8 range, and include species for instance cyclopentane, cyclohexane, methyl cyclopentane, dimethyl cyclohexane isomers and methyl cyclohexane. Among these, the cyclopentane has the highest octane number among the cycloalkanes. Since naphthenic compounds have low octane quality and they can be easily converted to aromatics via reforming, therefore their content of gasoline is limited to below 20 vol%.

Typical olefins range from C_5 to C_8 and include linear and branched pentene and hexene isomers. In their molecular structure presence double bonds, and therefore, they have high octane numbers, however, they also show high octane sensitivity. Olefins (alkenes) are also found in limited amounts in the fuel due to their poor oxidative stability, which reduces the storage life of gasoline fuels. Nevertheless, olefins are often useful precursors for other value-added chemicals (e.g., polymers).

Aromatics are the highest MW hydrocarbons in gasoline fuels, take place in the C_6 to C_9 carbon number range. The end of the gasoline distillation profile typically consists of high molecular weight alkylbenzenes. Characteristics of aromatics is the high octane number, but they are typically restricted to below 30-35 vol%, due to their propensity to increase soot, other called particulate matter emissions. Furthermore, benzene is a known carcinogen, the formation of cancer so its concentration in gasoline is restricted to below one vol%. For the foregoing reasons, the aromatic hydrocarbons are limited in gasoline fuel to toluene, m-xylene, oxylene, ethylbenzene, and various trimethyl benzene isomers. The most predominant aromatic found in gasoline is the toluene. (13)

Besides the hydrocarbon components, gasoline fuels should also contain various oxygenated additives. Many oxygenate such as ethyl t-butyl ether (ETBE), methyl t-butyl ether (MTBE), diisopropyl ether (DIPE), tamyl methyl ether (TAME), ethanol, methanol, and t-butanol have been blended to gasoline to improve its antiknock quality. Ethanol is the most widely used oxygenate additive for gasoline fuels, and it can be blended up to 85 vol% (E85) into the gasoline fuels. The most widely utilized blends contain 10 vol% (E10) in North America and in Europe. (25) Di Iorio et al. pointed out that blending oxygenates, such as MTBE, and ETBE or

even pure ethanol, increase the octane number of fuel, consequently improving combustion performance. This results in decreased HC and carbon monoxide emissions, and it has some positive effect in terms of lower particulate matter emissions in oxygenated fuels due to the displacing of aromatics. (26)

2.2 General Theory of Real Fuel Oxidation

The ignition has a significant influence on performance, emissions, and other characteristics, and the ignition can assign the performance of the whole system. Great reviews of ignition (27) can be found explaining chemical kinetics of hydrocarbon oxidation, thermal feedback, chemical kinetic chain-branching reactions, and other elements. However, ignition, in general, is a huge subject, and the present work will not provide thorough treatment but just the basic. (28)

The same principles apply to hydrocarbon oxidation like the chain character of the reaction of the H_2O_2 (hydroperoxide) system, and the formation of hydroperoxide is a key stage of the process as well. At first, oxygen enters into the hydrocarbon chains at any temperature and forms free radicals and radicals are transferred from one molecule to another (chain growth) until they form hydroperoxide. The combustion kinetic phenomena are principally affected by the fuel molecular structures. During the chemical reaction, important radical species are produced, such as H and O atoms, OH, CH_3, and HO_2, that have an effect on the endothermic and/or exothermic reactions over the reaction history, including initiation, propagation, branching, and termination. (28)

Detailed chemical kinetic mechanisms are used to describe the transformation of reactants into products at the molecular level, such as a very basic combustion of methane in the air. In case of perfect combustion, the final product CO_2 and H_2O, but as is well known, it proceeds through a large number of elementary steps. (27)

Initiation reactions generate radicals from stable species, such as the decomposition of propane:

$$C_3H_8 \rightarrow {}^*CH_3 + {}^*C_2H_5 \qquad \text{(Reaction 1)}$$

Chain propagation reactions keep the number of radical species by consuming OH and producing ethyl radicals:

$$C_2H_6 + {}^*OH \rightarrow {}^*C_2H_5 + H_2O \qquad \text{(Reaction 2)}$$

Chain termination reduces the number of radicals, as in recombination producing stable butane:

$$^*C_2H_5 + {}^*C_2H_5 \rightarrow C_4H_{10} \qquad \text{(Reaction 3)}$$

The key to understanding ignition kinetics is to identify the chain branching steps. In chain branching reactions, the number of radicals increases by consuming one oxygen atom and producing two radicals:

$$CH_4 + {}^*O \rightarrow {}^*CH_3 + {}^*OH \qquad \text{(Reaction 4)}$$

Respectively, the most relevant chain branching reaction consumes one Hydrogen atom and produces two radicals at high temperature:

$${}^*H + O_2 \rightarrow {}^*O + {}^*OH \qquad \text{(Reaction 5)}$$

The specific reaction sequences that provide chain branching change depends on the temperature, pressure, and reactant composition change. (28)

High-Temperature Ignition: at high temperatures above about 1200 K fuel oxidative pyrolysis (breaking down of hydrocarbons), fragment interactions (interaction of broken-down molecules) and, the reactions are key processes to determining heat release rate and radical histories. During the decomposition of hydrocarbon occurs from hundreds to thousands of subsequent steps. The dominant chain-branching step in hydrocarbon ignition is **Reaction 5**, with Hydrogen atoms that are generated by thermal decomposition of radicals such as vinyl, isopropyl, ethyl, formyl, and others. (28)

Intermediate Temperature Ignition: at temperatures above about 900 K but below 1200 K, **Reaction 5** is too slow to provide sufficient branching rates for ignition, and therefore a different reaction path will dominate. Key reactions are the following:

$${}^*H + O_2 + M \rightarrow {}^*HO_2 + M \qquad \text{(Reaction 6)}$$
$$RH + {}^*HO_2 \rightarrow {}^*R + H_2O_2 \qquad \text{(Reaction 7)}$$
$$H_2O_2 + M \rightarrow {}^*OH + {}^*OH + M \qquad \text{(Reaction 8)}$$

where R is an alkyl radical, RH supposed to be an alkane, and M is a third body. Collectively, these reactions consume one H-atom radical and produce two OH radicals, providing chain branching. (28)

Low Temperature Chemical Kinetics: In case of low temperature and negative temperature coefficient (NTC) kinetic behaviors (~500-900 K at 20 atm), organic free radicals formed by the addition of oxygen to alkyl radicals:

$${}^*R + O_2 + M \rightarrow {}^*RO_2 + M \qquad \text{(Reaction 9)}$$

The much larger alkylperoxy radicals (CH_3O_2) form through molecular oxygen addition reactions and due to oxygen, the large molecular will form and decompose to intermediate species. It subsequently, create "degenerate chain branching" of the radical pool through the

formation and decomposition of large molecular weight hydroperoxide intermediate species. (5)

Understanding the NTC behavior is very important for certain low-temperature combustion applications such as in controlling ignition timing in advanced combustion engines. The NTC behavior is caused by shifts in the equilibria of the RO_2 chemistry. As temperature increases the equilibrium of the reaction $R+O_2 <=> RO_2$ is shifted back towards the reactants. This equilibrium shift effectively shuts off the entire low-temperature ignition pathway. Thus, the ignition delay increases as temperature increases until the temperature reaches the point where high-temperature pathways for ignition become important. (29) Under low and NTC conditions the principal radicals are alkylperoxy and alkylperoxy derived radicals, that with OH and HO_2, which with H, O, CH_3, HCO, C_2H_5, C_2H_3 compose the "key radical pool" in a reacting system at higher temperatures, that lead to further oxidation of the original fuel species. The characteristics of the radical pool species and their concentrations define the rate of reaction, the temperatures at which it is established, and its dynamics. Therefore, the necessary requirement for a surrogate mixture is to be able to replicate the evolving behavior of the key radical pool of real fuel and so it will capable to reproduce real fuel, kinetically influenced combustion behaviors. (5)

We already know from kinetic modeling studies of pure hydrocarbon oxidation, that the formation of intermediates species of carbon numbers from C_1 to C_4 has a controlling role over the formation and behavior of the radical pool. These species are therefore playing a central role to the occurrence of combustion kinetic phenomena of all types of larger carbon number fuels and their mixtures. Consequently, a reasonable way to solve the challenge of combustion kinetics for surrogate fuel formulation strategies is to create mixtures of surrogate fuel components that consist of the same range of intermediate species, that formed from target real fuel during oxidation. Reactions, that involve these chemical intermediates characterize the small species radical pool, which has an influence on the important combustion processes (e.g., ignition delay, flame propagation, emissions formation). (5)

This idea remarkably simplifies the required surrogate fuel composition problem, because it makes unnecessary to describe every chemical functional class, that takes place in the target fuel (even if it is assumed that we know them). It is only needed to choose the surrogate components in the way that their intermediate species can react to each other of different chemical kinetic reactivity to establish radical pool production/consumption. (5)

For instance, several real fuel components contain an n-alkyl molecular functionality that can be combined with aromatic, cycloalkyl, alkenyl and isomerized alkyl functionalities to form a molecule. If the initial consumption of the molecule occurs, after that a generic collection of key distinct functionalities are formed. The following outcome of these groups is dependent on the thermochemical kinetic molecular environment. Because similar molecular environments are going to lead similar molecular processes in order to form a similar distribution of products. (5)
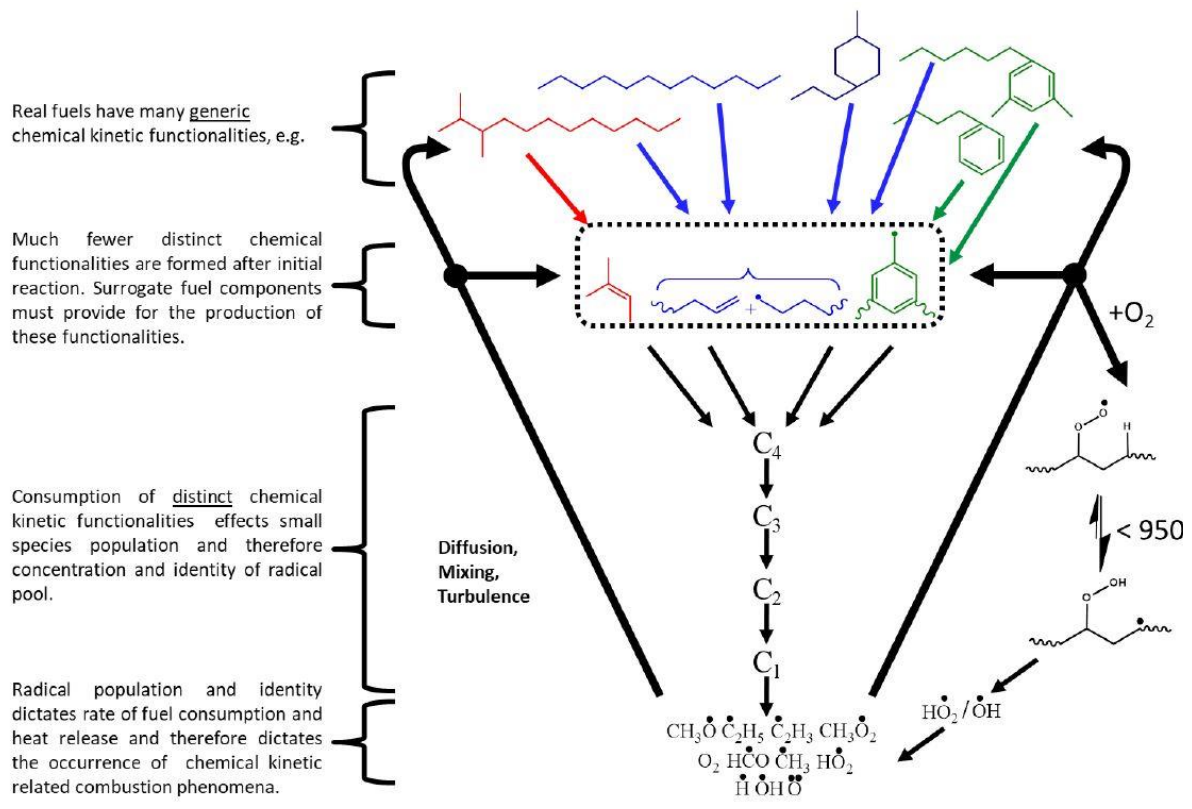
Figure 3: Schematic diagram of real fuel oxidation and concept of distinct chemical functionality as it applies at high and low temperature. (30)

This concept and strategy, as it refers to the combustion of generic liquid transportation fuels is represented in **Figure 3**. The models are made in a hierarchical system because the combustion executes through a sequence of elementary steps that fragments the parent fuel break down into smaller intermediate species, which afterward react to form stable products. The schematic illustration shows the importance of having a common high fidelity small-molecule reaction mechanism, on top of which the reaction mechanism for larger hydrocarbons can be produced. The reactions for larger hydrocarbons are added to the core reaction mechanism. These mechanisms typically include detailed reaction mechanisms for oxidation and pyrolysis of hydrogen and C_1-C_4 hydrocarbon species. Basically, this strategy does not require the identification of initial fuel molecular structures and therefore detailed knowledge of real fuel chemical composition does not need either. Preferably, the composition of surrogate fuel components is needed to be classified regarding the ability of their mixtures to repeat the same set of distinct chemical functionalities, that take place during the combustion of the target real fuel. The functionality set of n-alkyls, iso-alkenyls, and benzyl-type in the hydrocarbon liquid transportation fuels are already important fraction and distinctive form. The cycloalkyl, naphthenic and olefinic functionalities have distinctive reaction character as well, but these functionalities have significantly less impact than the principal key functionalities. Naphthenics and olefinics are generally limited by certification in real fuels and therefore these have even less influence in reaction. (30)

The motivation of experimental measurements encourages to test this approach well and support the conclusion that the important aspect in formulating surrogate compositions for chemical kinetic properties is to keep a reasonable number of the distinct chemical functionalities present in the real fuel and do not insist on the original fuel molecular structure or structural class characterization. (30)

2.3 Combustion Property Targets

A conceptual theory of real fuel oxidation is recommended to use in case of the creation of the formulation of surrogate fuels. In this section, some important factors will be highlighted. There are more aspects that we must pay particular attention to, when the formulation methodology of surrogate fuel is considered. Violi et al. (8) and Ranzi et al. (31), suggested four restrictive factors for surrogate fuel formulation methodology in their early work:

1. Feasibility: The detailed kinetic mechanisms of the chosen surrogate component must have well understood. For the numerical modeling of chemical reaction flow is particularly important, that the chemical kinetics of individual components being known. The science of thermochemistry is often overlooked but it is a critical element of this factor.
2. Cost and Availability: Surrogate pure components should be available at enough cleanness and reasonable cost to provide for the characterization of their combustion behaviors all over the place.
3. Simplicity: The surrogate should be as simple as is possible, and no more complicated that is necessary to describe the particular reacting processes. The too complicated mixture can lead to confusion at any system level.
4. High fidelity: For modeling goals of surrogate compositions should give back enough numbers of the real fuel physical and chemical properties, in a way that the global and detailed combustion behaviors of the two fuels are almost the same.

The cost and availability an important factor, but if we want to reclaim the accurate similarity between the surrogate and real fuel, this factor can be considered at least. (24) A more challenging task is, achieving a high-fidelity emulation of real fuel behaviors through a surrogate. It depends on the used pure components, the choice of physical and chemical property indicators and the surrogate mixture optimization method. (5)

To achieve the similarity factor, many suggestions have been made for the combinations of property indicators to be emulated for this and many other applications. In the case of real transportation fuels, the characterization of their combustion chemistries is not simple because of the numerous structural variations that are within each molecular class. The definition of the chemical character of real fuel inflicts challenges to explain the relationship of chemical characteristics and experimentally observed behaviors.

Consequently, an important challenge in order to formulate a surrogate fuel is to identify the components of the model fuel. To do this, a strategy of a predefined combustion property targets (CPTs) is developed of a select set of combustion property indicators. Each combustion property target is created to match fundamental molecular criteria that takes place in the combustion kinetic phenomena. (5)

The selected are strictly related to the engine application in which the fuel is used. Whereas gasoline fuels are used in both Spark Ignition (SI) and Compression Ignition (CI) engine applications, the combustion process in each is considerably different. Even within a specific technology, combustion processes can change, when the operating conditions are modified for example speed and load, and even if abnormal conditions occur (e.g., knock phenomena, pre-ignition, etc.). Therefore, it is essential to decide which target properties should be matched by a surrogate even if all or only a specific part of the target properties have to be emulated. When a surrogate is developed, target properties are prudently selected, with a knowledge of how they affect engine combustion and operating characteristics. Because each property influences the combustion process, the correlation between the target property and combustion performance must be considered. Target properties are categorized into physical and chemical characteristics. For example, physical properties, like fuel volatility has an impact on spray formation, which in turn influences combustion performance; an example of the chemical target property is the octane number, which has an impact on the knock-limited operating conditions. (13)

Based on fundamental basis and empirical analysis, three targets of the fuel properties were defined at first: the hydrogen to carbon ratio (H/C) of the specific real fuel; the average molecular weight (MW) of the real fuel and the measure of the real fuel sooting propensity (the Threshold Sooting Index or TSI) were found as "Combustion Property Targets". Each are individually prescriptive to one or more fundamental combustion behaviors.

With the combination of thoroughly justified Combustion Property Targets, the real fuel target, and the surrogate fuel mixture can be prescriptive for the emulation of real fuel fully pre-vaporized global combustion reactions. However, many studies have been stated, that two or three property targets are not enough to describe the real fuel for the surrogate fuel. Therefore, there was a demand for at least one additional combustion property target that will demonstrate the chemical reaction character of the real fuel and surrogate mixture. The "Derived Cetane Number" was hypothesized as a comparatively simple methodology that could indicate a combustion property target characteristic of the chemical reactivity of real fuels and surrogate components, and their mixtures. Then it was fully investigated the use of this descriptor, which proved a satisfying measure of the chemical kinetic reaction potential of the real fuel. (20)

These targets were selected because they are able to describe the important physical and chemical kinetic characteristics of real fuel. These are for instance: autoignition, heat release rate, laminar burning rate, adiabatic flame temperature, extinction, lean blowout limit, and sooting. An additional advantage of these combustion property targets for the surrogate components, surrogate mixtures, and real fuel samples, that their determining can be executed through simple small-scale experimental tests, each of them requires only small-

volume samples. It is known fundamentally that petroleum-derived fuels are formed principally of various fractions of paraffins and alkyl aromatics. Due to this information, a significant advantage of this approach is that no quantitative, detailed chemical analyses of the real fuel are needed to formulate the surrogate mixture. Through the proper mixture of surrogate components, the mixture has to be capable to reproduce the same combustion property targets as the target fuel. (5)

To confirm, that constraining the chemical composition of a surrogate mixture is very effective by four Combustion Property Targets, for replicating a real fuel Sang Hee Won (32) created a 12-component "Model Fuel" composed of known n-/iso-alkanes and alkyl aromatics. The construction of the Model Fuel was developed in a targeted way to emulate the combustion property targets of a global average used petroleum-derived jet fuel. Then, "2nd generation" surrogate mixtures composed developed by Sang Hee Won (32), which contains n-dodecane, iso-octane, n-propylbenzene, and 1,3,5-trimethylbenzene (40.41 / 29.48 / 7.28 / 22.83 mole %) are created to share different combinations of the four CPTs of the Model Fuel. The blends of the four surrogate components are systematically created under constraints. We consider that the discrete variation of 0.01 mole fraction changes for each mixture. Hypothetically, this would produce hypothetical total of 176,851 discrete mixtures, the H/C, TSI, MW and DCN for each of these compositions are then calculated as described in.
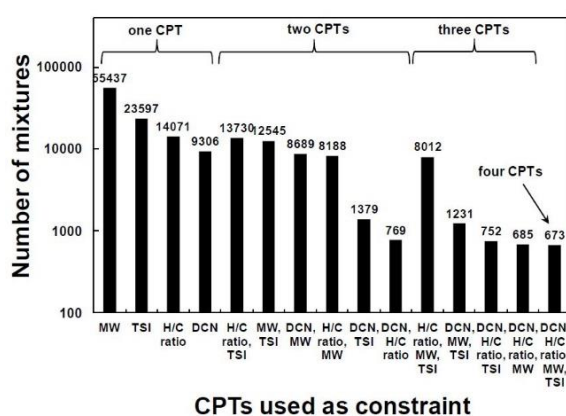
Figure 4: Number of possible mixtures matching the imposed CPT constraints for the Model Fuel. *(5)*

From the total 176,851 mixtures, considering specified uncertainty is found 673 sets of mixtures that replicate all four combustion property targets within three times. The measurement uncertainties are < 0.01 for H/C, < 6 g/mol for MW, < 1 for DCN, and < 1 for TSI. Summarizing the number of possible mixtures matching the forced Combustion Property Target constraints can see in **Figure 4**. Generally, we can say the more CPT parameters considered, the fewer the surrogate mixture possibilities are found to meet the Model Fuel target values. It is an impressive example, that using all four CPTs reduces the total number of possible mixtures from 176,851 to just 673 is a very significant outcome. The remaining 673 mixtures are less than 0.5% of the unconstrained mixture variabilities. However, fewer

mixtures would produce for each constraint condition if smaller uncertainty bands were applied to the similarity condition. The combustion property targets were chosen as targets of the fuel properties and the reasoning for their selection are explained below. (5)

2.3.1 H/C Molar Ratio

Hydrocarbon compounds mainly contain hydrogen and carbon elements and each practical fuel has a specific H/C ratio. The physical and chemical properties of practical fuels can be related to their H/C values. It can be stated that the H/C value appears likely to be a break-through milestone for the research of complex practical fuels. The composition of hydrocarbon fuels is always contained three main classes of compounds: paraffins, naphthenes, and aromatics. A different range of H/C values belongs to each class of compound, and the H/C value of a transportation fuel varies the proportions of the three classes of compounds. (33) Because of this reason, the H/C ratio was named as a combustion-related property. It was found that the hydrocarbon fuel with a higher H/C ratio has a higher net heating value. Moreover, decreasing the H/C ratio resulted in a lower smoke point (SP) for paraffins. The result was just the opposite for the aromatic homologous series. However, the properties of hydrocarbon fuels are mainly influenced not just by H/C but MW values as well. With a higher (H/C)/MW hydrocarbon fuel has a lower density. and so, the viscosity decreases with the increase of (H/C)/MW. The flash point (the lowest temperature at which a flammable liquid can form an ignitable mixture in the air) shows a decreasing tendency versus the increase of (H/C)/MW. (33)

According to the correlations between the properties (density, viscosity, net heating value, coke deposit, etc.) and (H/C)/MW values of hydrocarbon fuels, an appropriate range of H/C for a specific hydrocarbon fuel could be determined for a specific application. These conclusions may provide relevant information for the design of a new state of the art hydrocarbon fuel. Above all, the most important property the high net heating value because, it is essential for fuels to maximize the capacity of the engine. Both the weight energy content and volumetric energy content are required to be taken into consideration. The correlation between the net heat of combustion also known as lower heating value and H/C values is shown in *Figure 5*. The net heating values per unit mass increase gradually with the increase of H/C. For weight energy content based on the H/C content, the linear regression equation is: (33)

$$NHV = 4.596 \times H/C + 34.197 \qquad \text{(Equation 1) } (33)$$

The strong linear connection between H/C and net heat of combustion means that H/C can be utilized as a target for surrogate formulation for petroleum-derived and alternative jet fuels as well. (5) H/C can be measured by using an elemental analyzer, which has very low uncertainty (reproducibility). (33)
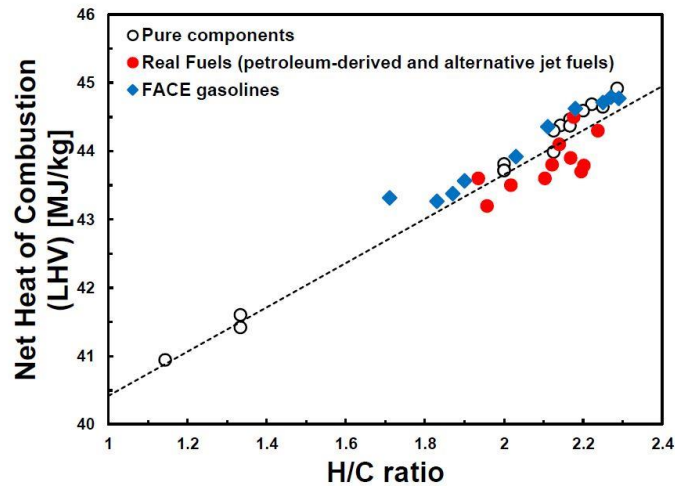
Figure 5: Net heat of combustion against H/C ratio for selected pure hydrocarbons, real aviation fuels, and the Fuels for Advanced Combustion Engines (FACE) gasolines. *(5)*

Concerning energy content, the net heat of combustion, (ΔH_c), is usually measured by indirect methods rather than from direct measurements. ASTM D4809 (34) utilizes an estimation technique for the net heat of chemical reactions or physical changes as well as heat capacity by correlation to other chemical and physical properties of the respective fuel.

However, an important aspect of the H/C ratio should be highlighted. Today, gasoline or diesel consists not only hydrocarbons, but it contains often oxygenated species (e.g. ethanol, methyl esters) as well. Therefore, the surrogate formulation is required to consider the net heat of combustion directly by considering the H/C/O ratio, which is a similar scaling derived for mixtures of oxygenated as demonstrated by Pera and Knop for gasoline. (35)

2.3.2 Average Molecular Weight

Gas-phase fuel diffusive properties correlate strongly with molecular weight. Hence, in order to emulate the different properties of real fuels in gas phase environments, a surrogate fuel must have a similar average molecular weight. If the surrogate fuel formulation has an available molecular weight range that is considerably lower than the average molecular weight of real fuels, this mismatch can cause to a loss of high fidelity in emulating combustion kinetic phenomena because that are heavily influenced by the rate of mass diffusions, such as diffusive extinction limits.

Furthermore, the molecular weight influences the physical properties of the fuel. Low molecular weight hydrocarbons have lower liquid density; therefore, their volumetric energy density is notably lower than higher molecular weight hydrocarbons. (30)

2.3.3 Threshold Sooting Index

The consequence of using internal combustion engines is produced particulate matter (PM) emissions, that are having a deleterious impact on public health and global temperature rise. In the premixed as well as for non-premixed systems, the distribution of controlling particulate mass and particulate matter size is a very important topic. Tightening regulations on PM

emissions have required producers to add a control measure system for reducing soot, like diesel particulate filters with a disadvantage, that it decreases the fuel efficiency and engine power. (36)

SI engines produce far less soot than CI engine, however, the modern development of gasoline direct injection engines has required a more thorough consideration of soot generation from gasoline-range fuels. Therefore, the soot formation is a vital factor to be judged in maximizing passenger car engine efficiency. (36)

The complex chemical mechanisms, that exist under soot formation are complicated to understand, therefore it is necessary to manage experimental testing of soot formation and PM emission. Basically, direct measuring the soot emissions from engines require intensive resources regarding labor equipment and large quantities of testing fuel. Therefore, it was called an effort to the formation of smaller bench-scale measurements on the basis for the research on the sooting tendencies of pure compounds. One of the oldest sooting indices is the smoke point, a measure of the maximum flame height possible by fuel in a test lamp without smoking in millimeter. Smoke Points are experimentally determined by the ASTM D1322. This test has been used for many years as a fast, comfortable and simple way to describe the sooting propensity of aviation fuels. (36)

The smoke point has been used to determine the chemical properties that influence sooting in gas turbines used fuel, but this indicator has not been utilized for diesel or gasoline engine applications. Normally, the same application method to hydrocarbons has been less successful because the highly sooting fuels with the low smoke point make it very difficult to get values with sufficient reproducibility. (37) However, several recent studies have been insisted on reviewing smoke point measurements for both diesel and gasoline fuel including emissions from SI engines, because the sooting indices measured in simple flames are important in emissions control from practical devices. Standardization of smoke point started with the Threshold Sooting Index (TSI), which is an apparatus-independent approach and it ranks fuels on a 0-100 scale based on defined reference values. The TSI estimates the Smoke Point based on the fuel's molecular weight, also using experimental constants to admit for Smoke Points measured with different apparatuses to be confidently compared: (36)

$$TSI = a \left(\frac{MW}{SP} \right) + b \qquad \text{(Equation 2) (36)}$$

where a and b constants are apparatus-dependent value if the smoke point is used.

The TSI has an unstandardized but practically used reference scale of 0 to 100 as determined by the Smoke Points from two reference fuels, n-hexane (TSI = 2, SP ~ 149 mm) and 1-methylnapthalene (TSI =100, SP ~ 5 mm). (5) (37)

Many studies declare, the methodology for determining TSI has several weaknesses, for example estimating the proper flame shape is not accurate enough, especially for compounds with a high smoke point. To improve the repeatability of sooting tendency measurements, a

proposal was recently made similar approaches, that measure not based on smoke point, including the micropyrolysis index (MPI) and yield sooting index (YSI). The YSI has been introduced as an alternative for estimating the sooting potential of highly aromatic fuels, avoiding some of the scaling limitations typical of the TSI methodology. (5) The YSI developed by McEnally & Pfefferle, precisely measures the sooting tendencies of small amounts of sample and correlates well with TSI. In the YSI test, laser incandescence is used to measure the maximum soot volume fraction. It is an important aspect to consider the TSI or YSI with regard to transportation fuels as a property that surrogate formulation should include. While useful, sooting indices measurements have one significant disadvantage: neither of them considers the particulate size distribution, which would be emerging as an important emission characteristic because of its health and global warming implications. (36)

The sooting tendency, as presented by the TSI depends on the molecular structure of fuel and its molecular weight in the following order: aromatics > cyclo-alkanes ≥ iso-alkanes > normal alkanes. This basic behavior is shown in *Figure 6*, which breaks the sooting propensity into two zones: Region I. includes the aromatic fuel components. Aromatic fuel components have a high sooting tendency as shown by the chart (TSIs > 30). Region II. includes the other hydrocarbon fuel components that show lower sooting tendencies. (5)

In general, the following set of statements are applicable:

- The soot is a polyaromatic hydrocarbon, therefore its initiation is very supported by the occurrence of any aromatic structures within the fuel before starting chemical reactions. This is the reason why aromatic containing fuels have higher sooting tendencies than fuels that do not include aromatics.

- In the case of normal paraffins, if its chain length increases, the sooting propensity increases as well, because the increasing chain length prefers the formation of ethylene over relatively reactive methyl radicals. And ethylene leads to acetylene which is an important soot causer.

- In the case of normal and isomerized paraffins, if its degree of branching increases (isomerization, methylation), the sooting propensity increases as well, because this provides more and larger joint alkenes and alkynes to be created, which are also important soot causers.

Obviously, the real fuels are way more complex mixtures, that consist of all of these molecular class components. Therefore, their sooting behavior is intermediate between the pure components. It was mentioned before that the smoke point and TSI is used alternative aviation fuels by choice, because they are simpler, containing purely paraffinic, H/C =~ 2.2, and are a great example to prove the observations above. They show a low TSI, because of their low degree of isomerization of the paraffins. From *Figure 6*, it is visible, that the sooting propensity of fuel is influenced by its molecular structure, even as presented by the most simplistic macroscopic composition parameters, such as H/C. (5)
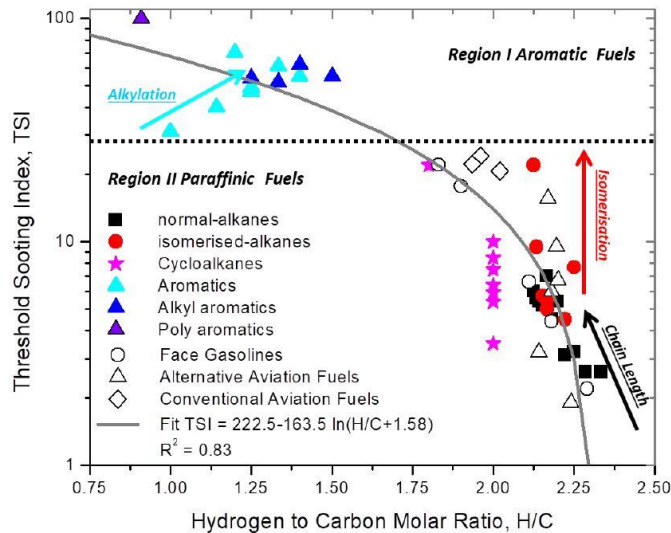
Figure 6: TSI of hydrocarbon fuels, pure components, conventional and alternative aviation fuels and the FACE gasolines.

A large number of existing experimental and theoretical studies have examined, that in the case of premixed, the soot formation characteristics of fully pre-vaporized combustion systems are principally correlated to the fuel H/C and fuel-air ratio that together controls the flame temperature. If the flame temperatures can be reduced for example by exhaust gas recirculation or by controlling local equivalence ratios, then soot formation proportion can also be reduced. This conclusion is very valuable in terms of determining the TSI of non-aromatic alternative fuels and their mixtures with petroleum-derived fuels as a real fuel Combustion Property Target. (5)

2.3.4 Derived Cetane Number

Given that this study is primarily based on the determination and evaluation of the derived cetane number of the surrogate fuels, more attention should be paid to this section in order to understand the significance of the DCN value in terms of CPTs.

Internal combustion engines mainly work either gasoline or diesel and mixtures thereof with biofuels and/or alternative fuels. CI engines keep going by temperature rise due to compression of air and ignition a liquid fuel spray injected into the combustion chamber. Therefore, CI engines need fuels with short ignition delay time (IDT), such as diesel. The readiness of CI engine fuel to ignite when injected into a diesel engine is indicated by its Cetane Number (CN) based on a cetane scale. Boetlage and Broeze proposed the cetane scale in 1932, or at the time of its establishment it was identified as the "cetene" scale. The test fuel was assigned a cetane number, comparing the combustion properties with the primary diesel reference fuels (PRF) on this scale. Originally, the diesel PRFs were cetane other called 1-hexadecene and mesitylene is known as 1,3,5-trimethylbenzene. Cetane is a long-chained olefin that has high reactivity and can easily ignite in a compression ignition engine, while mesitylene is an aromatic that has low reactivity beginning ignition difficult in a

compression ignition engine; therefore, cetane was assigned cetane numbers of 100 and for mesitylene was stated 0. Differences in ignition quality depending on the double bond position of cetane caused its replacement by cetane (n-hexadecane). Consequently, mesitylene was replaced by alfa-methylnaphthalene too. This scaling system was approved by American Society for Testing and Materials (ASTM) in 1935 to form the CN number, the first standard fuel metric to evaluate diesel fuels. However, this reference pure fuel was not good enough. The production of alfa-methylnaphthalene was very expensive and difficulty in handling, so it was replaced by a highly branched long-chain alkane, called iso-cetane (2,2,4,4,6,8,8-heptamethylnonane) in 1962, which has a reference CN of 15. If a fuel shows the same ignition delay time as a blend of the two primary reference pure fuels, then the cetane number can be calculated from the volume percent of cetane and heptamethylnonane. (38)

Nowadays, DCN measured by an ignition quality tester according to the ASTM D6890 standard (39) is an accepted fuel rating method for CI engine fuels. Please pay attention, that the Derived Cetane Number should not be confused with the Cetane Number.

The CN is produced by experimental testing. The most widely accepted is the Cetane engine namely Cooperative Fuel Research (CFR) engine ASTM D613 (40) developed in the 1930s. Some important features are the single-cylinder, the four-stroke, variable compression ratio diesel engine, and the 900 revolutions per minute. The method is the following: the compression ratio of the engine is gradually increased until the time reaches the 2.407 milliseconds between fuel injection and ignition. Then the resulting cetane number is calculated. A significant disadvantage is that this using this method is very expensive, and the process of CFR engine is very complex. Additionally, this method is also experimentally complex and time consuming to generate the required data, and each requires a considerable volume of fuel too. As these tests were complex and resource consuming methods, developing to determine IDTs with a constant volume combustion chamber (CVCC) was proposed. (38)

After several trials, the CVCC developed at Southwest Research Institute, and it was commercialized by Advanced Engine Technology, Ltd. (AET) in a limited number. (41) This instrument does the measurement much simpler than the CFR engine. The fuel is injected into a constant combustion chamber, which has a constant pressure and temperature about 575 °C. As the time difference between the start of injection and the start of combustion can be derived as the ignition delay if the fuel using an empirical inverse correlation. (39) It is a simple determinable scalable metric that is able to indicate a reactivity potential of real fuel and surrogate mixtures. To determine the overall absolute ignition delay, the DCN measurement does not distinguish the individual contributions of the low, intermediate, and high-temperature chemical kinetic properties. As the CN of fuel was not measured in the CFR engine but it was evaluated with the CVCC, the measured quantity called the DCN. (38)

Spark ignition engine fuels are characterized by two standard numbers: The Research Octane Number (RON) and the Motor Octane Number (MON) measured in a similar manner to CN of a fuel and are done in accordance with the ASTM D2699 (42) and ASTM D2700 (43) standards. The difference between RON and MON is described as octane sensitivity (OS). The negative temperature coefficient (NTC) behavior of Primary Reference Fuels mixtures,

and the shortage of NTC behavior in most practical gasoline fuels, results in differences in antiknock attribute under RON and MON conditions, which expresses itself as OS. These fuel rating metrics were defined in 1927 and they are still in use nowadays without meaningful changes. A fuel sample's RON and MON value is measured in an SI CFR F1/F2 engine, and comparing its antiknock quality of a blend of the two primary reference pure fuels, then the RON and MON can be calculated from the volume percent of n-heptane (RON and MON = 0) and iso-octane (2,2,4-trimethylpentane; RON and MON=100). (38)

Parallel, with the developments of IC engines, the standard CFR engine condition like pressure/temperature has shifted gradually and the outmoded fuel standards, ASTM D2699, and D2700 may not be able to precisely predict the autoignition characteristics of fuels in modern engines anymore. However, these two numbers are able to quantitatively evaluate the changes in autoignition chemistries of gasoline PRFs and gasoline fuels, therefore it makes sense to use the furthermore. (38) Note that in currently developing advanced IC engines particularly low-temperature combustion (LTC) engines, the ''ideal'' fuel may have autoignition behavior in between the typical gasoline and diesel fuels under controlled conditions. Additionally, it is assumed that the outlook for transportation fuels will change in the next decades. The demand will shift for relatively heavier transport fuels such as diesel and jet fuels. Therefore, it is important to understand fuel chemistry at conditions and not just a single condition prescribed by ASTM standards. The understanding of the relation between ONs and CNs is required.

Operation at the optimum ignition timing is critical regarding the optimum combustion process and therefore the fuel autoignition property is a vital chemical characteristic in both SI and CI engine. An advanced ignition timing leads to higher pressures, higher temperatures, and increased efficiency. The not corresponding fuel property effects knocking combustion. Engine knock, an abnormal combustion phenomenon that can occur in IC engines. (13)

In case of SI engine, probably the antiknock quality is the most important chemical property of gasoline fuel is, which is identified by the ability of the fuel/air mixture to resist autoignition. Knock phenomena occurs because of the autoignition of the unburned fuel/air mixture in the end-gas phase, ahead of the advancing flame front in a SI engine. The knocking tendency of a fuel/air mixture impends on the pressure and temperature progression with time passing and on the anti-knock quality of the fuel. The higher octane fuels enable an earlier spark timing, which can change for the better combustion efficiency and power output at higher compression ratios. (44)

In case of CI engine, it takes the fuel and air into a correlated mixture in the combustion chamber and creates the pressure and temperature environment that is needed for the chemical reactions to arise. The chemical processes occur the autoignition of the fuel and the following combustion process releases the energy in the fuel. The rate and scale of pressure rise going to depend on the quantity of fuel present in the combustion chamber, which in turn will be affected by the length of the ignition delay and the quantity of fuel injected during the delay time period. More numerous amounts of diesel fuel accumulate in the combustion chamber before ignition happens a greater knock result. This diesel knock corresponds to the

knocking of the spark-ignition engine. However, the problem here is not that the fast combustion is too early but that it occurs too late. (44)

The knocking combustion phenomena can cause major engine damage, and as well as it reduces the efficiency. Knock leads to disturbance of thermal boundary layers. The potential damage to the engine is manifold. Auto-ignition and knock lead to an increased heat flux on the cylinder wall. Erosion of the piston crown and cylinder head and there is the possibility of the breakage of piston rings or melting of the piston. Because of auto-ignition and knock, the optimal combustion phasing which would lead to the best thermal efficiency might not be reached and therefore knock limits the possible efficiency. The maximum engine power is reached when as much oxygen as possible is burned. However, this likely results in unburned fuel and hence reduced fuel efficiency. (45)

2.4 Experimental Studies and Results

The study provides the summary of discussion in this chapter by drawing examples from the literature and providing original contributions needed to illustrate particular arguments.

In modeling multi-component properties of real fuels, a simplified approach is required and currently being developed to include the fuel properties in a model, and have it predicted a punctual surrogate. Employing the concept of "chemical functional groups" have been recently utilized by Sang Hee Won's research group, which is an experimentally observed success in the surrogate approach. This approach is very similar, that have been widely utilized to estimate thermochemical properties as well as for estimating the physical properties of molecules. The chemical functional group approach can be considered as a low-dimensional descriptor, that can define the fuel reaction kinetic characteristics ergo characterize the combustion behaviors. A chemical functional group is a concept, that observes the molecules as a group of atoms (molecular fragments) that yield different chemical kinetic behaviors. The chemical functional group descriptor contains the n-alkyl, iso-alkyl, and aromatic functionalities that take place in most of the fuels' molecular structure. Chemical functional group descriptor of complex multi-component mixtures allows the creation of quantitative structure-property relationship (QSPR) regression models, creating a bridge between the functional group composition and the combustion behaviors. The QSPR regression model is based on a Scheffé's simplex-polynomial. From before mentioned reason, the DCN plays an important role in determining the distribution of key chemical functional groups, thus the "chemical potential" of the fuel. The QSPR regression model has been proposed for Derived Cetane Number of real liquid fuels with chemical functional group descriptors that are employed to study how the CPT-based surrogate approach can restrain the chemical kinetic characteristics in the multi-component surrogate formulation. A QSPR regression method for predicting DCN makes up six chemical functional groups like CH_2, $(CH_2)_n$, CH_3, C, CH, benzyl etc. For accurate prediction, the QSPR needs sufficient quantity of data available for calibration.

The CPT property target characterization and/or the chemical functional group application and/or the QSPR regression model was utilized in many studies and projects of the combustion research laboratory at the University of South Carolina successfully. In the

following section some example will be highlighted. The CPTs concept was used by Dooley et al. (46), where a series of experimental measurements are designed to demonstrate the influence of a generic cycloalkane chemical functionality on the global combustion behaviors of model fuels for real complex liquid transportation fuels. Another study used the CPTs conception by for instance, Won et al. (47)

Won et al. (48) made another study, where global combustion characteristics of iso-dodecane have been experimentally measured and it was compared to characteristic combustion behaviors of iso-octane, iso-cetane and a fifty-fifty molar blend of them. Combustion property targets, DCN and SP of these fuels, have been experimentally determined and chemical functional group analyses focusing on methylene (CH_2) and methyl (CH_3) groups have been performed. There were also some studies stated including the not just the CPTs and chemical functional group concept, but the QSPR regression model as well. For formulating a simple surrogates mixture that emulate combustion behaviors of complex chemical mixtures of real aviation fuel, a chemical functional group representation methodology has been investigated by Won et al. (49). A total of six chemical functional groups were analyzed, and their relations to the CPT surrogate formulation constraints were statistically examined. The goal was to address observation functional group-DCN trends, and the QSPR regression was developed. Another paper is about a methodology to simulate the chemical structure of complex chemical mixtures of real aviation fuel has been investigated by Won et al. (32) based on chemical functional group representation of a fuel. The relationships to the CPT constraints of six chemical functional groups were considered and they were statistically analyzed with a Model Fuel, that was composed of twelve components. QSPR regression has been performed using a DCN database, which was determined based on a statistical analysis revealing the strong relationship of chemical structure and DCN.

Applicability of chemical functional group descriptor as a tool of characterizing the real fuel global combustion behaviors has been investigated by Won et al. (50) using NMR spectra. Sensitivity analyses of low dimensional QSPR regression models were employed in the purpose of evaluating the role of chemical functional groups on vaporized fuel ignition delay characteristics. To prove the applicability of this experimental tool to characterize the ignition propensity of real fuels, the chemical functional groups were directly determined from NMR spectra and it was compared to the QSPR model predictions regarding alternative jet fuels.

The previously mentioned methods were not only used for studies, but also real project from companies. Won et al. (51) had to examine the possible influence of fuel chemical properties of crude oils in terms of stationary gas turbine combustion. The chemical properties of four light crudes have been compared based on their DCN behaviors and the understanding of 1H and 13C NMR spectral measurements. The obvious proportionality of measured DCN values with a growing ratio of paraffinic CH_3 and CH_2 groups encouraged the formulation of the simple QSPR regression analysis as well. The following two studies used the IQT specifically to determine the DCN. In the Haas et al. (52) paper was stated an issue, that next to fuel, some oil droplets can appear in the cylinder interior from the piston crown or cylinder walls. The oil-fuel ignition is one of several assumptions for low-speed pre-ignition (LSPI) phenomena recognized in higher-boosted, degraded-displacement downsizing of direct injection gasoline

engine technologies. To get insight into combustion processes influenced by such phenomena, the 95 RON gasoline surrogate, and base oil blends were examined in an IQT to determinate of DCN values for each mixture. The relationships between DCN and RON was also determined. DCN perceptions were shown to significantly react to the chemical structure characteristics based on 1H NMR observations.

Carpenter et al. (53) have been further investigated the role of cycloalkane functionalities on ignition propensity of multi-component mixtures by measuring DCNs of both saturated and alkylated cycloalkanes and their mixtures with n-alkane and iso-alkane. Based on the results of DCN measurements, it is utilized to apply the QSPR regression model compared to an extensive DCN database of species and mixtures of other cycloalkanes database. The abundances of chemical functional groups are quantified by interpreting 1H and 13C NMR spectra simultaneously. We can see now, that several studies and project has been investigated using the CPTs property target conception, and the QSPR regression model based chemical functional group to emulate the real transportation fuel by surrogate fuel, and with them getting a better insight in the chemical kinetic and hydrocarbon formulation during the combustion. However, to state confidentially, that the described model are reliable methods, the models must provide accurate and comprehensive results under all variable conditions. The relevant aspect is to test the model under real conditions, ensuring the functionality of the determined model in real life, and not only in laboratory circumstances. One of the most important condition, that is missing yet, is testing the applicability of the prediction model in the case, when nitric oxide (NO) is added to the experimental air, just like in the real engine condition. The IQT, when suitably modified, the device can serve the determination of DCN of fuel mixtures, that is closer to the real results. The rest of this chapter will convince the reader, why is this condition relevant and what is the reason behind the experiment.

The chemical kinetics drives the autoignition, and the thermodynamic condition inside the cylinder and the chemical composition of the reacting mixture controls the rate of this phenomena. The reacting mixture always contains a certain quantity of remaining combustion products from the previous combustion event in piston engines. These remaining gases contain certain species such as NO. Residual NO typically exists at concentrations of order from 10 up to100 ppm inside the cylinder after mixing with the fresh charge air. This has been reported to have a significant influence on autoignition in SI engines and HCCI engines. (54)
In advanced autoignition engines, the ability to control the ignition timing is dependent on the fuel's autoignition kinetics. Therefore, the understanding and improvement of chemical kinetic mechanisms are going to be very important in their design. To address these issues in SI engines, several advanced techniques have been employed. A variable intake charge temperature or exhaust gas recirculation (EGR) is applied to control the mixture auto-ignition phasing. An exhaust gas portion is re-injected inside the intake port by the EGR, and this reduces the combustion temperature. Another positive aspect is, that NO_x emissions are reduced by the reduction of the rate of production of thermal-NO. After the investigation of autoignition kinetics, it has appeared, that the autoignition kinetics are quite sensitive to trace

components in the unburned gas. This means, that the species in EGR can be essential for identifying the knock. Combustion engine exhaust gases are formed of many various species, which come from incomplete oxidization like carbon monoxide (CO), but nitric oxide can also be present in small quantities. (55)

The most SI engine study showed that the knock intensity of iso-octane was increased with NO. These studies suggested that the effect of NO could change the fuel structures and engine operating conditions. The promoting effect of knock is associated with the reaction:

$$HO_2 + NO \rightarrow OH + NO_2 \quad\quad\quad \text{(Reaction 10)}$$

, where from a less reactive HO_2 via NO, a reactive OH radical is produced, which accelerates oxidation.

How it was stated before, the hydrocarbon oxidation starts with H-abstraction from the fuel (RH) without NO, as the next sequence part, it followed by the ROO and QOOH steps, resulting to degenerate chain branching. Adding NO species introduces new reactions, for example, **Reaction 10**. On the other hand, NO reacting with OH creates a less reactive HONO which slows down oxidation:

$$NO + OH + M \rightarrow HONO + M \quad\quad\quad \text{(Reaction 11)}$$

Another reaction is NO with RO_2 radicals (**Reaction 12**). In some cases, this promotes ignition, due to RO_2 being converted to a more reactive RO radical. Nevertheless, in other cases prevents ignition, due to consuming the ROO radicals which can otherwise react in the low-temperature branching channel and it accelerates autoignition:

$$NO + RO_2 \rightarrow NO_2 + RO \quad\quad\quad \text{(Reaction 12)}$$

However, our knowledge is not deep enough to understand the NO oxidation kinetics and questions still remain as to how NO impacts different fuels. Many studies try to make up this shortage. (54)

Dubreuil et al. (55) have been studied the effect of the addition of changeable initial NO concentration from 0 to 500 ppm was also studied using IQT tester. Two surrogate transportation fuels were used (n-heptane/iso-octane and n-heptane/toluene) and they were compared to the pure n-heptane and the addition of NO up to 500 ppm. To draw the lesson from the paper is, that the cool flame ignition delay, 100 ppm of NO has maximum effect. Another paper from Chen et al. (56) studied the effect of NO on the onset of knock in a CFR engine. The experiments are conducted in the standard knock intensity (SKI) condition for the RON tests. The test fuel was iso-octane blend. The results of experiments show clearly that the knock onset is consistently kept down with increasing NO additions at the SKI condition. However, interesting trends can be seen in the richer condition. In case of increased NO addition first advancing knock onset and then its retarding phenomena. Further paper from Chen et al. (54) studies the influence of nitric-oxide on n-heptane combustion in a rapid

compression machine (RCM). The ignition of n-heptane was promoted by NO up to 100 ppm in the low-temperature oxidation regime (≤ 720 K) because it seemed higher NO levels do not further help ignition. The experimental results pointed out that NO support ignition almost in all cases, but it changed by both the NO concentration and the mixture temperature. NO presented a more obvious promoting effect within the NTC region and higher temperatures. The reason behind that the ignition delays decreasing monotonically when more NO was added. One more work form Chen et al. (57) examined the influence of NO on knock onset in a CFR engine under constant knocking, constant conditions. NO was investigated with 0–800 ppm concentration. Important outcomes of this study are on the first hand, the increasing effect became much more powerful as temperature increased, where the knock onset is monotonically raised with growing NO concentration at the intake temperature of 200 °C. On the other hand, the impact of NO varied with fuel chemical composition. Seven gasoline surrogate fuels of a similar octane number were created and showed that higher contents of toluene and ethanol led to more promoting effects which related to an increase of the octane sensitivity in these fuels. DelVescovo et al. (58) have been declared a very interesting fact, namely that the current trends among automotive manufacturers to develop downsized, boosted engines, which require to understand specific fuel chemistry interactions take place in this new operating condition. Under such high-pressure conditions, a phenomenon called pre-spark heat release has lately been recognized and is described by kinetically controlled heat release before spark, with resultant changes in end-gas thermodynamic state and composition. In the study, experimental engine data at boosted operating conditions proving pre-spark heat release were compared with simulations utilizing mechanisms showing the latest developments in gasoline kinetic modeling. Four chemical mechanisms were chosen, describing the state of the art in gasoline surrogate modeling. The two tested mechanisms which included NO_x were the best performing in terms of LTHR phase, which highlights the importance of NO_x chemistry in SI engine modeling. The results refer to the concept that to match only high-temperature ignition delay for autoignition prediction in boosted SI engines may be inadequate for the understanding of the robust chemical mechanisms because a mechanism must match the low-temperature ignition delay and heat release magnitude in order to precisely predict the thermodynamic conditions of the end-gas.

These were the most relevant suited regrind this subject. The literature review shows that, most of these studies were limited to small fuels and no data are available for diesel, gasoline or surrogate fuels. In engines, only a few studies concerning such promoting effects of NOx were reported. Due to the very limited available data base and the widely different experimental conditions used, new studies on the kinetics of surrogate liquid fuels oxidation and interaction with NO_x would be needed to develop operating modes with optimized ignition timing.

3 EXPERIMENTAL SETUP

The IQT is a combustion-based instrument that has a constant-volume combustion chamber and it provides fast and reliable determination of the compression-ignition characteristics of a wide range of middle distillate-type fuels, fuels blended with biodiesels, and pure biodiesels. More appropriate comprehension of the IQT combustion process may necessitate to its use as a development and validation principles for kinetic models of innovative fuels, and the machine ensures a well-controlled operation condition for many tests in contrast to a conventional engine. The IQT is a constant-volume spray combustion apparatus that allows combustion and ignition examinations of low-volatility fuels as well. The IQT has the opportunity to produce experimental data important to confirming kinetic ignition models by advantage of its well-controlled parameters such as chamber wall temperature, air temperature, charge pressure, oxygen concentration, and mass of fuel injected are easily and quickly quantifiable for model implementation. The IQT offers the supplementary advantage of a low fuel quantity requirement. Depending on how many tests are ordered, the machinery is needed for the testing approximately between 50 and 100 ml of fuel. (38)

The main components of the IQT can be seen in *Figure 7*, which are:

1. Base unit which includes a stainless-steel combustion chamber, fuel injection system, and associated valves, sensors and hardware,
2. A closed loop cooling system,
3. An electrical cabinet, which encloses all electrical and electronic components,
4. A computer-based system that performs data acquisition and analysis, control and diagnostic functions,
5. A wheeled cabinet on which the base unit rests and which houses the cooling system, and
6. An Uninterruptible Power Supply (UPS) which is used to provide conditioned power to the electrical cabinet, computer and cooling system.

Figure 7: Ignition Quality Tester Apparatus (59)

The 213 cm^3 combustion chamber is the heart of the system and it is constantly pressurized to approximately 21 bar before the injection of the fuel. The combustion chamber is equipped

with thermocouple ports, a pressure transducer port for measuring combustion pressure, inlet and exhaust ports with associated valves, and an end cap. The injector nozzle is a single-hole type inward opening nozzle, that is located inside the end cap at one end of the chamber, with the combustion pressure transducer located at the other end. The end cap and three insulating gaskets act as a shield for the fuel injector nozzle against the high-temperature conditions inside the chamber. The end cap is equipped with passages connected to the coolant system. The purpose of the coolant flow is to reduce the heat transfer from the chamber to the nozzle and maintain the nozzle at a constant temperature. Two separate heating systems are used to maintain the temperature of the various components of the system. The larger of the two contains nine electrical rod heaters, that are inserted around the heater cylinder and take place in the outer wall of the combustion chamber to heat it and its parts to the test temperature. These sustain a constant charge temperature of approximately 575 °C, especially in the region of the nozzle tip. However, the end temperature of the injection is lower because of the heat transfer to the coolant system around the injection nozzle body and surface, that is exposed to ambient air. In the second heating system, two heaters are used to heat and maintain the temperature of the injection pump body at 35 °C. (59) *Figure 9* illustrates a simplified schematic section of combustion chamber.

The test sequence is automated, and the process consists of charging the combustion chamber to the test pressure and injecting a small amount of the test fuel into the combustion chamber. The injection pressure, as empirically defined, is around 225 bar during the main injection period. Before each test, the injection pump, fuel line and injector nozzle are manually purged with 3.45 bar (50psi) nitrogen and then flushed of any remaining fuel from the previous test. Compressed air is used to drive the fuel injection system 12 bar (175 psi). The injection system is actuated by solenoid valve connecting the surge tank to the air cylinder. Upon release of the air by the solenoid valve, the piston of the air cylinder pushes on the plunger of the injection pump, forcing its movement, and thus injecting the fuel into the combustion chamber. Charging of the combustion chamber to the test pressure is initiated by actuating a solenoid valve, which connects a regulated compressed air source to the combustion chamber. The charge air pressure is 21.3 bar (310 psi). This an ultra-high purity mixture of 79% nitrogen and 21% oxygen from Praxair with 99.993% purity. The charging of the combustion chamber is preceded and followed by the closing of the air-actuated combustion chamber exhaust and inlet valves. After injection the exhaust valve, located at the bottom from the combustion chamber, is opened. This evacuates a portion of the combustion gases of the previous combustion events. To complete the purging sequence the inlet valve, located at the top of the combustion chamber, is opened to introduce a small quantity of air into the combustion chamber. Compressed gas requirements during the procedure: (59)

- Extra-dry compressed air (O_2 concentration: 20.9+/- 0.1% by volume) used to charge the combustion chamber to the test pressure,
- Industrial-grade compressed air used to drive the fuel injection system, and
- Compressed nitrogen used to pressurize and flush the fuel injection system during testing.

The process starts with the fuel injection into the combustion chamber at a pressure of 225 bar. In the chamber a piezo-electric pressure transducer is mounted, aligned the same axis as that of the fuel injector makes a chamber pressure signal, and this is collected by a data recovery system, simultaneously with the needle lift values from a needle lift sensor that takes place in front of the injector. These two signals are the major pillar of measuring ignition delay times of test fuels. (60)

The total ignition delay time is determined as the time difference between the start of injection and the rise in combustion pressure to the "pressure recovery point" that defines ignition delay. The start of injection was set as the point where the needle lift achieves its maximum. The start of ignition is defined by the IQT system software. **Figure 8** shows the time delay between the beginning of injection and the extension in combustion pressure to the combustion pressure retrieval point of injected fuel. Besides this diagram describes the displacement of the cone needle in the axial direction, when the fuel injected into the combustion chamber. (61)
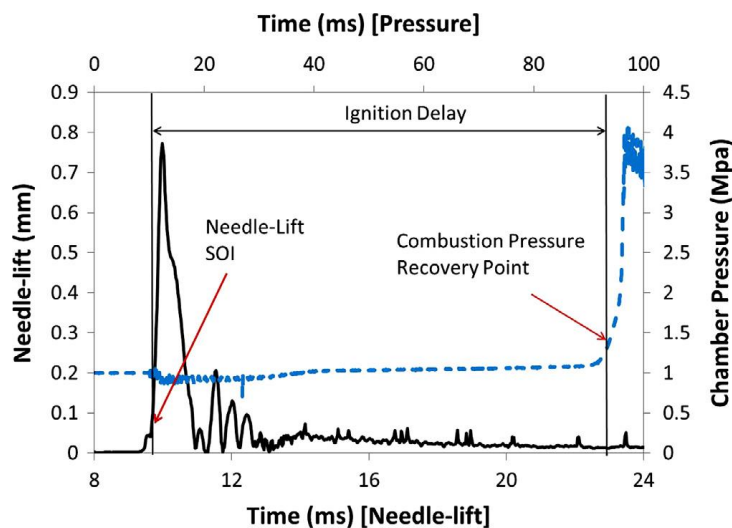
Figure 8: Ignition Quality Tester Apparatus (61)

The target of approving ignition kinetic models using the IQT needs an accurate perception of the combustion and injection processes within the IQT, since the measured ignition delay is a combination of the physical dynamics and the combustion chemistry. A total ignition delay time involves delays from both physical and chemical aspects during ignition. Physical ignition delay time defines the time needed for the injected liquid spray to atomize into fine droplets, heat, evaporate, and mix with an oxidizer to form a quasi-homogeneous fuel-oxidizer mixture that can ignite. (60) The reason why ignition process will not start quickly is that a short but limited time called the ignition delay time period is needed for the fuel spray to be divided into fine droplets to form a flammable mixture with the air, and also for the pre-flame reactions which commence to ignition to occur. Typically, one microsecond in the ignition delay is an accompanying part of the diesel combustion process, but the exact length of ignition delay going to depend on several factors. Just highlighted some of them: how easy the fuel can

oxidize, the temperature of the air, the size of the injected fuel droplets and the amount of fuel-air mixing. (6)

Chemical ignition delay time describes the time that the fuel molecules need to breakdown into smaller particles and reacts with oxidizer molecules to form adequate chain branching radicals that ignite the mixture. The ignition delay time is relatively much shorter for diesel fuels than for gasoline fuels such that the contribution from a physical process is supposed to be relatively small. (60) Some works have tried to separate the "physical delay time" including the evaporation process of the liquid fuel injection, from the "chemical delay time" including the chemical reaction. However, based on previous experience, it appears that this separation is irrelevant in terms of indicating the chemical reactivity of different fuels and surrogate mixtures. (5)

The ASTM method of D6890-08 was designed around the IQT device to enable a fast measurement of DCN. The D6890 method determines the DCN of pure fuel or even real transportation fuel based on the relationship of averaged ignition delay times. It uses as reference tests using the ASTM D613 engine test method. The DCN is calculated from the measured IDT using Equation 3 and Equation 4 as prescribed by ASTM D6890. The equations are defined depending on the range of the measured IDT. In the range of 3.1 to 6.5 ms is used the Equation 3, and outside the range is utilized the Equation 4. Extensive tests in this range have led to the development of precise correlation as given by Equation 3; however, the correlation given by Equation 4 is less precise. In spite of this, many recent publications have employed correlation Equation 4 to take DCN of fuels whose IDT is outside the range of 3.1-6.5 ms. (24)

$$DCN = 4.460 + \frac{186.6}{IDT} \qquad \text{(Equation 3) } (24)$$

$$DCN = 83.99\,(ID - 1..512)^{-0.658} + 3.547 \qquad \text{(Equation 4) } (24)$$

In the standard IQT test, each run involves 15 pre-injections to create a stable operating environment for the succeeding 32 main injections, that are performed to determine an average CN. As a reference fuel is used the n-heptane (≥99.5%) and it is also used for all experiments in this subject because of its use as a calibration fuel for the IQT. **n-Heptane** has a reference ignition delay time of **3.78** milliseconds and DCN number of **53.8**.

3.1 Modification on Ignition Quality Tester

There have been numerous studies to investigate creating a surrogate fuel methodology using the IQT apparatus. Most of the research in this field has been tested the various fuel blends in the way, that the combustion chamber of CVCC machines were completely purified before fuel-air injection due to the machine construction and used scientific air (21% oxygen and 79% nitrogen, analytical uncertainty by +/- 0.02% abs) for the fuel oxidization. The key problem with this technique is, that the scientific gas condition does not emulate the real conditions,

because, in the real, some NO_x remains in any time in the combustion chamber from the previous power-tact before the new portion of fuel-air is injected. As far as it is known, only very limited previous research has investigated the close to genuine conditions. One aim of this study is to create a new system to be able to test the real conditions and approve that the current surrogate fuel regression method is good enough to represent the real fuel chemical mechanism. Based on the results obtained, we have to evaluate the accuracy of the current developed descriptive model, and if necessary, it has to be adjusted. To do this we have to build a new gas supplier system for the existing IQT apparatus. The basic idea is that some Nitrogen-Oxide (NO) concentration has to be added to the air gas. NO is a colorless gaseous signaling molecule, and it is one of the basic oxides of nitrogen. It is a free radical thus it has an unpaired electron and it plays an important intermediate species in the chemical industry because nitric oxide transformations to NO_x during the combustion process. From the reason that we do not know yet, how many vol% NO is needed to obtain a significant change in DCN of certain fuels, the system must have the opportunity to change the NO fraction of supplied gas between the tests. Further important aspect is that it has to be evolved a dual-circuit air supply system and install a direct connection between existing regular air and the new system, given the possibility to switch from one to the other. To use the regular air system is necessary to calibrate the system, and make sure that the default setting still ensures the right value and that the new gas blend did not damage the prescribed operation of the apparatus. Furthermore, after the study the new system is not supposed to be disassembled, because further studies may be conducted with both air conditions.

Note that pure NO gas is not common available on the commercial market, because nitrogen oxides is toxic and very reactive gas. A dangerously big amount of inhaled dose is associated with serious lung injury. To avoid any possible dangers, the purchasable NO gas is balanced by pure N_2. In our system is built a N_2/NO (NO=5% and N_2=95%) gas tank. Therefore, to create a proper predetermined concentration gas mixture of NO-O_2-N_2 can be made from three separate tanks. A schematic P&ID diagram of the experimental setup is shown in *Figure 9*. The apparatus comprises a KR-IQT, a gas supply system, and several data acquisition setups. In the *Table 2*. the reader can see, in the different phase which valves should be opened or closed.

Given the information that the volume of the mixing tank is **4,2 dm³** and the IQT consumes **0,14 m³** pressurized air per test run, the pressure in the mixing tank can be calculated by dividing the needed gas quantity by the tank capacity. The needed pressure in the tank will be 1200 psi (82.7 bar) in case of two test runs and 1500 psi (103.4 bar) if the number of runs would be three. The pressure in any case is categorized as high pressure, therefore every parts of the system must be stressed on this requirement. A part list of the system and their most important features can be seen in *Figure 10*.
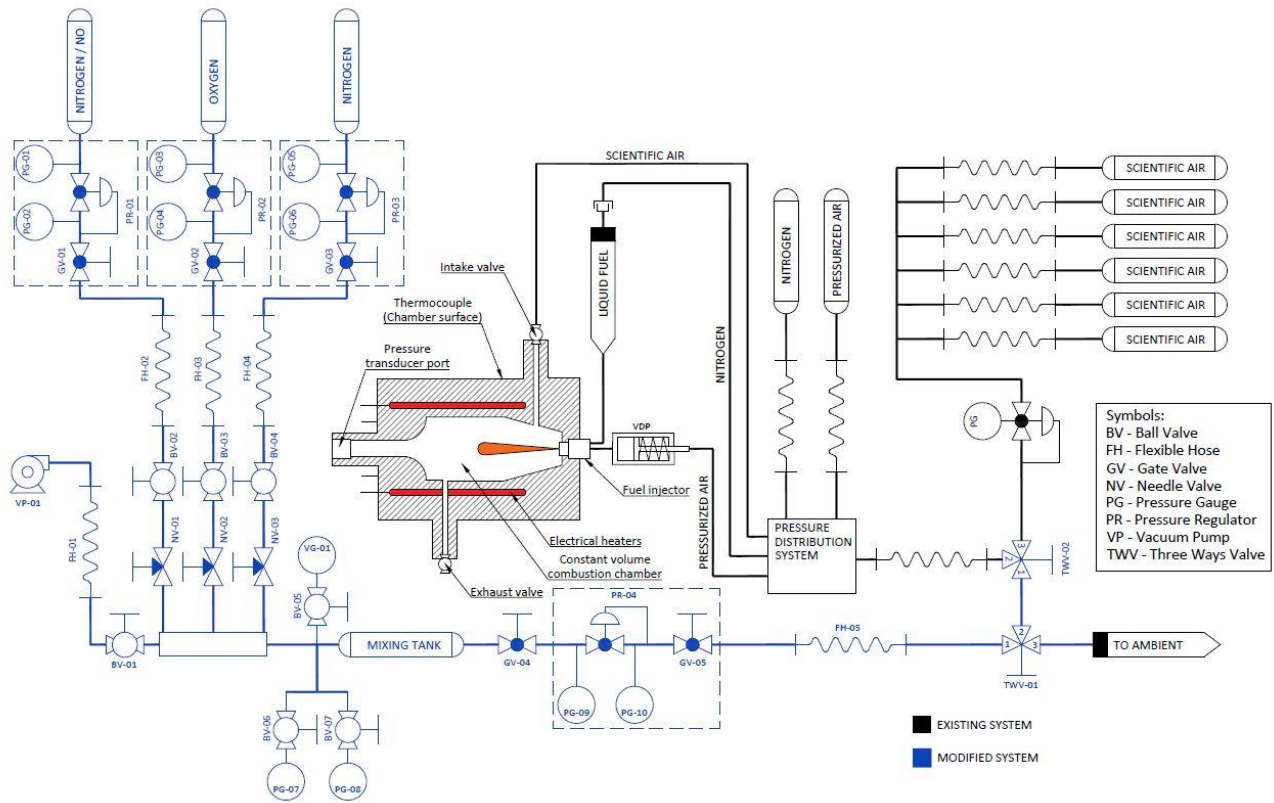
Figure 9: Modified gas supply system of Ignition Quality Tester

	ITEM #	UNIT	PART NAME	P&ID SYMBOLS	DESCRIPTION
1		1	Stainless Steel Mixing Tank	-	Material: stainless steel Max. Pres.: 2500 psi Volume: 4,2 dm3
2		3	On/Off Ball Valves	BV-02 BV-03 BV-04	Material: carbon steel Max. Pres.: 1500 psi Size: 1/4 NPT
3		2	Directional-Control Valves	TWV-01 TWV-02	Material: carbon steel Max. Pres.: 3000 psi Size: 1/4"
4		4	On/Off Ball Valves	BV-01 BV-05 - BV-07	Material: carbon steel Max. Pres.: 4500 psi Size: 1/4 NPT
5		1	Digital High-Accuracy Vacuum Gauges	VG-01	Pres. rate.: 0.145 to 25 psi Resolution: 0.1 psi Size: 1/8 NPT
6		1	Digital High-Accuracy Pressure Gauges	PG-07	Pres. rate.: 0 to 100 psi Resolution: 0.1 psi Size: 1/4 NPT
7		1	Digital Pressure Gauges	PG-08	Pres. rate.: 0 to 3000 psi Resolution: 1 psi Size: 1/4 NPT
8		3	Precision Flow-Adjustment Valves	NV-01 NV-02 NV-03	Material: carbon steel Max. Pres.: 5000 psi Size: 1/4 NPTF
9		5	High-Pressure Threaded Flow-Adjustment Valves	GV-01 ... GV-05	Material: carbon steel Max. Pres.: 1975 psi Size: 1/4 NPT
10		4	Pressure-Regulating Valves for Air and Inert Gas	PR-01 ... PR-04	Pres. rate.: 0 to 2500 psi
11		1	Vacuum Pump JB Industries DV-85N-250	VP-01	Perform.: 1/2 HP, 1725 RPM Intake port: 1/4"
12		5	Hose with Fittings for Plumbing Fixtures	FH-01 ... FH-05	Material: stainless steel Max. Pres.: 3250 psi Size: 3/8"

Figure 10: Part list of the modified gas supply system and their technical specifications

To handle the strength of extreme pressures, the used fittings are extreme-pressure stainless steel threaded pipe fittings. The stainless-steel fittings have excellent corrosion resistance, and they can be used to connect equipment in hydraulic fluid lines as well. The most weakness fitting is a male straight-reducer with the size of 1/2 x 1/4 NPT and its maximum allowable pressure is 7200 psi. Thread seal tape (also known as Teflon tape) is used for sealing pipe threads. It is a regulation to use it for pressurized systems because its lubricated feature allowing for a more profound seating of the threads, and it helps prevent the movement of the thread and its seizing when being unscrewed.

Table 2: Function diagram of modified gas supply system

PREPARATION		CHARGING #1 (NO/N2)		CHARGING #2 (O2)		CHARGING #3 (N2)		OPERATION		PURIFYING	
open	close	open	close	open	close	open	close	open	close	open	close
PR-01 & GV-01	BV-02	PR-01 & GV-01	VP-01	PR-01 & GV-01	VP-01	PR-01 & GV-01	VP-01	PR-01 & GV-01	VP-01	PR-01 & GV-01	VP-01
PR-02 & GV-02	BV-03	PR-02 & GV-02	BV-01	PR-02 & GV-02	BV-01	PR-02 & GV-02	BV-01	PR-02 & GV-02	BV-01	PR-02 & GV-02	BV-01
PR-03 & GV-03	BV-04	PR-03 & GV-03	BV-03	PR-03 & GV-03	BV-02	PR-03 & GV-03	BV-02	PR-03 & GV-03	BV-05	PR-03 & GV-03	BV-02
PR-04 & GV-05	BV-06	PR-04 & GV-05	BV-04	PR-04 & GV-05	BV-04	PR-04 & GV-05	BV-03	PR-04 & GV-05	BV-06	PR-04 & GV-05	BV-03
BV-01	BV-07	BV-02	BV-05	BV-03	BV-05	BV-04	BV-05	BV-07	BV-04	BV-07	BV-04
BV-05	NV-01	BV-06	NV-02	BV-07	BV-06	BV-07	BV-06	GV-04	NV-03	GV-04	BV-05
VP-01	NV-02	BV-07	NV-03	NV-02	NV-01	NV-03	NV-01	TWV-01 (1 to 2)	BV-02	TWV-01 (1 to 3)	BV-06
TWV-01 (1 to 2)	NV-03	NV-01	GV-04	TWV-01 (1 to 2)	NV-03	TWV-01 (1 to 2)	NV-02	TWV-02 (1 to 2)	BV-03		NV-01
TWV-02 (1 to 2)	GV-04	TWV-01 (1 to 2)		TWV-02 (1 to 2)	GV-04	TWV-02 (1 to 2)	GV-04		NV-01		NV-02
		TWV-02 (1 to 2)							NV-02		NV-03
											TWV-02

Before charging the gas into the mixing tank, it has to be made sure, that in the thank is no residue of other gases. To ensure a completely empty tank a vacuum pump was built in the system. The pump creates an almost perfect vacuum 0.01 bar (0.145 psi) within 1% of error rate, which is feasible. In this process phase an important point is, that the ball valves of the pressure gauges (BV-06 and BV-07) must be closed, otherwise the pressure gauges can damage, as they cannot measure in the negative direction.

The required pressure in the mixing tank should be divided between the different gases according to vol% of NO that we want to mix with the air. Considering that the pressure of inside the mixing tank is 1500 psi and the needed N_2/NO is 1000 ppm, the calculation method guides the following Equations. These values show the different pressure proportion of each gas.

$$P_{N_2/NO} = P_t * \frac{NO_{ppm} + \left(\frac{1-0.05}{0.05}\right) * NO_{ppm}}{1000000} = 1500 * \frac{1000 + \left(\frac{1-0.05}{0.05}\right) * 1000}{1000000} = \mathbf{30\ psi} \quad \text{Equation 5}$$

$$P_{O_2} = P_t * \frac{(1000000 - NO_{ppm}) * 0.21}{1000000} = 1500 * \frac{(1000000 - 1000) * 0.21}{1000000} = \mathbf{314.7\ psi} \quad \text{Equation 6}$$

$$P_{N_2} = P_t - P_{N_2/NO} - P_{O_2} = 1500 - 30 - 314.7 = \mathbf{1155.3\ psi} \quad \text{Equation 7}$$

where 'P_t' and 'NO_{ppm}' are variables and their values can be adjusted to the required conditions.

However, the exact amount of NO will be determined later from experimental results, but generally can be expected, that the NO/N_2 concentrate will not exceed 60 psi. This is followed

by oxygen and then pure nitrogen in increasing rates. Needle Valves (NV) are used to precisely control the gas flow into the tank. Respectively, the system is fitted with two pressure gauges with different sensitivity. The PG-07 pressure gauge can measure up to 100 psi at +/- 0.1 and the PG-08 pressure gauge up to 3000 psi at +/- 1.0 accuracy, which is an acceptable error rate. After reaching the vacuum, the ball valve (BV-05) of the vacuum gauge (VG-01) is closed and the NO/N_2 mixture is first allowed to release into the mixing tank while the BV-06 and BV-07 valves are opened. The gas is allowed to insert into the tank until the higher sensitivity pressure gauge shows just the desired values. The gas flow is then shut off, including the BV-06 valve of the PG-07, preventing it from being destroyed by subsequent high pressure. Oxygen and nitrogen are then added into the tank in a similar process.

During the operation, the charge air pressure is 21.3 bar (310 psi). This means that lower than this value the test process will abort, as the pressure is not high enough to maintain the system working. The consequence is that in the mixing tank will always remain at least 310 psi gas mixture, that must be released from the tank before the next mixture charging. However, the NO is a hazardous gas compound, therefore it cannot simply release into the laboratory atmosphere. In order to solve this issue, a right way is to build two three-ways-valve (TWV) in the system. During the purge process, the TWV-02 must be closed and the TWV-01 must be opened in the 1st to 3rd direction to release the remained gas into the outer ambient, outside the building.

Table 3: First results of DCN and IDT using the new gas supply system

Test #	Run #	Fuel	DCN	Std Dev DCN	IDT	Std Dev IDT	Charge Air	Set Point	Date	Run ID #
	Run #1	nC7	57.35	1.46	3.528	0.099	553.3	581	26/02/2020	2769
Test #1	Run #2	nC7	53.16	0.77	3.832	0.060	554.3	581	26/02/2020	2770
	Run #3	nC7	52.34	0.86	3.897	0.070	554.4	581	26/02/2020	2771
Test #2	Run #1	nC7	58.22	1.31	3.471	0.085	553.8	581	27/02/2020	2776
	Run #2	nC7	54.58	1.08	3.723	0.080	554.4	581	27/02/2020	2777
Test #3	Run #1	nC7	55.49	3.27	3.657	0.230	553.6	581	28/02/2020	2778
	Run #2	nC7	52.18	0.80	3.910	0.064	554.2	581	28/02/2020	2779
Test #4	Run #1	nC7	53.92	0.74	3.773	0.056	553.2	581	28/02/2020	2780
	Run #2	nC7	54.03	0.64	3.764	0.049	554.0	581	28/02/2020	2781
Test #5	Run #1	nC7	53.66	0.84	3.793	0.065	552.8	581	28/02/2020	2782
	Run #2	nC7	53.44	0.58	3.810	0.045	553.4	581	28/02/2020	2783

To verify the reliability of the new system, several tests are required, before the real blends are tested. A comprehensive test is required for the two different gas supply system with the same set condition and test fuel. The successful result can be stated, if the measurement results recorded consistent and reproducible. The IQT main parameters are: The chamber set point temperature was set to 581 degrees Celsius, as reference fuel is used the n-heptane (≥ 99.5%), number of runs are three, which consist of 9 pre-injections and 32 test injection after ASTM 6890. Before and after the test, it was made a check test again from regular air tank, with n-heptane and/or a diesel check fuel to ensure the IQT was still within calibration.

Furthermore, it is required, the same diesel check fuel is run in the middle of multiple runs to ensure calibration is constant and to lubricate the machine.

To verify the reliability of the gas system, five different tests were made with small modification on the system until the system proved to be reliable. The results of the various tests can be seen in the *Table 3*. Each run had its ignition delay, DCN, and standard deviation for each recorded.

For the **Test #1**, the mixing tank was filled with 21% oxygen (315 psi) and 79% nitrogen (1185 psi) for three test runs. The results of its runs were extremely different, where the value of the first run is significantly higher than by the following two. To prove the result of Test #1 another test was conducted. By **Test #2**, the conditions were the same except of the number of runs. We came to the conclusion, if the DCN result of the first and second run is identical or near identical, the test can be stated as an acceptable, successful experiment. Therefore, not just by Test #2, but in case of following tests were investigated by two runs. For financial reason, it seems a logical decision as well, however, when the real experiments will be started, it is recommended to use always at least three runs by every test. For two runs the required pressure in the mixing tank is 1200 psi consequently it had to be filled with 21% oxygen (252 psi) and 79% nitrogen (948 psi).

In the case of the second test, the same phenomena could be observed. The result DCN of the first run was higher than the second run. Note, that it was recognized that the output pressure of the mixing tank was not stable, and consequently the input gas flow of the IQT system neither. The pressure regulator required continuously a readjustment. At the experiments so far, in the output side of the new gas supply system was built a one-stage line regulator, which could cause the issue of unreliable pressure flow. To understand the importance of the types of pressure regulators, a brief summary of them is ensured in the following indention.

The pressure in the gas cylinders is extremely high, so a pressure regulator valve is required for their safe use. This is the most reliable means to reduce cylinder pressure to a usable level for operating instruments and equipment. There are two types of pressure regulators. On the one hand, the single-stage pressure regulators decrease cylinder pressure to outlet pressure in one single step. On the other hand, two-stage pressure regulators decrease cylinder pressure in two steps. What type should be used depends on requirements, since mechanical characteristics affect the performance of each regulator. The two most relevant differences are droop and supply pressure effect. Droop can be described as a difference in delivery pressure between the regulator's maximum flow capacity and zero flow conditions. The supply pressure effect can be described as the difference in delivery pressure. Supply pressure gets lower while the cylinder empties. Single- and two-stage regulators dispose of various droop characteristics and they react in a different way to changing supply pressure. Little droop with varying flow rates is showed by the single-stage regulator, but it has a relatively large effect on supply pressure. The two-stage regulator is just the opposite, it shows a significant droop, but only little supply pressure effects. If the inlet pressure does not vary significantly or if the regular readjustment of delivery pressure does not mean a problem, the single-stage regulator

is recommended. However, the advantage of the two-stage regulator is that it provides constant delivery pressure without any periodic readjustment.

Considering this information, the replacement of the one-stage line regulator to the two-stage regulator is reasonable. Furthermore, using instead of the line regulator with one pressure gauge (on the output side) should be used regulator with two pressure gauges on both input (PG-09) and the output side (PG-10). Knowing that a digital pressure gauge (PG-08) is already using to measure the pressure inside the mixing tank, to utilize an analog pressure gauge (PG-08) at the same time appears kind of unnecessary. However, the double-check of the pressure of the mixing tank is a rational decision, in that sensitive circumstances.

In spite of the modification, the result of the **Test #3** was not adequate either. However, the pressure flow from the mixing tank into the IQT gas distributor system was more balanced, nevertheless the value of the first run was still higher compare to the second run. This fact manifests, that there must be another issue, which causes this anomaly.

To find out the fault, it is advisable to investigate the gas blend itself inside the vessel. Worthy of mention, that oxygen above 51 bar (740 psi), and nitrogen above 34 bar (493 psi) at room temperature (20 ^{0}C) is not in gas phase anymore, but becomes a supercritical state. This can lead to an issue, because the mixture may not create a homogeneous compound. (62) To confute, that this is not the case, the real pressure-density relationship of both oxygen and nitrogen was drawn on *Figure 11*, and beside the ideal pressure-density relationship was calculated based on the ideal gas law for both types of gas:

$$\rho = \frac{P*MW}{R*T} \begin{cases} P*V = n*R*T \\ n = \frac{m}{MW} \to \frac{\rho*V}{MW} \\ \rho = \frac{m}{V} \to m = \rho*V \end{cases} \qquad \text{Equation 8 } (62)$$

, where the meaning of the symbols is the following:

P = Pressure (Pa)
V = Volume (m^3)
n = Amount of substance (mol)
R = Ideal Gas Law Constant (J * K^{-1} * mol^{-1})
T = Temperature (K)
m = mass (kg)
MW = Molecular Weight (g/mol)
ρ = Density (kg/m^3)
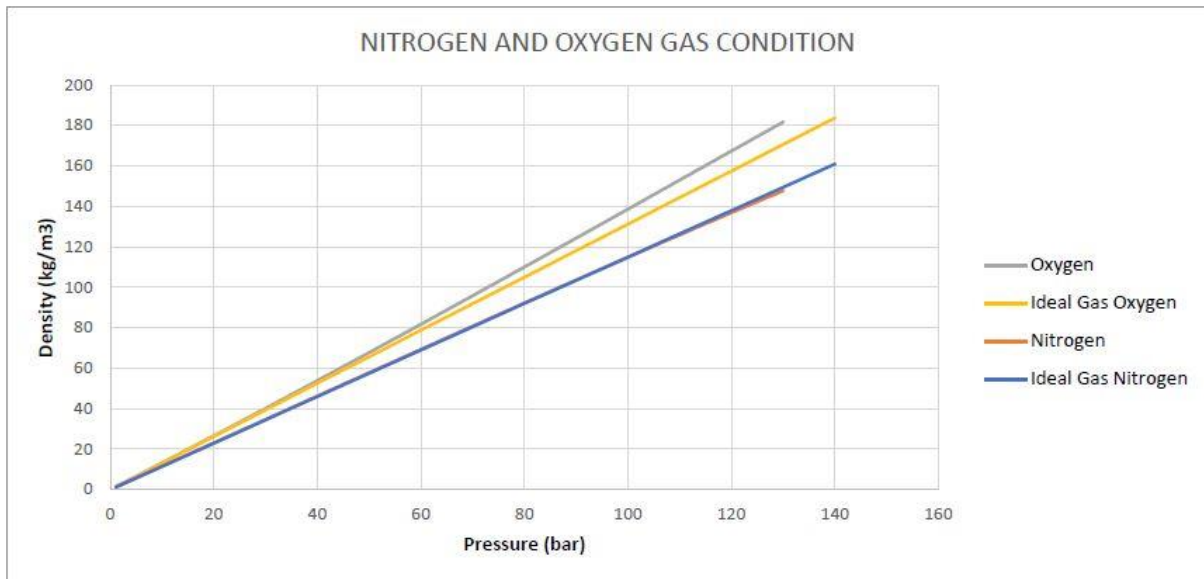
Figure 11: Ideal and real gas condition of oxygen and nitrogen in relation of pressure and density
(62)

Figure 11 shows us, that there is a neglectable difference between the real and ideal gas conditions until 120 bar, which is our maximum needed pressure for operation and according to the chart we can assume that the molecular is so slight, that it creates an almost homogeneous gas mixture each other.

Despite the result of the investigation of gas condition, it is assumed that the oxygen concentration at the outlet side of the tank is higher and towards the inlet side decreases, as first oxygen then nitrogen enters the system and they did not have time to mix with each other properly. This phenomenon may explain why the value of the first run of the tests was higher than that of the subsequent ones. Therefore, it is advisable to wait between 20-30 minutes after pressurizing the mixing tank, to provide enough time to the gas for blending homogeneous mixture all over the gas cylinder.
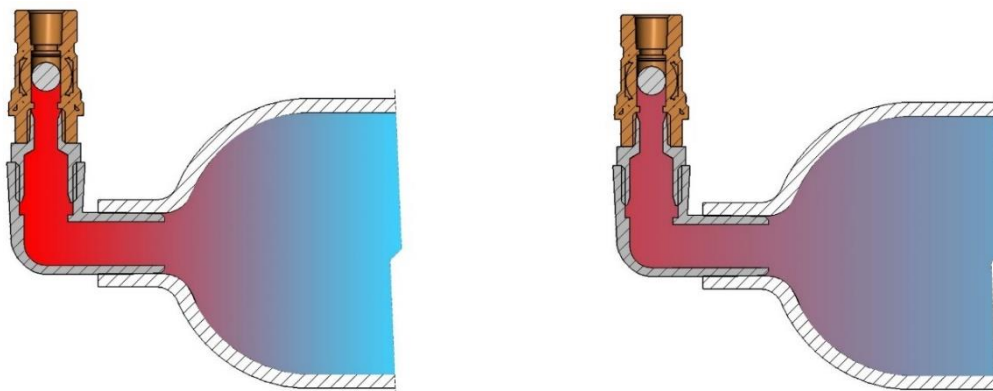
Figure 12: The degree of mixing of oxygen (red color) and nitrogen gas (blue color) at the outlet area of the mixing tank. Without waiting time (left side), with waiting time (right side)

On the *Figure 12* will be seen the degree of mixing of oxygen and nitrogen gas at the outlet area of the mixing tank. The longer the waiting time, the more homogeneous the mixture. Based on the pictures, further consideration can be taken. Because of the narrow area of bottleneck, fittings, and valves, the gas blend will be always oxygen-dominant in this cross-section. Therefore, additional advice is to release around 5 psi from the blend to the ambient before the mixed gas is loaded into the IQT gas supply system to avoid that some accumulated oxygen-rich gas, deflects the DCN value of the first run. Higher concentration of oxygen gas results more intensive combustion consequently shorter IDT and obviously higher DCN number.

Before starting a new test, another n-heptane check fuel was run after the previous experiments to again ensure the IQT was within acceptable calibration range. The test was performed within the above-determined limitations. The system reproducibility was proofed by two other tests. In case of **Test #4**, the first run has a value of 53,92, the second run of 54,03, which create an average value of **53.97**. In case of **Test #5**, the first run has a value of 53,66, the second run of 53,44, which create an average value of **53.55**. The first and second runs are almost identical, and the values are in the tolerance rate of the reference value of n-heptane (53.8 ± 1). It can be stated that the performance of the system is feasible.

Finally, we would like to draw particular attention to the fact, that the experiment is performed under hazardous conditions. Because the gas condition in the mixing tank is still supercritical, from safety reasons, the following section of the chapter must attract attention to some important criterion of supercritical fluid operation.

Equipment working with supercritical fluids and liquefied gases might have serious hazards that must be taken into account not only for equipment design and construction but for operation and maintenance as well. Safety considerations must influence any technical choice and operation and a detailed analysis of potential hazards must be specifically conducted for any case. In this section, some important points of the different classes of hazards will be manifest and how to cope with them, so that both the process designer and the operator are informed. Clearly, in any pressurized vessel presents a rupture hazard. Nevertheless, both design standards and official tests that are regulated by state standards (or equivalent), in combination with severe inspection policy decrease this hazard to a quasi-zero level, especially in the industry on large-scale units. However, some different types of hazards are often underestimated, especially on R&D (Research and Development) multipurpose equipment:

For example, a mechanical hazard might take place in the metal cylinder itself. The life duration of high-pressure vessels is connected to the number of pressurization and depressurization cycles. Usually, pressure tanks are authorized for 10,000 to 20,000 cycles, it depends on their design. By our experiments, it is very unlikely, that the pressurization reaches this amount of cycles, but still, it is an important point. Another potential mechanical hazard can be the tubing connection rapture. Fittings connections are usually used on most small-scale equipment when the operating pressure is below 400 bar (5800 psi). Normally,

these connections are perfectly safe and reliable as long as the screwing procedures are strictly followed. Otherwise, the thread is not strongly attached to the hole and a brutal rupture may occur on pressurization. It is recommended to always verify the good setting of the connections prior to high-pressure use. (63)

Besides mechanical, chemical and/or biological hazards can occur as well, as we utilize flammable fluids, co-solvents product. Explosion-proof equipment, buildings, and careful procedures must be executed when flammable fluids are used, especially for light hydrocarbons. Furthermore, handling any co-solvent, raw material or fluid that includes a kind of danger regarding chemical toxicity or pathogenic agents have to guide to intensive providing as supercritical fluid apparatus work at high pressure with potential leaks at any moment. The fluid leakage often promotes to the aerosol formation (droplets of extract, cosolvent, fluid in the gas flux) that are easily absorbed when breathing. Explosion atmosphere sensors must be installed and connected to power fans and valves that stop fluid reservoirs. (63)

We would stress the fact that a key for safe and reliable operation of supercritical fluid equipment, should include a cautious training of the operators. Detailed information exchange between the equipment designer and user should be the key for reliable and safe operation, both for lab/pilot scale versatile equipment and for large scale dedicated units. Such detailed discussions can avoid that they fall in different "traps" that could lead to accidents. Some recommendations are stated below:

- Be careful after tank decompression if exists a risk of plugging; wait several minutes before opening a decompressed autoclave.
- Never "over-screw" a leaking nut, as gas leakage causes a very suddenly temperature drop and leak cure is not possible, with the potential risk of nut break and metal piece ejection.
- Always verify the reliability of the instruments (pressure gauges).
- Always check what can happen if any electric power or instrument air fail; ensure that in case of electric power and/or instrument air recovery, nothing hazardous can happen.
- Never modify the equipment or introduce "new" type of spare parts without the checking of their suitability for operation condition.
- The remained gas in the vessel must release slowly, to avoid significant temperature changing, that could lead to loosed screws and fittings, and it may explode at any time.

3.2 Selection of the Target Fuels

Commercial transportation fuels like gasoline, diesel, kerosene etc. consist of complex mixtures from hundreds to thousands of hydrocarbons and oxygenated chemical species. therefore, to represent the corresponding real fuels, simple and reliable surrogate mixtures are needed for further experimental or computational studies and design practical engines. Since 2000, many comprehensive literature reviews have been published regarding the

simplified gasoline surrogate models. The most widely used gasoline surrogates can be made from the simplest two-component (iso-octane/n-heptane) called PRF, three-component (toluene/iso-octane/n-heptane) called TPRF, which are binary mixtures of iso-octane and n-heptane plus toluene and additional multi-component surrogates. The size of the model differs from a couple of species and it can cause hundreds to thousands of reactions. These models were verified against different targets including IDT, flame speeds (FS), speciation profiles estimated from flow reactors and premixed flames under various conditions. Sarathy et al. (13) studied the gasoline surrogate formulation approaches and made experimental and chemical kinetic studies on the important surrogates. Kalghatgi et al. (64) developed a method to define the composition of a TPRF (toluene/n-heptane/iso-octane/ethanol) by matching both RON and MON of target gasoline. (65)

Nowadays, the use of oxygenated types of gasoline, such as blending oxygenates, MTBE, ETBE, and ethanol blended to regular gasoline, has grown remarkably, as an effort to improve the anti-knock quality of fuel and to reduce the lifecycle (well-to-wheel) CO_2 emission. Because the need of ETBE is growing continuously, and strictly speaking, nowadays, it can be found in almost all types of engine fuel or as fuel additive, it has to be concerned, that the surrogate fuel of gasoline has to contain this kind of chemical compound as well. This fact was also stated by Tien Mun Foong et al. (66), Yang Li at al. (65), by whom this concept has been comprehensively validated.

The present study proposes to develop a four-component (toluene/n-heptane/iso-octane/ethanol) – TPRF-Ethanol gasoline surrogate model with an even fewer number of species and reactions for use in more computationally demanding multi-dimensional CFD model.

Table 4: Physical properties of target fuel compounds (1)

Compound Group	Formula	Structural Formula	Molecular Weight (g/mol)	Boiling Point, °C (101.3 kPa)	Density (g/cm3)	Octane Number		Cetane number
						RON	MON	
n-Heptane	C_7H_{16}		100.2	98.4	0.688	0.0	0.0	53.8
iso-Octane (2,2,4-trimethylpentane)	C_8H_{18}		114.2	99.2	0.690	100.0	100.0	17.4
Toluene	C_7H_8		92.1	110.6	0.871	120.0	103.5	6.0
Ethanol	C_2H_5OH		46.07	78.24	0.789	111	92	-

General properties of target fuel can be seen in *Table 4*. Heptane is an organic molecule and it is an alkane with the chemical formula C_7H_{16}. Heptane is a volatile, colorless liquid, in pure form is odorless. Heptane is an important hydrocarbon, along with pure isooctane, sets the octane rating scale. Heptane is an undesirable fuel component for spark engines since its autoignition happens under low pressure, causing engine knocking. This is why higher octane ratings are required for improving engine performance. Heptane is used to define the standard

zero point of ON. Besides setting the zero point for octane rating, heptane is commonly used as a laboratory solvent due to its low reactivity with other molecules. Many substances cannot dissolve in water, but it does in heptane. (1)

The scientific name of isooctane is 2,2,4-trimethylpentane. This compound is a colorless liquid substance with a petrol-like odor, that chemically belongs to the group of saturated, branched hydrocarbons (alkanes). Isooctane has eight carbon atoms and is also used as a fuel. It is a branched-chain hydrocarbon and is a five-carbon chain with three methyl groups at various points in the chain. Branched-chain hydrocarbons are more useful than straight-chain hydrocarbons in petrol. The straight-chain hydrocarbons cause irregular small explosions that cause performance loss, but the branched-chain hydrocarbons burn smoothly. Therefore, this compound was chosen as 100 on the octane scale. All octane can be used as solvents and cleaning agents, isooctane is contained in automotive and aviation fuels. (1)

Toluene is an aromatic hydrocarbon. The most beneficial gasoline aromatic is toluene (boiling point 110 °C) from the point of view of combustion and emissions. This chemical compound is hazardous chemical stuff because it is carcinogenic as well. This compound is colorless, in water is an insoluble liquid with the smell is similar to the paint thinners. It is a mono-substituted benzene derivative, its molecule consisting of one CH_3 group attached to a phenyl group. Toluene is especially used as an industrial feedstock and a solvent. Naturally in crude oil, toluene can be found occurs at low levels and is a byproduct of gasoline production and in making coke from coal. It is inexpensively produced industrially. Toluene can be used as an octane promoter in gasoline fuels for internal combustion engines as well as jet fuel. (1)

Ethanol, another called ethyl-alcohol is a volatile, colorless chemical compound that has a slight smell. This is simple alcohol with the chemical formula C_2H_5OH. During its burning, it has a smokeless blue flame that is not always visible in natural light. The physical properties of ethanol arise basically from the presence of its hydroxyl group and because of its carbon chain shortness. The hydroxyl group of ethanol can participate in hydrogen bonding, doing it more viscous and less volatile compare to less polar organic compounds of similar molecular weight, for example propane. (1)

Using ethanol in liquid transportation fuels has increased significantly in recent years. The forbidding of tetra-ethyl lead (TEL) from gasoline during the 1980s in the United States, and the possible way of its replacement MTBE, have led to increased use of ethanol as an oxygenate and octane enhancer. Nowadays, ethanol is used as a blending component of gasoline in ca. 5-15 v/v % or it is not rare to use it in ca. 85 v/v% (E85). The 2007 Renewable Fuel Standard requires, that the use of biofuels has to be increased to a total of 133.2 billion liters per year by 2022 in the United States. Ethanol is expected to supply the majority of this goal volume and could replace approximately 20% of gasoline need in the United States by then. These shifts in the energy segment indicate a continuing increase in ethanol production and use as a fuel in the near future. Ethanol presents significant potential for improving spark-ignition engine performance. It is already measured and accepted the fact that compare the

regular gasoline, ethanol has a significantly higher octane rating. (66) Although different RONs and MONs of pure ethanol have been reported beforehand, the RON value of ethanol was generally reported to be approximately 111 and the MON approximately 92. On the other hand, Gasoline has typically a RON value of at least 90 for regular fuel and up to 100 for premium gasoline. (1)

Based on the experiences of bioethanol programs worldwide, and various other research regarding ethanol, the advantages, and disadvantages of this fuel in Otto engines are quite obvious: (1)

Advantages:

- Gasoline octane number increasing with additive
- Contributes to the reduction of aromatic content of gasolines
- Improved combustion because it is an oxygen-containing compound
- Higher compression ratio, and thus higher efficiency of engine
- Enhanced the performance and increased torque
- Mixtures have higher volumetric energy content
- Environmental advantages in reducing emissions of some carbon compounds (e.g., ca. 60–65% carbon dioxide, ca. 50% carbon monoxide).

Disadvantages:

- Energy content lower by mass (i.e., performance declines as purity increases)
- Energy consumption highest with pure ethanol
- New gasoline blends not yet efficient at high blending vapor pressures

4 COMPUTATIONAL METHODOLOGY

An experiment called mixture experiment if the response is only a function of the proportion of components (constituents) being in the mixture and not a function of the total amount of the mixture. Experiments with mixture methodology are going to provide a functional relationship among proportions of inputs used and are helpful to add responses at points that have not been investigated in the experiment. In a mixture experiment, at least $q \geq 2$ components are mixed in different proportions, and one or more responses are investigated for all the mixtures. So, a mixture experiment includes mixing variable proportions of two or more ingredients to make various compositions of an end product. Suppose that N investigations are tried in an experiment that is a combination of the proportion of various components in the way that the sum of the proportions remains constant. If so, the 'N' investigations are acquired by splitting the fixed portion of inputs for employment in 'q' crop growth stages. If 'x_i' indicates the proportions of the 'i^{th}' element, then for mixture experiments: (67)

$$0 \leq x_i \leq 1 \qquad i = 1,2 \dots, q \qquad and \qquad \sum_{i=1}^{q} x_i = 1 \qquad \text{Equation 9 (67)}$$

where q signs the number of components. These kinds of experiments can be determined as mixture experiments in 'q' ingredients and 'N' design points. **Equation 9** is the basic constraints stated to the proportions involving the mixture experiment. Due to these limitations, the factors are not independent. The component proportions are also usually controlled by single or multiple-component constraints. The constraints in **Equation 9** is a simplex experimental field, while single- or multiple-component constraints commonly create a polyhedral constrained field. First, Cornell (1990) did research experimental design methods for simplex and restrained field mixture experiments. In a mixture experiment, one or more answers of inquiry are investigated for each composition. The main goal is to create a simple model for each reaction to promote the experimenter: first, examine the effects of each element on the responses, second, predict response values for recent mixtures, and/or third, formulate mixtures with acceptable or optimum responses. Cornell (1990) has been developed several classes of mixture experiment models, although the canonical polynomial models created by Scheffé are most frequently applied. To model responses as functions of the component proportions, the Scheffé mix models are often used. Scheffé (1963) described the polynomials for mixture experiments with the utilization of the constraint in standard polynomial and called them as canonical polynomials. The first (linear) polynomial model is given below, where the expected value of the response is marked by E(y).

$$E(y) = \sum_{i=1}^{q} \beta_i x_i \qquad \text{Equation 10 (67)}$$

The meaning of symbols briefly: 'β_i' represents the probable response to pure component 'i',

and 'x_i' indicates the proportions of the 'i'[th] element. (67) This formula (***Equation 10***) does not used very often because, there is a small possibility that each component has the same influence factor in the total mixture. This would assume that the model follows a linear relationship between the portion of mixture. In our experiment, it can be observed that change the proportion of different component drives a non-linear effect in the result. And so, using this formula results an inaccurate output for our regression model. This will be discussed later in the **Chapter 5**.

Furthermore, some researcher has examined to complete Scheffé linear models with squared terms. For three mixture components, Darroch and Waller (1985) suggested a quadratic model that can be parametrized to hold linear and squared terms for each substance at the same time. Chan, Meng, Jiang, and Guan (1998) and Chan, Guan, and Zhang (1998) developed two optimal experimental designs over simplex mixture fields for linear models completed with squared terms. Scheffé (1958) suggested the quadratic canonical polynomial model as well. The completed Scheffé quadratic (CSQ) model containing 'q' linear terms ($\beta_i x_i$, i = 1,2, ..., q) and Q = (q^2-q) / 2 quadratic cross-product terms ($\beta_{ij} x_i x_j$, where 1 ≤ i < j ≤ q) is often used. The quantity of quadratic cross-product terms 'Q' grows quickly as 'q' increases, and hence models including fewer interested quadratic terms. For the certain experiment concerning non-mixture factors 'x_i', where 'i' = 1,2, ..., q, the expected value of the response E(y) is usually sufficiently estimated by a quadratic polynomial model which is referred to as the CSQ model in this paper (***Equation 11***). (67)

$$E(y) = \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q-1} \sum_{j=i+1}^{q} \beta_{ij} x_i x_j \qquad \text{Equation 11 (67)}$$

The coefficients in canonical polynomials may be managed as usual regression coefficients β_i, where 'i' = 1,2 …, q may be taken as effect due to the 'i'[th] element and 'β_{ij}' represents the probable change in response (from linear blending) as a result of the quadratic blending of components 'i' and 'j'. If the blending of ingredient is rigidly an additive, then the linear canonical polynomial is the most suitable representation of the surface. However, when a curvature in the mixture surface exists resulting in a nonlinear blending between pairs of ingredients, then, the canonical polynomial of degree two or more are implemented as a representation of the surface. The components 'i' and 'j' are defined synergistic if the sign of 'β_{ij}' is positive, and the components 'i' and 'j' have antagonistic behavior if the sign of 'β_{ij}' is negative. In the mixture experiment literature, the terms of the general terminology of quadratic blending terms are used regarding '$\beta_{ij} x_i x_j$' as stated in ***Equation 11***. (67)

Basically, standard Scheffé polynomials are accessible up to the fourth order. Two of them were discussed above. Another two Scheffé models exist, that were specifically developed to treat the natural constraints of mixture designs. The remained two are the special-cubic and the full-cubic models. The special-cubic model is utilized, when there is three component blending. The formula is the following:

$$E(y) = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<1}^{q-1} \sum_{j}^{q} \beta_{ij} x_i x_j + \sum_{i<j}^{q-2} \sum_{j<k}^{q-1} \sum_{k}^{q} \beta_{ij} x_i x_j x_k \qquad \text{Equation 12 (67)}$$

It can be concluded that the difference between the cubic and quadratic models is an extra variable. The concept behind this is that with an additional parameter the result would be more accurate. In our experiment of three-components blend, the linear model has got three, the quadratic model has got six while the special-cubic model has got seven variables. An additional variable would make our conception more complicated to work with and leads to unanswered questions, and its result would be slightly better. Since the most important goal of the surrogate formulation is that it must be as simple as possible, the special-cubic model does not provide any benefit for us. Consequently, we propose CSQ models in this paper. The special-cubic polynomial model was investigated and found that this would be already over-parametrized for our experiment, therefore the full-cubic model will not discuss in this paper, as this is a more complicated formulation.

For the mixture experiments, it is sufficient to point out that, the inaccuracy of the system might be considered when this kind of works is performed. The main characteristics of many products composed by mixing numerous, individual components depend on their proportions in the mixture, nevertheless not on the volume of the mixture. Typical examples are the flavor of a mixture of fruit-juices obtained from different fruits owning individual taste-intensity or the strength of an alloy made by combining different metals owning individual features. Mixtures with required proportions of components are usually achieved by mixing predefined amounts of them. This is often done with tiny errors that appear negligible, can influence the properties of the mixture. Althubaiti et al. (68) investigated the impact of such errors caused by measurement mistakes on the statistical analysis of data obtained in experiments with mixtures and they suggest improvements to the original analysis that ignores the mixing errors. Their results also support for improving the manufacturing of mixture products in case of unavoidable mixing errors.

Several studies from Fuller (1987), Cheng and Van Ness (1999) and Carroll et al. (2006). summarizing the available techniques for handling such data. A significant difference between various cases is based on how the errors befall and what their distribution is. For instance, if an explanatory variable 'x' cannot be measured directly or precisely, the values adopted in the statistical analysis are $w_t = x_t + u_t$, t = 1, 2, …, n, where n is the number of observations. Several assumptions can be made regarding the so-called classical measurement errors 'u'. Most observed studies contain such classical measurement errors. Another contingency, when the final data are collected in a designed experiment and they are specified by the experimental design values 'w_t' are set with errors, i.e. $x_t = w_t + u_t$, t = 1, 2,…, n, the inaccurate values 'w_t' are regularly used in the evaluation of the statistical model of the data as the values 'x_t' are not known. In this case, the errors are avowed as Berkson's errors (Berkson, 1950). (68)

The reason why the mixing error problem should be considered is that in designed mixture experiments, the errors created in setting the correct amounts of any component propagates to the proportions needed by the experimental design for all components. Consequently, the mixing errors drive to a complicated error structure for the proportions of the mixtures. The results presented in the paper from Althubaiti et al. show that neglecting the mixing errors can lead to inaccurate estimation for the model parameters. The direction and the size of the distortion depend on many factors, but in particular on the size of the mixing error divergence. Nevertheless, the results that they present proof that the influence of the mixing errors cannot be eliminated entirely from the statistical analysis of the data. The rise in the variability of the results stimulates to the accuracy of the evaluation of the model parameters and so the prediction of the response. This is an especially important restriction when mixing errors cannot be avoided and the purpose of the experiment is to set the manufacturing frames of a mixture product. A typical quality feature of the product will be reduced by the mixing errors. Hence, perhaps not extraordinary to declare, if we do not use a more complex model to consider the mixing errors, at least trying to avoid or minimize the mixing errors might be the first thing to complete. (68)

As far as we handle mixtures for our experiences, the mixing errors should be taken into account. As it has written before, for estimation the DCN value, the Scheffé quadratic canonical polynomial model will be used in this paper. Considering the mixing errors the regression model would be the following:

$$Et(y) = \sum_{i=1}^{q} \beta_i x_{it} + \sum_{i=1}^{q-1} \sum_{j=i+1}^{q} \beta_{ij} x_{it} x_{jt} \qquad \text{Equation 13}$$

In the **Equation 13**, the 't' represents the measurement errors. It is presented in the different proportions of components in the mixture.

When a surrogate fuel mixture is made, it is recommended that the different components will not be measured by vol% (ml), because it can lead to inaccurate result when the components are blended. Instead of volume it is recommended to use the molecular mass (g/mol) of each component, which is concerted then into mass (g).

Mixing errors can enter into the system in several ways, when variant pure fuel components are blended. In particular there are three risky steps of blending process. Basically, calculating the proportions of the components based on molar mass and then conversion to mass provides the most accurate result possible. However, we do not consider the decimals, variations in totals can be due to the effects of rounding too few decimal places. Another problem is that measuring the components using a scale, if the scale is not calibrated or conditions are not appropriate, results in measurement inaccuracy. Finally, make sure that the time elapsed between the addition of each mixture during the preparation of the mixture is minimized and that the final mixture is placed quickly in a closed system so that it cannot evaporate further. Since our mission is to create a simple formulation methodology for surrogate fuel, we do not use a complicated regression model, that considers the mixing

errors. Therefore, trying to avoid or minimize the mixing errors as much as possible should be ensured.

In many areas of science and engineering field, computer codes or complex mathematical models are applied to model the output of a physical and chemical process and it is regularly of interest to conclude and characterize how the result is influenced by changes to the input factors. In our study, after the regression model is applied it is deserving to run a sensitivity analysis to identify how the result is influenced by the ratio of the components. Basically, two types of sensitivity analyses are distinguished. The global sensitivity analysis stands on understanding how the output is influenced by a set of input factors when the unused inputs have been combined out of the process. On the contrary, the local sensitivity analysis stands on understanding how the output is affected by very small adjustments in the input factors corresponding to a baseline. In many scientific perspectives, local sensitivity owns a very limited value since experimenters are interested in how significant the input affects the output. This is correct in both physical and chemical experiments in which experimenters wish to understand how the inputs globally change model outputs. The output of a physical process through visualization considered by Cornell (2002) what happens if there are small changes in a single input. Then a method was visualized between two components in a mixture by Piepel et al. (2002) through considering small changes of baseline or reference mixture. (69)

The process of re-calculating the results of the used model under alternative assumptions to define the influence of a variable by sensitivity analysis can be advantageous for a range of purposes, which includes:

- Testing the robustness of the outcomes of the used model or system in the occurrence of uncertainty.
- To understand the relationships between input and output variables in the model or system.
- Reduction of uncertainty by focusing on attention model inputs that cause remarkable uncertainty in the output in order to increase robustness.
- Searching for errors in the model (mixing errors etc.)
- Simplification of the model by identification input factors that have zero or small effects on the output.
- Development of the model by identification important connections between perceptions, model inputs, forecast and predictions.

The applied mathematical model in the field of climate change, economics, engineering, etc. can be very complex, and as a consequence, its relationship between input factors and outputs may be weakly understood. In these cases, the model can be defined as a "black box", that means the output is an untransparent function of its inputs. This happens, when some or all of the model inputs include uncertainty content, including errors of measurement, etc. That imposes a limit on our trust in the response of the model. Moreover, models may have to handle the intrinsic variability of the system, for instance, the occurrence of stochastic events. A good modeling requires that the researcher provide an evaluation of the trust in the model. This demands from the evaluation to know how much the input factors are contributing to the

output uncertainty. To solve this issue is addressed by sensitivity analysis, performing the task of ordering by relevance the strength of the inputs in the identification of the variation in the output. The selection of the method of sensitivity analysis is typically demanded by a number of issue constraints or settings. A large number of approaches exist to performing a sensitivity analysis. The different approaches are differentiated by the type of sensitivity measure, based on for example the variance decompositions, elementary effects or partial derivatives.

In the context of sensitivity analysis, the regression model involves elements of linear regression to the model response besides using standardized regression coefficients to direct measurement of sensitivity. This method is most suitable when the model response can be confirmed as linear, for instance, if the coefficient of determination is big. The benefits of regression analysis are simplicity and it has a low computational demand. Regression analysis is principally applied for two conceptually different purposes. On the first hand, regression analysis is widely utilized for prediction and forecasting. On the second hand, regression analysis can be applied to infer causal relationships between independent and dependent variables.

Sensitivity analysis determines how several values of an independent variable affect a dependent variable under a given assumption. The sensitivity coefficients show how much the measured value shifts for a given replacement in a single input quantity, whilst keeping all of the others constant, and noticing the output effect on the measured value. The sensitivity coefficient is often calculated mathematically by using the partial derivative of the measurement with respect to the input quantity. i.e.:

$$\boldsymbol{sen.C} = \frac{\frac{\Delta M}{M}}{\frac{\Delta x_i}{x_i}} \rightarrow \frac{\Delta M}{\Delta x_i}\frac{x_i}{M} \rightarrow \frac{\boldsymbol{\delta M}}{\boldsymbol{\delta x_i}}\frac{x_i}{\boldsymbol{M}} \qquad\qquad \text{Equation 14}$$

where 'x_i' is the examined independent variable or parameter and 'M' is the modelled value.

Over time, many dimensionless sensitivity coefficients have been suggested, using the partial derivative of the dependent variable to the independent variables. This technique is often the easiest approach to determining sensitivity coefficients if the measurement model pursues a straightforward relationship.

5 EXPERIMENTAL ANALYSIS AND RESULTS

In this work three different neat fuel components were studied. The iso-octane and/or toluene mixtures were measured with n-heptane and only n-heptane as a pure sample. However, as mentioned before, the ethanol would be an essential part of the surrogate fuel of gasoline, but in this study such a mixture with this component was not measured. It will be one of the future tasks for another study. 23 different mixtures were tested by IQT including seven n-heptane-iso-octane blends, eight n-heptane-toluene blends, single iso-octane-toluene blend, five n-heptane-iso-octane-toluene blend and the pure n-heptane and iso-octane as control measurements. The result of the different blended mixture's DCNs are located in **Table 5**. Since the DCN values of iso-octane and the toluene are lower than the n-heptane (53.8 by definition), the measured DCN values of the mixtures exhibit a fairly monotonic increase of DCN values as n-heptane increases in the mixture, indicating that the ignition propensity is considerably increased due to the increasing presents of the n-alkyl chain.

Table 5: Correlation development data of DCN of mixtures

No.	nC_7H_{16} (mol%)	nC_7H_{16} (vol%)	iC_8H_{18} (mol%)	iC_8H_{18} (vol%)	C_7H_8 (mol%)	C_7H_8 (vol%)	DCN	Ref.
1	100	100	0	0	0	0	53.8	(70)
2	0	0	100	100	0	0	18.9	(70)
3	75	72.5	25	27.5	0	0	47.8	(70)
4	50	46.8	50	53.2	0	0	41.0	(70)
5	25	22.7	75	77.3	0	0	32.0	(70)
6	80	77.9	20	22.1	0	0	48.3	This study
7	60	56.9	40	43.1	0	0	42.7	This study
8	40	37	60	63	0	0	36.4	This study
9	20	18	80	82	0	0	29.2	This study
10	75	80.5	0	0	25	19.5	46.6	(70)
11	50	57.9	0	0	50	42.1	36.5	(70)
12	25	31.4	0	0	75	68.6	24.2	This study
13	10	13.3	0	0	90	86.7	10.5	(70)
14	76	81.3	0	0	24	18.7	46.8	This study
15	54	61.8	0	0	46	38.2	38.1	This study
16	34	41.5	0	0	66	58.5	28.2	This study
17	16	20.8	0	0	84	79.2	15.7	This study
18	60	61.7	20	23.4	20	15	42.6	(70)
19	33.3	34.9	33.3	39.7	33.3	25.4	31.8	(70)
20	25	27.8	25	31.7	50	40.5	27.0	This study
21	20	19.5	60	66.4	20	14.2	28.4	This study
22	10	12.6	10	14.3	80	73.1	12.4	(70)
23	0	0	50	61	50	39	10.4	This study

Our research aims at finding a solution to predict an optional mixture's DCN without testing it for real. For this purpose, the above results were incorporated into the three different type of regression model, which were mentioned in the **Chapter 4**. These regression models are based off the mole fraction proportion of each mixture. After choosing the best fit model, it will be transformed into our concept using the chemical functional groups to ensure the most accurate predicted DCN. Each analysis made by Excel Solver to find an optimal value of the variables for the formula. To be more accurate, the linear regression detects the possible smallest sum of squared residuals on the dataset. Applying the model of **Equation 10**, the number of variables is three. After performing the calculation, the summarized residue is

130.09, which is the sum of squared difference between real DCNs and predicted DCNs and the value of R-squared is 0.9646. Statisticians announce that a regression model matches the data properly if the differences between the predicted values and the observations are small and not unusual. Not unusual means in this context, that the matched values are not too high or too low anywhere in the measurement space. Nevertheless, before evaluating numeric measures of goodness of result, such as R-squared, the residual plots should be evaluated. A biased model can be exposed far more effectively by residual plots than the numeric output is there are some problematic patterns in the residuals. If the model does not follow any consequence, the results cannot be trustworthy. If your residual plots seem sufficient, then R-squared and other statistics can be assessed. The scattering rate of the data points around the suited regression line is evaluated by R-squared. The R^2 is also called the coefficient of determination. For the same data set, the higher R-squared values mean smaller disparity between the observed initial data and the fitted values. This is the percentage of the dependent variable divergence and usually, the larger the R-squared, the better the regression model fits the observations.

In order to estimate whether the outcome of linear model is a good result, another type of regression model must be performed to have a benchmark. The second time, following the same calculation concept the quadratic model of **Equation 11** was used with six variables as a transfer function for regression analysis with **Table 6** summarizing the regression coefficients to predict the DCN. The summarized residue is **17.29** with the R^2 value of 0.995. **Figure 13** shows the entire result database with the experimentally measured DCN on the x-axis and the predicted DSN on the y-axis. This graph shows the quadratic regression model ability to predict a variety of fuels based off solely the fuels mole fraction proportion.
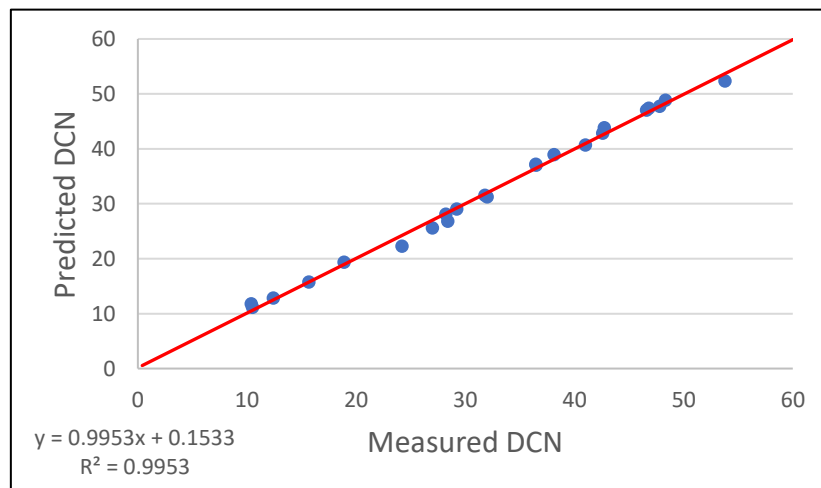
Figure 13: The measured DCN plotted against its predicted DCN

Table 6: Table showing each coefficient for the quadratic regression analysis

Variables: a_i	Fuel type	Value	Variables: a_{ij}	Fuel type	Value
a_1	nC_7H_{16}	52.36793	a_{12}	nC_7H_{16}-iC_8H_{18}	19.34508
a_2	iC_8H_{18}	19.36386	a_{13}	nC_7H_{16}-C_7H_8	37.87552
a_3	C_7H_8	2.743358	a_{23}	iC_8H_{18}-C_7H_8	2.970116

The graph shows that a vast majority of the DCN are feasible within 0.69 of the experimental measurements with only a few being outside of 1.94 DCN.

The Scheffé's polynomial quadratic regression model can provide a significant better result than the linear one. It was mentioned before that probably the linear type of model gives an inappropriate result, since evaluating the different mixtures can be seen for example that the different n-heptane concentrations and the corresponding DCN values follow a non-linear behavior. In the third time, using still the same calculation concept the special-cubic model of **Equation 12** was conducted with seven variables. The summarized residue is **13.16** with the R^2 value of 0.9964. The special-cubic compare to the quadratic model does not provide a significant better result. Keeping ourselves to the goal that the regression model should be as simple as possible besides providing reliable results, the quadratic model will utilize following in the study, since this is simpler and usually sufficient to predict an accurate DCN values.

5.1 QSPR regression model application for DCN

In previous work, a Scheffé's simplex polynomial was found to accurately predict the DCN of a surrogate mixture within the standard deviation of 0.88 (3 sigma) and a maximum error in predicted DCN of 1.94. Previously, the role(s) of chemical functional groups have been investigated by constructing a quantitative structure-property relationship (QSPR) regression analysis. The purpose of the QSPR is to determine the interactions between specific differing chemical functional groups. In organic chemistry, the role of functional groups is to define a specific group of atoms and atom constellations within a compound that is accountable for the characteristic of chemical reactions of the compound. The same functional group is going to act in a similar way, by conducting similar reactions, notwithstanding the compound of which it is a part. The basic idea is, if the regression model is used based on the chemical functional groups of organic compounds instead of the pure component's proportionality of mole fraction, the prediction will be more accurate. Moreover, the prediction of DCN value is possible by such fuels on which the exact proportionality of hundreds of components is not known.

As highlighted throughout the former chapters, it is absolutely necessary to minimize the dimensionality of our numerical models, to provide CFD numerical design tools to be most efficient. Keen functional group determination for improving structure-property relationships are necessary for a good approximation of these measures. It is desired that these associations preserve sufficient accuracy to also consider the underlying physical processes that would be significant in guaranteeing relationships that are predicted. If these methods can be testified against a range of combustion behaviors, a huge potential can be in the functional group relationships as an alternative low dimensional descriptor of gas-phase combustion kinetics. To ensure a mathematical model for the liquid fuel gas-phase combustion interaction that can be implemented based on functional group descriptions, which have to meet four intrinsic challenges: 1) The examined dataset must be considered the combustion behavior of known molecular structures and it must be sufficiently large and quantitatively accurate; 2) the functional groups must be identified, that principally consent to the examined combustion behavior; 3) having respect for the dominant physical and chemical fundamentals, an

analytical model must be derived, that correlates the activity of the chemical functionality and the combustion behavior. 4) the functional group descriptor must be quantitatively definable. The chemical functional group approach used in this study and in some other previous papers based on identifying the "key" carbon-hydrogen multi-atom functional groups existing in the real fuel. In this paper, six "key" molecular fragments were utilized as the feasible chemical functional groups to describing global combustion replies obtained for mixtures of n-alkanes, iso-alkanes, and aromatics. The molecular fragments considered in the present study are: 1) the linearly bonded methylene group ($(CH_2)_n$, where "n" indicates the resulting n-alkyl chain length and n > 3; 2) isolated methylene groups (referred to as CH_2); 3) the methyl group (CH_3); 4) the CH group (CH); 5) the C group bonded only to other carbons (C), and 6) the benzyl group (benzyl-type). Basically, these are the different chemical groups, that can be found in n-heptane, iso-octane and toluene. In numerical terms, the molecule of n-heptane consists five $(CH_2)_n$ and two CH_3 groups, the molecule of iso-octane includes five CH_3, and each one from CH_2, CH, C, furthermore the molecule of toluene is built from one CH_3 and one benzyl-type group.

The sequence of the next subject is the following: 1) determine all possible subsets terms of Scheffé polynomial; 2) for each polynomial subset with 'a_i' or 'a_{ij}' terms, determine which particular polynomial has either the highest coefficient of determination using sensitivity analysis; 3) removing all terms appear unnecessary; 4) the optimal polynomial is that with the fewest number of terms that has the minimum absolute error among all of the available concept.

The **Equation 15** below is a continuation of that work by including the chemical functional groups and is used as a transfer function for QSPR regression analysis with **Table 7** summarizing the regression coefficients to predict the DCN. This regression analysis is not only meant to ensure a comprehensive analysis, but to evaluate the roles of each of the key chemical functional groups in determining DCN.

$$DCN_{predicted} = a_0 + \sum_{i=1} a_i x_i + \sum_{i=1} \sum_{j=i+1} a_{ij} x_i y_j = a_1 x_1 + a_2 x_2 + a_3 x_3 + a_4 x_4 + a_5 x_5 + a_6 x_6 +$$

$$a_{12} x_1 x_2 + a_{13} x_1 x_3 + a_{14} x_1 x_4 + a_{15} x_1 x_5 + a_{16} x_1 x_6 + + a_{23} x_2 x_3 + a_{24} x_2 x_4 + a_{25} x_2 x_5 +$$

$$a_{26} x_2 x_6 + a_{34} x_3 x_4 + a_{35} x_3 x_5 + a_{36} x_3 x_6 + a_{45} x_4 x_5 + a_{46} x_4 x_6 + a_{56} x_5 x_6 \qquad \text{Equation 15}$$

Important note, that based on empirical research experience the equation need to be complemented with an additional coefficient. If the formula does not include a constant a_0, the equation, and the result suggests that if we have a progressively increasing number of functional groups, indicating that the molecular weight of the fuel becomes increasingly larger. This means the fuel becomes denser, consequently the DCN value going to be larger and larger. At the same time taking into account the physics of component, we know that the toluene (CH_3 and benzyl-type) has a negative impact on the DCN and it decreases the value. Consequently, certain types of functional groups even though there are added to the equation should not increase DCN. Therefore, to compensate the first-order term, a constant a_0 must

be added. The randomly given number of DCN as a_0 is able to abolish increasing the DCN through such groups as benzyl-type, CH_3 etc. groups. The additional coefficient can be arbitrary, and so we had chosen the DCN number belonging to **Blend #19**.

The same set of functional group descriptors mentioned above in this chapter are employed and each functional group mass fraction are interpreted by a Scheffé simplex-polynomial After running the Solver with all possible variables, the summarized residue is **17.29** with the R^2 value of 0.9953.

Table 7: Table showing each coefficient for the quadratic regression analysis

a_i or a_{ij}	Functional group	Value	a_i or a_{ij}	Functional group	Value
a_1	$(CH_2)_n$	4.12908	a_{23}	0.29019	CH_3-CH_2
a_2	CH_3	-4.42003	a_{24}	0.29019	CH_3-CH_2
a_3	CH_2	0.91433	a_{25}	0.29019	CH_3-CH_2
a_4	CH	0.91433	a_{26}	1.42517	CH_3-benzyl-type
a_5	C	0.91433	a_{34}	0.85603	CH_2-CH
a_6	benzyl-type	-26.0617	a_{35}	0.85603	CH_2-CH
a_{12}	$(CH_2)_n$-CH_3	0.87626	a_{36}	1.10655	CH_2-benzyl-type
a_{13}	$(CH_2)_n$-CH_2	0.75871	a_{45}	0.85603	CH-C
a_{14}	$(CH_2)_n$-CH	0.75871	a_{46}	1.10655	CH-benzyl-type
a_{15}	$(CH_2)_n$-C	0.75871	a_{56}	1.10655	C-benzyl-type
a_{16}	$(CH_2)_n$-benzyl-type	8.16628	a_0	31.8	-

Despite successful predictive abilities of QSPR models for DCN, no succinct fundamental knowledge for the result has been understood previously, and the experiments have been principally empirical, indicating predictive precision rather than fidelity and seeking fundamental understanding. Such in the thinking behind has been resulted in the consideration of larger numbers of independent variables to develop accuracy with only restricted guidance from kinetic insights to develop improved fidelity. Whilst a longer polynomial probably fits the development or validation data better, it is not a guarantee that this kind of advanced fit does not include significant reproducibility errors given from the fuels studied. Furthermore, even though a higher dimensional regression can provide a more precise replication of the pointed ignition delays values, the more complicated relations may hide the real sensitivity of the behaviors regarding the predicted chemical kinetic behaviors. Therefore, it was found, the shorter and simpler polynomial with a minimum absolute error can provide at least such a valuable solution. Removing all terms containing CH_2, CH and C furthermore the coefficients of a_{26}, a_{13}, a_{14}, a_{15}, the result will only slightly change. The remained five terms include a_1, a_2, a_6, a_{12}, a_{16} can see in the **Table 8** and they result a summarized residue of **17.89** with the R^2 value of 0.995, which indicates that there are no significant differences between the results and the latter is still an adequate output. Note, if we remove one of those five coefficients, then the result is not acceptable anymore, drawing the conclusion that DCN is capable of including not only primary but secondary interaction terms of chemical functional groups.

Table 8: Table showing the new values of the coefficients for the regression analysis of DCN prediction

a_i or a_{ij}	Functional group	Value
a_1	$(CH_2)_n$	2.56702
a_2	CH_3	-2.43833
a_6	benzyl-type	-26.29338
a_{12}	$(CH_2)_n$-CH_3	1.26410
a_{16}	$(CH_2)_n$-benzyl-type	8.70459
a_0	-	31.8

The data are presented in **Figure 14** indicate the comparison between the measured DCN and the predicted DCN values yielded from the regression. The QSPR database with the experimentally measured DCN on the x-axis and the predicted DCN on the y-axis. This graph shows the QSPR's ability to predict a variety of fuels based off solely the fuels chemical functional group and the resulting QSPR model reproduces the training data set results very well. This method allows for a useful and meaningful nuance: the degree to which the training data can be reproduced is dependent on the selection and number of chemical functionalities chosen as descriptors. The graph shows that a vast majority of the DCN are well within 0.7 of the experimental measurements with only a few being outside of 1.8 units which is the determined standard deviation between the measured and predicted values.

$y = 0,9951x + 0,1586$
$R^2 = 0,9951$
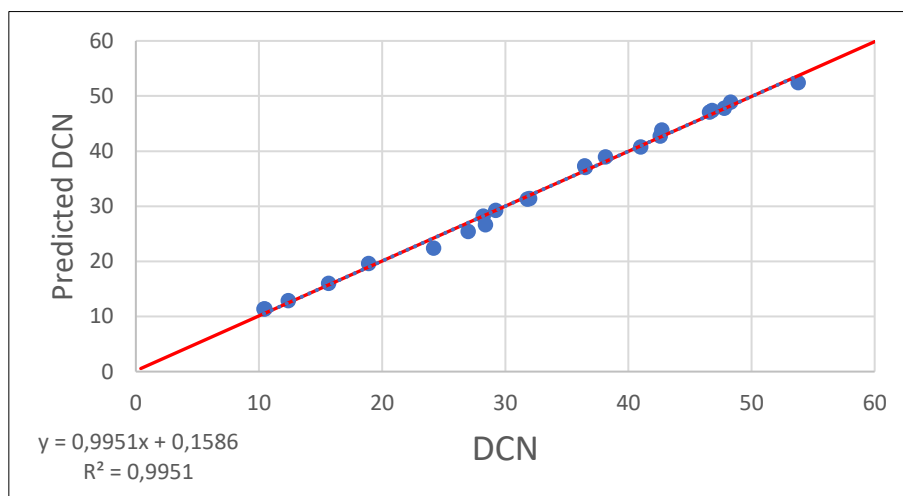
Figure 14: Comparison between measured and predicted DCN analyzing by the QSPR regression model

The QSPR regression model also allowed for analysis of the importance of each chosen chemical functionality in determining the DCN. **In Figure 15** the sensitivity analysis represents the impact of chemical functional groups of certain mixtures. The mixture number shown on the x-axis and the extent of effect on the y-axis. This helps to illustrate that $(CH_2)_n$ has the greatest impact on the ignition properties of fuels, which is in line with what is known in the field, confirming our physical understanding, and continues to show the validity of this regression analysis. The $(CH_2)_n$, the chemical functional characteristic inherently increases

the reactivity of the fuel, promoting higher DCNs. Due to the pressure and temperature conditions under which the DCN is determined in an Ignition Quality Tester, the mighty sensitivity of the $(CH_2)_n$ group can be linked to the chemical kinetic potential of such groups, because in low-temperature combustion, they promote chain branching reactions as a process of adding oxygen molecular to large hydrocarbon radicals, i.e. $R + O_2 = RO_2$. (5)
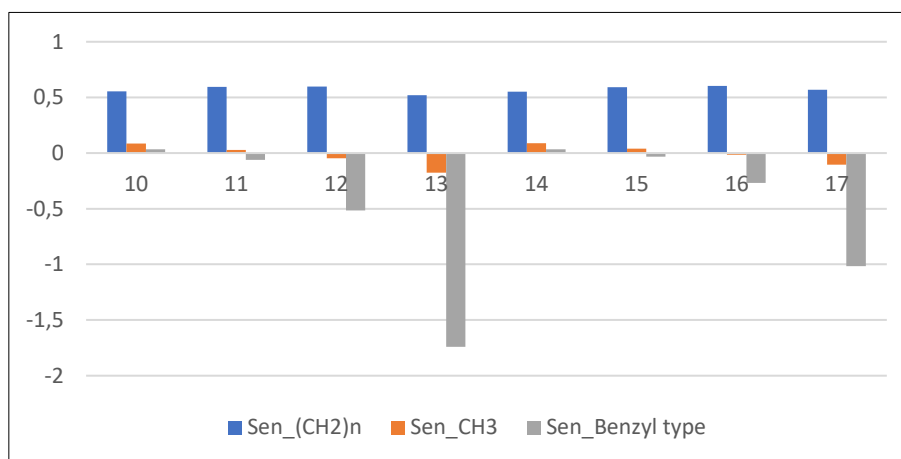
Figure 15: Sensitivity analysis of each chemical functional group regarding mixtures including n-heptane and toluene.

Adjacent CH_2 groups present in alkanes and aromatic side chains were found to play the most significant role in ignition propensity (chemical potential), followed by those associated with CH_3 and benzyl-type groups. The abundance of the CH_3 and the benzyl-type functionalities both influence the reactivity negatively. The methylene functionality is shown to be most influential on ignition delay predictions, especially at low temperatures. Both the methyl and benzyl functionalities contribute negatively to ignition delay. The surrogate-fuel kinetic model analysis replicates the behaviors of the QSPR functional group model. This supports that both respond in a manner consistent with the underlying fundamental physics.

5.2 QSPR regression model application for RON and MON

It is well known that the RON and MON values are utilized for gasoline characterization in terms of Knock Resistance. Our experiments confirm with previous results, that measuring the DCN value of mixture is possible by statistical analysis and the regression model represents an innovative alternative to identify the chemical and physical characterization of fuel blends. The formulation can be adapted to prediction RON and MON value of fuels as well. The **Table 9** includes different mixtures and their RON and MON values were taken from the paper written by Yuan et al. (71), who have been presented a similar method to ours, for correlating the octane numbers of fuel blends, and they applied this to the research of toluene reference fuels blended with ethanol. Remaining consistent to our previous work, only those mixtures were here considered, that include n-heptane, iso-octane and toluene in a certain proportion.

Table 9: Correlation development data of RON and MON of mixtures

No.	nC_7H_{16} (mol%)	nC_7H_{16} (vol%)	iC_8H_{18} (mol%)	iC_8H_{18} (vol%)	C_7H_8 (mol%)	C_7H_8 (vol%)	RON	MON	Ref.
1	27.2	34	0	0	72.8	66	85.2	74.8	(71)
2	23.7	30	0	0	76.3	70	89.3	78.2	(71)
3	20.3	26	0	0	79.7	74	93.4	81.5	(71)
4	16	20.8	0	0	84	79.2	97.7	86.2	(71)
5	20.8	26.6	0	0	79.2	73.4	92.3	80.7	(71)
6	16.5	21	3.5	5	80	74	96.9	85.2	(71)
7	12.6	16	7	10	80.4	74	99.8	88.7	(71)
8	8.7	11	10.5	15	80.8	74	103.3	92.6	(71)
9	4.8	6	14.1	20	81.1	74	107.6	96.6	(71)
10	13	12	66	73	21	15	91	88.4	(71)
11	16	17	45	53	39	30	91.4	86.1	(71)
12	18	20	27	35	55	45	91	83.5	(71)
13	13.5	16.7	12	16.7	74.5	66.7	98	87.4	(71)
14	16.9	16.7	59.9	66.7	23.2	16.7	87	84	(71)
15	10	9.9	65	72.2	25	17.9	93.7	90.3	(71)
16	15	16.5	35	43.5	50	40	93	85.8	(71)
17	13.7	14.7	42.8	51.5	43.5	33.8	93	86.7	(71)
18	9.8	10	56.5	65	33.7	25	95.2	90.5	(71)
19	13	15	27	35	60	50	96.3	87.3	(71)
20	17	16.6	63	69.2	20	14.2	86.6	84.2	(71)
21	17	16.2	69	74.1	14	9.7	85.7	84.6	(71)
22	12.3	13.7	34	42.8	53.7	43.5	96.3	88.3	(71)
23	8.5	8.5	61.3	69.4	30.3	22.1	96.1	91.8	(71)
24	18.1	17.5	64.7	70.5	17.2	12	85.1	83.8	(71)
25	12.4	13.5	39.5	48.4	48.2	38.1	94.8	87.8	(71)
26	19.6	20	50.5	58	29.9	22.1	85.1	81.6	(71)
27	0	0	18.4	26	81.6	74	113	100.8	(71)
28	0	0	39.2	50	60.8	50	110	99.3	(71)
29	0	0	85.2	89.9	14.8	10.1	101.9	–	(71)
30	0	0	60	70	40	30	105	–	(71)
31	0	0	39.1	49.9	60.9	50.1	108.5	–	(71)
32	0	0	18.4	25.9	81.6	74.1	113	–	(71)
33	0	0	6.7	10	93.4	90	115.3	–	(71)

The data on all fuel components is regressed globally to the same set of independent terms based upon the selected functional groups. Following the same calculation strategy used in case of DCN, has led us to the conclusion. Based on experiences we know that using the regression analysis without a_0 constant, the results still follow the physics in a relative way, nonetheless we had taken the $a_0 = 95$ coefficient for RON and MON prediction since the result will be more accurate. Furthermore, using the primary interaction terms from chemical functional group are enough to predict the RON and MON values appropriate. In both case the regression model is performed by three coefficients, which are a_1 $(CH_2)_n$, a_2 (CH_3), a_6 (benzyl-type). The coefficients of RON are: a_1= -17.78, a_2= 0.82, a_6= 18.78. The coefficients of MON are: a_1= -18.13, a_2= 0.95, a_6= 4.67. The **Figure 16** indicate the comparison between the measured and the predicted RON on the left side and the values belonging to MON on the right-side values yielded from the regression. The results are the following: the summarized residue of **2.40** with the R^2 value of 0.997 associated with the RON, while the summarized residue of **4.67** with the R^2 value of 0.9923 regarding MON. Both results can be considered effective.
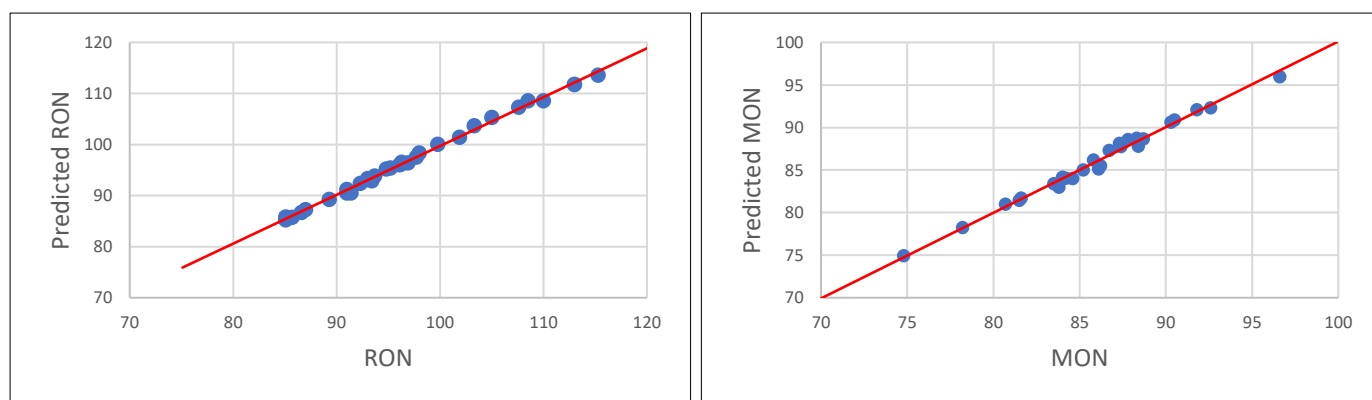
Figure 16: Comparison measured and predicted RON (left) and measured and predicted MON (right)
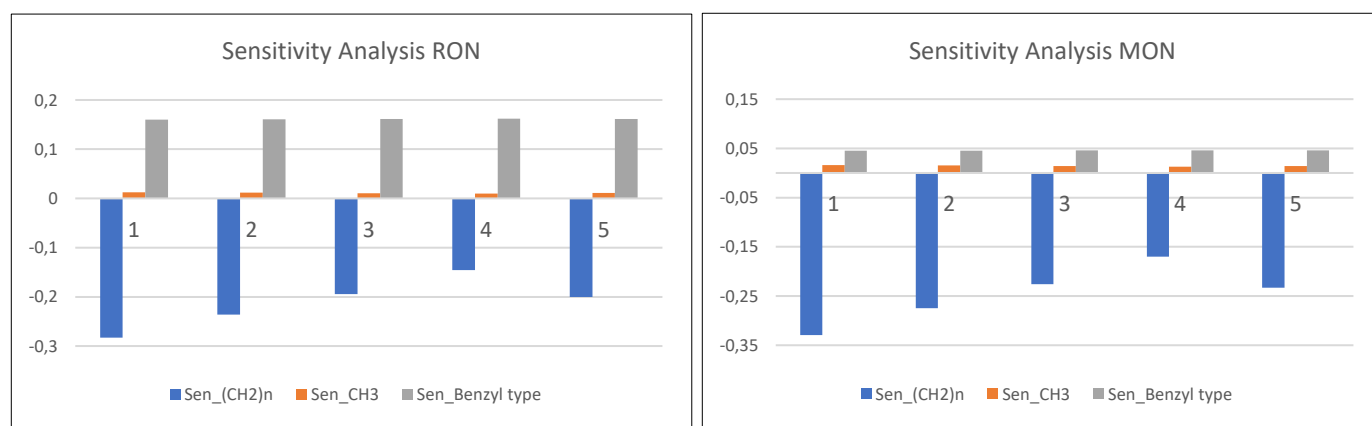
Figure 17: RON (left) and MON (right) sensitivity analysis of each chemical functional group regarding mixtures including n-heptane and toluene.

In Figure 17 the sensitivity analysis for both RON (left) and MON (right), that represents the impact of chemical functional groups of certain mixtures. The mixture number shown on the x-axis and the extent of effect on the y-axis. This helps to represents that $(CH_2)_n$ has the greatest impact on the ignition properties of the mixtures, which is in line with what is known in the field, confirming our physical understanding, and continues to show the validity of this regression analysis, namely the $(CH_2)_n$ has a negative impact on fuel mixture, when we measure its RON and MON value. This linear methylene group if followed by those associated with benzyl-type and CH_3 groups. The abundance of the CH_3 and the benzyl-type functionalities both influence the reactivity positively.

The analysis leads to the following conclusions, that the chemical group additivity and Quantitative Structure Property Relationship models are powerful tools for fundamentally rationalizing which components of a complex multicomponent fuel's chemical structure are most important to the occurrence of any combustion kinetic behavior. The Scheffé's simplex polynomial mathematical modelling can be utilized not only for DCN prediction of mixtures but for forecast of RON and MON as well.

Furthermore, the prediction model can be used for calculating the Octane Sensitivity (OS). To explain the importance of OS a short background information is provided in the next section.

The assessment of auto-ignition propensity in SI engines is a difficult project because the auto-ignition process heavily depends on the fuel nature and on the operating conditions too. As we know, to assist classify the fuels two standardized test methods have been established for normal spark-ignition operation, these are the RON and MON values. However, the RON and MON values only ensure two approximative classifications in terms of auto-ignition propensity that is not good enough under specific engine conditions. Researcher found that RON and MON are not good enough to determine what are the fuel chemical property and the RON or MON alone cannot describe the knocking behavior of a real transportation fuel in a SI engine adequately. Nonetheless, these index-numbers can still be applied as a reference if the impacts of the fuel nature and the operating circumstances are separated out. For a proper distinction of these impacts was introduced the Octane Index (OI). This OI gives a more precise classification of engine performances when results from different engines and different fuels are considered, which cannot be achieved only based off the RON and MON values, the formula is the following: (35)

$$OI = (1 - k) * RON + k * MON = RON - k * OS \qquad \text{Equation 16 (35)}$$

The Octane Sensitivity can be calculated by *OS = RON - MON*. Gasoline would regularly have a RON value in the range of 95-100 based on European prescription, a MON in the range of 85-93, and the sensitivity of about OS = 10. **Table 9** indicates that the RON and MON of mixtures are very small, that do not contain toluene and in this case those two measures are almost identical. When we start to add toluene for mixture then the numbers are starting to increase. The reason from our analysis says since we have large octane sensitivity the fuel is starting to have more aromatic.

The 'k' symbol is an empirically derived constant, that depends on the engine design and the operating conditions, where the 'k' has a value of 1 for the MON test and 0 for the RON test. If the temperatures for a certain pressure is higher than MON, the factor can be larger than 1, and, more importantly, if conditions are 'lower' than at the RON test, then this can be below 0. In other words, the 'k' gets lower as the temperature of the compressed unburnt gas decreases at a given pressure in the engine and it will be a negative number since this temperature is below than in the RON test. The development missions for SI engines have for long been raised pressures and reduced temperatures to increase the power density and efficiency of engines. The downsizing process and using turbocharging move values of 'k' to negative and so beyond RON. Several studies confirm that in conditions in which knock occurs, the negative 'k' values are prevalent in most advanced downsized turbocharged car engines. This implies that the MON test has become less relevant over time. (35)

Many researchers are debating the true importance of OI, as there are plenty of unanswered questions about it. Therefore, for now, this issue is a black box in this area of research.

5.3 Interaction between DCN, RON and MON

We have been used the quantitative structure-property relationship concept in our work so far to predict the DCN, RON and MON values of real liquid fuel mixtures. In the QSPR, the "quantitative" means the amount of each chemical composition, the "structure" represents the different chemical functional groups and the "property" indicates the measured reference DCN, RON or MON value.

If enough data are available for calibration, a new expression can be constructed on the basis of quantitative property-property relationship (QPPR) to predict the RON and MON based on DCN and vice-versa. With other words, the molecule structure of the fuel sample does not have to be known to be able to predict DCN and/or RON, MON measurements because it is enough, if one of them is known as initial data. Besides the DCN values for the fuel blends in **Table 5**, the RON and MON values were also predicted using the standard QSPR model. In the **Figure 18** can see the correlation between predicted DCN and RON. On combining this result, we deduce from the trend that RON and DCN measurements follow the same way. This means, between them does exist a strong relationship and taken the DCN, the RON indicator value can be predicted very well. On the other hand, the DCN does not correlate well to MON as it can be seen in the **Figure 19**, where the correlation between predicted DCN and MON is drawn. From the function's equation belonging to the trend line based on the measurement points we can build our own equation. This means more specifically, the RON values can be predicted based on DCN by using **Equation 17**, and the MON values can be predicted based on DCN by using **Equation 18**. And so, the QPPR model is formed.
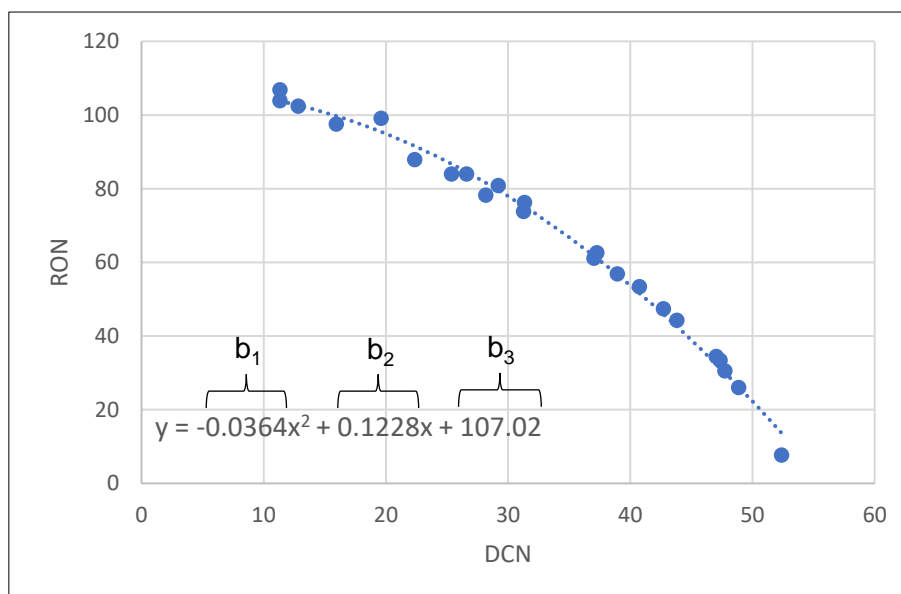
Figure 18: Correlation between predicted DCN and predicted RON

$$RON_{predicted} = b_1 * DCN_{ref.}^2 + b_2 * DCN_{ref.} + b_3 \qquad \text{Equation 17}$$
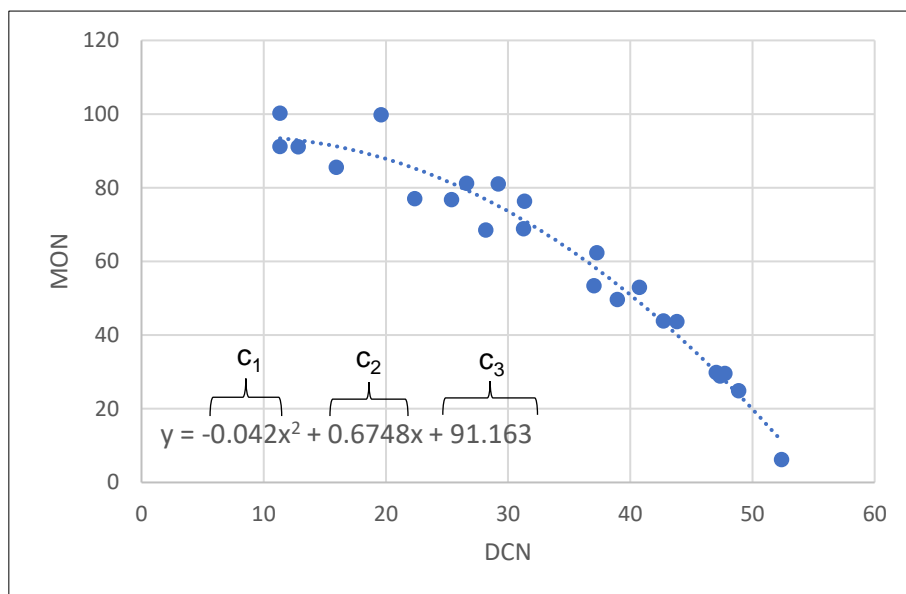
Figure 19: Correlation between predicted DCN and predicted MON

$$MON_{predicted} = c_1 * DCN_{ref.}^2 + c_2 * DCN_{ref.} + c_3 \qquad \text{Equation 18}$$

Further investigate the significant diversion which can be experienced between the predicted MON values measured by the two different models, their absolute difference was illustrated in the **Figure 20**. The red marked values differ with more than five order of magnitude. Based on the diagram, the trend of points position lets us conclude, the more n-heptane concentration has the mixture, the less the difference between the values measured by the two methods.
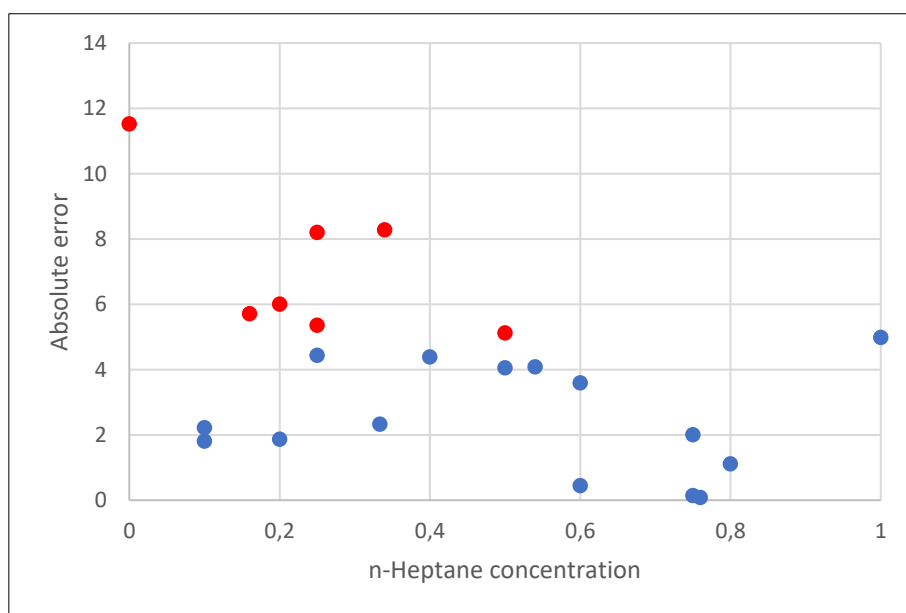
Figure 20: Uncertainty between MON number measured by QSPR and QPPR

Knowing, that n-heptane promotes the ignition and the more the n-heptane has the mixture the faster its ignition and shorter its ignition delay time. Based on our assumption, a better correlation may be achieved, once DCN measurements having NO in the background, since NO promotes the ignition. This hypothesis is also supported by Foucher and his colleague's treatise, who have investigated ignition enhancement by NO/NO_2 gas addition in the HCCI combustion engine of n-heptane, iso-octane, toluene, and their blends. Their work has pointed out that both the low-temperature and the high-temperature ignition stages are promoted by adding NO. Results provided the observation that NO increasing dramatically decreases the ignition delay time by promoting OH formation. (55) Presumably, when n-heptane dominated fuel blend is combusted in NO enriched environment, probably it cannot observe significant change in the combustion. On the other hand, the ignition of low concentrated n-heptane blends can be accelerated spectacularly by increasing NO concentration of the air.

Based on speculation, the DCN, RON, and MON measurements are all affected more by NO chemistry. However, the largest impact can reflect in MON measurement, since during MON measurement condition more NO_x is formed. This can be substantiated in two ways. The first is when the temperature of the combustion is investigated.

The thermodynamic process of mixture can be examined in isentropic process, there is no heat conversion Q beyond the system boundary (Q = 0). Under this condition, an isentropic change of state must obviously take place in an adiabatic system. Basically, no system is perfectly thermally insulated, so that an isentropic change of state can only be approximate. But even if systems are not particularly well insulated against heat flows, under certain conditions thermodynamic processes can be regarded as approximately isentropic. For example, when the changes in state occur so quickly that the system does not have time to exchange heat with the environment. The compression and expansion processes taking place in internal combustion engines are very often considered to be isentropic. Isentropic processes are therefore of great importance for simplified considerations of rapidly occurring processes. An isentropic process can therefore be implemented approximately in a cylinder with a movable piston, the cylinder walls of which are provided with insulating material and by allowing the change of state to take place very quickly. If the gas is compressed suddenly, the pressure is initially increased due to the reduction in volume. However, this also entails an increase in the temperature, since the sudden movement of the piston gives the gas particles an additional impulse when they hit the piston surface, thereby increasing their speed. (72)

A clear connection between two state variables can be derived if, in addition to the general gas equation, the special condition for the isentropic process with Q = 0 is also taken into account. After more complex mathematical derivation, a combination of both equations ultimately results in the following state connections in an isentropic process:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{k-1} \qquad \text{Equation 19 (72)}$$

where, the 'k' is the ratio of specific heats value. The standard values of 'k' used for air at 300K is 1.4. This value are functions of temperature, and therefore it can obtain significant errors in the extremely high temperature range in internal combustion engines. However, it was found that choosing the average values of 'k' gives results with reasonable accuracy, within around 1%. (62)

Knowing the initial data of measurement method of RON (42) and MON (43) standards, and using the **Equation 19**, the temperature of air can be calculated after compression, which is 590 K in case of RON, while 770 K by MON. Besides the inlet air temperature by the MON measurement is higher than by the RON measurement, the calculation allows the conclusion, that the temperature of fuel/air mixture after the compression is higher for MON measurement, which leads that the post-combustion temperature achieves higher values. And it will result higher temperature after the combustion, thus it might be producing more NO through the thermal NO_x formation mechanism. The nitrogen dioxide, NO_2, created in an SI engine is small amount compared to NO. The maximum NO_2 concentrations are reaching about 2% of the NO concentration. This indicates the necessity of NO addition, when MON is measured. Furthermore, the higher temperature results the fact, that the octane number received by the MON measurement is lower than the octane number received by the RON measurement because it is performed at lower compression ratios in case of the MON method. Depending on the design of the fuel, the MON rating value is with 8 to 12 points lower than the RON.

The other way to certify the more NO_x formulation during MON test can relate to the engine speed. The research motor runs with 600 rpm (42) in case of RON, where the compression time is 0.05 sec, while MON is tested with 900 rpm (43), so the compression time is 0.033 sec. The MON measurement is measured by higher RPM, and so the combustion does not have time to combust the mixture so well, and it might result in a larger amount of burned gas remaining in the engine cylinder, which is playing more impact in MON measurements. MON measurements are affected by the residue content of NO, which was not reflected in DCN our measurements, because the IQT was used scientific air without NO. Therefore, there is a higher probability for MON measurement to be more affected by NO chemistry interaction with fuel chemistry.

From these reasons, it was necessary to build the new gas supply system for the IQT apparatus, to be capable to add NO concentrated gas for the combustion, representing the real conditions of engine operation. There will be artificially added NO residual in DCN measurements, which probably seem similar to that in RON measurement, based on the fact that DCN correlates well with RON measurements. However, in the case of MON, the MON value might be well correlated with DCN, if so, it would confirm the hypothesis above.

5.4 Revision of current international fuel quality standards

One advantage of the prediction model is that numerous fuel mixtures can be measured by cost-effective manner. Hundreds of thousands of measurements can be performed in some seconds, and so many correlations and conclusions can be described based on the results. For example, it is worth looking at, how effectively can the today used fuel quality indicators characterize the chemical structure of fuels. Furthermore, it is worth paying attention to the correlations between the different quality indicator tools, if there exist.

Many people think that the quality of European gasoline is better than that US. This misunderstanding is founded based on the fact that the rating number of fuels, that can be read in the tank station is lower in the US than in Europe, but generally saying, there is no difference between the fuels regarding the quality. US and Europe calculate the quality of commercial fuel in a different way which makes US fuel look like it has a lower rating but, in the reality, they have got the same rating. Europe standard only shows the RON rating which has a higher value than the MON rating, while US standard shows the average value of the RON and MON rating, which called the Anti-Knock Index (AKI). The AKI value is calculated by the average of RON and MON. The AKI is sometimes also called pump octane number (PON), which is the result of try to find a road octane number that would provide similar conditions to the real operation of vehicles on the road. The AKI is used around the world, for example in the USA, Mexico or in Canada, while RON is applied in Europe, Australia and in Asia.

Based on the up to date standard in the EU, the fuel specifications require a minimum rating of RON 95 for regular, RON 98 for midgrade, and RON 100 for premium quality. In the US, gasoline typically has octane ratings of AKI 87 for regular, AKI 88-90 for midgrade, and AKI 91-94 for premium quality. In the further examinations, the regular fuel quality of both standards was considered. Depending on the design of the fuel, the MON of gasoline is about 8 to 12 octane rates lower than the RON. Both the EU and the US have minimum MON-requirements for commercial fuels. The minimum value of MON is 85 considering RON 95.
For this experiment, 5151 possible mixtures were created in a sequence, that all possible mole fraction proportion of n-heptane was listed from zero to 100 in steps of the order of 0.01. The iso-octane molar fractions are added belonging to each n-heptane fraction from zero to 100 in steps of the order of 0.01. The rest of the mixtures is implemented with toluene. Some mixture examples can see on the **Table 10** with their functional group distributions and their predicted indicator values such as RON, MON, AKI and OS.

Table 10: Examined mixtures and their predicted indicator values regarding RON, MON, AKI and OS

Mix #	Mol %			Functional Group Distribution						Indicator Values			
	nC_7H_{16}	iC_8H_{18}	C_7H_8	$(CH_2)_n$	CH_3	CH_2	CH	C	Benzyl-type	RON	MON	AKI	OS
1	0	0	1	0	1	0	0	0	1	114.61	100.63	107.62	13.98
2	0	0.01	0.99	0	1.04	0.01	0.01	0.01	0.99	114.46	100.62	107.54	13.84
3	0	0.02	0.98	0	1.08	0.02	0.02	0.02	0.98	114.30	100.61	107.46	13.69
4	0	0.03	0.97	0	1.12	0.03	0.03	0.03	0.97	114.15	100.60	107.37	13.54
5	0	0.04	0.96	0	1.16	0.04	0.04	0.04	0.96	113.99	100.59	107.29	13.40
2226	0.25	0	0.75	1.25	1.25	0	0	0	0.75	87.89	77.02	82.46	10.86
2227	0.25	0.01	0.74	1.25	1.29	0.01	0.01	0.01	0.74	87.73	77.02	82.37	10.72
2228	0.25	0.02	0.73	1.25	1.33	0.02	0.02	0.02	0.73	87.58	77.01	82.29	10.57
2229	0.25	0.03	0.72	1.25	1.37	0.03	0.03	0.03	0.72	87.42	77.00	82.21	10.42
2230	0.25	0.04	0.71	1.25	1.41	0.04	0.04	0.04	0.71	87.27	76.99	82.13	10.28
3826	0.5	0	0.5	2.5	1.5	0	0	0	0.5	61.16	53.42	57.29	7.74
3827	0.5	0.01	0.49	2.5	1.54	0.01	0.01	0.01	0.49	61.01	53.41	57.21	7.60
3828	0.5	0.02	0.48	2.5	1.58	0.02	0.02	0.02	0.48	60.85	53.40	57.13	7.45
3829	0.5	0.03	0.47	2.5	1.62	0.03	0.03	0.03	0.47	60.70	53.40	57.05	7.30
3830	0.5	0.04	0.46	2.5	1.66	0.04	0.04	0.04	0.46	60.54	53.39	56.97	7.16
4801	0.75	0	0.25	3.75	1.75	0	0	0	0.25	34.44	29.82	32.13	4.62
4802	0.75	0.01	0.24	3.75	1.79	0.01	0.01	0.01	0.24	34.28	29.81	32.05	4.47
4803	0.75	0.02	0.23	3.75	1.83	0.02	0.02	0.02	0.23	34.13	29.80	31.97	4.33
4804	0.75	0.03	0.22	3.75	1.87	0.03	0.03	0.03	0.22	33.97	29.79	31.88	4.18
4805	0.75	0.04	0.21	3.75	1.91	0.04	0.04	0.04	0.21	33.82	29.78	31.80	4.04
5147	0.98	0.01	0.01	4.9	2.02	0.01	0.01	0.01	0.01	9.70	8.09	8.90	1.60
5148	0.98	0.02	0	4.9	2.06	0.02	0.02	0.02	0	9.54	8.09	8.82	1.46
5149	0.99	0	0.01	4.95	1.99	0	0	0	0.01	8.78	7.16	7.97	1.63
5150	0.99	0.01	0	4.95	2.03	0.01	0.01	0.01	0	8.63	7.15	7.89	1.48
5151	1	0	0	5	2	0	0	0	0	7.72	6.22	6.97	1.50

The same coefficients were used for the prediction of indicator values, that were expounded in the **Chapter 5.2**.

The resulting mixtures must be narrowed according to the different standards. The criterion of RON is for instance, that the result of mixture must be in 95 ± 1, this criterion is 85 ± 1 for MON and for AKI is 87 ± 1. Considering the regular quality of fuel, the number of possible mixtures is 180 in case of RON, which is 184 for MON and 173 for AKI.

Based on the chemical function distribution of mixture we can calculate the constraining ability of RON, MON, AKI and RON & MON separately regarding each functional group of the possible mixtures, which can be determined by the Coefficient of Variation (CV). This indicator is used, if there is nothing to know about the data other than the mean. This is one way to describe the relative greatness of the standard deviation is dividing it by the mean. And so, the CV gives us the benefit to see that even a lower standard deviation does not mean fewer variable data and it is a simple method to calculate and helps a lot with perception of relative variability. The results are plotted on the **Figure 21** and the inference is the following:
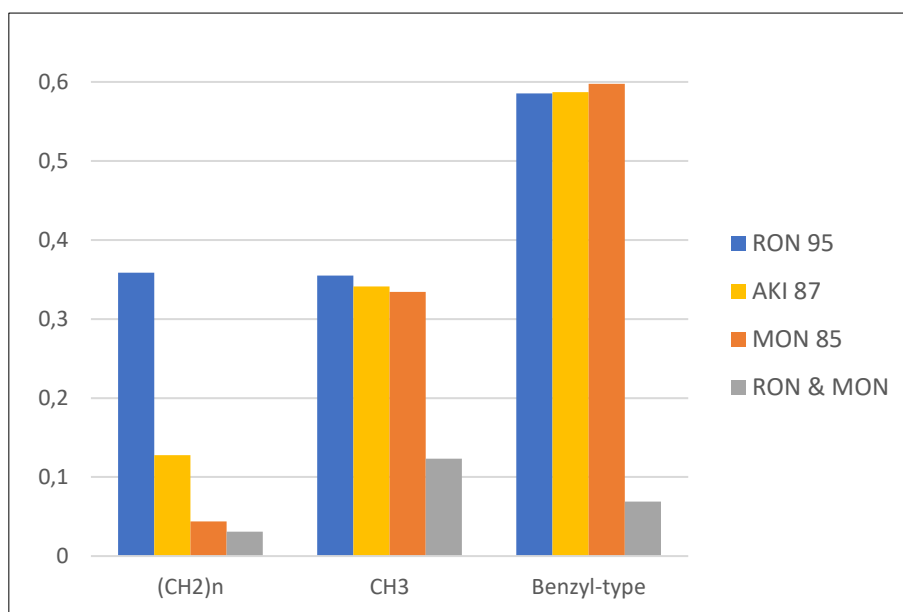
Figure 21: Constraining ability of RON, MON, AKI and RON & MON in terms of functional group distribution by $(CH_2)_n$, CH_3 and Benzyl-type

In case of RON, MON, and AKI standard, there is a lot of variation in benzyl-type functional group distribution. Neither can constrain the benzyl-type better than the other. The AKI American standard can constrain the $(CH_2)_n$ slightly better than RON European standard. However, summarized their results, both the US and EU standard cannot effectively constrain the relevant chemical structure of fuel. The MON is more effectively constrain the molecular structure of $(CH_2)_n$, then the RON and AKI. Very interesting observation is, when RON and MON are used simultaneously, $(CH_2)_n$, CH_3, and benzyl-type are well constrained. One research question is also why using both RON and MON together can constrain CH_3 and benzyl-type so effectively, if RON and MON cannot constrain them separately? Possible answers can be explained by further statistical analysis. How it was mentioned before, the Octane Sensitivity is calculated by subtraction of RON and MON, accordingly the OS is indirectly incorporated, when the data are analyzed. This means, that the OS might help us to understand the phenomena in question. To do that it is needed to find out what is the sensitivity of OS with chemical functional groups. The function of RON is f(CFG) and MON is g(CFG) and so, the OS can be derived as RON-MON= f(CFG)-g(CFG). From here we can easily calculate the coefficient of OS, which are a_1= 0.352, a_2= -0.13, a_6= 14.11. It shows up right away, that while the a_1 and a_2 is a very low value, the a_6, which is the benzyl-type has a high value. Consequently, it can be stated, that the OS is the function of only the benzyl-type. We can derive the sensitivity analysis of OS to each functional group, for the mixtures found in RON & MON matching mixtures. It is not surprising, after run the sensitivity analysis, the values of $(CH_2)_n$, CH_3 and benzyl-type are significant higher in case of OS, compare to values RON and MON. This indicates that by OS, all three functional group has a high impact in the results.

The promotion of changes in fuel technology, driven by the necessity to improve the efficiency of the SI engine is announced in various studies, written by Kalghatgi. (73) The energy demand transportation will have an intense impact on the specifications, properties, and production of future fuels and their alternatives. He has been emphasized frequently, that the current fuel specifications everywhere in the world should assume that MON consent to the antiknock quality and the fuel quality standards should be revised as the mismatch with engine requirements widens. The scientist's review highlighted a list of issues for combustion science that are important to gasoline fuel and SI engine development. He also recognized that neither RON nor MON characterizes the autoignition quality of gasoline satisfactorily. And he promotes the introduction of octane index officially, that can truly resistance to autoignition of real fuels. OI indicates the octane number of the PRF that meets the autoignition behavior of the fuel in a certain test under consideration. (73) The interested reader can find more detail about the OI and OS in chapter 5.2. Our experiments support Kalghatgi's assumption and we also promote his intention to use OI and the directly incorporated OS for measurement of fuel quality in long term instead of today utilized standards since the EU standard only use RON and this cannot constrain the chemical compositions in gasoline. The US standard seems to be slightly better since it utilized the average of RON and MON, but based on the analysis it can see, that neither the US standard can constrain the chemical compositions in gasoline properly.

5.5 Ignition propensity in low temperature combustion

In this current paper so far, we have done a QSPR regression modeling for investigation and prediction of DCN, RON and MON measurements as the first step. Due to this analysis, we could get an insight into the ignition propensities of fuel mixtures, defined by those three numbers, that are controlled by functional group distribution particularly $(CH_2)_n$, CH_3, CH_2, C, and benzyl-type, and their interaction terms. In the second step, we have been investigated the relationship among those three numbers. We have found, that between DCN and RON does exist a strong relationship, on the other hand, between DCN and MON does not obtain this interaction so efficiently. However, this kind of approach, that we did to find the correlation between the measurements is not good enough, since it does take into account only the distribution of chemical functional groups of the component in the mixtures. The Ignition Delay Time from Ignition Quality Tester is not only the consequence of chemical structure and chemical kinetics, but it depends on the spray injection phenomena, greatness of atomization and mixing quality as well.

In this subsection, we would like to examine the relationship among those three numbers considering more fundamental approach, which is the Ignition Delay Time of the homogenous fuel-air mixture and stoichiometric conditions. From our experience, one of the most important condition is the temperature in terms of combustion. The ignition temperature can be regulated well, and so the combustion can be controlled. Since we can identify, which is the temperature condition of each measurement in homogeneous IDT, that enables us to look at more fundamental detail, which we cannot perform with only RON, MON, DCN measurement. The benefit of this approach is that the temperature of the analysis with the detailed chemical

kinetic model can be precisely determined if the details of chemical kinetics in RON, MON, DCN measurement is required to be understood because at that temperature it does have a strong, linear correlation to RON, MON or DCN.

One initiative investigation of homogenous combustion phenomena made by Karla et al. (50) and her research fellows. A fundamental approach has done in Karla's study to investigate the chemical functional group approach to verify, that the low-dimensional descriptors are fundamentally applicable in the prognostication of global combustion behavior, as characterized by homogeneous shock ignition delay times, measured in a shock tube. To investigate whether such descriptors can properly follow the impact of these functionalities on ignition delay, a similar QSPR regression analysis was performed, like in this paper, with the formulation of analytical models based on an Arrhenius-type description. However, they did not utilize the same chemical functional groups, as we did in this paper. They did not different differentiate CH_2 from $(CH_2)_n$ and so the CH_2, CH_3, and benzyl-type were used as three key chemical functional groups, where the CH_2 represents the n-alkyl, the CH_3 imitates the iso-alkyl, and benzyl-type means the aromatic functionalities, respectively. The models are performed using literature measurements of reflected shock IDTs for stoichiometric fuel-air mixtures at 20 atm. The prediction analyses of constant-volume adiabatic ID applying detailed chemical kinetic models show the importance of n-alkyl, iso-alkyl, and aromatic functional groups in both, the low and high-temperature region. For the QSPR regression models applied sensitivity analyses show that the CH_2 functional group controls mostly chemical kinetic behaviors in low-temperature regions, and its importance decreases as the temperature decreases. The chemical kinetic affections of CH_3 and benzyl-type functional groups have no significant change neither in high nor in the low-temperature region. But generally, it can be said, that the importance of all of them diminishes as temperature increases. (50)

It was found that the IDT of all fuel compounds is typically dependent on temperature because the kinetic oxidative behavior of large alkyl radicals tends to follow a non-linear trend. The typical ignition delay behaviors can be diminished by three main factors, which are the branching rearrangements by alkyl-peroxy radicals, the negative temperature coefficient region, and the Arrhenius phenomena in the high-temperature region. Two analytical models were formulated including the above-mentioned main factors for both high and low-temperature properties. These formulations are described by Scheffé simplex-polynomial with a natural logarithm (L_n) for IDTs and the equations consider the temperature variances of each functional group mass fraction. The **Equation 20** bellow can be utilized for the high-temperature condition (≥1000 K). (50)

$$Ln(\tau_{IG})_{high\,T} \cong a_0 + a_1\frac{T_r}{T} + a_2 Y_{CH_3} + a_3 Y_{CH_2} + a_4 Y_{BZY} + a_5 Y_{CH_3}\frac{T_r}{T} + a_6 Y_{CH_2}$$
$$+ a_7 Y_{BZY}\frac{T_r}{T}$$

Equation 20 (50)

where the T_r = (1200 K) is added as a correction factor to ensure that the temperature to be consequent when the mass fraction in functional groups is using. **Equation 21** is based on a cubic polynomial formulation for low-NTC-intermediate temperature conditions (≤1000 K). (50)

$$Ln(\tau_{IG})_{low\ T} \cong a_0 + a_1 \frac{T_r}{T} + a_2 \left(\frac{T_r}{T}\right)^2 + a_3 \left(\frac{T_r}{T}\right)^3 + a_4 Y_{CH_3} + a_5 Y_{CH_2} + a_6 Y_{BZY}$$
$$+ a_7 Y_{CH_3} \frac{T_r}{T} + a_8 Y_{CH_2} \frac{T_r}{T} + a_9 Y_{BZY} \frac{T_r}{T}$$

Equation 21 (50)

In the equations used molecular fragment composition of real fuel was determined by Nuclear Magnetic Resonance (NMR) spectroscopy. The NMR spectrum can distinguish molecule types of ^{1}H or ^{13}C nuclei within a given fuel mixture by resonance frequencies. Both the ^{1}H and ^{13}C can be accurately identified and quantified specific hydrogen and carbon types respectively. This allows the classification and quantification of small chemical groups such as α-methyl (CH_3), and β-, γ-, δ-, and ε-methylenes (CH_2), etc. Not just small but larger structural groups can be identified that have a significant impact on combustion behavior. These are for example the benzyl groups, polyethylene, cyclo and/or branched paraffinic groups. The operating principle is the following: certain atomic nuclei exhibit nuclear spin and we can take advantage of that nuclear spin by subjecting a molecule to an external magnetic field. A magnetic field is induced, then we irradiate with light and we gather information about how the light interacts with that compounds. For instance, a resonance comes from CH_3 environment based on a ^{1}H or ^{13}C nucleus, it will indicate a different resonance frequency compare to a ^{1}H or ^{13}C nucleus in a CH_2 environment. The resonances that come from similar chemical functionalities will show up within narrow ranges of the spectrum, and so it is easy to differentiate each chemical group. Taken this advantage, NMR spectroscopy can ensure all the constructive and quantitative information to characterize fuels regarding their chemical functionalities. NMR analysis differs from other conventional molecular analysis methods, for example, gas chromatography, etc., but it can provide at least so reliable molecular composition estimation than the other tools. According to the opinion of scientists in combustion society, the NMR is a very promising tool, that lends them to relatively convenient, and fully quantitative analysis of fuel mixture structure.
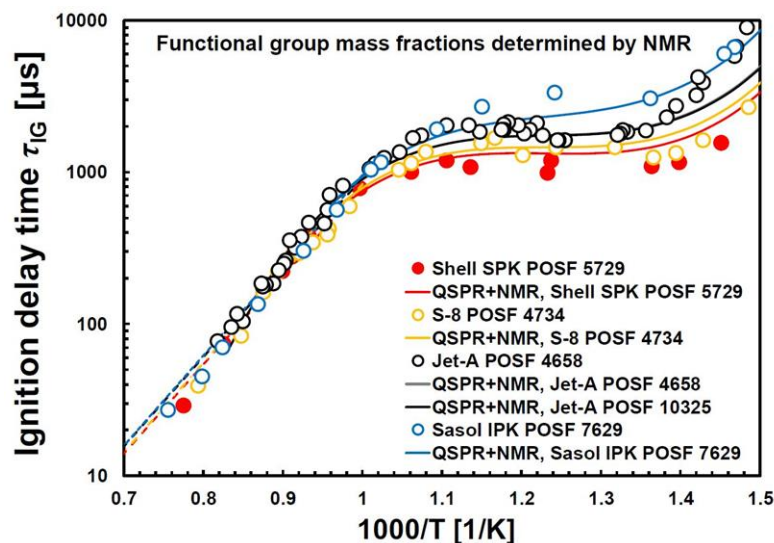
Figure 22: Comparison of real measured and QSPR model predicted values based on the molecular fragment compositions measured by NMR spectroscopy for four selected real jet fuels

From Karla's work, the success of the approach is shown in **Figure 22**. The QSPR formulation for prediction of the ignition delay time given in **Equation 20** and **Equation 21** was used based on the molecular fragment compositions measured by NMR spectroscopy for four selected kerosene range fuels. The result shows, that the predictions of ignition delay of the fuels show very high fidelity compare to the real measured values. In the diagram, the real measurements are displayed as points and the result of prediction is shown as a line. Summarized the result in both the low and high-temperature regions, the model can reproduce the measurements well with a fidelity of (R^2) of > 0.95, where, the R^2 means to the fidelity of the prediction model to the complete performed database.

In this chapter, we are going to use the prediction model for the low temperature, since the condition in the IQT reflects the low-temperature combustion phenomena. Comparing to Karla's work, one significant change will be, that instead of using the mass fraction of each functional group, we will consider the number-density of each functional group since we did this previously in this whole study.

For all mixtures, found in **Table 10**, was calculated the mass fraction of each functional group, consisting of each mixture. We can apply the above-mentioned **Equation 21** for the mixtures, using the QSPR regression coefficients for low temperature analytical models, see in the **Table 11**. For the temperature can be chosen a random number, before we optimize it.

Table 11: QSPR regression coefficients for low temperature analytical models. (50)

a_i or a_{ij}	Value	a_i or a_{ij}	Value
a_0	-86.146	a_5	1.952
a_1	189.141	a_6	0
a_2	-127.204	a_7	0.873
a_3	28.699	a_8	-2.308
a_4	-1.245	a_9	0.479

As we know from **Chapter 5.3** already, between DCN and RON (see on the **Figure 18**), and between DCN and MON (see on the **Figure 19**) does exist a linear relationship. Furthermore, if we observe the data trends on that two diagrams, we can state that between RON and MON does exist a linear relationship as well. Therefore, to find the optimal temperature, so that the DCN value has a linear relationship to the homogenous ignition delay time, a statistical model must be used, that can tell us the linear relationship between the two variables. Typically, if two measurements must be compared in terms of their grade of linear relationship, the Pearson's R correlation form can be used. The Pearson correlation is the most common measure of correlation. Pearson's R measured the strength of the linear relationship between two variables. The value of Pearson's is always between -1 and 1. If the r = 1.0 means, that we have a perfect positive relationship, and as x increases, y increases in exactly the same way. When the r = -1.0, the opposite is true, and as x increases, y decreases and this means a perfect negative relationship. If r = 0 means that among the data, it cannot identify any relationship, just have some random points and they do not seem related in any way, and it

makes to impossible to draw a line through that. We can obtain the R^2 to catch the result in percentage, by squaring the result of correlation.

The optimal temperature can be calculated by Excel Solver, in the form, that the R^2 must be maximized, while the temperature can vary under the condition that the temperature must be greater than 320 K. We did the same optimization calculation for DCN, RON, MON and OS as well. The results are the following: the temperature, where the DCN measurements should be performed is 592 K, because it has the strongest relationship to the homogenous IDT at this temperature, with an uncertainty of R^2=0.93. In case of RON, the temperature should be 635 K (R^2=0.83), the temperature of MON should be 601 K (R^2=0.74), and finally the temperature of OS should be 1340 K (R^2=0.99). The results explain that RON needs a higher temperature than MON to have better correlation. And comparing the DCN to MON, the temperature of DCN is lower than MON.
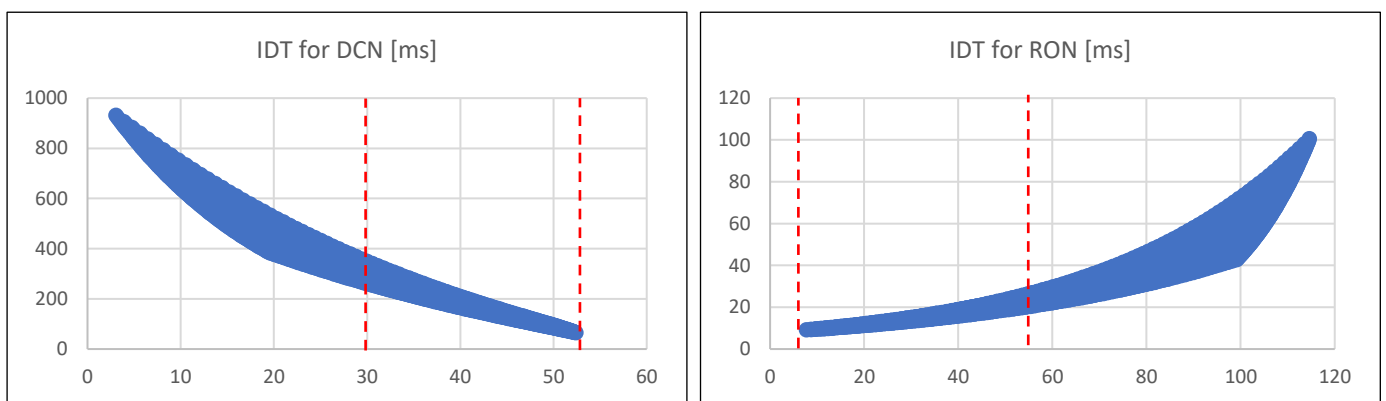
Figure 23: Relationship between homogeneous IDT-DCN (left) and homogeneous IDT-RON (right)
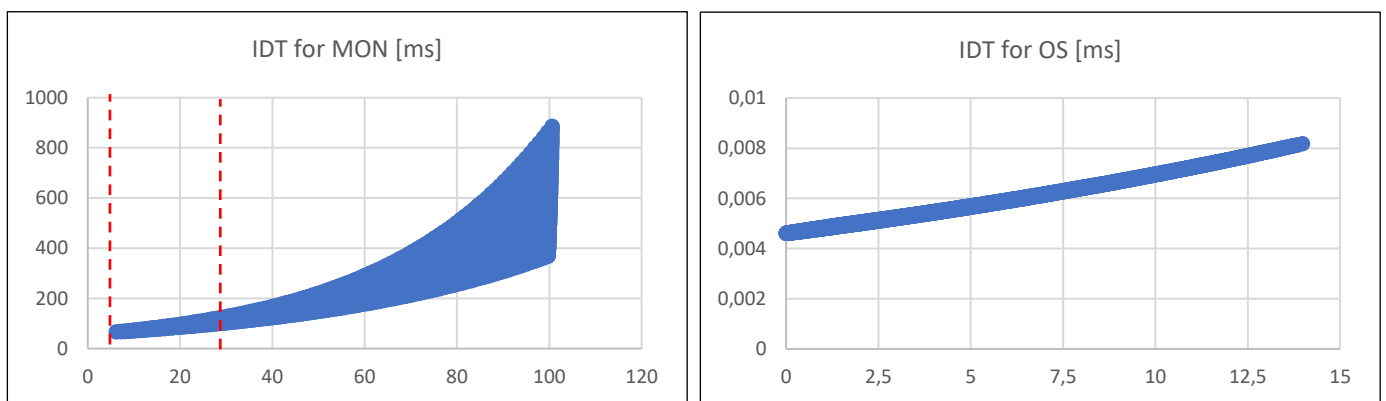
Figure 24: Relationship between homogeneous IDT-MON (left) and homogeneous IDT-OS (right)

Taken in consideration the optimal temperature of the different measurements, the correlation between the DCN, RON, MON, OS and homogenous shock tube IDT can be seen on the **Figure 23** and **Figure 24**. In the **Figure 23** left side can be seen, that DCN correlates with homogenous IDT quite well, if not the entire DCN measurements are investigated. Typically,

the DCN is good between 30 and 53 measurements. It means, that DCN has strong relationship to chemical properties within large range of DCN variation, like practical fuels. Considering volatility of RON and MON values in gasoline market, where the typically octane numbers vary from 70 to 100, in that range we have quite significant deviation (**Figure 23** right and **Figure 24** left side). This is exactly the range, where RON and MON cannot strongly constrain the chemical property of the fuel. Based on the results, the RON can constrain the chemical property of fuel only in the range between 0 and 56. And it becomes more substantial for MON. The dependency to the chemical reactivity defined by homogenous shock tube IDT from MON is not great compare to RON. However, the relationship the RON and DCN and their trends are quite similar. Note, that in both case of RON and MON the IDT is extremely sensible to the temperature changing. Just a small change of the temperature can cause a large deviation in ignition delay time. An interesting phenomenon can be seen by the Octane Sensitivity in **Figure 24** right side. It has a very strong linear relationship to homogenous IDT, however at a very high temperature. If we consider the OS at low temperature range, the correlation loses its strong constraining ability, and it becomes much looser and the deviation going to be larger.

The results of the analysis are very instructive. We have had the presupposition, that we can find a certain temperature for DCN, RON and MON, where they have a strong relationship to the homogenous ignition delay time. And, at that temperature, they can constrain the chemical property of the fuel. Nevertheless, this exact temperature does not exist by none of them. We can find a certain temperature for them though, but they do not follow a perfect linear relationship. This allows us to say, that the OS is not directly related to ignition delay time, and chemical potential of fuel in low temperature region. It is capable to define only the sensitivity of change of the chemical functional group distribution on the fuel, especially the amount of aromatics, as we have seen in the **Chapter 5.4**.

Besides the investigation of the relationship of the chemical property of DCN, RON and MON measurements, it is reasonable to investigate the relationship's grade of the physical property of the three measurements. The physical property of the mixture can be represented by the molecular weight. And so, the relationship between the MW and the DCN, RON, MON was investigated. To do that, the Pearson-R statistical analysis model, that shows how great is the linearity between the variables, cannot be used, since between the MW and DCN, MON, RON does not exist a linear relationship.

In this case the Covariance-R statistical model may be utilized, which shows us how much the variables correlated to each other. The result from Covariance correlation in terms of IDT is for DCN = -3880.44, RON = 399.05, MON = 3177.57. The result from Covariance correlation considering the MW is for DCN = 4.2, RON = 2.39, MON = 15.33. We can see here that there is a huge difference between the covariance values regarding each measurement. However, we cannot compare the results, since these values are not foundational values, and the covariance number changes based on the real change that we have. For example, IDT changes substantially, and so it has a large variation as well as DCN. Whereas, among the mixtures by MW the values do not change much, and so it does not have big variation,

because our mixtures consist only n-heptane, iso-octane, toluene, and their MW are almost identical. And considering the operation of the covariance equation, if I have a large variation, we are going to have a large value for covariance value. Therefore, we obtain a large covariance value for DCN, RON and MON, while we have small covariance value for MW. Therefore, it would be not correct to compare them on this level. However, if we normalized the covariance value, we could compare the results. The difference of normalized and unnormalized covariance value is, that the normalized covariance is dimensionless. Whatever unit have the original variables, the result always will be the same and this ensures that two variables can be compared simply by comparing their correlation. The result from normalized Covariance correlation in terms of IDT is for DCN = -0.19, RON = 0.14, MON = 0.14. The result from normalized Covariance correlation considering the MW is for DCN = 0.001, RON = 0.0003, MON = 0.002. It can be seen that still a big difference does exist between the MW and DCN, RON, MON. The results evidence, that the observed DCN, RON and MON do not correlate strong with physical property of mixture, but much more correlated with chemical properties.

In summary, the consideration of chemical group and quantitative structure property relationship analytical models seems to be a powerful approach to understand fundamentally which components of a complex fuel mixtures' chemical structure are most essential to any combustion kinetic behavior.

6 CONCLUSION

By liquid-fuel operated internal combustion engines will remain the most dominant drivers of road and air transportation for decades, or even for most of the 21st century. The world's demand for liquid transportation petroleum-derived and petroleum and/or alternative-derived blended fuels is already giant, and it will increase by a very long-term point when it becomes economically unsustainable and infeasible. The projected demand for fuels derived from petroleum and other fossil resources and developing propulsion technologies require to a growing necessity to fully understand the fuel's physical and chemical kinetic property impacts on internal combustion engine (multi-phase) performance and emissions. A greatly simplified surrogate fuel concept may be an answer to this research question since it can model the physical and chemical properties of real fuels that vary geographically and contain hundreds of individual species. If the surrogate fuel formulation is compact enough and it can replicate real fuel combustion behaviors, then it can be employed in engineering design tools (CFD simulations for advanced engine design) in order to predict fuel impacts on advanced combustion technologies, as well as for observation of the compatibility of non-petroleum derived alternative fuels on conventional burning equipment. A meaningful challenge does exist in terms of determining the number and type of surrogate components and their mixture formation needs to be modeled simultaneously by both physical and chemical kinetic properties. The key features named Combustion Property Targets (CPT) of the real fuel should be able to replicate any surrogate mixture, based on the qualitative comprehension of combustion kinetic characteristics influencing global combustion behaviors. Four targets of the fuel properties were defined: the hydrogen to carbon ratio (H/C), the average molecular weight (MW), the threshold sooting index (TSI) and derived cetane number (DCN). It was found, if these four features of the surrogate fuel match approximately with the same global combustion behavior of the real fuel, then the emulation will be successful.

This study provided a new approach to obtain thorough insights into the impacts of fuel composition on Derived Cetane Number (DCN), Research Octane Number (RON), Motor Octane Number (MON), and Octane Sensitivity (OS), which are all essential parameters for describing the antiknock quality of gasoline fuels. The CPT-based surrogate formulation approach was investigated by consideration of the chemical functional group of fuel mixtures. The chemical function group concept was examined with Quantitative Structure-Property Relationship (QSPR) regression analysis, which is a low dimensional descriptor.

In this current paper as the first step, we have performed the QSPR regression modeling for investigation and prediction of DCN, RON, and MON measurements. Due to this analysis, we could get an insight into the ignition propensies of fuel mixtures, defined by those three numbers, that are controlled by functional group distribution particularly $(CH_2)_n$, CH_3, CH_2, C, and benzyl-type, and their interaction terms. It was found, that the QSPR's ability to predict a variety of fuels based on solely the fuels chemical functional group and the resulting QSPR model reproduces the training data set results very well. The QSPR regression model also allowed for analysis of the importance of each chosen chemical functionality in determining the DCN, RON, and MON. Based on the sensitivity analysis can be stated, that the CH_2 groups

present in alkanes and aromatic side chains were found to play the most significant role in ignition propensity (chemical potential), followed by those associated with CH_3 and benzyl-type groups. The rest three functional groups can be neglected in terms of the success of the result.

In the second step, we have been investigated the relationship between DCN, RON, and MON. We have found, that between DCN and RON does exist a strong relationship, on the other hand, between DCN and MON does not obtain this interaction so efficiently. The reason behind might be explained that the characteristic of the condition of MON measurement is different than the RON. MON measurements are affected more by the residue content of NO, which was not reflected in DCN our measurements. From this reason, it was necessary to build the new gas supply system for the Ignition Quality Tester (IQT) apparatus, to be capable to add NO concentrated gas for the combustion, representing the real conditions of engine operation. Probably, the MON value might be well correlated with DCN, nevertheless, this experiment will be performed in the future. In the same work phase, a new expression was constructed based on a quantitative property-property relationship (QPPR) to predict the RON and MON based on DCN. From the correlation between DCN - RON and DCN - MON it can be deduced that RON and DCN measurements have a tight relationship, however, DCN and MON do not correlate well, probably from the reasons described above.

As the third step, we have examined the relationship among DCN, RON, MON, and Octane Sensitivity (OS) considering a more fundamental approach, which is the IDT (Ignition Delay Time) reflected shock tube of the homogenous fuel-air mixture and stoichiometric conditions. Since we can identify, which is the temperature condition of each measurement in homogeneous IDT, that enables us to look at more fundamental detail, which we cannot perform with only RON, MON, DCN measurement. From the analyses, we could realize, that at an optimized temperature, the DCN correlates with homogenous IDT quite well, if not the entire DCN measurements are investigated. Typically, the DCN is good between 30 and 53 measurements. Considering the volatility of RON and MON values in the gasoline market, where the typical octane numbers vary from 70 to 100, in that range, they have quite a significant deviation. Furthermore, if we consider the OS at the low-temperature range, the correlation loses its strong constraining ability, and it becomes much looser and the deviation going to be larger.

In summary, this study proves that chemical kinetic modeling is a powerful tool to understand the relationships between gasoline fuel mixture composition and antiknock quality (i.e., IDT). The simple correlations exhibited herein can be applied to monitor various fuel mixtures in terms of DCN, RON, MON, and OS. This is a small but important step in the path to enable developing the state-of-the-art simulation-driven fuel design tools, significantly reducing the demand for costly and time-consuming experiments, and ensuring new opportunities for advancing the performance and efficiency of spark-ignition engines.

7 RECOMMENDATION OF FUTURE WORK

Taken into account that the chemical functional group descriptor is an effective approach of providing the understanding of fuel chemical property contributions on different combustion behaviors, it would be reasonable to improve this kind of low-dimensional descriptor to be investigated not only in scientific conduction but closer to real conditions to prove that fuel-specific chemical kinetic models can be used for real transportation fuels.

In this paper, only TPRF mixtures (n-heptane, iso-octane, toluene) were investigated, however, if we want to keep up with the most recent regulations regarding fuel quality, the mixtures must be completed by ethanol as well.

From the paper, it was ascertained, that DCN and MON measurement does not correlate well to each other. Based on our assumption, MON measurements are affected by the residue content of NO, which was not reflected in DCN our measurements. We believe, as long as it does, the relationship between those two measurements will be better. This provides a good starting point for discussion and further research and future investigations are necessary to validate the kinds of the presumption that can be drawn from this study. To be able to add NO concentrated gas for the combustion, representing the real conditions of engine operation, the new gas supply system for the Ignition Quality Tester (IQT) apparatus had been built already. Future research should consider the potential effects of NMR (Nuclear Magnetic Resonance) spectroscopy more carefully. The NMR is perhaps one of the most important areas of current interest. It has been applied for many years as a powerful analytical tool in the petroleum refining and pharmaceutical fields, but it is only over the last decade or so has that NMR has emerged as a significant contributor to fundamental and applied combustion efforts. Since this new technology based on NMR spectroscopy can directly quantify chemical functional group distribution of real gasoline fuels, it allows us to combine the results presented in this thesis to the real fuel.

In this paper, the most analyses aimed to DCN, RON, and MON measurement, which are chemical property indicators. As future work, it is going to be necessary to perform a very well-defined examination model in a fundamental way, rather than using the indicators. The IQT measures the chemical potential of fuels and it can reflect the impact of different molecule structures of fuel, however, the DCN measurement itself contains other physics beyond just chemical potential of fuel. Physical properties like injections, spray dynamics, are included in DCN measurements. Our results and analyses suggest that it is also recommended to perform fundamental experience, where purely chemical properties of mixtures can be evaluated in a fundamental way. Those are for example gas-phase homogenous mixtures examined by shock tube etc.

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APPENDIX

	a1	a2	a3	a4	a5	a6
	(CH2)n	CH3	CH2	CH	C	Benzyl-type
n-heptane	5	2	0	0	0	0
iso-octane	0	5	1	1	1	0
toluene	0	1	0	1	0	1

a1	2.567022	a12	1.264109	a23		a34	
a2	-2.43834	a13		a24		a35	
a3		a14		a25		a36	
a4		a15		a26		a45	
a5	-26.2955	a16	8.70465			a46	
a6	31.8					a56	

Mixtures table:

Mix. #	nC7H16	iC8H18	C7H8	DCN
1	1	0	0	53.8
2	0	1	0	18.9
3	0.75	0.25	0	47.8
4	0.5	0.5	0	41
5	0.25	0.75	0	32
6	0.8	0.2	0	48.32
7	0.6	0.4	0	42.73
8	0.4	0.6	0	36.45
9	0.2	0.8	0	29.23
10	0.75	0	0.25	46.6
11	0.5	0	0.5	36.5
12	0.25	0	0.75	24.2
13	0.1	0	0.9	10.5
14	0.8	0	0.2	46.80
15	0.5	0	0.5	38.14
16	0.3	0	0.7	28.21
17	0.2	0	0.8	15.65
18	0.6	0.2	0.2	42.6
19	0.33	0.33	0.33	31.8
20	0.25	0.25	0.5	27
21	0.2	0.6	0.2	28.4
22	0.1	0.1	0.8	12.4
23	0	0	0.5	10.4
24				

Chemical functional group table:

(CH2)n	CH3	CH2 (3)	CH (4)	C (5)	Benzyl type
5	2	0	0	0	0
0	5	1	1	1	0
3.75	2.75	0.25	0.25	0.25	0
2.5	3.5	0.5	0.5	0.5	0
1.25	4.25	0.75	0.75	0.75	0
4	2.6	0.2	0.2	0.2	0
3	3.2	0.4	0.4	0.4	0
2	3.8	0.6	0.6	0.6	0
1	4.4	0.8	0.8	0.8	0
3.75	1.75	0	0	0	0.25
2.5	1.5	0	0	0	0.5
1.25	1.25	0	0	0	0.75
0.5	1.1	0	0	0	0.9
3.8	1.76	0	0	0	0.24
2.7	1.54	0	0	0	0.46
1.7	1.34	0	0	0	0.66
0.8	1.16	0	0	0	0.84
3	2.4	0.2	0.2	0.2	0.2
1.67	2.67	0.33	0.33	0.33	0.33
1.25	2.25	0.33	0.25	0.25	0.5
1	3.6	0.6	0.6	0.6	0.2
0.5	1.5	0.1	0.1	0.1	0.8
0	3	0.5	0.5	0.5	0.5
0	0	0	0	0	0

Sum of residue^2 = 17.89497981

DCN_Predicted	(DCN-DCN_predicted)^2
52.39952666	1.961325569
19.60831125	0.501704824
47.75702975	0.001846442
40.74432821	0.065368062
31.36142205	0.407781804
48.87514551	0.304496673
43.83383339	1.225818143
37.2755903	0.687114394
29.20041626	0.000875198
47.04220182	0.195542451
37.034539086	0.285732028
22.37653844	3.325012073
11.34957586	0.721779138
47.3457813	0.297877231
38.94826783	0.647919537
28.18913759	0.000585434
15.96125549	0.094816053
42.71473906	0.013156051
31.26582818	0.285339529
25.37149964	2.652013423
26.62203663	3.161153737
12.82117633	0.177389502
11.33825557	0.880323514

(CH2)n Sen_(CH2)n	CH3 Sen_CH3	CH2 Sen_CH2	CH Sen_CH	C Sen_C	Benzyl-type Sen_Benzyl type
0.48619146	0.148177	0	0	0	0
0	-0.62176	0	0	0	0
0.4745366	0.132561	0	0	0	0
0.42898021	0.062015	0	0	0	0
0.31645113	-0.1163	0	0	0	0
0.47907425	0.139274	0	0	0	0
0.45253889	0.098845	0	0	0	0
0.39546721	0.009163	0	0	0	0
0.27838995	-0.17694	0	0	0	0
0.55445233	0.085639	0	0	0	0.033740844
0.59508711	0.02924	0	0	0	-0.061183938
0.5963638	-0.04794	0	0	0	-0.516589625
0.51947875	-0.17506	0	0	0	-1.739890897
0.55227068	0.087925	0	0	0	0.034389751
0.59048327	0.038542	0	0	0	-0.032962125
0.60343085	-0.01375	0	0	0	-0.269148642
0.5686171	-0.10371	0	0	0	-1.017274847
0.51564033	0.076076	0	0	0	-0.00084052
0.47120292	-0.02827	0	0	0	-0.125650627
0.48103151	-0.07611	0	0	0	-0.303739439
0.33275985	-0.15879	0	0	0	-0.132137243
0.44562626	-0.21132	0	0	0	-1.369056124
0	-0.64516	0	0	0	-1.159502103

$$DCN_{predicted} = a_0 + \sum_{i=1} a_i x_i + \sum_{i=1, j=i+1} a_{ij} x_i x_j = a_1 x_1 + a_2 x_2 + a_3 x_3 + a_4 x_4 + a_5 x_5 + a_6 x_6 +$$

$$a_{12} x_1 x_2 + a_{13} x_1 x_3 + a_{14} x_1 x_4 + a_{15} x_1 x_5 + a_{16} x_1 x_6 + a_{23} x_2 x_3 + a_{24} x_2 x_4 + a_{25} x_2 x_5 +$$

$$a_{26} x_2 x_6 + a_{34} x_3 x_4 + a_{35} x_3 x_5 + a_{36} x_3 x_6 + a_{45} x_4 x_5 + a_{46} x_4 x_6 + a_{56} x_5 x_6$$

$$sen.\,C = \frac{\frac{\Delta DCN}{DCN}}{\frac{\Delta x_i}{x_i}} = \frac{x_i}{DCN}\frac{\Delta DCN}{\Delta x_i} = \frac{x_i}{DCN}\frac{\delta DCN}{\delta x_i}$$

QSPR regression model based on chemical funct. group

y = 0.9951x + 0.1587
R² = 0.9951

(axes: Predicted DCN vs DCN)

previsious data

Composition table

	a1	a2	a3	a4	a5	a6
	(CH2)n	CH3	CH2	CH	C	Benzyl type
n-heptane	5	2	0	0	0	0
iso-octane	0	5	1	1	1	0
toluene	0	1	0	0	0	1

a1	-17.7867	a12	a23	a34	a45	a56
a2	0.824582	a13	a24	a35	a46	
a3		a14	a25	a36		
a4		a15	a26			
a5	18.78535	a16				
a6	95					
a0						

Mixture composition and RON

Mix. #	nC7H16	iC8H18	C7H8	RON
1	0.272	0	0.728	85.2
2	0.237	0	0.763	89.3
3	0.203	0	0.797	93.4
4	0.16	0	0.84	97.7
5	0.208	0	0.792	92.3
6	0.165	0.035	0.8	96.9
7	0.126	0.07	0.804	99.8
8	0.087	0.105	0.808	103.3
9	0.048	0.141	0.811	107.6
10	0.13	0.66	0.21	91
11	0.16	0.45	0.39	91.4
12	0.18	0.27	0.55	91
13	0.135	0.12	0.745	98
14	0.169	0.599	0.232	87
15	0.1	0.65	0.25	93.7
16	0.15	0.35	0.5	93
17	0.137	0.428	0.435	93
18	0.098	0.565	0.337	95.2
19	0.13	0.27	0.6	96.3
20	0.17	0.63	0.2	86.6
21	0.17	0.69	0.14	85.7
22	0.123	0.34	0.537	96.3
23	0.085	0.613	0.302	96.1
24	0.181	0.647	0.172	85.1
25	0.124	0.395	0.481	94.8
26	0.196	0.505	0.299	85.1
27	0	0.184	0.816	113
28	0	0.392	0.608	110
29	0	0.852	0.148	101.9
30	0	0.6	0.4	105
31	0	0.391	0.609	108.5
32	0	0.184	0.816	113
33	0	0.067	0.933	115.3

Group contributions

	(CH2)n	CH3	CH2	CH	C	Benzyl type
1	1.36	1.272	0	0	0	0.728
2	1.185	1.237	0	0	0	0.763
3	1.015	1.203	0	0	0	0.797
4	0.8	1.16	0	0	0	0.84
5	1.04	1.208	0	0	0	0.792
6	0.825	1.305	0.035	0.035	0.035	0.8
7	0.63	1.406	0.07	0.07	0.07	0.804
8	0.435	1.507	0.105	0.105	0.105	0.808
9	0.24	1.612	0.141	0.141	0.141	0.811
10	0.65	3.77	0.66	0.66	0.66	0.21
11	0.8	2.96	0.45	0.45	0.45	0.39
12	0.9	2.26	0.27	0.27	0.27	0.55
13	0.675	1.615	0.12	0.12	0.12	0.745
14	0.845	3.565	0.599	0.599	0.599	0.232
15	0.5	3.7	0.65	0.65	0.65	0.25
16	0.75	2.55	0.35	0.35	0.35	0.5
17	0.685	2.849	0.428	0.428	0.428	0.435
18	0.49	3.358	0.565	0.565	0.565	0.337
19	0.65	2.21	0.27	0.27	0.27	0.6
20	0.85	3.69	0.63	0.63	0.63	0.2
21	0.85	3.93	0.69	0.69	0.69	0.14
22	0.615	2.483	0.34	0.34	0.34	0.537
23	0.425	3.537	0.613	0.613	0.613	0.302
24	0.905	3.769	0.647	0.647	0.647	0.172
25	0.62	2.704	0.395	0.395	0.395	0.481
26	0.98	3.216	0.505	0.505	0.505	0.299
27	0	1.736	0.184	0.184	0.184	0.816
28	0	2.568	0.392	0.392	0.392	0.608
29	0	4.408	0.852	0.852	0.852	0.148
30	0	3.4	0.6	0.6	0.6	0.4
31	0	2.564	0.391	0.391	0.391	0.609
32	0	1.736	0.184	0.184	0.184	0.816
33	0	1.268	0.067	0.067	0.067	0.933

Prediction and sensitivity analysis

Sum of residue^2: **2.407706704**

RON_Predicted	(RON-RON_predicted)^2	Sen_(CH2)n	Sen_CH3	Sen_Benzyl type
85.53475517	0.112061022	-0.282807208	0.0122625	0.159885096
89.27604587	0.0005738	-0.236089997	0.0114253	0.160549446
92.91044255	0.239666495	-0.19431244	0.0106766	0.161143582
97.50688542	0.037293243	-0.145931446	0.0098097	0.161831561
92.37597245	0.005771813	-0.200248144	0.010783	0.161059141
96.43036961	0.220552707	-0.152171843	0.0111591	0.155845898
100.0571907	0.066147046	-0.111991852	0.011587	0.150947861
103.6840118	0.147465027	-0.074622818	0.0119849	0.146392487
107.2953458	0.092814177	-0.039785474	0.0123885	0.141990468
90.49227265	0.257787064	-0.127760336	0.0343529	0.04359403
90.5377263	0.743515934	-0.157164547	0.0269585	0.080919696
91.18750954	0.035159829	-0.175550204	0.0204365	0.11304343
98.32079349	0.102908461	-0.122110379	0.0135444	0.142341035
87.2681141	0.071885171	-0.172224646	0.0336851	0.049940354
93.85396345	0.023704745	-0.094757058	0.0325074	0.050038768
93.15536853	0.024139379	-0.143201497	0.0225718	0.100828043
93.33700321	0.113571162	-0.130536181	0.0251694	0.087549692
95.38414821	0.033910565	-0.091372195	0.0290294	0.066370168
96.53221055	0.053921739	-0.119766481	0.0188779	0.116761111
86.68112245	0.006580852	-0.174416907	0.0351023	0.043343571
85.75190124	0.002693738	-0.176306917	0.0377905	0.030669274
96.19637727	0.01073767	-0.113713122	0.0212839	0.104866021
96.0303935	0.004845064	-0.078718064	0.0303711	0.059076867
85.24200889	0.020166524	-0.188337867	0.0364591	0.037904781
95.23769714	0.191578783	-0.115791582	0.0234116	0.094875791
85.83775546	0.544283123	-0.203068194	0.0308938	0.065435294
111.7603169	1.536814188	0	0.0128084	0.137158193
108.5390167	2.134472241	0	0.0195094	0.105229357
101.4149874	0.235237253	0	0.0358404	0.027414403
105.3177165	0.100943757	0	0.0266202	0.071347339
108.5545037	0.002970654	0	0.0194762	0.105387394
111.7603169	1.536814188	0	0.0128084	0.137158193
113.5722983	2.984953267	0	0.0092062	0.154322216

(Sen_CH2, Sen_CH, and Sen_C columns are all 0.)

Sensitivity Analysis RON

Legend: Sen_(CH2)n, Sen_CH3, Sen_Benzyl type

Predicted RON vs RON

y = 0.9565x + 4.0743
R² = 0.997

previsious data

Input matrix

	a1 (CH2)n	a2 CH3	a3 CH2	a4 CH	a5 C	a6 Benzyl type
n-heptane	5	2	0	0	0	0
iso-octane	0	5	1	1	1	0
toluene	0	1	0	0	0	1

Coefficients

	value					
a1	-18.1388	a12	a13			
a2	0.954565	a14	a15	a23	a24	a25	a26
a3		a16		a34	a35	a36
a4				a45	a46
a5				a56
a6	4.672915				
a0	95				

Data table

	nC7H16	iC8H18	C7H8	MON
1	0.272	0	0.728	74.8
2	0.237	0	0.763	78.2
3	0.203	0	0.797	81.5
4	0.16	0	0.84	86.2
5	0.208	0	0.792	80.7
6	0.165	0.035	0.8	85.2
7	0.126	0.07	0.804	88.7
8	0.087	0.105	0.808	92.6
9	0.048	0.141	0.811	96.6
10	0.13	0.66	0.21	88.4
11	0.16	0.45	0.39	86.1
12	0.18	0.27	0.55	83.5
13	0.135	0.12	0.745	87.4
14	0.169	0.599	0.232	84
15	0.1	0.65	0.25	90.3
16	0.15	0.35	0.5	85.8
17	0.137	0.428	0.435	86.7
18	0.098	0.565	0.337	90.5
19	0.13	0.27	0.6	87.3
20	0.17	0.63	0.2	84.2
21	0.17	0.69	0.14	84.6
22	0.123	0.34	0.537	88.3
23	0.085	0.613	0.302	91.8
24	0.181	0.647	0.172	83.8
25	0.124	0.395	0.481	87.8
26	0.196	0.505	0.299	81.6
27	0	0.184	0.816	100.8
28	0	0.392	0.608	99.3

Descriptor table

(CH2)n	CH3	CH2	CH	C	Benzyl type
1.36	1.272	0	0	0	0.728
1.185	1.237	0	0	0	0.763
1.015	1.203	0	0	0	0.797
0.8	1.16	0	0	0	0.84
1.04	1.208	0	0	0	0.792
0.825	1.305	0.035	0.035	0.035	0.8
0.63	1.406	0.07	0.07	0.07	0.804
0.435	1.507	0.105	0.105	0.105	0.808
0.24	1.612	0.141	0.141	0.141	0.811
0.65	3.77	0.66	0.66	0.66	0.21
0.8	2.96	0.45	0.45	0.45	0.39
0.9	2.26	0.27	0.27	0.27	0.55
0.675	1.615	0.12	0.12	0.12	0.745
0.845	3.565	0.599	0.599	0.599	0.232
0.5	3.7	0.65	0.65	0.65	0.25
0.75	2.55	0.35	0.35	0.35	0.5
0.685	2.849	0.428	0.428	0.428	0.435
0.49	3.358	0.565	0.565	0.565	0.337
0.65	2.21	0.27	0.27	0.27	0.6
0.85	3.69	0.63	0.63	0.63	0.2
0.85	3.93	0.69	0.69	0.69	0.14
0.615	2.483	0.34	0.34	0.34	0.537
0.425	3.537	0.613	0.613	0.613	0.302
0.905	3.769	0.647	0.647	0.647	0.172
0.62	2.704	0.395	0.395	0.395	0.481
0.98	3.216	0.505	0.505	0.505	0.299
0	1.736	0.184	0.184	0.184	0.816
0	2.568	0.392	0.392	0.392	0.608

Predictions and residuals

Sum of residue^2: **4.675728187**

MON_Predicted	(MON-MON_predicted)^2
74.94734417	0.021710303
78.25177334	0.002680479
81.46179025	0.001459985
85.52151753	0.460338468
80.98972894	0.08394286
85.01954327	0.032564632
88.67170854	0.000800407
92.32387382	0.076245668
95.97518444	0.390394485
87.78981266	0.372328587
85.13669248	0.927518301
83.40251526	0.009503275
87.7792654	0.143842245
84.15986843	0.025557916
90.63072708	0.109380404
86.16651067	0.134330071
87.32720694	0.393388543
90.89219734	0.153818752
88.12312836	0.677540305
84.03896185	0.025933287
83.98768251	0.374932712
88.7241883	0.179935718
92.07853327	0.077580785
82.98589782	0.662762365
88.58276998	0.612728845
81.69107499	0.008294653
100.4702228	0.108752983
100.2924545	0.984965844

Sensitivity

(CH2)n Sen_(CH2)n	CH3 Sen_CH3	CH2 Sen_CH2	CH Sen_CH	C Sen_C	Benzyl type Sen_Benzyl type
-0.329147676	0.0162008	0	0	0	0.045390293
-0.274683324	0.0150897	0	0	0	0.045563618
-0.226006133	0.0140967	0	0	0	0.045718527
-0.1696769	0.0129476	0	0	0	0.045897786
-0.232922544	0.0142378	0	0	0	0.045696516
-0.176012419	0.014652	0	0	0	0.043970264
-0.128873494	0.0151358	0	0	0	0.042370035
-0.08546403	0.0155813	0	0	0	0.040896411
-0.045358681	0.0160329	0	0	0	0.039486601
-0.134300419	0.0409923	0	0	0	0.011177972
-0.170443393	0.0331879	0	0	0	0.02140595
-0.195736353	0.0258663	0	0	0	0.030815654
-0.139482577	0.0175625	0	0	0	0.039659952
-0.182120902	0.0404352	0	0	0	0.012881629
-0.100069717	0.0389701	0	0	0	0.012889985
-0.157881371	0.0282493	0	0	0	0.027115608
-0.142281729	0.0311421	0	0	0	0.023277029
-0.097786209	0.0352663	0	0	0	0.017325714
-0.133792443	0.0239391	0	0	0	0.031816265
-0.183462108	0.0419132	0	0	0	0.011120829
-0.183574122	0.0446665	0	0	0	0.007789333
-0.125730665	0.0267141	0	0	0	0.02828265
-0.083721822	0.0366676	0	0	0	0.015326268
-0.1978119	0.0433538	0	0	0	0.009685276
-0.126955221	0.0291382	0	0	0	0.025373693
-0.217600353	0.0375791	0	0	0	0.017103478
0	0.0164937	0	0	0	0.037952523
0	0.0244417	0	0	0	0.028328474

Sensitivity Analysis MON (bar chart; legend: Sen_(CH2)n, Sen_CH3, Sen_Benzyl type; axis 0.1 to -0.35)

Predicted MON vs MON (scatter plot)
y = 1.0064x - 0.5283
R² = 0.9923
Axes: Predicted MON (vertical), MON (horizontal)

MON

a0	95
a0	-18.1388
a1	0.954565
a6	4.672915
b1	-0.042
b2	0.6748
b3	91.163

RON

a0	95
a0	-17.786651
a1	0.82458167
a6	18.785347
b1	-0.0364
b2	0.1228
b3	107.02

DCN

a0	31.8
a1	2.567028802
a2	-2.438335777
a6	-26.29338592
a12	1.264108236
a16	8.704597205

	a1	a2	a3	a4	a5	a6
	(CH2)n	CH3	CH2	CH	C	Benzyl type
n-heptane	5	2	0	0	0	0
iso-octane	0	5	1	1	1	0
toluene	0	1	0	0	0	1

Mix. #	nC7H16	iC8H18	C7H8	(CH2)n	CH3	CH2	CH	C	Benzyl type
1	1	0	0	5	2	0	0	0	0
2	0	1	0	0	5	1	1	1	0
3	0.75	0.25	0	3.75	2.75	0.25	0.25	0.25	0
4	0.5	0.5	0	2.5	3.5	0.5	0.5	0.5	0
5	0.25	0.75	0	1.25	4.25	0.75	0.75	0.75	0
6	0.8	0.2	0	4	2.6	0.2	0.2	0.2	0
7	0.6	0.4	0	3	3.2	0.4	0.4	0.4	0
8	0.4	0.6	0	2	3.8	0.6	0.6	0.6	0
9	0.2	0.8	0	1	4.4	0.8	0.8	0.8	0
10	0.75	0	0.25	3.75	1.75	0	0	0	0.25
11	0.5	0	0.5	2.5	1.5	0	0	0	0.5
12	0.25	0	0.75	1.25	1.25	0	0	0	0.75
13	0.1	0	0.9	0.5	1.1	0	0	0	0.9
14	0.8	0	0.2	3.8	1.76	0	0	0	0.24
15	0.5	0	0.5	2.7	1.54	0	0	0	0.46
16	0.3	0	0.7	1.7	1.34	0	0	0	0.66
17	0.2	0	0.8	0.8	1.16	0	0	0	0.84
18	0.6	0.2	0.2	3	2.4	0.2	0.2	0.2	0.2
19	0.33	0.33	0.33	1.666667	2.666667	0.333333	0.333333	0.333333	0.33333
20	0.25	0.25	0.5	1.25	2.25	0.25	0.25	0.25	0.5
21	0.2	0.6	0.2	1	3.6	0.6	0.6	0.6	0.2
22	0.1	0.1	0.8	0.5	1.5	0.1	0.1	0.1	0.8
23	0	0.5	0.5	0	3	0.5	0.5	0.5	0.5

Quantitative structure property relationship

DCN_Predicted	RON_Predicted	MON_Predicted
52.39955481	7.715908551	6.215217327
19.60832112	99.12290837	99.77282382
47.7570508	30.56765851	29.60461895
40.74434385	53.41940846	52.99402057
31.36143395	76.27115842	76.3834222
48.87516784	25.99730851	24.92673863
43.83385098	44.27870848	43.63825992
37.27560424	62.56010844	62.34978122
29.20042762	80.84150841	81.06130252
47.04219409	34.43941357	29.81828286
37.03452777	61.16291859	53.4213484
22.37655584	87.88642361	77.02441393
11.34962599	103.9205266	91.18625325
47.34577439	33.37047337	28.87416024
38.94825492	56.88715779	49.64485791
28.18914094	78.2659618	68.52731034
15.96129113	97.50688542	85.52151753
42.71474098	47.37611253	43.80919105
31.26583679	73.81624852	68.87184021
25.37151521	84.01466854	76.81075002
26.62205191	83.93891246	81.23223365
12.82122206	102.3718246	91.10078769
11.33829971	106.8664185	100.2001516

Quantitative Property-Property Relationship

RON_Pre.	Error	MON_Pre.	Error
13.5106996	5.794791	11.2022591	4.987042
95.4326021	3.690306	88.2462723	11.52655
29.865779	0.701879	27.59855	2.006069
51.5957088	1.8237	48.9330179	4.061003
75.0703448	1.200814	71.017035	5.366387
26.0702047	0.072896	23.8151179	1.111621
42.4636006	1.815108	40.04301	3.59525
61.0207118	1.539397	57.958095	4.390972
79.5688075	1.272701	75.0555197	6.005783
32.2447453	2.194668	29.9624155	0.144133
61.6431926	0.480274	58.548537	5.127189
91.5419879	3.655564	85.2328693	8.208455
103.724904	0.195623	93.4115392	2.225286
31.2390075	2.131466	28.9637897	0.08963
56.5852629	0.301895	53.7326869	4.087829
81.5571794	3.291218	76.8106703	8.28336
99.7066801	2.199795	91.233641	5.712124
45.8517831	1.524329	43.3558451	0.453346
75.2765319	1.460283	71.2039796	2.332139
86.7044403	2.689772	81.2477195	4.43697
84.4912832	0.552371	79.3607474	1.871486
102.610878	0.239054	92.9106438	1.809856
103.732867	3.133552	93.414689	6.785463

Uncertainty of MON

Scatter plot: Absolute error vs n-Heptane concentration.

RON vs DCN chart: $y = -0.0364x^2 + 0.1228x + 107.02$, $R^2 = 0.9932$

MON vs DCN chart: $y = -0.042x^2 + 0.6748x + 91.163$, $R^2 = 0.9626$

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Parameter tables

RON	
a0	-17.79
a1	2.5670
a2	0.8246
a6	18.785

MON	
a0	-18.139
a1	0.955
a2	4.673

DCN	
a0	31.8
a1	2.5670
a2	-2.438
a6	-26.29
a12	1.2641
a16	8.7047

	a0	-86.146	a5	1.952
	a1	189.141	a6	0
	a2	-127.204	a7	0.873
	a3	28.699	a8	-2.308
	a4	-1.245	a9	0.479
			Tr(K)	1200

	Nor. Cov
Cov. (MW, DCN)	0.001389383
Cov. (MW, RON)	0.000318559
Cov. (MW, MON)	0.002181822

Equation:

$$LN(\tau_{IG})_{Low\ T} = a_0 + a_1\frac{T_t}{T} + a_2\left(\frac{T_t}{T}\right)^2 + a_3\left(\frac{T_t}{T}\right)^3 \\ + a_4 Y_{CH_3} + a_5 Y_{CH_2} + a_6 Y_{BZY} \\ + a_7 Y_{CH_3}\frac{T_t}{T} \\ + a_8 Y_{CH_2}\frac{T_t}{T} + a_9 Y_{BZY}\frac{T_t}{T} \quad (2)$$

	Nor. Cov	Covariance	Covariance		Nor. Cov
	-0.197133537	0.140578594	0.144043392	Covariance	0.002576679
Covariance	-3880.447271	399.049045		Cova^2	6.63979E-06
Cova^2	15057871.02	159240.1403		Pearson R	0.997523969
Pearson R	-0.963832305	0.909061566		R^2	0.995054069
R^2	0.928972711	0.82639293			

Cov. (MW, DCN)	4.203172268
Cov. (MW, RON)	2.398509271
Cov. (MW, MON)	15.32714302

QSPR regression model for homogenous reflected shock IDT

	Temp. (K) 592.78	Temp. (K) 635.01	Temp. (K) 601.21	Temp. (K) 1340.74
	IDT for DCN [ms]	IDT for RON [ms]	IDT for MON [ms]	IDT for OS

Component group definitions

	(CH2)n	CH3	CH2	CH	C	Benzyl-type
nC7	5	2	0	0	0	0
iC8	5	5	1	1	0	0
toluene	0	1	0	0	0	1

MW (g/mol)	(CH2)n 14	CH3 15	CH2 14	CH 13	C 12	Benzyl-type 77	MW
nC7	0.7	0.3					100
iC8	0	0.658	0.123	0.114	0.105		114
toluene	0	0.163				0.837	92

Molecule weight: 100 114 92

Mixture table — mole fractions and functional group distribution

Mixt. #	X_nC7	X_iC8	X_toluene	(CH2)n	CH3	CH2	CH	C	Benzyl-type
1	0	0	1	0	1	0	0	0	1
2	0	0.01	0.99	0	1.04	0.01	0.01	0.01	0.99
3	0	0.02	0.98	0	1.08	0.02	0.02	0.02	0.98
4	0	0.03	0.97	0	1.12	0.03	0.03	0.03	0.97
5	0	0.04	0.96	0	1.16	0.04	0.04	0.04	0.96
6	0	0.05	0.95	0	1.2	0.05	0.05	0.05	0.95
7	0	0.06	0.94	0	1.24	0.06	0.06	0.06	0.94
8	0	0.07	0.93	0	1.28	0.07	0.07	0.07	0.93
9	0	0.08	0.92	0	1.32	0.08	0.08	0.08	0.92
10	0	0.09	0.91	0	1.36	0.09	0.09	0.09	0.91
11	0	0.1	0.9	0	1.4	0.1	0.1	0.1	0.9
12	0	0.11	0.89	0	1.44	0.11	0.11	0.11	0.89
13	0	0.12	0.88	0	1.48	0.12	0.12	0.12	0.88
14	0	0.13	0.87	0	1.52	0.13	0.13	0.13	0.87
15	0	0.14	0.86	0	1.56	0.14	0.14	0.14	0.86
16	0	0.15	0.85	0	1.6	0.15	0.15	0.15	0.85
17	0	0.16	0.84	0	1.64	0.16	0.16	0.16	0.84
18	0	0.17	0.83	0	1.68	0.17	0.17	0.17	0.83
19	0	0.18	0.82	0	1.72	0.18	0.18	0.18	0.82
20	0	0.19	0.81	0	1.76	0.19	0.19	0.19	0.81
21	0	0.2	0.8	0	1.8	0.2	0.2	0.2	0.8
22	0	0.21	0.79	0	1.84	0.21	0.21	0.21	0.79
23	0	0.22	0.78	0	1.88	0.22	0.22	0.22	0.78
24	0	0.23	0.77	0	1.92	0.23	0.23	0.23	0.77
25	0	0.24	0.76	0	1.96	0.24	0.24	0.24	0.76
26	0	0.25	0.75	0	2	0.25	0.25	0.25	0.75
27	0	0.26	0.74	0	2.04	0.26	0.26	0.26	0.74
28	0	0.27	0.73	0	2.08	0.27	0.27	0.27	0.73
29	0	0.28	0.72	0	2.12	0.28	0.28	0.28	0.72
30	0	0.29	0.71	0	2.16	0.29	0.29	0.29	0.71
31	0	0.3	0.7	0	2.2	0.3	0.3	0.3	0.7
32	0	0.31	0.69	0	2.24	0.31	0.31	0.31	0.69
33	0	0.32	0.68	0	2.28	0.32	0.32	0.32	0.68
34	0	0.33	0.67	0	2.32	0.33	0.33	0.33	0.67
35	0	0.34	0.66	0	2.36	0.34	0.34	0.34	0.66
36	0	0.35	0.65	0	2.4	0.35	0.35	0.35	0.65
37	0	0.36	0.64	0	2.44	0.36	0.36	0.36	0.64
38	0	0.37	0.63	0	2.48	0.37	0.37	0.37	0.63
39	0	0.38	0.62	0	2.52	0.38	0.38	0.38	0.62
40	0	0.39	0.61	0	2.56	0.39	0.39	0.39	0.61
41	0	0.4	0.6	0	2.6	0.4	0.4	0.4	0.6
42	0	0.41	0.59	0	2.64	0.41	0.41	0.41	0.59
43	0	0.42	0.58	0	2.68	0.42	0.42	0.42	0.58
44	0	0.43	0.57	0	2.72	0.43	0.43	0.43	0.57
45	0	0.44	0.56	0	2.76	0.44	0.44	0.44	0.56

Results — DCN, RON, MON, OS, functional group distribution and MW

Mixt. #	DCN	RON	MON	OS	CH3	CH2	CH	C	Benzyl-type	MW [g/mol]
1	3.068	114.610	100.627	13.982	0.163	0.000	0.000	0.000	0.837	92.0
2	3.234	114.455	100.619	13.836	0.168	0.001	0.001	0.001	0.829	92.2
3	3.399	114.300	100.610	13.690	0.173	0.002	0.002	0.002	0.820	92.4
4	3.564	114.145	100.602	13.543	0.178	0.003	0.003	0.003	0.812	92.7
5	3.730	113.990	100.593	13.397	0.183	0.004	0.004	0.004	0.803	92.9
6	3.895	113.836	100.585	13.251	0.188	0.005	0.005	0.005	0.795	93.1
7	4.061	113.681	100.576	13.105	0.193	0.006	0.006	0.006	0.787	93.3
8	4.226	113.526	100.568	12.958	0.198	0.007	0.007	0.007	0.778	93.5
9	4.391									93.8
10	4.557									94.0
11	4.722									94.2
12	4.888									94.4
13	5.053									94.6
14	5.218									94.9
15	5.384									95.1
16	5.549									95.3
17	5.715									95.5
18	5.880									95.7
19	6.045									96.0
20	6.211									96.2
21	6.376									96.4
22	6.542									96.6
23	6.707									96.8
24	6.872									97.1
25	7.038									97.3
26	7.203									97.5
27	7.369									97.7
28	7.534									97.9
29	7.699									98.2
30	7.865									98.4
31	8.030									98.6
32	8.196									98.8
33	8.361									99.0
34	8.526									99.3
35	8.692									99.5
36	8.857	109.189	100.328	8.861	0.336	0.043	0.040	0.037	0.544	99.7
37	9.023	109.035	100.320	8.715	0.341	0.044	0.041	0.038	0.536	99.9
38	9.188	108.880	100.311	8.568	0.346	0.045	0.042	0.039	0.527	100.1
39	9.353	108.725	100.303	8.422	0.351	0.047	0.043	0.040	0.519	100.4
40	9.519	108.570	100.294	8.276	0.356	0.048	0.044	0.041	0.511	100.6
41	9.684	108.415	100.286	8.130	0.361	0.049	0.046	0.042	0.502	100.8
42	9.850	108.260	100.277	7.983	0.366	0.050	0.047	0.043	0.494	101.0
43	10.015	108.105	100.269	7.837	0.371	0.052	0.048	0.044	0.485	101.2
44	10.180	107.951	100.260	7.691	0.376	0.053	0.049	0.045	0.477	101.5
45	10.346	107.796	100.251	7.544	0.381	0.054	0.050	0.046	0.469	101.7

IDT values

Mixt. #	IDT for DCN [ms]	IDT for RON [ms]	IDT for MON [ms]	IDT for OS
1	1863.196	100.611	886.104	0.008
2	1846.739	99.756	878.340	0.008
3	1830.427	98.908	870.645	0.008
4	1814.260	98.068	863.016	0.008
5	1798.235	97.235	855.455	0.008
6	1782.352	96.409	847.960	0.008
7	1766.609	95.590	840.530	0.008
8	1751.005	94.778	833.166	0.008
…				
36	1365.850	74.637	651.205	0.007
37	1353.786	74.003	645.500	0.007
38	1341.829	73.374	639.844	0.007
39	1329.977	72.751	634.238	0.006
40	1318.230	72.132	628.681	0.006
41	1306.586	71.520	623.173	0.006
42	1295.046	70.912	617.713	0.006
43	1283.607	70.310	612.301	0.006
44	1272.269	69.712	606.936	0.006
45	1261.032	69.120	601.618	0.006

Charts: IDT for DCN [ms], IDT for RON [ms], IDT for MON [ms], IDT for OS