ϕsensitivity

A step forward in future fuels evaluation

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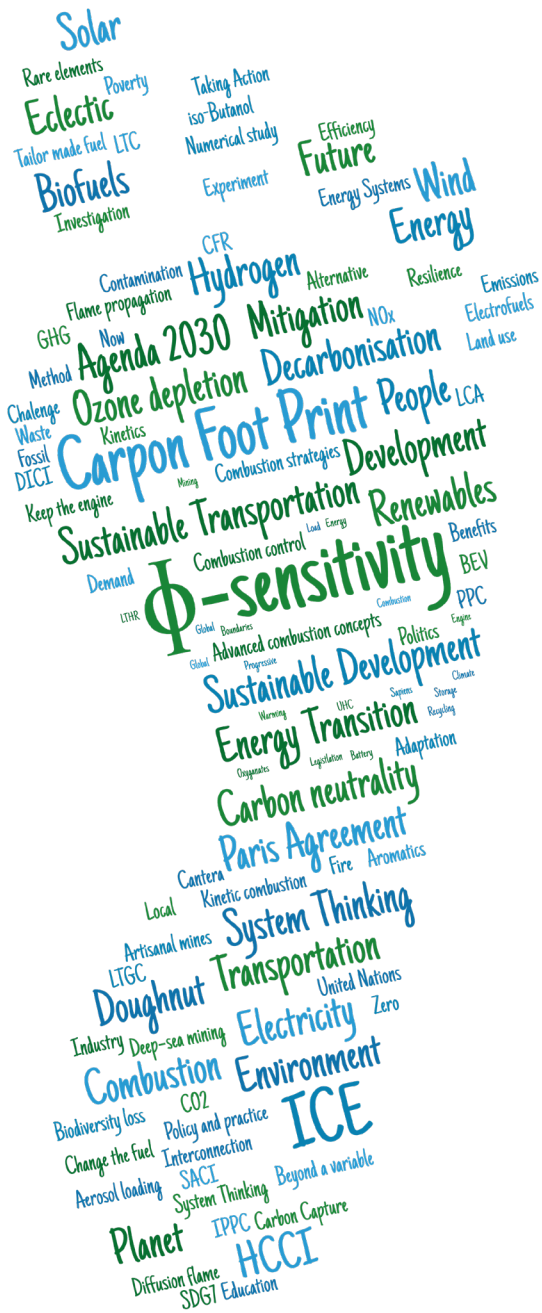

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A step forward in future fuels evaluation

by Nika Alemahdi

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UNIVERSITY

DOCTORAL DISSERTATION

Thesis for the degree of Doctor of Philosophy at the Faculty of Engineering

To be publicly defended on Friday, 14 of October at 10:15 in KC: A lecture hall, Department of Energy sciences, Kemicentrum, Naturvetarvägen 18, Lund

Thesis advisor: Professor Martin Tunér, Professor Antonio Garcia Martinez

Faculty opponent: Professor Pilar Dorado

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Abstract

Internal combustion engine is a developed and established technology which contributes largely to the transportation of goods and people. In one hand, the burning of fossil fuels is the main reason for the combustion engines to be considered unsustainable while on the other hand, the combustion behaviour of renewable fuels is not fully understood yet. This lack of knowledge is more pronounced when it comes to the combustion behaviour of renewable fuels in advanced combustion engine concepts.

In this PhD study a new empirical methods of fuel testing has been developed to quantify the equivalence ratio-sensitivity of different liquid fuels. Equivalence ratio (ϕ) is the ratio of the actual fuel-air ratio to the stoichiometric fuel-air ratio. ϕ-sensitivity is a decisive fuel property when it comes to the modern low temperature combustion technologies. The developed method in this study, characterize the ϕ-sensitivity property of liquid fuels. ϕ-sensitivity is fundamentally the sensitivity of auto-ignition temperature or ignition delay to the variation of fuel equivalence ratio in the combustion. This property is important to understand since it separates different fuels impact on efficiency and emissions for modern engines where current fuel characterization methods (octane rating and cetane number) are indifferent. Therefore, ϕ-sensitivity is needed to be understood for the development of renewable fuels in both conventional and advanced combustion engines. In this study a special test engine which is designed to be used for gasoline octane rating is the experimental apparatus. The Cooperative Fuel Research (CFR) engine is how this engine is called. In this engine, the height of cylinder head is adjustable to provide different Compression Ratio (CR). The variable CR of this engine make it versatile for testing different fuels having different physical and chemical properties.

Since the aim of this study was to develop an empirical ϕ-sensitivity test method, different surrogate gasoline have been designed to cover a wide range of Research Octane Number (RON) values (≈105-63). Surrogate fuels are single-component fuels, binary blends, and multi-component blends that are prepare in a way that emulate the desirable physical or chemical property of a more complex hydrocarbon like gasoline. In this study four components are used to prepare desirable surrogate fuels. These components are toluene, ethanol, iso-octane, and n-heptane. After method development step, four different alcohols are evaluated using the method. Due to the property similarity of iso-butanol and n-butanol to conventional gasoline, these two alcohols have been evaluated. Furthermore, blends of iso-butanol with RON (87) surrogate gasoline are evaluated. The results of this study shows that the developed test method (Lund ϕ-sensitivity number) is an appropriate platform to evaluate and tailor fuels with a preferable ϕ-sensitivity at a desirable octane number. Liquid fuels from renewable to conventional, to blends of renewable and conventional can be evaluated using Lund ϕ-sensitivity method. Using this method provides required knowledge for application of different renewable fuels in internal combustion engines.

Key words Equivalence ratio, ϕ-sensitivity, Cooperative Fuel Research engine, Method development, Biofuels.

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LUND
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A doctoral thesis at a university in Sweden takes either the form of a single, cohesive research study (monograph) or a summary of research papers (compilation thesis), which the doctoral student has written alone or together with one or several other author(s).

In the latter case the thesis consists of two parts. An introductory text puts the research work into context and summarizes the main points of the papers. Then, the research publications themselves are reproduced, together with a description of the individual contributions of the authors. The research papers may either have been already published or are manuscripts at various stages (in press, submitted, or in draft).

Cover illustration front: the potential application of ϕ-sensitivity property to evaluate renewable future fuels to tailor those in accordance with the needs in a sustainable transport system. Drawing created at draw.io.

Cover illustration back: A word cloud of my PhD thesis created at wordclouds.com.

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To the memory of my grandfather,
to whom I owe my curiosity and scientific thinking.

Table of Contents

Acknowledgements

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A special feeling of gratitude to my loving parents, Mohammad and Sara, for all humanity values that they taught me by being who they are.

Thank you “Soren Best” for being so kind to “Mim,” for all nice “fikas” you were preparing for me when I was working hard, I promise we will spend more time together.

My dear Ali, this journey was not coming to an end if I didn’t have your unconditional love and support. Thank you for always believing in me and encouraging me to work towards my dreams, you are the one for me!

Popular summary

Internal combustion engine is a developed and established technology which contributes largely to the transportation of goods and people. In one hand, the burning of fossil fuels is the main reason for the combustion engines to be considered unsustainable while on the other hand, the combustion behaviour of renewable fuels is not fully understood yet. This lack of knowledge is more pronounced when it comes to the combustion behaviour of renewable fuels in advanced combustion engine concepts.

In this PhD study a new empirical methods of fuel testing have been developed to quantify the equivalence ratio-sensitivity of different liquid fuels. Equivalence ratio (ϕ) is the ratio of the actual fuel/air ratio to the stoichiometric fuel/air ratio. ϕ-sensitivity is a decisive fuel property when it comes to the modern low temperature combustion technologies. The developed method in this study, characterize the ϕ-sensitivity property of liquid fuels. ϕ-sensitivity is fundamentally the sensitivity of auto-ignition temperature or ignition delay to the variation of fuel equivalence ratio in the combustion. This property is important to understand since it separates different fuels impact on efficiency and emissions for modern engines where current fuel characterization methods (octane rating and cetane number) are indifferent. Therefore, ϕ-sensitivity is needed to be understood for the development of renewable fuels in both conventional and advanced combustion engines. In this study a special test engine which is designed to be used for gasoline octane rating is the experimental apparatus. The Cooperative Fuel Research (CFR) engine is how this engine is called. In this engine, the height of cylinder head is adjustable to provide different Compression Ratio (CR). The variable CR of this engine makes it versatile for testing different fuels having different physical and chemical properties.

Since the aim of this study was to develop an empirical ϕ-sensitivity test method, different surrogate gasoline has been designed to cover a wide range of Research Octane Number (RON) values (≈105-63). Surrogate fuels are single-component fuels, binary blends, and multi-component blends that are prepared in a way that emulates the desirable physical or chemical property of a more complex hydrocarbon like gasoline. In this study four components are used to prepare desirable surrogate fuels. These components are toluene, ethanol, iso-octane, and n-heptane. After method development step, four different alcohols were evaluated using the method. Due to the property similarity of iso-butanol and n-butanol to conventional gasoline, these two alcohols have been evaluated. Furthermore, blends of iso-butanol with RON (87) surrogate gasoline were evaluated. The result of this study shows that the developed test method (Lund ϕ-sensitivity number) is an appropriate platform to evaluate and tailor fuels with a preferable ϕ-sensitivity at a desirable octane number. Liquid fuels from renewable to conventional, to blends of renewable and conventional can be evaluated using Lund ϕ-sensitivity method.

Using this method provides required knowledge for application of different renewable fuels in internal combustion engines.

Populär sammanfattning

Förbränningsmotor är en utvecklad och etablerad teknik som i hög grad bidrar till transport av varor och människor. Förbränning av fossila bränslen den främsta orsaken till att förbränningsmotorerna anses ohållbara, n samtidigt som förbränningsbeteendet för förnybara bränslen ännu inte är helt klarlagda. Denna brist på kunskap är mer uttalad när det gäller förbränningsbeteendet hos förnybara bränslen i avancerade förbränningsmotorkoncept.

I denna doktorandstudie har en ny empirisk metod för bränsletestning utvecklats för att kvantifiera ekvivalensförhållandets känslighet för olika flytande bränslen. Ekvivalensförhållandet (ϕ) är förhållandet mellan det faktiska bränsle/luftförhållandet och det stökiometriska förhållandet för bränsle/luft. ϕ-känslighet är en avgörande bränsleegenskap när det kommer till modern lågtemperaturförbränningsteknik. Metoden som utvecklats i denna studie, karakteriserar ϕ-känslighetsegenskapen hos flytande bränslen. ϕ-känslighet är i grunden känsligheten hos självantändningstemperaturen eller tändfördröjningen för variationen av bränsleekvivalensförhållandet i förbränningen. Den här egenskapen är viktig att förstå eftersom den separerar olika bränslens påverkan på moderna motorers effektivitet och emissioner där nuvarande bränslekarakteriseringsmetoder som oktantal och cetantal är otillräckliga. Därför behövs ϕ-känslighet för att vägleda utvecklingen av förnybara bränslen för både konventionella och avancerade förbränningsmotorer. I denna studie har en speciell testmotor av typen Cooperative Fuel Research (CFR) använts. Den är utvecklad för att bestämma oktantalet för bensin. I denna motor är höjden på topplocket justerbar för att ge olika kompressionsförhållande, vilket gör den mångsidig för att testa olika bränslen med olika fysikaliska och kemiska egenskaper.

Eftersom syftet med denna studie var att utveckla en empirisk testmetod för ϕ-känslighet har olika typer av surrogatbensin designats för att täcka ett brett spektrum av oktantal (RON) från 63 till 105. Surrogatbränslen är enkomponentsbränslen, binära blandningar och flerkomponentsblandningar som framställs på ett sätt som efterliknar de önskvärda fysiska eller kemiska egenskaperna hos ett mer komplext kolväte som bensin eller diesel. I denna studie används fyra komponenter för att framställa önskvärda surrogatbränslen. Dessa komponenter är toluen, etanol, iso-oktan och n-heptan. Efter steget med metodutveckling utvärderas fyra olika alkoholer med metoden. På grund av likheten i egenskaper mellan iso-butanol och n-butanol med konventionell bensin, har dessa två alkoholer utvärderats. Dessutom utvärderades blandningar av iso-butanol med surrogatbensin. Resultaten av denna studie visar att den nyutvecklade testmetoden (Lund ϕ-känslighetstal) är en lämplig plattform för att utvärdera och skräddarsy bränslen med önskvärd ϕ-känslighet vid ett önskvärt oktantal. Förnybara och konventionella flytande bränslen, och blandningar dem emellan kan utvärderas med

Lunds ϕ-känslighetsmetod. Att använda denna metod ger erforderlig kunskap för tillämpning av olika förnybara bränslen i förbränningsmotorer.

List of publications

This thesis is based on the following publications, which will be referenced by roman numerical in the body text of this thesis. The papers are appended in the order listed below:

I **The effect of 2-ethyl-hexyl nitrate on HCCI combustion properties to compensate ethanol addition to gasoline**
Alemahdi N, Tuner M
Fuel, vol. 270, p. 117569, 2020
https://doi.org/10.1016/j.fuel.2020.117569

II **Development of a fast-virtual CFR engine model and its use on auto-ignition studies**
García A, Monsalve-serrano J, Lago Sari R, Fogué-Robles Á, **Alemahdi N,** Tunér M
Fuel processing technology, vol. 224, p. 107031, 2021
https://doi.org/10.1016/j.enconman.2022.115257

III **Development of an empirical test method to quantify the ϕ-sensitivity**
Alemahdi N, García A, Boufaim E, Aferiat G, Tunér M.
Energy conversion and managements, vol. 24515, p.115257, 2022
https://doi.org/10.1016/j.fuproc.2021.107031

IV **Understanding the ϕ-sensitivity of toluene & ethanol reference fuels at different intake temperatures**
Alemahdi N, García A, Tunér M
Review comments received: International journal of engine research

V **Nonlinear ϕ-sensitivity behaviour of iso-butanol blends with surrogate gasoline**

Alemahdi N, García A, Tunér M.
Status: Manuscript

Author contributions

Paper I

The study was designed by me and the co-author. I performed the measurements. I did the analysis of the experimental results, authored the draft paper, and revised the paper after the peer-reviews.

Paper II

I have designed the experimental part of this study. I performed the measurements. I did the analysis of the experimental results and provided data for simulation. Two of the co-others did the numerical study. I wrote the experimental part of the paper, and they wrote the numerical part.

Paper III

I have designed the experiments. I have performed the measurements or supervised the other co-authors when they were collecting the data. I did the data analysis, authored the draft paper, and processed the peer-reviews.

Paper IV

I have designed the study, performed the measurements, and did the analysis of the experimental results. I authored the draft paper and at the moment revising the paper after the peer-reviews.

Paper V

For this paper, I have designed the experimental campaign and performed the engine measurements. I post-processed the data, analysed it, and authored the paper.

List of acronyms and symbols

AcHR	Accumulated heat release
ATDC	After top dead centre
BTDC	Before top dead centre
CA50	Crank angle degree at which 50% of total accumulated heat is released
CAD	Crank angle degree
CFR	Cooperative fuel research
COV_{IMEP}	Coefficient of variation of indicated mean effective pressure
CR	Compression ratio
DCR	Digital counter reading
ERHR	Early reaction heat release
GDI	Gasoline direct injection
HCCI	Homogeneous-charge compression ignition
HoV	Heat of vaporization
HRR	Heat release rate
HTHR	High-temperature heat release
ID	Ignition delay
LTC	Low-temperature combustion
LTGC	Low-temperature gasoline combustion
ITHR	Intermediate- temperature heat release
LTHR	Low-temperature heat release
MON	Motored octane number
OI	Octane index
PFS	Partial fuel stratification
PPC	Partially premixed combustion
PRR_{Max}	Maximum pressure rise rate
P_{SMC}	Pressure at start of main combustion
Pin	Intake pressure
RON	Research octane number
SI	Spark ignition
S	Octane sensitivity: S= RON-MON
TAcHR	Total accumulated heat release
TDC	Top dead centre

TERF	Toluene-ethanol reference fuel
TRF	Toluene reference fuel
ERF	Ethanol reference fuel
Tin	Intake temperature
UHC	Unburned hydrocarbon
ϕ	Equivalence ratio

Chapter 1

The urgency of taking action!

Sapiens have been changing the ecosystem from the first decades of their existence on the planet [1]. In the late nineteenth and early twentieth centuries humans became aware of their negative impact on the environment and the necessity of protecting it [2]. Early examples of environmental legislation were enacted to manage the contamination and pollution of the environment, for human beings' own comfort and not to protect the ecosystem [2–5]. In 2012, at the United Nations conference on sustainable development in Rio de Janeiro, for the first time, 17 goals were introduced as the sustainable development goals (SDGs) [6]. Later in 2015 those goals were adopted as the core of the "2030 Agenda for Sustainable Development" by all United Nations member states [6]. The objective of defining those goals was to develop a set of universal goals that help the nations to achieve social development within the planetary boundaries. Planetary boundaries were first introduced by Johan Rockström et.al in 2009 in an attempt to define "the safe operating space for humanity with respect to the earth system, associated with the planet's biophysical subsystems or processes" [7]. The most noted and known planetary boundary is the climate change but this is only one of the 9 defined planetary boundaries. The other 8 are rate of biodiversity loss, nitrogen and phosphorus cycle, ozone depletion, ocean acidification, global freshwater use, change in land use, atmospheric aerosol loading and chemical pollutions [7–10].

The doughnut model by Raworth Kate illustrates that living within the sustainable development doughnut, is the only "safe and just space for humanity" [8]. Fig. 1.1 is the illustration of the doughnut model [8]. The outer circle of the model represents the limit for the 9 planetary boundaries. The inner circle is based on the 11 dimensions of social foundation. It means that human development must grow in a way that fulfils the availability and accessibility of social foundations for everyone on the planet, and at the same time does not push the planetary boundaries out of their limits. Is it possible to live within the doughnut?

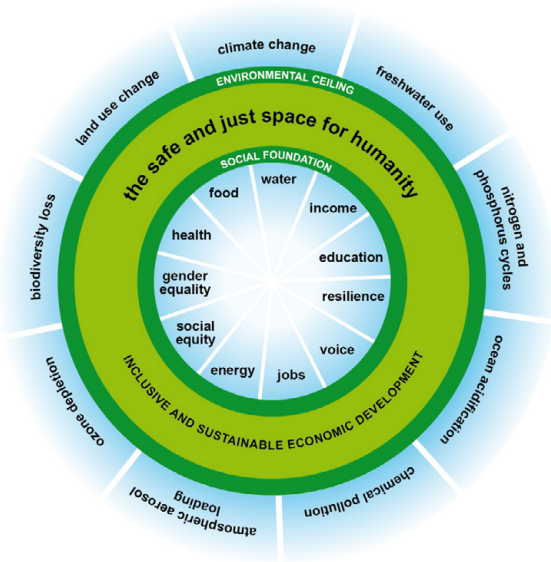


Fig. 1.1.Doughnut model by Raworth Kate [8]

In other words, is it possible to achieve the sustainable development defined by Gro Brundtland, "to meet the present needs without compromising the ability of future generations to meet their own needs" [9]?

Statistics indicate that the lifestyle of the 10% of the wealthiest people of the world is the cause of the largest planetary-boundary stress. This stress mainly comes from the contribution of different companies to the consumption of natural resources and the pollution formation to produce goods and services for that 10% of world population. As an example, 11% of the world population generates 50% of global carbon emissions [8].

We, human beings, should not overestimate the resilience of the planet's ecological system to maintain the Holocene state. We are ethically responsible to actively plan and contribute to both mitigation and adaptation with maximum capacity and urgency [11]!

1.1 Transition toward a sustainable energy system (SES)

Energy has an essential role in providing human being's needs from survive to thrive, from the considerably basic needs like food, clothes, and shelter to the secondary ones like health and employment. Therefore, any transition toward a sustainable society requires an energy transition towards a sustainable energy

system (SES). As it has been stated before, both adaptation and mitigation strategies are important for a sustainable energy system (SES). Mitigation aims for lowering the impact of human being's activities on the planetary boundaries, while adaption tries to suggest different solutions for living on a planet which has been already changed due to the human activities [12–14]. Mitigation strategies in the energy sector are suggested to be based on the reduction of fossil fuel consumption and equipping fossil fuel power plants with 'lock-in' GHG emissions infrastructures, increasing usage of low-emission energy sources, accelerating deployment of renewable energy sources, and finally increasing energy efficiency [12,13].

In the energy sector, emissions reduction is the core of mitigation strategies, while increasing resilience is the basis for adaptation strategies. To achieve resilience in power systems (from generation to distribution), infrastructure resilience and diversification of energy resources are claimed to have a significant effect [14].

1.1.1 Progressive demand of Energy

"Ensure access to affordable, reliable, sustainable and modern energy for everyone," is the sustainable development goal (SDG) number 7. All SDGs are strongly interconnected as the planetary boundaries are. Access to clean, affordable, and reliable energy means more children can turn on the light at night and study to become more successful at their education and therefore find a better job and escape poverty! No poverty is the first SDG. Fig. 1.2 displays the energy consumption of entire world by sector.

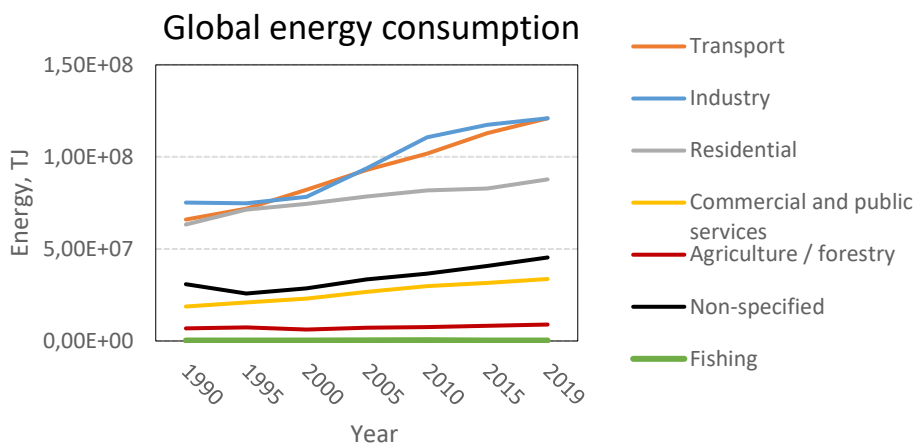


Fig. 1.2.Global energy consumption by sector.[15]

It is expected that in the global move towards development, the need for energy increases. Industry and transport sectors have the highest amount of energy consumption and the sharpest increase in the energy demand (Fig. 1.2).

Most of these sharp increases are not to help developing countries to become sustainable societies, but to provide for the 10% richest population of the world [16]. Now, roughly 20 % of world population does not have access to electricity. The energy needed for providing electricity to them results in less than one percent increase in global CO2 emissions [8].

Fig. 1.3 displays the energy production share of each energy source. It shows, more than 70% of energy supply in the global scale is produced from fossil fuels. According to the International energy agency database, fossil fuels are responsible for more than 99% of CO_2 emissions in the energy sector.

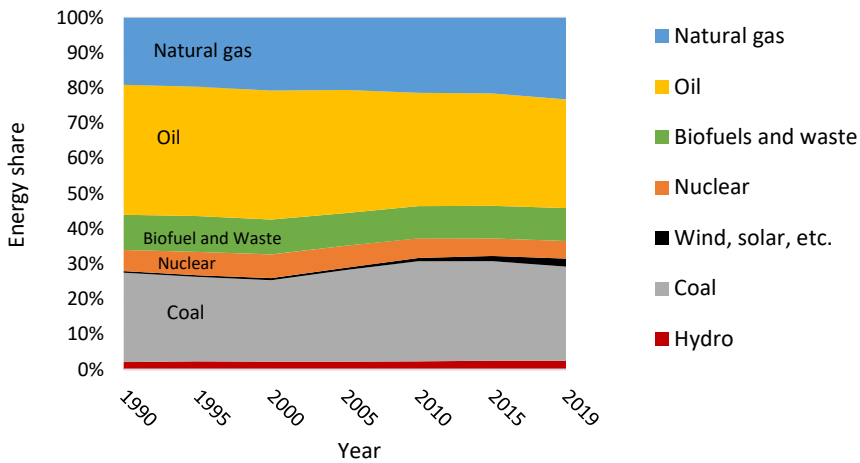


Fig. 1.3.Global energy production share by source[15]

Now of writing these lines, 137 days have passed from Russia's invasion of Ukraine. Taking another look at Fig. 1.3, makes it easier to figure out how Russian government dares to continue the invasion for 137 days. Russia holds about 24% of the world's total natural gas reserves, which ranks Russia first in the world [17]. The high dependency of the world energy sector on natural gas, financially enables Russia to continue killing innocent people and create all forms of sustainable development challenges from social to environmental and economical in Ukraine and even create food crisis far from Ukraine, in Africa! The global energy sector is not divers enough, and as a result it is not enough resilience to ban Russian natural gas! EU needs Russian natural gas to secure people's normal life, and therefore, let

Putin step on all values of humanity! Are policy makers able to guaranty that a new single technology transport system of full electric fleet, will not create another war somewhere else? Maybe in Congo which is the largest cobalt exporter, or South America which is a source of lithium!

1.2 Sustainable transport system

Our current transport system is pushing all the planetary boundaries to their thresholds to different extents. Greenhouse gasses, primarily CO_2, are the main contributors to the climate change [10,18]. Although all the planetary boundaries from land use (roads, mines, and factories) to loss of biodiversity (mining for different elements, pollutions, and roads) are threaten by our transport sector, the most known planetary boundary which is associated with the transport sector is climate change [9,18]. Fig. 1.4 depicts the contribution of different sectors to global CO_2 emissions. The data is extracted from the IEA 2021 report [19]. In 2019 the CO_2 emissions share of transport sector has increased 2% compared to 1990. It may not seem that bad, but since the total CO_2 emissions increased 65 % from 1990 to 2019 the actual increase in CO_2 emissions of transport sector is 78% [19,20]; And as Fig. 1.4 indicates, over one quarter of global CO_2 emissions are emitted from the transport sector.

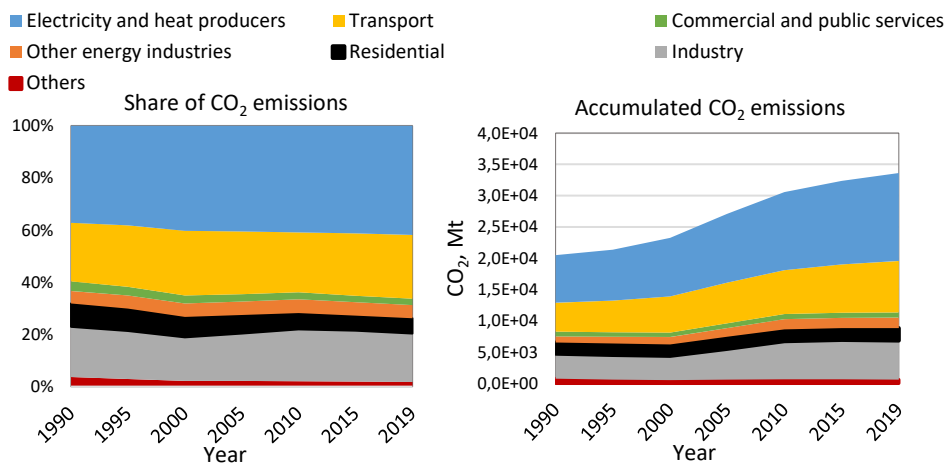


Fig. 1.4.Global CO2 emissions by sector from 1990 till 2019 [19].

Considering the mentioned statistics in Fig. 1.4, it is expected to see many researchers searching for different strategies to lower the CO_2 share from the transport sector. These strategies contain improvement in public transport systems,

high speed electric trains, hybrid, and battery-electric personal vehicle, improving ICE technology and replacing fossil fuels with renewable substitutes [21]. Due to the high demand in the transport sector, not any of these technologies alone would be able to solve the problem. I have explained in section 1.1 that resilience and diversification are the key factors for mitigation and adaptation in the energy sector. Considering this statement, how can we expect that a single technology insures both diversity and resilience in an unknown future which unpredictable challenges and natural disasters are an inseparable part of it? Let us take a moment and think about what Kelly Senecal and Felix Leach discuss in their recent book (Racing Toward Zero): "The future is ECLECTIC" [22]. The importance of an eclectic and not only electric transport system is the resilience which is the result of diversity.

1.2.1 A local benefit at the cost of others

Global warming and climate change, as the names suggests, are global problems, must be investigated, and treated globally [21]. Like any other industrial process, the powertrain of a battery-electric vehicle (BEV), contributes to the production of CO_2 emissions in different ways. The CO_2 emissions of electricity production power plants used for charging; the CO_2 emissions emitted in battery production process; as well as battery recycling in the end of battery life´s, are some of the examples [23–25]. The required minerals for battery production are rare compared to a conventional ICE. Mining for rare battery minerals highly contaminants freshwater resources and the ecosystem as well as the high toxicity for human [26]. Recently deep-sea mining has become an option to provide for the high demand of battery rare minerals [25]. Deep-sea mining could severely impact the deep-sea ecosystem.

The other challenge with the large-scale production of batteries, using the current technology (cobalt or lithium) is promoting child labour. A known example is Democratic Republic of the Congo (DRC), central Africa. Approximately 50-70% the world's cobalt is from the DRC, and 20% of it is extracted by artisanal miners [27]. Artisanal mines are informal, illegal, nonindustrial mines which are a hole deep to 30 m or more underground, not reinforced, with considerable risk of death for the artisanal miners [26,28].

The miners dig these tunnels using hand tools, they do not use any safety protection equipment. It is common to use children for their smaller body size [26,27]. Around 40,000 children work in southern DRC in cobalt mines [26]. The cobalt supply chain is not transparent and the large companies which are consumers of cobalt do not have appropriate tools and authority to control the supplied cobalt [26]. I am not going to explain more about children's working conditions in the artisanal mines, what I would like to conclude is that lack of system thinking is dangerous. Focusing too much on the single technology of BEV, we will improve the air quality of cities in developed countries but the children who must work without any basic protection and safety in artisanal mines might pay for it! Excessive demand of cobalt (as an

example) will threaten the sustainable development of the exporter countries with the child labour issue. The children will not live a healthy life due to the close contact with hazardous material (SDG 3), their schooling will be interrupted by work (SDG4), and due to insufficient education, will have less chance of skipping poverty in the future (SGD1).

Yet, all these costs do not result as much in **global** benefits as expected [29]. Different life cycle assessment studies are comparing the GHG emissions from BEVs to those of ICE vehicles mainly fuelled with fossil fuels. Excluding the driving force of vehicles as well as the battery production emissions from the LCA, during the manufacturing phase, results in a similar global warming potential (GWP) for both BEVs and ICEVs; the equivalent CO_2 emissions for this GWP reported to be around 2.5 megatons [30]. The most challenging part of LCA studies of BEVs, is the battery production phase; this challenge is due to the uncertainty in the estimated emissions of the battery production [25,31]. LCA studies of BEVs are sensitive to the vehicle lifetime as well as the source of electricity used for charging [25,32].

1.2.2 Combustion Engines, to be or not to be

One of the most proposed suggestions to reduce transport sector emissions is banning the Internal Combustion engines (ICE) and go for a fully electric transport system, due to their lower tailpipe emissions. In the best scenario this strategy will only diminish part of the local emissions which are coming directly out of the exhaust pipes, while creating other planetary stresses, as well as pollutions, and leading to the collapse of the transport system [22,23,25]! All the pollutions that are associated with a vehicle itself will still exist, even if we replace the combustion engine of a vehicle with a sail and hope for a back wind whenever we want to drive. Therefore, at least with the current vehicle production technology the term “zero emissions” simply does not exist. The other point is that, despite fascinating developments and innovations in battery and hybrid powertrain technologies, as well as smart roads and renewable electricity power plants, only 1.1% of light-duty transportation vehicles in Europe had electrical powertrains by 2020 [10] and 63.1% of the electricity production in world was fossil thermal electricity [20]. Fig. 1.5 shows global electricity production share of different resources at 2019.

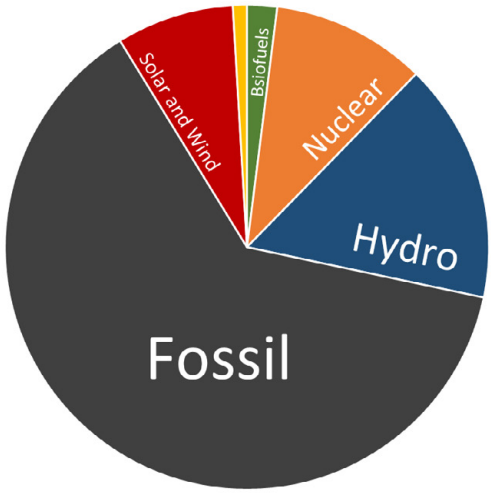


Fig. 1.5. World total electricity production share of different resources, 2019.[15]

This chart clearly depicts the large share of fossil fuels in electricity production industry. This dependency suggests that there is still a long way towards decarbonisation of global electricity production.

There is a lot of discussions about the benefits of electric cars even in the case of using fossil electricity to charge them. Decrease in local emissions level and improvement of the air quality in large cities are two major benefits of using electric cars regardless of electricity sources [23]. With this approach, the emissions are displaced from large cities to the fossil thermal power plants, where the possibility of carbon capture is higher, but with an increase in battery production industries, with potentially huge negative environmental impacts [22,23,25].

There are some simple facts about combustion engines in the transportation systems that are worth to consider. The combustion engine is a well-established technology and contributes largely to the transportation of goods and people in both light and heavy-duty transports. Combustion engines are already a huge part of the market and the transition to cleaner engines could be done quickly. There is no need to change the infrastructure, as such, which will save money and does not contribute to the emissions associated to provide the infrastructure. Replacing fossil fuels with renewable substitutes and applying more efficient combustion strategies are available solutions to fit ICE in a sustainable framework. The low-temperature combustion (LTC) concept is one of the basic concepts of these high-efficiency and low-emissions combustion technologies. Homogeneous-charge compression ignition (HCCI), partially premixed combustion (PPC), and premixed charge compression ignition (PCCI) are some examples of these technologies [33–37].

To develop a sustainable transportation system, an inclusive strategy is required. Electrical battery, hybrid, and fuel cell powertrains together with the well stablished ICE technology are required to engender the transition of the transport sector towards sustainability.

1.2.3 Decarbonisation of combustion engines

Carbon dioxide (CO_2) is the main greenhouse gas contributing to the global warming [3]. The 2020 and 2021 reports of the United Nations Environment programme emphasise the importance and urgency of taking effective actions on the decarbonisation of different industries and sectors [3,18]. In these reports, it has been stated that even if the Paris Agreement countries follow current legislation, global temperature will exceed 3°C by the end of the century [3,18]. Elevated risk of this temperature increase is the main reason for urgency of decarbonisation and the transport sector is not an exception. The motivation is that after reaching this threshold the changes in the planet ecosystem will be irreversible [13].

Would it be possible to decarbonize combustion engines? Besides increasing the efficiency, using renewable substitutes to replace fossil fuels is the other story line in ICE journey towards sustainability. Burning fossil fuels will keep the emissions problem of ICE unsolved even if the ICE technology improves further. The possibility of burning renewable fuels in both conventional and modern engines is an attractive area in ICE research that many researchers have investigated it [38–45]. Some researchers and companies moved one step further and have designed or manufactured special engines compatible with specific fuels like bio hydrogen [46,47]. There are three known options for decarbonisation of combustion engine's fuel [48,49]:

1. Fuels that store the already emitted CO_2, (e.g., Methane, Methanol (MeOH), and DME) [50]
2. Biofuels that store biogenic carbon, (e.g., Biomethane and biodiesel) [51]
3. Carbon free fuels, (e.g., ammonia, hydrogen) [48]

The type of renewable fuel is another challenge that needs to be addressed. Apart from the sustainability and scalability of renewable fuels, these fuels must be cost effective too [52]. Appropriate and applicable renewable fuels for combustion engines used in transports, must have high energy density to be feasible carrying on board [48,53].

In fact, the burning of fossil fuels is the main reason for the combustion engines to be considered unsustainable. Why not "keep the engine and change the fuel" [51,53,54]!

1.3 Summary and conclusion

The move towards a sustainable transport system and decarbonisation of energy sector is urgent. The global temperature will not wait for us to develop a neutral carbon emissions technology of BEV. We must use all our knowledge and technical capacities to decarbonize the energy and transport sector as fast as possible. Tackling a local air pollution problem, is not necessarily the same as solving the global warming challenge. If nations do not contribute to the mitigation urgently, the possibility of adaptation would be lost too.

1.4 Thesis outline and structure

The thesis consists of seven chapters. Chapter 1 provides a brief overview of the context of the performed research, as well as the relevance of this work for transition to a sustainable transport? Energy system. Chapter 2 provides information on the working principals of ICE with the focus on LTC and different fuel indexes, as well as the motivation behind this thesis work. Chapter 3 presents the experimental methodology of this research. Chapter 4 discusses the prerequisite studies that are performed to define criteria for the method development. Chapter 5 depicts the method development and discusses the effective parameters on the defined method. Chapter 6 presents the evaluation of two different alcohols using the defined method and compare these with each other. Finally, Chapter 7 concludes this thesis work and suggests future possible works.

Chapter 2

Engine and Fuel interplays

Fire! “The greatest discovery made by humanity, excepting only language,” as Charles Darwin believed [55]. This best-known exothermic reaction has transformed the life of human beings as well as nature [56]. Fire control had a substantive impact on human evolution [57]. With the beginning of the industrial revolution open fire technologies started a transformation toward hidden fire technologies, like **Internal Combustion Engines** (ICEs). Internal combustion engines had a significant impact on human beings’ development. ICE gave the possibility of fresh foods and goods transportation for longer distance than before. ICE also made public transportation possible and contributed to the development of cities and societies [58].

2.1 Conventional combustion technologies

Combustion is a series of high temperature exothermic chemical reactions. The two components of these reduction-oxidation reactions are fuel as the reductant and oxygen (air) as the oxidant. Fuel and air can be mixed to form a combustible mixture at different ratios. Fuel/air mixture strength is described using the fuel/air equivalence ratio (ϕ) concept. Fuel/air equivalence ratio is the actual ratio of fuel to air in the unburnt gas to the ratio of fuel to air in the stoichiometric mixture of that fuel [59,60]. A stoichiometric mixture is a specific blend of fuel and air which during the combustion process where all the air and the fuel molecules will be consumed [59,60].

A combustion engine is a controlled environment where these reactions occur to produce work, out of the released heat. A combustion engine is a heat engine which converts the chemical energy of the fuel to the mechanical work. There are different combustion concepts and as a result different combustion engine technologies. The

conventional combustion engines can be categorized in two distinct groups in term of ignition; Compression ignition (CI) engines and spark ignition (SI) engines. The working principles of these engines are based on two idealized thermodynamic cycles of Diesel and Otto [60].

2.1.1 CI engines

In CI engines, as the name suggests, combustion is driven by auto ignition which is facilitated by compression. Conventional CI engines are Direct Injection Compression Ignition (DICI) engines. Fig. 2.1 shows the sequence of events in a four-stroke diesel engine. As the diagram demonstrates, the air enters the cylinder and at a close timing to the TDC, fuel is directly injected into the compressed air-filled cylinder. Injection provides a heterogeneous charge inside the cylinder. After the fuel ignition delay time, ignition begins, and combustion starts at the surface of the fuel spray. Combustion and mixing continue in parallel, until the end of the injection process [60].

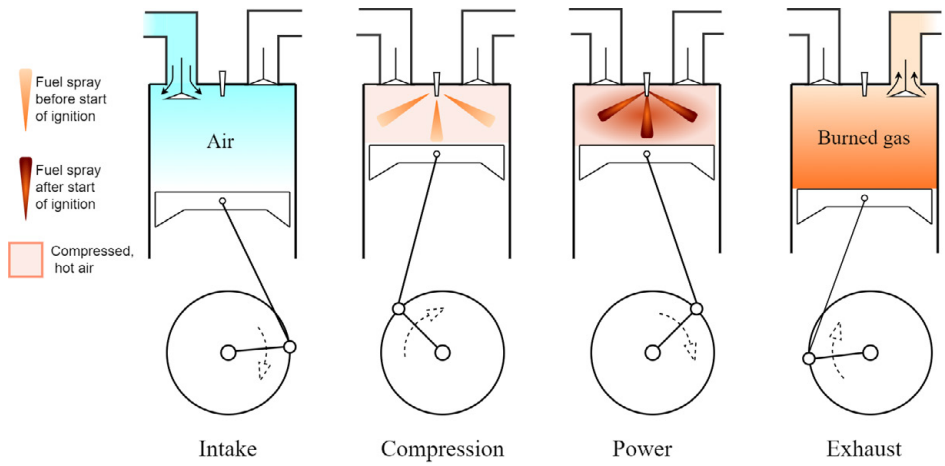


Fig. 2.1.The sequence of events in a four-stroke diesel engine, modified diagram from [61].

In conventional CI engines, the global fuel/air equivalence ratio (ϕ) inside the combustion chamber is less than 1 (lean mixture), while locally close to the injectors more than 1 (rich mixture) and at the combustion zone is around the stoichiometric value [60,62,63]. For a stoichiometric mixture, the ratio of fuel and oxygen is chemically ideal and both fuel and oxygen are completely consumed at the end of combustion [59,60]. Therefore, in a DICI engine, three types of mixture strengths are engaged in the combustion process at the same time. DICI engines have up to 40% more fuel efficiency compared to conventional SI engines (PFI-SI), mainly because of higher compression ratio, lower pumping losses and higher energy per

unit of volume of diesel fuel than gasoline [34,60]. Due to the remarkably high combustion efficiency, DICI engines produce lower CO_2 emissions compared to PFI-SI engines. DICI engines have high soot and nitrogen oxide (NOx) emissions due to a very rich zone and high combustion temperature in the combustion chamber [64,65].

2.1.2 SI engines

Spark ignition engines are the most common internal combustion engines widely in use. SI engines can be found in personal cars, small boats and even chainsaws! Combustion in a spark ignition (SI) engine is fundamentally different from a CI engine. SI engines burn a homogeneous and around stoichiometric mixture in a flame propagation process [60,66]. Port fuel injection spark ignition (PFI-SI) engines are conventional SI engines. Opposite to the DICI engines, in PFI-SI engines, fuel is injected into the intake manifold and premixed with air before entering the combustion chamber. The mixture gets compressed inside the cylinder and an electrical spark ignites it. Spark plug is the means of ignition onset, and the combustion phasing control is done through the spark timing. Flame propagation is the process of burning a homogeneous fuel-air mixture, starting from the spark plug and propagating to the cylinder walls. Knock, which is driven by the unfavourable auto ignition of the end gas, is an issue in SI engines which decreases the combustion efficiency and in case of super knock causes engine damage [67–69]. An alternative to PFI-SI combustion engine is direct injection spark ignition (DISI) engine. These engines are categorized as single mode homogeneous DISI and mixed mode stratified-combustion DISI (SC DISI). In these types of engines, gasoline is directly injected into the combustion chamber. For SC DISI, mixture composition in low load and speed is stratified having a lean global equivalence ratio. For higher load mixture composition is homogeneous and around stoichiometric [70–72]. PFI-SI engines are easy to control, have lower production costs compared to DICI engines and three-way catalysts to reduce the emissions [73,74]. High pumping losses in partial load is a known challenge for PFI-SI engines. This loss happens due to the controlling of the engine load by a throttle. Low fuel efficiency and knock are the other challenges of PFI-SI engines [20,65,75].

2.2 Advanced combustion concepts

Each of these engine technologies (DICI and PFI-SI) have advantages and disadvantages. Engine researchers have tried to combine the advantages of DICI and PFI-SI engines and create new combustion concepts and technologies with high fuel efficiency and low emissions. Fig. 2.2 is the modified conceptual model proposed by Bengt Johansson [76]. This triangle has two edges of CI and SI. The

third edge is homogeneous charge compression ignition (HCCI) concept which is a combination of SI and CI concept.

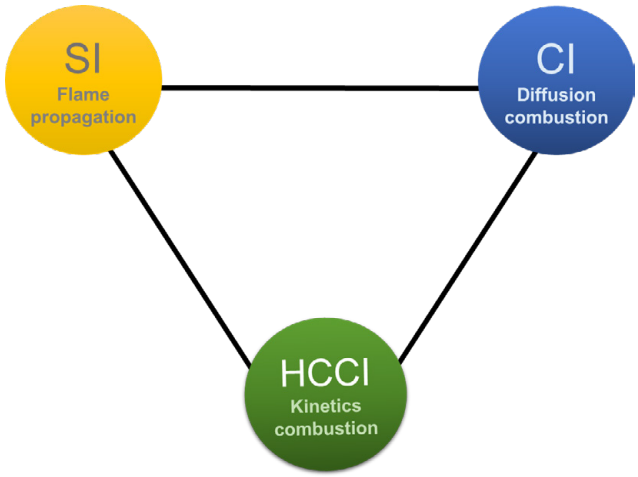


Fig. 2.2. The three fundamental combustion concepts [76].

These three edges of the combustion concepts triangle are three major combustion processes [76]. In the combustion concepts triangle, the properties of three major combustion concepts of CI and SI and HCCI are merging each other at different extent to create modern combustion concepts. These modern combustion technologies combine the advantages of SI and CI and HCCI and try to avoid the disadvantages of these technologies [35,77,78]. HCCI Combustion duration is comparatively shorter than CI or SI engines. This is mainly due to the high required CR to trigger auto-ignition and spontaneous combustions in the entire combustion chamber [79,80]. It is difficult to control combustion phasing in case of an extremely short combustion duration. Therefore, the HCCI engine is operated on globally lean mixture to lower the combustion rate and increase the combustion controllability. This results in a low temperature combustion (LTC) phenomenon in the combustion chamber. Low temperature combustion (LTC) is the basic concept of most of the proposed low emissions and high efficiency combustion technologies. Fig. 2.3 shows the combustion concepts triangle, including alternative combustion concepts on the triangle sides [61]. The two main categories of the LTC concept are homogeneous charge compression ignition (HCCI), the lower edge in combustion concepts triangle at Fig. 2.3, and stratified charge compression ignition (SCCI), the right and left sides of the combustion concepts triangle.

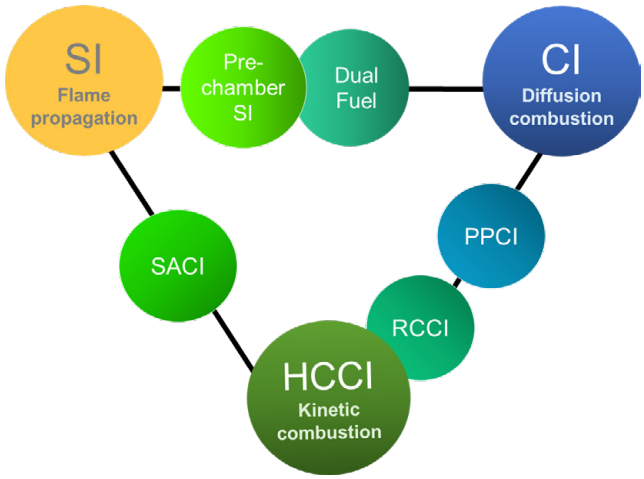


Fig. 2.3. Fundamental and alternative combustion concepts [61].

The right side of the combustion concepts triangle represents "fuel concentration SCCI," including two main categories of partially premixed compression ignition (PPCI) and reactivity-controlled compression ignition (RCCI) modes. In Fig. 2.3 , the left side of combustion concepts triangle represents "thermal SCCI", and includes spark assisted HCCI (SA-HCCI) also called spark assisted CI (SACI) combustion mode [35,77,78,81]. Besides high efficiency the ultralow NOx and soot emissions reduces the dependency of LTC engines on NOx and soot exhaust after treatment systems to meet the emissions regulations compared to DICI engines [35,81,82].

Fig. 2.4 is a schematic figure that demonstrates different mixture preparation in the combustion chamber of CI engines.

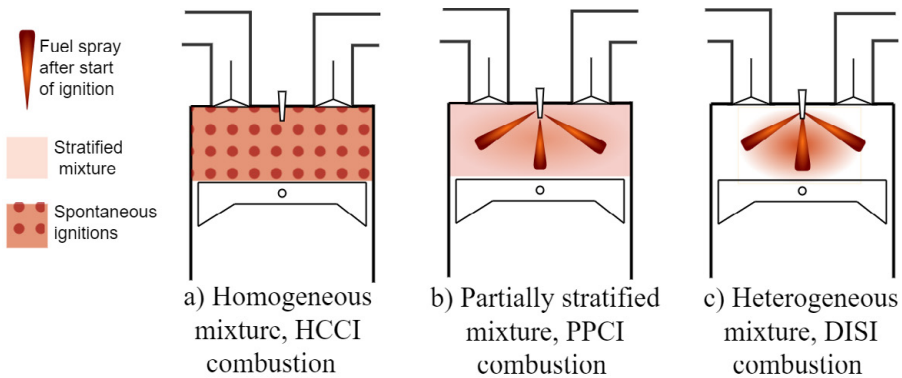


Fig. 2.4. Schematic of different concepts in CI combustion strategies, inspired from [83].

Modern CI combustion concepts try to overcome DICI drawbacks by avoiding heterogeneity and introducing HCCI and fuel concentration SCCI concepts. As it is explained earlier, in an HCCI engine, theoretically spontaneous ignition starts in all the combustion chamber and a homogenous charge burn, as illustrated in Fig. 2.4, a.

The mixture stratification process in fuel concentration SCCI including PPCI and RCCI combustions, is a midway process between HCCI and DICI. The concept of SCCI was introduced to overcome DICI emission problems and HCCI combustion controllability problems, while keeping the combustion efficiency high [35,84]. As an example, for a PPCI combustion, Fig. 2.4 direct injection begins during the compression stroke, therefore mixture in PPCI combustion is not homogeneous and not completely heterogeneous [33,34,85,86]. In fact, unlike DICI, in PPCI, injection and combustion are not parallel. The goal in PPCI injection strategy is to have a separation between injection and start of ignition, to provide enough time to form a partially premixed mixture for combustion, illustrated in Fig. 2.4. b. [35,36,87]. The conventional CI engines are demonstrated in Fig. 2.4, c (explained in section 2.1.1)

2.2.1 HCCI combustion

In this study the engine operating mode is HCCI. Therefore, in this section we will have a closer look at the HCCI combustion mode. Fig. 2.5 demonstrates the sequence of events in a four-stroke HCCI engine.

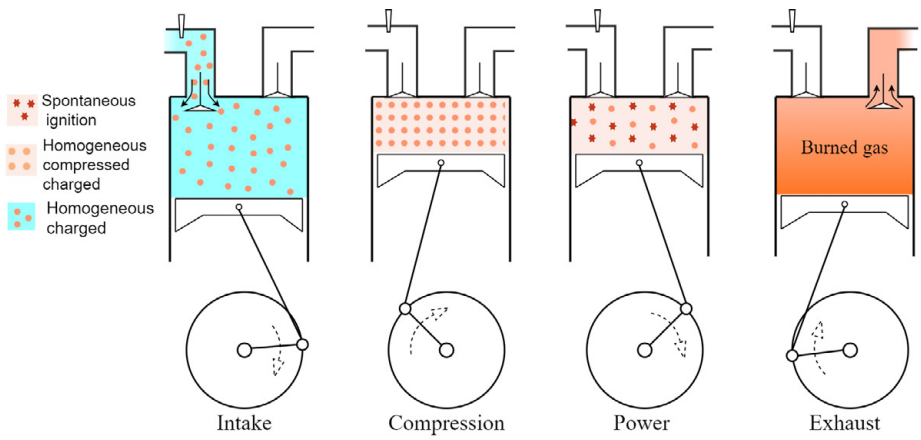


Fig. 2.5 The sequence of events in a four-stroke HCCI engine.

In an HCCI engine a homogenous mixture of fuel and air enters the combustion chamber, similar to PFI-SI, or forms inside the combustion chamber, like a DISI engine. The piston compresses the fuel-air mixture and the temperature increase during the compression, drives the auto-ignition of the mixture, like DICI combustion [88,89]. It should be considered although the HCCI concept known as

“homogenous” charge compression ignition combustion, but in a real engine, there are always thermal stratifications or other inhomogeneities. Also, fuel stratifications and inhomogeneities may also happen due to the asperities in preparing a fully homogeneous charge [79,88].

Because of the kinetics combustion characteristics of HCCI ignition, HCCI combustion is not affected from flame propagation like SI engines; And due to the homogenous mixture, not any diffusion flame like DICI engines happens during an HCCI combustion. Therefore, this combustion technology is widely used for fundamental fuel and combustion studies [90–96]. Due to this different working principle of HCCI combustion, the appropriate input parameters for the PFI-SI and DICI engines necessarily are not optimal for an HCCI engine, and vice versa. As an example, the intake temperature of a conventional engine is preferable to be the ambient temperature and in case of EGR, cooled EGR is recommended to lower the NOx emissions [97–100]. High intake temperature is less a limiting factor for HCCI combustion because HCCI is a type of LTC, and a high intake temperature will not effect the NOx formation within it [80,101,102]. High intake temperature facilitates the homogeneous charge preparation. Preheating of air and fuel mixture before or inside the intake manifold is a promising way for preparing a homogenous charge [103,104]. Apart from preheating the air and fuel mixture there are different methods for preparation of homogeneous mixture of an HCCI combustion. Injection timing, using high EGR and negative valve overlap (NVO) are other methods [103,105–109]. The NVO method benefits from variable valve timing and traps the exhaust gases inside the combustion chamber and increases the initial in-cylinder temperature. The NVO method increases the internal EGR. In this method the exhaust valves are closed before the exhaust gases are completely discharged from the combustion chamber [110] . The HCCI concept has high fuel efficiency, extremely low NOx and soot and is fuel flexible [94,111,112]. The main challenges of HCCI engines, which slows down the commercial production of them, are cold start problems, difficulty in combustion phasing control, limited operating range and higher hydrocarbon (HC) and carbon monoxide (CO) emissions [35,90,111,113,114].

HCCI combustion phasing control

First, the reason behind the importance of combustion phasing control in HCCI should be understood. In an HCCI engine the fuel-air mixture enters the combustion chamber and compresses to the point that the pressure and temperature is exactly right for the auto-ignition of the mixture. If the optimum pressure-temperature point for the auto-ignition of a specific mixture, happens before TDC, the piston has to work against the high combustion pressure. The early combustion increases the compression work and decreases the expansion work, and as a result decreases the efficiency [115–117]. The excessive pressure rise during the early combustion increases the mechanical stress on the engine parts which could damage the engine.

This early reaction will also increase the NOx level [88]. If for the same mixture, the intake temperature or the pressure is reduced, the combustion phasing continuously retards and become more stable and efficient. If this reduction continues further, fuel consumption, cycle to cycle variation, hydrocarbon (HC) and carbon monoxide (CO) emissions will increase. When the temperature–pressure is not optimum to ignite or lead to a complete combustion anymore, misfire happens [76,79,114]. Since HCCI combustion is a kinetics combustion, it is overly sensitive to pressure, temperature, mixture strength and fuel properties or any other parameters that controls those factors [79,104]. HCCI combustion does not have any direct means of ignition timing control, like spark or injection timing [114]. Every parameter that can affect the combustion phasing, like the fuel-air mixture strength or the auto-ignition properties of it, has the potential to be used as an HCCI combustion timing actuator [84,114,117–119].

Operating range limits

Another limitation towards commercialization of HCCI engines is the operating range limit in terms of load [120,121]. The theoretical operating range of an HCCI engine is much wider than the practical range of it. In practice, the HCCI range depend on the acceptable fuel efficiency, emission levels and noise [88]. If we take another look on the combustion concepts triangle in Fig. 2.2, we can claim that on each edge, there is a specific mixture strength; the SI edge has stoichiometric charge, equivalence ratio (ϕ) $\approx$1, the CI has rich mixture (ϕ>1) in the combustion zone in a globally lean condition, and finally the HCCI combustion occurs in lean (ϕ<1) condition. We can conclude that HCCI concept is optimum to work at lean condition. But how lean? Low combustion efficiency, misfire and therefore excessive HC and CO are the low load limits of HCCI combustion, with this limit around $\phi \approx 0.25$ [88,117,122]. Excessive pressure rise rate, too fast combustion, and possibility of NOx formation at high load are limiting factors for richer mixture in an HCCI combustion. The rich limit for HCCI combustion in around $\phi \approx 0.4$ [75,88,114,117].

2.3 The Kinetics behind two-stage combustion

In an HCCI engine, when the premixed fuel-air mixture is heated up to approximately 750 K or higher, chain branching reactions accelerate the radical generation. The radical generation in the presence of heat, leads to a thermal runaway: so, called auto ignition [84,123]. Undesirable auto-ignition might damage the engine, like knock or super-knock in an SI engine. A controlled auto-ignition is desirable since the auto-ignition is the onset of HCCI or DICI combustion. In an HCCI combustion, an array of consequential auto-ignition events throughout the combustion chamber happens and releases the heat. The onset of significant

reactions is extremely temperature dependent and takes place after the reactant temperatures exceeds 550K [104]. In two stage combustion the main chain branching exothermic reaction pathway of alkyl radicals (R) and (H_2O) with O_2 are responsible for LTHR [92,111,124]. ITHR is caused by the early reactions before the start of the main combustion and after the LTHR reactions. The main exothermic combustion reactions are $H_2O_2 + M = OH + OH + M$, where M is called the third body and could be any molecule in the mixture [78,99,120].

2.4 Beyond a variable

The strength of fuel/air mixture is described using the fuel/air equivalence ratio (ϕ). Fuel/air equivalence ratio is the actual ratio of fuel to air in the unburnt gas to the ratio of fuel to air in the stoichiometric mixture of that fuel (Equation 2.1) [59,60].

$$\phi = \frac{(F/A)_A}{(F/A)_s} \qquad \text{Equation 2.1}$$

The potential of LTC technology as an ultralow emissions and high efficiency combustion technology has been previously discussed. Both fuel and thermal stratifications are effective strategies for achieving LTC (right and left side of the combustion triangle in Fig. 2.3). ϕ is an important parameter controlling the combustion behaviour of a fuel-air mixture in LTC engines. A better understanding of the combustion characteristics of fuel/air mixtures at different ϕ levels will increase the chance of success in combustion phasing control of LTC. Apart from the strong impact of ϕ variation on emissions, fuel efficiency, combustion phasing and combustion stability, in all types of engines, ϕ variation affect knock in SI engines. Avoiding knocking is a major reason for the low CR of conventional SI engines. A proper understanding of the heat release rate (HRR) and auto-ignition behaviour of homogeneous mixtures of various fuels and blends with different ϕ levels

Auto–ignition of a homogenous charge is a desirable phenomenon in an HCCI engine. I have explained earlier that every parameter that can affect the combustion phasing has the potential to be used as an HCCI combustion timing actuator. Therefore, the ϕ level of a mixture and the auto–ignition properties of it could perfectly be used as a control actuator [84,114,117–119].

Due to the fast kinetics HCCI combustion, the optimum operating range for an HCCI engine is in the lean range and between $\phi \approx 0.25$ and $\phi \approx 0.4$; and again, due to the fast kinetics characteristic of HCCI combustion fuel/air equivalence ratio (ϕ) has a significant role in combustion control. Even in this range, that might seem narrow the variation of ϕ will significantly affect the combustion phasing [88,131]. ϕ is therefore not only a variable in HCCI combustion but an actuator for

combustion phasing control. There are diverse ways to effect ϕ or charge dilution. Increase or decrease oxygen concentration by adjusting air flow, boosting or exhaust gas recirculation (EGR), or vary the fuel flow are most common strategies for ϕ variation

2.5 Various fuel indexes

The most known fuel indexes are the research octane number (RON), motor octane number (MON) and cetane number (CN) test methods. RON and MON are design for SI engines and gasoline like fuels. These two test methods give an understanding of any fuels resistance to knock [132,133]. The CN test method is designed for CI engines and evaluates the auto-ignitability of the diesel like fuels. The HCCI fuel index [93], and Lund-Chevron HCCI number [95] are two more recent test methods that explain the fuel combustion behaviour under HCCI combustion. The modified version of the combustion concepts triangle [76] based on the relevant fuel testing methods would look like Fig. 2.6. There is established methods for the edges of combustion concepts triangle but not for the sides!

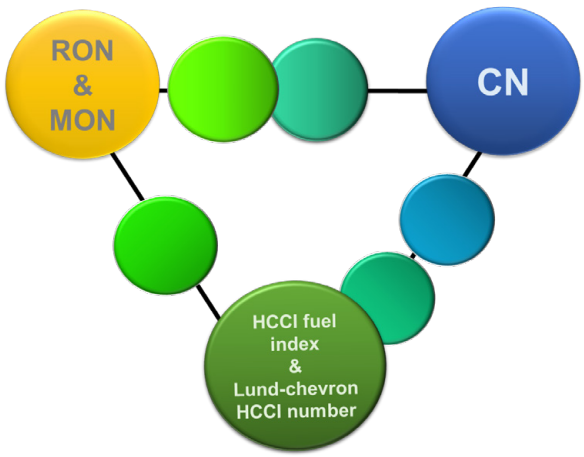


Fig. 2.6 modified combustion triangle based on the fuel indexes.

In modern combustion engines the unburned gas has comparatively lower temperature and higher pressure than the older-generation engines of the same combustion concepts [74]. For this reason, many researchers claim that regardless of combustion technologies, RON and MON are not any more proper indicators of fuel behaviour or antiknock quality of a fuel in modern engines [68,73,74]. Other indexes such as the toluene number [68], octane index [134,135], HCCI Fuel Index [93], and Lund-Chevron HCCI number [95] are more appropriate for modern engines and modern combustion concepts. This method may be able to explain the combustion behaviour of fuels on the edges of combustion triangle to some extent

but will not provide inclusive information about stratified LTC which are located on the sides of the triangle. Due to the complexity of combustion phenomenon none of these indexes can provide a full image of combustion phenomenon and fuel behaviour in combustion chamber. Consideration of all these indexes together may provide some information to estimate the fuel behaviour in combustion concepts located on the triangle's sides (mixed mode combustions) [88]. None of these methods, specifically evaluate the effect of dilution or ϕ on the combustion behaviour of fuel. It might be the case that using conventional ICE did not bring up the need or interest to develop a specific method for explaining combustion behaviour in thermal or fuel stratified combustion, but the development of LTC concepts was a game changer.

2.5.1 What is ϕ-sensitivity?

Creating various levels of thermal or fuel stratifications inside the combustion chamber is a method to lower the combustion pressure rise rate (PRR) in HCCI engines and develop new combustion concepts such as PPCI, RCCI and SACI [35,76]. But how do these stratifications promote combustion smoothness?

Auto–ignition properties of fuel/air mixture with different ϕ levels are different. As an example, pressure-temperature trajectories of these mixtures have different ignition delays and to have the same ignition delays, different thermodynamic boundaries are needed to be set. These different ignition delays or thermodynamic boundaries are not similar for different fuels. A suitable fuel for stratified combustion is a fuel that its auto-ignition properties are sensitive to variations in ϕ. Therefore, the fuel stratification (different ϕ inside the combustion chamber at the same time) produces asynchronous auto-ignition and as the result a staged heat release rate (HRR). The grade of auto-ignition properties sensitivity of a fuel at different ϕ levels is known as the ϕ-sensitivity property of that fuel [96,127,136].

There are several studies performed during the last years to try to identify the impact of ϕ on auto–ignition behaviour of various levels of fuel/air mixture's strength [96,127,136–139]. Since the HCCI combustion is kinetics combustion and not affected from flame propagation or diffusion flame, HCCI has been selected widely as the combustion mode for auto-ignition studies of homogeneous mixture at different ϕ levels [96,136,139]. These studies aim for designing a strategy based on fuel stratification to control low-temperature gasoline combustion (LTGC). Understanding the effect of low-temperature reactions (LTRs) on LTGC was another challenge that these studies tried to overcome. John Dec and Magnus Sjöberg has introduced the initial ϕ-sensitivity number in 2006 [127,136]. They have continuously worked on the idea and in 2019 based on the kinetics simulation using the chemical kinetics simulation software, ANSYS CHEMKIN-PRO, they defined the ϕ-sensitivity number as:

$$\text{Norm } \phi - \text{sensitivity} = -\frac{1}{T}\frac{dT}{d\phi} \qquad \text{Equation 2.2}$$

where T is the ITHR ignition delay, which refers to the end of the ITHR stage [96].

Afterwards, in the research on the ϕ-sensitivity concept, the effect of early reactions on ϕ-sensitivity was recognized [128]. The exothermic reactions that occur before the main combustion and high temperature heat release (HTHR) are called early reactions. These exothermic reactions lead the combustion event at the cylinder temperatures between 600 and 800 K. These reactions produce free radicals as feedstock for the main combustion [89,126]. Early reactions generate both low temperature and intermediate temperature heat releases. Fig. 2.7 shows the early heat release of HCCI combustion of PRF63.

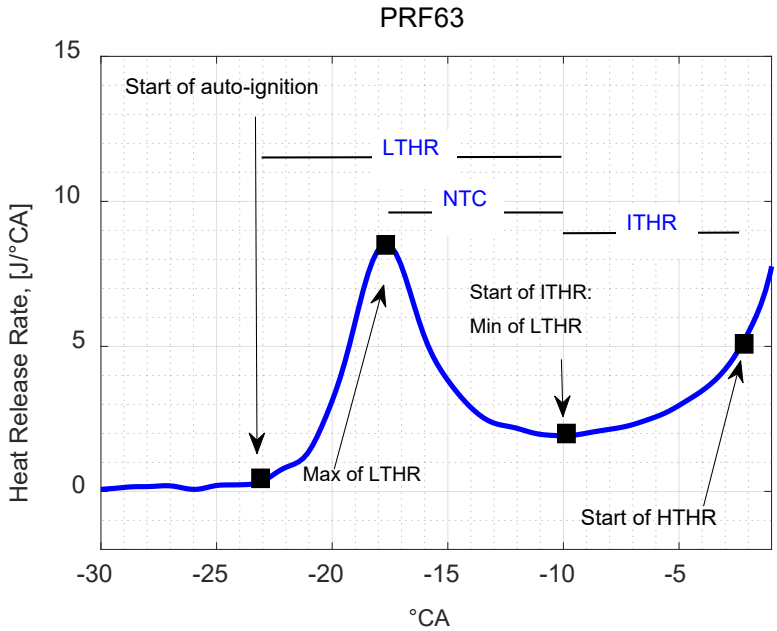


Fig. 2.7. Heat release by early reactions in a two-stage HCCI combustion.

ϕ-sensitivity research suggests that ITHR has a key role in ϕ-sensitivity of low temperature gasoline combustion (LTGC) [96]; especially because, high octane gasoline does not exhibit LTHR in naturally aspirated or low boost condition and ITHR is the main early heat release in their combustion process.

These studies also indicate that despite the start of main combustion which is ϕ-sensitive, the start of LTHR is not ϕ-sensitives [96]. Low intake temperature and high in-cylinder pressure or boosting are boundary conditions that promote the ϕ-sensitivity of different fuels. The combustion response of different fuel/air mixtures to the ϕ variation is not the same. In the other word, different fuels have different ϕ-

sensitivities [96,136,140]. As discussed in section 2.2.1, HCCI combustion is extremely sensitive to ϕ variation. The ϕ sweep in a conventional engine at constant intake pressure and temperature has two main limiting factors. At a higher ϕ levels an excessive pressure rise rate and at a lower ϕ levels misfire are the limiting factors. The ϕ sweep in a conventional engine does not affect the timing of LTHR [136].

The sensitivity of HCCI combustion to ϕ variation, complicates the design and data processing of experimental ϕ-sensitivity studies. To achieve a constant and stable combustion phasing during ϕ sweep experiments, the intake temperature (Tin) or CR must be adjusted proportional to the ϕ level. During a ϕ sweep experiment, some fuels do not need great adjustments of required CR or Tin to keep the combustion phasing constant. These fuels have a lower level of ϕ-sensitivity [136]. Low ϕ–sensitivity and high RON fuels have lower $COVI_{MEP}$ and PRR_{max} during homogeneous SI at both low and high loads [96]. In an SI engine in case of any thermal stratification in the combustion chamber or inhomogeneities in the fuel/air mixture with low ϕ-sensitivity, different local ϕs have similar auto–ignition properties and ignition delays and therefore, have higher knock resistance [90,96]. These blends generate less early heat release compared to the fuels with higher ϕ-sensitivity. High ϕ–sensitivity–low RON fuels are appropriate for stratified combustions like DICI engines. High ϕ–sensitivity–high RON fuels are compatible with LTGC application; and high ϕ-sensitivity–medium RON work well in PPC engines [82,89,111,123,139,141].

2.6 Renewable fuels, a problem, or an opportunity?

A major step to transition of ICE towards sustainability, is replacing the fossil fuels with renewable substitutes. In this section the advantages and obstacles for renewable fuels as an option for future transportation is discussed briefly.

Biofuels are the very first renewable fuels used by human beings [142]. The first–generation biofuels were ethanol from sugarcane and biodiesel from soybeans [25,52]. The biomass feedstock for both fuels was food–crop. Using food–crops as a feedstock for biofuel production is not always a sustainable approach, both due to the negative possible impact on food security and because of the impact of referred cultivation to several planetary boundaries´ threat, (e.g., land use and freshwater use) [25,143].

There are many different pathways and feedstocks for renewable fuels or biofuels production [142]. Electrofuels are another category of renewable fuels that are available as gaseous and liquid fuels [65]. Hydrogen is an ideal example of future electrofuel. It can be used as a carbon free fuel for ICEs and serve the role of energy storage for renewable solar and wind electricity. Hydrogen can act as an intermediate substance to produce electro hydrocarbon and value-added chemicals.

Fig. 2.8 demonstrates different energy conversion pathways for renewable fuels (including electrofuels and biofuels) production.

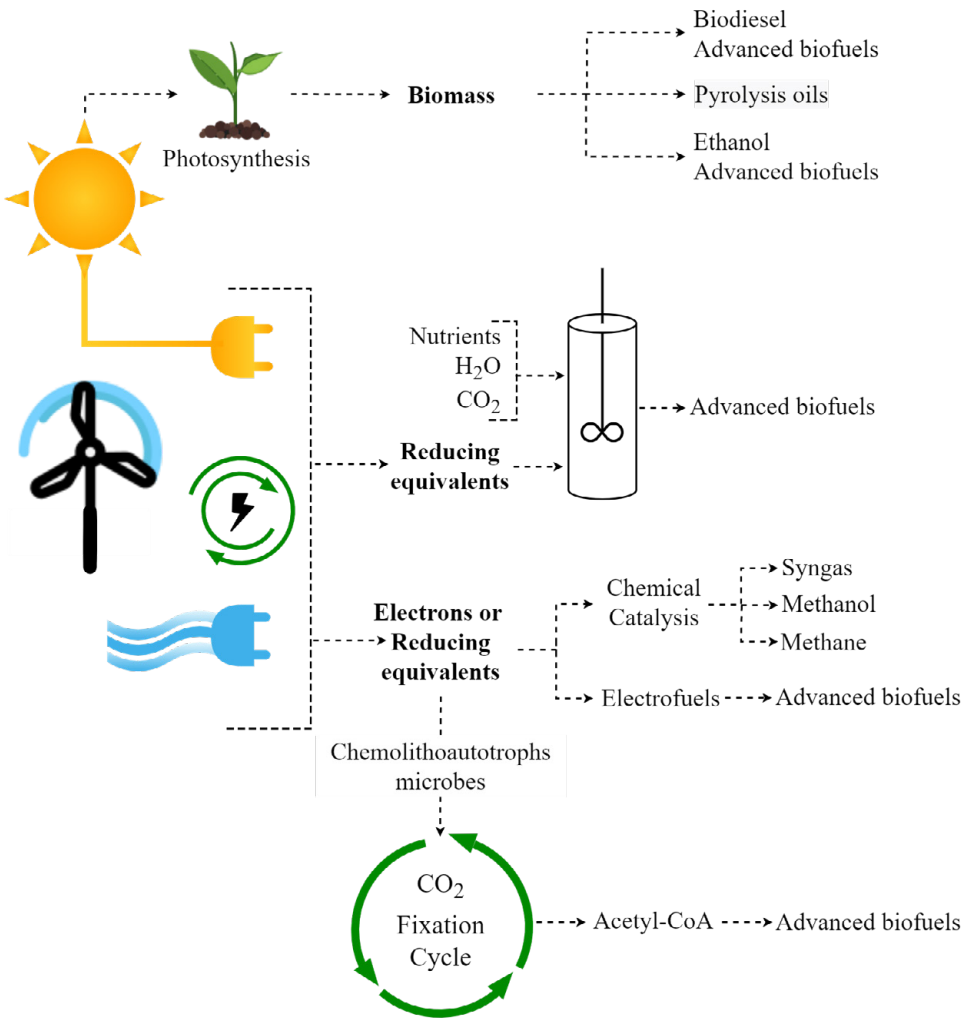


Fig. 2.8. Energy conversion pathways for biofuel production, inspired from[49].

This diagram is inspired from chapter 38, "Advanced biofuels and bioproducts" book [142]. There are some terms in the Fig. 2.8 that might need more explanations.

- Reducing equivalent based on "Encyclopaedic Dictionary of Polymers[144] "is: "An amount of a reducing compound that donates the equivalent of 1 mole of electrons in an oxidation-reduction reaction. The electrons may be expressed in the form of hydrogen atoms."

- Chemoorganotrophs obtain chemical energy through oxidation (electrons or reducing equivalent) to consume inorganic substances and produce organic ones. Reductive acetyl-CoA is one of the by-products of these carbon fixation cycles that can rapidly generate different liquid fuel molecules [49].

Ethanol and methanol, so called low molecular weight alcohols, contain high percentage of oxygen. Therefore, ethanol and methanol have lower energy density compared to the conventional gasoline [44]. Both (ethanol and methanol) will enhance the anti–knock quality of conventional fuels, lower the emissions, and consider as renewable fractions of fossil fuels [83,145,146]. Both ethanol and methanol have high hygroscopicity property (water absorption and adoration) which is a disadvantage for a fuel. Methanol has another drawback, blend of this light alcohol with gasoline inhibits highly corrosive substances that can damage engine components [65,147]. There are some higher alcohols (higher molecular weight) which have less oxygen content, higher energy density, less hygroscopicity. These alcohols are compatible with the current engine design and material. Butanol isomers are among these higher alcohols which many studies are conducted on the production and application of them as renewable soot free fuels or additive in ICEs [43,44,148,149].

Different renewable fuels can be used as both combustion fuels and energy storage. This dual application of renewable fuels in connection with other renewable energy systems enables the transition of energy and transport sector to a sustainable system.

2.7 Approach of the study

2.7.1 Research questions

The purpose of this Ph.D. work is to characterize renewable fuels in connection with both modern and conventional combustion concepts, using experimental approaches that lead to the development of an empirical ϕ–sensitivity test method. This test method expected to be able to quantify the relative ϕ–sensitivity of different liquid fuels using a CFR engine; and evaluate the ϕ–sensitivity of fuels independent of numerical methods and kinetics mechanisms. This PhD work is an effort to answer the following questions:

1. What are the determinative input and output parameters of a CFR engine in HCCI combustion?
2. How to isolate the fuel's ϕ-sensitivity from the fuel reactivity?

3. How to formulate the dependency of early reactions to the changes of equivalence ratio using a CFR engine in form of a ϕ-sensitivity index?
4. What is the dependency of ϕ-sensitivity to the intake temperature heat of vaporization and combustion phasing?
5. How does the blending ϕ-sensitivity change for alcohols?
6. What is the conclusion of ϕ-sensitivity test method for designing load adaptive fuels effective for different combustion concepts?

2.7.2 Research objectives

Different fuels exhibit different pressure and temperature sensitivities to ϕ variation, and the ϕ-sensitivity is different for the fuel with similar octane number and different composition [96,150]. The objective of this study is to develop an empirical test method for evaluation and quantification of liquid fuel's ϕ–sensitivity. A standard method, which can be quickly performed in refineries and fuel production industries independent of complex prerequisite data such as detailed kinetics mechanisms. This method is expected to:

1. Provide supplementary knowledge for knock resistance evaluation of SI engine fuels
2. Facilitate fuel tailoring for thermal or fuel stratified combustions as well as homogenous combustions
3. Provide knowledge for designing control strategies of LTC at different engines loads
4. Provide knowledge for tailoring load adaptive fuels that can tolerate different loads with minor combustion instability for different combustion concepts
5. Provide knowledge about future fuels response to modern combustion concepts in future ICEs.

2.7.3 Thesis contribution

This PhD work uses the complex science behind the combustion behaviour of surrogate gasolines and alcohols, to establish a technically simple to implement and calculate test method. Apart from the possible application of this method at the refineries, there is possibility of using the produced database for future numerical studies. A part of this extensive database was used for numerical auto ignition investigation which proves the validity of this database for application in future numerical studies too.

The proposed Lund ϕ-sensitivity test method provides the opportunity to compare different fuels and blends to each other and evaluate the knock intensity of them further than conventional methods such as research and motor octane numbers. This test method also facilitates the tailoring and evaluation of future fuels for future LTC combustion engines.

Chapter 3

Experimental facilities and tools

The experimental work in this thesis was conducted on a modified Cooperative Fuel Research F1/F2 (CFR-F1/F2) engine. The experimental facilities include an engine, an emissions measurement system, and a data acquisition system. In this chapter, all the experimental facilities are introduced. Moreover, the heat release calculation and some other calculations behind the data post processing are briefly explained.

3.1 Experimental facilities

The modified CFR-F1/F2 engine of this study is installed in an instrumented test cell which allows to monitor and control the required boundary conditions during the experiment.

The control system for the engine is an in-house control system, and control of different parameters is performed by a LabVIEW interface from a control room beside the test cell. A Horiba Mexa 7500 is used as an emissions analyzer. Fig. 3.1illustrates the schematic of the test cell facilities.

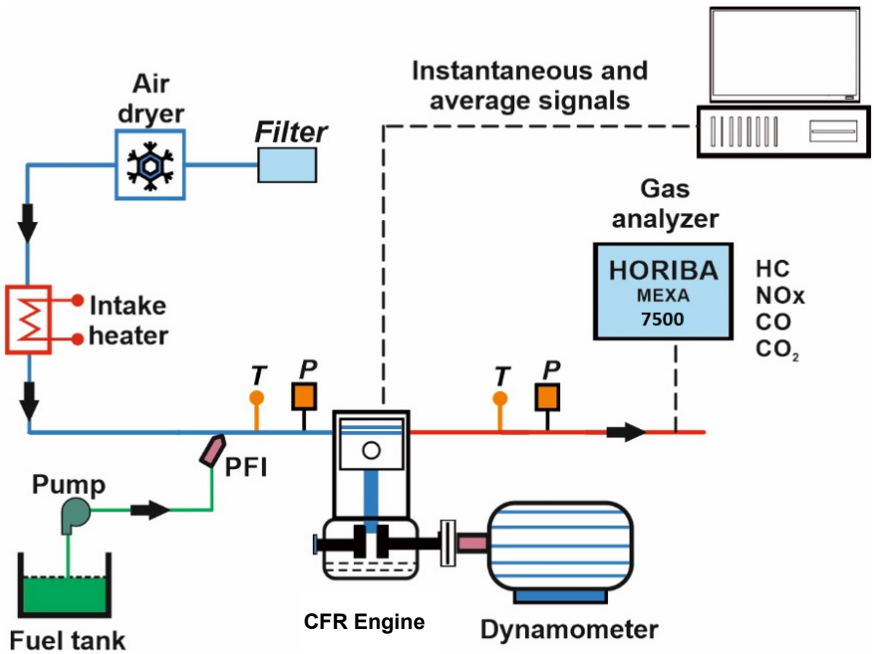


Fig. 3.1.Schematic of the modified CFR F1/F2 engine, PFI (port Fuel Injector), P (pressure sensor) and T (temperature sensor)

3.1.1 Research engine

A Cooperative Fuel Research F1/F2 (CFR-F1/F2) engine is a fuel test device which has variable compression ratio (CR) on its single cylinder. This engine is designed to be used in developing gasoline knock-test methods (RON and MON). Due to its variable compression ratio, it is versatile to be used with different fuels that have different physical and chemical properties [80,132,133,151]. The engine specifications are presented in Table 3.1.

Table 3.1.CFR engine specifications.

CFR engine	
Displacement volume	612 cm3
Number of cylinders	1
Bore	83 mm
Stroke	114 mm
CR	Variable (4:1 to 18:1)
Number of valves	2
Intake valve opens	10° ATDC ± 2.5°
Intake valve closes	146° BTDC ±2.5°
Exhaust valve opens	140° ATDC ± 2.5°
Exhaust valve closes	15° ATDC ± 2.5°

By deactivating the spark plug and replacing the engine original carburettor with port fuel injectors, the CFR engine was modified for HCCI combustion. The port fuel injection system together with an intake air heater, provides a homogeneous charge at favourable temperature. Fig. 3.2 shows the modified CFR engine used for this PhD study.

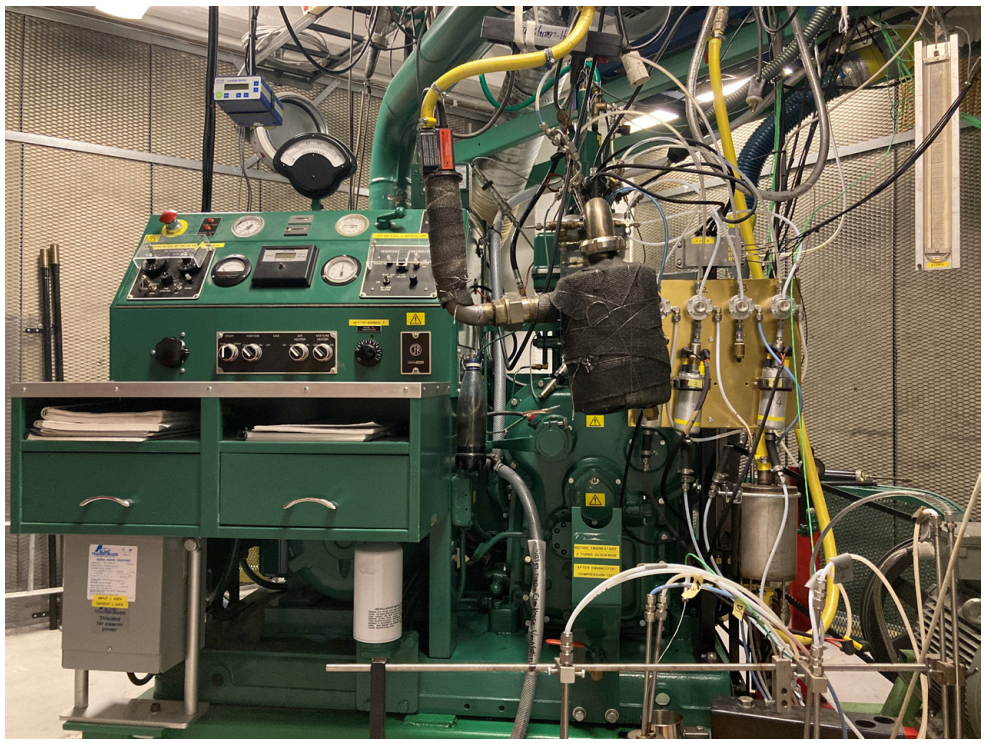


Fig. 3.2.The modified CFR engine at the Energy sciences lab of Lund university.

The engine works in a naturally aspirated condition. To make sure that the incoming air is dry and provides constant intake air humidity, an intake-air refrigerator unit is used. The engine cooling system provides a water temperature of 373 K.

3.1.2 Data acquisition system

Using a data acquisition system (DAQ) is one of the solutions to measure different engine and combustion parameters, A DAQ system measures electrical or physical parameters such as current, voltage, temperature, or pressure from an experimental apparatus. This system consists of sensors, measurement hardware and software. There are two types of signals in terms of frequency, low and high frequency signals.

Low sampling frequency data

Low frequency signals are up to 50 Hz. In the experimental apparatus of this study there were two type of low frequency signals, data logger and exhaust gas data.

The intake, exhaust, and cooling system signals are collected via a logger unit. The inlet charge temperature is measured by a thermocouple mounted in the intake manifold and close to the inlet valve. The exhaust gas temperature is located in the exhaust manifold close to the exhaust valve. Both intake and exhaust pressures are measured via piezo electric Kistler sensors. All these pressures and temperatures are time-averaged.

Exhaust gas analyser

In this study only gaseous emissions are measured. The emission measurement is performed using a Horiba Mexa 7500 equipped with a heated oven. The Mexa 7500 of this work uses a non-dispersive infrared measurement technique to measure CO and CO_2 cold and dry. THC and NOx are measured hot and wet using a flame ionization detector (FID) and a chemiluminescence technique, respectively. The emission analyser is calibrated with synthetic calibration gases before each engine test. Oxygen is calculated from the measured exhaust gas emissions.

In this research work fuel/air equivalence ratio (ϕ) is calculated based on the relative air/fuel ratio (λ). The lambda is calculated from the exhaust gas emissions, and for redundancy measured using ETAS sensor; then lambda is converted to the equivalence ratio as, Equation 3.1.

$$\phi=\frac{1}{\lambda} \qquad \textit{Equation 3.1}$$

High sampling frequency data

The high frequency signals are up to 30 kHz and are based on the engine crank angle. The CFR engine of this study is equipped with a rotary encoder with a 0.2 CAD resolution and provides the crank position measurement and a TDC position. The In-cylinder pressure is acquired using a Kistler 6125C pressure transduce. The cylinder pressure measurements are filtered and ensemble-averaged for every experimental point.

3.2 Fuel selection

This study consists of three main parts: pre-evaluation, method definition and method implementation. Different fuels and blends from conventional gasoline to surrogate gasoline and neat alcohols, as well as blends of alcohols with surrogate gasoline are used in different steps.

Gasoline is not a single molecule fuel, but a complex mixture of hundreds of different hydrocarbons. Moreover, gasoline does not refer to a sole product. A variety of fossil fuels with different octane numbers and different physical and chemical properties name gasoline [85,86,152]. These complexities make gasoline inappropriate as a reference fuel. Selecting a suitable surrogate gasoline instead of gasoline is an important aspect that helps researchers to limit the chemical and physical complexity of tested fuels and establish a baseline for further experiments on renewable future fuels [68,153,154]. Surrogate gasolines are categorized as single-component, binary and multi-component blends [89,155]. The most well-known surrogate gasolines are primary reference fuels (PRFs). These fuels are blends of two paraffins, iso-octane and n-heptane and have been used for the development of the gasoline octane rating test methods (RON and MON). Each PRF has an equal value for RON and MON, meaning that the octane sensitivity (S) of PRFs is zero. Conventional gasoline and all types of alcohols have different RON and MON, meaning an octane sensitivity above zero (S>0). Therefore, a surrogate gasoline that accounts for octane sensitivity, and is relevant for gasoline and future renewable fuels must be selected. Aromatics are known to be responsible for S in gasoline. Toluene is the most important aromatic component of gasoline, and its content can reach up to 35% in commercial gasoline [89,156,157]. Toluene reference fuels (TRFs) are blends of toluene and n-heptane and/or iso-octane. Oxygenates are other components of surrogate fuels. Ethanol is widely used as a gasoline additive to increase the octane number. Ethanol and other alcohols are also widely used as a renewable fraction for fossil fuels [80,120,155]. Thus, for this study toluene-ethanol reference fuels (TERFs) which are oxygenated reference fuels, are also considered. In surrogate gasolines iso-octane and n-heptane are the two paraffins, toluene is the aromatic and ethanol is the oxygenate component of the blend. The properties of the blend components are presented in Table 3.2.

***Table 3.2. Properties of fuel blend components. iso–Octane and toluene data from* [60]*, n–heptane data from* [115].**

Hydrocarbon class	Fuel	Molecular formula	RON	S	Boiling point, °C	HoV, KJ/Kg	Calorific value, MJ/ Kg
Aromatics	Toluene	$C_6H_5CH_3$	121	11	110	412	40.58
iso-paraffins	iso-octane	C_8H_{18}	100	0	99	305	44.46
n-paraffins	n-heptane	C7H16	0	0	98.5	321	44.56

Since the approach of this PhD study was the evaluation of future fuels through an innovative test method, apart from ethanol, two other alcohols (n–Butanol and iso–butanol) and the volumetric blends of iso–butanol are evaluated.

Table 3.3 shows the physical and chemical properties of alcohols of this study in comparison to gasoline. The source of this data is the data sheet provided by the fuel company Preem, one of the partners of this PhD project.

Table 3.3.Physical and chemical properties of alcohols and gasoline.

	Gasoline	Ethanol	n-butanol	iso-butanol
Chemical formula	C4-C12	C2H5OH	C4H9OH	C4H9OH
Molar weight [kg/kmol]	-	46.07	74.12	74.12
H/C-ratio	1.795	3	2.5	2.5
Oxygen content by mass [%]	0	34.7	21.6	21.6
O/C-ratio	0	0.5	0.25	0.25
Density [kg/m3]	720-775	798.3	809.8	801.1
Viscosity [cST]	0.37-0.44	1.5	3.6	8.3
Solubility in water [wt%]	Negligible	Miscible	7.7	8.7
Flash point [°C]	-45	14	35	28
Auto-ignition temperature [°C]	232-280	362	343	415
Boiling point [°C]	25-210	78	117.6	108
Reid vapour pressure [kPa]	54-103	16	2.2	3.3
LHV [MJ/kg]	41-44	26.8	33.2	33.1
Energy density [MJ/l]	30-33	21.3	26.9	26.6
HoV [kJ/kg]	373	838	584	566
RON	88-98	108	98	105
MON	80-88	90	85	90
Stoichiometric air/fuel ratio	14.7-14.8	9	11.1	11.1

3.3 Experimental test matrix and methodology

In this study, HCCI combustion has been performed at different ϕ levels, three engine speeds of 600, 900, and 1200 RPM and three intake temperature (Tin) of 323, 373, and 423 K. The crank angle degree at which 50% of total accumulated heat is released (CA50) has been maintained constant. The intake temperature or compression ratio (CR) are two options to be used for the adjustment of combustion phasing at different ϕ levels of a fuel. Since the CFR engine has variable CR, the adjustment of CA50 was achieved by means of adjusting the CR. The target

equivalence ratio is achieved by variation of fuel mass. The details of the experimental set up for each campaign is presented under the related sections. Table 3.2 presents the engine operating condition for different campaigns.

Table 3.4. Engine operating condition.

Input parameters	Unit	Value	Variation
Tin	K	323,373, 423	± 1 K
Pin	bar	0.98	± 0.03
Engine speed	RPM	600, 900,1200	± 8
Coolant temperature	K	373 K	± 1
Oil temperature	K	330 K	± 8.5
CA50	°CA	8,5,and 3	± 0.5
CR	-	Variable	-
ϕ	-	0.25,0.31, 0.33, 0.35, 0.37, 0.4	± 0.005

3.4 Pre and post calculations

To design the experiment and to evaluate the results some pre- and post- calculations and data processing were needed. The most important calculations of this study are presented in this section.

3.4.1 RON and MON calculations

Designing the experiment requires fuel design as well. Considering one of the objectives of this study, isolating the effect of RON number from the fuel ϕ-sensitivity, a quadratic regression model developed by Solaka Aronsson et. al [158] was used to estimate RON and MON of the designed blends. Solaka Aronsson et. al have used toluene-ethanol reference fuels to map RON and MON.

After RON and MON estimation using the mentioned model, the designed blends were sent to Saybolt AB (project partner) for RON and MON measurements. More details are presented in the relevant result and discussion section.

3.4.2 Heat release calculation

In this study a single zone heat release model is used to calculate the heat release based on the pressure trace. The Woschni heat transfer model is used according to Heywood [60]. It has been assumed that the in-cylinder gas temperature when the inlet valve closes (TIVC) is known. TIVC is calculated based on the measured intake temperature considering the effect of residual gas and the heat transfer to the

walls [126]. The heat release calculations are performed for each individual cycle and the presented figures in this thesis are based on the mean value of 300 combustion cycles. More details about heat release calculation can be found in [94]. The average of 50 sampled motored cycles are used to tune the heat release as close to zero as possible for the motored pressure trace.

Equation 3.2 calculates the rate of heat release as a function of crank angle degree, with negligible crevice flow losses [60]. Since the combustion mode is HCCI, it is assumed that assuming that the temperature and the gas composition inside the cylinder are uniform.

$$\frac{dQ}{d\theta} = \frac{\gamma}{\gamma-1}\left[\frac{PdV}{d\theta} + \frac{VdP}{d\theta}\right] + \frac{dQ_{HT}}{d\theta} + \frac{dQ_{crevice}}{d\theta} \qquad \textit{Equation 3.2}$$

Where:
V and P are the cylinder volume and pressure respectively
γ is the ratio of specific heats (Cp/Cv).
θ is the crank angle degree
Q is heat release and QHT is heat transfer

3.4.3 Definition of CAD selection for the start of combustion

The identification of the auto-ignition points and the start of main combustion of a fuel in a CI engine have many different definitions and criteria [95,105,159,160]. Selecting the crank angle at which a certain percentage of accumulated heat is released is a method that is widely used [80]. This method is valid at constant load because the total accumulated heat release (TAcHR) is almost constant at different operating points for a single fuel. Since this method is a relative method, when the TAcHR is high, the percentage-wise selected auto-ignition point will move closer to the top dead centre (TDC), and when the TAcHR is low, this point will move away from the TDC. Instead, using an absolute value of the HRR in some studies is a way to exclude the effect of TAcHR on the selection of auto-ignition point or start of main combustion [95,105,152]. In this study, the crank angle degree (CAD) at which the rate of heat release reaches 0.2 J/CAD is selected as the auto-ignition point or the start of combustion and early reactions [152,157]. The start of the main combustion or the high-temperature heat release (HTHR) is selected as the crank angle degree at which the rate of heat release reaches 5 J/CAD. Fig. 3.2 illustrates the crank angle degree selection for the start of distinct phases of combustion in this study.

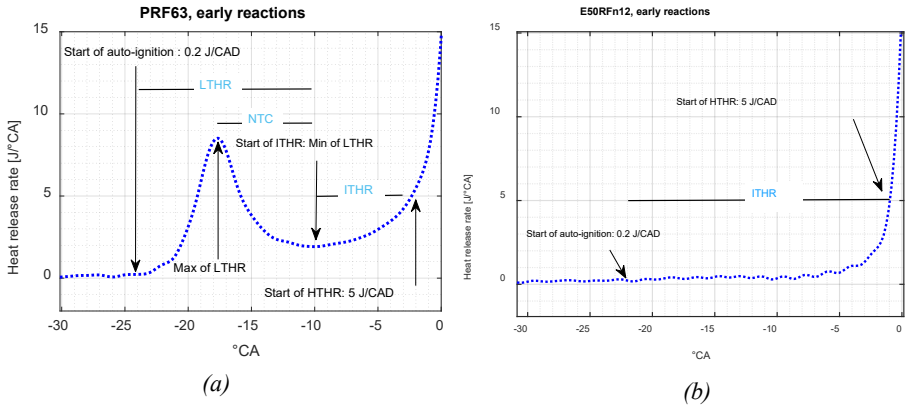


Fig. 3.3. CAD selection for start of LTR and HTR: a) HRR during the early reactions for two-stage combustion; b) HRR during the early reactions for single-stage combustion

3.5 Numerical tools

Extending the ignition delay assessment capability was the reason for using a numerical approach for a part of this PhD project. GT-power and Cantera are two simulation tools which are widely used by researchers and industrial companies and used in this part of the study. Using both tools allow to combine the calculation of pressure-temperature trajectories and mixture composition with reaction kinetics calculations.

3.5.1 GT- power

GT-Power is one of the packages of GT-suite simulation tools developed by Gamma technologies. GT-suite addresses a wide range of problems in the transport sector and is used by all major engine manufacturers. The GT-Power package is a 0D/1D/3D multi physics simulation tool which can model and connect the engine related components to predict engine performance quantities such as fuel consumption, airflow, volumetric efficiency, power, and torque.

In this study the CFR engine is modelled using GT-Power aiming at predicting mixture composition and the pressure-temperature trajectory prior combustion under different ϕ levels at HCCI combustion[112].

3.5.2 Cantera

Cantera is an open-source code which provides a 0-D/1D reaction kinetics solver. In this study the solution of 0-D reactors is used for ignition delay determination of HCCI combustion in variable ϕ and CR conditions. The formulation provided by the closed ideal constant volume reactor, is based on solving the mass conservation equation, Equation 3.3, for each species as well as the energy equation, Equation 3.4.

$$m\frac{dY_k}{dt} = \sum_{in}\dot{m}_{in}\left(Y_{k,in} - Y_k\right) + \dot{m}_{k,gen} - Y_k\,\dot{m}_{wall} \qquad \textit{Equation 3.3}$$

$$mc_v\frac{dT}{dt} = -p\frac{dV}{dt} - \dot{Q} + \sum_{in}\dot{m}_{in}\left(h_{in} - \sum_k u_k Y_{k,in}\right) - \frac{pV}{m}\sum_{out}\dot{m}_{out} - \sum_k \dot{m}_{k,gen}u_k \qquad \textit{Equation 3.4}$$

Where:
m, v, and p are the reactor mass, volume, and pressure respectively,
t is the time, T is temperature and Y_k is the mass fraction of each species,
u is the internal energy, h is enthalpy and $\dot{Q}$ is the total heat transfer.

3.6 Error Analysis

To check the repeatability of the experiments, the hypothesis was: "performing the experiments on different days have statistically significant impact on the result parameters (Hα)" [161]. There is always the risk that the hypothesis holds due to the chance and logically proving of a hypothesis using observation is impossible [161]. For this reason, a null hypothesis with the assumption that the Hα is incorrect needs to be statistically evaluated. In this study a null hypothesis was considered as: "performing the experiments on different days does not have statistically significant impact on the result parameters (H0)". In our case we wanted to prove the H0 and reject the Hα. Therefore, we need the p value to be more than 0.05 (α) to be able to prove the validity of H0, at 95% confidence level.

H0: Three sets of data are similar.
Hα: Three sets of data are NOT similar.

Due to the limited numbers of fuel pumps and the necessity of flushing out the previous fuel before using the same pump and injector for another fuel, it was impossible to randomize all the operating points. Therefore, for each experimental campaign, one or more fuels were selected and all the operating points for that fuel were replicated three times randomly to check if the null hypothesis of this study holds. The analysis of variance technic (ANOVA) was used. This statistical technic is used to spot the differences between several samples (more than two)[161].

Since each operating point was average of 300 combustion cycles the high degree of freedom gives the chance of having narrow limit for significance.

In one case in which two sets of data was engaged in the comparison, a paired t-test was performed to spot the possible differences. More details are presented in the result and discussion sections of each campaign.

Chapter 4

Prerequisite studies for the method development

In this chapter the prerequisite studies for the development of the Lund ϕ-sensitivity number are explained in detail. To have a successful test method, it is necessary to develop the test method progressively. The simplified flow chart diagram in Fig. 4.1 demonstrates the steps of method development in this study.

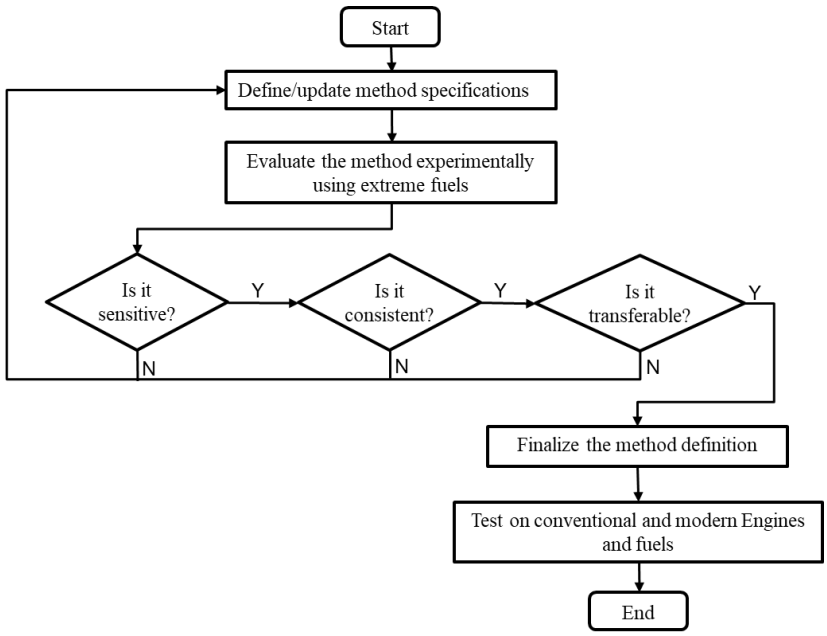


Fig. 4.1. Flow chart diagram of the method definition.

As the flow chart displays, the method should be sensitive enough to show a clear variation in result parameters when changing the input parameters, consistent enough to be repeatable and produce same output for the same input every time and transferable to conventional and future fuels and engines.

Before starting the experimental campaign for the method development and even before designing the experiment, it was necessary to find out the limitations and possibilities of the experimental facilities to be able to define more appropriate method specifications. Therefore, three experimental campaigns and one numerical study was performed to provide a better understanding of limitations and possibilities of the experimental apparatus.

4.1 Evaluation of CFR engine speed reliability

Due to the importance of repeatability of the experiments, it was crucial to select an engine speed which does not impact the reliability of the collected data. To nail this objective, the Lund–Chevron HCCI number [95] for seven different binary reference fuels (PRFs; PRF60,70,80, 85, 90, 95 and 100) in three different engine speeds of 600, 900 and 1200 and three intake temperature 323, 373,423 K were evaluated. The Lund–Chevron HCCI number evaluates the auto ignitability of different fuels in HCCI combustion using a standard CFR engine. To perform the Lund–Chevron HCCI number test method, ϕ was adjusted to 0.33 (λ≈3), CA50 (the engine crank angle at which 50% of total heat is released) was adjusted at 3 crank angle degree after TDC. This combustion phasing was achieved by changing the CFR engine compression ratio (CR).

The null hypothesis was “doing the experiment at different days does not affect the results.” Therefore, paired t-test was used to check if the data sets of this campaign are the same as similar campaign performed by another operator at different time using the same PRFs. The HCCI number was selected as the result parameter and four PRFs (60, 80, 90 and 100) were selected for the statistical evaluation. Equation 4.1 presents the t_{obs} calculation method[161]

$$t_{obs} = \frac{\bar{x}-\mu}{s/\sqrt{n}} \qquad \textit{Equation 4.1}$$

Where:
$\bar{x}$ is the mean difference between two samples
μ is the hypothetical mean which is zero
n is the population
s is the standard deviation of the difference.

The results show that for the engine speed of 1200 RPM and high octane PRFs (90 and100), there was a significant difference between the CA50 of the two data sets. The differences were more pronounced at 373 K.

This result concludes that the outcome of performing HCCI combustion at the engine speed of 1200 RPM using Lund CRF engine is not repeatable, whereas the experimental results at the engine speeds of 600 and 900 RPM are shown to be repeatable and reliable.

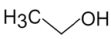
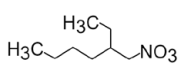
4.2 A detailed evaluation of two-stage combustion

At this step after narrowing the engine speed range to 600 and 900, the engine was tested using conventional gasoline and different volumetric percentage of additives. Again, the Lund-chevron HCCI number was measured. Due to the results of the previous campaign this campaign was performed only at the two engine speeds of 600 and 900 RPM. The aim of this campaign was a better understanding of conventional gasoline behaviour in the experimental apparatus of this study and to have a closer look at two-stage combustion and the effect of ignition improver on LTHR.

4.2.1 Fuel selection

Due to the existence of oxygenates in most commercial gasolines, 10% ethanol at volumetric ratio, was added to a gasoline (RON=85.9) which boosts the octane number and decreases the fossil CO_2. 2-ethyl-hexyl nitrate (2-EHN) is known as an ignition improver. It is a low-cost commercial additive used to enhance auto-ignition quality of diesel and diesel-like fuels [162–164]. Adding ethanol to gasoline decreases the reactivity of the fuel and consequently increases the required CR in HCCI combustion to keep the combustion phasing constant. While 2-ethyl-hexyl nitrate (2-EHN) has an opposite effect and increases fuel reactivity and as the consequence decreases the required CR to keep the combustion phasing constant [80]. The properties of the blend components are presented in Table 4.1.

Table 4.1. Properties of blend components[80]***.***

Competent	RON	MON	Q_{LHV} MJ/Kg	Chemical structure	Molecular weight (g/mol)	Flash point (°C)
Gasoline	85.5	81.5	42.73	$C_nH1.87_n$	~110	-45
Ethanol	108	90	26.8		46.07	14
2 -Ethylhexyl nitrate					175.23	76

4.2.2 Experimental test matrix and methodology

The modified CFR engine was used to measure the Lund-Chevron HCCI number for the blends of this campaign. A gasoline with RON=85.9 was the base fuel and 10% (v/v) ethanol with 99.6 purity was mixed with it. Different percentages of 2-EHN (0.25%, 0.50%, 1%, and 2.5 %) were added to the prepared E10 to enhance the auto-ignitability of the E10. The engine operating conditions are presented in Table 4.2.

Table 4.2. Engine operating condition.

Input parameters	Unit	Value	Variation
Intake charge temperature, Tin,	K	323,373, and 423	± 1 K
Pin	bar	0.98	± 0.03
Engine speed	RPM	600, 900	± 8
Coolant temperature	K	373 K	± 1
Oil temperature	K	330 K	± 8.5
CA50	°CA	3	± 0.5
CR	-	Variable	-
ϕ	-	0.33	± 0.005

The Lund-Chevron HCCI numbers [95] of the six prepared blends were measured at 600 and 900 RPM, and three different intake temperatures of 323, 373, and 423 K.

4.2.3 Results and discussion

As expected, the 10% added ethanol decreased the fuel reactivity and increased the required CR to auto ignite the fuel and maintain the combustion phasing constant. On the other hand, the added 2-EHN, compensated for the effect of ethanol on fuel reactivity and decreased the required CR to maintain the CA50 constant. The Lund-Chevron HCCI number is a function of CR [95]. Fig. 4.2 shows two graphs representing the required CR to maintain the CA50 constant at two engine speeds. These plots clearly demonstrate the effect of different blend components on the required CR to maintain the CA50 constant. Moreover, the comparison of 600 and 900 RPM plots depicts at a higher engine speed due to the less available time for auto ignition reactions, the required CR increases [40,137]. Moreover, the differences between the RCR to maintain the combustion phasing constant is more pronounced at the higher engine speed.

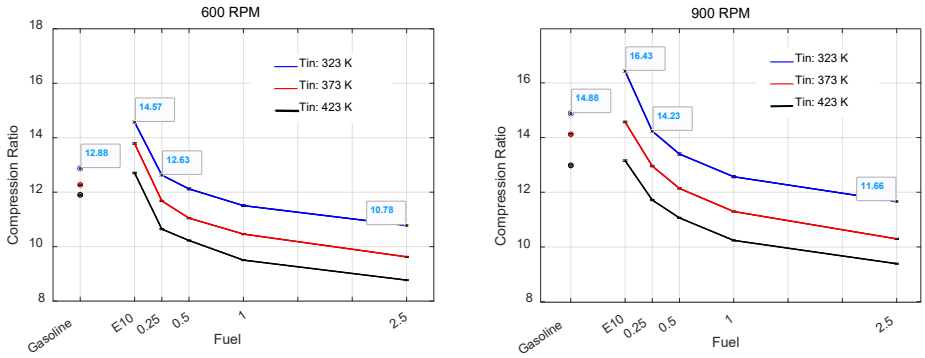


Fig. 4.2.Required CR to maintain the CA50 constant at 3°CA aTDC for 600 and 900 PRM.

The heat release profile is an appropriate indicator of the combustion phenomenon. To increase the clarity of the graphs, only three out of six fuels are presented here, gasoline, E10 and E10 containing 2.5% 2-EHN. HRR plots of all six fuels are available in the first paper of this thesis [80]. The quenching effect of ethanol on LTHR is clearly visible in Fig. 4.3.b. This effect is due to the role of ethanol as a radical sink at the beginning of LT reactions [165]. The higher peak of HRR for E10 (Fig. 4.3.a) is a result of higher RCR to maintain the CA50 constant (Fig. 4.2). The heat release profile of these fuels also shows that 2-EHN can compensate for the quenching effect of ethanol on LTHR and return the LTHR to the heat release profile of E10 (gasoline with 10% ethanol). The decomposition of 2-EHN to NO_2 and alkoxy radicals (C8H17O) happens at a lower temperature than the fuel auto-ignition temperature (in the range of 450–550 K). This is the main reason for the behaviour of 2-EHN as an ignition improver [80,164,166].

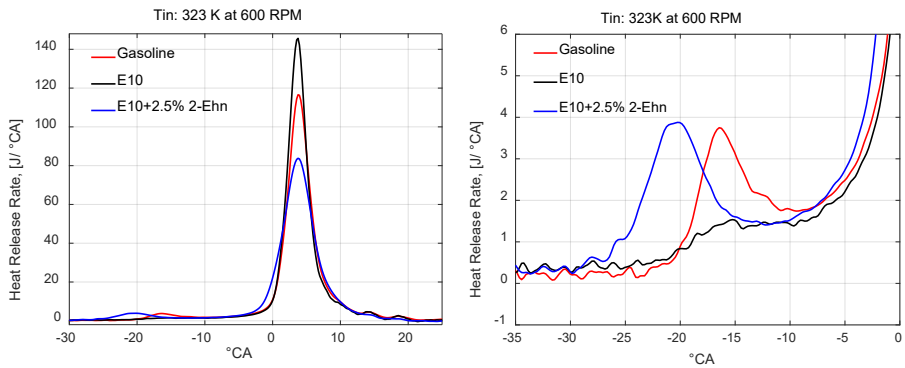
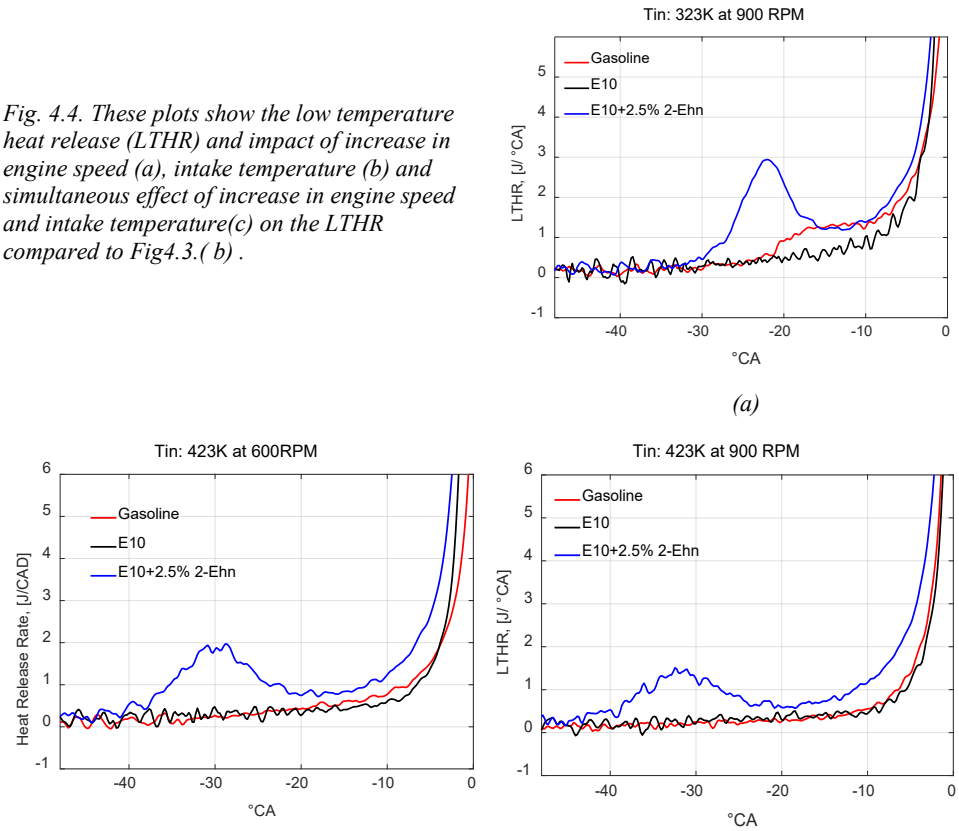


Fig. 4.3. a) Heat release rate for different blends at Tin: 323 K.; b) Low temperature heat release.

The HCCI combustion evaluation of these blends at different intake temperatures and engine speeds depicts the effect of these two variables on LTHR of the blends. Fig. 4.4 is a demonstration of this effect.it can be conclude that LTHR is more

pronounced at lower intake temperature, higher pressure (CR) and lower engine speed. The figure suggests that the burning of the 2-EHN content of the blend is not as sensitive as the low temperature reactions to the intake temperature and engine speed variation. Increasing the engine speed and intake temperature supressed the LTHR of gasoline but did not have the same impact on the blend of gasoline-ethanol and 2-EHN (E10+2.5%2-EHN).

Fig. 4.4. These plots show the low temperature heat release (LTHR) and impact of increase in engine speed (a), intake temperature (b) and simultaneous effect of increase in engine speed and intake temperature(c) on the LTHR compared to Fig4.3.(b) .



At low intake temperature and engine speed, the added 2-EHN does not drive burning of more gasoline content of the E10 during the LTHR compared to the LTHR of gasoline combustion at the same operating condition. While, at the higher intake temperature and engine speed that the LTHR of gasoline is supressed due to the thermodynamic condition of the combustion chamber, the added 2-EHN slightly increases the resistance of LTHR to the high intake temperature and engine speed. It should be considered that the added 2-EHN burns and releases heat as well. Adding ethanol to the gasoline increases the octane number of gasoline making it more appropriate as an SI fuel, while adding only 0.25% of 2-EHN increases the fuel reactivity and make it more appropriate for HCCI combustion [80]. This study

shows that the added 2-EHN increases the resistance of LTHR of the base fuel to the quenching effect of the higher intake temperature and engine speed.

4.3 Increasing the ϕ range

In this campaign two methods were used to check the potential increase of ϕ range. The first method was knock-stability limit and the second one was throttling. Although there were several studies performed by other researchers specifying the HCCI limits [88], it was still important to evaluate these limits to be able to define robust criteria for the method development. PRF63 is a binary reference fuel which has two-stage combustion. This surrogate gasoline was selected for this campaign. It is important to note that the appropriate HCCI combustion strength ($\phi \approx 0.3$) is much leaner than the lean limit of SI combustion. In an SI engine maintaining fuel-air ratio around the stoichiometric value is a crucial factor for optimum laminar flame speed. A ϕ around 0.55-0.62 is the leanest condition where laminar flames can propagate [167,168]. In HCCI combustion there is not any laminar flame, and the laminar flame is not favourable either. The latter is another reason that the mixture strength in an HCCI engine must be much leaner than the lean limit of SI engine [88].

4.3.1 Experimental test matrix and methodology

Although it was observed in the previous campaign that the higher engine speed has a quenching effect on LTHR, the engine speed of 900 RPM was selected. The reasoning behind this selection was the fact that in modern engines the engine speed is much higher than 600 and even 900 RPM. Moreover, at 900 RPM the differences between the required CR of different fuels are more pronounced, which supports the sensitivity of the test method.

Knock-stability limit method

Knock-stability limit is a point where the effect of increasing ϕ on the combustion phasing cannot be further compensated by decreasing the CR and retarding the combustion phasing. At this point any further increase in ϕ leads to knocking while any further decrease of CR causes misfire.

For this campaign, first, the HCCI combustion of PRF63 started at $\phi \approx 0.33$, and later by increase or decrease of fuel mass, gradually the higher or lower ϕ were achieved. Table 4.3 presents the operating points for each fuel. This decrease and increase of ϕ is continued to the point that the combustion either was too aggressive, or the misfire was preventing the data collection.

Table 4.3. Experimental test matrix.

Fuel	ϕ [-]	T_{in} [K]	P_{in} [bar]	Engine speed [RPM]
PRF63	0.20,0,25 0.33, 0.37,0.47	323	0.98±0.03	900

The combustion phasing was maintained constant at CA50≈3°CA for all the operating points except knock-stability point. Fig. 4.5 illustrates HRR of PRF63 HCCI combustion. ϕ more than 0.37–0.38 was not achievable at CA50≈ 3° CA. Therefore, the RCR was decreased and gradually the ϕ was increased up to CA50≈ 21 °CA after TDC, where the knock-stability limit was. Designing a test method based on the collected data of such late combustion phasing is not robust. Instead, such kind of experiments is interesting for LTHR studies.

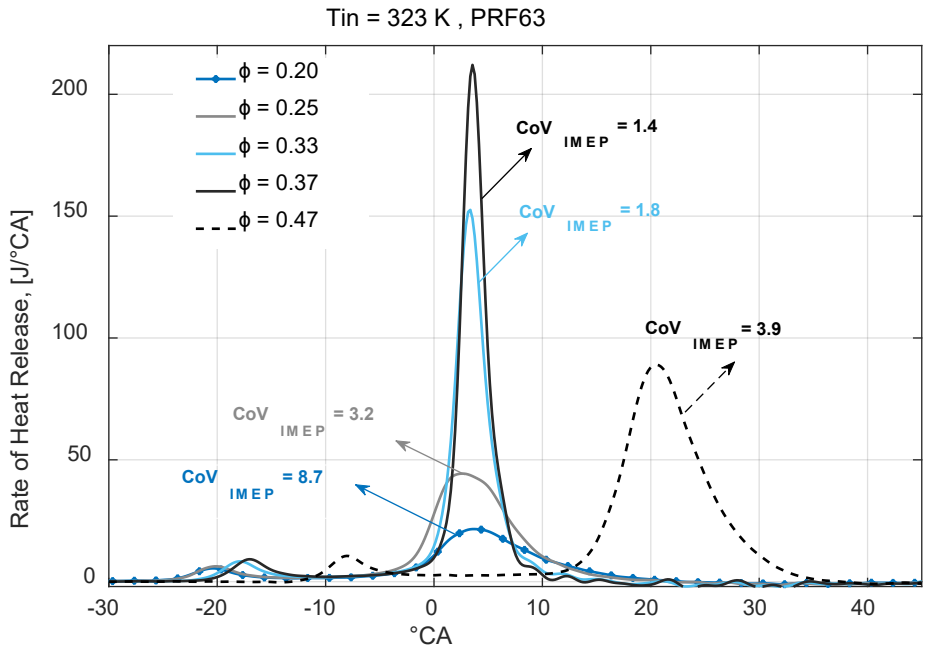


Fig. 4.5. HCCI combustion of PRF up to the knock-stability limit.

The CoV_{IMEP} of each HRR profile is presented in Fig. 4.5. As expected for a constant combustion phasing, a leaner combustion increases the CoV_{IMEP}. The high ϕ knock stability limit of PRF63 has a high CoV_{IMEP} too.

Engine throttling for ϕ adjustment

This method was another effort and investigation to increase the ϕ high limit further (at a constant combustion phasing of CA50 ≈ 3° aTDC). Instead of variation of fuel mass for this campaign, a throttle was used to decrease the intake air. The result was not promising. This method had several disadvantages compared to the other ϕ

adjustment method (changing fuel mass at constant air flow). Due to the throttling the intake pressure was changing, and throttling losses were affecting the thermodynamic condition inside the combustion chamber. The CFR engine did not have any air flow meter which therefore impacted the measurement accuracy. This air flow uncertainty will also affect the internal residual gases. Therefore, the residuals will affect in-cylinder temperature in an uncontrolled way. Consequently, throttling will decrease the calculation's accuracy.

4.4 Numerical method for ϕ range extension

Due to the experimental limitation of the ϕ range, a numerical study was proposed to evaluate the possibility of ϕ range extension. The main objective of this numerical evaluation was to develop a numerical model which combines the calculation of pressure-temperature trajectories and mixture composition with reaction kinetic calculations, to enable the prediction of the ignition delay of different fuels in response to HCCI combustion. In this study the timing between the start of auto-ignition and the start of the main combustion is defined as the ignition delay (ID). To aim the objective, GT-power as a thermodynamic solver for full cycle simulation was coupled with Cantera as a reaction kinetics solver for ignition delay determination [112].

4.4.1 Methodology

Ethanol and PRF63 were selected for this evaluation. Details are presented in Table 4.4.

Table 4.4. Operating conditions for both Ethanol and PRF63 evaluations.

Fuel	ϕ [-]	Tin [K]	Pin [bar]
Ethanol	0.37,0.35,0.33, 031, 0.27	373, 423	0.98±0.03
PRF63	0.37,0.35,0.33, 031	323, 373, 423	0.98±0.03

HCCI combustion of ethanol is single-stage while PRF63 has two-stage HCCI combustion. These two contrasting fuels were investigated experimentally to provide a database for the model development. An extensive analysis was performed to characterize the most accurately defined low, intermediate, and high temperature species for ignition delay recognition. Then the CFR engine was modelled using GT-Power. The model was used to predict mixture composition and the pressure-temperature trajectory prior to the combustion at different ϕ levels of HCCI combustion. Then, the results provided by GT-Power were used as boundary conditions for the detailed chemical kinetic solver, Cantera. Each engine-state was

modelled in Cantera via a constant volume reactor. Each individual state was then correlated by applying the Livengood and Wu method. This method allows to combine the calculation of pressure-temperature trajectories and mixture composition with reaction kinetic calculations.

4.4.2 Results and discussion

Fig. 4.6 illustrates the CFR engine model, developed in GT-Power. This model consists of the inlet and exhaust environment, manifold and ports and the engine cylinder.

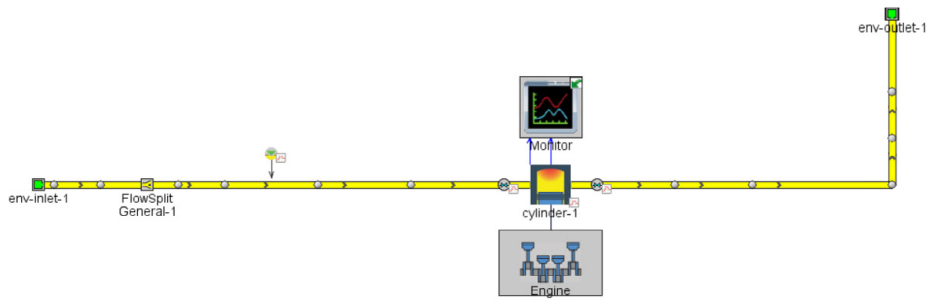


Fig. 4.6. CFR engine model, developed in GT Power[112].

Fig. 4.7 depict a detailed comparison between two different chemical reaction mechanisms in terms of their ability in predicting the occurrence of LTHR, ITHR, and HTHR according to representative species of each zone.

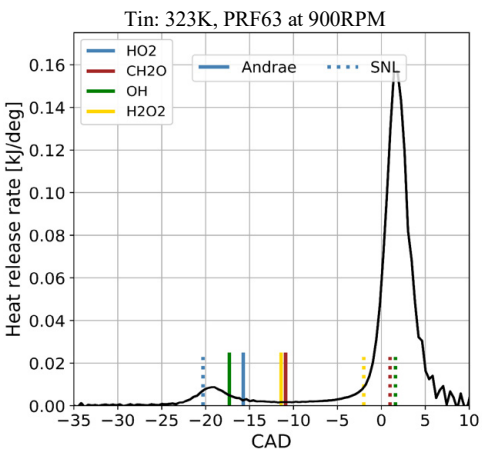


Fig. 4.7.Onset of low, intermediate and high temperature ignition delay, Andrae VS SNL.

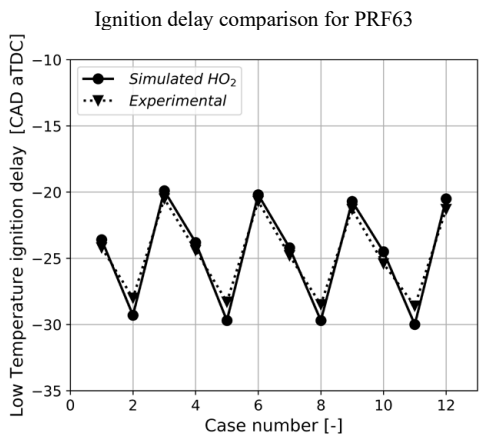


Fig. 4.8. Low temperature ignition delay, simulation VS experiment.

The plot shows that there are significant differences in the predictions depending on the selected mechanism. Andrae's mechanism tends to predict an earlier start of intermediate temperature reaction compared to SNL. This is even more pronounced in the case of main combustion delay (HTHR). Fig. 4.8 shows the PRF63 results for the low temperature ignition delay. It can be concluded that the proposed framework enables the determination of the ignition delay values with reasonable accuracy.

4.5 Conclusion

The most important conclusion of these prerequisite studies presented in this chapter can be summarized as below.

- Comparing the results of three engine speeds of 600, 900 and 1200 RPM, 900 RPM is selected for the test method development due to statistically more reliable results compared to 1200 RPM and more sensitive results compared to 600 RPM.
- A Phi range of 0.30–037 is demonstrated to be the most stable and reliable equivalence ratio range for HCCI combustion while maintaining the CA50 constant at 3°CA.
- The feasibility of quantifying the auto-ignition behaviour of both single and two stage combustion fuels using numerical evaluation studies has been proved. Moreover, the use of non-reactive conditions from GT-Power provides an alternative to explore conditions that are experimentally limited.

Chapter 5

Lund ϕ-sensitivity method development

In the previous chapter the preliminary studies were presented. The method definition flow chart (Fig. 5.1) shows that the preliminary studies have already provided the data for the method specification, limitations, and criteria definition (the blue box in Fig. 5.1). The next step would be going through the steps in the dashed black box of the flow chart.

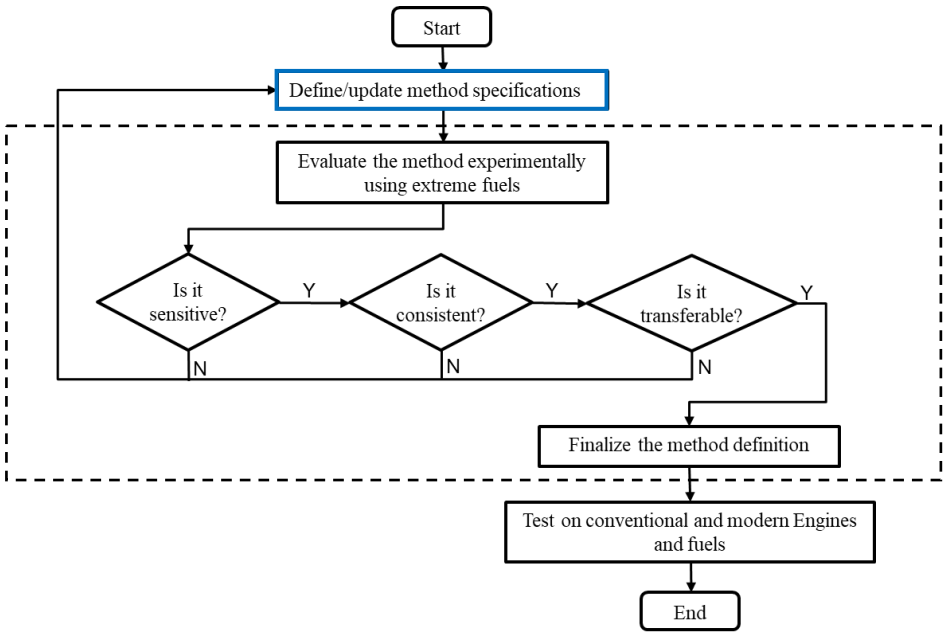


Fig. 5.1. The flow chart diagram of the method definition.

The experiments of this section aim to provide robust and reliable data for the method development, data which is sensitive, consistent, and transferable. In this chapter, the details of the experimental set up, data analysis and method definition will be discussed.

5.1 Fuel selection

Surrogate fuels can be designed and prepared in a way that emulate the desirable physical or chemical property of a more complex hydrocarbon like gasoline. Surrogate fuels have been widely used in fundamental research. Using surrogate fuels help researchers to limit chemical and physical complexity of the tested fuels, and also make a baseline for further experiments on unknown renewable future fuels [67,95,116,140,158]. Future gasoline-like fuels are expected to have a RON above 100 [169,170]. Such high RON enables higher CR and boost pressure, which typically offers increased power and efficiency in SI engines. Low RON gasoline is suggested to be a promising fuel for DICI engines, using LTC strategies [88]! In this campaign, three RON numbers were selected as low (RON≈60), medium (RON≈85) and high (RON≈105) levels; then using a regression model [158], explained in chapter 3, three groups of surrogate gasoline were designed. Blends in each group prepared with the aim of having a similar RON. The fuel components ratio was adjusted in a way that results in as close MON as possible within each RON group. After tailoring the blends using the model, the blends were sent to "Saybolt Sweden AB" for RON and MON measurement. Table 5.1 presents the prepared blend and their measured and estimated values. Dividing blends to different RON groups, facilitated a ϕ-sensitivity study independent of RON. Each group consists of:

- One TERF (four components surrogate gasoline, containing oxygenates and aromatics), (e.g., T10E10RFn49)
- One TRF (non-oxygenated, three components surrogate gasoline), (e.g., T40RFn48)
- One ERF (oxygenated, non-aromatic surrogate gasoline), (e.g., E20RFn55)
- One base fuel (ethanol, PRF84 or PRF63)

The study of blends consists of different components while their RON are similar, which provides information regarding the effect of fuel composition on the fuel ϕ-sensitivity property.

Table 5.1. The fuel matrix for the method development.

Fuel		n-heptane, vol.%	Ethanol, vol.%	Toluene, vol.%	Calculated RON*	Measured RON	S*	S[1]	HoV J/g
1	**T20E40RFn10**	10	40	20	108.3	105.5[4]	13.2	14.4[4]	552
2	**Ethanol**	0	100	0	-	108	-	14	846
3	**T65RFn5**	5	0	65	108.72	105.9[4]	14.31	9.3[4]	387
4	**E50RFn12**	12	50	0	108.8	105.3[4]	12.1	14[4]	591
5	**T25E30RFn40**	40	30	25	84.52	85.4[4]	6.9	7.8[4]	503
6	**E38RFn43**	43	38	0	84.4	84.4[3]	5.4	5.7[3]	532
7	**T50RFn30**	30	0	50	82.7	83.8[2]	8.5	7.6[2]	368
8	**PRF84**	16	0	0	-	84	-	0	307
9	**T10E10RFn49**	49	10	10	63.0	63.1[4]	4.0	5.1[4]	384
10	**E20RFn55**	55	20	0	63.7	63.2[4]	4.2	4.9	432
11	**T40RFn48**	48	0	40	63.3	63.7[2]	6.9	5.7	361
12	**PRF63**	37	0	0	-	63	-	0	310

**Calculated based on a model introduced in (Solaka Aronsson, Tuner et al. 2014)*[158]
[1] *based on the measured RON and MON from different references.*
[2] *(G. Kalghatgi, Babiker et al. 2015)*[68]
[3] *(Solaka Aronsson, Tuner et al. 2014)*[158]
[4] *(measured by project partner, Saybolt Sweden AB)*

As an example of naming convention for the blends, T20E40RFn10 is a blend, consisting of 20% toluene, 40% ethanol and 10% n-heptane, while the iso-octane is used as the filler. Therefore, for this particular case 30% iso-octane was used.

5.2 Experimental methodology

The presented experimental campaign in this section was the basis for method definition. The CA50 was maintained constant for all the blend at different ϕ levels. One engine speed, three intake charge temperatures and four ϕ levels are evaluated. Operating conditions of the CFR engine for this campaign are presented in Table 5.2.

Table 5.2. Engine operating conditions

Input parameters	Value	Variation
Intake Charge Temperature, Tin	323, 373, 423 K	± 1 K
Pin	0.98 bar	± 0.03
RPM	900 RPM	± 2
Coolant Temp	373 K	± 1 K
Oil temperature	330 K	± 8.5 K
CA50	3 °CA	± 0.5 °CA
CR	Variable	-
Equivalence ratio ϕ	0.31, 0.33, 0.35, 0.37	± 0.005

5.3 Error analysis

For each RON group, one fuel was selected and all the operating points for that fuel were replicated three times randomly to check if the null hypothesis holds. Then analysis of variance (ANOVA) was used to check if the H_0 holds:

H_0: Three sets of data are similar.
H_α: Three sets of data are NOT similar.

In this campaign CA50 was selected as the variable.

Error bars in the plots of this study are the representative of the standard deviation of each parameter from the mean.

5.4 Method development

The method definition is extracted from the data evaluations that are presented in this section. The combustion behaviours of blends are evaluated and then the validity of CR as an indicator of ϕ-sensitivity is discussed.

5.4.1 Combustion and heat release behaviour

HCCI combustion is a kinetics combustion driven by a consequence of spontaneous auto-ignition of fuel-air mixtures in a pressurized combustion chamber. In any experimental combustion study, the rate of heat release is a key parameter of combustion investigation. The rate of heat release (HRR) versus crank angle degree (CAD) is also called heat release profile. The heat release profile of different fuels provides an inclusive image of the combustion phenomenon inside the cylinder. The distinction between two-stage combustion and single stage combustion by looking at a heat release profile is straight forward. A small bump before the main heat

release peak is the sign of the existence of low temperature heat release (LTHR). Other information like combustion duration, maximum HRR, CAD of start of combustion are also calculable from the HRR data.

In this section, the HRR of TERF of each group, as the representative of that group, is presented and discussed. These selected blends are four components surrogate gasoline. It means these blends contain oxygenates, aromatic, iso-paraffin, and n-paraffin. Fig. 5.2 shows the HRR of these three TERFs. Graph a, b, and c depict full heat release rate profiles and d, e, and f, focus on early reactions. SER pinpoints the start of early reactions for each fuel and SMC is the start of main combustion. The method for the detection of the start of early reactions and the start of main combustion is explained in chapter 3 of this document. $\phi \approx 0.33$ is selected for the presented plots in Fig. 5.2.

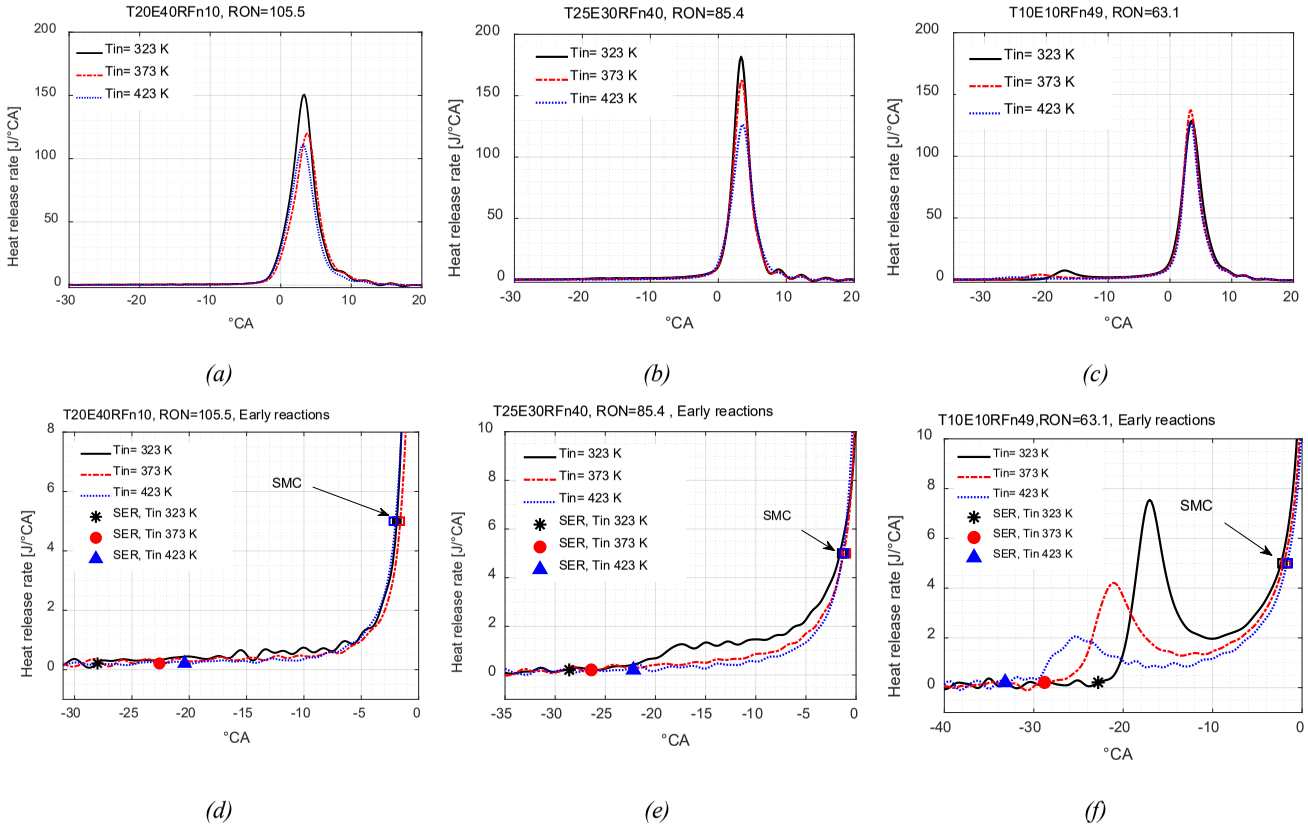
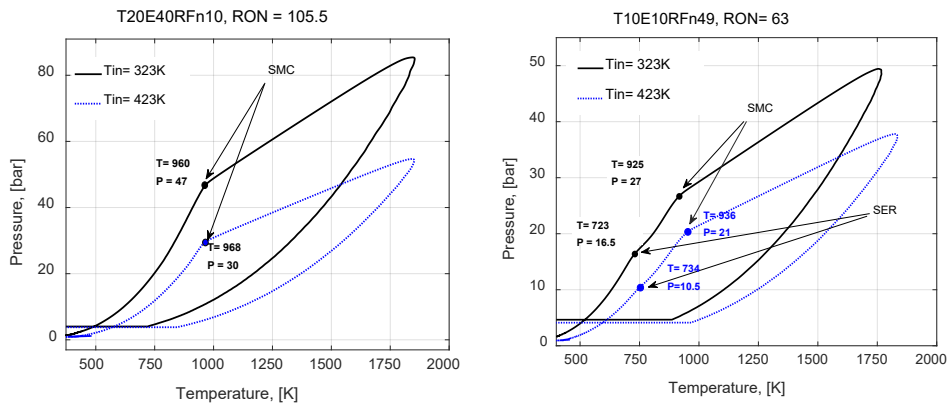


Fig. 5.2. a, b, and c) Full HRR versus CAD for TERF of each RON group at three intake charge temperatures; d,e, and f) Early heat release for the same operating points.

In this study the timing between the start of auto-ignition and the start of the main combustion is defined as the ignition delay (ID). Increasing intake temperature increases fuel reactivity and decreases the intake air mass. Due to this higher fuel reactivity, a lower CR is needed to maintain the CA50 at 3° CA aTDC. Higher Tin also lowers the intake air mass and decreases the required fuel mass to achieve the same ϕ. Lower CR and lower fuel mass decreases the total accumulated and the rate of heat release at higher Tin.

As the plot d and e in Fig. 5.2 show, at a single stage combustion, the ignition delay has correlation with the Tin; an increase in Tin increases the ignition delay. In fact, lower in–cylinder pressure, which is the direct consequence of lower CR, leads to a later start of combustion at a higher Tin. This statement is, however, only valid for single stage combustion. For the blends with two stage combustion (plot c and f in Fig. 5.1) the ignition delay decreases by increasing the Tin and the auto-ignition happens more advanced. The main reason for this behaviour is that the low temperature reactions occur at much lower temperature and pressure, and a minor variation in intake temperature or pressure will affect their onset [80,102,112,127].

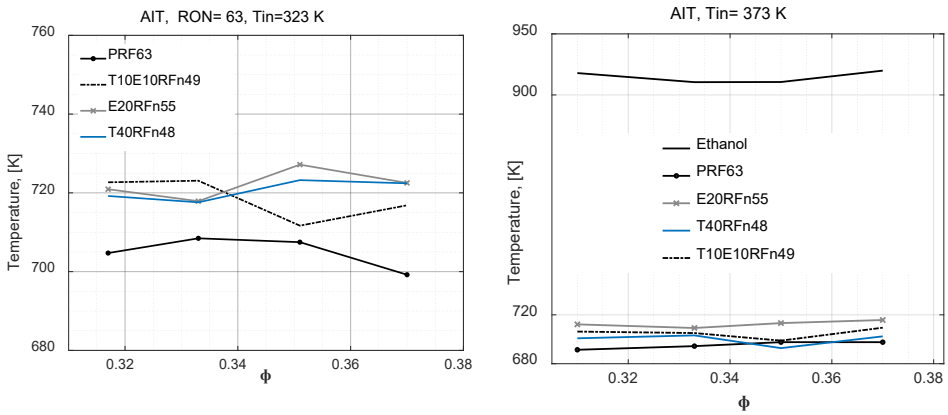
Fig. 5.3 shows the P-T diagram for single-stage combustion and two-stage combustion fuels which are previously presented in Fig. 5.2. The data for Tin= 373K are removed to avoid congestion in the figures. These pressure-temperature trajectories clearly show that the driving factor for the start of combustion is the in-cylinder temperature. The in-cylinder pressure is important as a driving factor for the in-cylinder temperature. In other words, high pressure at a low in-cylinder temperature will not trigger auto-ignition of fuel-air mixture. This is a basic chemistry fact that to combust the fuel-air mixture, it must be heated up to the threshold of breaking the chemical bounds of the molecules and the initiation of the exothermic chemical reactions [167].



(a) *(b)*

Fig. 5.3. Pressure-temperature trajectories, a) single stag combustion, b) two stage combustion.

The study of the HR profiles of different fuels at different operating conditions in this campaign, indicates auto-ignition temperature variation from the highest to the lowest ϕ is exceedingly small. Fig. 5.4 shows the auto ignition temperature (AIT) for two-stage combustion fuels (a) at Tin=323 K. The variation is small, but the different behaviour of oxygenated and non-oxygenated blends is recognizable. This small variation is also reported by other researchers [88,94].



(a) *(b)*

Fig. 5.4. Auto-ignition temperature, a) Low RON group, b) Low RON group and ethanol.

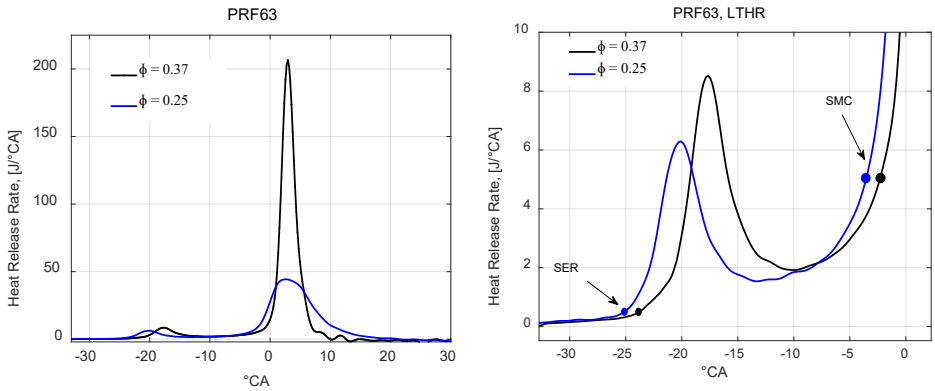
The auto-ignition temperature (AIT) of a fuel or blend is not a specific unique value. Beside energy, the auto-ignition process of fuel-air mixture requires time. In an engine, available time for auto-ignition depends on the engine speed. As explained before, intake temperature and the rate of charge-heating by the compression are the two main sources for pre-combustion heating.

5.4.2 Compression ratio as a compensator for ignition delay

In this study, ignition delay (ID) is defined as the timing between the start of auto-ignition and the start of the main combustion. In an HCCI engine with a constant CR, any changes in ϕ affects the ID [96,137]. To avoid this ID variation, intake temperature can be adjusted to maintain the combustion phasing stable. The other possibility for maintaining combustion phasing at a desirable value is the CR. Since a CFR engine has variable CR, maintaining a constant combustion phasing (e.g., CA50) while varying the ϕ would be possible by adjusting the CR. Although the CR adjustment range, same as Tin, is limited.

The evaluation of different parameters in this campaign explains the dependency of ΔCR on the fuel ϕ-sensitivity. The ϕ-sensitivity of a fuel is more pronounced at higher intake pressure and lower intake temperature [96,139]. Therefore, the results from the experiments at Tin=323 K are selected for the method development. Fig.

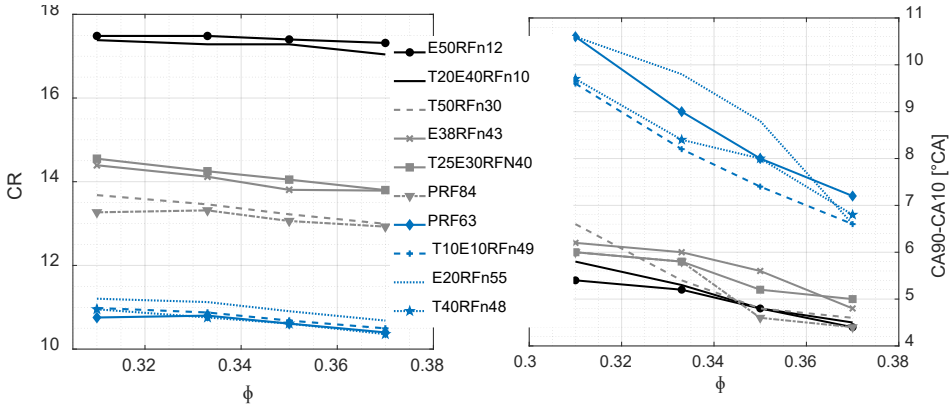
5.5 shows the HRR of PRF63 at two different ϕ levels. Fig. 5.5, b focuses on LTHR, start of early reactions and the start of main combustion at two different ϕ levels.



(a) *(b)*

Fig. 5.5. Heat release rate of PRF63 at Tin= 323K, a) HRR at two ϕ levels, b) LTHR

Not only Fig. 5.5, but also, the ID calculations for different blends of this campaign show that: "Adjusting the CR to achieve a constant combustion phasing of CA50 ≈ 3° aTDC compensates for the effect of changing ϕ on the ID [90]." This effect is due to the impact of variation in ϕ and CR on the in-cylinder pressure, temperature, volume, mass, and the internal residual gases. Variation in these parameters changes the timing of both start of early reactions and main combustion, and therefore maintains the ID with a high confidence. However, the main combustion duration shows a high sensitivity to ϕ variation. Fig. 5.6, a, shows the required CR to maintain the CA50 constant for 10 out of 12 blends which auto-ignited at Tin=323K; and Fig. 5.6, b, shows the effect of ϕ variation on the combustion duration of these 10 blends (CA10-CA90).



(a) (b)

Fig. 5.6. Required CR to keep the CA50 constant (a) and main combustions duration (b) at different ϕ for all of the blends.

Fig. 5.6 shows that despite a lower CR for the higher ϕ, the duration of main combustion decreases. The higher energy content in a mixture with higher ϕ is the driving factor in this case.

The fuel ignition delay was introduced as a ϕ-sensitivity indicator by Pintor et.al. [96]. More explanation is presented in the second chapter of this thesis. To have a better overview of the effect of simultaneous variation in ϕ and CR to maintain a constant CA50, a few parameters were normalized to exclude the impact of the initial values on them. Fig. 5.7 shows the normalized variation of CR, the pressure at the start of main combustion (P_{SMC}), and the ignition delay.

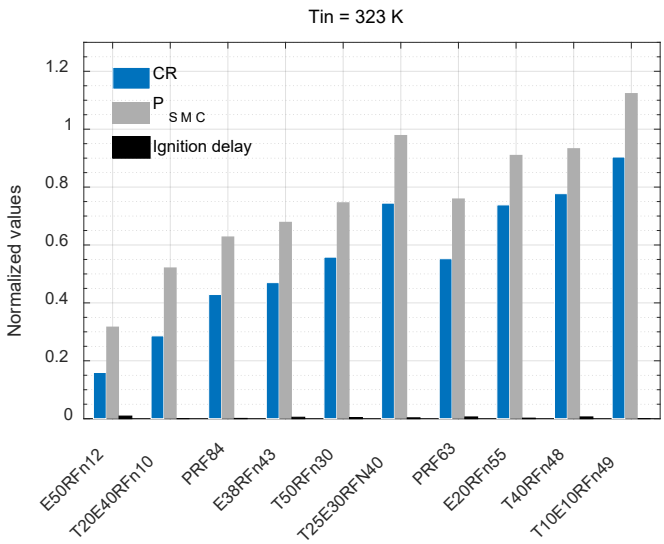


Fig. 5.7. Normalized parameters.

The variation of a desirable parameter at a higher ϕ is normalized based on the value of that parameter for the lower ϕ (Equation 5.1-3).

$$\text{Norm CR} = -\frac{1}{\text{CR}}\frac{\Delta \text{CR}}{\Delta \phi} \qquad \text{Equation 5.1}$$

$$\text{Norm P}_{\text{SMC}} = -\frac{1}{\text{P}_{\text{SMC}}}\frac{\Delta \text{P}_{\text{SMC}}}{\Delta \phi} \qquad \text{Equation 5.2}$$

$$\text{Norm ID} = -\frac{1}{\text{ID}}\frac{\Delta \text{ID}}{\Delta \phi} \qquad \text{Equation 5.3}$$

The bar chart in Fig. 5.6 illustrates that the CR adjustment to keep the CA50 constant clearly compensates for the impact of ϕ variation on the ID. The bar chart also shows that the (P_{SMC}) follows the same trend as variation in CR does.

As discussed before, early reactions have considerable impact on the fuel ϕ-sensitivity [40,96]. Fig. 5.8 shows the LTHR and ITHR as percentages of the TAcHR for each blend at Tin 323K and ϕ≈0.37.

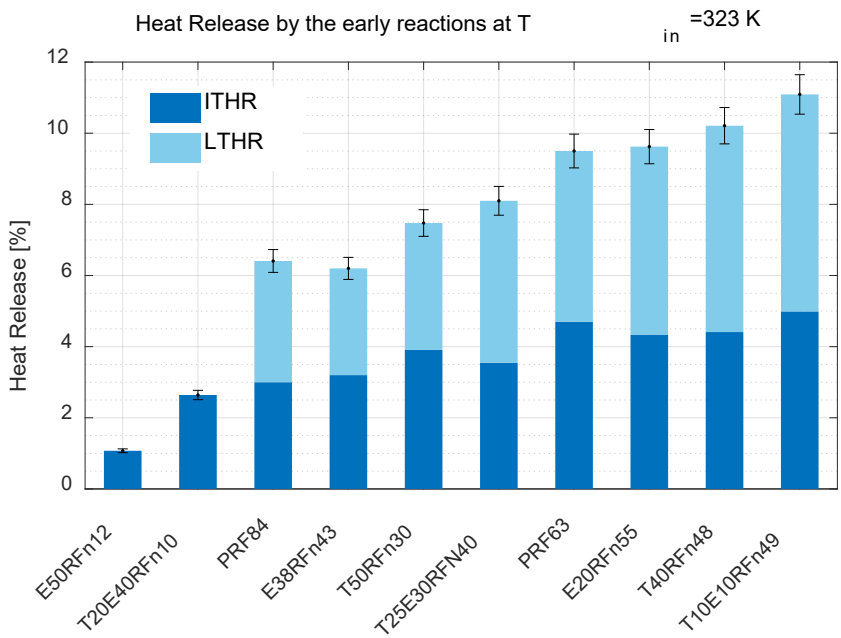


Fig. 5.8. Fraction of accumulated heat release during the early reaction to the total accumulated HR at T_{in}= 323 K.

Considering 3-5% error for each blend, the ratio of accumulated heat release during the early reactions (ITHR and/or LTHR) follows the trend of normalized P_{SMC} and CR. It can be observed that the coexistence of toluene and ethanol together with iso-octane and n-heptane (TERF) maximizes the Norm CR (Equation 5.1) as well

as the ratio of accumulated heat release during the early reactions to the total accumulated heat release. Although at first glance it might be unexpected, there is an explanation. A numerical study of ϕ-sensitivity has also reported this co-effect of oxygenates and aromatic on the fuel ϕ-sensitivity. Ethanol is known for its scavenging effect on LTHR [80,112,138,171–173]. This quenching effect is the result of radical consumption ($O\dot{H}$ and $H\dot{O}_2$) and RCHO and HO_2 formation. RCHO and HO_2 are stable at low temperatures [43,129,150,173,174]. Ethanol delays the start of early reactions but not the start of high temperature reactions (main HR); while toluene delays both early reactions and the high temperature reactions (main combustion). Therefore, the quenching effect of ethanol on total accumulated heat release during the early reactions is more pronounced than toluene [96,172,173,175]. Apart from this, ethanol has high HoV and therefore a high charge cooling effect. The intake temperature for the presented results in Fig. 5.7 is 323 K which is much lower than the boiling point of ethanol. Therefore, there is a change that ethanol content of the blend is not fully vaporized and as a result has a charge cooling effect. This charge cooling effect increases the required CR to maintain the CA50 constant. Higher CR means higher pressure and higher pressure increases the ϕ-sensitivity of fuels [96,128].

In conclusion, the Lund ϕ-sensitivity number was built upon the results of this campaign and defined as bellow:

$$\text{Lund } \phi\text{-sensitivity number} = -\frac{1}{CR}\frac{\Delta CR}{\Delta \phi} \qquad \text{Equation 5.4}$$

This number is a comparative scale for the ϕ-sensitivity evaluation of different fuels, and it is an indicator of fuel response to ϕ variation during HCCI combustion[90]. The advantages of this method for ϕ-sensitivity evaluation compared to the other available method is that the Lund ϕ-sensitivity method is empirical and does not depend on complex kinetic mechanism that are often unavailable.

5.4.3 Correlation with other indexes and parameters

In this section Lund ϕ-sensitivity number is compared with other indexes to evaluate the possibility of any correlation between them. In Fig. 5.9 the Lund-Chevron HCCI number, S and HoV of different blends of this campaign are measured or calculated and compared with the Lund ϕ-sensitivity number. This bar chart illustrates that at Tin=323K, the Lund ϕ-sensitivity number, the Lund-Chevron HCCI number, HoV, and S are not linearly correlated. However, these presented indexes can be a used as a guide for tailoring fuels to any favourable combustion strategy. It was also important to evaluate the correlation between the Lund ϕ-sensitivity number and the load range of the fuels to check if the Lund ϕ-sensitivity number might be used as a criterion for tailoring load adaptive fuels.

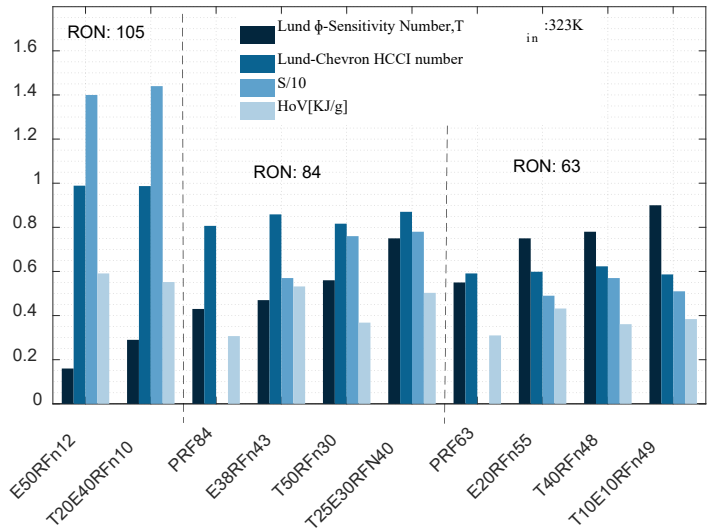


Fig. 5.9. Comparison of Lund ϕ-sensitivity number with other fuel indexes.

According to this study, there is a correlation between load adaptability and the Lund ϕ-sensitivity numbers of the blends (Fig. 5.10).

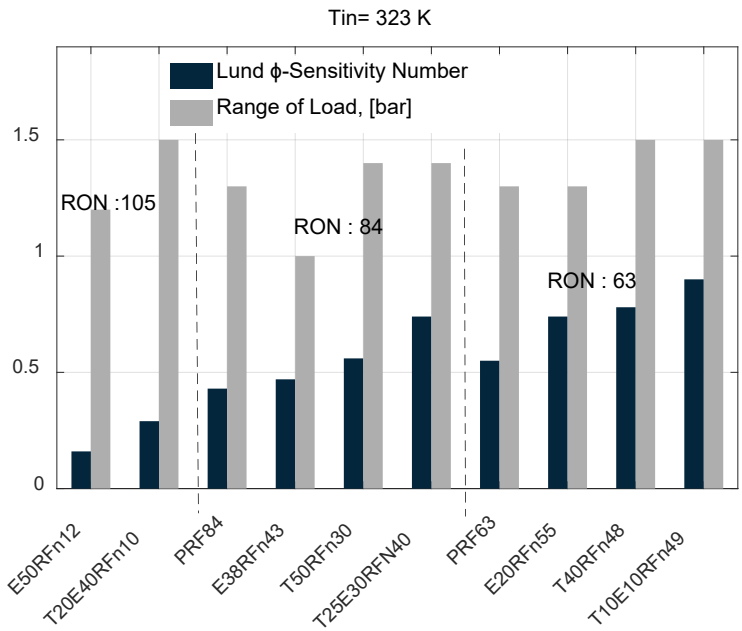


Fig. 5.10. The load range indexes with Lund ϕ-sensitivity number.

Based on this graph, ethanol reference fuels (ERF) have a lower Lund ϕ-sensitivity number and load range compared to the toluene-ethanol reference fuels (TERF) or toluene reference fuels (TRF) of the same RON group. Combination of the aromatic's ignition delay property, and the charge cooling effect of ethanol increases both the Lund ϕ-sensitivity number and the load range for TERFs compared to the other blends.

5.4.4 Fuel composition and ϕ-sensitivity

The effect of ethanol (oxygenate) and toluene (aromatic) has been mentioned in this thesis several times. The role of fuel composition in the ϕ-sensitivity of a fuel is determinative. Consequently, the Lund ϕ-sensitivity number is influenced by the fuel composition.

This study shows that different blends with similar RON still can have different Lund ϕ-sensitivity numbers. A summary of the fuel composition impact on the Lund ϕ-sensitivity number is presented in Fig. 5.11.

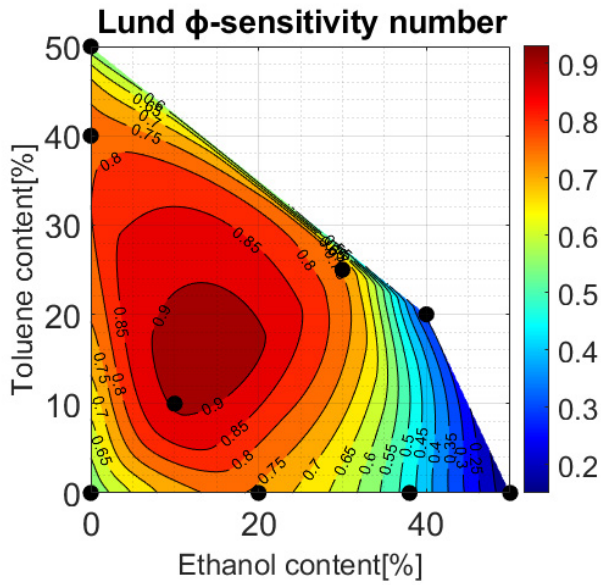


Fig. 5.11. Lund ϕ-sensitivity number as a function of ethanol and toluene

This plot shows that a low percentage of ethanol (less than 25%) together with toluene (up to 35%) will maximize the Lund ϕ-sensitivity number of the tested TERFs.

5.4.5 Intake temperature and ϕ-sensitivity

Charge preheating is a way of preparing a homogenous mixture for HCCI combustion. Applying hot EGR is another way to ensure mixing and increase the dilution level. Both these methods increase the charge temperature and as a result the fuel reactivity increases [66,94,96,130,176]. This means that the pressure sensitivity of the fuel increases and that fuel auto-ignites at a lower pressure. How does this lower pressure and higher temperature of auto-ignition, influence the Lund ϕ-sensitivity number?

Since a higher Tin increases the fuel reactivity a lower CR (pressure) is required to maintain the CA50 constant. Fig. 5.12 shows the required CR to maintain the CA50 constant for two blends of the low RON group.

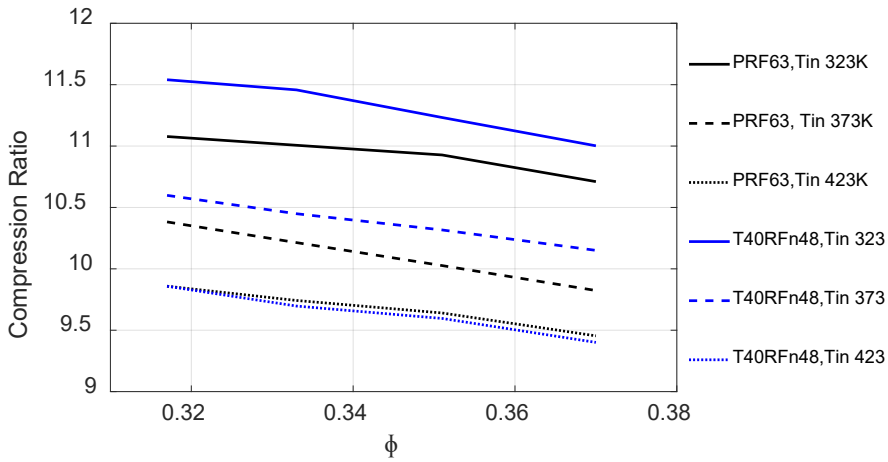


Fig. 5.12. Required CR for two blends (same RON) at different Tin.

Fig. 5.12 clearly depicts that increasing the intake temperature (moving from solid lines to dashed and doted lines) decreases the required CR to maintain the CA50 constant. Fig. 5.13 illustrates the percentage of accumulated HR during the early reactions at Tin=423 K.

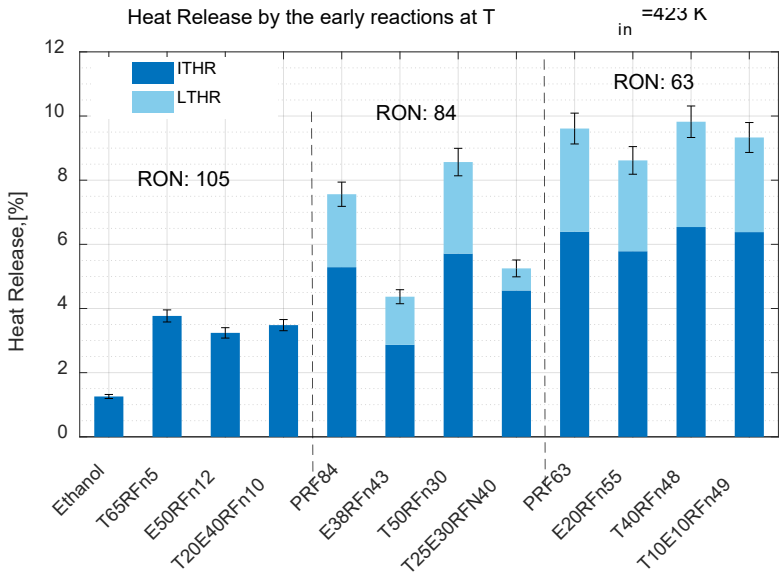


Fig. 5.13. The percentage of AcHR during the early reactions at Tin: 423 K and ϕ≈ 0.37.

The link between HoV (Table 5.1.) and LTHR is clearly noticeable in this plot. As an example, the higher ethanol content of a blend increases the HoV of it and decreases the LTHR due to the quenching effect of ethanol on early reactions [177].

The latent heat of vaporization of a blend does not show an explicit effect on the Lund ϕ-sensitivity number, but together with the ratio of accumulated heat release during the early reactions to the total accumulated heat release creates a meaningful co-effect. Whenever a blend has the lowest LTHR/TAcHR but at the same time the highest HoV in the RON group, that blend will not show the lowest ϕ-sensitivity of its RON group, which is expected from the ratio of LTHR/TAcHR of the blend. Instead, the high HoV of the blend increases the ϕ-sensitivity. This effect is expected to be the result of possible thermal stratification inside the combustion chamber.

To evaluate the impact of high intake temperature on the Lund ϕ-sensitivity number of the blend, the Equation 5.4 is used to calculate the ϕ-sensitivity of the blends at the Tin=423 K. Fig. 5.14 depicts the Lund ϕ-sensitivity number at 323 and 423 K for 10 out of 12 blends of this study which had stable auto-ignition at Tin=323K. In this comparison, for 6 out of 10 blends, the variation of Tin has a significant impact on the Lund ϕ-sensitivity number. For two out of these six blends, the Lund ϕ-sensitivity number decreases at Tin=423 K compared to Tin=323 K.

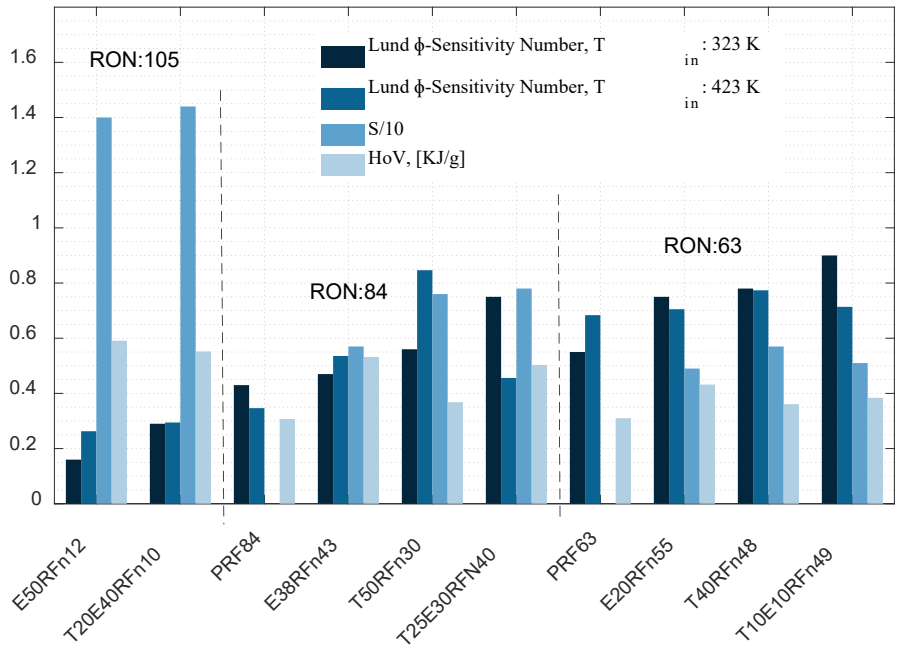


Fig. 5.14. Lund ϕ-sensitivity number of the blends at two different intake temperatures.

The highest percentage of AcHR of TRFs, during the early reactions in each RON group at 423 K, explains the higher fuel ϕ-sensitivity of these blends [90,96,121,136].

A remarkable observation from Fig. 5.14, is the decrease in the Lund ϕ-sensitivity number of TERFs by increasing Tin. It means that the TERFs despite the other blends, are less sensitive to both thermal and fuel stratification at a higher intake temperature.

Toluene content in a blend, delays both low and high temperature reactions of a fuel and as a result, increases the ignition delay [173,178]. Toluene is known as a radical sink and consumes very reactive radicals of O$\dot{H}$ and $\dot{H}$ and replaces them with the unreactive benzyl radical ($C_6H_5C\dot{H}_2$) which therefore delays the early reactions [171]. The low concentration of O$\dot{H}$ radicals delay both the cool flame and the main combustion. At the same time, $H\dot{O}_2$ radicals produce H_2O_2 that stays until the thermodynamic condition for the decomposition is reached. The decomposition reactions of H_2O_2 terminates the toluene radical consumption reactions and initiates the main combustion reactions. In fact, for the toluene blends, the oxidation of intermediary species such as the benzyl radical controls the reaction system and not the direct oxidation of the fuel. This indirect pathway decreases the rate of H_2O_2 production and therefore delays the start of the main combustion further [171].

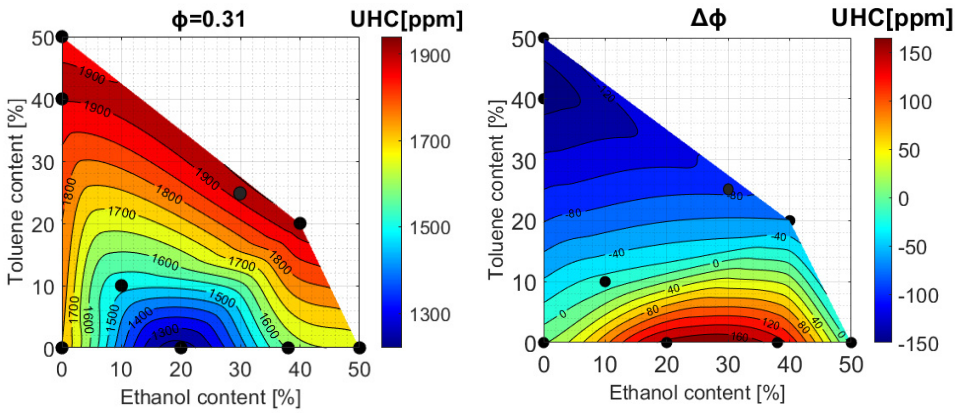
The increased Lund ϕ-sensitivity number of TERFs by increasing Tin, seems to be the result of the reactions described in the previous paragraph. For the same reason, TRFs exhibit the highest Lund ϕ-sensitivity number in each RON group at Tin 423K.

5.4.6 Emissions and Lund ϕ-sensitivity number

The variation of emissions during the ϕ sweep were evaluated to determine if the emissions could act as a ϕ sensitivity indicator. The correlations were inconsistent but as expected, emissions and fuel composition were correlated.

Unburned hydrocarbon (UHC)

UHC are usually the most polluting emissions from HCCI engines. These high UHC emissions are due to the trapped homogeneous charge in the crevices during the combustion stroke. This trapped mixture is not exposed to enough heat to combust and therefore ends up as unburned hydrocarbons in the exhaust. Several studies indicate that increasing in-cylinder temperature will not burn these trapped gases completely [101,106,179]. Increasing ϕ, results in a lower required CR to maintain the CA50 constant. Decrease in CR lowers the ratio of crevice volume to the total in-cylinder volume, consequently, the UHC decreases. Fig. 5.15 presents the UHC emissions of the blends evaluated in this campaign. Fig. 5.15, (a) shows the UHC emissions for the lowest ϕ and Fig. 5.15, b) shows the variation of UHC emissions due to the variation of ϕ. Variation of ϕ is symbolized by Δϕ.



(a) *(b)*

Fig. 5.15. (a) UHC emissions in the leanest condition; (b) the effect of ϕ increase on UHC reduction for different blends.

Blends with aromatic content display a decrease in UHC emissions in response to an increase in ϕ. When ethanol is the only source of octane sensitivity (S) in the blends, this expected decrease of UHC (in response to an increase in ϕ) no longer occurs. The ethanol content of the blends at higher ϕ, increases the UHC emissions in respect to the lower ϕ. This effect is due to the charge cooling effect of oxygenated blends. The key point to consider is that despite this effect, due to the oxygen content of the blends, oxygenated blends emit less UHC than do other fuels with the same RON. It can be concluded that both the UHC level and UHC variation pattern are highly dependent on the fuel composition.

Carbon monoxide (CO) emissions

Fig. 5.16, (a) displays CO emission levels of all blends at ϕ≈0.31 and Fig. 5.16, (b) illustrated the effect of ϕ increase on the CO emissions level. Oxygenated reference fuels show lower UHC, and CO emissions compared to non-oxygenated blends. This effect is due to the presence of oxygen in the fuel composition [34,35,40,80]. In this campaign, all the blends show a decrease in CO emissions corresponding to an increase in ϕ.

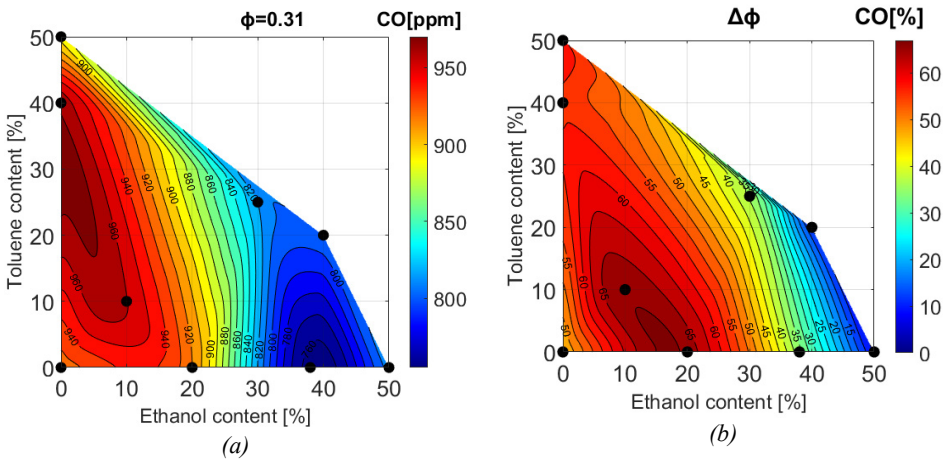


Fig. 5.16. CO emissions at a specific ϕ (a), effect of ϕ increase on the CO emissions reduction for different blends(b).

Decreasing the CR to maintain the CA50 constant at a higher ϕ, decreases the in-cylinder pressure and since the fuel mass has been increased, the energy in the combustion chamber increases and therefore the in-cylinder temperature increases. Fig. 5.17 shows the percentage of increase in maximum in-cylinder temperature due to the ϕ increase as a function of toluene and ethanol content of the blend. The plot suggests that the blends exhibiting less increase in maximum in-cylinder temperature, show a smaller decrease in CO emissions.

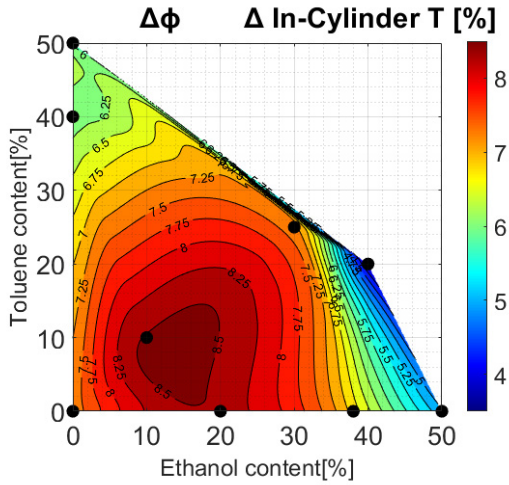


Fig. 5.17. ΔT due to $\Delta\phi$ as a function of fuel composition.

The results show that emissions are directly influenced by the fuels compositions, the change of CFR engine geometries, CR and in-cylinder temperature. An experiment which isolates the effect of the variation of CR and crevice volume ratio must be designed to enable the study of the effect of ϕ-sensitivity on emission formation. Such experiments were beyond the scope of this study, but it would be interesting to investigate this effect in future works.

5.5 Conclusion

In this chapter based on the HCCI combustion of 11 toluene-ethanol reference fuels together with pure ethanol, an empirical method was developed. Based on this method the ϕ-sensitivity of fuels would be measurable using a CFR engine with the CR as the main output parameters to calculate Lund ϕ-sensitivity number as below:

$$\text{Lund } \phi\text{-sensitivity number} = -\frac{1}{\text{CR}}\,\frac{\Delta\text{CR}}{\Delta\phi}$$

The study shows that the determination of ϕ-sensitivity for different fuels using Lund ϕ-sensitivity number provides clear and consistent results. This method empirical, quick, and unlike the other available ϕ-sensitivity method [96] independent of detailed kinetic mechanisms as prerequisites data. The Lund ϕ-sensitivity number, together with RON and MON, can be used for fuel characterization.

Chapter 6

Lund ϕ-sensitivity evaluation of butanol isomers

Higher molecular weight alcohols, also called longer chain alcohols (for instance iso-butanol and n-butanol), have higher energy content compared to ethanol and methanol. Longer chain alcohols are also typically more compatible with conventional engines, compared to lighter alcohols. Several established sustainable production pathways for iso-butanol and n-butanol production exist. In this chapter the results of the Lund ϕ-sensitivity number evaluation for iso-butanol and n-butanol are presented.

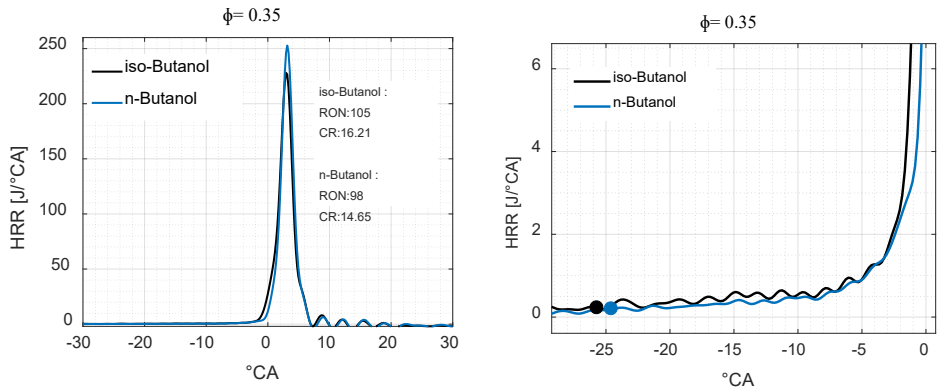
6.1 ϕ-sensitivity evaluation of butanol isomers

Different strategies are used for evaluation of butanol isomers. First, the Lund ϕ-sensitivity numbers of iso-butanol and n-butanol at CA50≈3°CA after TDC were measured. Then, the Lund ϕ-sensitivity number of iso-butanol at two different combustion phasings' of CA50=8 and CA50=6 is evaluated. This evaluation is performed to investigate the effect of retarded combustion phasing on the Lund ϕ-sensitivity number of iso-butanol. Finally, the volumetric blends of iso-butanol and surrogate gasoline (RON≈87) were prepared at 0.85, 0.50, 0.30, 0.10 v/v% and the ϕ-sensitivity of these blends measured using the Lund ϕ-sensitivity method at CA50≈6. The objective of this part was to study the blending ϕ-sensitivity of iso-butanol. Table 3.1 presents the different operating conditions of this campaign.

Table 6.1. Operating conditions for different sets of experiments.

Input parameters	Isomers evaluation	CA50 evaluation	Blends evaluation	Variation
Intake Charge Temperature, Tin	323K	323K	323K	± 1 K
Pin	0.98 bar	0.98 bar	0.98 bar	± 0.03
RPM	900 RPM	900 RPM	900 RPM	± 2
Coolant Temp	373 K	373 K	373 K	± 1 K
Oil temperature	330 K	330 K	330 K	± 8.5 K
CA50	3 °CA	6, 8 °CA	6 °CA	± 0.5 °CA
CR	Variable	Variable	Variable	-
Equivalence ratio ϕ	0.25, 0.30, 0.33, 0.35	0.25, 0.30, 0.33, 0.35, 0.40	0.25, 0.30, 0.33, 0.35, 0.40	± 0.005

Fig. 6.1 presents the HR profile of (iso-butanol and n-butanol) at ϕ≈0.35. In a CRF engine, a lower CR is provided by increasing the in-cylinder volume (moving the cylinder head upward). Since the HCCI combustion is very lean (excess air) the residual gas inside the combustion chamber (IGR) has oxygen content. Therefore, a higher in-cylinder volume provides a higher oxygen concentration. Which requires a higher fuel mass to prepare the same ϕ. This effect is experimentally tested by the author. Decreasing the CR was lowering the ϕ too. To compensate the lower ϕ, longer injection duration was needed. iso-Butanol and n-butanol have similar stoichiometric values and the observed difference in the maximum HRR in Fig. 6.2, is due to the lower required CR to maintain the CA50 constant for n-butanol, and therefore an associated higher energy content in the combustion chamber.



(a) *(b)*

Fig. 6.1.HRR of iso-butanol and n-butanol. a) Complete HRR, b) Early HR.

The HoV of n-butanol is higher than iso-butanol while the n-butanol RON is lower (Table 3.3). Therefore, the Lund ϕ-sensitivity number for n-butanol is expected to be higher than iso-butanol. Fig. 6.3 shows the measured ϕ-sensitivity of iso-butanol and n-butanol using the Lund ϕ-sensitivity method. It clearly depicts a similar trend

of the Lund ϕ-sensitivity number and the normalized in-cylinder pressure at the start of main combustion which shows the correlation between the CR and the pressure at the start of main combustion in these experiments.

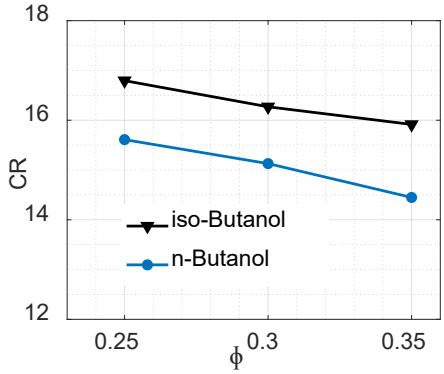


Fig. 6.2. Required CR to maintain the CA50 constant at 3 ° aTDC.

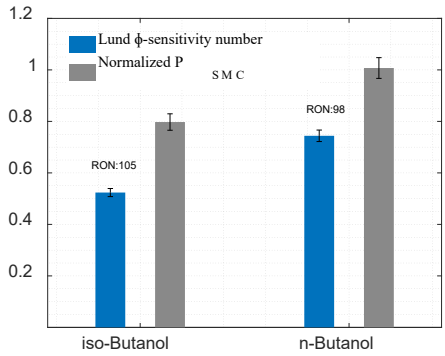


Fig. 6.3. Lund ϕ-sensitivity number and normalized in-cylinder pressure at the start of main combustion.

A high combustion phasing sensitivity of n-butanol is observed and reported in other HCCI engine studies too [180]. Since in the Lund ϕ-sensitivity method, the combustion phasing is maintained constant, the high combustion phasing sensitivity of n-butanol is projected on the CR. Fig. 6.4 shows the CoV_{IMEP} as a function of ϕ for iso-butanol and n-butanol. n-Butanol exhibits higher combustion stability and less cycle-to-cycle variation than iso-butanol in response to HCCI combustion. This property is more pronounced at lower ϕ. As Fig. 6.5 suggests, n-butanol shows slightly higher maximum pressure rise rate at each ϕ level compared to iso-butanol. This difference is due to the lower CR and therefore higher fuel mass in the combustion chamber for n-butanol.

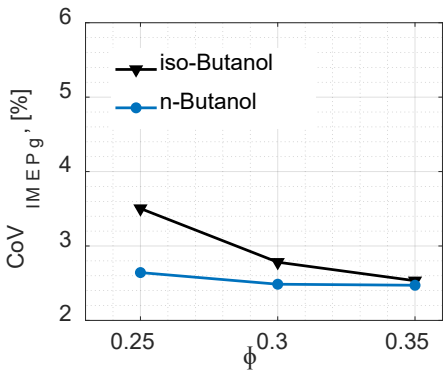


Fig. 6.4. Coefficient of variation IMEPg.

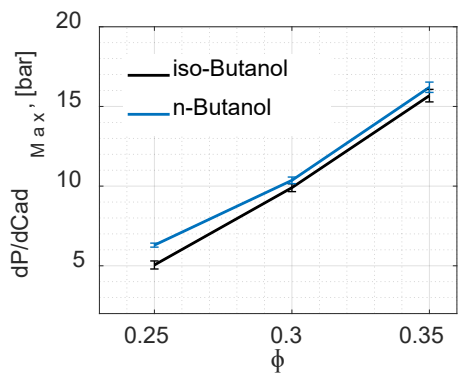


Fig. 6.5. Maximum pressure rise rate per °CA.

Fig. 6.6 shows the combustion duration of iso-butanol and n-butanol at three different ϕ levels of this campaign, while Fig. 6.7 depicts the combustion efficiency of the same operating points. The combustion duration data (CA10–90) are in line with presented observations in chapter 5, indicating the impact of fuel mass and energy content on the combustion duration.

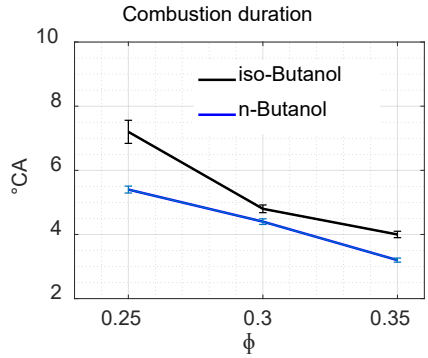


Fig. 6.6. Combustion duration of iso-butanol and n-butanol at three different ϕ levels.

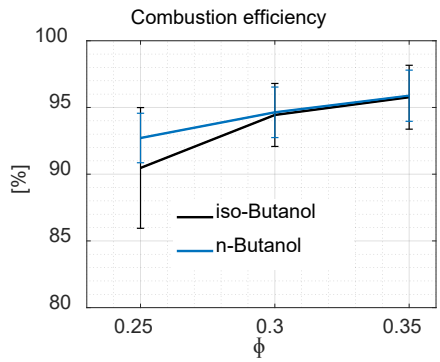


Fig. 6.7. Combustion efficiency of iso-butanol and n-butanol at three different ϕ levels.

Again, due to the higher volume of combustion chamber at a lower CR, more fuel mass is needed to provide a specific ϕ in respect to a higher CR. Therefore, n-butanol which requires lower CR to auto ignite, requires a higher fuel mass which shortens the combustion duration.

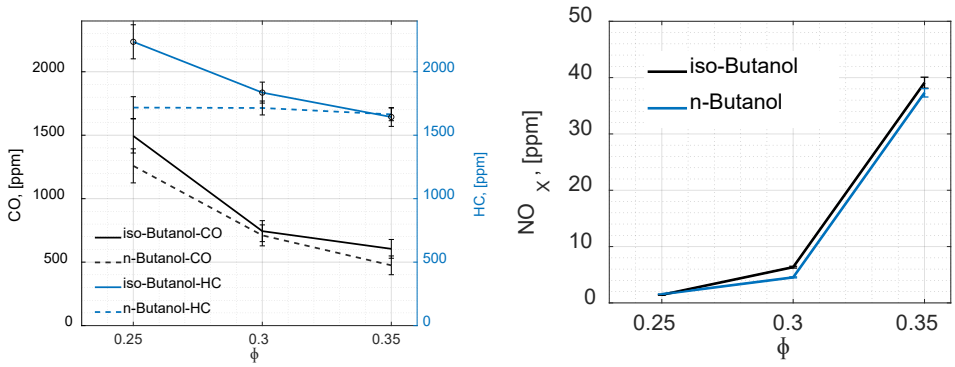


Fig. 6.8. Produced emissions of iso-butanol and n-butanol at three different ϕ levels. (a) Carbon monoxide and unburdened hydrocarbon emissions; (b) Nitrogen oxide emissions

Except for the leanest operating point, the combustion efficiencies of iso-butanol and n-butanol are similar. Higher HC and CO emissions for iso-butanol at the lowest ϕ indicates the existence of misfire or incomplete combustion at this operating point and confirms the lower combustion efficiency of iso-butanol at lower ϕ (Fig. 6.8).

6.2 Combustion phasing sweep and Lund ϕ-sensitivity number

The highest nominal CR of a CFR engine is 18. During HCCI combustion in a CFR engine, some technical conditions decrease this upper limit. Combustion instability and the risk of engine damage are two examples of these technical challenges. HCCI combustion is driven by auto-ignition, and high-octane fuels need higher CR to auto-ignite. A higher intake temperature increases the fuel reactivity and lowers the required CR to maintain the CA50 constant, but also strongly effects the early reactions that are proven to be responsible for ϕ-sensitivity. Retarding the combustion phasing is another way to decrease the required CR to auto-ignite the fuel-air mixture. In this campaign the Lund ϕ-sensitivity method for measuring the ϕ-sensitivity of iso-butanol at CA50≈6 and 8 respectively, is applied. The results are compared to the Lund ϕ-sensitivity number of iso-butanol at CA50≈3. Fig. 6.9 shows the HRR of iso-butanol at three different combustion phasing of 8, 6 , and 3 crank angle degree after TDC and the equivalence ratio of ϕ≈ 0.35.

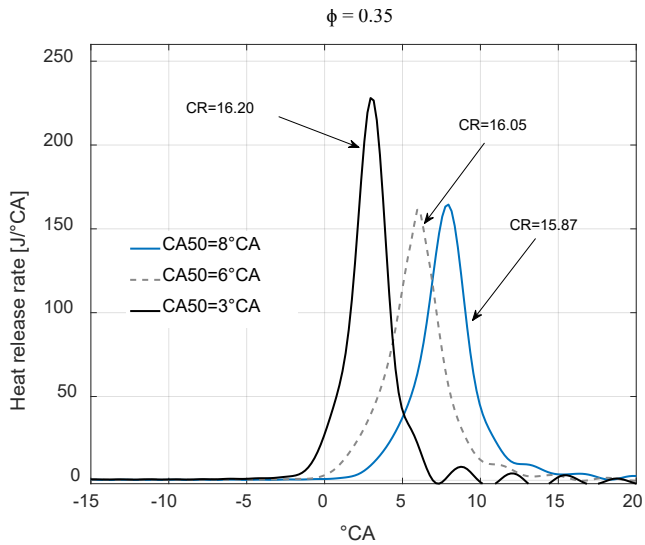


Fig. 6.9. HRR for HCCI combustion of iso-butanol at different combustion phasing.

Fig. 6.9 show the impact of a later CA50 on the required CR. Retarding the combustion phasing, results in a slightly higher maximum ϕ of 0.40 compared to the maximum ϕ at CA50≈3°CA. There were not any differences between experiments with CA50≈6°CA and 8 in terms of maximum ϕ limit. Fig. 6.9 also suggests that retarding the combustion phasing decreases the sensitivity of combustion phasing the CR variation. This observation became more noticeable when the Lund ϕ-sensitivity number confirms this effect too. Fig. 6.10 shows the Lund ϕ sensitivity number of iso-butanol for different CA50 adjustments. The bar

chart clearly indicates the lower Lund ϕ sensitivity number of iso-butanol at the latest CA50. This decrease is due to the lower required CR (Fig. 6.11) and therefore lower compression pressure inside the combustion chamber (Fig. 6.12). Lower pressure is one of the known reasons for the lower ϕ-sensitivity property of different fuels [96].

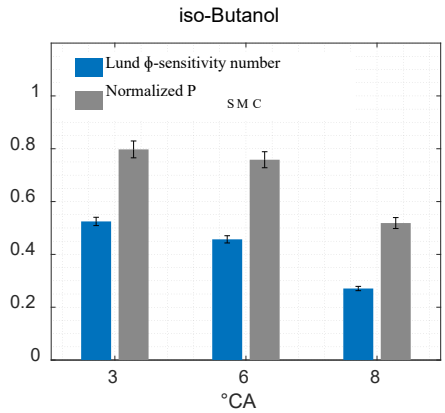


Fig. 6.10. Lund ϕ-sensitivity number at three different CA50.

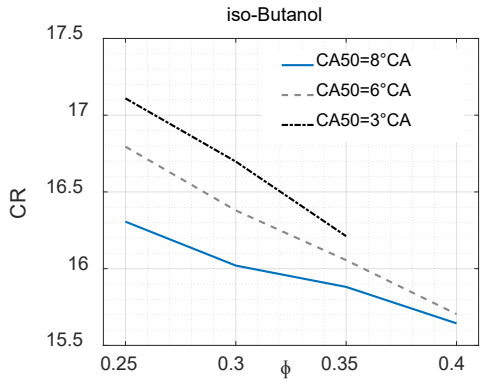


Fig. 6.11. Required CR to maintain the CA50 constant at the different CADs for iso-butanol.

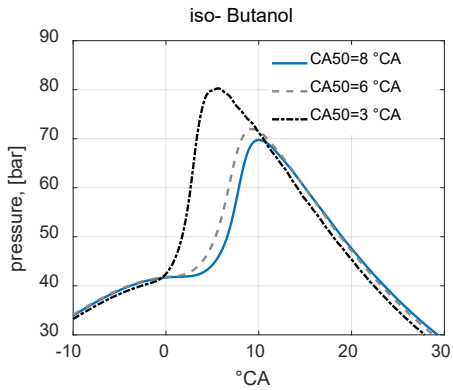


Fig. 6.12. The in-cylinder pressure at different operating point.

6.3 Blending ϕ-sensitivity of iso-butanol

Some properties of alcohols are affected by blending and may exhibit a nonlinear behaviour. Octane number is one of these properties. Does the Lund ϕ-sensitivity number also show a nonlinear behaviour in response to blending?

In this campaign, T30RFn20, a surrogate gasoline containing 30% toluene, 50% iso-octane and 20% n-heptane (volumetric ratios), with the resulting RON≈87 and Lund-Chevron HCCI number ≈ 86 was the base fuel. Blends of iso-butanol and T30RFn20 were prepared at 0.85, 0.50, 0.30, 0.10 v/v and both the Lund-Chevron HCCI number and the Lund ϕ-sensitivity number of these blends were measured. Table 6.2 presents these numbers as well as the calculated heating values of the blends.

Table 6.2. Blends of iso-butanol and T30RFn20.

Blends	Lund-Chevron HCCI number	Lund ϕ-sensitivity number at CA50 ≈ 6° CA	QLHV, [MJ/Kg]
Iso-Butanol	95.10	0.44	33.10
Iso-Butanol-85	96.74	0.38	34.5
Iso-Butanol-50	96.98	0.41	37.97
Iso-Butanol-30	96.62	0.43	40.02
Iso-Butanol-10	90.99	0.88	42.13
T30RFn20	88.06	0.82	43.2020

Fig. 6.13 presents the Lund ϕ-sensitivity number at different iso-butanol concentration and CA50≈6 °CA and illustrates the nonlinear behaviour of Lund ϕ-sensitivity number for iso-butanol blends with T30RFn20. Adding 10% iso-butanol to T30RFn20 increases the Lund ϕ-sensitivity of the blend even though it will increase the RON too. This likely is due to the high heat of vaporization of iso-butanol which increases the charge cooling effect, and as it has been discussed in chapter 5 it will enhance the ϕ-sensitivity. In contrast, adding more iso-butanol to the base fuel does not result in higher ϕ-sensitivity, instead more than 10% iso-butanol in the base fuel, decreases the ϕ-sensitivity number of the blend gradually up to a value less than the ϕ-sensitivity of neat iso-butanol.

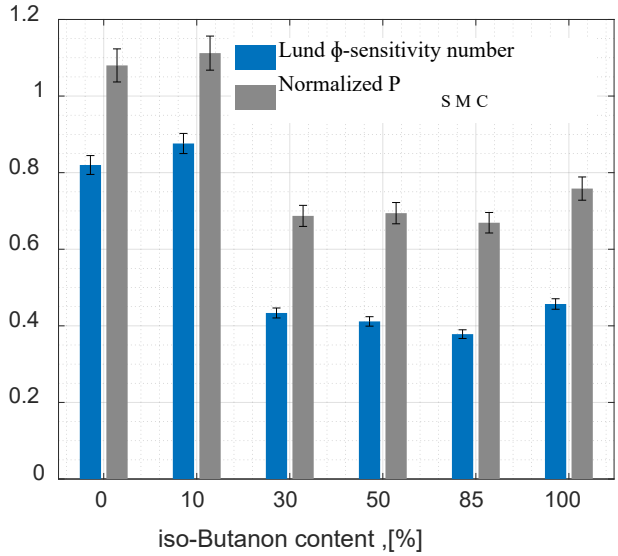


Fig. 6.13. Lund ϕ-sensitivity number at different iso-butanol concentration and CA50≈6 °CA.

Fig. 6.14 depicts the rate of HR for blends of iso-butanol and T30RFn20 at ϕ≈0.35. The lower heating values of the blends are presented in Table 6.2. Simultaneous increase in iso-butanol content and required CR to maintain the CA50 constant, varies both combustion chamber volume and the energy content of the fuel/air mixture. The blend composition and in-cylinder volume affect the energy content inside the cylinder. Increasing the CR for fuel with higher Lund-Chevron HCCI number, decreases the required fuel mass to achieve a specific ϕ. Since the stoichiometric value of the blend is increasing too, the required fuel mass needs to increase. The QLHV of those blends with higher Lund-Chevron HCCI number are lower, which cause less heat release during the combustion. Fig. 6.14 exhibits the rate of HR for blends of iso-butanol and T30RFn20 at ϕ≈0.35. This figure shows the combined effect of CR, fuel mass and QLHV on the HRR. Blends containing 85% and 50 % iso-butanol have lower stoichiometric value than neat iso-butanol. As a result, less fuel is required to generate the same ϕ. The required CR to maintain a constant CA50 is also increasing. Therefore, the in-cylinder volume decreases and compensate for the less fuel mass due to the lower stoichiometric value and results in a remarkably similar heat release rate for iso-butanol 50, 85 and 100.

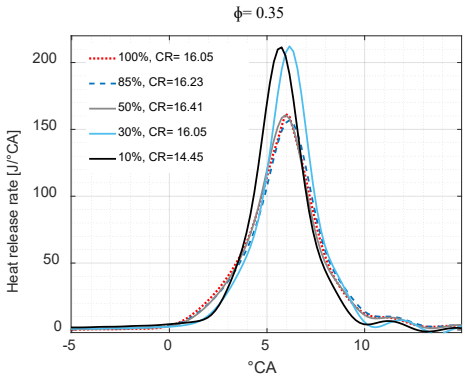


Fig. 6.14. Rate of HR for blends of iso-butanol and T30RFn20 at ϕ≈0.35.

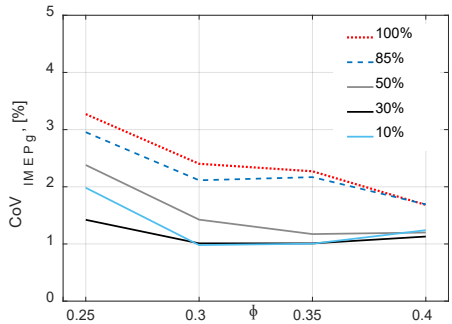


Fig. 6.15. CoV_{IMEP} for iso butanol blends at different ϕ levels.

Fig. 6.15. Shows the CoV_{IMEP} for iso-butanol blends at different ϕ levels. It shows that increasing iso-butanol content will increase combustion instability, especially at lower ϕ. The high charge cooling effect of iso-butanol increases the risk of miss-fire at very lean conditions where the in-cylinder temperature is low.

6.4 Conclusion

In this chapter the results of ϕ-sensitivity evaluation of iso-butanol and n-butanol are presented and discussed. The impact of retarded combustion phasing on the Lund ϕ-sensitivity number of iso-butanol is investigated and finally, the blending ϕ-sensitivity of iso-butanol as an alcohol example is evaluated.

As expected, the Lund ϕ-sensitivity number of n-butanol is higher than iso-butanol which is due to the higher octane reactivity of n-butanol. The retarded combustion phasing decreases the Lund ϕ-sensitivity number of evaluated fuel. The reason for the decrease in the Lund ϕ-sensitivity number, is the lower required compression ratio (CR) to auto ignite the fuel at a later combustion phasing. Because lower CR decreases the in-cylinder pressure and lower pressure is a known condition that decreases the ϕ-sensitivity. As expected, retarding the combustion phasing, increased the ϕ range of the experiment by lowering the maximum pressure rise rate. The Lund ϕ-sensitivity number shows a nonlinear behaviour in connection with the variation of iso-butanol content in the base fuel.

Chapter 7

Conclusions and suggestions for future work

7.1 Summary and conclusions

Sustainable transportation of people and goods is a considerable challenge for the transition toward a sustainable society. One of the suggested practical approaches for achieving a reliable and sustainable transport system is using renewable drop-in fuels for combustion engines. Even though the combustion engine is a well stablished technology, there is still room for research and improvements in this field. During this PhD study the author has developed an empirical test method for the evaluation of the ϕ-sensitivity property of different liquid fuels. The main rational for performing research about ϕ-sensitivity, is the role of this property in tailoring fuels for low temperature combustion (LTC) combustion. The LTC concept is the basis for some of the high-efficiency, low-emission combustion technologies that can facilitate a transition of the transport sector towards sustainability.

In this study, a modified cooperative research engine (CFR) engine for homogeneous charge compression ignition (HCCI) combustion, is used as the experimental apparatus. Different surrogate fuels and alcohols are evaluated at different ϕ levels, and the Lund ϕ-sensitivity method is developed. The proposed Lund ϕ-sensitivity method is the only empirical test method, available now, for the evaluation of ϕ-sensitivity of liquid fuels. The Lund ϕ-sensitivity method has a rather simple technical implementation. Therefore, this method has the potential to be established as an appropriate platform to characterize liquid fuels in refineries and other fuel related industries and applications.

During this PhD study the research questions (previously stated in chapter 2) are answered as below:

1. What are the determinative input and output parameters of a CFR engine in an HCCI combustion?

The results suggests that intake temperature, engine speed and equivalence ratio are the determinative input parameters. The required CR to maintain the CA50 constant, amount of heat release during the early reactions and in-cylinder pressure at the start of the main combustion are sensitive to the variation of those parameters. Moreover, a stable HCCI combustion is limited by the range of these parameters.

2. How to isolate the fuel's ϕ-sensitivity from the fuel octane reactivity?

Different blends that were used for the core experiments of the method development, were tailored to fit in three RON groups. In each group blends have similar RON number which is equal to a similar octane reactivity. Using this approach, the effect of octane reactivity was eliminated from the ϕ-sensitivity in each RON group.

3. How to formulate the dependency of early reactions to the changes of equivalence ratio using a CFR engine in form of a ϕ-sensitivity index?

The compression ratio (CR) adjustment for maintaining a constant combustion phasing during the ϕ sweep, compensates for the effect of ϕ variation on the ignition delay and the heat release ratio during early reaction to total accumulated heat release (TAcHR). Therefore, the CR variation during the test method application can be interpreted as a ϕ-sensitivity indicator. This approach results in a test method that can be used to quantify the ϕ-sensitivity of different fuels with the same RON.

This test method is a platform to evaluate and tailor fuels with a preferable ϕ-sensitivity at a desirable RON. Liquid fuels from renewable to conventional, to blends of renewable and conventional can be evaluated using the Lund ϕ-sensitivity method. The advantages of this method compared to numerical investigation of the ϕ-sensitivity property of fuels, is that the Lund ϕ-sensitivity method is applicable for compounds which do not have a detailed kinetics mechanism. The method provides a clear and consistent determination of ϕ-sensitivity of different liquid fuels via quick sets of experiments and simple calculations. Since the method is based on experiment, it does not rely on complex prerequisite data such as detailed kinetics mechanisms, which not always exist.

The following equation depict the Lund ϕ-sensitivity number formula:

$$Lund\ \phi\text{-}sensitivity = -\frac{1}{CR}\frac{\Delta \mathrm{CR}}{\Delta \phi}$$

4. What is the dependency of ϕ-sensitivity to the intake temperature, heat of vaporization, fuel composition and combustion phasing?

Since the ϕ-sensitivity property of a fuel is temperature-pressure sensitive, at different intake temperatures the ϕ-sensitivity of a fuel might defer. At 323K intake temperature the coexistence of oxygenated and aromatic hydrocarbons together with paraffin maximizes the Lund ϕ-sensitivity of the blends, while at the intake temperature of 423 K the unoxygenated octane sensitive blends (Toluene reference fuel: TRFs) have the highest Lund ϕ-sensitivity number in each research octane number (RON) group. This effect is due to the quenching effect of toluene on the cool flame and delaying the main combustion event. These multiple effects together, increase the ignition delay of aromatic blends and therefore increases the ϕ-sensitivity of the blends. At the lowest intake temperature, the charge cooling effect of ethanol compound of the blend, increases the fuel capability of adapting a higher CR that results in a higher in-cylinder pressure and therefore, increases the fuel ϕ-sensitivity. The results show, the intake temperature variation does not affect the Lund ϕ-sensitivity numbers of different blends in an analogous way. This study confirms the effect of early reactions heat releases (ERHR) on the ϕ-sensitivity of different fuels and consequently, on the Lund ϕ-sensitivity number.

Although the results do not suggest a correlation between the latent heat of vaporization of fuels and the Lund ϕ-sensitivity number, but a co-effect of HoV and ERHR is noticeable. The latent heat of vaporization of a blend does not show an explicit effect on the Lund ϕ-sensitivity number, but together with the ratio of accumulated heat release during the early reactions to the total accumulated heat release does create a meaningful co-effect; in each RON group, the blend with the lowest ERHR/TAcHR, and at the same time the highest HoV, does not exhibit the lowest ϕ-sensitivity of that RON group (associated with the lowest LTHR/TAcHR ratio). Instead, the high HoV of the blend increases its ϕ-sensitivity. This effect is expected to be the result of possible thermal stratification inside the combustion chamber.

A retarded combustion phasing decreases the Lund ϕ-sensitivity number of a fuel. This decrease is a result of the lower required CR to auto-ignite the fuel/air mixture, at the retarded CA50. Lower CR decreases the compression pressure inside the combustion chamber. Lower pressure is one of the known reasons for the lower ϕ-sensitivity property of different fuels.

5. How does the blending ϕ-sensitivity change for alcohols?

An evaluation of iso-butanol blended with T30RFn20 indicates that the Lund ϕ-sensitivity number do not show a linear behaviour in connection with the variation of alcohol content in the base fuel. Adding 10% iso-butanol to the surrogate gasoline increases the Lund ϕ-sensitivity number of the blend compared to the surrogate gasoline. Adding more iso-butanol decreases Lund ϕ-sensitivity number gradually, and for neat iso-butanol the ϕ-sensitivity increases again.

6. What is the conclusion of using the ϕ-sensitivity test method for designing load adaptive fuels effective for different combustion concepts?

The study suggests that there is a link between the Lund ϕ-sensitivity number and the fuel load adaptability property. The expected properties for a fuel to be load adaptive depends on the combustion concept. Fuels with high Lund ϕ-sensitivity number and high RON are expected to be more load adaptive for low temperature gasoline (LTG) engines while a low Lund ϕ-sensitivity number for a high-octane fuel makes it more appropriate for SI combustion and is also more knock resistance. Stratified combustion schemes like PPC, are expected to work well with fuel having medium RON and high Lund ϕ-sensitivity number.

7.2 Suggestions for future work

Modern combustion engines are working at high intake pressure, so called boosted condition. Experimental evaluation of ϕ-sensitivity of different fuels under boosted conditions seems therefore necessary. It would also be valuable to tailor different blends using the Lund ϕ-sensitivity method and then evaluate those fuels in a conventional engine at PPC, HCCI or other modern combustion concepts.

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Scientific publications

I **The effect of 2-ethyl-hexyl nitrate on HCCI combustion properties to compensate ethanol addition to gasoline**
Alemahdi N, Tuner M
Fuel, vol. 270, p. 117569, 2020
https://doi.org/10.1016/j.fuel.2020.117569

II **Development of a fast-virtual CFR engine model and its use on auto-ignition studies**
García A, Monsalve-serrano J, Lago Sari R, Fogué-Robles Á, **Alemahdi N,** Tunér M
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III **Development of an empirical test method to quantify the ϕ-sensitivity**
Alemahdi N, García A, Boufaim E, Aferiat G, Tunér M.
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IV **Understanding the ϕ-sensitivity of toluene & ethanol reference fuels at different intake temperatures**
Alemahdi N, García A, Tunér M
Review comments received: International journal of engine research

VII **Nonlinear ϕ-sensitivity behaviour of iso-butanol blends with surrogate gasoline**
Alemahdi N, García A, Tunér M.
Status: Manuscript