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**“Computational Studies on HCCI
Engines”**

School of Engineering
Department of Automotive, Mechanical and
Structures Engineering
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MPhil Thesis

Cranfield
UNIVERSITY



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2010

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This thesis is submitted in partial fulfilment of the requirements for the degree of
Master of Philosophy.

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ABSTRACT

Emission legislation is changing in an effort to reduce exhaust emissions from the IC engines. Research and development has been focused on improving both spark-ignition and compression ignition engines to make them more efficient. Over the last decade, research has been increasing in Homogeneous Charge Compression Ignition (HCCI) engines. This alternative combustion process has the potential to combine the best of spark-ignition engines, namely the cleaner combustion with virtual no emission of NO_x and soot, with the best of compression ignition, the increased engine efficiency with low fuel consumption and consequently lower carbon dioxide emissions.

In this thesis, the effect upon HCCI combustion of different additives has been investigated. These additives can be used, to control the start of auto-ignition and/or to extend the load limits in which HCCI operation is possible.

As part of this work, the HCCI combustion capability of running with different fuels was investigated. In order to study these effects on HCCI combustion, a detailed chemistry fuel oxidation mechanism was used together with a powerful chemical kinetic modelling tool, CHEMKIN. Simulations of the HCCI combustion were performed using a single-zone zero dimensional model and later a simpler multi-zone model comprising three different zones.

Using the single-zone CHEMKIN model, additives influence on combustion was studied.

From this study more complex mixtures were defined and more simulations were done, this time including different fuels such as ethanol, iso-octane and mixtures of both.

A more complex model other than the single-zone tool available at CHEMKIN was developed and comparisons between the two simulation methods were performed.

The results obtained from the simulations performed confirmed the fuel tolerance of HCCI combustion and the capability of running water diluted mixtures.

ACKNOWLEDGMENTS

My first acknowledgment goes for Professor Doug Greenhalgh who made all this possible. His enthusiasm for the subject when I first came for my interview made me embrace this adventure.

That first interview was the beginning of a new stage in my life that I am truly enjoying! Thanks!

Also to Professor Nick Vaughn who was my supervisor at Cranfield after Doug and James had left to embrace their new projects.

Thanks Nick for some directions given with regards to writing the thesis and with help getting all the extensions.

To Adam, Alessio, Christelle, Edouard, Fatiha, with whom I shared the office where I worked, thank you for your friendship during the course of time we spent together.

To all my friends in Brentwood, Andre B, Andre F, Adriana, Bia, Mauro, Nicola, thanks for the support given to help me out finish writing my thesis! Well, not really as some of you were always trying to make me go out instead of working!

A big thanks to Fran and Derek, where I lived during the course of my studies. You were a family to me and the support and stability you all gave me was fantastic! The friendship we have now is one of the best things I take from my experience abroad.

To my parents, whose encouragements and support have always given me strength and of course without whom never of this would have been possible.

Thanks for everything!

TABLE CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	v
ABBREVIATIONS AND DEFINITIONS	ix
LIST OF FIGURES	xi
LIST OF TABLES	xv
CHAPTER 1	1
1.1 Overview	1
1.2 Combustion and Emissions	3
1.3 Aim of the Thesis	7
1.4 Methodology	8
1.4.1 Literature Review	8
1.4.2 Computational Simulations	8
1.4.3 Data Analysis and Discussion of Results	8
CHAPTER 2	11
2.1 Internal Combustion Engines	11
2.2 Review on HCCI Combustion Literature	14
2.2.1 HCCI – The Beginning	17
2.2.2 Compression Ratio	20
2.2.3 Exhaust Gas Recirculation, EGR	22
2.2.4 Forced Induction	24
2.2.5 Turbulence	26
2.2.6 Fuel Injection and Spark Ignition	28

2.2.7 Hybrid Engines	31
2.2.8 Reformed Fuel	33
2.2.9 Different Fuels	36
2.2.10 Summary	38
2.3 Emission Formation	39
2.3.1 Carbon Dioxide Formation	40
2.3.2 Carbon Monoxide and Unburned Hydrocarbons Formation	41
2.3.3 Soot Formation	42
2.3.4 Nitrogen Oxides Formation	43
CHAPTER 3	45
3.1 Chemical Kinetics for the HCCI Combustion Process	45
3.1.1 Low-Temperature Paraffin Oxidation	47
3.1.2 Low-Temperature Olefin Oxidation	49
3.1.3 Low-Temperature Aromatic Oxidation	50
3.1.4 Intermediate-Temperature Paraffin Oxidation	52
3.1.5 High-Temperature Paraffin and Olefin Oxidation	53
3.1.6 High-Temperature Aromatic Oxidation	55
3.1.7 Influence of NO in Combustion	56
3.2 HCCI Engine Simulation	58
3.2.1 Single Zone Chemical Kinetics Models	60
3.2.2 Multi Zone Chemical Kinetics Models	61
CHAPTER 4	63
4.1 CHEMKIN Set-Up	63
4.2 CHEMKIN Initial Simulations	66
4.2.1 Additives Influence in Combustion	69

4.2.2 Summary	76
4.3 CHEMKIN Simulations with Different Fuels	77
4.3.1 Iso-Octane	78
4.3.2 Ethanol	82
4.3.3 Iso-Octane /. Ethanol	86
4.3.4 Summary	88
CHAPTER 5	91
5.1 Multi-Zone Simulation	91
5.2 Single Zone vs Multi-Zone Results	93
5.2.1 Ethanol Fuelled HCCI	95
5.2.2 E85 Fuelled HCCI	100
5.2.3 E24 Fuelled HCCI	104
5.2.4 E10 Fuelled HCCI	107
5.2.5 Iso-Octane Fuelled HCCI	110
5.3 Discussion of Results	113
5.4 Recommendations and Future Work	115
REFERENCES	117
BIBLIOGRAPHY	127
APPENDIX 1	
APPENDIX 2	
APPENDIX 3	
APPENDIX 4	

ABBREVIATIONS AND DEFINITIONS

ATDC	After Top Dead Centre
ATM	Atmospheres
BTDC	Before Top Dead Centre
CAD	Crank Angle Degree
CAI	Controlled Auto-Ignition
CO	Carbon Monoxide
DI	Direct Injection
DP / DT	Pressure Release per Crank Angle
EGR	Exhaust Gas Recirculation
ETOH	Ethanol
EVC	Exhaust Valve Closing
EVO	Exhaust Valve Opening
HC	Hydrocarbon
HCCI	Homogeneous Charge Compression Ignition
IC	Internal Combustion
IGN	Ignition
IOCT	Iso-Octane
IVC	Intake Valve Closing
IVO	Intake Valve Opening
NOx	Nitrogen Oxides
NTC	Negative Temperature Coefficient
NVO	Negative Valve Overlap
PFI	Port Fuel Injection
PPM	Parts Per Million
SI	Spark Ignition
SOC	Start of Combustion
TDC	Top Dead Centre
CHEMKIN	Code and format for chemical kinetics modelling
WAVE	Commercial 1-D engine cycle simulation code
LabView	Software used for experimental data acquisition

LIST OF FIGURES

Figure 1.1 - Variation of pollutant concentrations in the exhaust of a conventional SI engine with fuel/air equivalence ratio.^[7]

Figure 2.1 - Ignition and combustion process for CI, SI and HCCI engines.^[21]

Figure 2.2 - Plasmatron engine concept.^[57]

Figure 2.3 - Summary of HC, CO and NO pollutant formation mechanisms in a spark-ignition engine.^[7]

Figure 4.1 - Comparison between temperature vs crank angle data.^[66]

Figure 4.2 - Temperature profile against crank angle for an initial temperature of 500K.

Figure 4.3 - Pressure release per crank angle, for an initial temperature of 500K.

Figure 4.4 - CO₂ influence on temperature profile and pressure release rate.

Figure 4.5 - CO influence on temperature profile and pressure release rate.

Figure 4.6 - H₂ influence on temperature profile and pressure release rate.

Figure 4.7 - H₂O influence on temperature profile and pressure release rate.

Figure 4.8 - O₂ influence on temperature profile and pressure release rate.

Figure 4.9 - N₂ influence on temperature profile and pressure release rate.

Figure 4.10 - NO influence on temperature profile and pressure release rate.

Figure 4.11 - CH₄ influence on temperature profile and pressure release rate.

Figure 4.12 - CH₃OH influence on temperature profile and pressure release rate.

Figure 4.13 - C₂H₆ influence on temperature profile and pressure release rate.

Figure 4.14 - C₂H₂ influence on temperature profile and pressure release rate.

Figure 4.15 - CH₂O influence on temperature profile and pressure release rate.

Figure 4.16 - Ignition delays and peak temperatures for different iso-Octane mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11.

Figure 4.17 - Pressure release per C.A. for different iso-Octane mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11.

Figure 4.18 - Ignition delays and peak temperatures for different iso-Octane mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11.

Figure 4.19 - Pressure release per C.A. for different iso-Octane mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11.

Figure 4.20 - Ignition delays and peak temperatures for different ethanol mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11,5.

Figure 4.21 - Pressure release per C.A. for different ethanol mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11,5.

Figure 4.22 - Ignition delays and peak temperatures for different ethanol mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11,5.

Figure 4.23 - Pressure release per C.A. for different ethanol mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11,5.

Figure 4.24 - Ignition delays and peak temperatures for different iso-octane / ethanol mixtures ran with different equivalence ratio and a compression ratio of 11,5.

Figure 4.25 - Pressure release per C.A. for different iso-octane / ethanol mixtures ran with different equivalence ratio and a compression ratio of 11,5.

Figure 5.1 - Schematic representation of the multi-zone model used.

Figure 5.2 - Pressure vs crank angle comparison between simulations for 90% EtOH/water mixture diluted with CO₂.

Figure 5.3 - Pressure release per crank angle vs crank angle comparison between simulations for 90% EtOH/water mixture diluted with CO₂.

Figure 5.4 - Pressure vs volume comparison between simulations for 90% EtOH/water mixture diluted with CO₂.

Figure 5.5 - Pressure vs crank angle comparison between simulations for 90% E85/water mixture diluted with CO₂.

Figure 5.6 - Pressure release per crank angle vs crank angle comparison between simulations for 90% E85/water mixture diluted with CO₂.

Figure 5.7 - Pressure vs volume comparison between simulations for 90% E85/water mixture diluted with CO₂.

Figure 5.8 - Pressure vs crank angle comparison between simulations for 90% E24/water mixture diluted with CO₂.

Figure 5.9 - Pressure release per crank angle vs crank angle comparison between simulations for 90% E24/water mixture diluted with CO₂.

Figure 5.10 - Pressure vs volume comparison between simulations for 90% E24/water mixture diluted with CO₂.

Figure 5.11 - Pressure vs crank angle comparison between simulations for 90% E10/water mixture diluted with CO₂.

Figure 5.12 - Pressure release per crank angle vs crank angle comparison between simulations for 90% E10/water mixture diluted with CO₂.

Figure 5.13 - Pressure vs volume comparison between simulations for 90% E10/water mixture diluted with CO₂.

Figure 5.14 - Pressure vs crank angle comparison between simulations for 90% iso-octane/water mixture diluted with CO₂.

Figure 5.15 - Pressure release per crank angle vs crank angle comparison between simulations for 90% iso-octane/water mixture diluted with CO₂.

Figure 5.16 - Pressure vs volume comparison between simulations for 90% iso-octane/water mixture diluted with CO₂.

Figure 5.17 - Comparison between simulation results, for peak pressure, when the fuel used was ethanol.

LIST OF TABLES

Table 1.1 - EU Emission standards for passenger cars, g/Km.^[4,6]

Table 3.1 - Comparison between different HCCI models.^[76]

Table 4.1 - Results for mixtures of Iso-Octane.

Table 4.2 - Results for mixtures of Ethanol.

Table 4.3 - Results for mixtures of Iso-Octane / Ethanol.

Table 4.4 - Results for different mixtures that achieved desired results.

Table 5.1 - Mixtures used in the CHEMKIN simulations.

Table 5.2 - Summary of the results obtained when fuel used was ethanol.

Table 5.3 - Summary of the results obtained when fuel used was E85.

Table 5.4 - Summary of the results obtained when fuel used was E24.

Table 5.5 - Summary of the results obtained when fuel used was E10.

Table 5.6 - Summary of the results obtained when fuel used was iso-octane.

CHAPTER 1

INTRODUCTION

Chapter 1 provides a synopsis of this thesis. A brief introduction on engine emissions, the legislation driving the motor companies and the way OEM are addressing them, is given. A succinct description of HCCI combustion and its potential is also found on this chapter. It ends with the aim of the thesis and with the methodology followed during the course of this work.

1.1 Overview

The increasing concern about the environment has been one of the major forces behind ongoing research to obtain cleaner sources of energy and to optimize the use of existing technologies. Internal combustion engines (ICE) have been around for more than one century and have been identified as one major source of air pollution. The exhaust gases from the ICE are mainly constituted by carbon dioxide (CO₂) and water (H₂O) together with nitrogen oxides (NO_x), carbon monoxide (CO), unburned hydrocarbons (UHC) and smoke (soot).

It is well known that CO₂ emissions are a serious environmental problem due to its contribution to the greenhouse effect. Several studies show that nitrogen oxides, beyond the capability to form smog by interacting with sunlight and UHC, can also contribute to the greenhouse effect, making this pollutant another global warming agent coming out from the exhaust of automotive engines.

The other exhaust emissions (CO, UHC and soot) were found to have a negative impact on air quality as well as being toxic for humans.^[1,2]

In this context, worldwide motor industries are gradually introducing new technologies to minimize emissions and improve fuel economy making ICE more and more efficient. Nowadays automotive research and development is

driven by the environmental pressure that worldwide motor companies are facing.

The new emerging technologies should be applied to mass production satisfying all customer requirements, as improved fuel economy, performance, driveability, while being available at an acceptable cost.

Within the next years, legislation by the Environmental Protection Agency (EPA) and the European Union (EU) will become further stringent.

It was recently proposed by the European Commission to reduce CO₂ emissions to an average of 120g/Km by 2012 (a reduction of around 25% from today levels), which will correspond to an average fuel consumption of 4.5 L/100Km (around 60mpg).^[3,4]

In table 1.1 it is possible to see how the legislation for exhaust gas emissions is becoming stricter. In the past 10 years all the allowed exhaust emissions from new cars has decreased to at least half of the previous values and the future, will yield more changes for even more rigorous legislation.^[1-5]

Table 1.1 – EU Emission standards for passenger cars, g/Km.^[5,6]

Tier	Date	CO	HC	HC+NOx	NOx	PM
Diesel						
Euro 1	Jan 1989	2.72	-	-	0.97	0.14
Euro 2, IDI	Jan 1993	1.00	-	-	0.70	0.08
Euro 2, DI	Jan 1993	1.00	-	-	0.90	0.10
Euro 3	Dec 1997	0.64	-	0.50	0.56	0.05
Euro 4	Jan 2003	0.50	-	0.25	0.30	0.025
Euro 5	Sep 2009	0.50	-	0.18	0.23	0.005
Euro 6	Sep 2014	0.50	-	0.08	0.17	0.005
Petrol (Gasoline)						
Euro 1	Jan 1989	2.72	-	-	0.97	-
Euro 2	Jan 1993	2.20	-	-	0.5	-
Euro 3	Jan 1997	2.30	0.20	0.15	-	-
Euro 4	Jan 2003	1.00	0.10	0.08	-	-
Euro 5	Sep 2009	1.00	0.10	0.06	-	-
Euro 6	Sep 2014	1.00	0.10	0.06	-	0.005*

*Applies only to vehicles with direct injection engines.

1.2 Combustion and Emissions

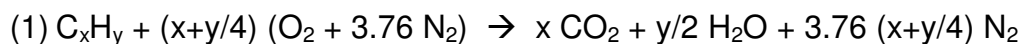
Internal combustion engines (ICE) release energy by burning/oxidizing the fuel inside the engine in the combustion chamber. The exothermic reaction of the fuel with the oxidizer (oxygen) creates gases of high temperature and pressure that will expand producing force and work on the piston head causing a downwards movement of it inside the cylinder. In theory if sufficient oxygen is available, a hydrocarbon fuel can be completely oxidized. The carbon (C) in the fuel is then converted to carbon dioxide (CO₂) and the hydrogen (H₂) to water (H₂O) whereas the nitrogen (N₂) theoretically remains unchanged.

In practice, the exhaust gas of an ICE contains several incomplete combustion products, such as carbon monoxide (CO), unburned hydrocarbons (UHC), nitrogen oxides (NO_x), soot, as well as complete combustion products, nitrogen (N₂), carbon dioxide (CO₂) and water (H₂O).

Generally, under lean operating conditions the amounts of incomplete combustion products are smaller. On the other hand, under fuel rich operating conditions, these amounts become more substantial since there is insufficient oxygen to complete combustion reaction.

From the combustion stoichiometry, the relationship between reagents and products in chemical reactions, it is verified a direct relationship between the initial fuel quantity and the quantity of combustion products.

The following reaction (theoretical combustion chemistry reaction of a C_xH_y fuel molecule) shows the mentioned relationship.



According to what have been explained it is possible to conclude that lean combustion looks like one of the most practical solutions to face the constant need to reduce exhaust emissions and improve fuel consumption.^[7,8,9]

Figure 1.1 on the next page, shows the variation of exhaust emissions (NO, HC and CO) with equivalence ratio.

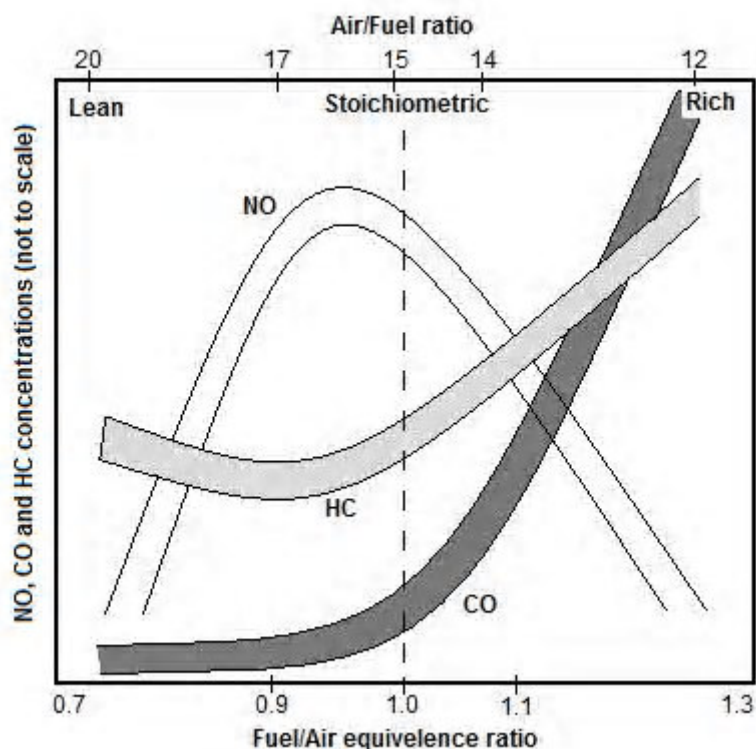


Figure 1.1 – Variation of pollutant concentrations in the exhaust of a conventional SI engine with fuel/air equivalence ratio.^[7]

The equivalence ratio is defined as the ratio of the fuel-to-oxidizer, to the stoichiometric fuel-to-oxidizer ratio. Equivalence ratios greater than one represent excess fuel than the one required for complete combustion, while ratios smaller than one represent a deficit of fuel in a mixture.

The richer the mixture is, the lower will be the formation of NO_x, due to the lack of available oxygen to recombine with nitrogen to form nitric oxides. This insufficient oxygen will not be able to oxidize all fuel to CO₂ and so carbon monoxide and UHC concentration will increase with rich mixtures. When the equivalence ratio is in the range of 0.8-1.0, CO and UHC emissions will be low, but NO_x emissions will reach a peak. This is caused not only by the availability of oxygen, but also because NO_x formation is highly dependent on temperature and at that range of equivalence ratios is where the peak temperatures are higher.

Going leaner in the mixture range will continue to decrease formation of all emissions, until a point is reached where irregular combustion and misfire start to occur with the natural consequence of increasing UHC.

There is potential to reduce fuel consumption and to reduce exhaust emissions, by using several different approaches or combinations of different concepts such as improved ignition systems, turbulence, fuel reforming, direct injection, stratified charge, amongst others.

Research and development will always be required to optimize ICE in order to achieve the maximum efficiency from the engine with minimum formation of pollutants. This is nowadays, the major driving force within the automotive industry.^[7,8,10]

One new emerging engine combustion technology is Homogeneous Charge Compression Ignition (HCCI). The idea behind this concept consists in the compression of a lean homogeneous air-fuel mixture to a point that will auto-ignite uniformly throughout all the mixture without the creation of rich spots.

This would allow diesel like fuel consumption and engine efficiency without the formation of soot or NO_x, due to the absence of localized rich zones.^[11]

The fundamentals of this combustion concept are not new at all. In the late 19th century, Akroyd Stuart developed the so called hot bulb engine where the heat created by the piston during the compression stroke ignited the fuel that it was introduced during the normal intake stroke. At their time this type of engines were popular, but the development of the diesel engine technology made the hot bulb engine obsolete specially for applications where a broad range of engine operation was necessary.^[12]

The HCCI concept started to be again object of study in the late nineteen seventies, however with two stroke engines applications in sight. Researchers could see opportunities for re-developing this engine concept. However, with the engine technology available at that time, implementing this combustion mode for automotive applications, where a broad range of engine speed in necessary, was an almost impossible task.

Since the late nineties with the development of sophisticated engine control systems including fuel injection, valve timing, spark ignition, the HCCI concept started to be of interest again and the amount of research going into it, increased exponentially.

The complex engine control systems are one key requirement for this combustion concept as there are no direct control methods to start combustion. While in a SI engine the spark timing defines the ignition and in a CI engine the fuel injection has this role, in a HCCI engine complex chemistry governs the start of ignition. Understanding and controlling the chemistry behind is the main challenge with this engine technology.^[13,14,15]

1.3 Aim of the thesis

The study undertaken in this thesis served several objectives.

The first objective was to understand the effect of different fuel additives that can be found either in the exhaust gas or as products of reformed fuel, on HCCI combustion.

Other important objective of this thesis was to prove the capability of HCCI combustion to use different fuels. On this thesis iso-octane, ethanol and mixtures of both this fuel were studied using simulation tools.

Another objective of this thesis was to develop a more accurate simulation model, based on more than one zone, to try to account for deviations in the homogeneous assumption. This model was run in CHEMKIN using a detailed chemical kinetic mechanism.

1.4 Methodology

The work developed on this thesis was accomplished by following well defined steps as literature review, simulation work, experimental work, data analysis and discussion of results.

1.4.1 Literature Review

The existing automotive ICE engines, spark ignition and compression ignition were briefly reviewed where advantages and disadvantages were pointed out. In this context it was showed the potential advantages of HCCI over the current existing engine technologies. Emission formation and combustion chemistry were also covered, since the latest plays the controlling role on achieving auto-ignition conditions on the HCCI combustion engine.

1.4.2 Computational Simulations

Computer simulations using CHEMKIN were used to model a single cylinder engine operating under HCCI conditions. The effect of different fuels and additives was studied. A more complex simulation model was developed to try to improve the results obtained with the single-zone model.

1.4.3 Data Analysis and Discussion of Results

Both simulation outputs were compared. The results are discussed and the findings reported.

Recommendation for future work is also presented.

CHAPTER 2

LITERATURE REVIEW

Chapter 2 starts with a brief overview of internal combustion engines where the advantages and disadvantages of SI and CI engines are presented.

A literature review on HCCI combustion is then given, where it is possible to identify the advantages and some of the current issues with this combustion concept.

A brief insight on emission formation is also given at the end of this chapter.

2.1 Internal Combustion Engines

The majority of engines used in vehicles today are spark-ignition (SI) engines and compression ignition (CI). The continuous development of our society, and more importantly, the emerging new economies from underdeveloped countries as China and India, mean that there will be an increase in the demand for cars. This situation will increase by a large factor the exhaust emissions from the automotive sector.

Hydrogen fuel cell technology arises theoretically as a solution for this problem, since it is capable of emitting no harmful products and has the potential of not to depend on fossil fuels. The drawback with fuel cell technology is that it is not believed it will be readily available at a reasonable cost for at least 10-15 years. Besides the technical side of running a car with this technology, there is also the entire hydrogen infrastructure required, the so called hydrogen economy.

Production of hydrogen should come from a renewable energy and that is far from achievable in the near future. Also, an all new logistic system for hydrogen transport and storage would need to be in place, which again does not seem viable in the near future.^[16,17]

As a consequence of this, it is concluded that ICE will still be around for some years, making the research on improving them, a priority. There are already a number of innovative technologies that have been recently introduced or are

expected to make their way into the market soon, such as: more flexible valve timing and control, lean burn combustion, gasoline direct injection, cylinder deactivation, better engine control systems, exhaust gas recirculation, new exhaust after-treatment systems, among others. Although these technologies allow better efficiency, improve fuel consumption and minimize emissions, further research must be undertaken to continuously improve them.

The SI engine is a lightly built engine and hence has a lower first cost than a CI engine. In SI engine the fuel is mixed with air before entering the combustion chamber, once there the homogenous charge is compressed and a spark initiates combustion. A flame is developed and propagates through the premixed homogeneous mixture. This combustion method offers the advantage of virtually no soot being produced as well as low formation of NO_x. However, this type of engines offer poor part load efficiency, due to large pumping losses during gas exchange, and low combustion and thermodynamically efficiency, which translates as not being as fuel efficient as CI engines are.^[11,13,18,20]

The CI engine is much more efficient. These engines operate un-throttled, since the engine air flow is unchanged (not completely true once today the majority on CI engines are turbo-charged). They have higher fuel conversion efficiency mainly by operating with lean mixtures at higher compression ratio which improves the fuel consumption and lowers the CO and CO₂ emissions, since they are directly proportional to the amount of fuel consumed. The combustion starts when the fuel is injected into the cylinder, at the end of the compression stroke where the air is at a higher temperature than the one required to ignite the fuel. The late injection of the fuel makes the mixture inhomogeneous, which result in high emissions of unburned particles (soot) and favours the formation of NO_x in localized areas of the combustion chamber, where the temperature is high and the oxygen is readily available.^[11,13,18]

As mentioned a big array of new technologies is been used to improve both the SI and CI engines.

On SI engines the direct injection systems are now more common. Amongst other consequences this allows an engine to operate with higher compression

ratios due to the cooling effect of the fuel being injected directly onto the combustion chamber. Higher compression ratios directly reflect an improvement on the engine efficiency with benefits on the fuel consumption. Together with direct injection, variable valve timing also helps improving the overall efficiency of the system.

A recent trend in the SI engines is the use of forced induction to maintain or improve power with the downsizing of the engine volume.

On CI engines one of the systems that take more focus of research is the injection system with the development going on the direction of even higher pressure injection systems. This would allow for better fuel atomization which will help reducing the formation of particulates and the smoke associated with CI engines. The development of new variable turbo charged systems also helps ensuring better efficiency in all engine ranges.

Another common strategy in place on both types of engine is, exhaust gas recirculation. Employing this strategy reduces the in-cylinder charge temperature which in turn helps minimizing the formation of NOx.

Beyond the improvement of these two types of engines, research is focusing on alternative combustion modes such as Homogeneous Charge Compression Ignition (HCCI). This is a promising concept, as it has the potential to combine the best of spark ignition (SI) and of compression ignition (CI) engines.

The engine operates with lean mixtures which may give CI equivalent fuel consumption, and due to the homogeneous charge without rich or stoichiometric zones the peak temperatures will be lower and the production of soot and NOx can be avoided.^[11,16]

At present there are still several challenges that must be addressed before HCCI can go into production, but this is a promising concept.

HCCI combustion is the topic of this thesis, and the next section discusses it in detail.

2.2 Review on HCCI combustion literature

The basic principle behind HCCI combustion is to compress a homogeneous air-fuel mixture to a certain point so that it auto-ignites close to top dead centre (TDC). This operation can be described as a combination of a SI and a CI engine. A homogeneous charge is prepared in the inlet manifold where fuel and air are mixed before the intake stroke of the engine – just like in an SI engine. After the intake stroke, valves are closed and the onset of combustion is governed by compression of the pre-mixed charge – similar operation as in CI engines.^[11,18]

Unlike SI or CI engines in an HCCI engine combustion is initiated by auto-ignition (a process dominated by chemical kinetics of the air-fuel mixture), which theoretically occurs simultaneously throughout the cylinder volume rather than in a flame front (SI, CI engines). Potentially, HCCI combustion is a third combustion principle for internal combustion engine applications.

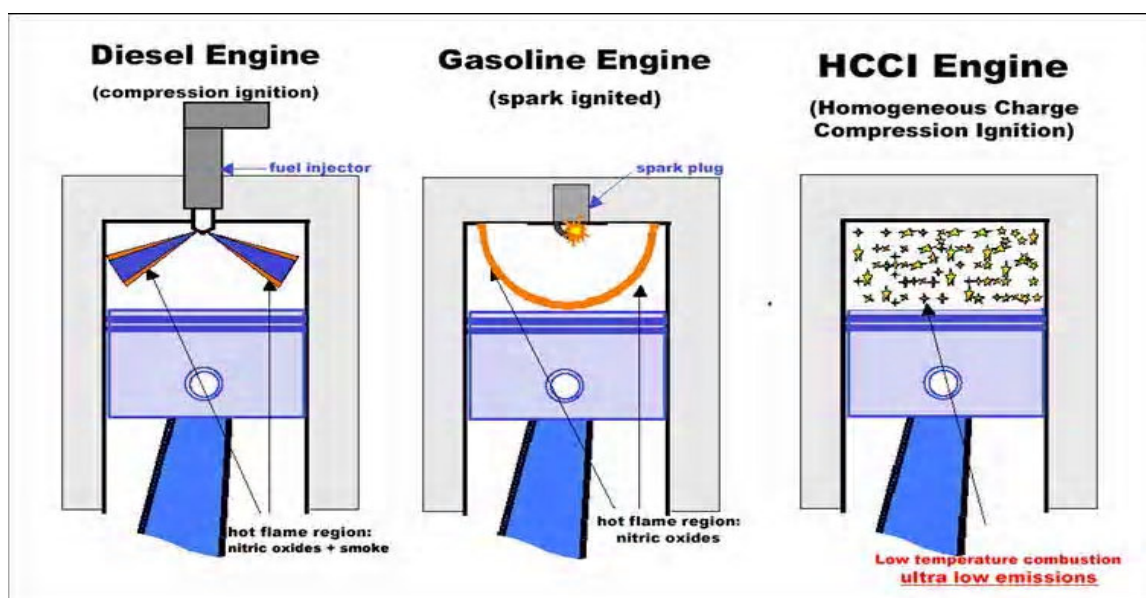


Figure 2.1: Ignition and combustion process for CI, SI and HCCI engines.^[21]

In the definition of HCCI (Homogeneous Charge Compression Ignition) combustion it is assumed that the air-fuel mixture is homogeneous, however in reality it is not. During the compression process, different parts of the charge mixture will have different heat capacities due to local in-homogeneities, which

results in non-uniform temperature distribution throughout the combustion chamber. This is the practical deviation to the theoretical assumed homogeneous mixture.

The first part of the mixture to ignite is the hottest region (may be constituted by only few hot spots), which will then compress the rest of the charge, leading to the ignition of all the mixture. Too fast burn durations lead to fast high heat release rates and consequently knock, which limit the upper load limit of HCCI operation. On the other hand too slow fast burn durations will cause incomplete combustion and misfire which will limit the lower load limit of HCCI.^[22-25]

HCCI combustion is achieved with very lean air-fuel mixtures that apart from contributing to minimizing fuel consumption, will also address the problem of fast high heat release rates. Due to the high dilution of the mixture, the gas temperature after combustion can ideally be lower than 1800-1900K, so the formation of NO_x in the combustion chamber can be minimized. Also due to the fact that the mixture in the cylinder is premixed, the formation of soot can be extremely low.^[25]

As just pointed, HCCI combustion has the potential to suppress the main problems that are currently associated with CI engines (the high emission formation of soot and NO_x) maintaining the lower fuel consumption due to lean air-fuel mixture operation.

There are, however some disadvantages with this concept which are; high UHC and CO emissions (which can be easily removed using actual technology, namely the current range of catalytic converters), reduced operating range (due to high heat release rates on the upper limit and misfire on the lower limit), low power density per displacement (forced induction might be a solution) and difficulties in starting and controlling combustion.

This represents a difficult problem in HCCI combustion, due to its extreme sensitivity to temperature, pressure and composition of the air-fuel mixture during the compression stroke.

It is generally accepted that HCCI combustion is mainly chemically controlled. Therefore a deep understanding of HCCI reaction chemistry is required to develop valuable control strategies.

Consequently the control system is fundamentally more complex than using a spark plug or fuel injector to determine start of ignition. ^[13,26-28]

2.2.1 HCCI – The beginning

As already explained, HCCI is a combustion concept where neither a spark nor fuel injection initiates the ignition in the combustion chamber.

This is maybe the older concept of an internal combustion engine. Ackroyd Stuart in the 1890s developed the so called hot bulb engine. The operation of this engine is simple and does not require any advanced fuel system or spark ignition. The main feature of it is a hot bulb that must be heated externally prior to engine start. Once the bulb is hot and the piston is rotating the principle is similar to a 4 stroke engine. During the intake stroke, air is drawn into the cylinder and fuel is sprayed into the hot bulb. Due to the sprayer action and the temperature in the hot bulb the fuel is vaporized. On the compression stroke the air temperature inside the cylinder rises, the vaporized fuel is mixed (through an opening on the hot bulb) and ignition takes place. At the time of its invention the main advantages were its economy, simplicity and tolerance to a large spectrum of fuels. The development of CI and SI engines made the hot bulb engine obsolete, especially for automotive applications, where its band of operation was too narrow.^[12,29]

Based on the auto-ignition concept of a homogenous charge due to the air temperature in the cylinder (same fundamentals as the hot bulb engine), Onishi et al in 1979, reported a new combustion concept called Active Thermo Atmosphere Combustion (ATAC). This was the modern predecessor of HCCI combustion. This concept was developed as an alternative lean combustion mode for two-stroke internal combustion engines. From the observations made, it was concluded that ATAC was initiated by auto-ignition that occur spontaneously at several different points within the combustion chamber. Stable combustion was achieved with lean air-fuel mixtures and exhaust emissions and fuel economy were remarkably improved.^[14]

At the same time another group of investigators led by Noguchi and Tanaka, was performing optical experiments to study this new concept. Apart from observing that ignition took place at numerous points inside the cylinder, they did not record any flame front being developed during combustion. Also, they

realized that the combustion duration is much shorter than the one it takes place on conventional SI or CI engines. The spectroscopy methods employed allowed the detection of intermediate species such as CH_2O , HO_2 and O that appeared in a specific sequence, before auto-ignition occurs. These species served as ignition kernels for combustion. This sequence of events, differs from conventional engines where all the radicals present appear at almost the same time.^[15]

In 1983, Najt and Foster's work was the predecessor for the studies on modeling kinetics and fuel oxidation on HCCI combustion. They were also the first researchers to report HCCI combustion in 4-stroke engines. From their work, important contributions to the knowledge of the ignition and the energy release process were withdrawn. They found that chemical kinetics played a vital role in HCCI combustion and through temperature control and species concentration control, it was possible to control combustion. They found that two different temperatures were of major importance on HCCI; low temperature hydrocarbon oxidation, which occurs below 950K and is responsible for controlling ignition, and a high temperature hydrocarbon oxidation that occurs above 1000 K, that controls the energy release process.^[30]

Since the first work on 4-stroke HCCI engines until today, hundreds of papers have been published by an increasing amount of research groups. The amount of work that has been put into this concept demonstrates the potential that is seen on it. The studies performed, have been able to demonstrate the potential of this combustion concept to produce fuel economy comparable with a CI engine with low levels of NO_x and soot emissions. Several conclusions have been reached as result of the investigation done so far. It was underlined that HCCI operation required high levels of EGR and high intake temperatures. It was pointed that it is not possible to operate under HCCI conditions for the whole engine range (lower boundaries defined by misfire, while the higher limit is set by engine knock), the levels of carbon monoxide (CO) and unburned hydrocarbons (UHC) are high, there is also low power density as a consequence of lean operation. Also there is an inability to control the initiation

and rate of combustion, which is due to the fact that combustion is controlled by the chemical kinetics of the fuel-air mixture.

To tackle these technical difficulties several different approaches have been studied to make HCCI a practical combustion mode. Efforts are still being made to develop a practical and feasible way to address HCCI problems and some strategies are discussed on the next sections.^[11,16,23,26,31]

2.2.2 Compression Ratio

Experimental research done in HCCI combustion is often performed in experimental engines with variable compression ratio (VCR), several studies show that almost any liquid fuel can be used in a HCCI engine using this type of strategy.

On the work done by Christensen et al, it is shown that operation with pure n-heptane required a compression ratio of about 11:1 to get auto-ignition at TDC, without the use of inlet air preheating. Under the same conditions, iso-octane required 21.5:1. It was found that the increase in compression ratio did not impact negatively on the formation of NO_x formation.

However, the indicated efficiency did not improve with increased compression ratio as expected. This parameter was studied by looking at the composition of the exhaust gases. More concentration in the exhaust gases of CO and UHN would translate in lower combustion efficiency.^[33]

Some initial work done in HCCI combustion showed that lower compression ratios were more suited for this kind of combustion concept. High CR offer the potential to enable HCCI at low loads at the expense of decreasing the higher load limit, due to excess pressure and heat release rates being created inside the cylinder, which ultimately lead to engine knock. A higher CR could be the solution to tackle the problem of the high initial temperatures required, but generally research has gone in the direction of choosing the CR that allows better efficiency at upper limits.^[16,32,33]

An engine capable of dynamically change its CR during cycles could offer good potential in terms of extending the HCCI operation limits. On lower load regions an engine like this would operate with high CR while when approaching higher load limits the CR would be decreased to prevent unwanted spontaneous detonations.

As pointed by some researchers, it is possible to run HCCI mode during a complete drive cycle with this type of control. However for driveability reasons (and power requirements, during specific situations) switching from HCCI mode to conventional SI will be desired/required.^[32]

The transitions between this two very different combustion modes present new challenges such as moving from a highly diluted environment to stoichiometric conditions. These transitions can be facilitated by adjusting the CR.^[32,33]

2.2.3 Exhaust Gas Recirculation, EGR

As stated previously, one of the requirements of HCCI combustion to reach the auto-ignition temperature is a higher initial temperature of the fuel-air mixture. This can be achieved in several different ways; increasing the compression ratio, using auxiliary intake air heaters or more simply and effectively by using residual gases, which are hot from previous cycles. There are two different strategies to use residual gases.

External EGR, where recirculation is achieved by driving the exhaust gases from the exhaust manifold into the inlet manifold. A control valve (EGR valve) within the circuit is used to control the gas flow in such way so that the engine requirements are satisfied.

The most common strategy used, is by trapping the exhaust gases within the cylinder by not fully expelling them during the exhaust stroke. This is called internal EGR and it is achieved by changing the valve timing which is used to control the amount of residual gas. The exhaust valves close earlier and are totally shut before the intake valves open. This allows trapping exhaust residual gas in the cylinder on the latter stages of exhaust stroke with consequent compression and increase in temperature. As the piston subsequently descend on the induction stroke, the inlet valves open late, so that a fresh mixture of fuel and air is drawn into the cylinder that, has already been partially filled with the trapped residuals. The cold fresh charge mixes with the hot residual gases, and gains thermal energy. Shortly afterwards the intake valves close and the in-cylinder charge is compressed by the ascending piston, the auto-ignition of the fuel/air mixture and the subsequent combustion around TDC occurs.^[34-38]

It is then possible to conclude that the use of EGR on HCCI combustion has the potential to extend its operation envelope. The burned exhaust gases from previous cycles will help raise the initial temperature of the charge which may help enabling auto-ignition conditions.

Work done by Cairns and Blaxill showed that by employing external exhaust gas, there was a 20 to 65% increase in the engine load. This increased

efficiency is due to the reduced rate of heat release, with consequences such as prolonging combustion and extending the knock limit, especially at higher pressures. By external gas, these authors refer to the same exhaust gas but that is passed by an external circuit which has the effect of cooling down the gases.

On the work done by these authors a combination of the use of internal EGR with external EGR is studied. This combined EGR technique proved to bring several benefits. Besides the advantage just pointed, the hotter internal EGR can help on the lower load conditions, where raising the air-fuel charge is essential to achieve auto-ignition. Another benefit of it is when the engine is transitioning from HCCI to SI conditions, as this transition seems to be smoother.^[36]

One other requirement of HCCI combustion is the need to use lean diluted mixtures. This demand is also attained with the use of EGR. The presence of residual gas increases the total thermal mass of the cylinder charge which results in increased heat capacity. This will lower the peak temperatures in the cylinder, slowing down combustion at high loads (avoiding knock) and consequently reducing the amount of NO_x that is produced (NO_x production is highly dependent on the temperature).^[27,36-39] This strategy for NO_x emissions abatement is nowadays of common use in diesel engines. It is worth to refer that HCCI combustion is governed by three important temperatures. There is the auto-ignition temperature (low temperature hydrocarbon oxidation), below 950 K. The temperature should then increase to at least 1500 K to allow good combustion efficiency (high temperature hydrocarbon oxidation), but it should not be increased to more than 1800 K to prevent NO_x formation.^[11,16,36]

2.2.4 Forced Induction

The use of forced induction by means of superchargers or turbochargers has also been studied as another control method for HCCI engines.

Forced induction brings not only the advantage of increasing the power density of HCCI engines (which is generally low), but also the control on the amount of EGR and engine load achieved.

Turbochargers or superchargers will increase mixture density and temperature; on the other hand the use of intercoolers will decrease mixture temperature. Since forced induction technology is familiar to manufacturers and it is not expensive to implement it is regarded as one extra promising control method for HCCI.

Due to the high levels of EGR and consequently lean mixtures that are used on HCCI combustion, the power density coming from this concept is low. To compensate the charge dilution effect, one of the methods used to recover some of the power is to introduce more air into the engine allowing also more fuel while maintaining overall diluted mixtures. Forced induction is an effective solution to introduce the extra amount of air into the engine to increase power.

The work performed by Wyszynski et al, proves that NO_x emissions are reduced considerably in the case of supercharged HCCI. The use of excess air which provides more thermal ballast without the regions of high temperature, reduces the NO_x production (highly temperature dependent). Besides the fact of reducing NO_x emissions formation, the excess air helps reducing the high temperature regions and consequently has a positive effect on decreasing knock occurrence.

Lower combustion temperatures are preferable as they allow for heat release without reaching the NO_x-critical temperature. Summarizing the studies completed by this author it is possible to state that boosting the engine and providing excess cold air to the combustion chamber, NO_x formation is decreased and the knock limits are improved.^[40]

There is published work where the exhaust gases were either recycled or rejected and the temperature of the mixture was increased or decreased as needed with the help of the supercharger and intercooler. This method has been shown to be effective in raising the usable HCCI operation load without any inlet heating required.

The limits of the load range obtained were the maximum boost pressure and unstable combustion. At the maximum allowed boost pressure for the system used, the indicated mean effective pressure (IMEP) was approximately 75% of the total engine load possible in this same engine running in SI configuration. This represents a substantial increase over the engine load range for naturally aspirated HCCI combustion with residual gas trapping.

Also, it was found that NO_x emissions can be low due to the advanced exhaust valve timings and high boost pressures. This will increase the charge dilution by exhaust residuals creating the necessary buffer in the combustion chamber that does not allow combustion peak temperatures to be too high.

On the other hand, NO_x emissions can be relatively high when there is a smaller percentage of trapped residuals coupled with low boost pressures, resulting in minimal amounts of dilution.^[41]

Summarizing the work described in this particular section, it is fair to say that results show that HCCI operation was successful with good efficiency and low NO_x emissions under a wide range of conditions. Boosted HCCI combustion has been shown to have largely extended the upper load ranges as compared to naturally aspirated HCCI, while providing more power density from this type of engines.^[40-42,88]

2.2.5 Turbulence

The auto-ignition timing is crucial to HCCI operation, and it is a function of complex chemistry, temperature, pressure and turbulence of the mixture fuel/air/residuals.^[34,43,44]

It is reported in several papers that turbulence and mixing are important factors in HCCI combustion and they have an indirect effect on the auto-ignition timing by altering the temperature distribution within the cylinder, boundary layer thickness, heat losses and the charge homogeneity. Small temperature differences in the cylinder may have a considerable effect on combustion, since chemical kinetics are very sensitive to temperature, therefore turbulence indirectly determines the speed of combustion.

It is however, accepted that once auto-ignition occurs, turbulence plays a minor role on combustion. After the ignition event, combustion propagate from the initial ignition points as a pressure wave across the combustion chamber, without a flame front.^[44-46]

Christensen et al in 2002 used two different pistons tops to study the influence of turbulence in HCCI combustion. A low turbulence flat-top piston and a high turbulence square-bowl piston were used. Several parameters were possible to be studied and compared by varying the levels of turbulence inside the combustion chamber with the two piston designs.

It was observed that with the flat-top piston (low turbulence inducer) the heat release rate was much higher than the one obtained with the square bowl-piston.

With such increased in the heat release ratio, it was expected that the NO_x formation and emission would be substantially higher for this case, however the results obtained in the work performed only showed a slightly increase in this emissions.

It is worth to highlight that with late combustion timing, less than 1 ppm of NO_x were generated in all cases.

Regarding HC and CO emissions, their formation was more sensitive to combustion timing with the high turbulence combustion.

The square bowl piston (high turbulence inducer), produced longer combustion duration than the low turbulence piston. In some cases this duration was almost twice as long. Also by using this piston, it was verified that the inlet air temperature required to achieve auto-ignition conditions (and the same combustion phasing) was lower than when using the low turbulence flat-top piston. This effect is seen probably due to the higher wall temperature and higher residual gas fraction.^[89]

It is possible to say that combustion chamber design, by increasing turbulence and with that allow different mixture formation, can be used as a tool for indirectly increase and allow better control the HCCI load range and start of combustion.

This method offers another control mechanism over HCCI combustion.

Summarizing some of the trends seen, higher turbulence promote a broader temperature distribution, which enhanced heat transfer with the result of longer burn duration, which in turn is reflected in a lower heat release rate. In some cases the combustion duration for the high turbulence piston was twice as long as when low turbulence piston was used, making the use of high turbulence systems more desired.^[44,45,90]

2.2.6 Fuel Injection and Spark Ignition

One of the simplest ways to control HCCI combustion after IVC is by adding fuel, or providing additional energy to trigger ignition (spark).

Fuel injection offer the advantage of having the fast response that is demanded in an engine and also has the potential effect of suppressing knock (cooling effects), expanding the load range.^[34] This strategy offers a promising way to help controlling HCCI combustion.

The work of Wang et al in 2005 is one of many that used gasoline direct injection as a strategy to control HCCI combustion. In his work he shows that this technique can be used to control ignition timing and also the burn duration. Fuel injection offers the possibility of stabilizing HCCI combustion together with the potential of extending the higher load range by suppressing knock.^[47]

With the use of retarded start of injection (SOI) which therefore increases the fuel stratification, HC emissions were found to decrease, indicating improvement in combustion efficiency. The formation of NO_x emissions increased however at late SOI, indicating that local combustion temperatures were consequently increased. Due to fuel impingement the formation of soot also increased which was indicated by carbon deposit on the piston surface. The emissions formation of CO, generally remained constant. It was observed that with increased fuel stratification the variation in maximum peak pressure was three times larger than with homogeneous mixture.^[48]

Several other studies performed so far, show that by using direct injection in HCCI combustion and consequently increasing charge stratification has the potential to improve combustion at the lower lean limits making it more stable. Generally, it has been observed that stratified operation generates faster heat release rates (HRR) and decreases the burn duration time. Consequently this operation is knock limited and creates more NO_x emissions which is consistent with the higher HRR achieved. One way of tackling this drawback us by using split-injections which are proven method to reduce HRR and increase the combustion stability.^[48,49,50]

Using spark-ignition in HCCI combustion offers an improvement in the operating range and some control over the start of ignition. The spark provide an energy input to help raising the temperature and pressure in order to trigger the main ignition event that occurs under HCCI conditions. This control method has been tried by several researchers with different degrees of success. Overall the operating range is increased, since it is possible to reach lower loads with the additional energy supplied. Also, for the same combustion phasing, compression ratio and inlet air temperature can be decreased with spark assistance.^[32]

One of the difficulties of using spark-ignition within HCCI conditions is to develop a flame (from the spark) under such lean conditions. The weak flame developed can also introduce higher cyclic variability which will be reflected in combustion variability, with a penalty in emissions formations (HC and CO) and also potential driveability, noise, vibration and harshness issues .^[51,52]

Beyond the fact that the use of spark-ignition can help starting an HCCI engine, it can also assist in transitions from conventional combustion to HCCI combustion.

This is of particular relevance, as it has been pointed in several studies that Homogeneous Charge Compression Ignition is more likely to be used in a hybrid engine.

The work done by Hyvönen et al in 2005, focus precisely on this point. It was shown on his work that spark assistance is an effective method to control the combustion phasing during a mode transfer between HCCI and SI combustion. The challenges associated with this transitions are the large combustion fluctuations in the intermediate regions where some cycles have both spark ignited flame propagation and auto-ignition and other cycles have only partially burnt flame propagation.

The partially burnt cycles produce much more unburned hydrocarbon emissions, whereas the auto-ignited cycles have high audible noise due to the decreasing amount of dilution in the intermediate combustion region.

Close loop controls of several parameters are needed to make a smooth and fast combustion mode transfer possible. Also the intermediate combustion cycles have to be minimized to a minimum possible to ensure a smoother combustion mode transfer.^[32]

2.2.7 Hybrid Engines

As showed in several studies, HCCI combustion has a narrow operating limit. Misfire prevents HCCI combustion being used at low load conditions, while knock resulting from very rapid heat releases limits the maximum load that HCCI combustion can operate. To address this problem, it has been suggested using a hybrid engine that operates on HCCI whenever possible while it changes to SI or CI combustion when the operating conditions fall outside the HCCI operation envelope.^[34,53,54]

To switch from HCCI to SI, the engine must move from highly diluted hot auto-ignition conditions, to stoichiometric cold spark ignition conditions with flame propagation. Worth to highlight that, theoretically, HCCI peak temperatures are lower than in SI engines although pre-ignition (or auto-ignition) temperatures need to be hotter for HCCI combustion so that auto-ignition conditions are met. These factors make the transitions from one combustion mode to the other even more difficult.

During the intermediate combustion region, the exhaust emissions of UHC and NO_x tend to be high due to partial burn and the decrease in the amount of dilution, respectively. Some combustion cycles will show auto-ignition and others partial flame propagation. The auto-ignited cycles produce high noise due to the decreasing amount of dilution with residuals in the intermediate combustion region. The intermediate combustion cycles have to be minimized in a combustion mode transfer.^[32,33,48,52]

These cycles during a mode transfer will have mixed combustion with both flame propagation and auto ignited HCCI behavior.

During the mixed combustion region, the in-cylinder conditions will not cause auto-ignition, so a temperature and pressure increase will be needed. Flame propagation alone is not sufficient (the lean in-cylinder conditions will most probably cause flame quenching and partial burned cycles). Hence, a combination of spark initiated flame propagation and auto-ignited HCCI combustion is needed.

The drawback with spark ignition of lean mixtures is, as discussed before, the cycle-to-cycle variability. Also there is a narrow time window to apply the spark so efficient combustion can be initiated.

If the spark ignition is too early, cycle-to cycle variation in flame kernel development increases. If the spark ignition is excessively late, temperature and pressure in the cylinder never reach auto-ignition conditions. The combustion stability can also be improved in spray guided gasoline direct injection HCCI engines with split injection and a stratified charge around the spark plug. With a proper control of the spark ignition flame kernel initiation, fast compression ratio and throttle control, a mode transfer is feasible for air diluted high compression ratio HCCI concepts. Higher HC and CO emissions can be avoided in the mixed combustion cycles if partial burnt.^[32,38]

This is a complicated transient process which involves crossing a boundary after which the combustion events are significantly different at each side. Yet, this difference must not be translated into engine power output. Variable valve timing to allow transitions between the two combustion modes has been studied, however this approach on its own leads to an increase in the airflow rate during the combustion mode which may cause torque perturbations, generally affecting the smoothness of the engine operation.

An accurate prediction of engine conditions would be necessary, so auto-ignition timing and burning rate can be controlled. These characteristics are affected by several conditions and engine parameters, making a precise and fast combustion control necessary to change different engine parameters like, fuel injection strategy, spark ignition timing, valve timing, EGR control, compression ratio, forced induction, etc, accordingly.^[54,55]

Work done in Tsinghua University using a direct injection gasoline engine, showed smooth and reliable transition from HCCI combustion to SI operation. This was achieved with a two stage cam system and with the help of direct injection which offers fuel injection flexibility. Although the transition was fast and reliable there were still some fluctuations when going from SI to HCCI mode. This has to do with the concepts behind SI and HCCI combustion.^[91]

2.2.8 Reformed Fuel

Reformed fuel can be obtained by using a fuel oxidation device. For example a plasmatron was the equipment used by Ivani and Ayala^[57] to produce reformed fuel. This type of device receives a fraction of the fuel that normally goes into the intake port and oxidizes it to a mixture containing H_2 , CO and N_2 and small amounts of H_2O and CO_2 . This mixture will then be combined with the regular air-fuel charge to form a homogeneous mixture before combustion.

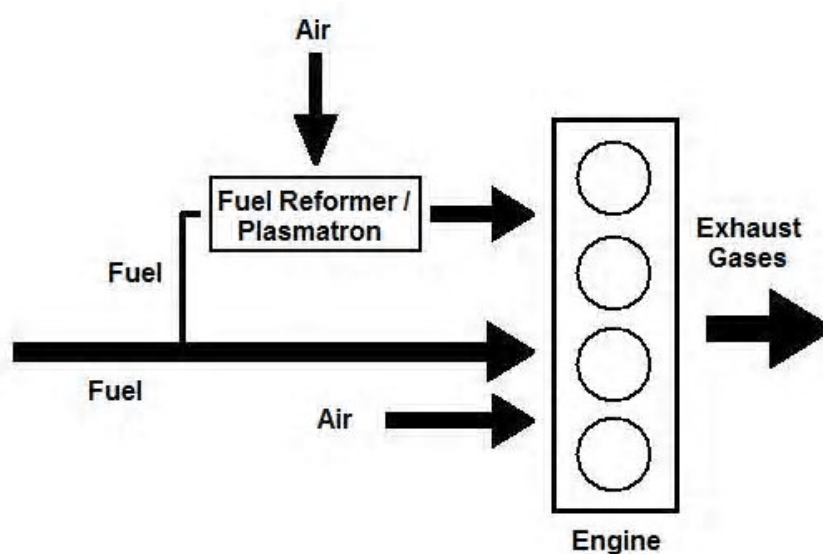


Figure 2.2 – Plasmatron engine concept.^[57]

This concept has some disadvantages such as, demand for extra electrical power (required to oxidize the fuel-air mixture), fuel conversion efficiency, and of course the complexity added to the engine, which involves a larger cost for the consumer.^[57]

The use of reformed fuel can extend the operational range of an HCCI engine, both increasing the high limits of operation (that is dominated by knock) and also by extending the lean limits (limited by misfire). This increased operational envelope will translate into reduction of fuel consumption and increase in engine efficiency.

Tully and Heywood showed in their work that the addition of reformed fuel had a beneficial effect on combustion than for example, the addition of H_2 on its own. The CO in the reformed fuel (originated by the plasmatron) is capable of diluting

the air-fuel charge bringing direct benefits to combustion, such as increased efficiency, improved emission results and better combustion stability.^[56]

There are other alternatives to the plasmatron, like internal fuel reforming. This is accomplished by manipulating the valve timing to create an NVO (which retain products from previous cycles) and by injecting fuel into these trapped exhaust gas residuals.

The mixture will then undergo compression and reformation during the exhaust stroke when the EV is already close. This approach will create species and radicals inside the cylinder that are combustion facilitators, since they are very reactive.

It has been seen, that fuel injection during the negative valve overlap interval, with the purpose of reforming the fuel and improving ignitability, was found to expand the lean limit of HCCI combustion substantially without any increase in NO_x emissions like that observed when the lean limit was expanded by forming a stratified charge mixture.

The lean limit of HCCI combustion can be further expanded when a portion of the fuel is injected in the NVO interval, while the remaining quantity is injected during the intake stroke. This, in comparison with the result achieved when injection of all the fuel occurred in the overlap interval.

This split fuel injection strategy brought as well the advantage of decreasing total fuel consumption.^[61]

Combustion enhancement via H₂ addition has been proved before and when associated to an HCCI engine has the potential to extend the HCCI operational limits, reducing NO_x emissions due to the lower peak temperatures achieved and improving engine efficiency.

The presence of H₂ will help, for a given temperature, to achieve lower loads, which translates into an extension of the HCCI lower load boundary. This is due to the specific properties of hydrogen, which is a highly flammable gas with capability to rapidly ignite in extremely lean conditions. Another important property of H₂ is its high knock resistance, which make it an optimal additive to HCCI engines, increasing its high load boundary for operation.^[58-61]

By using reformed fuel, HCCI combustion can be achieved with less pre-heating of intake air. It also allows the increase of EGR concentration in the cylinder (decreasing peak temperatures) with advantages in the formation of NO_x, without compromising engine performance.^[59,60]

The use of such technology is an additional/alternative method to control the onset of combustion in an HCCI engine. Study made by Hosseini and Checkel, showed that the use of reformed gas can be an effective and fast method to change ignition timing for HCCI applications.^[92]

2.2.9 Different Fuels

One important characteristic of HCCI engines is their fuel flexibility. This is of special interest, not only from the control point of view but also because of environmental considerations.

Several studies have been performed with different fuels, from conventional gasoline and diesel, to natural gas, methanol, ethanol, biodiesel, hydrogen, dimethyl ether (DME) and also their mixtures.

Some of the early enthusiasm for this variety of fuels disappeared as the research increased and their limitations started to be exposed.

The oxygenated fuels, methanol and ethanol can be produced from renewable raw materials and help reducing the fossil fuels dependency. As a setback, the fuel supply system of a conventional engine needs changing.

Natural gas, in which methane is its main constituent, has a high auto-ignition temperature requiring high compression ratios and/or intake charge heating to achieve HCCI operating conditions.

When hydrogen is used as main fuel, theoretically at least, its combustion can result in zero emissions. However, it requires substantial intake heating and its rate of combustion is too rapid to be effectively controlled. Besides that, there are other relevant issues to be considered regarding demand, production, storage and safety.

Because of properties such as low auto-ignition temperature and potential for smokeless emissions, DME was regarded as an attractive diesel alternative for HCCI engines. However its low viscosity causes poor lubrication which results in leakages and early abrasion wear. Currently it is only being used as an additive to improve ignition on difficult fuels to auto-ignite.^[62]

With increasing demand for renewable fuels, there has been increased interest in bio-ethanol as a replacement fuel for gasoline, since it can offer substantial reduction in the consumption of fossil fuels and in the total emission of greenhouse gases.

Due to the high octane number of bio-ethanol, exhaust gas trapping is a requirement to achieve auto-ignition temperatures at moderate compression

ratios and with low requirements of external charge heating. HCCI has been achieved in bio-ethanol fuelled engines and when compared to gasoline, allows leaner mixtures to be ignited and can also extend the operating range to higher speeds.^[93]

The load range can be controlled by the degree of internal trapping of exhaust gas, supplemented by moderate intake charge heating.^[63-65,94]

Regarding the use of more conventional fuels such as gasoline or diesel, several publications have been released using them and they continue to be by far the type of fuel where more research has been put into.

However, many researchers have been using reference fuels such as iso-octane (octane number 100) and heptane (octane number 0), instead of using the regular available fuel at the pumps, which are constituted by a big array of different and complex molecules. On the work done by Christensen et al, different mixes of the reference fuels were used. By mixing them, any octane number between 0 and 100 can be achieved. Also, different mixture ratios of gasoline and diesel fuel were tested.

It has been seen that the combustion duration decreases with increased fuel octane number as the overall combustion temperature becomes higher. The high octane number means implies higher auto-ignition temperature, which gives a higher overall combustion temperature.^[33]

As pointed before, gasoline and diesel are two fuels with very different characteristics. With their wide availability they were blended as a HCCI engine fuel. Some experimental results show that better combustion stability is obtained when gasoline/diesel blended fuel is used instead of gasoline-fuelled HCCI. As pointed in other studies the use of this mixture reduces the audible knocking limit and increases the HCCI operation envelope. It is possible to say that diesel fuel has remarkable influence on gasoline HCCI combustion. Ignition timing is advanced, the combustion duration is shortened and the IMEP range achievable in the unheated NVO mode is widened as diesel content increases. Exhaust emissions, especially HC and NO_x, show a large improvement compared with gasoline HCCI.^[62]

2.2.10 Summary

HCCI is a state of the art engine technology that has the potential to overcome the current fundamental NO_x and particulate emissions of CI engines maintaining its efficiency and fuel economy.

Although HCCI proves to have good characteristics regarding emission levels and efficiency, there are some drawbacks using this concept. There is the inability to control the initiation and rate of combustion over the required speed and load range of engine, and due to very rapid energy release during combustion, HCCI is restricted to very lean mixtures, resulting in low power density. Also the formation of carbon monoxide (CO) and unburned hydrocarbons (UHC) tend to be rather high.

These factors, presently, are limiting the commercialization of the HCCI concept, and many of these issues are associated with the fact that HCCI combustion is mainly chemically controlled.

2.3 Emission Formation

Exhaust emissions consist mainly of direct combustion products, such as water and carbon dioxide, and pollutants such as CO, UHC, soot and NO_x (which refers to the combination of NO and NO₂).

In appendix 2, information can be found on current technologies used to abate the exhaust emissions from ICE, either SI or CI engines.

Figure 2.3 gives a general summary of the formation mechanisms for some pollutants.

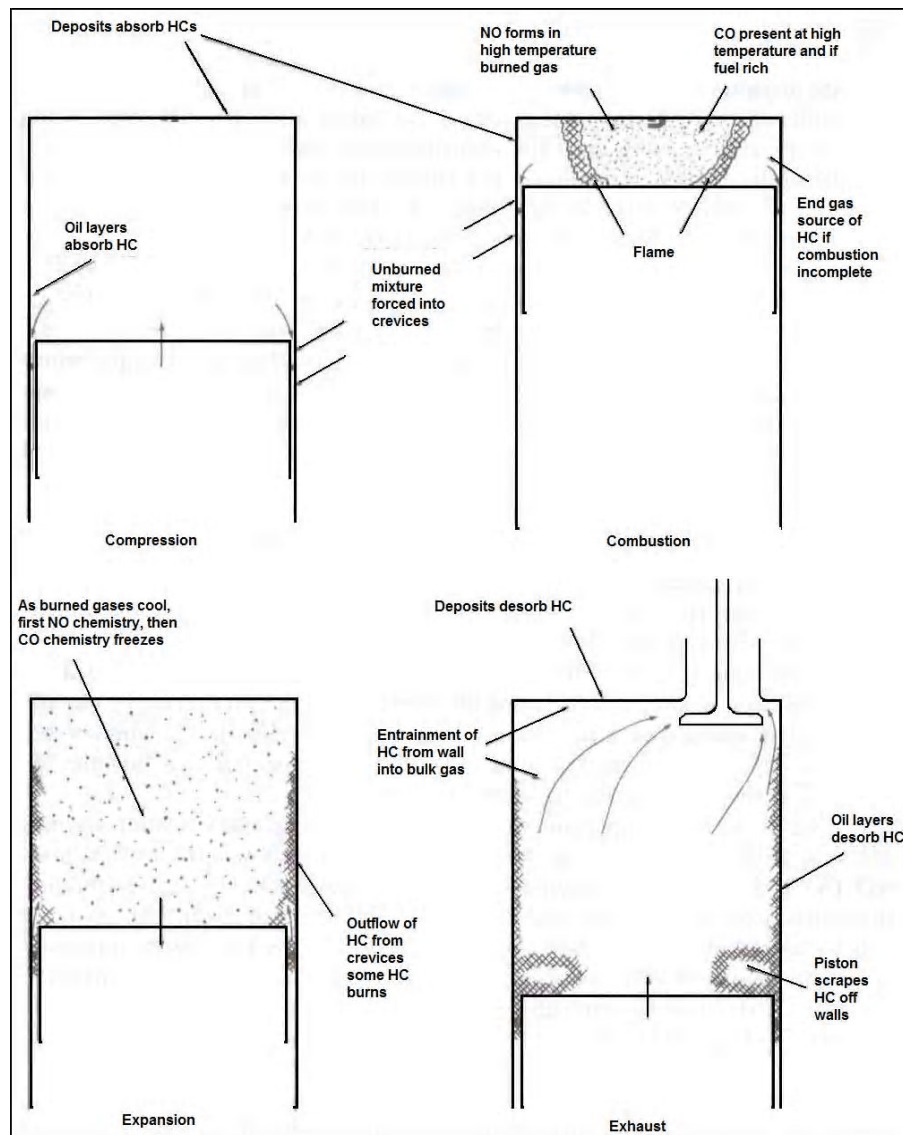
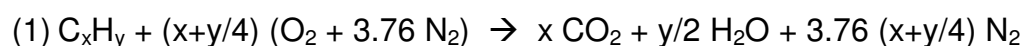


Figure 2.3: Summary of HC, CO and NO pollutant formation mechanisms in a spark-ignition engine.^[7]

2.3.1 Carbon Dioxide formation

Carbon dioxide is a product of hydrocarbon combustion and it is directly proportional to the amount of fuel consumed. Therefore the only way to reduce CO₂ emission is by reducing fuel consumption.

As seen in chapter 1, the theoretical stoichiometric combustion equation is,



From here it is possible to see the relationship between carbon monoxide formed and carbon content on the initial fuel molecule.

An increase in the fuel quantity will increase the amount of carbon atoms available in the combustion chamber and consequently that implies their conversion into CO₂.

2.3.2 Carbon Monoxide and Unburned Hydrocarbons formation

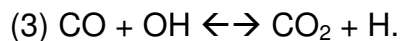
The CO and UHC pollutants are a consequence of incomplete combustion.

With rich air-fuel mixtures there is not enough oxygen to ensure oxidation of the carbon in the fuel to CO₂, also the carbon monoxide oxidation also freeze with the drop in temperature during the expansion stroke.

To improve driveability during cold starts, the fuel flow is increased to compensate for slow fuel vaporization. However, this strategy leads to an increase in CO emissions as well as UHC. The CO formation can be summarized in the following reaction



where R is the hydrocarbon radical. The carbon monoxide formed is then oxidized to carbon dioxide at a slower rate via the principal oxidation reaction,



There are several ways leading into the formation of unburned hydrocarbons.

Due to the increasing cylinder pressure forces during the compression stroke part of the air-fuel mixture is trapped into the crevices, this mixture will not be exposed to the high temperatures and it will remain unburned. These unburned gases will then leave the crevices during exhaust stroke. Other sources of formation of UHC are the cold cylinder walls that lead to flame termination before the completion of the oxidation reactions. Engine oil left in thin films on the cylinder wall and piston can absorb and desorb hydrocarbons before and after combustion, contributing as well to the formation of UHC.

2.3.3 Soot formation

Soot consists of agglomerates with a diameter of up to several hundred nanometers which have a fine structure of spherical primary particles. Soot formation starts with the pyrolysis of fuel molecules and the formation of polycyclic aromatic hydrocarbons (PAH). The most important precursor of the formation of higher hydrocarbons is acetylene (C_2H_2). Finally a rearrangement produces spherical primary particles which continue growing at their surface.

It is generally accepted that the formation of soot consists of four steps; nucleation, surface growth, agglomeration (and also oxidation) and adsorption (and condensation).

Soot or carbon particulates formation takes place in the rich part of the mixture within the flame zone. These particulates are formed in the diesel combustion environment at temperatures between 1000K and 2800K, at pressures of 50 to 100 atm. The formation process starts with a fuel molecule containing 12 to 22 carbon atoms and ends up with particles containing around 10^5 carbon atoms.

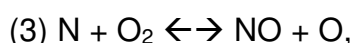
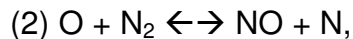
2.3.4 Nitrogen Oxides formation

The formation of NO_x is a complex process that involves the reactive combination of nitrogen found within the combustion air and organically bound nitrogen within the fuel itself. NO_x is a thermally produced gas and therefore its formation is largely dependent on the control of the combustion temperature.

There are many other mechanisms from which NO_x can be produced, but thermal and prompt NO are the more relevant in the internal combustion engines application.^[66-69]

Thermal NO

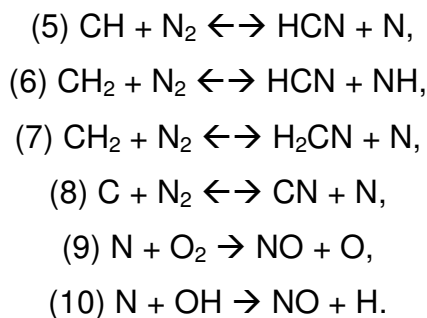
In the combustion of clean fuels (fuels not containing nitrogen compounds), oxidation of atmospheric nitrogen by the thermal mechanism is a major source of NO_x emissions. The three principal reactions that comprise the thermal NO formation mechanism are,



The first two reactions compose a chain sequence in which a small amount of atomic oxygen can produce large amounts of NO. This mechanism, often called the Zeldovich mechanism, is very sensitive to temperature not only because the high activation energy of the first reaction, but also because the concentration of oxygen atoms in flames increases rapidly with increasing temperature.^[66-69]

Prompt NO

Nitric oxide formation rates in combustion of hydrocarbon fuels can exceed those attributable to the thermal mechanism discussed above, especially for fuel-rich conditions. This rapidly formed NO was termed prompt NO, since it's rapid and is confined to regions near the flame zone.



It has been shown that, prompt NO in hydrocarbon flames is formed primarily by a reaction sequence of hydrocarbon radicals with molecular nitrogen, leading to formation of amines or cyano compounds that subsequently react to form NO. Numerous studies showed that CH and CH₂ are the hydrocarbon radicals that most contribute to the formation of prompt NO.^[66-69]

In HCCI, combustion occurs through chemical oxidation, thus, the reached maximum temperature is determined by the energy content of the fuel/air/residuals mixture, giving lower maximum temperatures than comparable with SI or CI.

While the Zeldovich mechanism (thermal NO) is adequate for calculating NO_x emissions in SI or CI engines, it is safe to say that it doesn't accurately predict these emissions on HCCI combustion. Studies on lean combustors showed that NO_x is largely formed through N₂O paths. It appears believable that N₂O reaction pathways would play an important role for NO_x formation also for HCCI engines.^[66-69]

CHAPTER 3

LITERATURE REVIEW

Chapter 3 gives an explanation of the theoretical background of the oxidation chemistry of fuels and additives such as NO that are behind HCCI auto-ignition and combustion. This subject is of great relevance since this is one of the key factors to control HCCI.

The chapter ends with a brief review on computational work models used to study HCCI combustion, where, different approaches as single zone and multi zone HCCI modelling are explained.

3.1 Chemical Kinetics for the HCCI Combustion Process

In HCCI engines, fuel oxidation chemistry determines the auto-ignition timing, the heat release, the reaction intermediates, and the ultimate products of combustion.

There are many critical issues to be addressed with HCCI engines and many of these issues are associated with the fact that combustion is mainly chemically controlled.^[43]

Due to auto-ignition of a homogeneous mixture, no flame propagation is present and instead the whole bulk will begin to oxidize almost simultaneously. It is commonly accepted that the onset of combustion is controlled by the chemical kinetics. As the mixture is compressed the temperature and pressure increase. Temperature and pressure history, together with the concentration of O₂, different fuel contents and combustion products, govern how combustion is initiated. As a consequence the auto-ignition timing will be influenced by equivalence ratio, inlet temperature, compression ratio, residual gases and EGR.

The most significant challenge of HCCI combustion is using the available mechanical measures (fuel injection timing, valve events, etc.) to control both the auto-ignition timing and the combustion duration.^[69-71]

The energy release rate from HCCI combustion depends not only, on the unique reaction chemistry of the fuel, but also on the thermal conditions that the mixture goes through, during compression.^[72,73]

In order to be able to control the ignition and overall combustion rate of HCCI combustion it is important to have an understanding of the interaction between the chemical kinetics of the fuel/air/residual gas mixture, and the temperature-pressure history of the cylinder, during the compression process.

The oxidation mechanisms of hydrocarbon fuels change substantially, over the ranges of pressure and temperature encountered in an HCCI engine. There are three fundamental “regimes” of hydrocarbon oxidation chemistry.

In the low-temperature regime, the reaction rate increases with increasing temperature and the dominant reactions are oxygen addition to form alkylperoxy radicals and olefins, followed by radical isomerisation and decomposition.

As the temperature is increased further the alkylperoxy radicals decompose back into initial reagents, the production of olefins and hydroperoxy radical is favoured, and the overall reaction rate decreases with increasing temperature. This is the classical negative temperature coefficient (NTC) behaviour observed in low-temperature oxidation of paraffinic fuels.

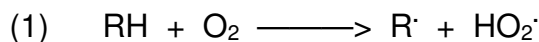
As the temperature is further increased, the reaction rate increases, as more olefinic hydrocarbons and hydrogen peroxide are produced. Eventually, the temperature is increased high enough so that hydrogen-oxygen branching reactions control the reaction rate in high-temperature regime.^[30,70]

The oxidation of the fuel plays an important role in HCCI combustion, and it depends of different factors, as pointed before.

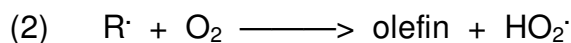
A crucial factor influencing the oxidation of the fuel is the composition of itself. An average gasoline is composed of roughly 60 % paraffins (single C – C bond), 10 % olefins (double C = C bond), and 30 % aromatics (benzene ring).^[30]

3.1.1 Low-Temperature Paraffin Oxidation

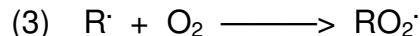
The first step is the abstraction of a hydrogen atom by oxygen, to form an alkyl radical ($R\cdot$) and a hydroperoxy radical ($HO_2\cdot$).



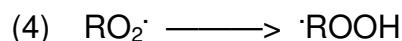
The hydrogen abstraction results in a variety of alkyl radicals. The fate of these radicals governs the subsequent chemical pathways. One important pathway is abstraction of another hydrogen atom by oxygen to form a conjugate olefin and a hydroperoxy radical.



Alternatively, rather than abstracting a hydrogen atom, in a second pathway the oxygen adds to the radical to form an alkylperoxy radical ($RO_2\cdot$).



The $RO_2\cdot$ radical undergoes internal isomerisation, the oxygen abstracts a hydrogen atom from a C-H bond elsewhere within the molecule, to form a hydroperoxyalkyl radical ($\cdot ROOH$).

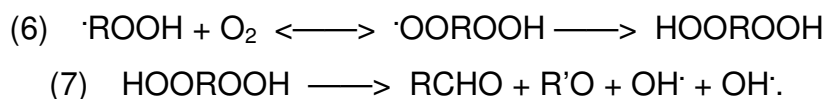


The $\cdot ROOH$ radical is consumed through two basic routes. In the first path an $OH\cdot$ radical is produced when the hydroperoxyalkyl radical either spontaneously decomposes into a lower molecular weight alkene, or forms cyclic ether and an $OH\cdot$ radical.



In the second path, the $\cdot ROOH$ radical undergoes a second oxygen addition to form a hydroperoxyalkylperoxyl radical ($\cdot OOROOH$), followed an internal H atom abstraction to produce an alkylhydroperoxide ($HOOROOH$). The

alkylhydroperoxide then decomposes into an aldehyde (RCHO) and two OH radicals

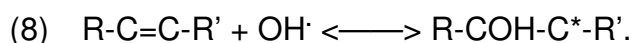


The production of the alkylperoxy radicals (reaction 3) is faster than olefin formation (reaction 2) at all temperatures. However, as the temperature is increased above 500 K at atmospheric pressure (700 K at 10 atmospheres pressure) the reverse of reaction 3 is favoured, and olefin production increases. The fuel consumption rate decreases as the rate of olefin formation increases. It is the competition between reaction 2 and 3 that defines the transition between the low- and intermediate-temperature regimes.^[16,30,70]

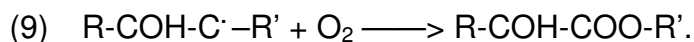
3.1.2 Low-Temperature Olefin Oxidation

Paraffin auto-ignition chemistry inherently involves olefin oxidation chemistry.

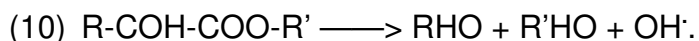
The first step in low-temperature olefin oxidation, involves the reaction of radical $\text{OH}\cdot$ with the parent fuel. This radical adds to the double bond to yield a hydroxyl group on one of the carbon atoms at the former double bond site and a free-valence electron at the other carbon atom



The resulting radical is highly energetic making the reverse reaction very important. There are two possible reaction paths for the radical. One is, decomposing into a carbonyl and an alkyl radical. The other is that the radical becomes stabilized by collision with another molecule. After the radical is stabilized it can undergo oxygen addition at the radical site via,



This radical decomposes following the reaction,



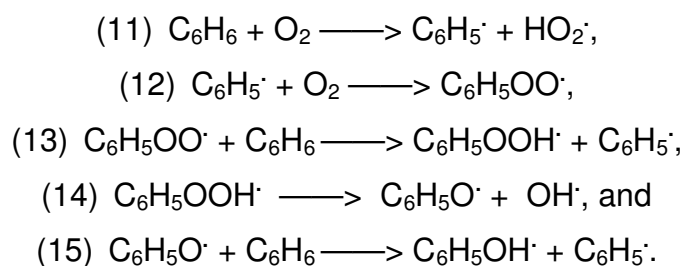
At the higher pressures experienced in engines, mechanism 9 dominates over unimolecular decomposition of the radical formed in reaction 8.

Larger olefinic molecules can also undergo “paraffinic” type reactions on the paraffinic portion of the molecules. These kind of reactions follow a similar pathway to reaction 2, and a diene (two $\text{C}=\text{C}$ bonds) species is formed.^[16,30,70]

3.1.3 Low-Temperature Aromatic Oxidation

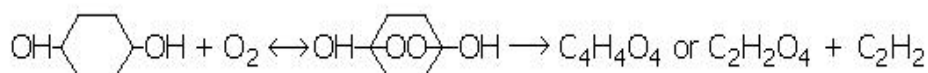
Aromatics have high octane ratings and are specifically blended into gasoline in order to increase the octane rating.

The low temperature oxidation of benzene takes place through a series of reactions analogous to those of paraffins, involving the formation of peroxy species.



Removal of an H atom from benzene by O_2 attack is slow. Additional reactions for the initiation step (reaction 11) are H atom abstraction by $\text{H}\cdot$, $\text{O}\cdot$ and $\text{OH}\cdot$ radicals. The $\text{C}_6\text{H}_5\text{OH}\cdot$ radical produced in reaction 15 reacts through the same sequence of reactions to produce $\cdot\text{HOC}_6\text{H}_4\text{OH}$. The addition of the two OH groups to the aromatic ring greatly reduces the ring stability.

(16)



After oxygen addition the ring ruptures to form maleic acid ($\text{C}_4\text{H}_4\text{O}_4$) or oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) and acetylene (C_2H_2). At low temperatures oxygen bridging is necessary to obtain ring rupture. At temperatures higher than 600 K the bridged benzyl peroxide becomes unstable and the reverse reaction is favoured. Thus the high-temperature oxidation of benzene proceeds through a different mechanism than reaction 16.

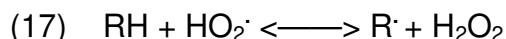
Aromatic compounds in fuel typically have large branched paraffinic (alkyl) side groups attached to the aromatic ring. Because the high stability of benzene, the first step in the oxidation of alkylated aromatics is an attack on the alkyl group. Thermal cleavage (homolysis) follows the initial H atom removal, and the

resulting alkyl radical reacts through a series of mechanisms that follow along the general lines for alkyl radical already discussed.

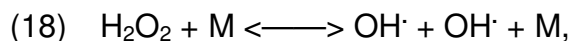
As a result, the low temperature oxidation of the higher carbon number alkyl benzenes exhibit NTC behaviour similar to that observed from the oxidation of the corresponding paraffinic species. ^[16,30,70]

3.1.4 Intermediate-Temperature Paraffin Oxidation

As the temperature is increased further into the intermediate-temperature regime reaction 2 produces more olefinic hydrocarbons and hydroperoxy radicals. Hydrogen peroxide (H_2O_2) production becomes significant by HO_2 radicals abstracting a hydrogen atom from the fuel,



As the temperature is increased there is a build up of hydrogen peroxide in the system that eventually decomposes and produces two hydroxyl radicals from each H_2O_2 molecule contributing to the increase of the overall reaction rate.



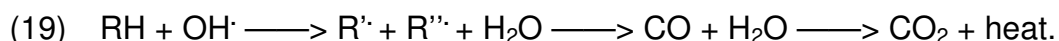
In the intermediate temperature regime, the $\text{HO}_2 \cdot$ radical replaces the $\text{RO}_2 \cdot$ radical of the low-temperature regime and H_2O_2 replaces HOOROOH as the degenerate branching agent.

At atmospheric pressures and temperatures higher than roughly 800 K the alkyl radicals are decomposed into smaller hydrocarbon radicals and olefins by C-C bond scission one bond away from the radical site.^[16,30,70]

3.1.5 High-Temperature Paraffin and Olefin Oxidation

The high temperature oxidation of hydrocarbons can be described as a sequential three-step process: (1) the parent fuel is converted to lower molecular weight hydrocarbons and water with little energy release, (2) the intermediate hydrocarbon species are converted to CO and water, and (3) CO is oxidized to CO₂ and the large fraction of the energy is released.

The reaction sequence can be conceptualized as,

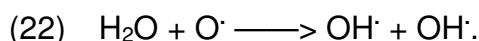
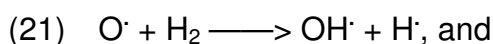
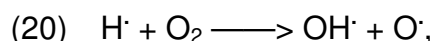


At the high-temperature regime (950 K at atmospheric pressure), the initiation reaction for paraffins is typically H atom abstraction by a radical. After the initial abstraction the alkyl radicals can decompose into smaller alkyl radicals and olefinic species. For olefins, the initiation reaction is the radical addition to the double bond, which is eventually followed by fragmentation at the double bond site. At temperatures well into the high-temperature regime, the initiation reaction can be unimolecular thermal decomposition of the parent fuel, or decomposition by collision with a third body.

Radicals continue to abstract H atoms from the intermediate hydrocarbon species and there is a cascading of the species, formaldehyde (CH₂O), formyl radicals ($\cdot\text{CHO}$) and CO. The final reaction in all hydrocarbon combustion systems is the oxidation of CO to CO₂. Because the radicals preferentially react with any hydrocarbons present in the mixture, CO oxidation is delayed until after the majority of the hydrocarbons are consumed.

The chain-carrying radicals in the high-temperature regime are OH \cdot , H \cdot and O \cdot .

The important chain-branching reactions in this regime are:

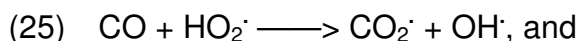
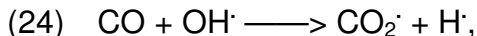


At the high pressures obtained in engines, radical recombination reactions are also important,



The hydroperoxy radical is relatively stable and is transported to the wall where it is destroyed (on the above reaction, M represents a third body). The transition between the intermediate and high-temperature kinetic regimes is generally defined as the condition where the branching reaction 20 dominates over the recombination reaction 23. At atmospheric pressure with nitrogen as the third body, the transition to high temperature kinetics occurs at roughly 950 K, while at 10 atmospheres pressure the transition does not occur until 1400 K.

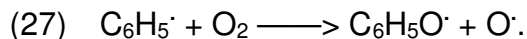
The final stage of the energy release at high temperature is CO oxidation, where a significant portion of the energy release (45 to 50 %) from hydrocarbon fuels is generated.



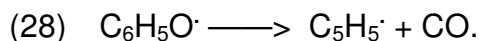
At high temperatures nearly all the CO is consumed by OH \cdot radicals via reaction 24 (CO oxidation is inhibited by the presence of hydrocarbons).^[16,30,70]

3.1.6 High-Temperature Aromatic Oxidation

The primary H atom removal will happen by direct radical attack, to produce a phenyl radical ($C_6H_5\cdot$),



The aromatic ring is fractured when the phenoxy radical ($C_6H_5O\cdot$) ejects a CO and produces a cyclopentadienyl radical ($C_5H_5\cdot$),



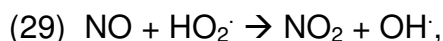
This mechanism for ring fracture explains the early presence of CO in aromatic combustion experiments. The cyclopentadienyl radical decompose through an analogous reaction pathway as the phenyl radical.

The high-temperature oxidation of alkylated aromatics can be reduced to the oxidation of the side chain, followed by oxidation of the phenyl radicals or benzene.^[16,30,70]

3.1.7 Influence of NO in Combustion

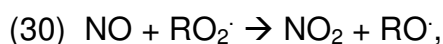
Recent studies in flow reactors have shown, that small concentrations of nitric oxide (NO) can change pre-ignition oxidation behaviour of alkenes and significantly enhance reactivity at intermediate temperatures promoting auto-ignition.

The increased reactivity of the fuel with the NO addition can be caused by the conversion of a radical $\text{HO}_2\cdot$ to a very reactive $\text{OH}\cdot$ radical,



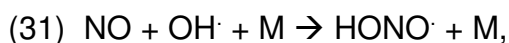
this reaction can be viewed as branching reaction since the formed $\text{OH}\cdot$ radicals will react mainly with fuel molecules, promoting auto-ignition.

Another set of important reactions are,



which can be viewed as an extension of reaction 29.

However when NO is present in higher concentrations there is a reduction in reactivity which might be explained by several termination reactions that take place and consume the reactive $\text{OH}\cdot$ radical.



The reaction 31 is in concurrence with reaction 29 and consumes hydroxyl radicals needed for the consumption of the fuel molecules.

At an inlet temperature of 673 K, up to 350 ppm NO enhanced reactivity whereas 400 ppm significantly reduced reactivity. Reaction 31 has been suggested as a possible reason for the decrease in reactivity. With 350 ppm of NO, 20 % of it is consumed via the chain breaking reaction (reaction 31). This percentage is increased to 40 % at 1400 ppm NO.

At higher temperatures all concentrations of NO seem to enhance combustion reactivity. In the absence of NO the reactivity at these temperatures can be very low.

At the higher NO concentrations the chain terminating path is consuming OH \cdot at a rate faster than is being produced via reaction 29 or from the baseline chemistry. The rate of reaction 29 is probably limited by the HO $_2\cdot$ concentrations produced as a result of the low temperature chemistry.

At higher temperatures the baseline chemistry itself produces a higher yield of HO $_2\cdot$ and, at higher NO concentrations it is possible that the reactivity is enhanced due to a higher rate of OH \cdot production by reaction 29.

Coupled to this is the fact that the rate constant of reaction 31 decreases with an increase in temperature, which would weaken the chain terminating pathway.^[74]

3.2 HCCI engine simulation

Engine simulation has demonstrated great benefits in the research and development phases of all modern engine technologies by improving the understanding of engine processes and providing guidelines for engine design. This has enabled the reduction of time and cost during engine development. Therefore, modelling studies of HCCI engines are highly desirable, either before or in parallel with an extensive experimental program.

HCCI engine modelling is a relatively new area and thus a complete code for HCCI combustion engine is not yet available.^[75]

Up to now, there are six categories of models applied to HCCI engine modelling. These six categories are listed in Table 2.1, along with their advantages, disadvantages and applications.

Table 3.1 – Comparison between different HCCI models.^[76]

HCCI model	Advantages	Disadvantages	Application Cases	Executing time (min)
0D single-zone with detailed chemistry	Lowest computational cost	HC and CO cannot be predicted	Ignition timing prediction. Fast parameter studies	< 10
Quasi-dimensional multi-zone with detailed chemistry	Temperature and concentration inhomogeneity considered	Initial conditions of each zone are necessary	HC, CO prediction. Heat release rate	< 10 ²
1D engine cycle with detailed chemistry in-cylinder	No initial conditions of cylinder specification. Parameter studies for engine performance	Fuel spray, flow and turbulence, mixture formation cannot be considered	Engine performance prediction. Optimize of gas exchange system and VVT strategies	< 10 ²
Multi-CFD with multi-zone detailed chemistry	Temperature and concentration inhomogeneity considered	Turbulence cannot be considered	HC, CO prediction. Heat release rate	< 10 ³
Multi-CFD with simplified chemistry	Fuel spray, flow and turbulence, mixture formation considered	Simplified combustion	Optimization of combustion system	< 10 ³
Multi-CFD with detailed chemistry	Detailed chemistry and fluid-dynamics, turbulence influence mixture formation and combustion rate considered	Highest computational cost	HC, CO, NO _x prediction. HCCI physicochemical process studies. Combustion optimization	10 ³ ~ 10 ⁵

Single-zone models are useful for parameter studies, by predicting trends in auto-ignition timing variations, as result of the effect of changing engine operating conditions. Quasi-dimensional multi-zone model with detailed chemistry has the capability in predicating UHC and CO emissions because the cylinder is divided into different zones, which provides more realistic distribution of the charge temperature and concentration inside the cylinder. 1D engine cycle model with detailed chemistry, is applied to simulate HCCI engine working process both in steady and transient operation, and is suitable to study the performance of HCCI engine. Multi-CFD model with multi-zone detailed chemistry is used for predicting emissions more accurately because inhomogeneities can be considered by using CFD as pre-processor. Considering turbulence, multi-CFD model with simplified chemistry is suitable for optimization of combustion systems in acceptable and practical engineering time. Finally, multi-CFD model coupled with detailed chemistry can be utilized to simulate the intake, two-stage spray, compression and combustion process of the HCCI engine.^[75,76]

3.2.1 Single Zone Chemical Kinetic Models

These models assume homogeneous distribution of temperature and species at the start of the calculations, being one of their big limitations the inability to account that the mixture inside the cylinder is not fully homogeneous due to limitations in mixing within the time slot available. This will reflect in the temperature distribution difference between the wall and hot gases, and also due to mixing of hot internal EGR.

They tend to over predict rate of heat release, pressure rise and can not account accurately for UHC, CO, CO₂ and NO_x emissions.

However they can reasonably predict the auto-ignition timing and the trends in pressure rise and heat release rate.

They are extensively used to compare experimental results with kinetic calculations, to improve and develop kinetic codes and to test the main effects of various engine parameters as speed, air-fuel ratio, EGR, on HCCI combustion.^[76,77]

3.2.2 Multi Zone Chemical Kinetic Models

Some of the limitations of single-zone HCCI models can be overcome, by performing multi-zone modelling instead. In this kind of models, the combustion chamber is divided into an arbitrary number of volumes. These do not have dimensions and so, the multi-zone models are therefore zero-dimensional, just like their single-zone counterparts. Since the zones in the multi-zone models can represent crevices, boundary layers and core zones, the models are also referred to as being quasi-dimensional.

The multi-zone model is much more suitable for predicting realistic cylinder pressure histories and emissions of NO_x, CO and HC.

The disadvantage in the use of multi-zone models is the increased computational costs with the increasing number of zones.^[38,75-77]

CHAPTER 4

INTRODUCTION

Chapter 4 covers the work involved in setting up the CHEMKIN program to run in HCCI mode. The single-zone computational work done in CHEMKIN is presented throughout this chapter. This model is based on the assumption of perfect homogeneous mixture, i.e. the thermodynamic properties, such as pressure, temperature and species concentrations, have the same values at all locations inside the cylinder. The preliminary work done with CHEMKIN is given as well as a study of the influence in HCCI combustion of several different additives that can be found in the composition of exhaust gas or in the composition of reformed fuel.

4.1 CHEMKIN Set Up

The package used to model combustion and chemical kinetics of the HCCI combustion is called CHEMKIN. This software is one of the most known packages for solving complex chemical kinetics problems and allows the user to calculate species concentrations, heat release rate, temperature and pressure history of the combustion.

One of the objectives of this thesis is to investigate the influence of different additives and fuels in HCCI combustion. The author of this thesis decided to use zero-dimensional single-zone thermo-kinetics mode, which enables to study the influence of different combustible mixtures with minimum computational time.

Before the start of modelling in CHEMKIN a pre process is required. This pre process will check if the basics to run the desired simulations are present.

The two sets of data that need to be pre processed prior to the actual modelling are the gas-phase kinetics input and the species thermodynamic data without each, no complete information is available to run the chemical kinetic equations.

On the gas-phase kinetic input data, all the chemical elements and species are accounted for, and every reaction between them is shown with the correspondent reaction rate coefficients. These chemistry sets can be prepared by the user or can be obtained from different resources, namely previous work done by other researchers.

The chemistry set used for this thesis was obtained from Curran et al.^[78,79]. Because this mechanism didn't take into account the formation of NO_x, all the NO_x reactions available at GRIMECH 3.0 mechanism were added to it.

The other file that requires pre process is the thermodynamic data. On this file all the information regarding thermodynamic properties of the species involved on every reaction are specified. Again this file can be built by the user using thermodynamic data as information or complete sets developed already can be used.

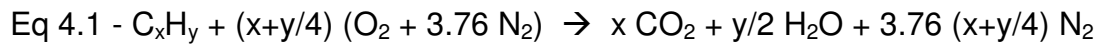
More information on the mechanism and species used can be found in Appendix 3.

The next stage of the modelling process is where a specific reactor is selected to cope with the demands of the desired simulation.

The CHEMKIN input for the simulation was based on the HCCI model that the package from Reaction Design, already includes.

The input parameters used were; simulation end time, 0.043s; engine compression ratio, 10; engine displacement volume, 665cc; engine connecting rod to crank radius, 3.3; engine speed, 1000 rpm; start crank angle, -142°; temperature 500, 600, 700 K; pressure, 0.8 atm; equivalence ratio, 0.485; heat transfer correlation, $a=0.035$, $b=0.71$, $c=0.0$; chamber bore diameter, 9.7 cm; wall temperature, 400 K; Woschini correlation of average cylinder gas velocity, $c_{11}=2.28$, $c_{12}=0.308$, $c_2=3.24$; ratio of swirl velocity, 0.0.

From equation 4.1 the composition of the initial gas mixture for the iso-octane combustion was calculated. As HCCI allows lean combustion, all calculations were done for an equivalence ratio (ϕ) of 0.4.



An excel spreadsheet was developed to quickly calculate several different initial conditions that were run during the simulations.

4.2 CHEMKIN Initial Simulations

The first work done on CHEMKIN was compared with available data^[66] to check how the model used was performing.

In figure 4.1 is possible to observe that the peak temperatures are similar and the ignition delay is longer for the CHEMKIN simulation.

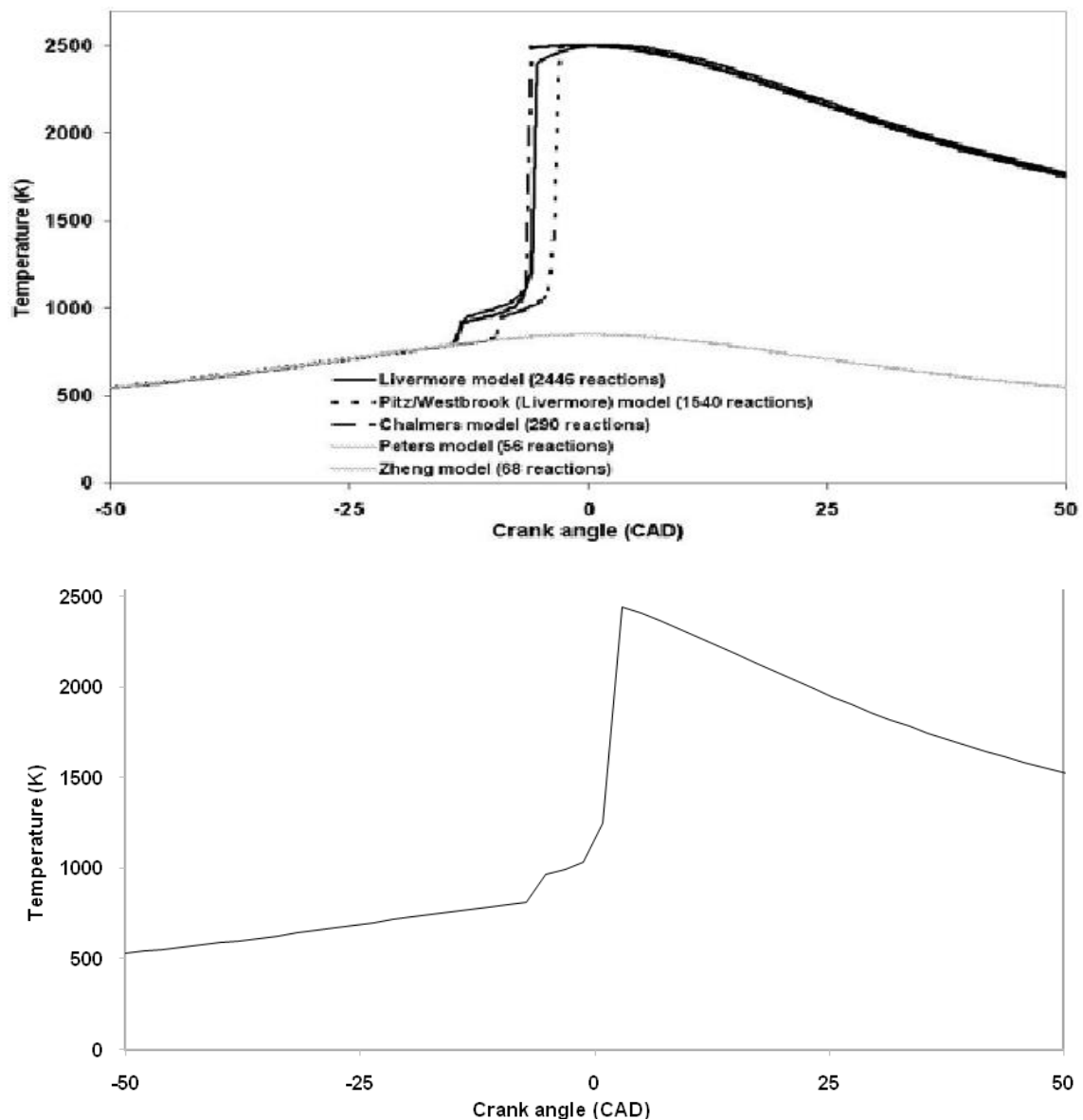


Figure 4.1 – Comparison between temperature vs crank angle data.^[66]

In the next set of simulations, a fix initial temperature of 500K and initial pressure of 0,8 atm were set. EGR was introduced in CHEMKIN simulations, varying it from 0% to 50%. Two different types of EGR were assumed. One

called neutral EGR was constituted by CO_2 , H_2O , N_2 , O_2 . The other was called active EGR where CO , H_2 and NO were added. The aim with these two distinct EGR was to study the differences caused by the addition of species that could enhance combustion.

The quantities of the components present in EGR were calculated by running a simulation in CHEMKIN with only air and fuel and analyzing the mol fractions produced of the gases in which the interest rely.

This allowed us to have an approximation of the exhaust gases produced.

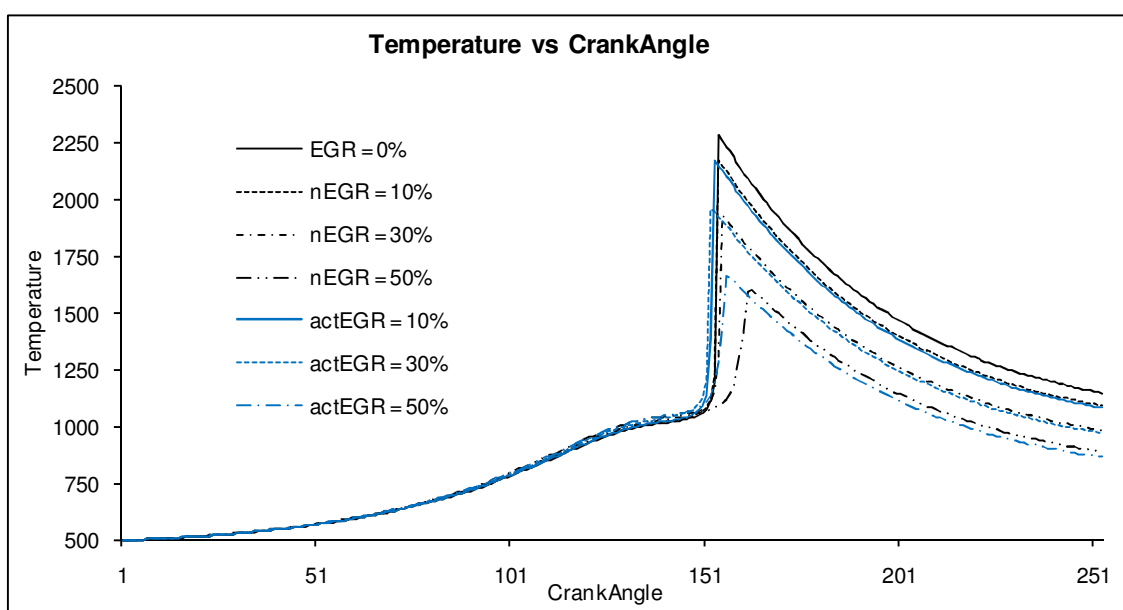


Figure 4.2 – Temperature profile against crank angle for an initial temperature of 500 K.

It is possible to see from figure 4.2 and 4.3 that the ignition is delayed by the charge dilution and peak temperatures decrease.

One of the operating problems with HCCI combustion is the rate of pressure released per crank angle degree, which tends to be high, leading to high mechanical stress within the engine. From these simulations is possible to highlight the difference between neutral and active EGR. Although the differences are small, it is possible to see that the presence of CO , H_2 and NO helped triggering the ignition leading to higher peak temperatures, as well as higher pressure released per crank angle (this effect is more pronounced for EGR=50%).

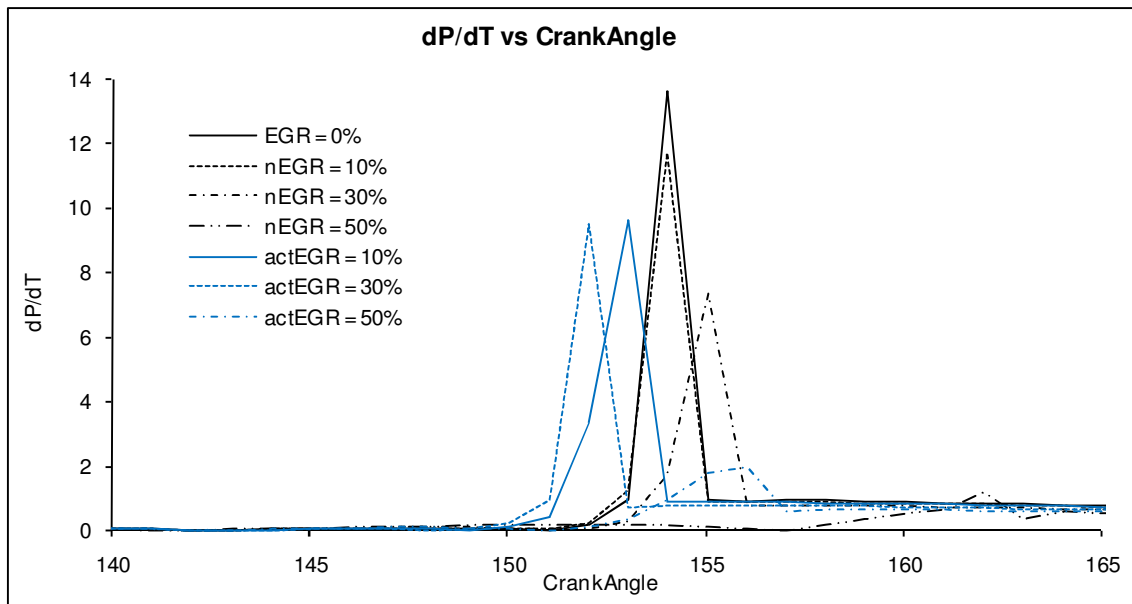


Figure 4.3 – Pressure release per crank angle, for an initial temperature of 500 K.

According to the results obtained, the ones that can be suitable for operation in an engine are the ones obtained with the high levels of EGR. The high dilution levels with exhaust recirculation gases, lead to a smoother pressure released per crank angle which is an important factor to produce smooth engine operation as well as to minimize the noise level.

4.2.1 Additives Influence in Combustion

The assumed EGR constitution was CO_2 , CO , H_2 , H_2O , O_2 , N_2 and NO . Some simulations were made to identify the contribution/influence of each one of these components in a combustion cycle. To perform this study, the initial temperature of 500 K was fixed and 1%, 5% and 10% of each element under study was added into the initial air-fuel mixture.

The results obtained are shown in the next plots.

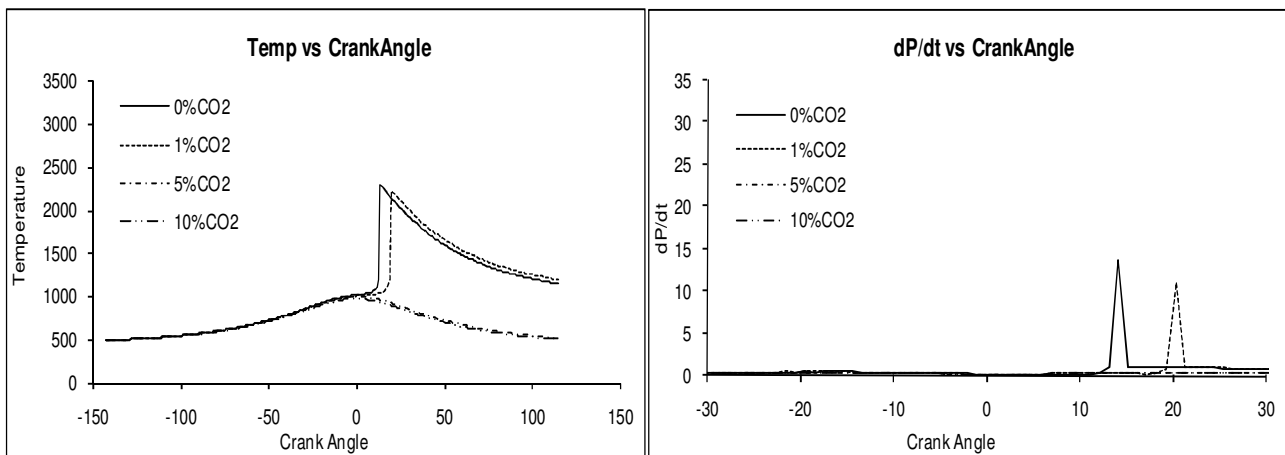


Figure 4.4 – CO_2 influence on temperature profile and pressure release rate.

When 1% of CO_2 was added, a slight decreased in the peak temperature as well as in the pressure release rate, was observed. Combustion was not achieved when 5 and 10% of CO_2 were added. These results are in agreement with what was expected once CO_2 is fully oxidized and not very reactive or flammable, so it can be used as an additive to slow down combustion.

When CO was added to our combustion simulation, the following results were obtained.

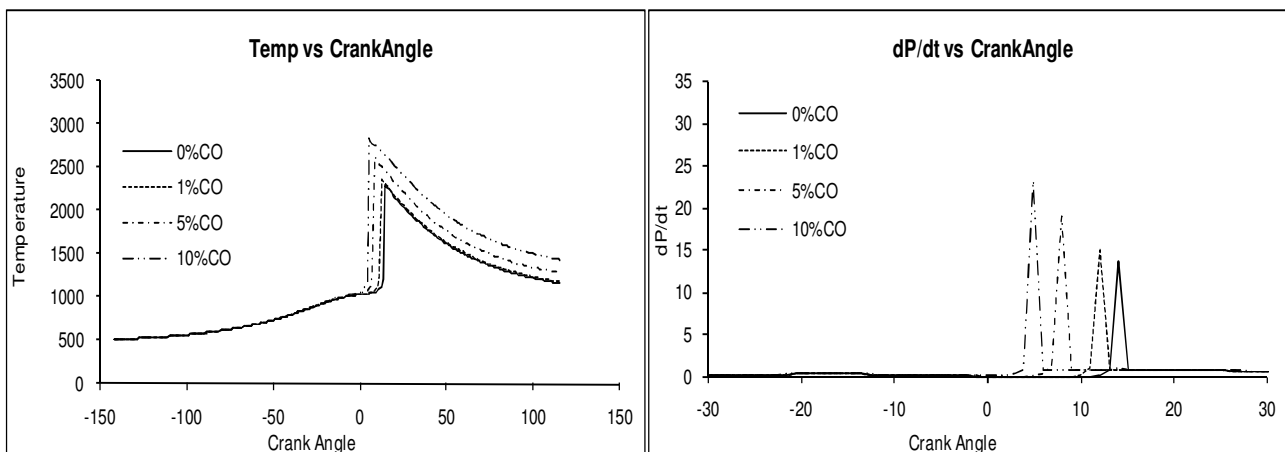


Figure 4.5 – CO influence on temperature profile and pressure release rate.

Increasing the quantity of CO produced a slightly increase in the peak temperature as well as in the pressure released rate. Also the addition of CO shortened the ignition delay by as much as 10 degrees for the case when 10% was added. CO is a flammable and combustible gas in the presence of an ignition source so it is easy to understand the behaviour of combustion when this gas was added.

On the next experiment it was added 1, 5 and 10 % of H₂ into the initial air-fuel mixture.

The results obtained are shown in figure 4.6.

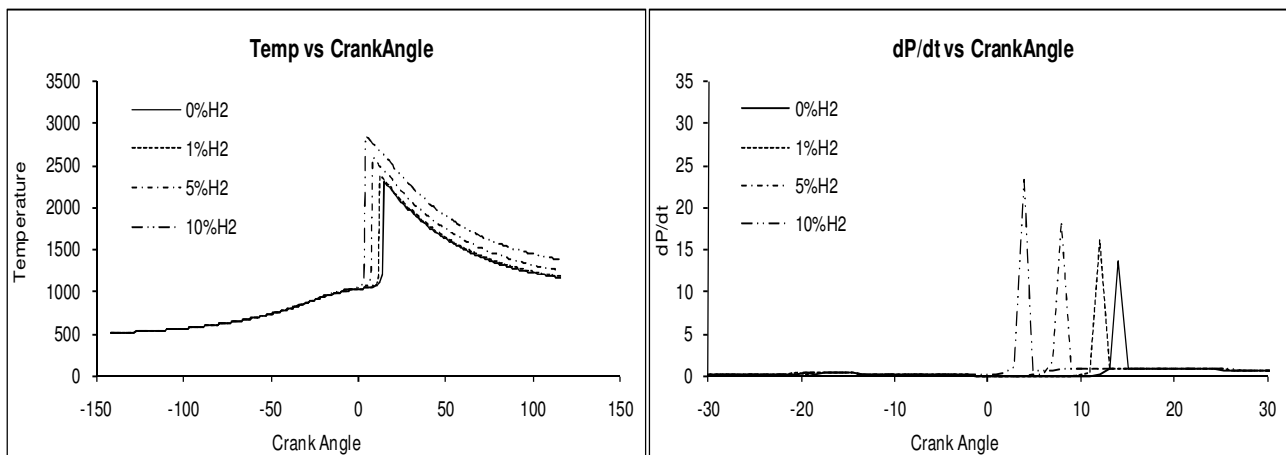


Figure 4.6 – H₂ influence on temperature profile and pressure release rate.

As expected increasing the initial concentration of H₂ will increase the peak temperatures, the pressure release rate and will shorter the ignition delay. These effects are due to the properties of H₂ like high flame speed and wide range of flammability. It is confirmed with this simulations that this gas can be used as a combustion enhancer. It is worth to note that H₂ as good anti knock properties which might make this additive even more desirable.

Figure 4.7 on the next page, exhibits the influence of water in our combustion simulations.

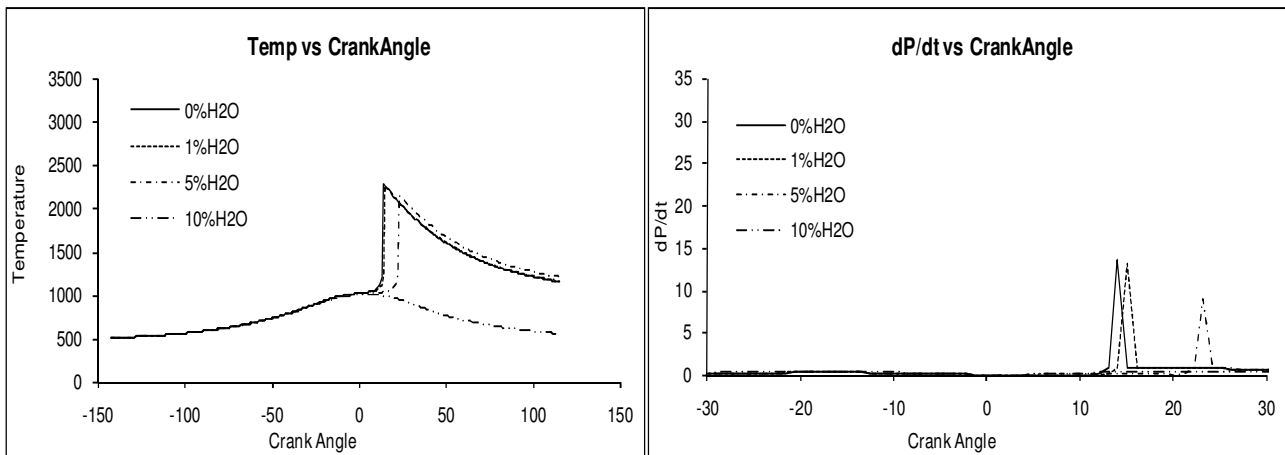


Figure 4.7 – H₂O influence on temperature profile and pressure release rate.

Increasing the initial concentration of H₂O will decrease the peak temperatures, the pressure released rate and will longer the ignition delay. With 10% of H₂O no combustion was achieved. These results are related with the non flammability of water and are expected. It is showed that water can be added into HCCI combustion to slow the combustion rate down, expanding the high load limits.

Increasing the amount of O₂ to the combustion cycle will slightly decrease the peak temperatures (almost negligible effect), and will produce no difference in pressure release rate however will shorter the start of ignition.

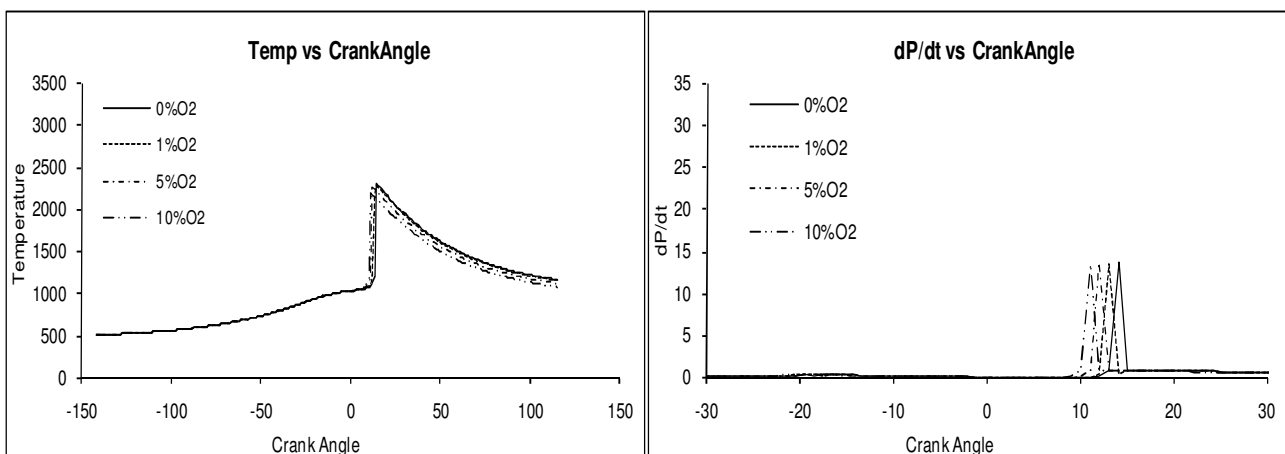


Figure 4.8 – O₂ influence on temperature profile and pressure release rate.

The following, figure 4.9, shows no noticeable differences in combustion when the amount of initial N₂ is changed.

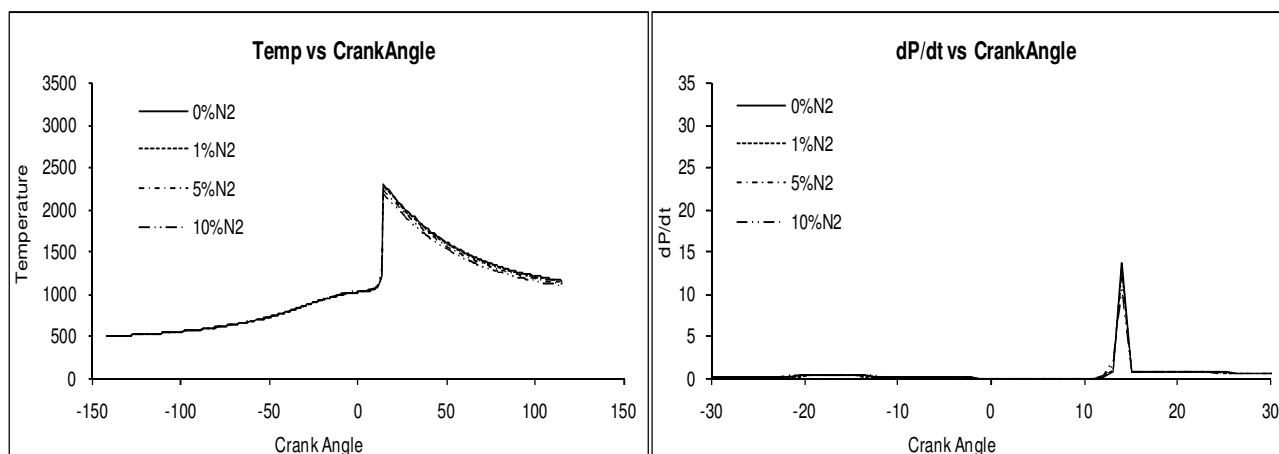


Figure 4.9 – N_2 influence on temperature profile and pressure release rate.

When NO was added to the combustion cycle (figure 4.10) significant changes in the combustion were produced. When 1% and 5% is added the peak temperature suffers a slightly almost not noticeable change. However when 10% is added, combustion is not achieved. With 1% the ignition delay is much shorter and the pressure release is slightly higher. For 5% the ignition delay is longer than for 1% but is shorter than for the case without any additive. The peak pressure for this case is slightly lower than the others.

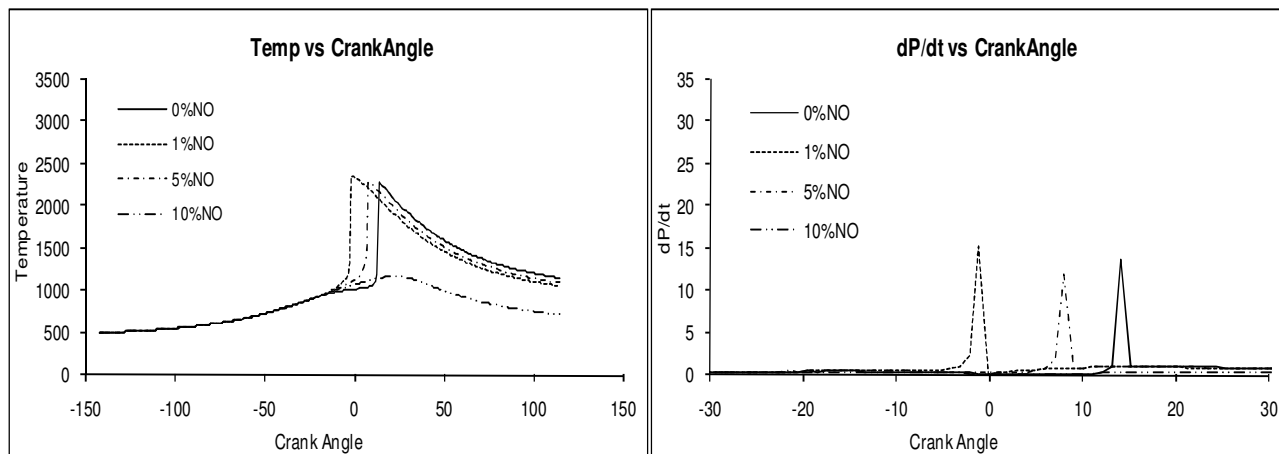


Figure 4.10 – NO influence on temperature profile and pressure release rate.

Nitric oxide is highly reactive and is capable of participating in many chemical reactions.

All the results obtained were expected. The NO added in small concentrations will enhance the auto-ignition chemistry, by producing more $OH\cdot$ radicals, on the other hand when large quantities of this additive (NO) is added, the chemistry will favour reactions that consume $OH\cdot$ radicals, that is fundamental to combustion.

In the next set of simulations performed, we studied the effect of several others additives like methane (CH_4), methanol (CH_3OH), ethane (C_2H_6), acetylene (C_2H_2), formaldehyde (CH_2O), hydrogen (H_2) and carbon monoxide (CO), that can be part of the constitution of reformed fuel.

Figure 4.11 shows the effect of adding methane as an additive to combustion. With 1% of CH_4 the peak temperature was increased. The ignition delay was longer and the pressure release rate smoother. Adding 5 and 10% of this additive lead to no combustion.

Methane has a very high auto-ignition temperature, and that might be the reason for the increased ignition delay when 1% was added, and the reason why the mixture, did not ignite when larger quantities were available. The slightly increase in temperature, when 1% of methane was added, is probably related with the series of reactions that methane can undergo after forming methyl radical.

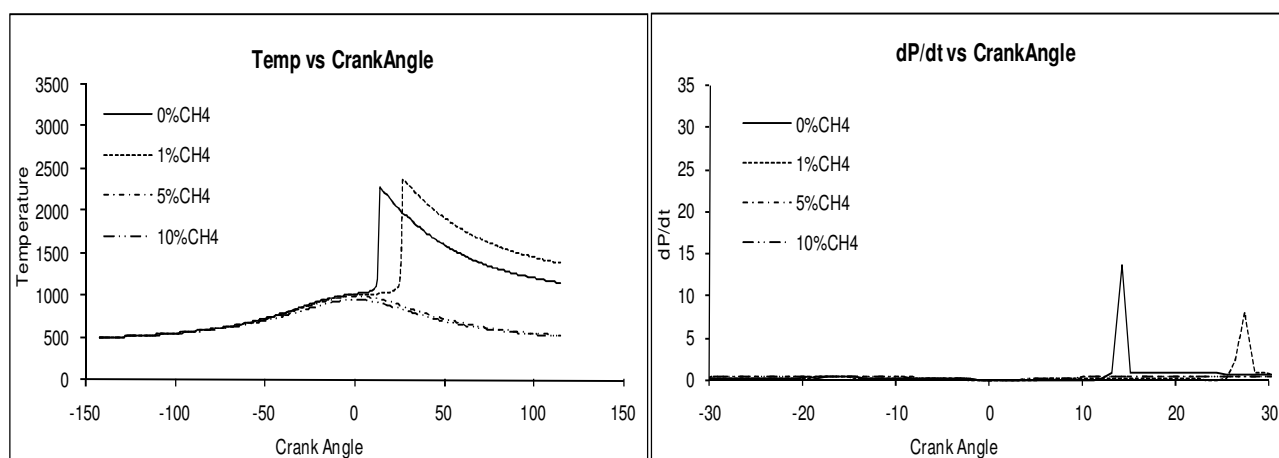


Figure 4.11 – CH_4 influence on temperature profile and pressure release rate.

Figure 4.12, which can be found on the following page, shows the impact on combustion, of the presence of methanol.

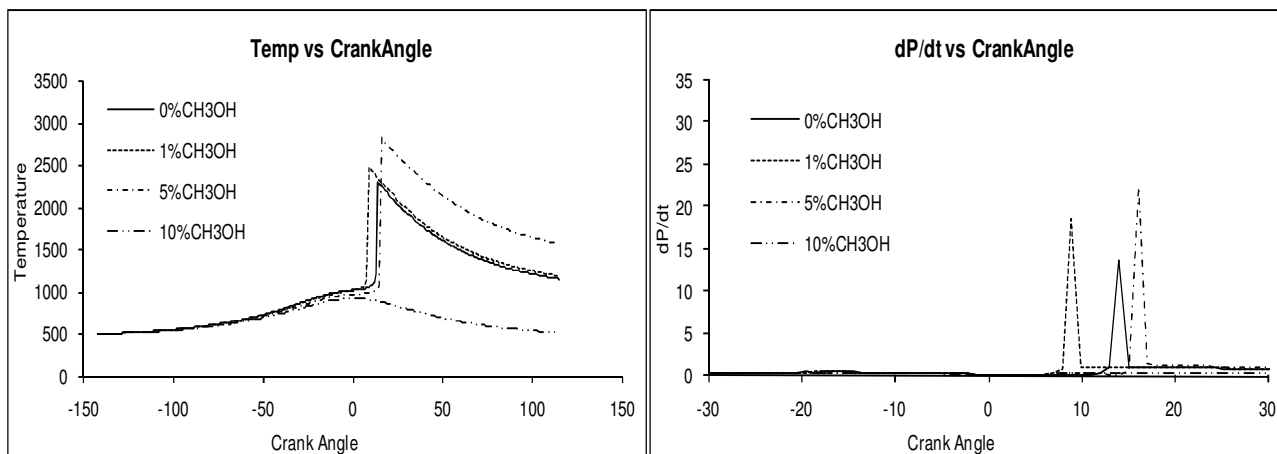


Figure 4.12 – CH_3OH influence on temperature profile and pressure release rate.

Increasing the amount of CH_3OH will, increase the peak temperatures and the pressure release rate. The ignition delay was shortened, when 1% was added, but the addition of 5% of methanol, made the ignition delay longer when compared with the reference case. Both experiments where 1 and 5% of methanol was added produced higher peak temperature. For 10% of CH_3OH no combustion was achieved. The explanation to such behaviour is probably the high octane number of alcohols.

The addition of C_2H_6 inhibits combustion due to his higher auto-ignition temperature and high antiknock properties. Such effect is shown in figure 4.13.

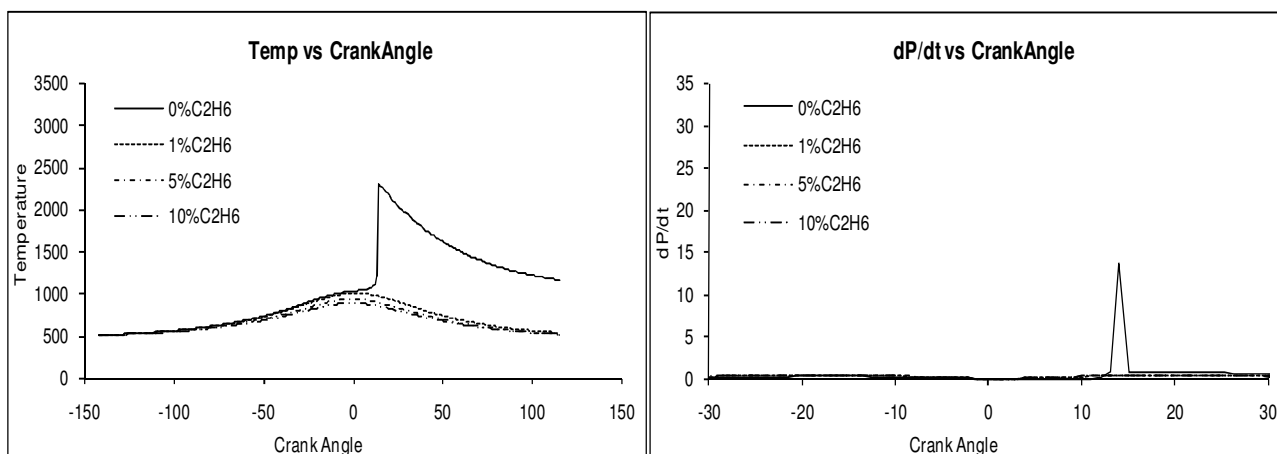


Figure 4.13 – C_2H_6 influence on temperature profile and pressure release rate.

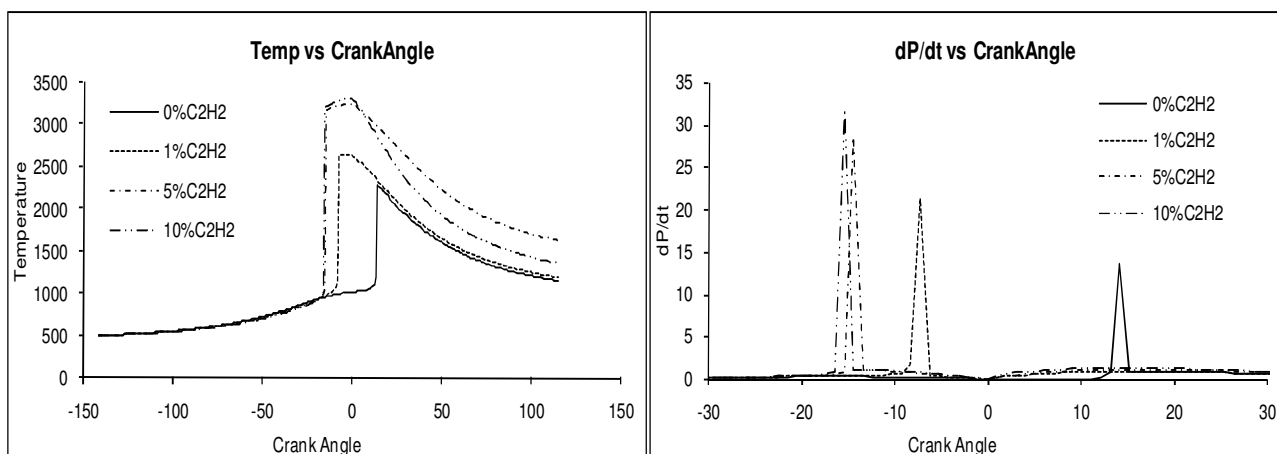


Figure 4.14 – C_2H_2 influence on temperature profile and pressure release rate.

On figure 4.14 the effect of acetylene is shown. Acetylene is highly combustible, extremely flammable gas, and his auto-ignition temperature is low. Another property of this gas is its tendency to produce very hot flames when combined with oxygen. As can be seen from results obtained, acetylene is a combustion enhancer. Increasing its initial concentration will increase the peak temperatures, the pressure release rate and will shorter the ignition delay.

Formaldehyde (CH_2O) is another gas with the capability to enhance combustion. In figure 4.15, it is possible to observe that increasing its initial concentration, the peak temperatures and the pressure released rate increased, while the ignition delay became shorter. Like acetylene, formaldehyde is a very reactive gas that can suffer oxidation easily, helping combustion.

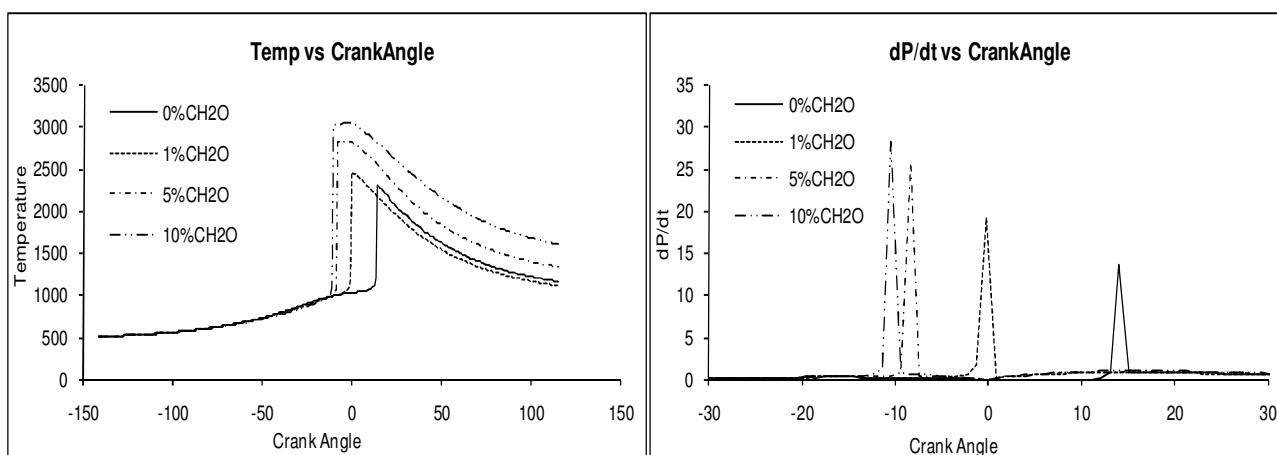


Figure 4.15 – CH_2O influence on temperature profile and pressure release rate.

4.2.2 Summary

With the simulations performed, it was possible to have an insight of the influence of each individual additive (CO_2 , CO , H_2 , H_2O , O_2 , N_2 , NO , CH_4 , CH_3OH , C_2H_6 , C_2H_2 and CH_2O) that was used. These particular additives were chosen as they are part of the constitution of EGR and it was good to understand the influence of each one of them by itself. Figures 4.15, 4.16 and 4.17 show the influence in combustion of each one of the additives studied, for a fixed amount.

Among these additives, there were some that enhance combustion (CO , H_2 , NO , CH_4 , CH_3OH , C_2H_2 and CH_2O), there were others that slow it down (CO_2 , H_2O and C_2H_6) and others that produced no noticeable effect (O_2 and N_2).

Some of the additives used, in small concentrations improve combustion decreasing the ignition delay and increasing peak temperatures, but when added in large concentrations had the opposite effect (NO , CH_4 and CH_3OH).

All the results obtained with our model were in agreement with theory.

4.3 CHEMKIN Simulations with Different Fuels

In this section results from CHEMKIN simulations done with different fuels, iso-octane, ethanol and mixtures between these fuels are presented.

It was also investigated in more detail the influence on combustion of mixtures where water, carbon dioxide and nitric oxide were added.

The aim of having different initial fuels and different amounts of diluents was to achieve a tolerable pressure release rate per crank angle and investigate the flexibility of HCCI combustion regarding the use of different fuels. Ethanol was used in this study as it has the potential to play an important role in future as an alternative fuel.

To model HCCI combustion in CHEMKIN using ethanol as fuel, a new chemical reaction mechanism was needed. An oxidation mechanism for methyl ether^[80,81] was used since it included all the relevant oxidation reactions for combustion of ethanol. As in the iso-octane oxidation mechanism, this one did not include reactions for NO_x formation, so again those reactions were added from GRIMECH 3.0 mechanism.^[82]

4.3.1 Iso-Octane

The effect of water, carbon dioxide and nitric oxide was investigated in this set of simulations using iso-octane as the initial fuel. Water was added from 1 to 25%, carbon dioxide from 1 to 10% and nitric oxide from 0,1 to 0,5%.

To determine the maximum quantities available of CO₂ and of NO from exhaust gases a CHEMKIN simulation was ran only for fuel-air mixture. Water is used in larger quantities since it can be easily available from external source. The results for peak temperatures and peak pressure releases obtained are shown in figure 4.16.

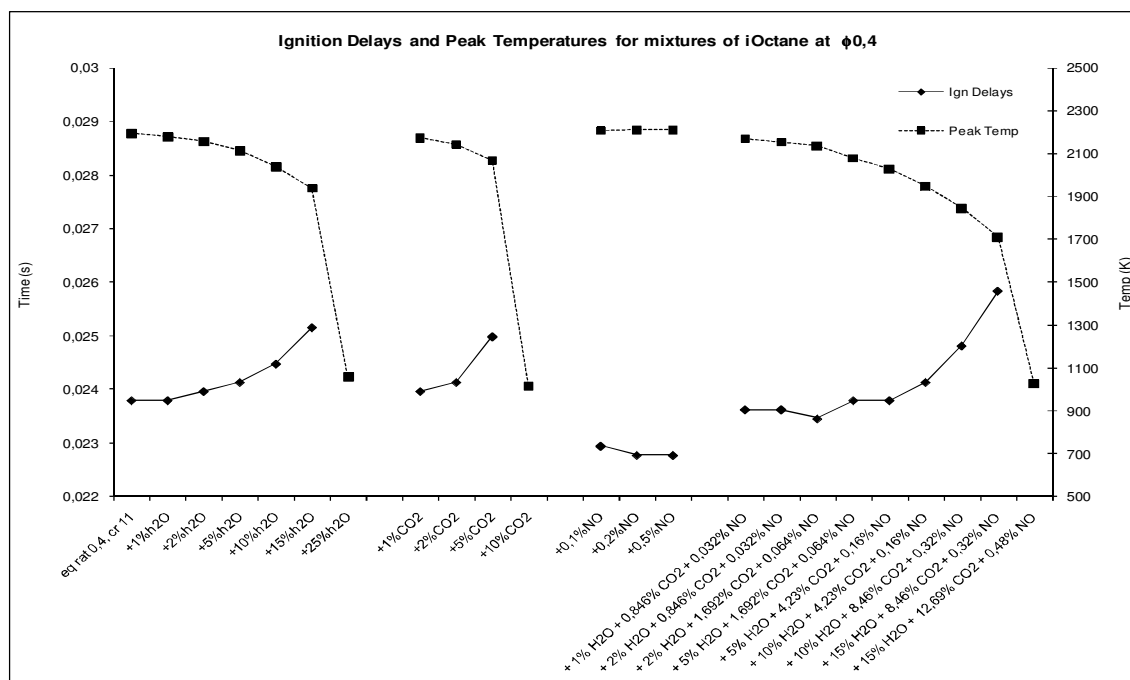


Figure 4.16 - Start of ignition and peak temperatures for different iso-Octane mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11.

Water and carbon dioxide had the same effect in combustion, although for carbon dioxide this effect is more pronounced. Increasing the quantity of these additives led to a decrease in the peak temperatures and an increase in the start of ignition. It was possible to dilute the fuel with 15% of water and still achieve combustion. For CO₂ the allowed quantity was lower, beyond 5% there was no combustion. As expected, adding nitric oxide decrease the ignition delay and produce a slight increase in the peak temperature. From 0,2% to 0,5% of nitric oxide there was no noticeable change.

Adding the complex mixture of water, carbon dioxide and nitric oxide, led to the results expected. Due to the presence of NO it was possible to increase the charge dilution. A mixture constituted by 15% of water, 8,46% of CO and 0,32% of NO was still ignitable.

As expected due to charge dilution with additives that slow down combustion, a decrease in peak temperatures and increase in the start of ignition was achieved.

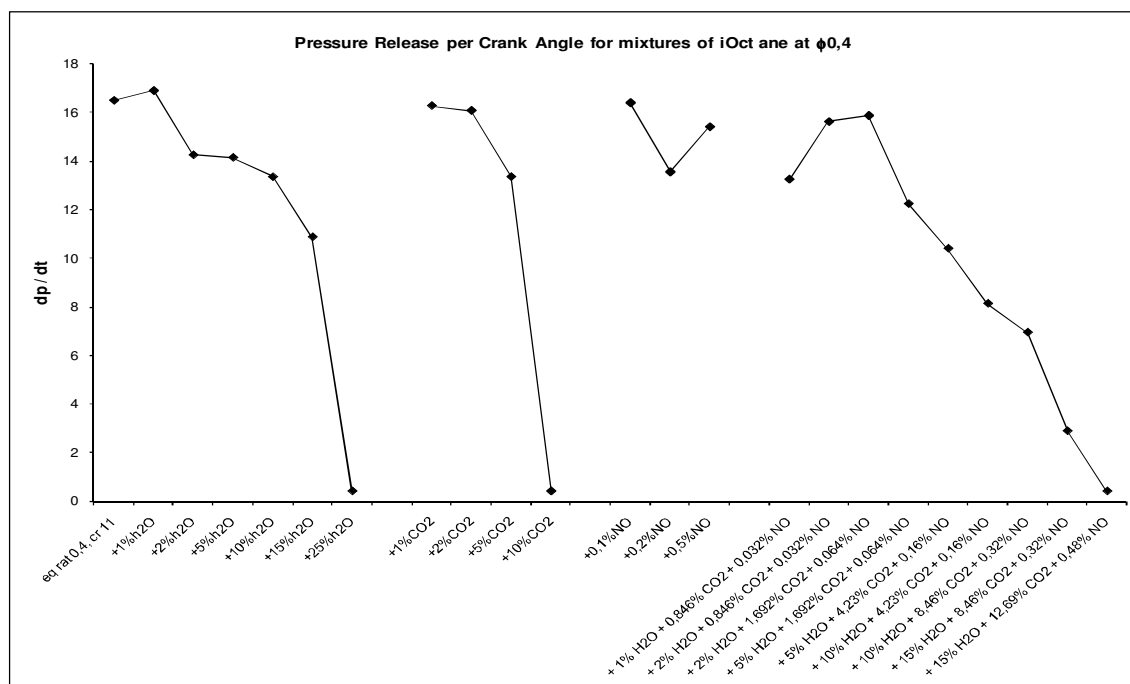


Figure 4.17 – Pressure release per CA for different iso-Octane mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11.

Figure 4.17 show the variation of the pressure released per ca with the additives added where is possible to visualize the trends already described. The addition of water and carbon monoxide lead to a decrease in the rate of pressure released. This parameter varied fairly in the same way as the peak temperatures.

When the equivalence ratio was increased to 0.6 the results obtained were similar. However, because the higher initial quantity of fuel the peak temperatures achieved were higher as well as the pressure release rates.

The two main differences when the initial fuel was increased are, with 25% of water combustion was still achieved although still reaching higher value for

pressure release rate, and there were no results for pressure release that could fit into the operating range of a normal engine.

The next table show the simulations that were performed as well as some of the results obtained when equivalence ratio was set to 0.4.

Table 4.1 - Results for mixtures of Iso-Octane.

	Ign Delay (s)	T(K) max	P(atm) max	dP/dt max
+15% H ₂ O + 8,46% CO ₂ + 0,32% NO	0,02635	1715,93	22,8	2,72
+15% H ₂ O + 8,46% CO ₂ + 0,0% NO	-	1001,57	16,4	0,39
+ 15% H ₂ O + 8,46% CO ₂ + 0,1% NO	-	1022,83	16,72	0,39
+ 15% H ₂ O + 8,46% CO ₂ + 0,2% NO	0,02669	1689,56	20,74	2,2
+ 16% H ₂ O + 8,46% CO ₂	-	1000,41	16,38	0,39
+ 16% H ₂ O + 8,46% CO ₂ + 0,32% NO	0,02669	1670,94	20,38	1,96
+ 17% H ₂ O + 8,46% CO ₂ + 0,32% NO	0,02788	1602,6	16,92	0,78
+ 18% H ₂ O + 8,46% CO ₂ + 0,32% NO	-	1224,39	16,83	0,39

From the table above it is possible to say that presence of NO have big influence whether combustion is achieved or not. Combustion is not achieved when 16% of water is added if NO is absent from the initial mixture. When a small percentage of this additive is included in the initial mixture the amount of water can be increased till 17%.

The results shown on the table can be observed in the next two plots.

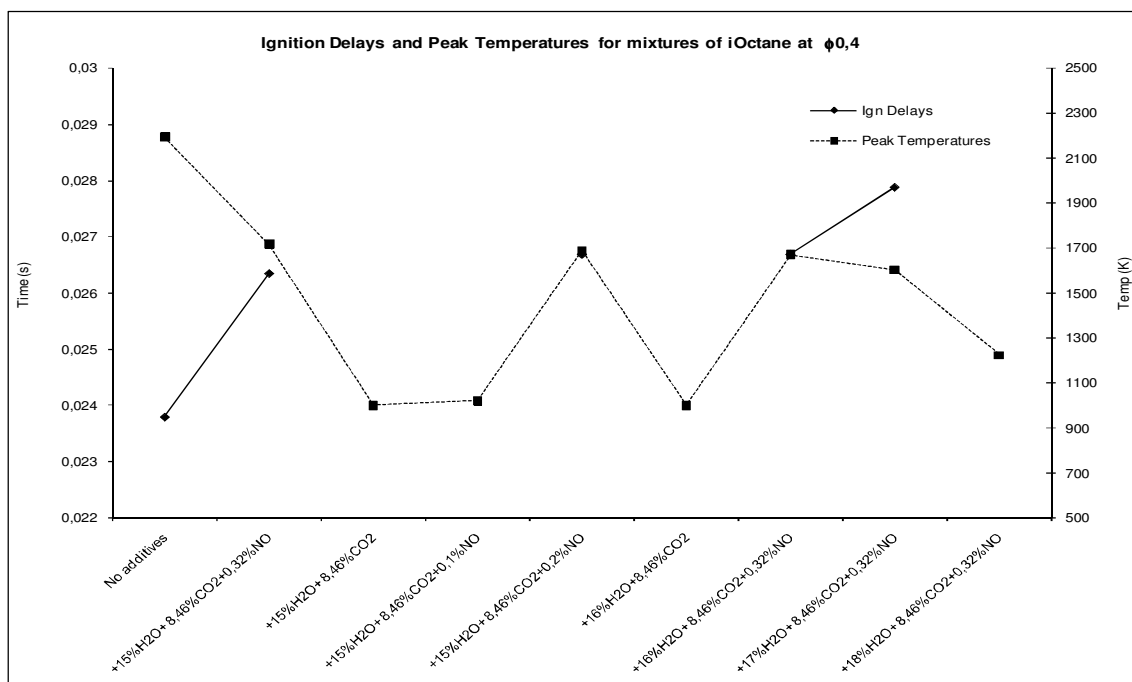


Figure 4.18 - Start of ignition and peak temperatures for different iso-Octane mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11.

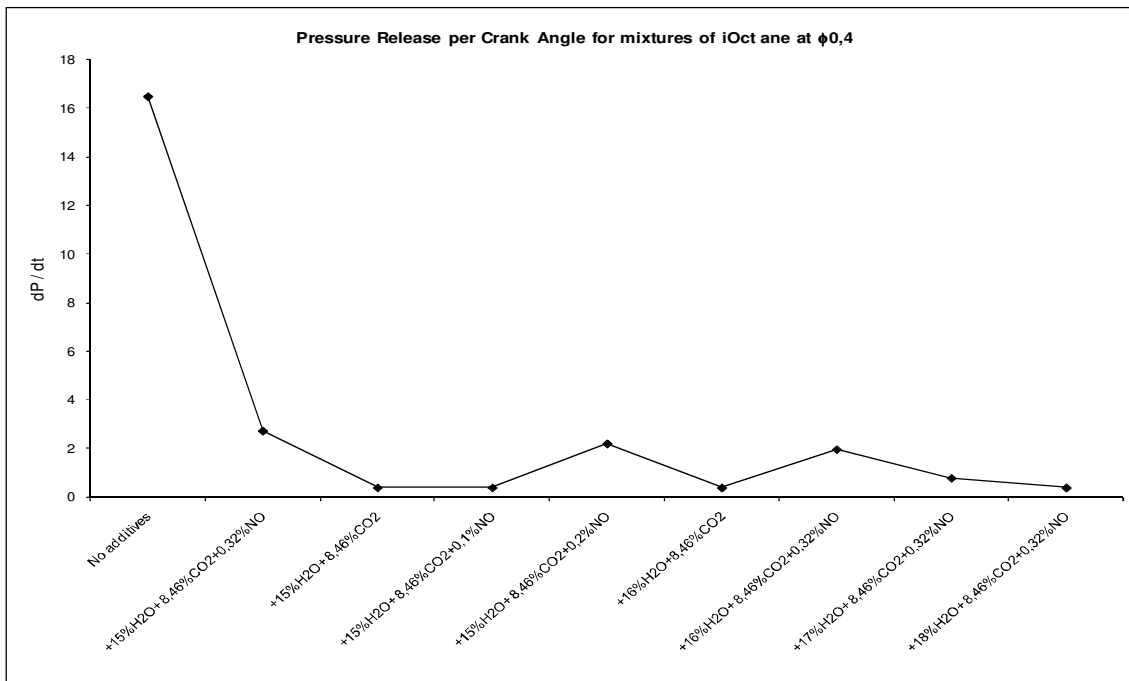


Figure 4.19 – Pressure release per CA for different iso-Octane mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11.

As seen before the presence of NO in small quantities will enhance the low temperature oxidation, extending the dilution limits for a certain mixture, with benefits in the smoother dP/dt values obtained and the lower peak temperatures achieved, which in turn, can decrease the formation of NO_x.

4.3.2 Ethanol

The fuel used on the following simulations was ethanol. As before the influence of adding water (from 1 to 25%), carbon dioxide (1 to 10%), nitric oxide (0,1 to 0,5%) was investigated. The simulations made with ethanol as initial fuel required a higher compression ratio of 11.5, 0,5 higher than the used for the case of iso-octane. This was due to the inability of achieving combustion at a compression ratio of 11. The higher compression ratio required by ethanol is understandable since this fuel has a higher octane number (107) than iso-octane (100) making it more difficult to ignite.

In figure 4.20 and 4.21, it is possible to see the results obtain for the different simulations, changing initial fuel and additives.

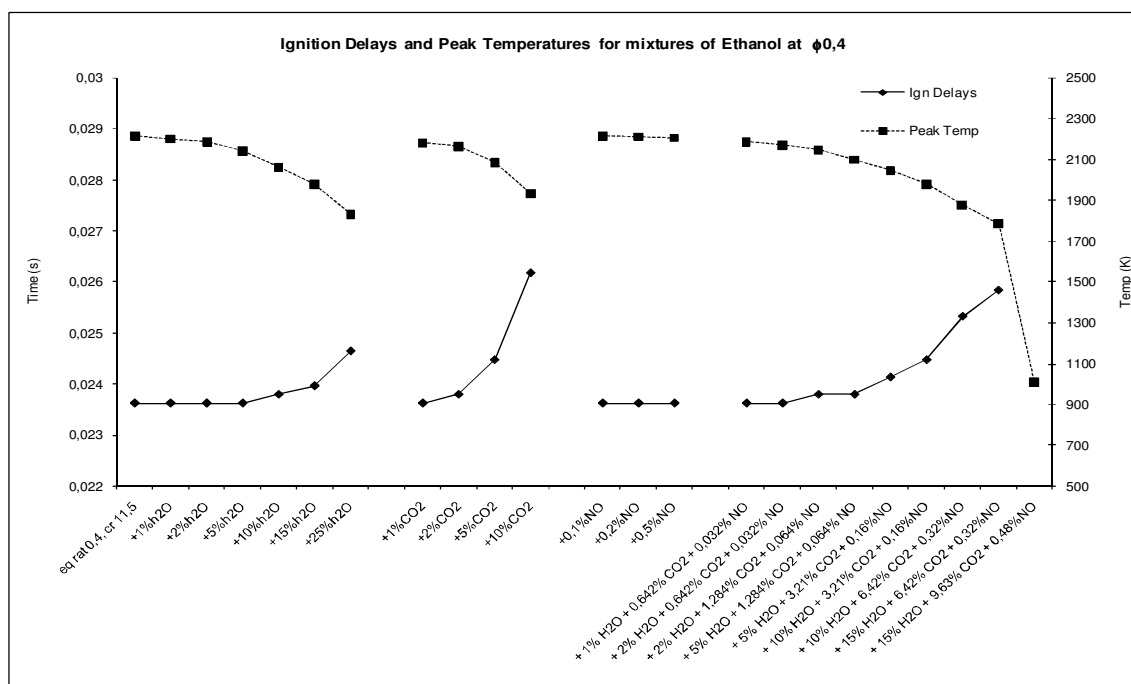


Figure 4.20 – Start of ignition and peak temperatures for different ethanol mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11,5.

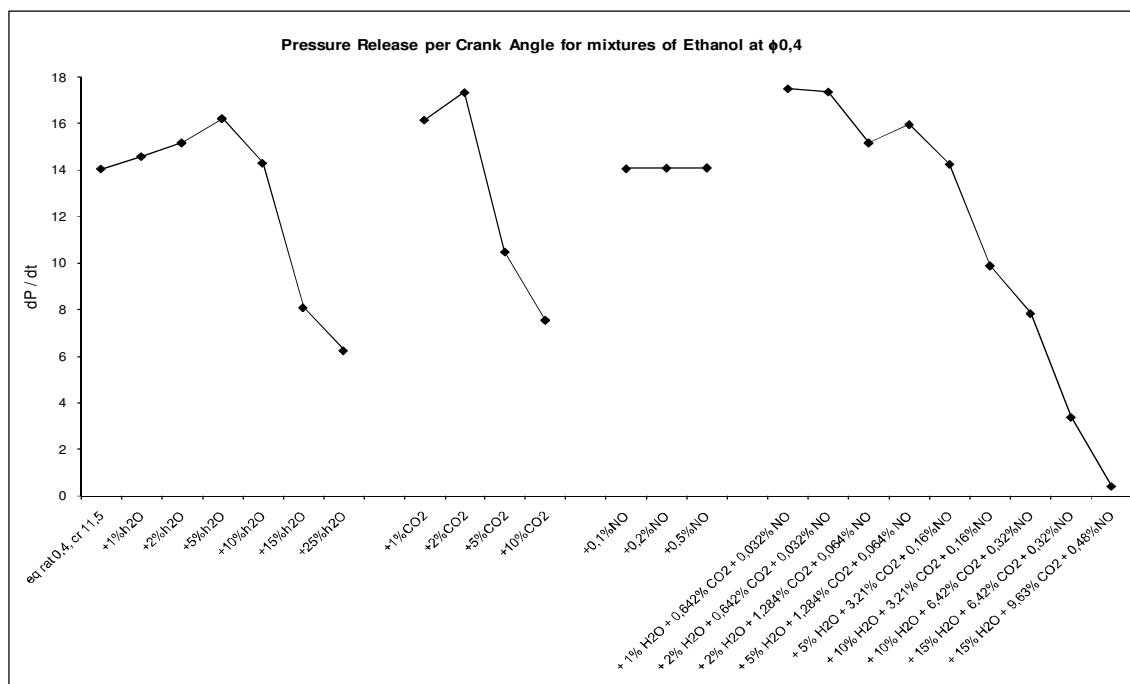


Figure 4.21 – Pressure release per CA for different ethanol mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11,5.

The results obtained were similar to the ones obtained with iso-Octane. The same trends can be observed and the same conclusions can be drawn.

The main difference when using ethanol as a fuel is that combustion is achieved even when 25% of water was added. These results show that ethanol has more capacity of being diluted with water.

Despite the very similar peak temperatures and start of ignition the combustion of ethanol is smoother as the results for the pressure release show.

When the quantity of fuel was increased to an equivalence ratio of 0,6 and 0,8, the results were similar. However, because we had a larger initial quantity of fuel, the peak temperatures achieved were higher as well as the pressure release rates.

These results will not be further investigated because the pressure released figures would be high and fall out of the operating window for a regular engine.

For the simulations made with ethanol, the addition of nitric oxide did not influence combustion, so it is well possible that the chemistry of NO do not play such an important role with ethanol as it did when the fuel was iso-octane.

Table 4.2, shows the simulations that were performed, as well as a summary of the results obtained, where start of ignition, peak temperatures and pressures achieved and pressure release per ca are showed.

Table 4.2 - Results for mixtures of Ethanol.

	Ign Delay (s)	T(K) max	P(atm) max	dP/dt max
+ 15% H ₂ O + 6,42% CO ₂ + 0,32% NO	0,02601	1785,19	25,27	3,39
+ 15% H ₂ O + 6,42% CO ₂	0,02618	1790,92	25,35	2,89
+ 16% H ₂ O + 6,42% CO ₂	0,02635	1770,11	24,41	3,48
+ 17% H ₂ O + 6,42% CO ₂	0,02669	1737,58	22,68	1,98
+ 18% H ₂ O + 6,42% CO ₂	0,02703	1702,75	20,99	1,79
+ 19% H ₂ O + 6,42% CO ₂	0,02771	1647,27	18,18	1,18
+ 20% H ₂ O + 6,42% CO ₂	0,02907	1519,56	17,38	0,45
+ 21% H ₂ O + 6,42% CO ₂	-	1201,4	17,35	0,42

Several of the simulations conducted achieved a smooth operation (maximum dP/dt lower than 3). As expected, adding water and carbon dioxide to the mixture led to a decrease in the peak temperatures as well as a decrease in the dP/dt value.

These results are particularly important as ethanol can play an important role as an alternative fuel (either use in a pure form or in gasoline-ethanol mixtures). It is also important to highlight that ethanol is a suitable fuel when mixed with water, which may have important implications in lowering the cost of the distillation processes to obtain this alcohol, since there is no requirement for it to be pure.

Figures 4.22 and 4.23 show the results summarized in table 4.2.

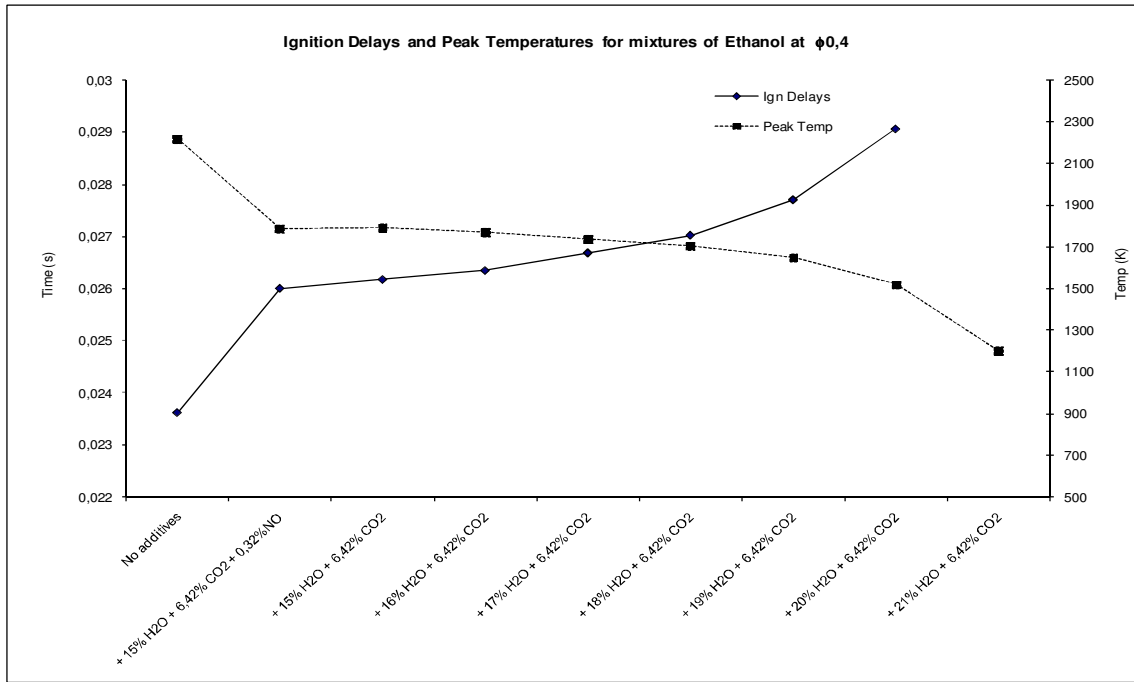


Figure 4.22 – Start of ignition and peak temperatures for different ethanol mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11,5.

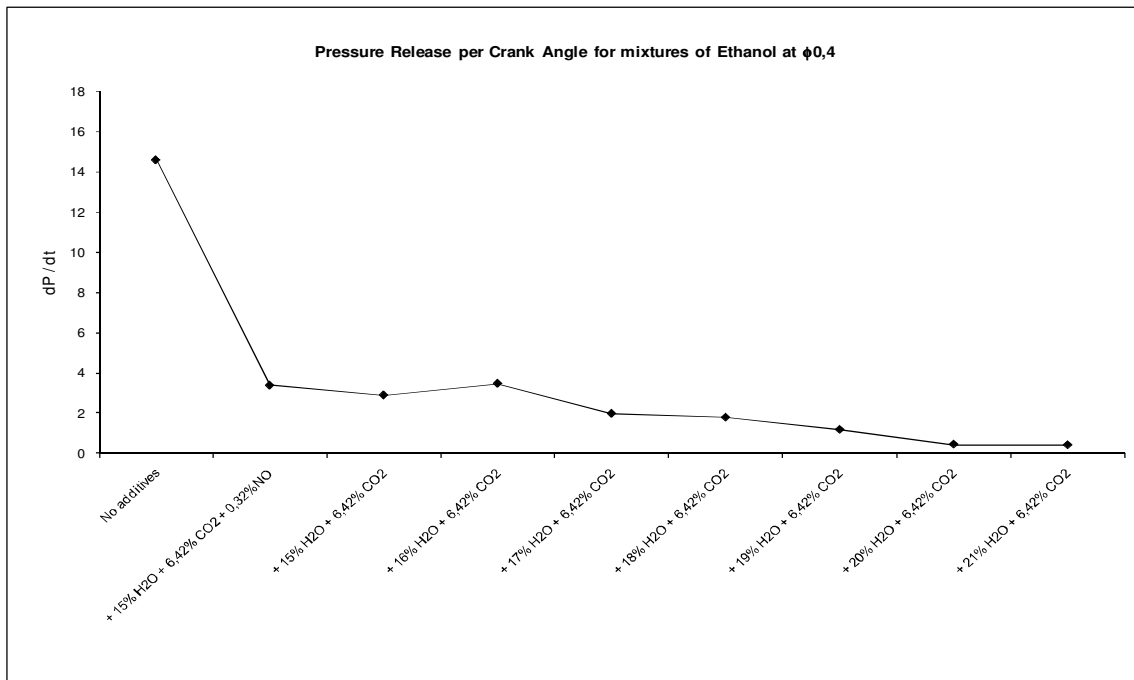


Figure 4.23 – Pressure release per CA for different ethanol mixtures ran with an equivalence ratio of 0,4 and a compression ratio of 11,5.

4.3.3 Iso-Octane/Ethanol

In the next set of simulations several different mixtures of iso-octane-ethanol were used. These mixtures are of particular economical importance as they can decrease the demand of fossil fuels. Also, several countries are already using a mixture of these two fuels. For example, in the United States, ethanol made from corn, is used in an 85% ethanol mixture called E85. In Brazil, ethanol from fermentation of sugarcane is used pure or blended with gasoline to yield gasohol, which contains 24% ethanol, which is the maximum concentration of ethanol tolerated by a current production engine without any modification.

The following table shows the results obtained, regarding start of ignition (s), peak temperatures (K), peak pressures (atm) and data for the pressure released rate per crank angle.

Table 4.3 - Results for mixtures of Iso-Octane / Ethanol.

	Ign Delay (s)	T(K) max	P(atm) max	dP/dt max
90% <i>i</i> Oct + 10% EtOH	0,0238	2193,94	36,74	16,42
90% <i>i</i> Oct + 10% EtOH + 5% <i>H</i> 2O + 3,2% <i>CO</i> 2	0,02584	1997,38	28,6	8,82
90% <i>i</i> Oct + 10% EtOH + 7% <i>H</i> 2O + 3,2% <i>CO</i> 2	0,02635	1945,22	25,92	5,89
90% <i>i</i> Oct + 10% EtOH + 10% <i>H</i> 2O + 3,2% <i>CO</i> 2	0,02822	1807,79	17,59	3,12
90% <i>i</i> Oct + 10% EtOH + 11% <i>H</i> 2O + 3,2% <i>CO</i> 2		1042,73	16,94	0,4
76% <i>i</i> Oct + 24% EtOH	0,0238	2193,41	36,73	16,29
76% <i>i</i> Oct + 24% EtOH + 5% <i>H</i> 2O + 3,2% <i>CO</i> 2	0,02584	1993,3	28,55	5,3
76% <i>i</i> Oct + 24% EtOH + 7% <i>H</i> 2O + 3,2% <i>CO</i> 2	0,02618	1958,42	26,77	8,88
76% <i>i</i> Oct + 24% EtOH + 10% <i>H</i> 2O + 3,2% <i>CO</i> 2	0,02771	1836,43	19,55	3,58
15% <i>i</i> Oct + 85% EtOH	0,0238	2193,87	36,81	16,14
15% <i>i</i> Oct + 85% EtOH + 5% <i>H</i> 2O + 3,2% <i>CO</i> 2	0,0255	2013,82	30,13	9,94
15% <i>i</i> Oct + 85% EtOH + 7% <i>H</i> 2O + 3,2% <i>CO</i> 2	0,02567	1977,59	29	10,23
15% <i>i</i> Oct + 85% EtOH + 10% <i>H</i> 2O + 3,2% <i>CO</i> 2	0,02703	2194,58	26,56	10,91

Simulations for three cases of iso-octane/ethanol mixtures were ran. The first simulation was made using 90% of iso-octane while the second and third simulations were ran using 76 % and 15 % of iso-octane respectively.

When ethanol was added to iso-octane (and subsequently the quantity of iso-octane decreased), the peak temperatures decreased, the start of ignition increased and the pressure released rates decreased as well.

These effects are probably due to the easier ignitability of iso-octane when compared with ethanol. For iso-octane the octane number is 100 while for ethanol it is 107, making the latter harder to ignite.

Figure 4.24 and 4.25 show some of the results obtained.

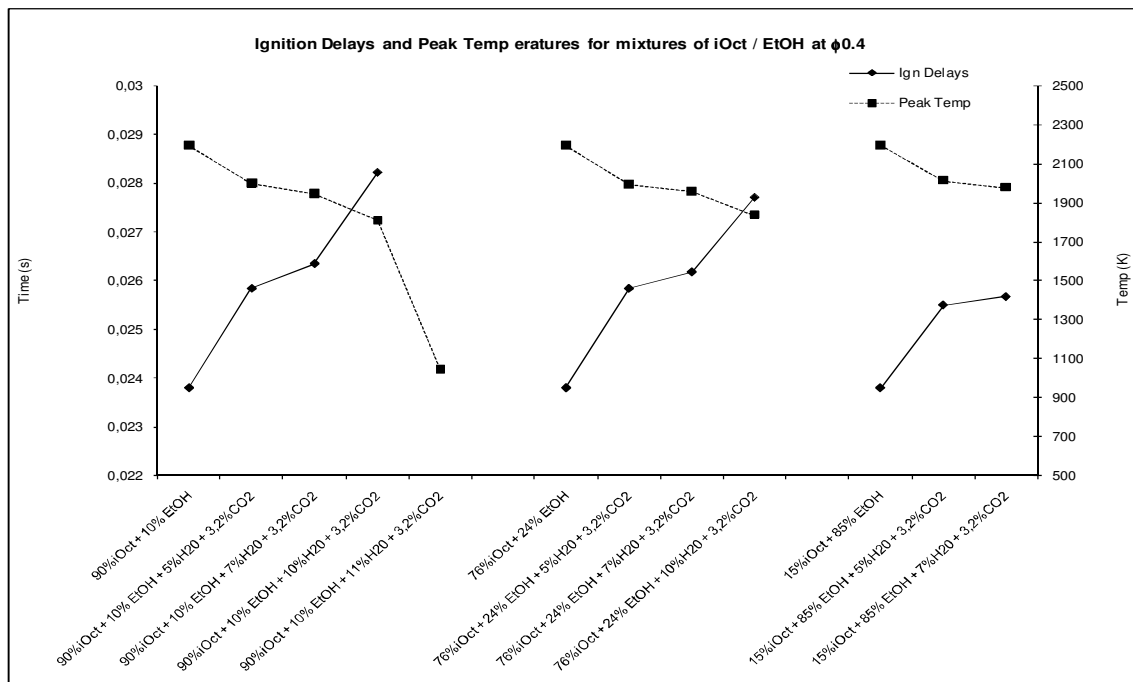


Figure 4.24 – Start of ignition and peak temperatures for different iso-octane / ethanol mixtures ran with different equivalence ratio and a compression ratio of 11,5.

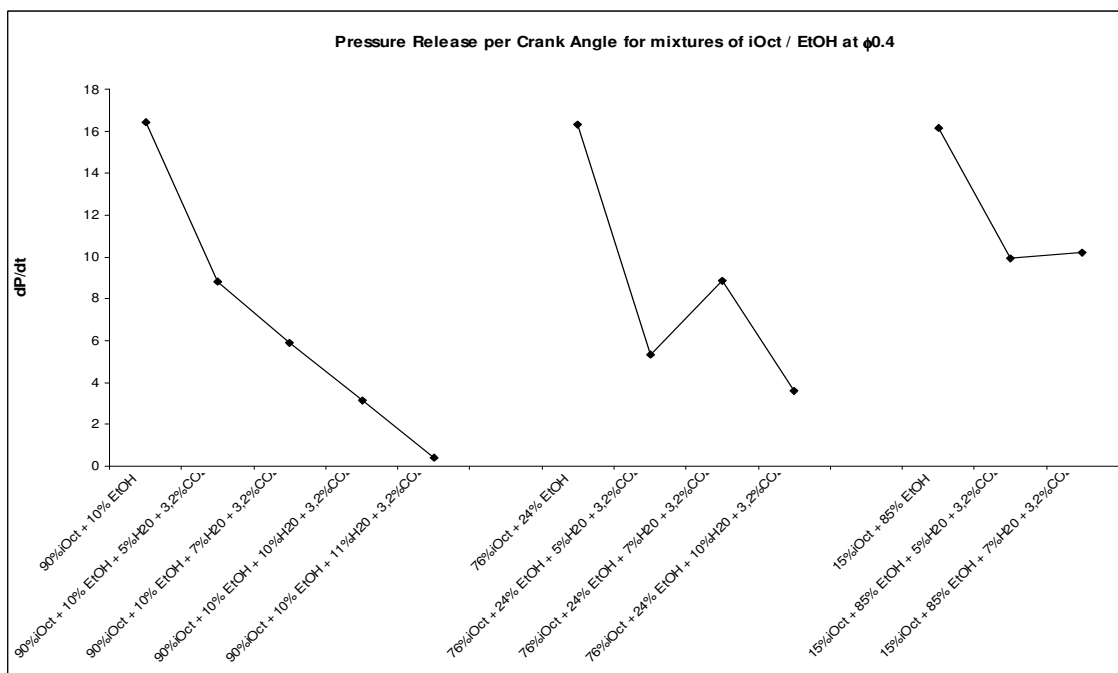


Figure 4.25 – Pressure release per CA for different iso-octane / ethanol mixtures ran with different equivalence ratio and a compression ratio of 11,5.

4.3.4 Summary

The work presented in chapter 4 refers to HCCI simulations performed using CHEMKIN. This work was carried with the aim of studying HCCI combustion and understanding the effect that different fuels and additives have in combustion.

It is possible to conclude from the results obtained, that nitric oxide plays an important role in the combustion of iso-octane as a combustion enhancer. The presence of this additive when ethanol was the fuel produced no significant changes. In HCCI, due to the spontaneous auto-ignition through the all charge, high heat released rates make combustion a very harsh process. By adding elements with the capacity to absorb part of this heat, combustion can be smoothed, as it was observed when added water and carbon dioxide were supplied as additives to a combustion mixture.

The mixtures that looked more suitable for engine operation, from the simulations made, were selected to be tested experimentally. These mixtures are presented in table 4.4 with the results for the start of ignition (s), peak temperatures (K), peak pressures (atm) and data for the pressure release rate per crank angle.

Table 4.4 - Results for different mixtures that achieved desired results.

	Ign Delay (s)	T(K) max	P(atm) max	dP/dt max
iOct + 15% H ₂ O + 8,46% CO ₂ + 0,32% NO	0,02635	1715,93	22,8	2,72
iOct + 15% H ₂ O + 8,46% CO ₂ + 0,2% NO	0,02669	1689,56	20,74	2,2
iOct + 16% H ₂ O + 8,46% CO ₂ + 0,32% NO	0,02669	1670,94	20,38	1,96
iOct + 17% H ₂ O + 8,46% CO ₂ + 0,32% NO	0,02788	1602,6	16,92	0,78
EtOH + 15% H ₂ O + 6,42% CO ₂ + 0,32% NO	0,02601	1785,19	25,27	3,39
EtOH + 15% H ₂ O + 6,42% CO ₂	0,02618	1790,92	25,35	2,89
EtOH + 16% H ₂ O + 6,42% CO ₂	0,02635	1770,11	24,41	3,48
EtOH + 17% H ₂ O + 6,42% CO ₂	0,02669	1737,58	22,68	1,98
EtOH + 18% H ₂ O + 6,42% CO ₂	0,02703	1702,75	20,99	1,79
EtOH + 19% H ₂ O + 6,42% CO ₂	0,02771	1647,27	18,18	1,18
EtOH + 20% H ₂ O + 6,42% CO ₂	0,02907	1519,56	17,38	0,45
90%iOct + 10% EtOH + 10%H ₂ O + 3,2%CO ₂	0,02822	1807,79	17,59	3,12
76%iOct + 24% EtOH + 10%H ₂ O + 3,2%CO ₂	0,02771	1836,43	19,55	3,58

When iso-octane was used as the fuel, nitric oxide played an important role. The chemistry involved when this additive was added promoted the oxidation of initial fuel which enabled further dilution of the initial fuel/air mixture to unreachable values, without the presence of nitric oxide (Section 2.2.8).

When the fuel was changed to ethanol a higher percentage of water was tolerable, in comparison when iso-octane was used. Ignition was still possible with 20% (per mass) of water inside the combustion chamber. By allowing the dilution with large amounts of water, combustion with smoother pressures released was achieved in several mixtures. The influence of nitric oxide when ethanol was the fuel was negligible, most possibly due to an oxidation mechanism where NO do not intervene.

When mixtures of iso-octane and ethanol were used the maximum amount of water was restrained to 10%. The mixtures containing 90% and 76% of iso-octane produced some results that may fall inside the operating window for engine (regarding pressures release per ca). For the 15% iso-octane mixture there were no smooth results achieved.

CHAPTER 5

INTRODUCTION

Chapter 5 gives an explanation of the modifications done to CHEMKIN single-zone to make it able to work as simplified multi-zone model. It also summarizes the results obtained when simulation models were employed (single and multi-zone simulation) in CHEMKIN. A discussion of the results obtained is given and the chapter ends with the conclusions of the work done as well with a scope of what could be done to further study the HCCI concept at Cranfield University.

5.1 Multi-Zone Simulation

Some of the limitations of the single-zone HCCI modelling can be overcome by performing a multi-zone modelling approach. In this particular modelling, the combustion chamber is divided into an arbitrary number of volumes, representing different zones such as crevices, boundary layers and core zones.

During the course of this work comparisons were made between single zone simulation and multi-zone model that was developed during the course of this work. In the multi-zone model developed on this thesis, three different zones were used. They represented the crevices and cylinder walls and two different core zones with different initial constitutions and temperatures. This is to account for deviations from the theoretical homogeneous charge that would be in the cylinder.

A schematic of the model used in this work is shown in figure 5.1.

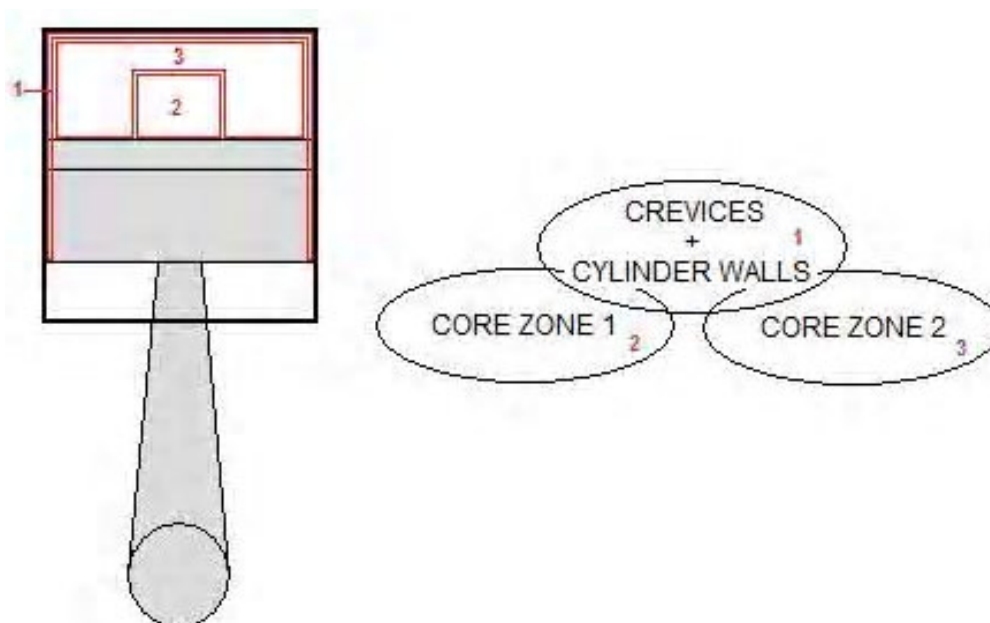


Figure 5.1 – Schematic representation of the multi-zone model used.

On this simplified model there was no exchange mass between the defined zones and no interaction between the three different zones.

Zone 1, as seen in the pictures represents the crevices and the cylinder walls. Its initial volume and air-fuel mixture was set to 5% of the original values while the initial temperature was defined as 350K, an assumption. Zone 2 and 3 represented two different core zones. One smaller zone (typically 35% of the original volume and air-fuel ratio) accounted for a hotter zone, and the bigger zone (60% of the original volume and air-fuel mixture) which was slightly cooler.

This approach allowed a better representation of the combustion phenomenon and the results obtained show some differences with regards to the single zone simulations results.

5.2 Single Zone vs Multi-Zone Results

After running several simulations in CHEMKIN with different air-fuel mixtures (comprising combinations of different initial fuels and different amounts of carbon dioxide) all the results obtained were analyzed.

Carbon dioxide properties make it a good additive for engine use when the goal is to decrease the heat release rate from the combustion event. This additive was used as diluent into the air-fuel mixture to absorb part of the heat release during the spontaneous auto-ignition process with the intent of making combustion smoother and decrease the mechanical stress imposed to the piston and to the engine.

Table 5.1, show the mixtures that were selected to run the comparisons done with both simulation models.

Table 5.1 – Mixtures used in the CHEMKIN simulations.

	iC8H18 (g/min)	C2H5OH (g/min)	H2O (g/min)	CO2 (g/min)
100% iOct	9.40	-	-	12.50
95% iOct	8.93	-	0.47	12.50
90% iOct	8.46	-	0.94	12.50
85% iOct	7.99	-	1.41	12.50
100% EtOH	-	18.10	-	12.50
90% EtOH	-	17.19	0.91	12.50
80% EtOH	-	14.48	3.62	12.50
70% EtOH	-	12.67	5.43	12.50
60% EtOH	-	16.26	10.84	12.50
55% EtOH	-	15.73	12.87	12.50
50% EtOH	-	14.30	14.30	12.50
45% EtOH	-	12.87	15.73	4.22
40% EtOH	-	10.84	16.26	4.22
100% E85	2.11	11.99	-	12.50
95% E85	2.06	11.69	0.35	12.50
90% E85	2.01	11.39	0.71	12.50
85% E85	1.96	11.09	1.06	12.50
100% E24	7.14	2.26	-	12.50
95% E24	6.97	2.20	0.24	12.50
90% E24	6.79	2.14	0.47	12.50
85% E24	6.61	2.09	0.71	12.50
100% E10	10.62	1.18	-	4.22
95% E10	10.35	1.15	0.29	12.50
90% E10	10.09	1.12	0.59	12.50
85% E10	9.82	1.09	0.89	12.50

The development of a simple multi-zone model within CHEMKIN should improve the simulation results and lead to more realistic pressure and peak pressures traces.

In appendix A4 is possible to find graphs for pressure (in atmospheres) inside the cylinder, against the position of the piston in crank angles, for all mixtures showed on table 5.1. It is also possible to find graphs showing the pressure release per crank angle.

On each graph, results for the single-zone model and for multi-zone model are showed, making a direct comparison possible.

5.2.1 Ethanol Fuelled HCCI

Section 5.2.1 compares the results obtained when the initial fuel used was ethanol. This fuel is of particular relevance and interest as it can be obtained from an alternative source other than by processing fossil fuels, which makes it a candidate to play an important role to decrease the global fossil fuel consumption on the automotive sector.

The 90/10 mixture ethanol/water was selected for graphic analysis. This mixture as the name anticipate is made of 90% ethanol and 10% of water. A mixture with this concentration was prepared and the pressure vessel that worked as fuel supply to the injector was filled with it.

Looking at the pressure trace from figure 5.2 obtained with either the single-zone and multi-zone simulation model it is possible to identify a initial increase in pressure, from -50 CA. These behaviour, showed on both simulation results corresponds to the oxidation reactions that take place on the low temperature regime. For the pressure trace that refers to the single-zone model is possible to observe a plateau just before TDC (0 CA degrees) where pressure seems to stabilize before the ignition event occurs, this behavior is explained by the so called negative temperature coefficient, explained in more detail on chapter 3 under section 3.2.

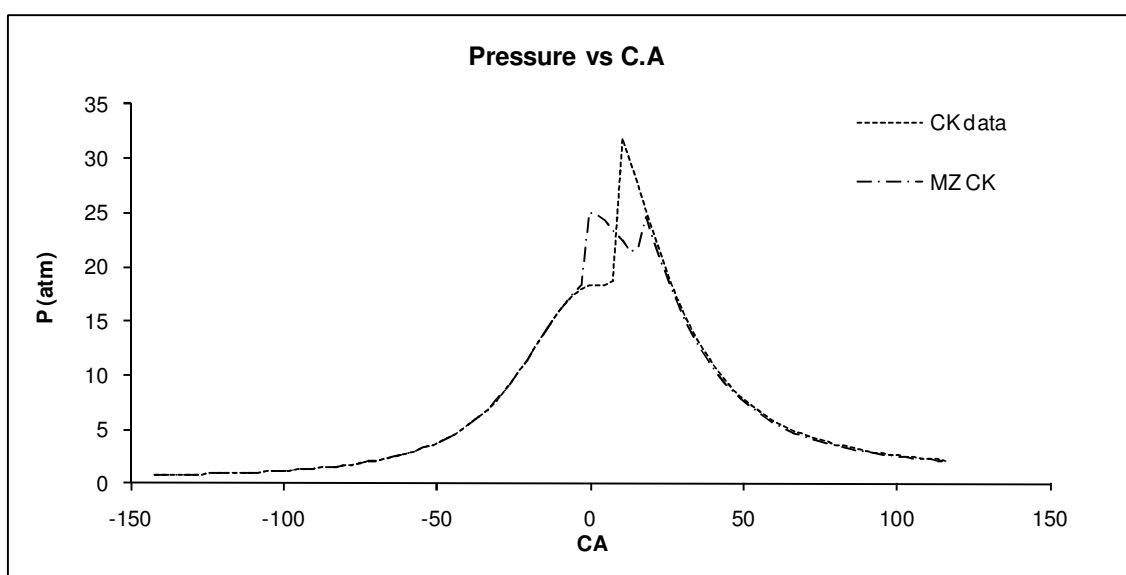


Figure 5.2 – Pressure vs crank angle comparison between simulations for 90% EtOH/water mixture diluted with CO₂.

Looking at the single-zone data, auto-ignition of the air-fuel mixture takes place at a later stage (compared with the other profiles). This only happens when specific temperature and pressure conditions inside the cylinder are met. This explanation is theoretically only as it assume a completely homogeneous charge where at once all the mixture auto-ignites. This theory is the exact assumption behind single-zone simulation. In real world there is no perfect homogeneous mixture that will ignite all at once, inside the cylinder different zones will behave slightly different and ignition will occur first on one spot and then will expand through the all mixture. This is what the introduction of a multi-zone model (even as simple as the one used on this work) try to reproduce.

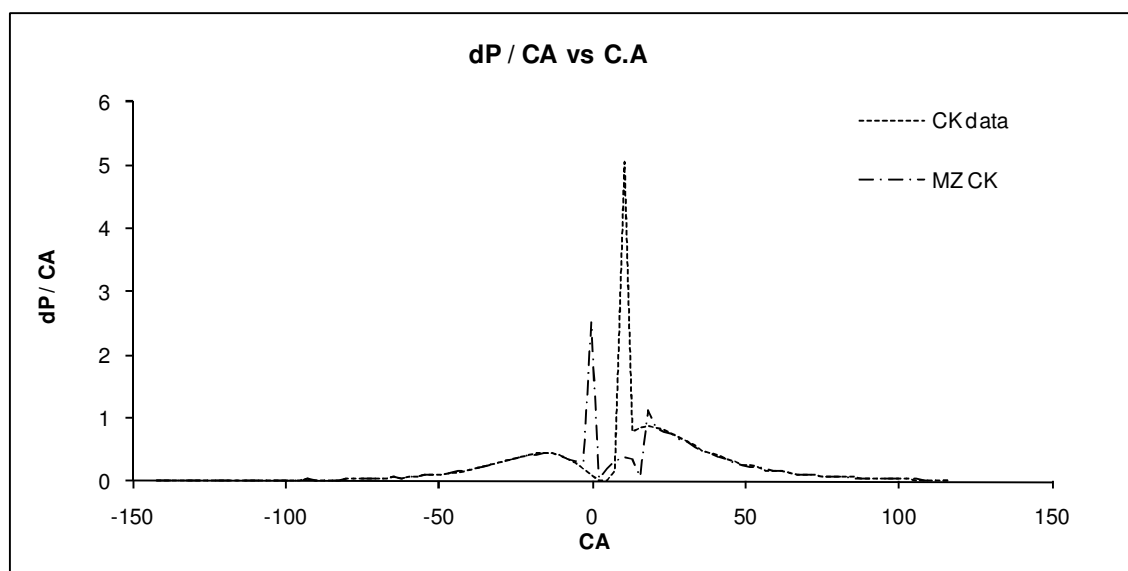


Figure 5.3 – Pressure release per crank angle vs crank angle comparison between simulations for 90% EtOH/water mixture diluted with CO₂.

The data obtained with the multi-zone model shows what it seems to be an improvement when compared with single-zone model. Although it shares the first initial behavior with the simpler model, from TDC the profile is different. This improvement in the simulation results is directly related with the different approach that includes different zones inside the cylinder which simulate the real deviation to the charge inhomogeneity.

Figure 5.4 shows the pressure–volume diagram obtained with the simulations. Due to the fact that CHEMKIN simulations only comprised the compression and the power stroke, the figure only show this part of the cycle, making it possible

to identify only the gross indicated work per cycle and not the net indicated work, were losses on the intake and exhaust strokes would be identifiable.

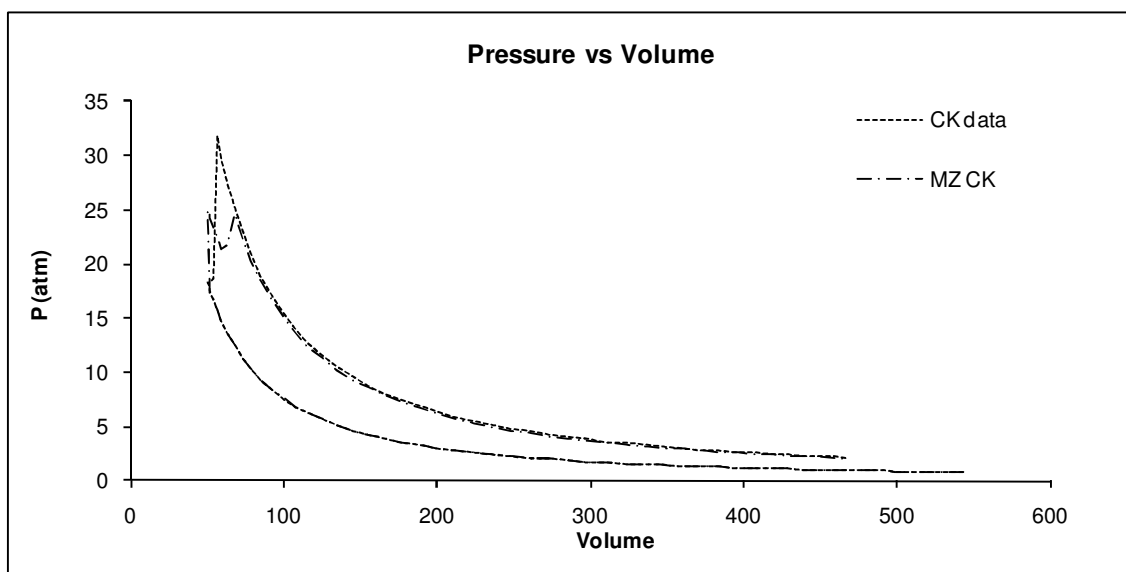


Figure 5.4 – Pressure vs volume comparison between simulations for 90% EtOH/water mixture diluted with CO₂.

Looking at the graph traces it is possible to see that as expected the multi-zone model produces lower peak pressures.

With regards to absolute values of area, gross indicated work, the single-zone model produces larger values than the multi-zone model.

These results are presented in the following table 5.2.

Several different mixtures having ethanol as base fuel were used and table 5.2 summarizes all these results. Data is shown for peak pressure achieved in the combustion chamber (in atmospheres), gross indicated mean effective pressure (in bar), pressure released per crank angle (unitless) and start of ignition (in seconds).

Several comparisons are possible by looking at the data provided. The differences between the use of single and multi-zone model are easily identified.

This data also offers a good comparison between the results obtained when the dilution with water increased.

Table 5.2 – Summary of the results obtained when fuel used was ethanol.

Fuel	Results	P max (atm)	GIWC(bar)	dP / dt	Start of Ig (ca)
100% EtOH	CK	31.19	23.92	2.67	10
	MZ CK	26.41	19.31	2.15	2
90% EtOH	CK	31.80	21.85	5.05	10
	MZ CK	25.10	19.90	2.52	0
80% EtOH	CK	30.14	19.50	4.26	10
	MZ CK	23.56	17.79	2.21	0
70% EtOH	CK	26.85	16.90	1.60	10
	MZ CK	25.92	15.94	2.45	2
60% EtOH	CK	26.85	14.57	1.37	8
	MZ CK	23.91	13.66	0.95	13
55% EtOH	CK	25.64	13.26	1.51	10
	MZ CK	22.84	9.68	1.05	10
50% EtOH	CK	25.05	11.96	1.10	8
	MZ CK	22.74	11.20	0.69	18
45% EtOH	CK	24.74	10.67	0.86	5
	MZ CK	22.72	10.01	0.65	18
40% EtOH	CK	22.29	9.26	0.62	21
	MZ CK	21.36	7.71	0.56	21

Looking at the data provided in the table is possible to see that the mixture ethanol/ water 90% is the one that achieved an higher peak pressure inside the cylinder. This mixture also showed the higher pressure release per crank angle.

The continuous addition of water leads to a decrease in pressures. This behaviour is expected as water is added into the mixture partly with the intent to decrease the combustions harshness by absorbing part of the heat released during the auto-ignition of the fuel-air mixture.

Other possible comparison to make based on the values given from table 5.2 is the one between the GIWC (gross indicated work per cycle) values. Generally, it follow the same trend as the peak pressures. According to the data obtained when a multi-zone model is used, the highest GIWC obtained was for a 90% ethanol /10% water mixture. A plausible explanation for this behaviour is that the addition of water delayed the auto-ignition event to its most favourable point in terms of piston position, also it is possible to argue that adding water made

combustion slower which in turn made it last longer producing effective work during more time on the power stroke.

As a high level summary of this section is possible to say that the multi-zone model produced slightly different results than the single-zone model, as expected. It is believed that the results obtained with the more complex model, better reproduce reality. This is due to the fact that the conditions that implied on a multi-zone model are more in agreement with reality. There is no perfect homogeneous charge, as simulated in single zone models, and the mixture will never ignite all at once. Richer spots inside the combustion chamber will always happen and those will tend to ignite first and drive the remainder of the air-fuel mixture towards auto-ignition.

With regards to the fuel constitution it was interesting to verify that combustion was achieved with ethanol over a large spread of dilution with water. HCCI combustion was still achieved with a mixture containing only 40% of ethanol and 60% of water.

The most suitable mixtures for HCCI operation in the conditions tested were the 90, 80 and 70% ethanol/water mixtures. It is important to highlight that all mixtures were ran in the presence of carbon dioxide. The role of this additive was, as with water, to absorb part of the heat release and make combustion smoother. For the highly water diluted mixtures the quantity of carbon dioxide had to be decreased to allow for combustion.

5.2.2 E85 Fuelled HCCI

The results obtained when the initial fuel used was E85 (name given to a fuel mixture containing 85% ethanol and 15% petrol) are shown on this section. This fuel mixture is available for consumer use at different countries such as Brazil, Canada, Sweden, UK, and USA, amongst others. This fuel appears as an effort to bring alternative fuels into the market and reduce the fossil fuel dependence. Because E85 can play an important role as an alternative fuel its potential as HCCI combustion fuel was studied.

Figure 5.5 to figure 5.7 show the data obtained in a graphical mode. As before the plotted results are, pressure vs CA (figure 5.5), pressure release per CA (figure 5.6) and pressure vs volume (figure 5.7).

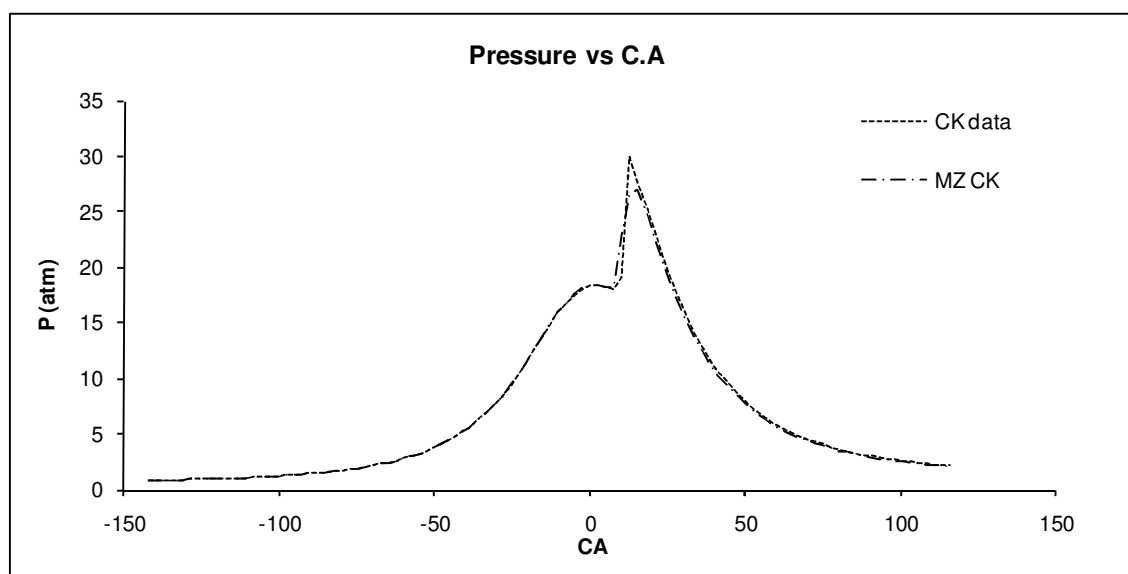


Figure 5.5 – Pressure vs crank angle comparison between simulations for 90% E85/water mixture diluted with CO₂.

The simulation results show low temperature oxidation of the fuel with combustion ramping up from around -50 CA. The multi-zone model shows a lower peak pressure when compared to the single-zone model. Besides there is not any other noticeable advantages by using the more complex simulation model, by looking at the above figure.

By looking at figure 5.6 is possible to note that both simulation models have the same start of ignition with the difference between them being the pressure release figures achieved. As expected in the multi-zone model the ignition occurs in a smoother process as the charge ignites in steps, instead of all igniting at once leading to larger pressure release rates.

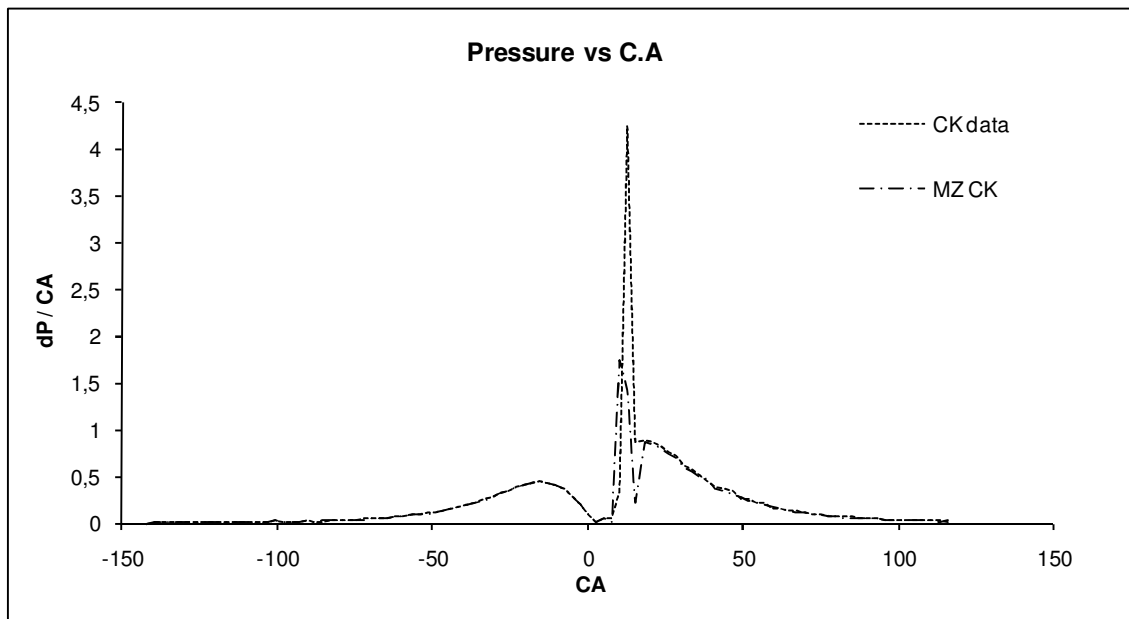


Figure 5.6 – Pressure release per crank angle vs crank angle comparison between simulations for 90% E85/water mixture diluted with CO₂.

The following figure, 5.7, shows the pressure vs volume graph. Very similar profiles were obtained for both the simulation models.

Only after carefully observation at the picture it is possible to identify that the multi-zone model has a lower peak pressure. This is in agreement with figure 5.5 where it is possible to identify the differences between the pressure traces.

As stated before on the analysis of the results obtained in this set of simulations, the improvement of the multi-zone model is only on peak pressures obtained which are lower and should reflect better, reality.

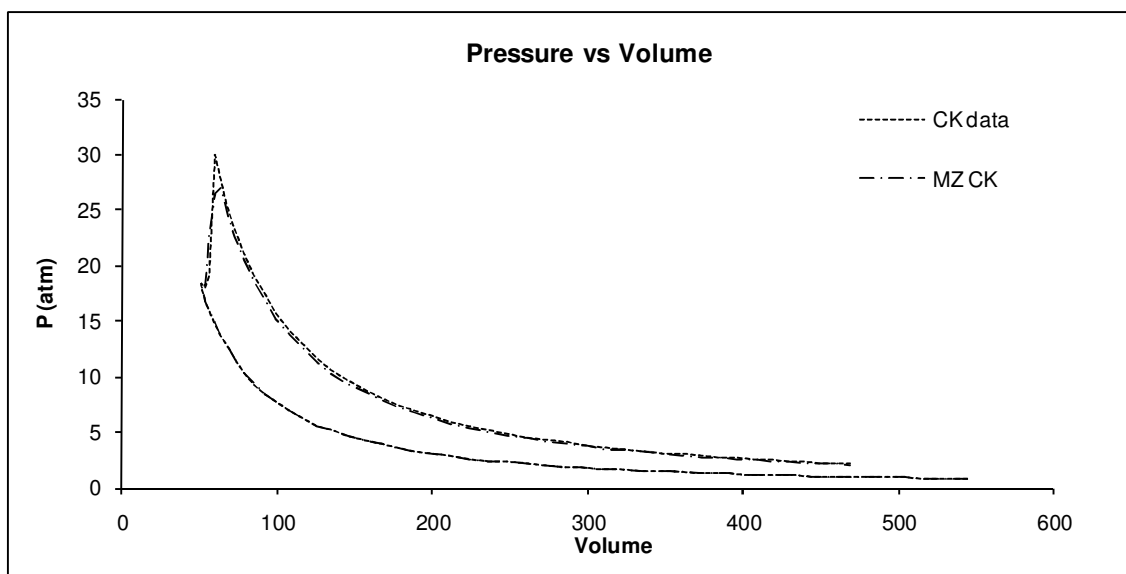


Figure 5.7 – Pressure vs volume comparison between simulations for 90% E85/water mixture diluted with CO₂.

To summarize the results obtained for the set of simulations done using E85 as fuel, table 5.3 on the next page is displayed.

This set of results showed that the addition of water did not bring any particular advantage with regards to combustion or engine operation. The only advantage of adding water into this mixture would be economic.

Table 5.3 – Summary of the results obtained when fuel used was E85.

Fuel	Results	P max (atm)	GIWC(bar)	dP / dt	Start of Ign (ca)
100% E85	CK	31.49	23.91	5.16	13
	MZ CK	25.58	22.32	2.18	10
95% E85	CK	30.71	22.77	4.69	13
	MZ CK	25.60	20.42	2.20	2
90% E85	CK	30.00	21.57	4.26	13
	MZ CK	27.06	20.43	1.75	10
85% E85	CK	29.28	20.45	3.85	13
	MZ CK	27.15	19.47	1.79	8

During this series of simulations the effect of the increase in water percentage did not seem to influence the start of ignition.

Looking at the gross indicated work per cycle (GIWC), the results followed the more expected trend. The pure mixture was the one that produced more work

during the cycle whereas the addition of water did generally lead to a decrease on the amount of work produced.

The differences in the results when using the multi-zone CHEMKIN model over the single-zone model are noticeable and are expected to be closer to real engine behaviour.

5.2.3 E24 Fuelled HCCI

The name given to a mixture of 24% ethanol and 76% gasoline is E24.

This mixture was selected to be used, as it is already in use in Brazil on cars without any engine modifications. This can be too much of a push forward as other studies say that no more than 10% of ethanol should be present in an unmodified engine, due to corrosion of fuel lines. However, as said before for the case of E85 this future can be of importance in the mid term future and for that reason was object of study with regards to application on a HCCI engine.

Figure 5.8 shows the in-cylinder pressure when the fuel is E24.

It is possible to see a differences in the pressure profile obtained when using single or a multi-zone model approach.

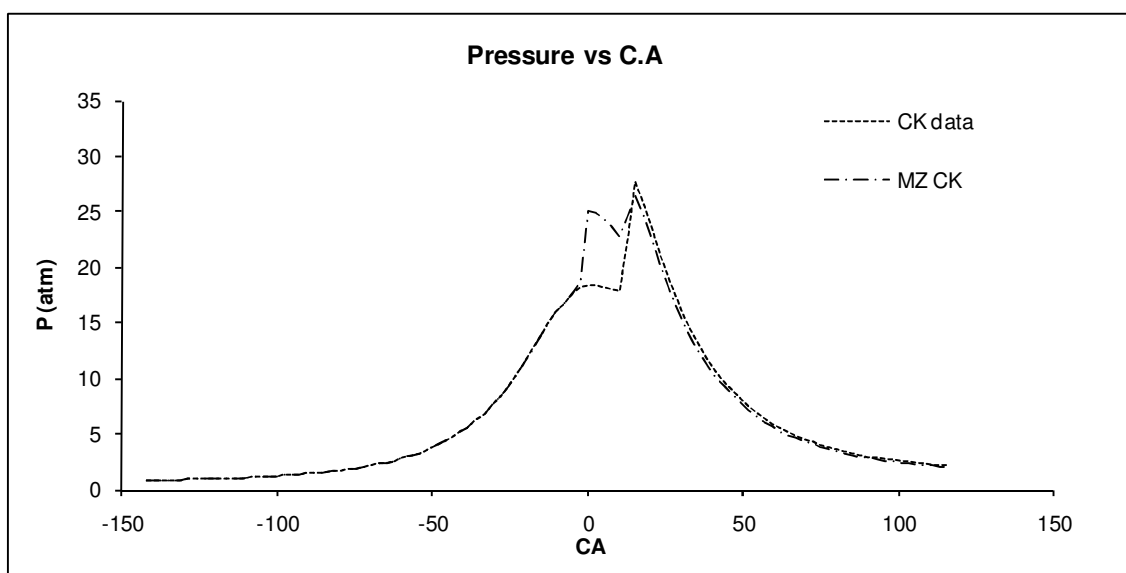


Figure 5.8 – Pressure vs crank angle comparison between simulations for 90% E24/water mixture diluted with CO₂.

By looking at figure 5.8 it is possible to see that there is no improvement on peak pressure achieved. Both simulation models are close to each other with regards to peak pressure achieved, however it is possible to note that the multi-zone model predicts start of ignition to happen earlier than single-zone model does.

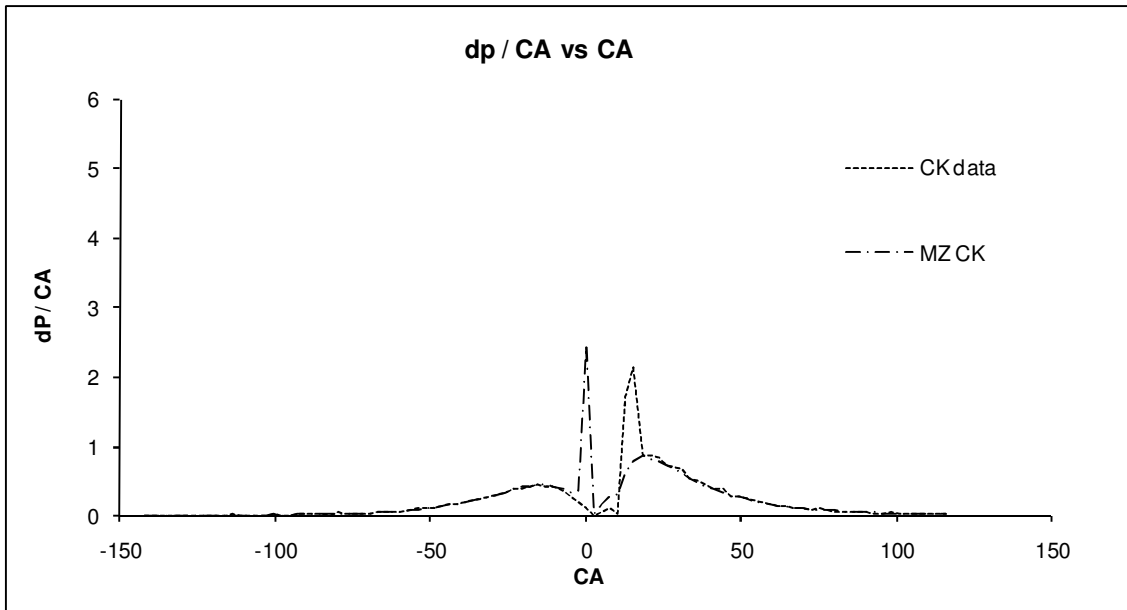


Figure 5.9 – Pressure release per crank angle vs crank angle comparison between simulations for 90% E24/water mixture diluted with CO₂.

The pressure release per crank angle analysis from figure 5.9 just confirms what has been pointed in regards to the differences seen with the use of the more complex simulation model. The simulations performed in the multi-zone model also show a slightly lower value for pressure release data.

Figure 5.10 shows the pressure vs volume diagram obtained for the particular mixture consisting of 90% E24 and 10% water.

The two profiles obtained are similar, and by looking at the figure is not possible to estimate which of the traces corresponds to more work done in the cycle.

That is only possible to compare by looking at the results in table 5.4.

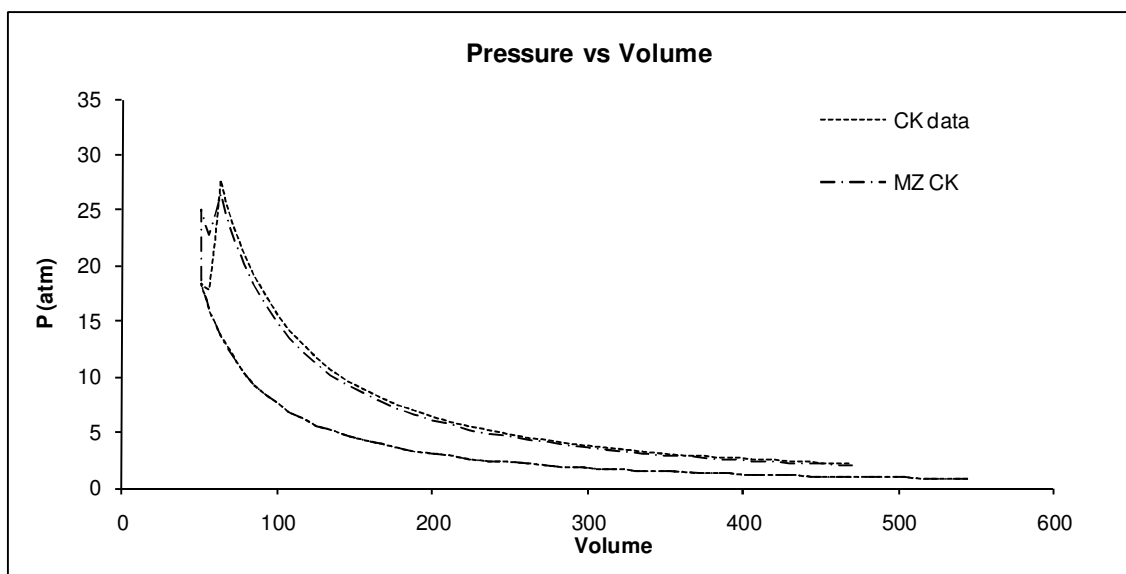


Figure 5.10 – Pressure vs volume comparison between simulations for 90% E24/water mixture diluted with CO₂.

Table 5.4, show all the results obtained when the fuel used was the E24 mixture. The mixture that reaches higher peak pressure and highest pressure release per CA is the no diluted mixture.

Table 5.4 – Summary of the results obtained when fuel used was E24.

Fuel	Results	P max (atm)	GIWC(bar)	dP / dt	Start of Ign (ca)
100% E24	CK	29.10	23.26	3.78	15
	MZ CK	26.16	21.97	2.36	10
95% E24	CK	28.46	22.17	3.00	15
	MZ CK	24.31	9.20	2.05	0
90% E24	CK	27.75	21.12	2.13	15
	MZ CK	26.62	19.91	2.44	0
85% E24	CK	27.06	19.99	1.96	13
	MZ CK	26.04	19.91	1.82	2

The introduction of water in the initial fuel mixture did not produce much difference.

Nevertheless it is important to know that the presence of water do not have a negative impact on combustion as this characteristic may be of importance from an economic point of view.

5.2.4 E10 Fuelled HCCI

This section presents the results obtained when the fuel used was E10. The name refers to the composition of 10% ethanol and 90% iso-octane. This fuel is already being used in several countries around the world. There seems to be a general agreement from car manufacturers that a fuel containing this much amount of ethanol is safe to be used in an engine without any modifications done into it and without affecting reliability.

Looking at figure 5.11 it is possible to see that the multi-zone simulation model brought some advantages over the simpler single-zone model. The start of ignition is quicker when comparing with the single-zone model.

On this particular case, where 10% of water was added, the peak pressure data obtained with the single-zone model is lower than the one obtained with the multi-zone model, which is somehow unexpected.

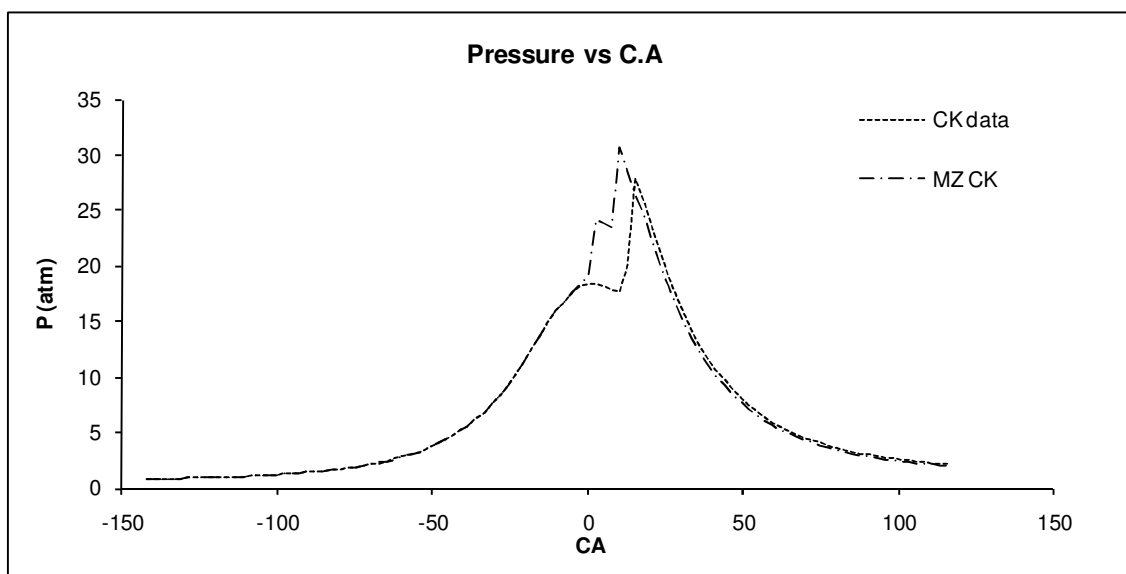


Figure 5.11 – Pressure vs crank angle comparison between simulations for 90% E10/water mixture diluted with CO₂.

The graph where pressure release per crank angle is plotted against crank angle, figure 5.12, shows what has been described previously. The multi-zone model predicts a start of ignition slightly earlier than the single-zone model. The pressure release per crank angle values is similar on both simulation models.

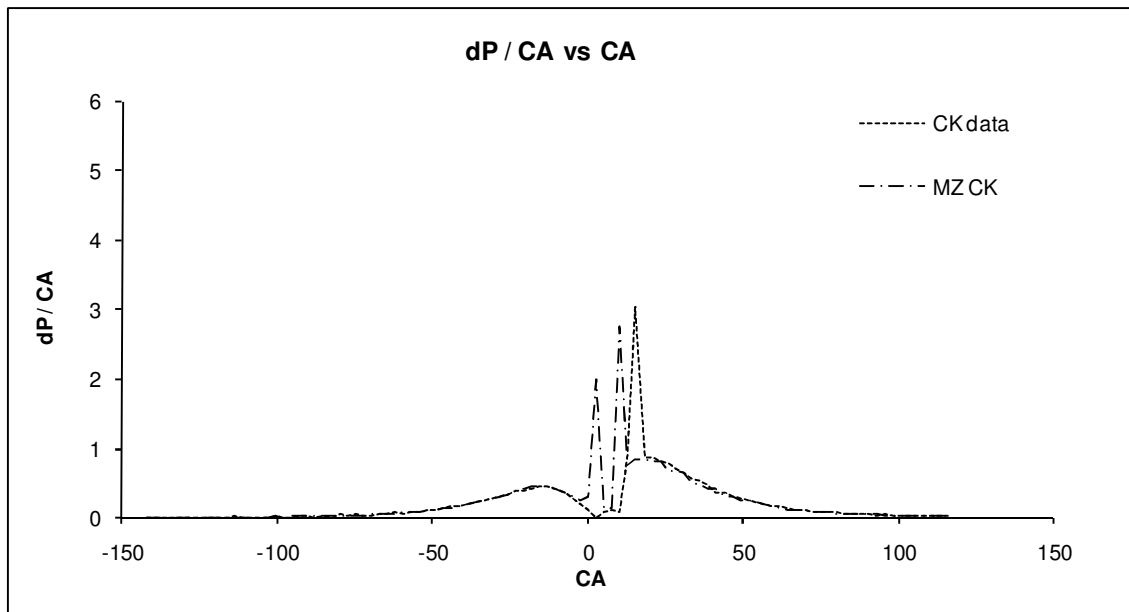


Figure 5.12 – Pressure release per crank angle vs crank angle comparison between simulations for 90% E10/water mixture diluted with CO₂.

The pressure vs volume graph, on figure 5.13, shows once more very similar profiles obtained for both simulation models.

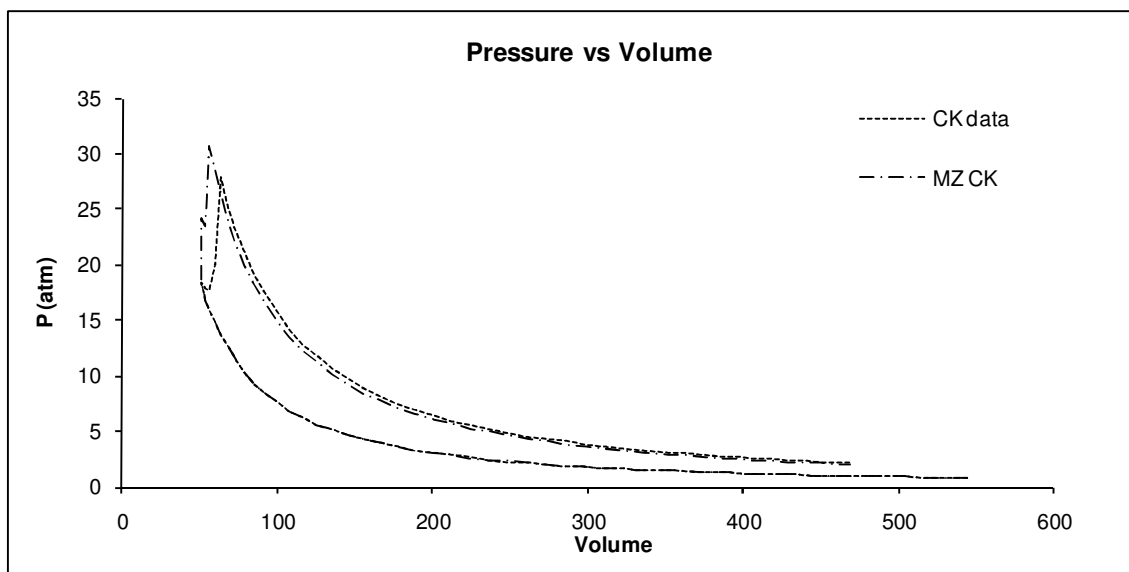


Figure 5.13 – Pressure vs volume comparison between simulations for 90% E10/water mixture diluted with CO₂.

Data provided in table 5.5 summarizes the simulation results obtained.

The peak pressure data obtained by using the multi-zone simulation model is generally lower than the peak pressures obtained with the single-zone model.

Regarding the pressure releases per crank angle, we can see that as expected the addition of water leads to a decrease in these values.

Table 5.5 – Summary of the results obtained when fuel used was E10.

Fuel	Results	P max (atm)	GIWC(bar)	dP / dt	Start of Ign (ca)
100% E10	<i>CK</i>	<i>29.16</i>	<i>23.28</i>	<i>4.15</i>	<i>15</i>
	MZ CK	26.13	19.91	2.45	10
95% E10	<i>CK</i>	<i>28.46</i>	<i>22.07</i>	<i>3.58</i>	<i>15</i>
	MZ CK	27.30	21.03	2.10	2
90% E10	<i>CK</i>	<i>27.80</i>	<i>21.02</i>	<i>3.04</i>	<i>15</i>
	MZ CK	30.61	20.28	2.75	2
85% E10	<i>CK</i>	<i>27.10</i>	<i>19.87</i>	<i>2.53</i>	<i>15</i>
	MZ CK	21.68	8.56	1.11	10

5.2.5 Iso-Octane Fuelled HCCI

Instead of using regular unleaded gasoline, iso-octane was used during the course of this work. To reproduce a regular unleaded fuel in CHEMKIN a much more complex mechanism for fuel oxidation would have to be used with the increased cost in computational time. This would be due to the fact that the unleaded fuel available from pumps is constituted by a very complex mixture of hydrocarbons and several different additives.

Figure 5.14 shows the comparison between simulation models when the fuel used was iso-octane, for pressure vs crank angle. Although peak pressures achieved are similar in both simulation models, the start of ignition predicted from the more complex simulation model happens earlier and it is expected to be a better match to what would happen in an engine.

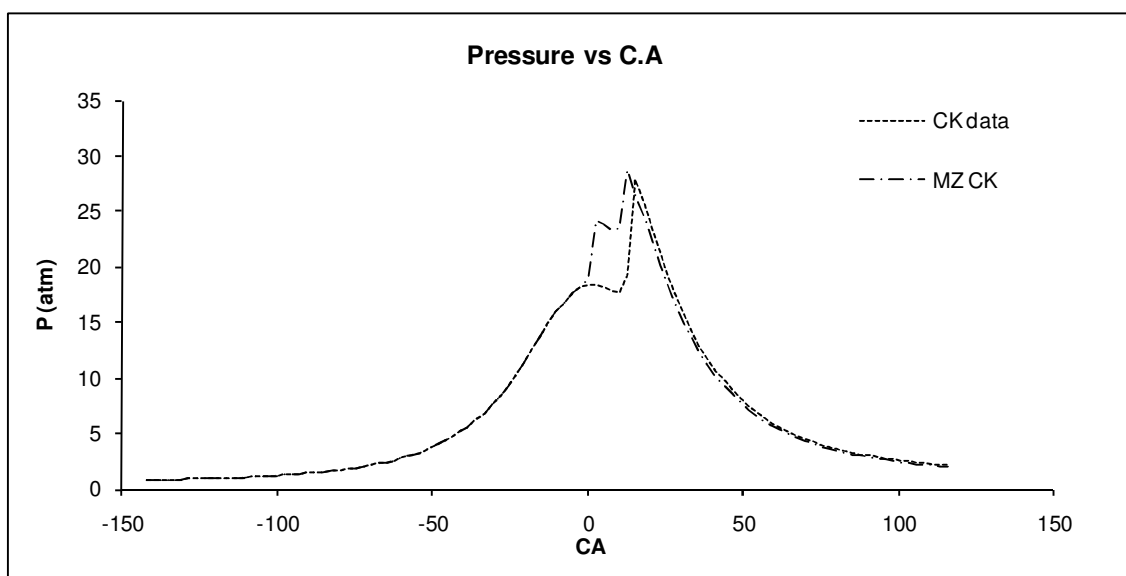


Figure 5.14 – Pressure vs crank angle comparison between simulations for 90% iso-octane/water mixture diluted with CO₂.

From figure 5.15 it is possible to graphically visualize the improvement in the start of ignition predictions from the simpler to the more complex approach. Again and as expected the pressure release rate is lower for the multi-zone model.

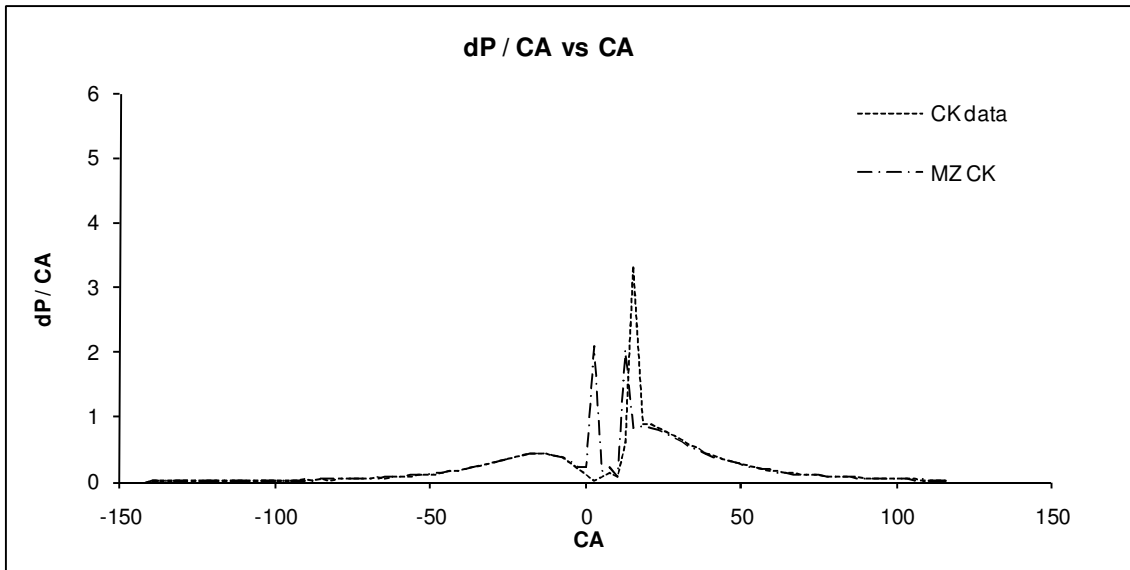


Figure 5.15 – Pressure release per crank angle vs crank angle comparison between simulations for 90% iso-octane/water mixture diluted with CO₂.

The pressure vs volume traces that can be found in figure 5.16 do show a similar profile for the results obtained via modelling.

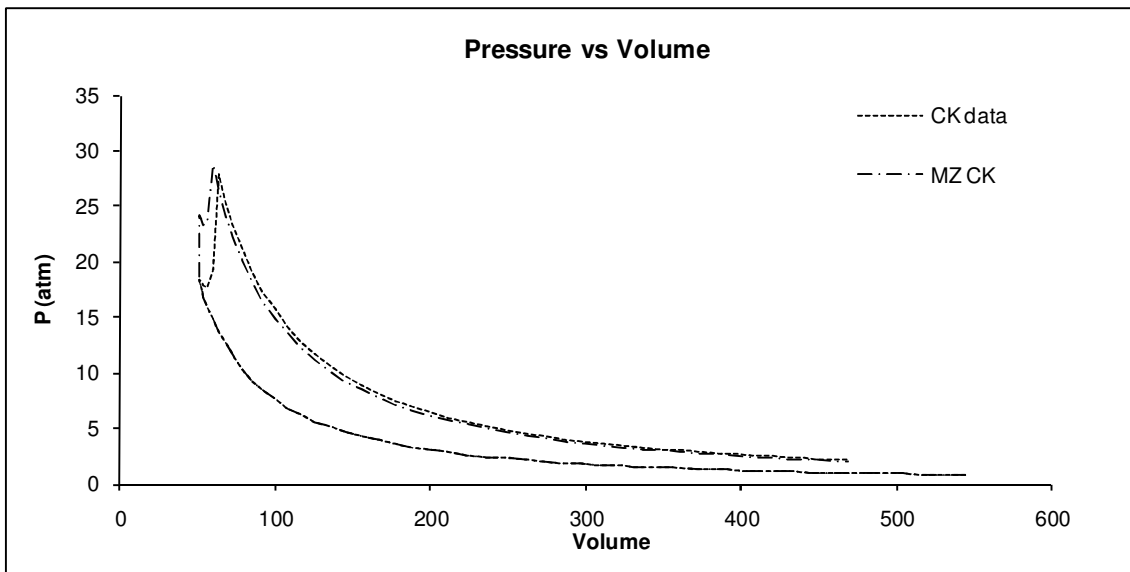


Figure 5.16 – Pressure vs volume comparison between simulations for 90% iso-octane/water mixture diluted with CO₂.

Table 5.6 summarizes the results obtained when the fuel used was iso-octane.

Table 5.6 – Summary of the results obtained when fuel used was iso-octane.

Fuel	Results	P max (atm)	GIWC(bar)	dP / dt	Start of Ignition (ca)
100% iOct	CK	29.19	23.24	4.30	15
	MZ CK	31.31	22.58	2.86	10
95% iOct	CK	28.50	22.13	3.82	15
	MZ CK	28.18	21.24	2.64	8
90% iOct	CK	27.81	20.98	3.33	15
	MZ CK	28.72	20.11	2.09	2
85% iOct	CK	27.11	19.85	2.89	15
	MZ CK	22.70	8.41	0.80	5

5.3 Discussion of Results

The comparison between the two CHEMKIN models showed an enhancement when using the more complex approach. The results obtained with the multi-zone model are believed to be more realistic due to the assumptions made. As mentioned in a single-zone model the combustible mixture is assumed to be perfectly homogeneous and to ignite all at once and in a very rapid process, following this theory the simulated results should always be an over predicted representation of what happens in reality, this with regards to the peak pressures and pressure release rates results obtained. These results tend to be higher than the results achieved when a more complex approach to modelling is employed.

The results obtained for start of ignition tend also to show what is believed to be an improvement when using the multi-zone model, as they are generally shorter than the results obtained with the single-zone modelling. The rationale behind is that assuming that the charge is perfectly homogeneous the auto-ignition conditions (temperature, pressure, chemical radical's concentration) will take longer to be met than that for example a heterogeneous mixture where at some localized spots high temperatures would be achieved and auto-ignition would take place, pushing the remaining mixture to auto-ignite as well.

As explained before and illustrated in figure 5.1, this model was constituted by three different zones. Two zones simulate the core areas inside the combustion chamber and the third zone simulated the cylinder walls and crevices. Generally, this model produced what is believed to be an improvement in the predicted results over the single-zone model.

This is summarized in figure 5.17 (for the case when ethanol was used as fuel).

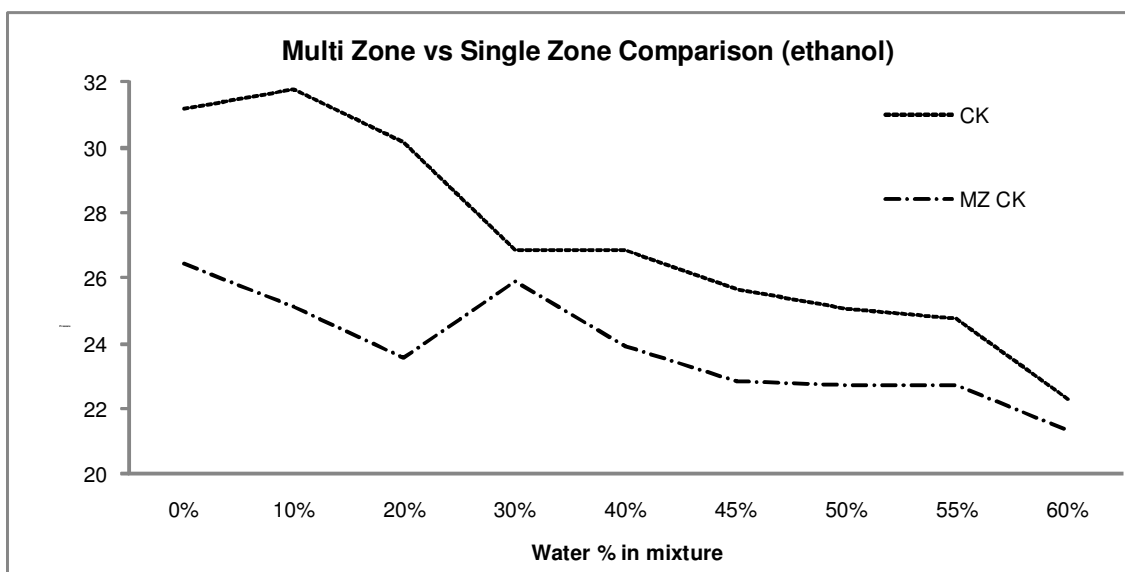


Figure 5.17 – Comparison between simulation results, for peak pressure, when the fuel used was ethanol.

The complete set of data can be found in appendix 4.

A noticeable characteristic of all results produced with the multi-zone model is the two ignition stages that are possible to observe by looking at the pressure vs crank angle figures. These reflect the different ignition timing that occurs on the two core zones that were defined. With some extra refinement those inhomogeneities of results would probably disappear and the results would probably be more accurate.

Generally the effect of water not only made combustion smoother, as it is possible to observe when looking at the pressure release per crank angle data, but also in some cases, improved the work done on each combustion cycle. An explanation for this may be the fact that with water combustion will take more time until completion which will increase the time window where force is being made on the piston. (Exception to this behaviour seems to be the case when the initial fuel used was E85).

Adding to the improvements seen in the majority of the cases it is worth to highlight that economically the addition of water can be of importance. By reducing the amount of fuel since water is added into the combustible mixture and when refining bio-fuels since this work proves that there is no need of having pure ethanol to run in a HCCI engine.

5.4 Recommendations and Future Work

The simulation work done on this thesis is of particular relevance as it studies in detail the effect of different additives and fuels in HCCI combustion.

The flexibility that HCCI combustion allows with regards to the type of fuel used was confirmed during the course of this work, several simulations indicate that HCCI would be successfully achieved on experimental engine using ethanol, iso-octane and mixtures of both these fuels.

There are numerous research projects that can be done at Cranfield University to further investigate HCCI combustion, to study its characteristics, understand its limitations and identify strategies to overcome some of its difficulties.

With the set up currently in place at Cranfield University and with minor modifications it would be possible to experimentally study HCCI combustion on the single cylinder Ricardo E6 engine available. Study the effect of exhaust gas recirculation as a more complex mixture would be extremely interesting. By employing this strategy the need of having external heating elements would be decreased and some comparisons would be possible, such as the direct effect of using exhaust gas recirculation on emissions formation.

One other aspect to study that would be to screen for HCCI viability within different engine speeds and try to determine the low and high rev limit tolerable to accomplish HCCI combustion.

As seen in several references a precise control method for fuel injection it is an advantage when running HCCI combustion.

It would be interesting to develop a more sophisticated injection method. Maybe even direct injection in the piston with different split injections to deviate from the concept of having a homogenous charge and try to create a stratified charge that would ignite easily. With direct injection earlier on the intake stroke would also allow the formation of homogeneous mixtures and comparisons would be possible.

Using spark assistance to start the engine and study transitions between spark ignition combustion to HCCI combustion would be of great interest, however this study would involve several modifications on the cylinder head used and much more complex engine management systems would be required to allow for the control of the spark timing.

Regarding the simulation work, there is also potential to further investigate the use of CHEMKIN to simulate HCCI conditions.

It would be extremely useful to obtain the required licences to be able to run CHEMKIN linked with a one dimensional engine cycle simulation program (e.g. WAVE from Ricardo which is already available at Cranfield University).

By joining forces between this two computational simulation programs a more detailed study regarding engine behaviour and performance would be possible and better predictions should be achieved.

The development of a more complex multi-zone model would also be extremely valuable. Beyond increasing the number of zones, when comparing with the simple approach used on this thesis, developing some interaction between the different zones would be the way forward that would most probably lead to better simulation results that would correlate better with experimental work to take place in parallel. Besides some licence requirements that would be needed, recommendations for a project like the one mentioned is not to initiate it without computational programming support or without a researcher with vast experience in code writing.

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APPENDIX 1

Appendix 1 gives an overview on the contribution of the automotive sector on global emissions in a group of European countries. An overview on the automotive legislation for exhaust emissions in Europe is also given, where stricter limits on pollutant emissions, particularly for nitrogen oxides and particulates, are going to be introduced.

A1.1 Automotive Contribution on Emission Formation

The figure presented bellow, summarise the emission results of a group of 27 European countries in 2006.

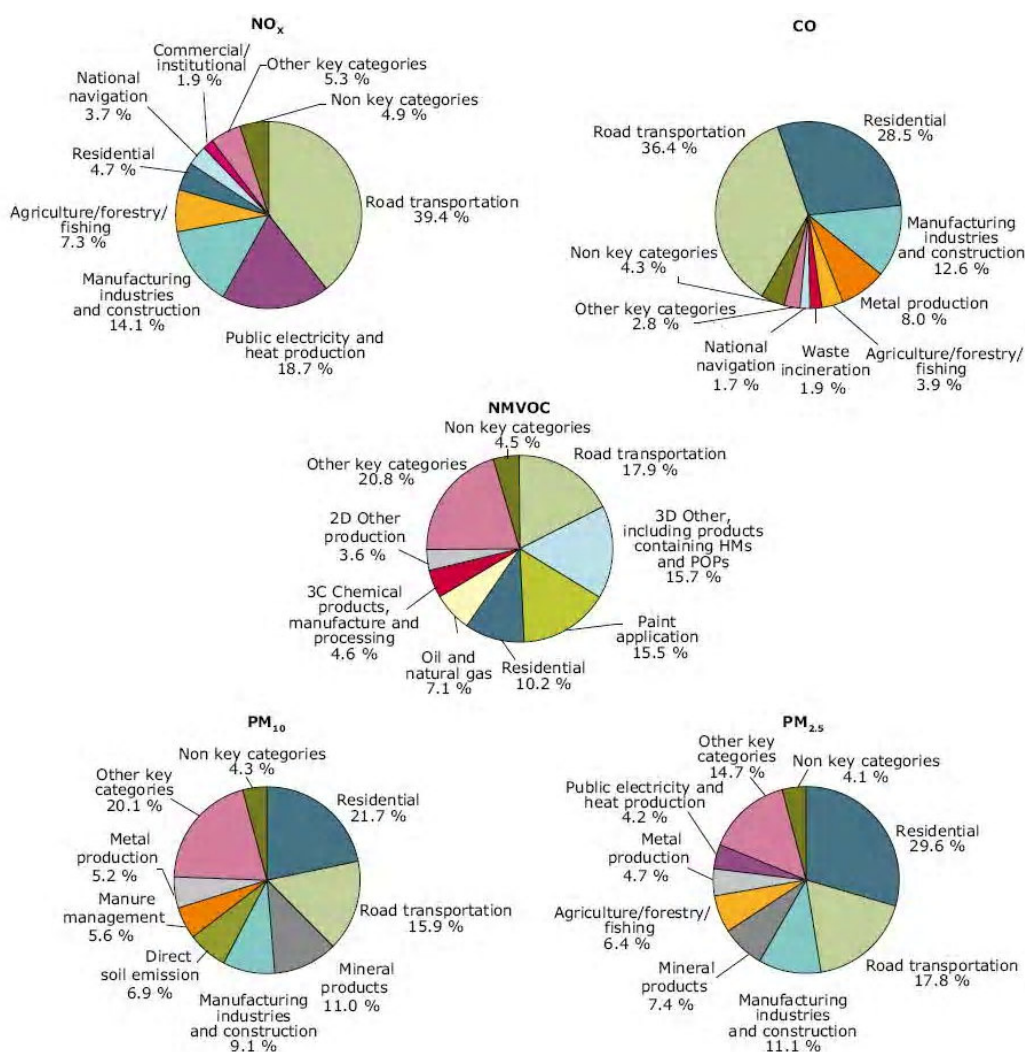


Figure A1.1 – Contribution of key categories to EU-27 emissions of NO_x, CO, NMVOCs, PM10 and PM2.5.

From figure A1.1 it is possible to see the contribution of road transportation on the overall emissions. In Europe the automotive sector alone is responsible for 39% of the nitrogen oxide emissions far from the second responsible for these emissions, the power sector which is responsible for 18.7%. It is also the main responsible for the emission of carbon monoxide and non-methane volatile organic compounds. Regarding the emission of particulates, the automotive sector is the second most important source, just behind the residential sector.

A1.2 Emission Limits

To address the problem described above new legislation for the automotive sector is going to be in place in a short period of time.

A1.2.1 Euro 5 standard

Emissions from diesel vehicles:

- carbon monoxide: 500 mg/km;
- particulates: 5 mg/km (80% reduction of emissions in comparison to the Euro 4 standard);
- nitrogen oxides (NO_x): 180 mg/km (20% reduction of emissions in comparison to the Euro 4 standard);
- combined emissions of hydrocarbons and nitrogen oxides: 230 mg/km.

Emissions from petrol vehicles or those running on natural gas or LPG:

- carbon monoxide: 1 000 mg/km;
- non-methane hydrocarbons: 68 mg/km;
- total hydrocarbons: 100 mg/km;
- nitrogen oxides (NO_x): 60 mg/km (25% reduction of emissions in comparison to the Euro 4 standard);
- particulates (solely for lean burn direct-injection petrol vehicles): 5 mg/km (introduction of a limit that did not exist for the Euro 4 standard).

A1.2.2 Euro 6 Standard

All vehicles equipped with a diesel engine will be required to substantially reduce their emissions of nitrogen oxides as soon as the Euro 6 standard enters into force. For example, emissions from cars and other vehicles intended to be used for transport will be capped at 80 mg/km (an additional reduction of more than 50% compared to the Euro 5 standard). Combined emissions of hydrocarbons and nitrogen oxides from diesel vehicles will also be reduced. These will be capped at, for example, 170 mg/km for cars and other vehicles intended to be used for transport.

A1.2.3 Implementation of the standards

As soon as the Euro 5 and Euro 6 standards enter into force, Member States must refuse the approval, registration, sale and introduction of vehicles that do not comply with these emission limits. Time frame:

- the Euro 5 standard will come into force on 1 September 2009 for the approval of vehicles, and from 1 January 2011 for the registration and sale of new types of cars;
- the Euro 6 standard will come into force on 1 September 2014 for the approval of vehicles, and from 1 January 2015 for the registration and sale of new types of cars;

Tax incentives granted by Member States and intended to encourage earlier use of the new limits will be authorised if:

- they apply for all new vehicles available for sale on the market of a Member State, which meet the requirements of this Regulation before their entry into force;
- they end on the date the new limits come into force;
- are worth less than the cost, including fitting, of the devices used on any type of motor vehicle in order to guarantee that the values laid down are not exceeded.

A1.2.4 Other Obligations on Manufacturers

In addition to complying with the emission limits mentioned above, vehicle manufacturers must also ensure that devices fitted to control pollution are able to last for a distance of 160 000 km. In addition, conformity must be checked for a period of 5 years or over a distance of 100 000 km.

Given the need for uniform standards, the Commission will establish committees to devise, before 2 July 2008, procedures, tests and specific requirements for the following:

- tailpipe emissions, including test cycles, low ambient temperature emissions, emissions at idling speed, exhaust gas opacity, and the proper functioning and regeneration of after-treatment systems.
- evaporative emissions and crankcase emissions;
- on-board diagnostic systems and the performance of anti-pollution devices while the vehicle is running;
- durability of anti-pollution devices, replacement parts for emissions control systems, in-service conformity, conformity of production and technical control;
- carbon dioxide emissions and fuel consumption;
- hybrid vehicles;
- extension of approvals and requirements for small manufacturers;
- requirements for testing equipment;
- reference fuels, such as petrol, diesel fuel, gas and biofuels.

Easy and clear access to information on vehicle repair and maintenance is key to guaranteeing free competition on the internal market for information and repair services. To this end, manufacturers must ensure that independent operators have easy, restriction-free and standardised (particularly in terms of compliance with the OASIS standard) access via the internet to information on the repair and upkeep of vehicles, without discrimination in favour of dealerships and official repair workshops. This obligation covers on-board diagnostic systems and their components, diagnostic tools and testing

equipment. Charges for accessing such information are permitted if they are reasonable and proportionate.

APPENDIX 2

No matter how efficient an engine can be made, exhaust emissions are a side product of combustion. Unburned hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides will always be present as combustion by products. To control the emission of these gases into the atmosphere strategies must be employed.

Appendix 2 presents a summary of the exhaust after treatments systems used by motor companies to meet emission legislations.

A2.1 Gasoline after treatment systems

Since the late eighties gasoline powered vehicles have been using three way catalysts, TWC. The name is due to the capability of the catalytic converter of oxidizing UHC and CO to CO₂ and water and the capability of reducing NO_x to N₂.

The basics behind the catalytic converters are the same as before, but development brought new materials which are more efficient on abating emissions, more cost effective and more durable. The effectiveness of the removal of the three species is generally limited to the stoichiometric region, as it is possible to observe in figure A2.1.

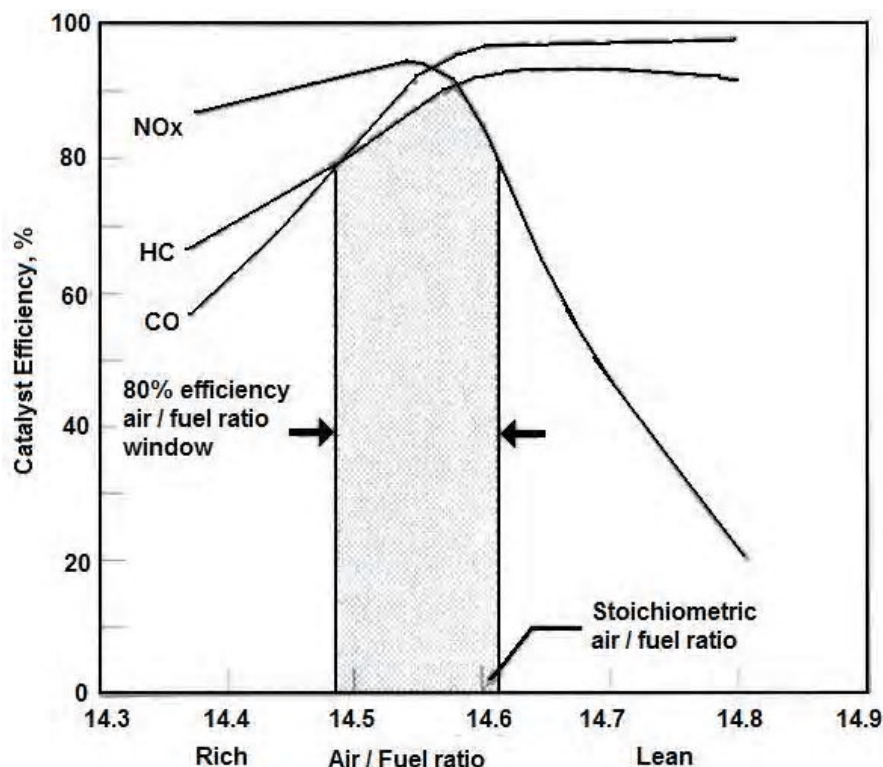


Figure A2.1: Conversion efficiency for NO, CO and HC for a TWC as a function of air/fuel ratio.^[7]

The oxygen concentration in the exhaust gas is key on the catalytic conversion process. At rich engine operation, the conversion efficiency on the oxidizing reactions that convert UHC and CO is reduced. There is not enough oxygen for these reactions to take place. When the engine is running lean, the oxidation is effective but the reduction of NOx suffers dramatically. Too much oxygen available makes it difficult for reduction reactions to take place. This goes against chemical equilibrium rules where it is stated that in a rich species environment the formation of more of that specie will not be favoured.^[7,83]

Together with tight engine control systems (exhaust oxygen sensors) that feedback into the engine management system and have direct effect on the fuel quantity injected, oxygen storage capacity OSC, is an important characteristic of a TWC. A good catalyst should have the capability of store oxygen during lean engine operation and release it, during rich conditions where oxygen concentration is scarce.^[84]

Lean combustion together with direct injection is seen as the natural development for gasoline engines. They will improve the fuel economy and

consequently will diminish the CO₂ coming out from the exhaust pipe. However, as explained before an engine operating for the majority of its time under lean conditions, do not favour the performance of the catalytic converter. It generates a rich oxygen environment in which the three way catalyst (TWC) efficiencies are lower.

To overcome this problem, new technologies for NO_x abatement are being developed. As seen before an oxidation catalyst can work effectively under a lean atmosphere, so the problem lies in the reduction of nitrogen oxides to nitrogen.

Two technologies under the focus of research are lean NO_x traps and Selective Catalytic Reduction, SCR.

The first technology works by adsorbing NO₂ during the engine lean operation. In the rich oxygen environment the NO_x is oxidized to NO₂ which is stored. Once the engine switches to stoichiometric or rich operation the NO₂ is desorbed and reduced by hydrocarbons, hydrogen and carbon monoxide to N₂. The second processed pointed is more complex. Ammonia, NH₃ can react with NO_x to produce elemental nitrogen. Ammonia is supplied externally under the form of urea which will be stored in a tank. Via a urea fuel system, amounts of this product are injected into a filter capable of trapping NO_x. Reduction reaction will than take place with the formation of nitrogen as a product of it.^[83]

To finalize the after treatment systems on gasoline applications, it is important to refer that from the implementation of euro 6 onwards (2014), direct injection gasoline engines will have to meet particulate emissions as well.

Because of this requirement, gasoline particulate filters are being developed.

As they will be generally similar to diesel particulate filters, an overview on this technology is given on the next section together with other diesel after-treatment systems.

A2.2 Diesel after treatment systems

Diesel engines are more fuel efficient than gasoline engines due to its lean combustion operation, which results in the production of less CO₂. The lean nature of diesel engine operation results in a cooler combustion with less NO_x, CO and UHC emissions, however the design of the combustion process results in high particulate emissions levels. On the forthcoming years emission legislation on diesel engines will become tighter and new after treatment systems will be required particularly to reduce PM and NO_x emissions.

Due to lean operation, with excess oxygen always present in the exhaust gases and with cooler temperatures, a different type catalyst than the one required in gasoline applications is used. Diesel oxidation catalyst, DOC, is the common after treatment system found in all diesel vehicles. These type catalysts, as the name say, have the capability to oxidize UHC and CO to CO₂. They work in a similar way to TWC in gasoline applications but without the capability of reducing nitrogen oxides.

One other after treatment technology commonly used in diesel engines as an addition to the DOC and with the intent to reduce PM emission levels of diesel exhaust is the diesel particulate filter (DPF).

The DPF is designed to remove the PM from the exhaust gas of a diesel engine. It does that by collecting the PM. All filters will have a maximum amount of PM they can collect and when that limit is reached the filter must have the capability of regenerate itself. This process is called DPF regen and basically it consists in burning the trapped particulates to CO₂. There are several strategies to allow for filter regen, but the most common is by creating higher temperature conditions in the filter so the oxidation of the particulates can be successful.^[83]

As said before, direct injection gasoline engines will have to meet a particulate number legislation from euro 6, which means that gasoline engines will have to employ a similar system to the one described.

On diesel engines, euro 6 will bring much tighter emissions for NO_x. Controlling this emission in diesel engines will pass by using a dedicated and specific new

after-treatment system. As pointed before automotive manufacturers are developing systems like NOx traps or Selective Catalyst Reduction. A brief summary on these technologies is found on the previous section.

A2.3 HCCI after treatment systems

An HCCI engine will run lean and one of the theoretical advantages it will bring is the reduced particulate matter and NO_x emission formation, when compared with a diesel engine. As explained before, this is achieved by burning a lean homogeneous mixture that will combust at cooler temperatures without the formation of rich spots.

As a TWC catalyst will not work in a lean environment, it is expected that this type of engines will have to use an after treatment system consisting of a oxidation catalyst (DOC like) and a dedicated system for abatement of NO_x emissions (Lean NO_x traps or SCR).

APPENDIX 3

On appendix 3 it is possible to see all the species included in the CHEMKIN detailed kinetic mechanisms. All the species are constituted by a combination of the elements; hydrogen, carbon, oxygen, nitrogen and argon.

The complete set of chemical equations is not presented as it too extended. It can be found at,

https://www-pls.llnl.gov/?url=science_and_technology-chemistry-combustion-ic8h18

to the mechanism and thermodynamic data that can be found in the link above more reactions and data were added from,

<http://www.me.berkeley.edu/gri-mech/version30/text30.html>

to allow for NO_x formation modelling.

Bellow the elements and species used on the mechanism mentioned can be found.

Elements:

h c o n ar

Species:

h	nh	hcn	hco	ch3o
h2	nh2	h2cn	co2	c2h6
o	nh3	hcn	ch2(S)	c2h4
o2	nnh	hcn	c	c2h5
oh	no	hocn	ch3	ch2
h2o	no2	hnco	ch4	ch
n2	n2o	nco	ho2	c2h
n	hno	co	h2o2	c2h2
	cn		ch2o	

c2h3	ac5h11	nc3h7o2h	pc4h9o	cc5h10ooh-b
ch3oh	bc5h11	ic3h7o2h	sc4h9o	cc5h10ooh-d
ch2oh	cc5h11	nc3h7o2	ic4h9o	dc5h10ooh-a
ch2co	dc5h11	ic3h7o2	tc4h9o	dc5h10ooh-b
hcco	ac5h10	c3h6o1-3	pc4h9o2h	dc5h10ooh-c
c2h5oh	bc5h10	ic4h8o	sc4h9o2h	ac5h10ooh-ao2
pc2h4oh	cc5h10	ic4h8oh	ic4h9o2h	ac5h10ooh-bo2
sc2h4oh	ic5h9	io2c4h8oh	tc4h9o2h	ac5h10ooh-co2
ch3co	nc5h12	ic4h7o	tc4h9o2	ac5h10ooh-do2
ch2cho	c5h11-1	c4h7o	ic4h9o2	bc5h10ooh-ao2
ch3cho	c5h11-2	c4h8oh-1	sc4h9o2	bc5h10ooh-co2
c3h4-a	c5h11-3	c4h8oh-2	pc4h9o2	bc5h10ooh-do2
c3h4-p	neoc5h12	c4h8oh-1o2	ch3coch2o2	cc5h10ooh-ao2
c3h6	neoc5h11	c4h8oh-2o2	ch3coch2o2h	cc5h10ooh-bo2
c4h6	c2h5o	c4h8ooh1-2o2	ch3coch2o	cc5h10ooh-do2
nc3h7	ch3o2	c4h8ooh1-3o2	neoc5ketox	dc5h10ooh-ao2
ic3h7	c2h5o2	c4h8ooh1-4o2	neoc5kejol	dc5h10ooh-bo2
c3h8	ch3o2h	c4h8ooh2-1o2	ac5h11o2	dc5h10ooh-co2
ic4h7	c2h5o2h	c4h8ooh2-3o2	bc5h11o2	a-ac5h10o
ic4h8	c2h3o1-2	c4h8ooh2-4o2	cc5h11o2	a-bc5h10o
c4h7	ch3co2	tc4h8ooh-io2	dc5h11o2	a-cc5h10o
c4h8-2	c2h4o1-2	ic4h8ooh-io2	ac5h11o2h	a-dc5h10o
c4h8-1	c2h4o2h	ic4h8ooh-to2	bc5h11o2h	b-cc5h10o
sc4h9	o2c2h4oh	c4h8ooh1-2	cc5h11o2h	b-dc5h10o
pc4h9	ch3co3	c4h8ooh1-3	dc5h11o2h	c-dc5h10o
tc4h9	ch3co3h	c4h8ooh1-4	ac5h11o	c5h11o2-1
ic4h9	c2h3co	c4h8ooh2-1	bc5h11o	c5h11o2-2
ic4h10	c2h3cho	c4h8ooh2-3	cc5h11o	c5h11o2-3
c4h10	c3h5o	c4h8ooh2-4	dc5h11o	c5h11o2h-1
ch3coch3	c3h6ooh1-2	ic4h8o2h-i	ac5h10ooh-a	c5h11o2h-2
ch3coch2	c3h6ooh1-3	ic4h8o2h-t	ac5h10ooh-b	c5h11o2h-3
c2h5cho	c3h6ooh2-1	tc4h8o2h-i	ac5h10ooh-c	c5h11o-1
c2h5co	c3h6ooh1-2o2	c4h8o1-2	ac5h10ooh-d	c5h11o-2
c5h9	c3h6ooh1-3o2	c4h8o1-3	bc5h10ooh-a	c5h11o-3
c5h10-1	c3h6ooh2-1o2	c4h8o1-4	bc5h10ooh-c	c5h10ooh1-2
c5h10-2	nc3h7o	c4h8o2-3	bc5h10ooh-d	c5h10ooh1-3
ic5h12	ic3h7o	cc4h8o	cc5h10ooh-a	

c5h10ooh1-4	o2cho	hoc3h6o2	c3h6cho-3	c3h6coc2h5-3
c5h10ooh1-5	ocho	o2c2h4o2h	c3h6cho-2	nc3h7coc2h4p
c5h10ooh2-1	ch2(s)	ch2o2hcho	c2h5chco	nc3h7coc2h4s
c5h10ooh2-3	c3ket12	ic4h7ooh	ic3h5coch3	ic3h7coc2h5
c5h10ooh2-4	c3ket13	ic3h5cho	ic3h5coch2	ic3h6coc2h5
c5h10ooh2-5	c3ket21	tc3h6ocho	ac3h4coch3	tc3h6coc2h5
c5h10ooh3-2	nc4ket12	tc3h6cho	sc3h5coch2	ic3h7coc2h4p
c5h10ooh3-1	nc4ket13	ic3h7cho	ch3chocho	ic3h7coc2h4s
c5h10ooh1-2o2	nc4ket14	ic4h7oh	ch3chcho	ic3h7coc2h3
c5h10ooh1-3o2	nc4ket21	ic3h6co	sc3h5cho	ic3h6coc2h3
c5h10ooh1-4o2	nc4ket23	ic4h6oh	sc3h5co	tc3h6coc2h3
c5h10ooh1-5o2	nc4ket24	ic3h5co	ic3h6cho	ic3h5coc2h5
c5h10ooh2-1o2	ic4ketii	ic3h7co	c3h6cho-1	ac3h4coc2h5
c5h10ooh2-3o2	ic4ketit	tc3h6o2cho	c2h5coc2h5	ic3h5coc2h4p
c5h10ooh2-4o2	neoc5ket	tc3h6o2hco	c2h5coc2h4p	ic3h5coc2h4s
c5h10ooh2-5o2	nc5ket12	ic3h5o2hcho	c2h5coc2h4s	nc4h9cho
c5h10ooh3-1o2	nc5ket13	tc3h6ohcho	c2h5coc2h3	nc4h9co
c5h10ooh3-2o2	nc5ket14	tc3h6oh	pc2h4coc2h3	ac3h5cho
c5h10o1-2	nc5ket15	ic3h5oh	sc2h4coc2h3	ac3h5co
c5h10o1-3	nc5ket21	tc4h8cho	ic3h6chcho	c2h3chcho
c5h10o1-4	nc5ket23	o2c4h8cho	ic3h6chco	c4h8cho-1
c5h10o1-5	nc5ket24	o2hc4h8co	ac3h5chcho	c4h8cho-2
c5h10o2-3	nc5ket25	o2hc4h7cho	ic3h6chcoch3	c4h8cho-3
c5h10o2-4	nc5ket31	c3h5oh	ac3h5chcoch3	c4h8cho-4
neoc5h11o2	nc5ket32	ch2cch2oh	ic3h6chcoch2	neoc5h9q2
neoc5h11o2h	ic5ketaa	nc3h7cho	nc3h7coch3	neoc5h9q2-n
neoc5h11o	ic5ketab	nc3h7co	nc3h7coch2	ic4h6q2-ii
neoc5h10ooh	ic5ketac	ch2ch2coch3	c3h6coch3-1	hoch2o
neoc5h10ooh-	ic5ketad	c2h5coch2	c3h6coch3-2	hocho
o2 neo-c5h10o	ic5ketca	c2h5coch3	c3h6coch3-3	ic6h14
c3h5-a	ic5ketcb	ch2choohcoch3	ic3h7coch3	ac6h13
c3h5-s	ic5ketcd	ch3choohcoch3	ic3h7coch2	bc6h13
c3h5-t	ic5ketda	ch3choococh3	ic3h6coch3	cc6h13
c3h3	ic5ketdb	ch3chcoch3	tc3h6coch3	dc6h13
c3h2	ic5ketdc	c2h3coch3	nc3h7coc2h5	ec6h13
c3h6o1-2	ic4h7-i1	ch3chco	c3h6coc2h5-1	ac6h12
ho2cho	c3h6oh	ch2ch2cho	c3h6coc2h5-2	

bc6h12	ec6h12ooh-b	ic6ketac	c4h7cho2-1	fc6h12ooh-fo2
cc6h12	ec6h12ooh-c	ic6ketad	c4h7co2-1	fc6h12ooh-go2
dc6h12	ec6h12ooh-d	ic6ketae	c4h6cho2-11	fc6h12ooh-ho2
ic6h11	a-ac6h12o	ic6ketca	nc5h11cho-2	gc6h12ooh-fo2
ac6h13o2	a-bc6h12o	ic6ketcb	nc5h11co-2	gc6h12ooh-ho2
bc6h13o2	a-cc6h12o	ic6ketcd	c5h10cho1-2	hc6h12ooh-fo2
cc6h13o2	a-dc6h12o	ic6ketce	c5h10cho2-2	hc6h12ooh-go2
dc6h13o2	a-ec6h12o	ic6ketda	c5h10cho3-2	f-fc6h12o f-
ec6h13o2	b-cc6h12o	ic6ketdb	c5h10cho4-2	gc6h12o f-
ac6h13o2h	b-dc6h12o	ic6ketdc	c5h10cho5-2	hc6h12o
bc6h13o2h	b-ec6h12o	ic6ketde	ic4h9coch3	g-hc6h12o
cc6h13o2h	c-dc6h12o c-	ic6ketea	ic4h9coch2	neoc6ketff
dc6h13o2h	ec6h12o d-	ic6keteb	ic3h6ch2coch3	neoc6ketfg
ec6h13o2h	ec6h12o	ic6ketec	ic3h7chcoch3	neoc6ketfh
ac6h13o	ac6h12ooh-ao2	ic6keted	tc3h6ch2coch3	neoc6ketgf
bc6h13o	ac6h12ooh-bo2	nc4h9cho-2	neoc6h14	neoc6ketgh
cc6h13o	ac6h12ooh-co2	nc4h9co-2	fc6h13	neoc6kethf
dc6h13o	ac6h12ooh-do2	c4h8cho1-2	gc6h13	neoc6kethg
ec6h13o	ac6h12ooh-eo2	c4h8cho2-2	hc6h13	tc4h9cho
ac6h12ooh-a	bc6h12ooh-ao2	c4h8cho3-2	neoc6h12	tc4h9co
ac6h12ooh-b	bc6h12ooh-co2	c4h8cho4-2	neoc6h11	neoc5h11cho
ac6h12ooh-c	bc6h12ooh-do2	ic4h9cho	fc6h13o2	neoc5h11co
ac6h12ooh-d	bc6h12ooh-eo2	ic4h9co	gc6h13o2	tc4h9chcho
ac6h12ooh-e	cc6h12ooh-ao2	ic3h6ch2cho	hc6h13o2	tc4h8ch2cho
bc6h12ooh-a	cc6h12ooh-bo2	tc3h6ch2cho	fc6h13o2h	ic4h7cho
bc6h12ooh-c	cc6h12ooh-do2	ic3h7chcho	gc6h13o2h	ic4h7co
bc6h12ooh-d	cc6h12ooh-eo2	ic5h11cho	hc6h13o2h	ac3h4ch2cho
bc6h12ooh-e	dc6h12ooh-ao2	ic5h11co	fc6h13o	ic3h5chcho
cc6h12ooh-a	dc6h12ooh-bo2	ac5h10cho	gc6h13o	ic5h11cho-b
cc6h12ooh-b	dc6h12ooh-co2	bc5h10cho	hc6h13o	ic5h11co-b
cc6h12ooh-d	dc6h12ooh-eo2	cc5h10cho	fc6h12ooh-f	ic5h10cho-ba
cc6h12ooh-e	ec6h12ooh-ao2	dc5h10cho	fc6h12ooh-g	ic5h10cho-bc
dc6h12ooh-a	ec6h12ooh-bo2	c4h7cho1-4	fc6h12ooh-h	ic5h10cho-bd
dc6h12ooh-b	ec6h12ooh-co2	c4h7co1-4	gc6h12ooh-f	c4h7cho1-2
dc6h12ooh-c	ec6h12ooh-do2	c4h6cho1-43	gc6h12ooh-h	c4h7co1-2
dc6h12ooh-e	ic6ketaa	c4h6cho1-44	hc6h12ooh-f	c4h6cho1-23
ec6h12ooh-a	ic6ketab		hc6h12ooh-g	c4h6cho1-24

c4h7cho2-2	x1o2	oc7h14	oc7h14ooh-no2	cc8h17o2
c4h7co2-2	xc7h14ooh-	pc7h14	oc7h14ooh-qo2	dc8h17o2
c4h6cho2-21	x2o2	pc7h13	pc7h14ooh-no2	ac8h17o2h
c4h6cho2-24	xc7h14ooh-	nc7h15o2	pc7h14ooh-qo2	bc8h17o2h
ch2cchch3	y1o2	oc7h15o2	oc7h14ooh-po2	cc8h17o2h
tc4h9coch3	xc7h14ooh-	pc7h15o2	pc7h14ooh-oo2	dc8h17o2h
tc4h9coch2	y2o2	qc7h15o2	n-nc7h14o	ac8h17o
tc4h8coch3	xc7h14ooh-zo2	nc7h15o2h	n-oc7h14o	bc8h17o
ch2ccho	yc7h14ooh-	oc7h15o2h	n-pc7h14o	cc8h17o
c7h162-4	x1o2	pc7h15o2h	n-qc7h14o	dc8h17o
xc7h15	yc7h14ooh-	qc7h15o2h	o-pc7h14o	ac8h16ooh-a
yc7h15	x2o2	nc7h15o	o-qc7h14o	ac8h16ooh-b
zc7h15	yc7h14ooh-	oc7h15o	p-qc7h14o	ac8h16ooh-c
xc7h14	y2o2	pc7h15o	neoc7ketnn	ac8h16ooh-d
yc7h14	yc7h14ooh-zo2	qc7h15o	neoc7ketno	bc8h16ooh-c
xc7h13	zc7h14ooh-xo2	nc7h14ooh-n2	neoc7ketnp	bc8h16ooh-a
xc7h15o2	zc7h14ooh-yo2	nc7h14ooh-q	neoc7ketnq	bc8h16ooh-d
yc7h15o2	x-x1c7h14o	qc7h14ooh-n	neoc7keton	cc8h16ooh-d
zc7h15o2	x-x2c7h14o	nc7h14ooh-o	neoc7ketop	cc8h16ooh-b
xc7h15o2h	x-y1c7h14o	nc7h14ooh-p	neoc7ketoq	cc8h16ooh-a
yc7h15o2h	x-y2c7h14o	qc7h14ooh-o	neoc7ketpn	dc8h16ooh-c
zc7h15o2h	x-zc7h14o	y- qc7h14ooh-p	neoc7ketpo	dc8h16ooh-d
xc7h15o	yc7h14o	oc7h14ooh-n	neoc7ketpq	dc8h16ooh-b
yc7h15o	y-zc7h14o	oc7h14ooh-q	neoc7ketqn	dc8h16ooh-a
zc7h15o	c7ket24xx1	pc7h14ooh-n	neoc7ketqo	ic8eteraa
xc7h14ooh-x1	c7ket24xy1	pc7h14ooh-q	neoc7ketqp	ic8eterab
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xc7h14ooh-z	c7ket24xy2	pc7h14ooh-o	ac8h17	ic8eterad
xc7h14ooh-y2	c7ket24xx2	nc7h14ooh-	bc8h17	ic8eterbc
xc7h14ooh-x2	c7ket24zx	n2o2	cc8h17	ic8eterbd
yc7h14ooh-x1	c7ket24zy	nc7h14ooh-qo2	dc8h17	ic8etercd
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yc7h14ooh-x2	oc7h15	nc7h14ooh-po2	ic8h14	ac8h16ooh-bo2
zc7h14ooh-x	pc7h15	qc7h14ooh-oo2	ic8h15	ac8h16ooh-co2
zc7h14ooh-y	qc7h15	qc7h14ooh-po2	ac8h17o2	ac8h16ooh-do2
xc7h14ooh-			bc8h17o2	bc8h16ooh-co2

bc8h16ooh-ao2	tc4h9coc2h5	yc7h14oh-z	c6h13-2	c6h12ooh1-5o2
bc8h16ooh-do2	tc4h8coc2h5	ic4h7oh-i1	c6h13-3	c6h12ooh2-1o2
cc8h16ooh-do2	tc4h9coc2h4s	oc7h14oh-p	c6h12-1	c6h12ooh2-3o2
cc8h16ooh-bo2	tc4h9coc2h4p	pc7h14oh-o	c6h12-2	c6h12ooh2-4o2
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dc8h16ooh-co2	neoc5h10coch3	pc7h14oh-q	c6h11	c6h12ooh2-6o2
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ic8ketdd	yc7h13ooh-x1	qc7h14o-po2h	c6h13o2-3	nc6ket26
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cc6h12cho-d	yc7h13o-x2	cc8h16oh-do2	c6h12ooh3-2	c7h15-2
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	zc7h14oh-y		c6h12ooh1-4o2	c7h13

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c7h15o2-3	c7h14ooh3-6	c7h14o1-2	nc7ket35	c5h9ooh1-5
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c7h15o-2	c7h14ooh1-4o2	c7h14o2-6	nc5h11co	ar
c7h15o-3	c7h14ooh1-5o2	c7h14o3-4	c5h10cho-1	
c7h15o-4	c7h14ooh2-1o2	c7h14o3-5	c5h10cho-2	
c7h14ooh1-2	c7h14ooh2-3o2	nc7ket12	c5h10cho-3	
c7h14ooh1-3	c7h14ooh2-4o2	nc7ket13	c5h10cho-4	
c7h14ooh1-4	c7h14ooh2-5o2	nc7ket14	c5h10cho-5	
c7h14ooh1-5	c7h14ooh2-6o2	nc7ket15	nc4h9coch3	
c7h14ooh2-1	c7h14ooh3-1o2	nc7ket21	nc4h9coch2	
c7h14ooh2-3	c7h14ooh3-2o2	nc7ket23	c4h8coch3-1	
c7h14ooh2-4	c7h14ooh3-4o2	nc7ket24	c4h8coch3-2	
c7h14ooh2-5	c7h14ooh3-5o2	nc7ket25	c4h8coch3-3	
c7h14ooh2-6	c7h14ooh3-6o2	nc7ket26	c4h8coch3-4	
c7h14ooh3-1	c7h14ooh3-7o2	nc7ket31	c4h7ooh1-4	
c7h14ooh3-2	c7h14ooh4-1o2		c4h7o1-4	

APPENDIX 4

On appendix 4 it is possible to find graphs for pressure against the position of the piston in crank angle, graphs showing the pressure release per crank angle and graphs for pressure vs volume. On each graph, results for the single-zone model and of the multi-zone model are showed, making a direct comparison possible.

Ethanol Fuelled HCCI – 100% Ethanol

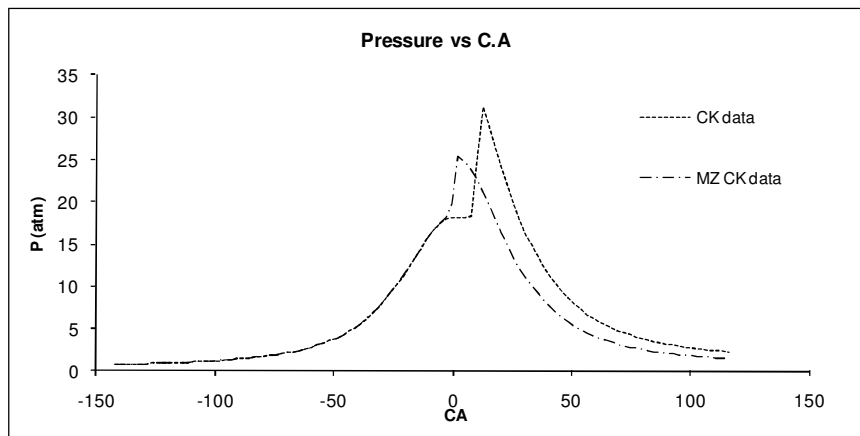


Figure A4.1 – Pressure vs crank angle comparison between simulation for 100% EtOH mixture diluted with CO_2 .

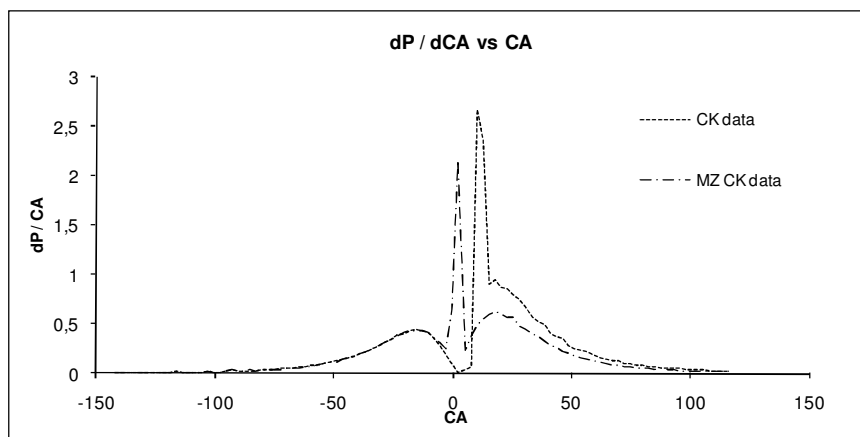


Figure A4.2 – Pressure release per crank angle vs crank angle comparison between simulations for 100% EtOH mixture diluted with CO_2 .

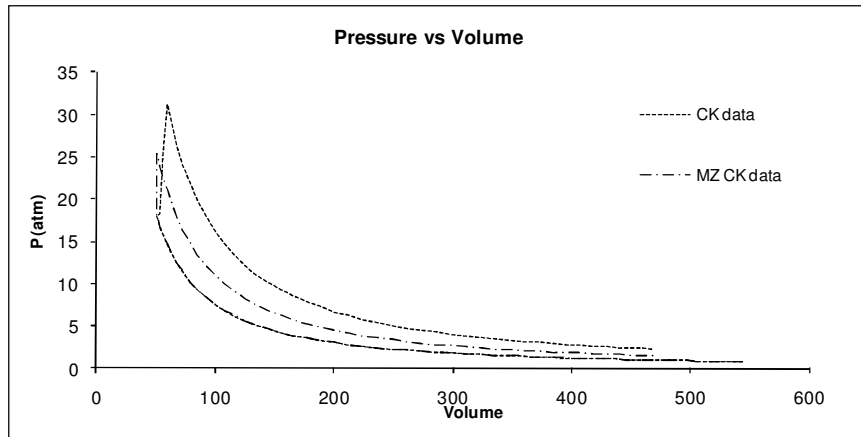


Figure A4.3 – Pressure vs volume comparison between simulations for 100% EtOH mixture diluted with CO₂.

Ethanol Fuelled HCCI – 90% Ethanol

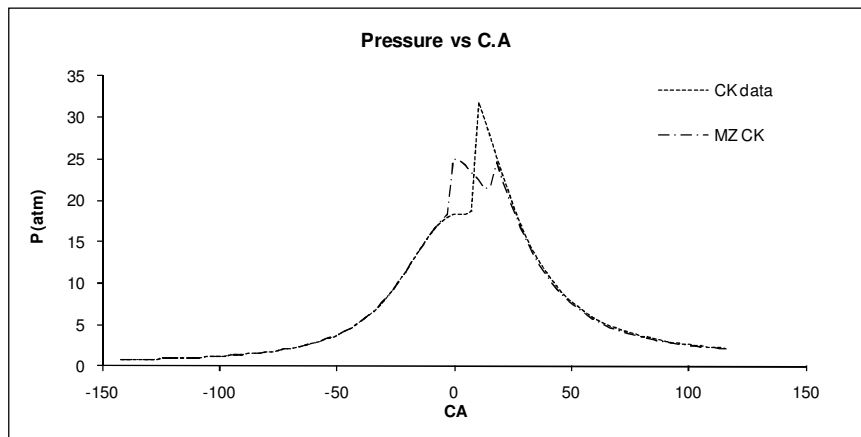


Figure A4.4 – Pressure vs crank angle comparison between simulation for 90% EtOH/water mixture diluted with CO₂.

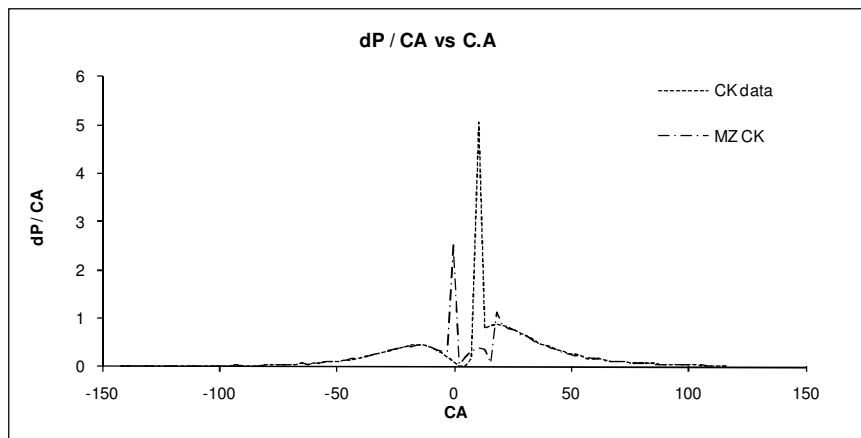


Figure A4.5 – Pressure release per crank angle vs crank angle comparison between simulations for 90% EtOH/water mixture diluted with CO₂.

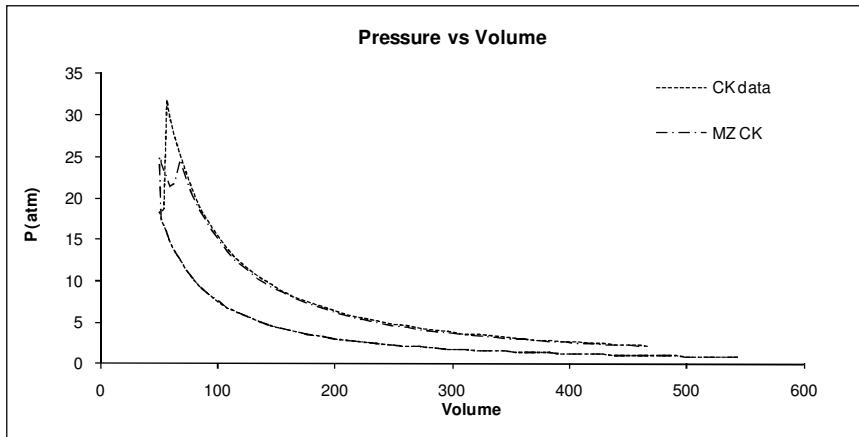


Figure A4.6 – Pressure vs volume comparison between simulations for 90% EtOH/water mixture diluted with CO₂.

Ethanol Fuelled HCCI – 80% Ethanol

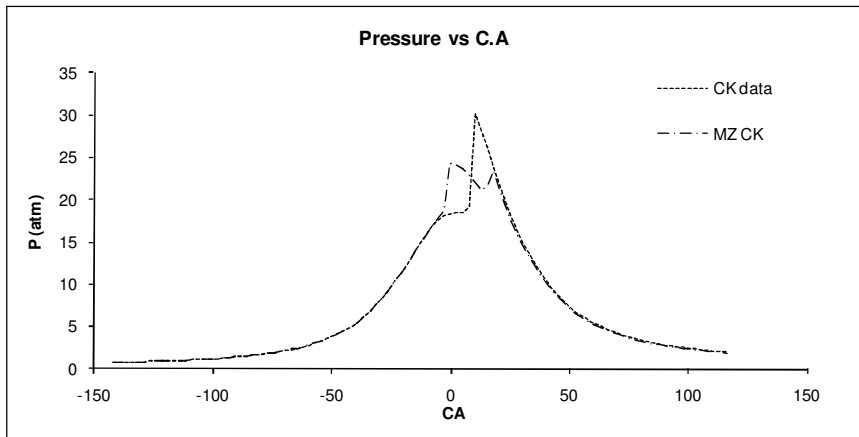


Figure A4.7 – Pressure vs crank angle comparison between simulation for 80% EtOH/water mixture diluted with CO₂.

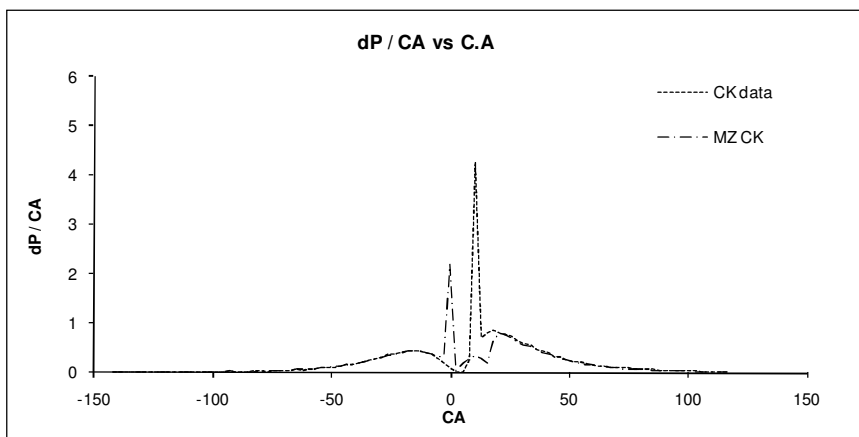


Figure A4.8 – Pressure release per crank angle vs crank angle comparison between simulations for 80% EtOH/water mixture diluted with CO₂.

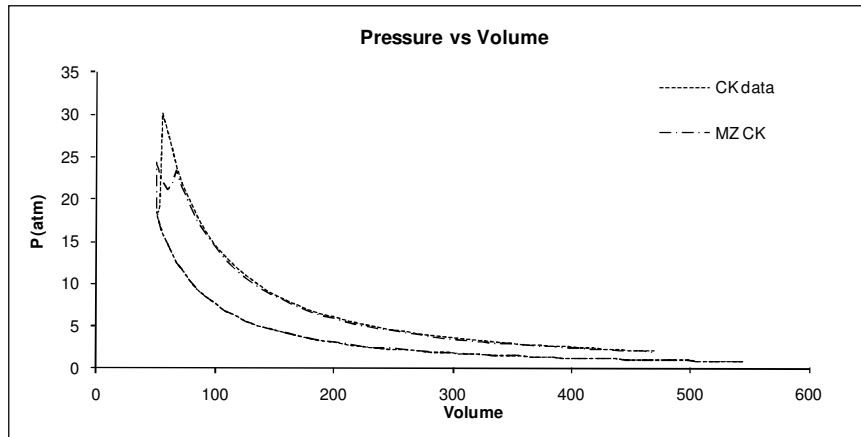


Figure A4.9 – Pressure vs volume comparison between simulations for 80% EtOH/water mixture diluted with CO₂.

Ethanol Fuelled HCCI – 70% Ethanol

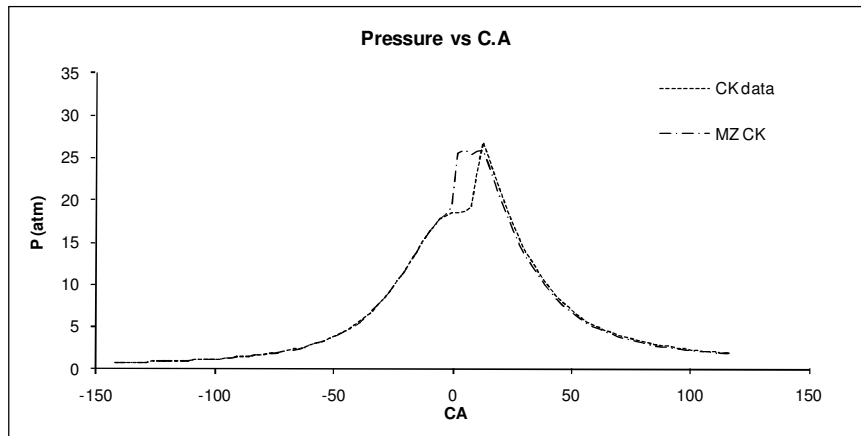


Figure A4.10 – Pressure vs crank angle comparison between simulation for 70% EtOH/water mixture diluted with CO₂.

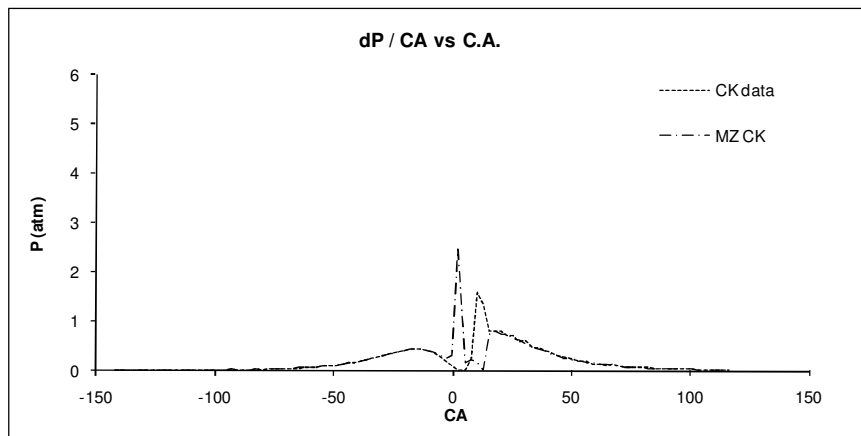


Figure A4.11 – Pressure release per crank angle vs crank angle comparison between simulations for 70% EtOH/water mixture diluted with CO₂.

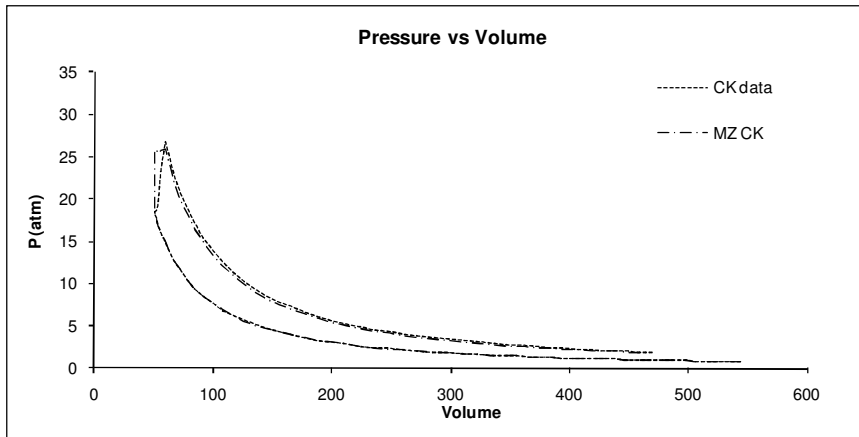


Figure A4.12 – Pressure vs volume comparison between simulations for 70% EtOH/water mixture diluted with CO₂.

Ethanol Fuelled HCCI – 60% Ethanol

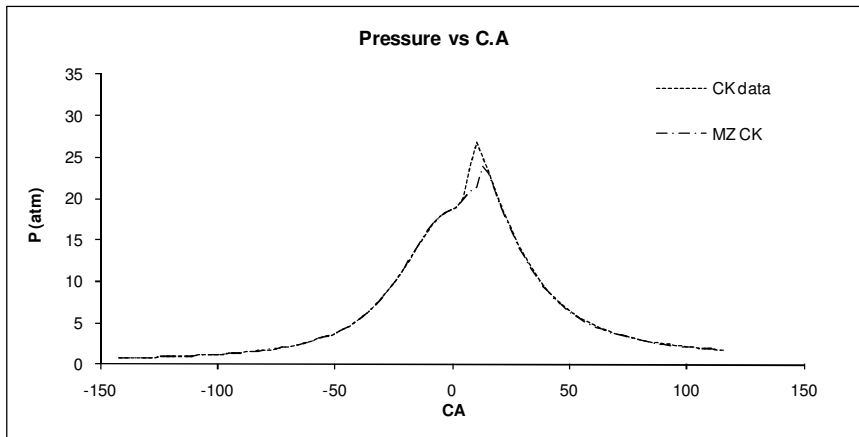


Figure A4.13 – Pressure vs crank angle comparison between simulation for 60% EtOH/water mixture diluted with CO₂.

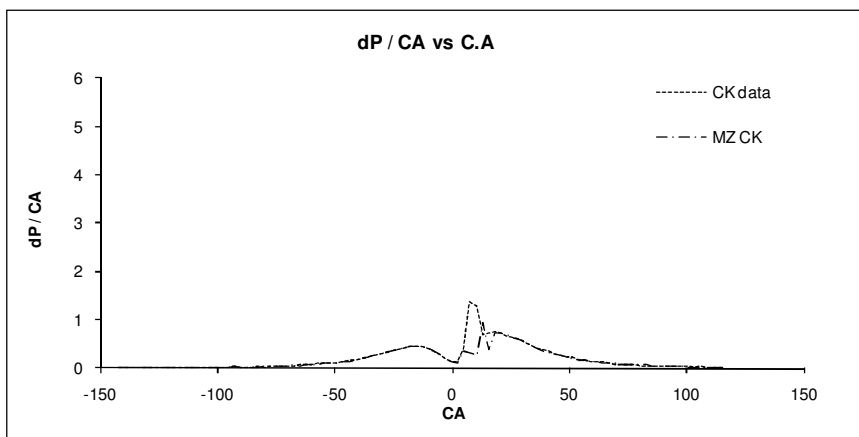


Figure A4.14 – Pressure release per crank angle vs crank angle comparison between simulations for 60% EtOH/water mixture diluted with CO₂.

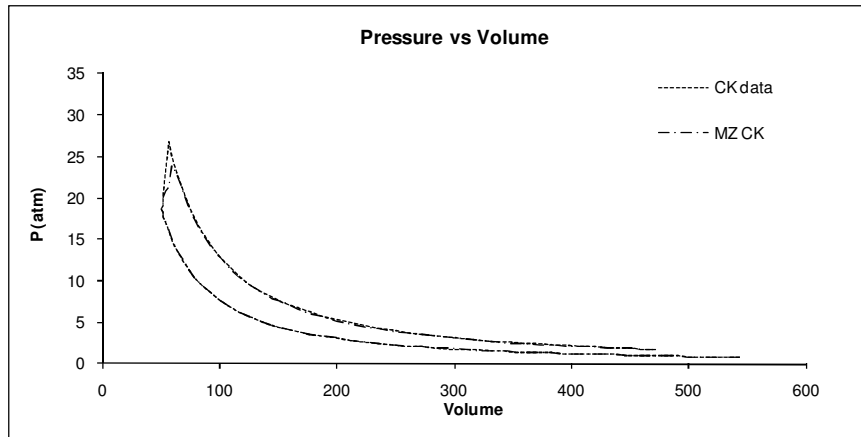


Figure A4.15 – Pressure vs volume comparison between simulations for 50% EtOH/water mixture diluted with CO₂.

Ethanol Fuelled HCCI – 55% Ethanol

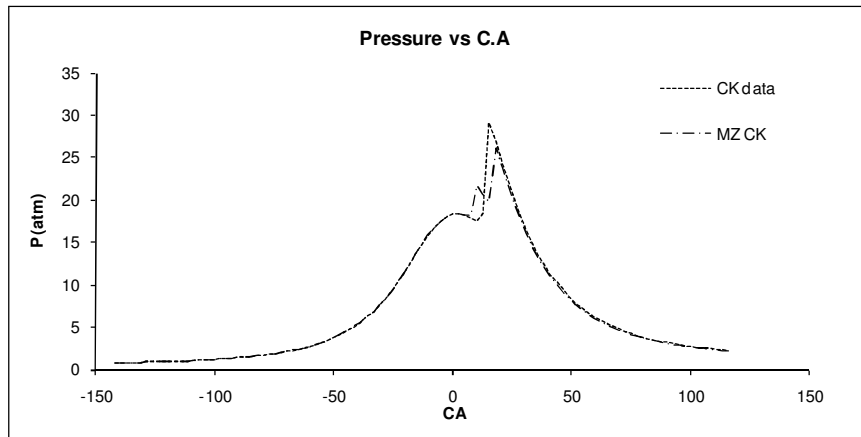


Figure A4.16 – Pressure vs crank angle comparison between simulations for 55% EtOH/water mixture diluted with CO₂.

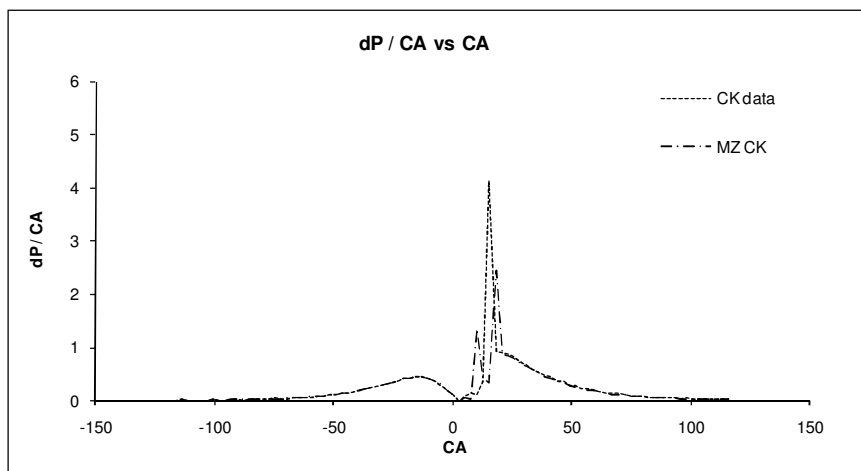


Figure A4.17 – Pressure release per crank angle vs crank angle comparison between simulations for 55% EtOH/water mixture diluted with CO₂.

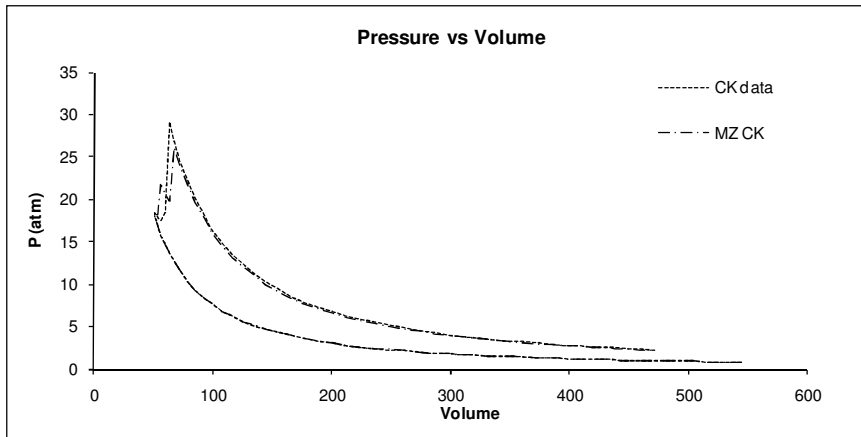


Figure A4.18 – Pressure vs volume comparison between simulations for 55% EtOH/water mixture diluted with CO₂.

Ethanol Fuelled HCCI – 50% Ethanol

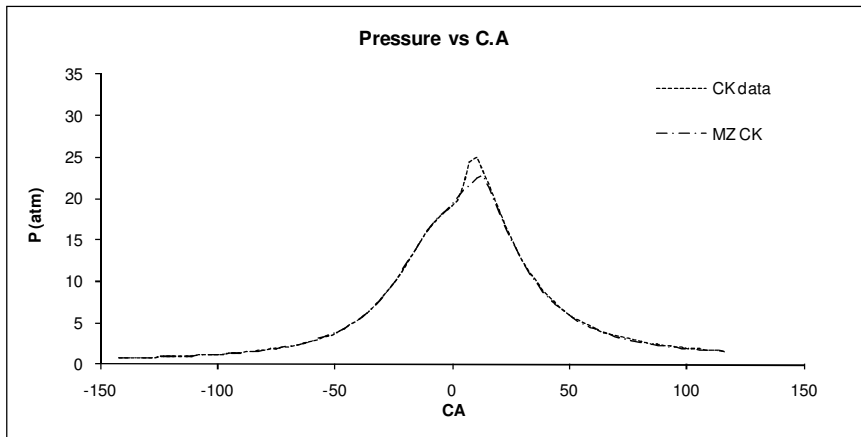


Figure A4.19 – Pressure vs crank angle comparison between simulations for 50% EtOH/water mixture diluted with CO₂.

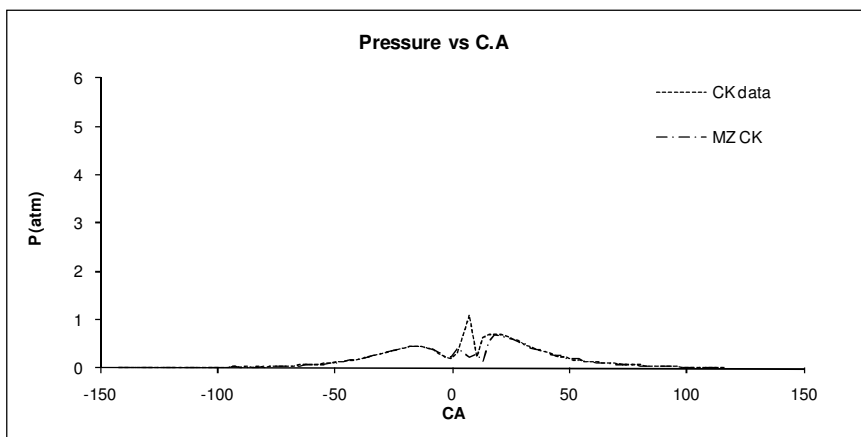


Figure A4.20 – Pressure release per crank angle vs crank angle comparison between simulations for 50% EtOH/water mixture diluted with CO₂.

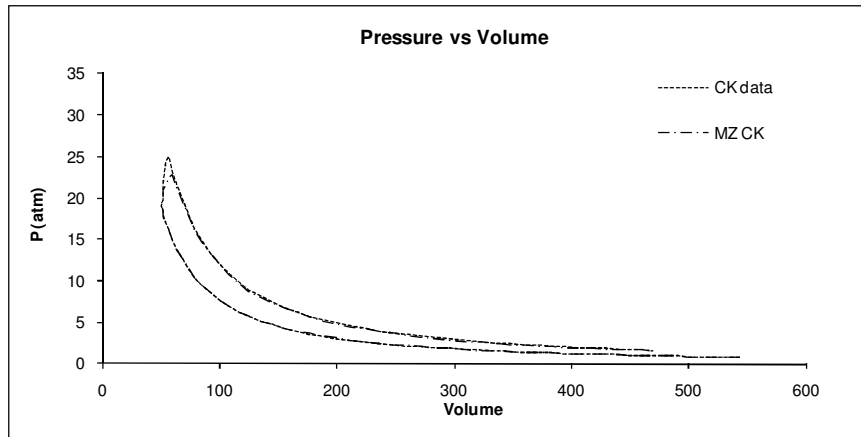


Figure A4.21 – Pressure vs volume comparison between simulations for 50% EtOH/water mixture diluted with CO₂.

Ethanol Fuelled HCCI – 45% Ethanol

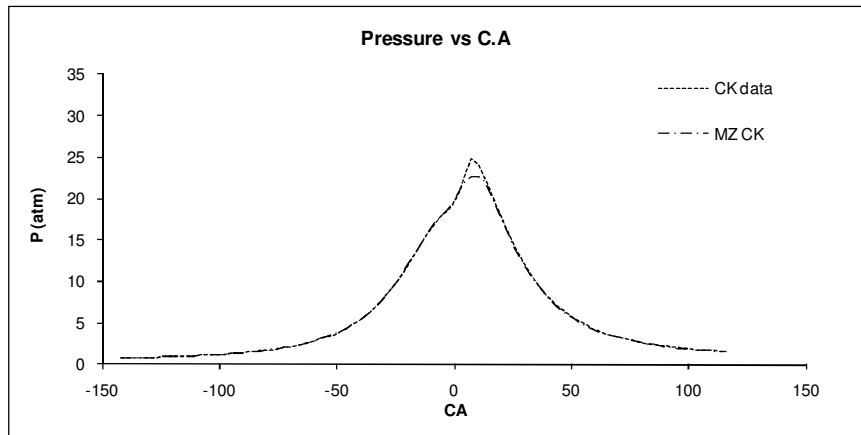


Figure A4.22 – Pressure vs crank angle comparison between simulations for 45% EtOH/water mixture diluted with CO₂.

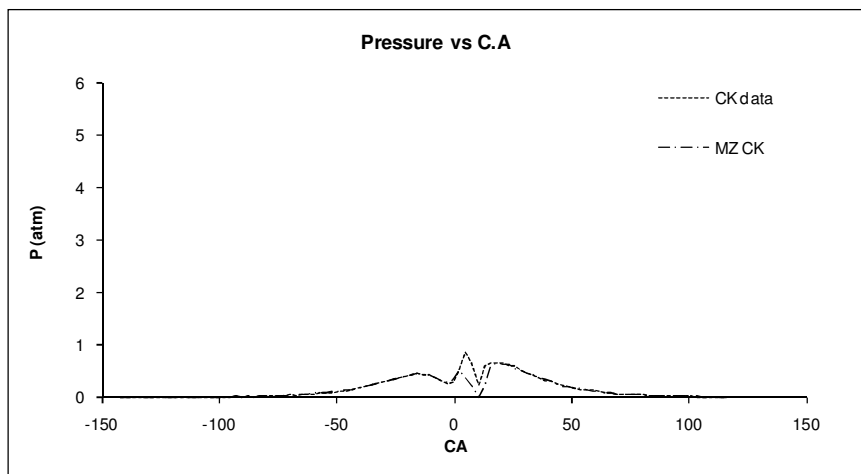


Figure A4.23 – Pressure release per crank angle vs crank angle comparison between simulations for 45% EtOH/water mixture diluted with CO₂.

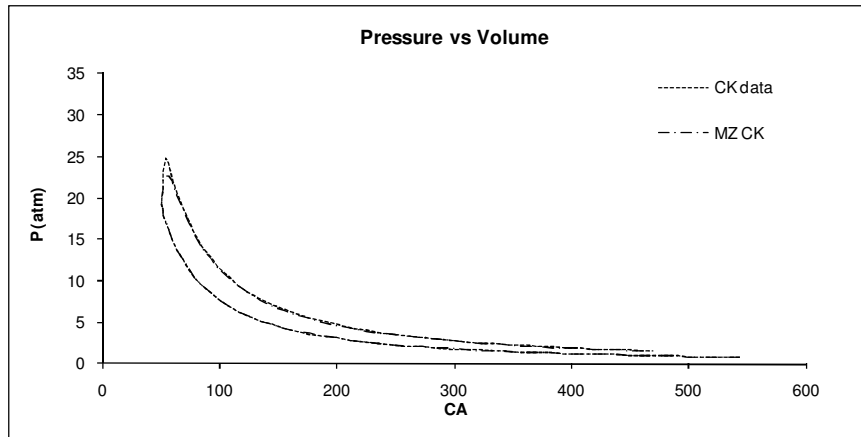


Figure A4.24 – Pressure vs volume comparison between simulations for 45% EtOH/water mixture diluted with CO₂.

Ethanol Fuelled HCCI – 40% Ethanol

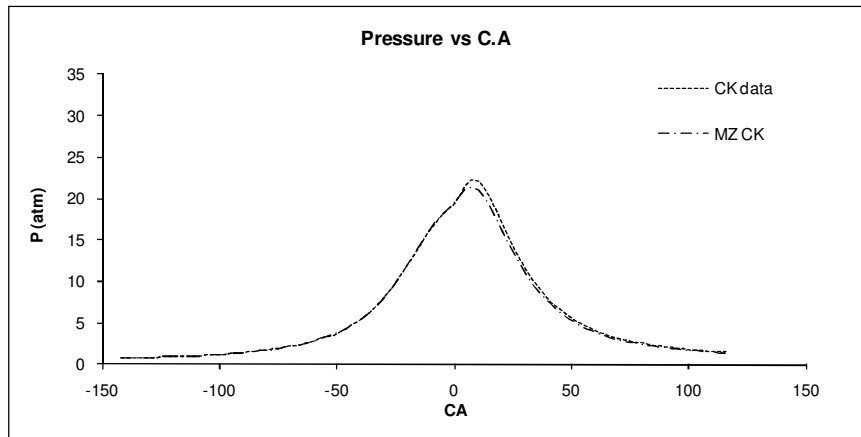


Figure A4.25 – Pressure vs crank angle comparison between simulations for 40% EtOH/water mixture diluted with CO₂.

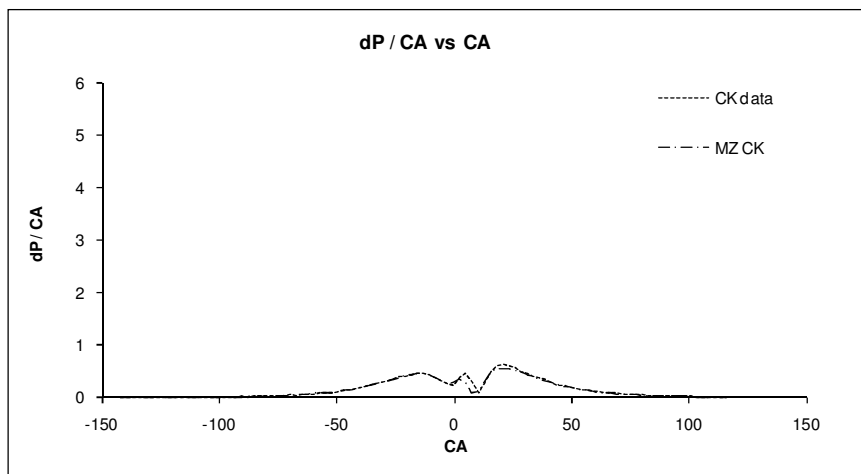


Figure A4.26 – Pressure release per crank angle vs crank angle comparison between simulations for 40% EtOH/water mixture diluted with CO₂.

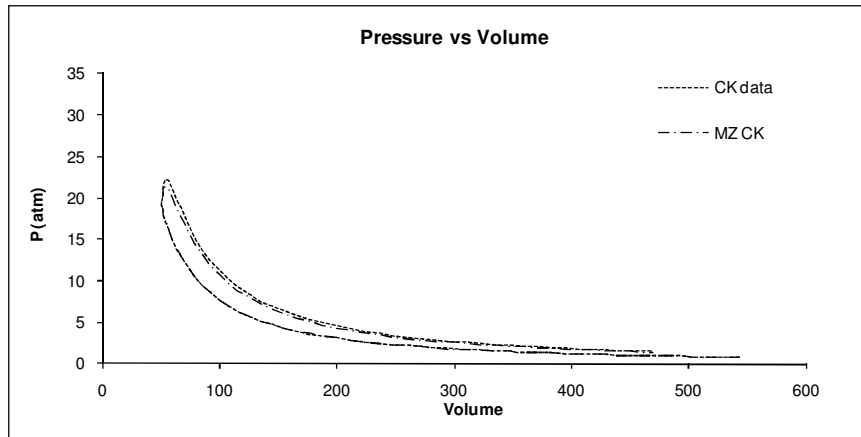


Figure A4.27 – Pressure vs volume comparison between simulations for 40% EtOH/water mixture diluted with CO₂.

E85 Fuelled HCCI – 100% E85

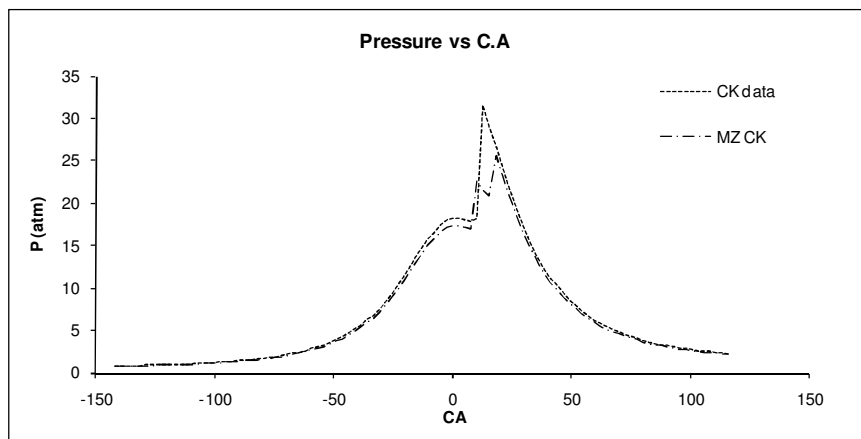


Figure A4.28 – Pressure vs crank angle comparison between simulations for 100% E85 mixture diluted with CO₂.

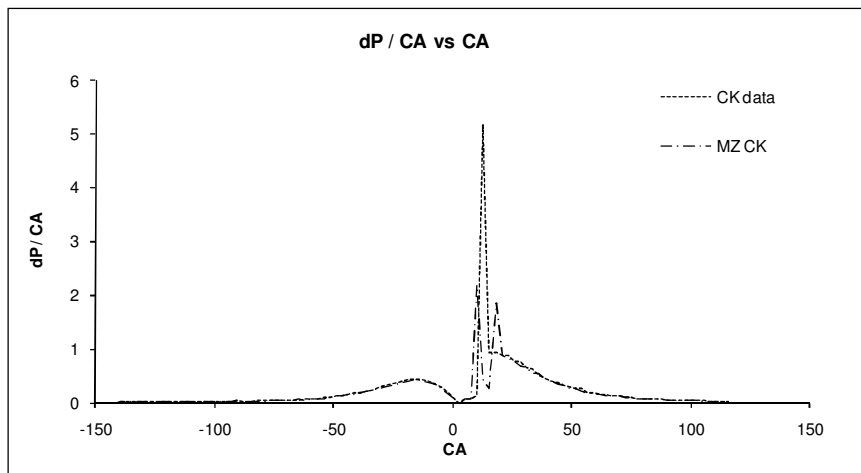


Figure A4.29 – Pressure release per crank angle vs crank angle comparison between simulations for 100% E85 mixture diluted with CO₂.

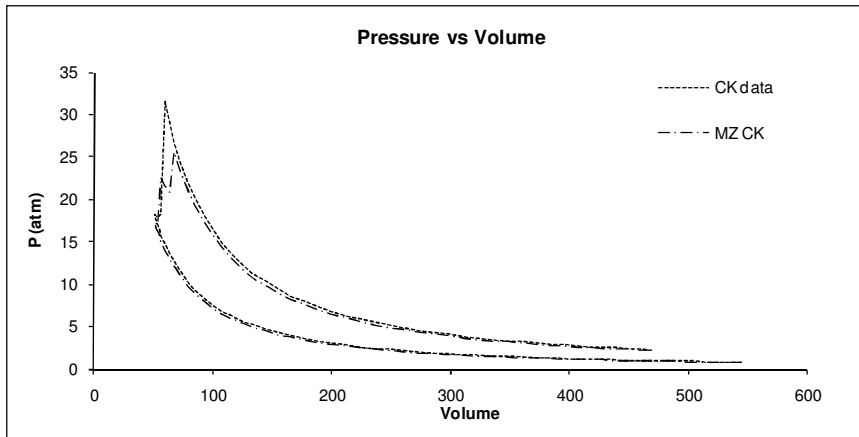


Figure A4.30 – Pressure vs volume comparison between simulations for 100% E85 mixture diluted with CO₂.

E85 Fuelled HCCI – 95% E85

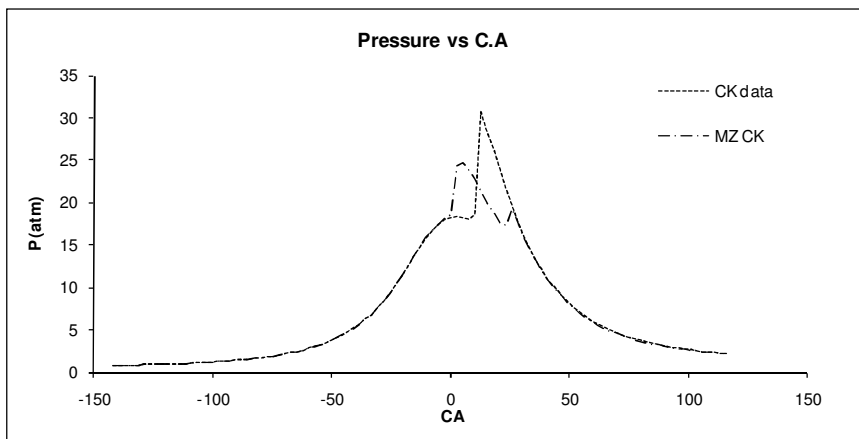


Figure A4.31 – Pressure vs crank angle comparison between simulations for 95% E85/water mixture diluted with CO₂.

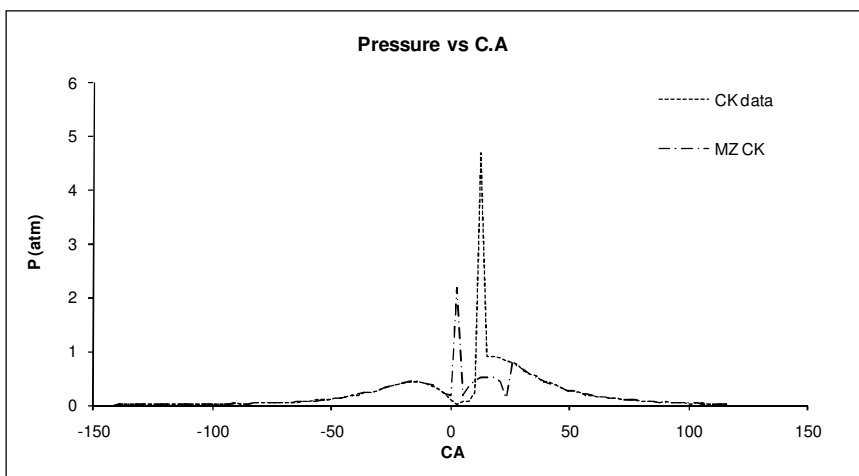


Figure A4.32 – Pressure release per crank angle vs crank angle comparison between simulations for 95% E85/water mixture diluted with CO₂.

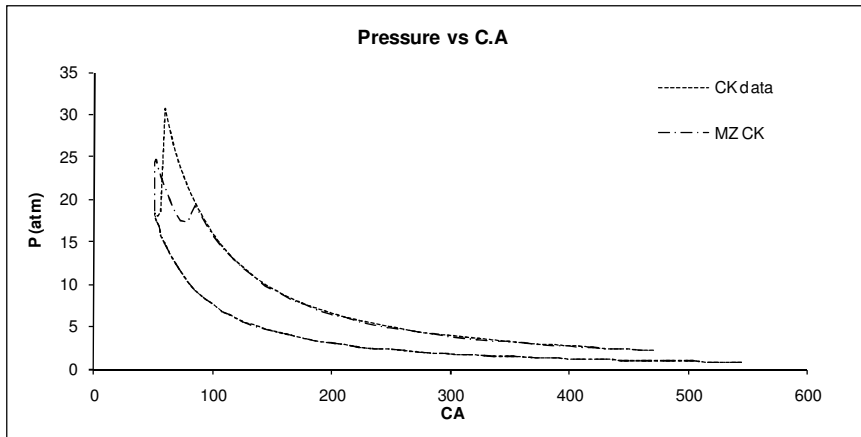


Figure A4.33 – Pressure vs volume comparison between simulations for 95% E85/water mixture diluted with CO₂.

E85 Fuelled HCCI – 90% E85

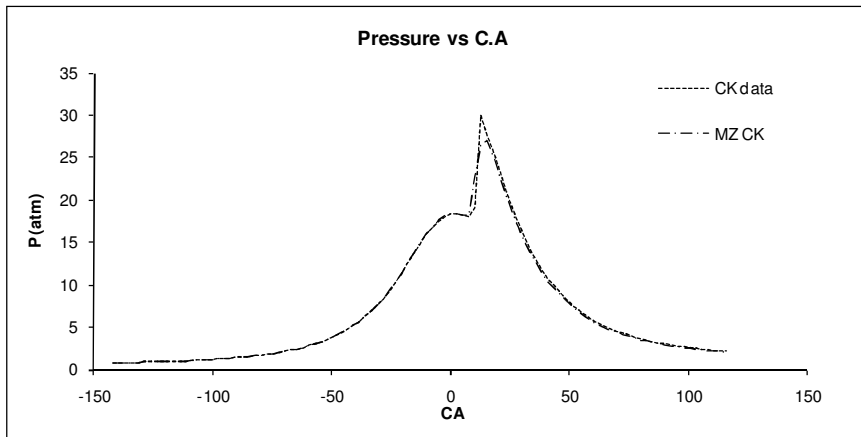


Figure A4.34 – Pressure vs crank angle comparison between simulations for 90% E85/water mixture diluted with CO₂.

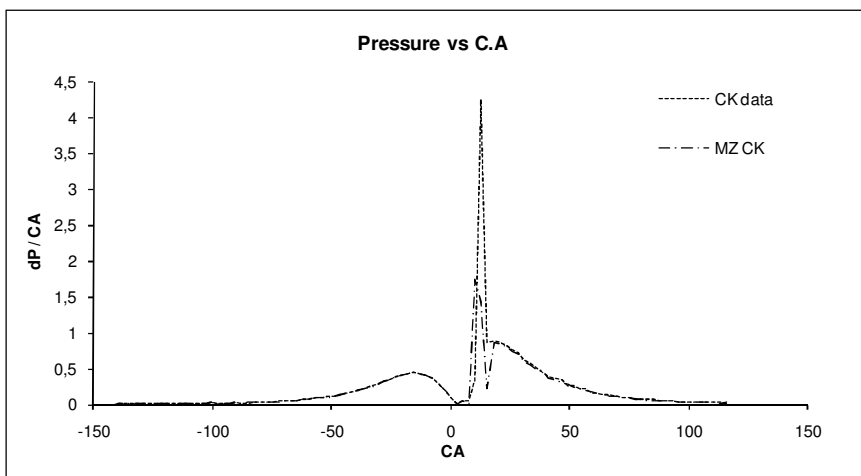


Figure A4.35 – Pressure release per crank angle vs crank angle comparison between simulations for 90% E85/water mixture diluted with CO₂.

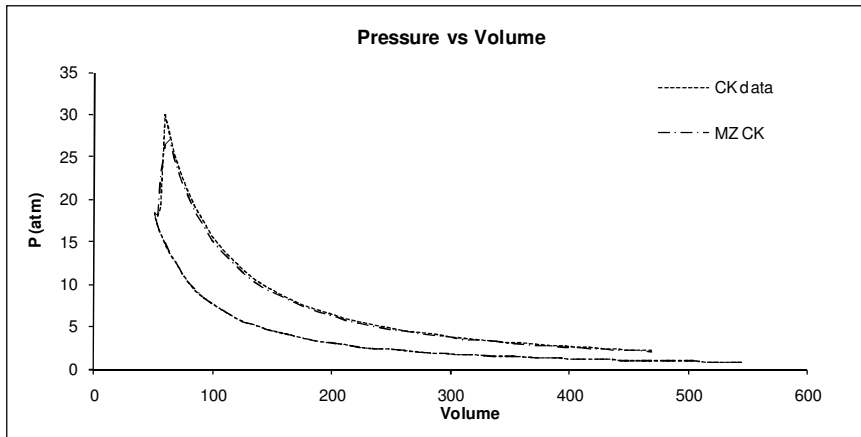


Figure A4.36 – Pressure vs volume comparison between simulations for 90% E85/water mixture diluted with CO₂.

E85 Fuelled HCCI – 85% E85

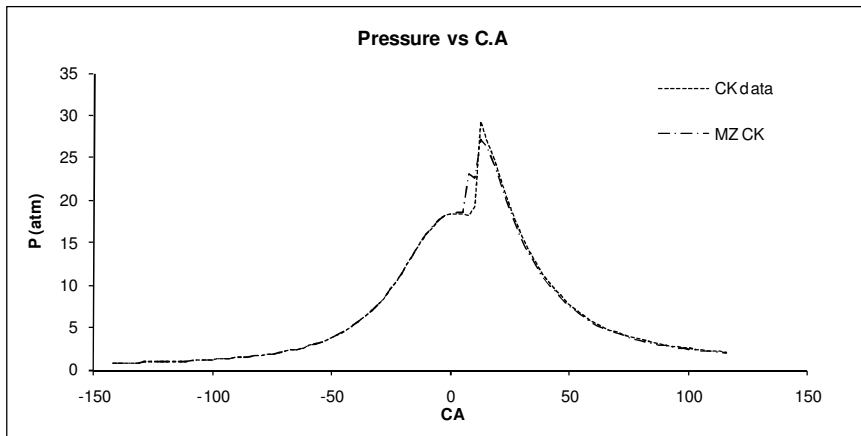


Figure A4.37 – Pressure vs crank angle comparison between simulations for 85% E85/water mixture diluted with CO₂.

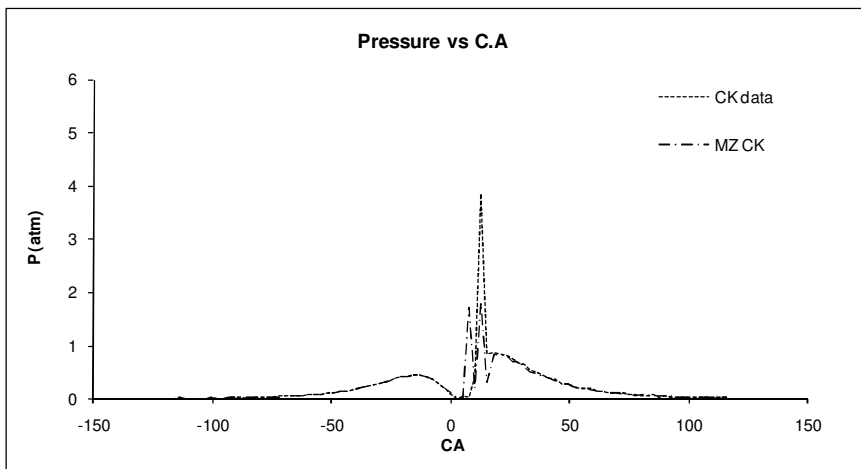


Figure A4.38 – Pressure release per crank angle vs crank angle comparison between simulations for 85% E85/water mixture diluted with CO₂.

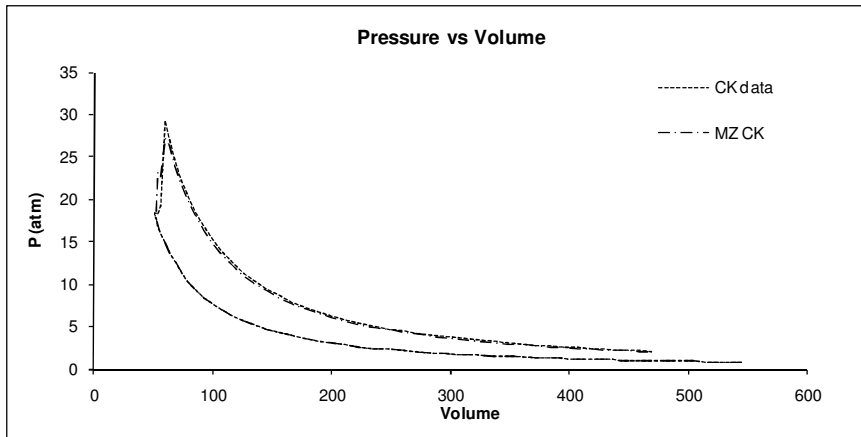


Figure A4.39 – Pressure vs volume comparison between simulations for 85% E85/water mixture diluted with CO₂.

E24 Fuelled HCCI – 100% E24

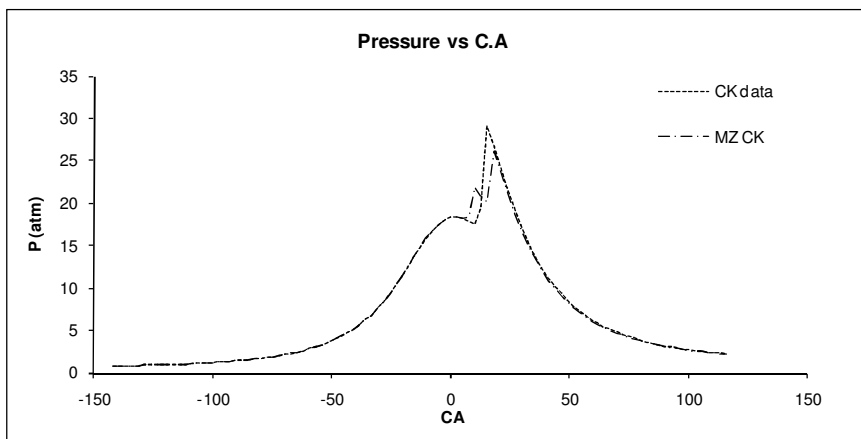


Figure A4.40 – Pressure vs crank angle comparison between simulations for 100% E24 mixture diluted with CO₂.

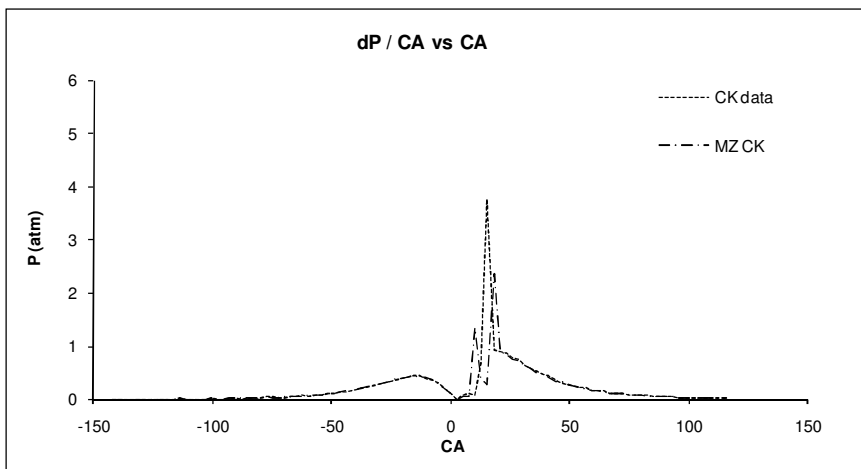


Figure A4.41 – Pressure release per crank angle vs crank angle comparison between simulations for 100% E24 mixture diluted with CO₂.

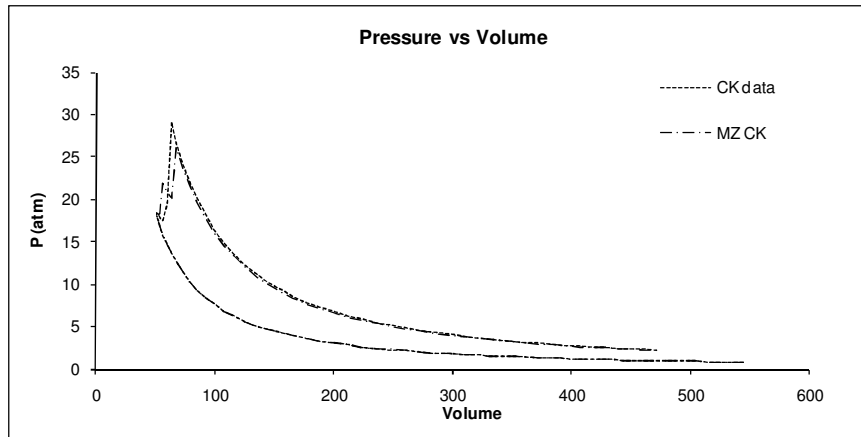


Figure A4.42 – Pressure vs volume comparison between simulations for 100% E24 mixture diluted with CO₂.

E24 Fuelled HCCI – 95% E24

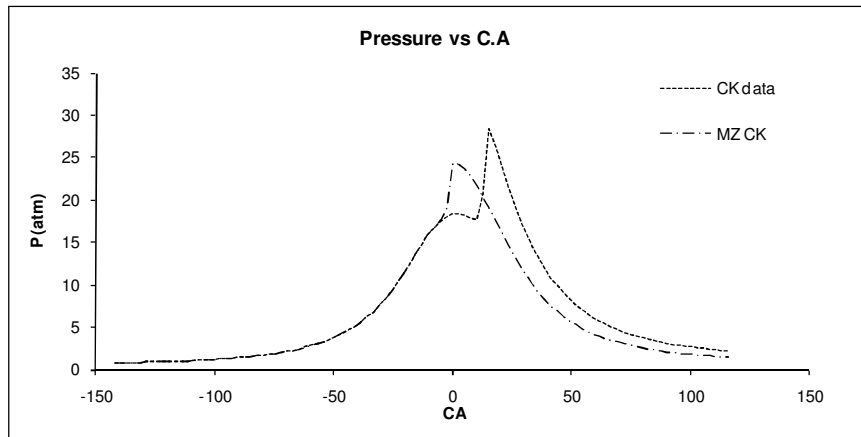


Figure A4.43 – Pressure vs crank angle comparison between simulations for 95% E24/water mixture diluted with CO₂.

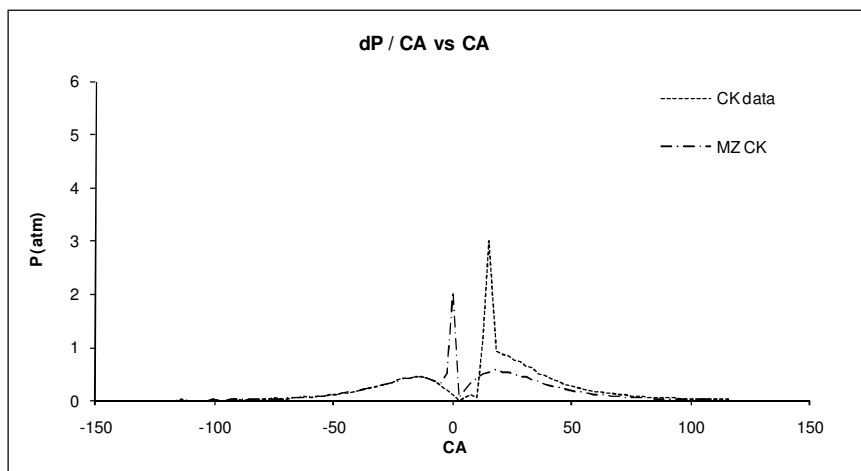


Figure A4.44 – Pressure release per crank angle vs crank angle comparison between simulations for 95% E24/water mixture diluted with CO₂.

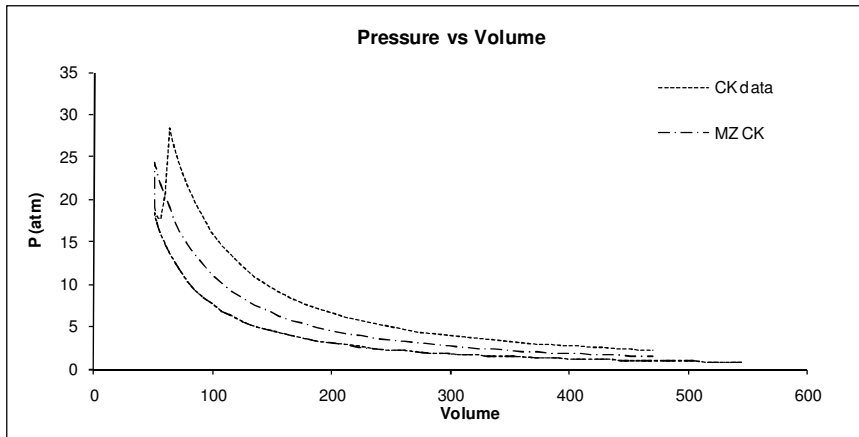


Figure A4.45 – Pressure vs volume comparison between simulations for 95% E24/water mixture diluted with CO₂.

E24 Fuelled HCCI – 90% E24

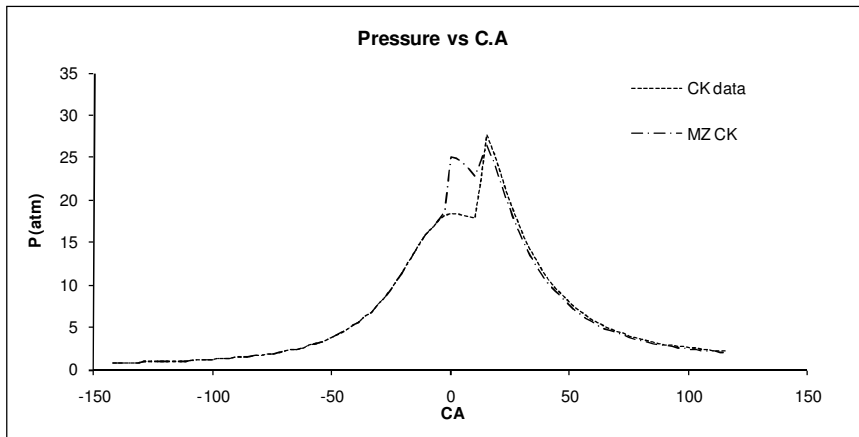


Figure A4.46 – Pressure vs crank angle comparison between simulations for 90% E24/water mixture diluted with CO₂.

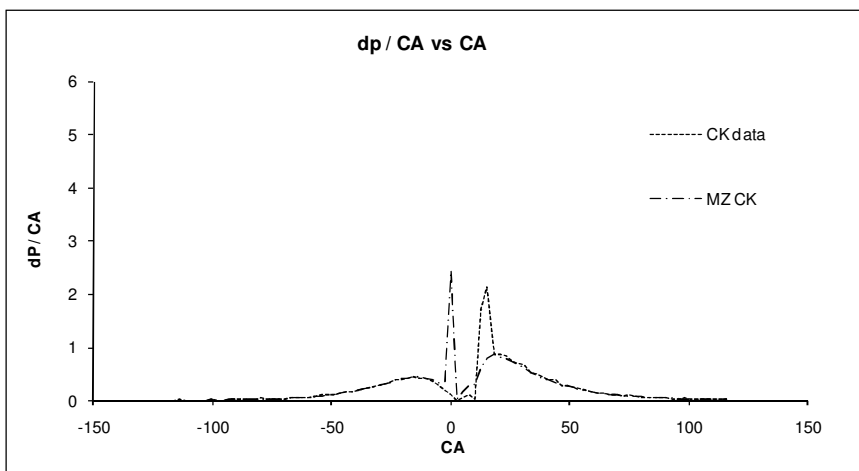


Figure A4.47 – Pressure release per crank angle vs crank angle comparison between simulations for 90% E24/water mixture diluted with CO₂.

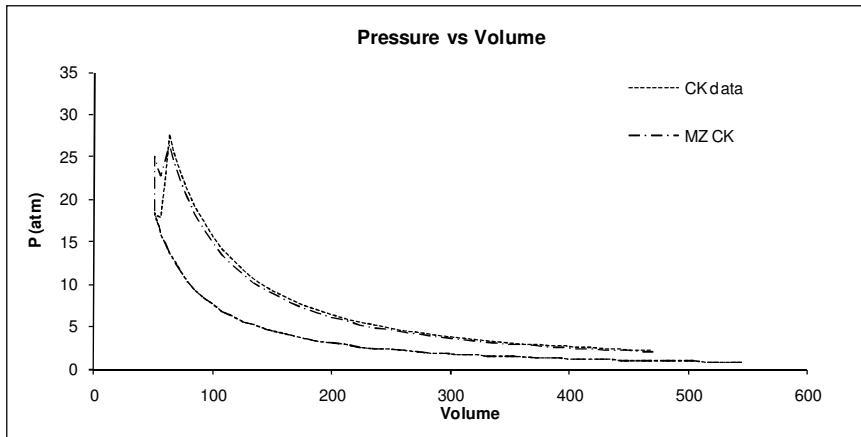


Figure A4.48 – Pressure vs volume comparison between simulations for 90% E24/water mixture diluted with CO₂.

E24 Fuelled HCCI – 85% E24

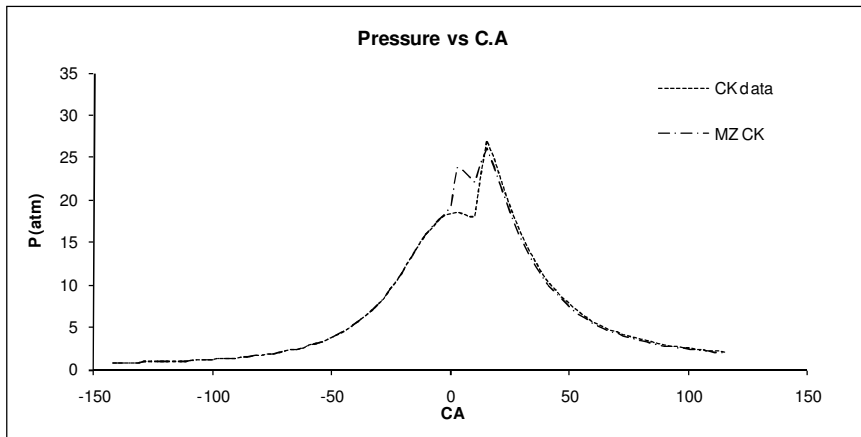


Figure A4.49 – Pressure vs crank angle comparison between simulations for 85% E24/water mixture diluted with CO₂.

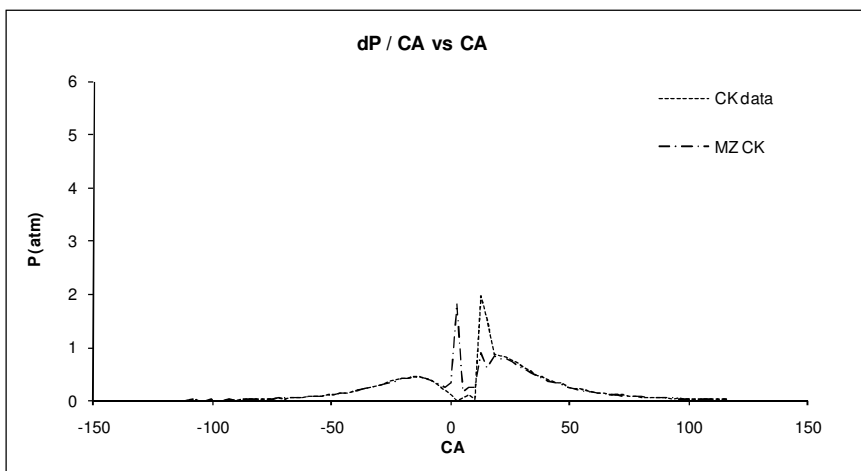


Figure A4.50 – Pressure release per crank angle vs crank angle comparison between simulations for 85% E24/water mixture diluted with CO₂.

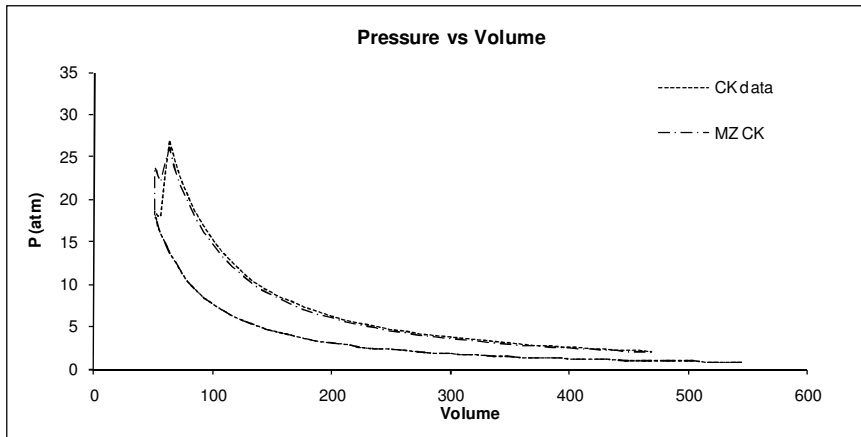


Figure A4.51 – Pressure vs volume comparison between simulations for 85% E24/water mixture diluted with CO₂.

E10 Fuelled HCCI – 100% E10

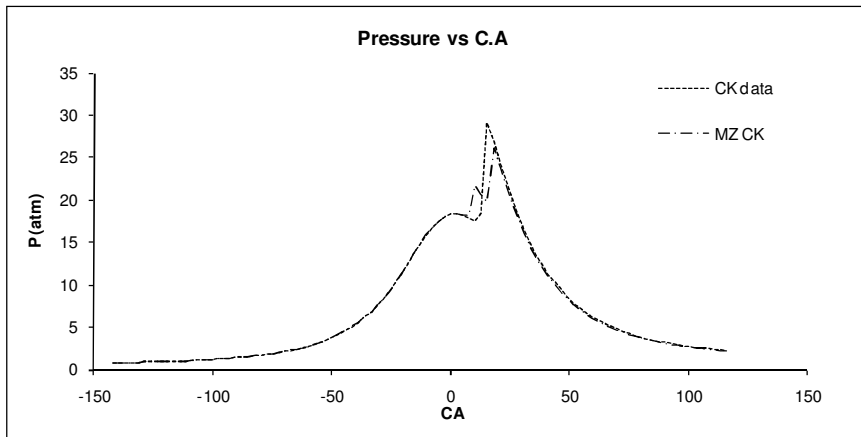


Figure A4.52 – Pressure vs crank angle comparison between simulations for 100% E10 mixture diluted with CO₂.

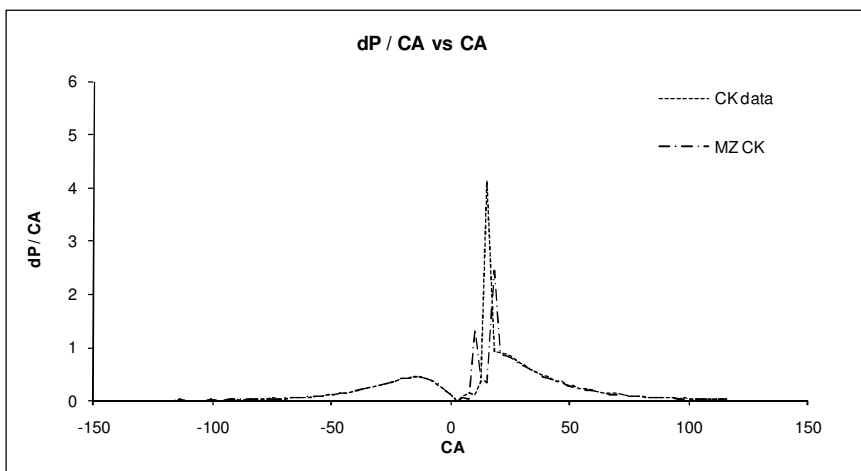


Figure A4.53 – Pressure release per crank angle vs crank angle comparison between simulations for 100% E10 mixture diluted with CO₂.

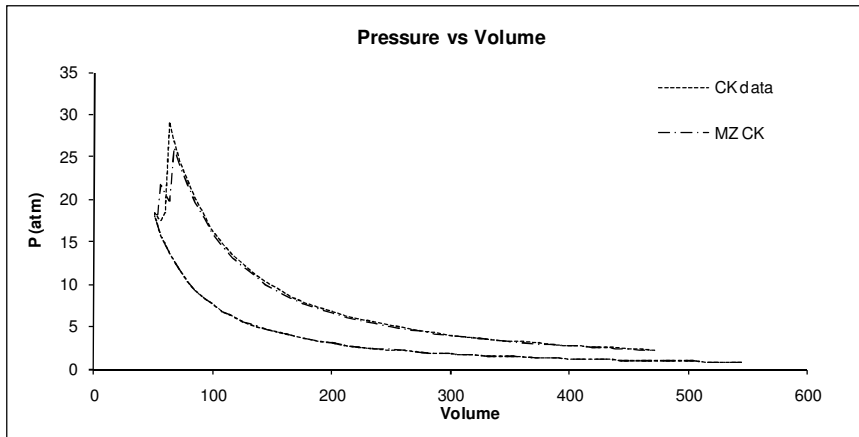


Figure A4.54 – Pressure vs volume comparison between simulations for 100% E10 mixture diluted with CO₂.

E10 Fuelled HCCI – 95% E10

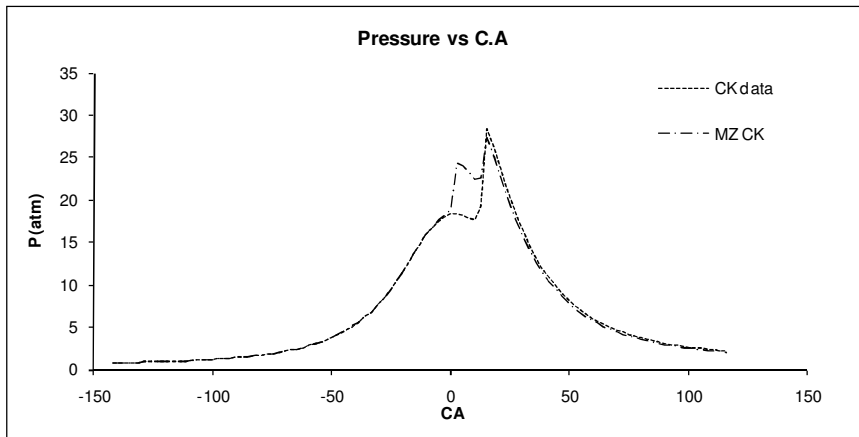


Figure A4.55 – Pressure vs crank angle comparison between simulations for 95% E10/water mixture diluted with CO₂.

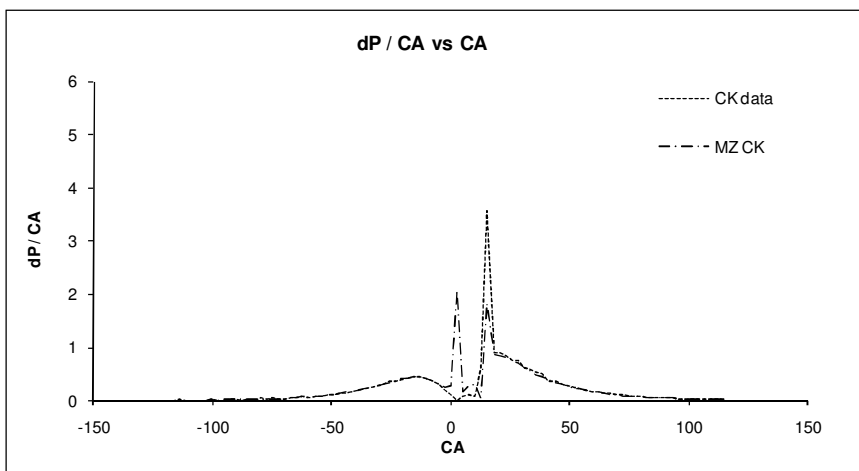


Figure A4.56 – Pressure release per crank angle vs crank angle comparison between simulations for 95% E10/water mixture diluted with CO₂.

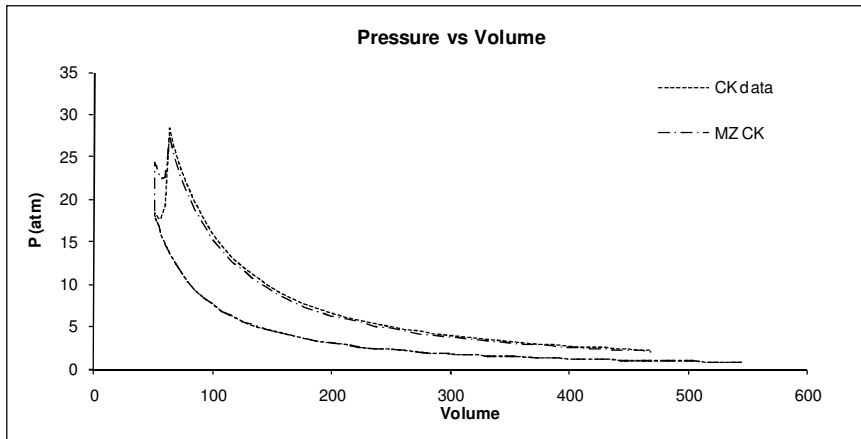


Figure A4.57 – Pressure vs volume comparison between simulations for 95% E10/water mixture diluted with CO₂.

E10 Fuelled HCCI – 90% E10

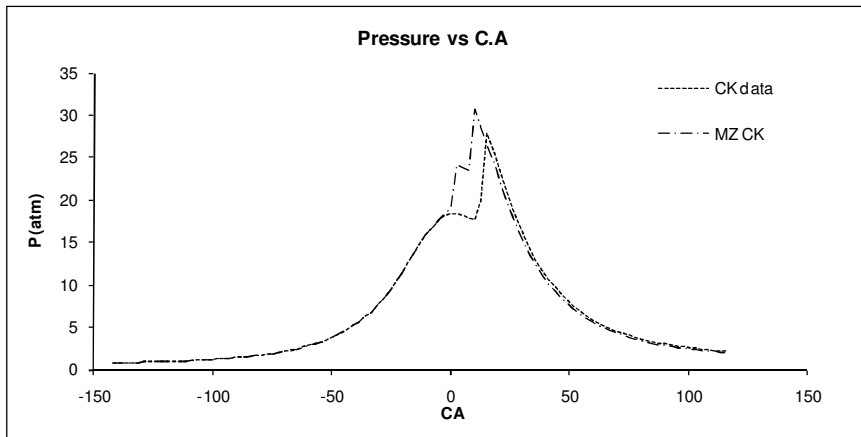


Figure A4.58 – Pressure vs crank angle comparison between simulations for 90% E10/water mixture diluted with CO₂.

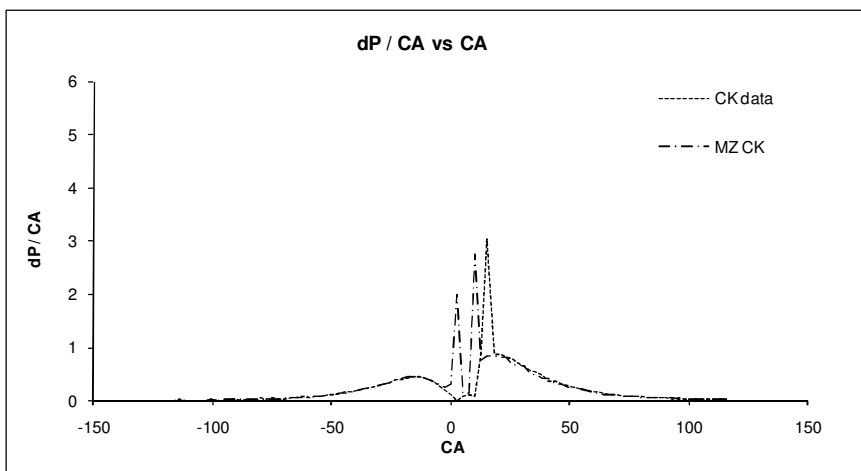


Figure A4.59 – Pressure release per crank angle vs crank angle comparison between simulations for 90% E10/water mixture diluted with CO₂.

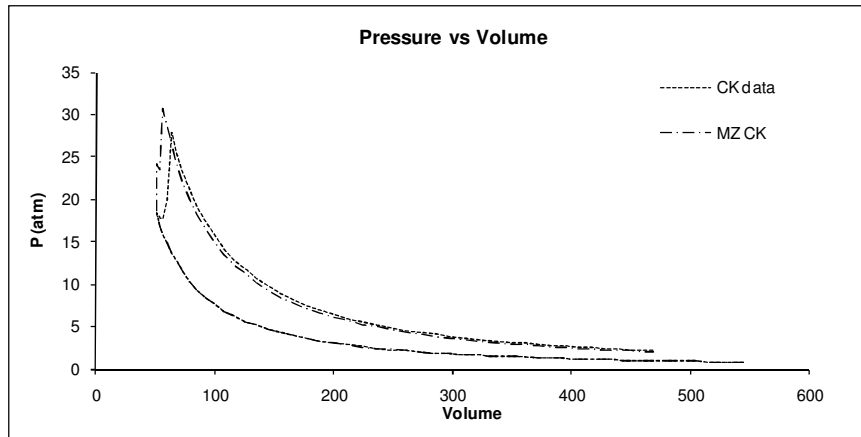


Figure A4.60 – Pressure vs volume comparison between simulations for 90% E10/water mixture diluted with CO₂.

E10 Fuelled HCCI – 85% E10

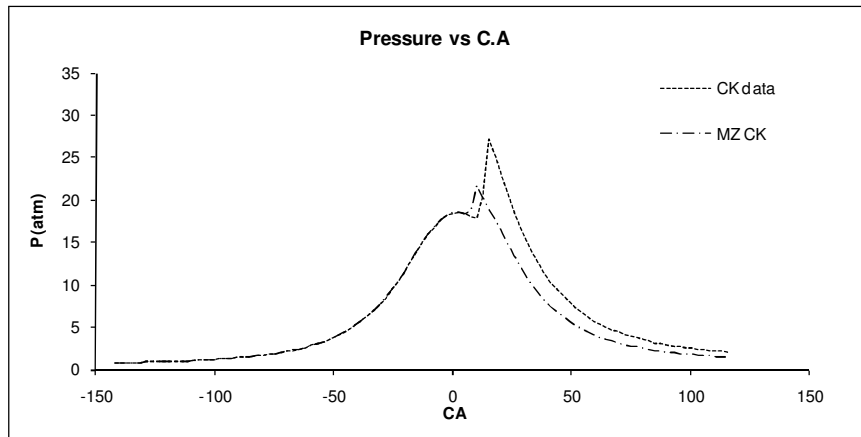


Figure A4.61 – Pressure vs crank angle comparison between simulations for 85% E10/water mixture diluted with CO₂.

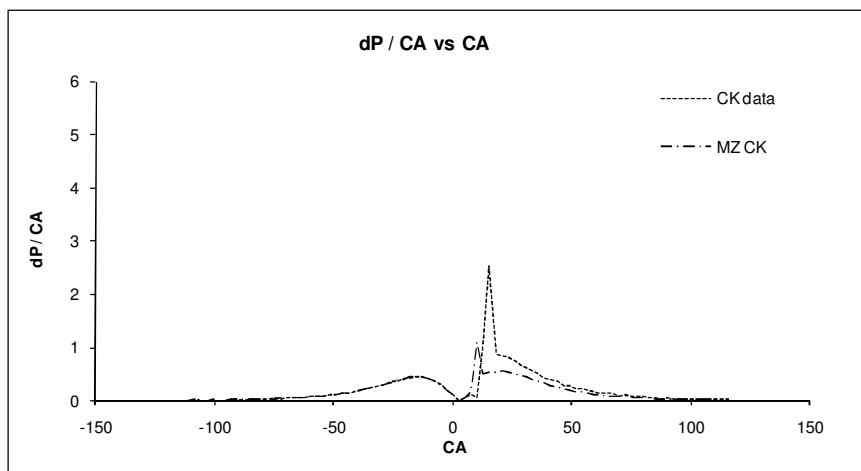


Figure A4.62 – Pressure release per crank angle vs crank angle comparison between simulations for 85% E10/water mixture diluted with CO₂.

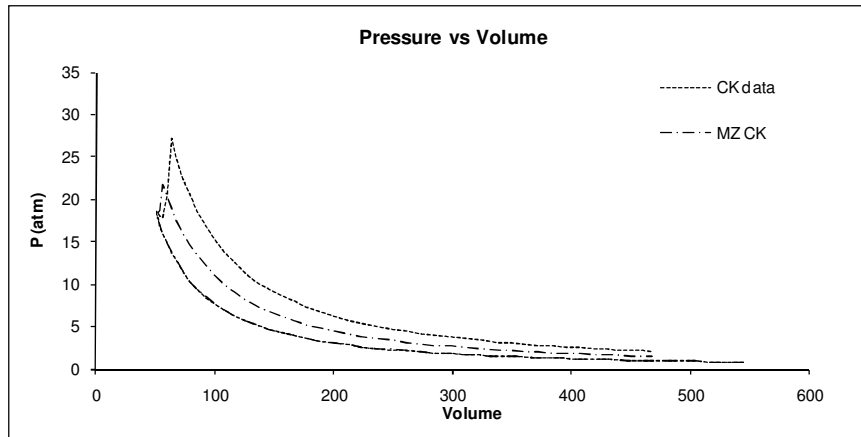


Figure A4.63 – Pressure vs volume comparison between simulations for 85% E10/water mixture diluted with CO₂.

Iso-Octane Fuelled HCCI – 100% iso-Octane

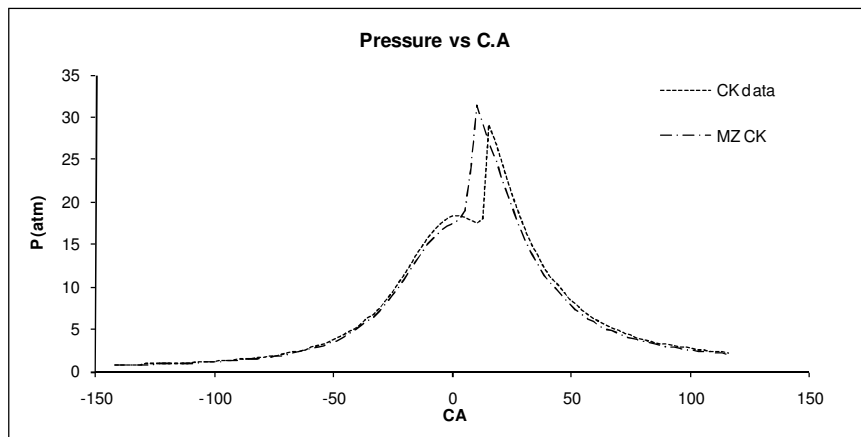


Figure A4.64 – Pressure vs crank angle comparison between simulations for 100% iso-octane mixture diluted with CO₂.

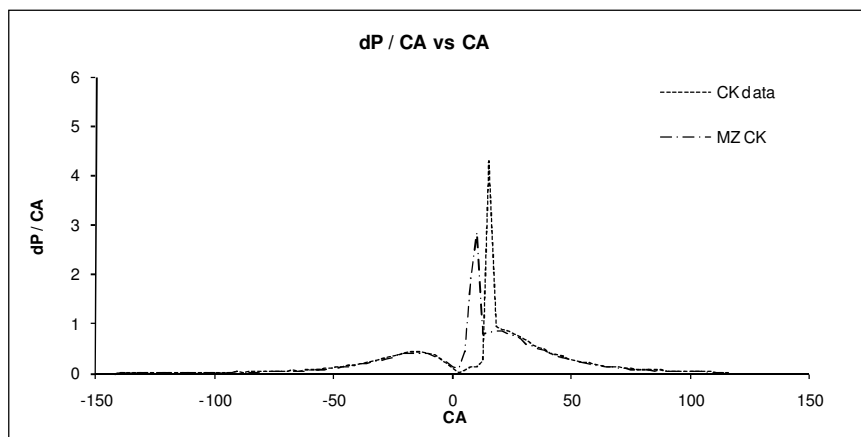


Figure A4.65 – Pressure release per crank angle vs crank angle comparison between simulations for 100% iso-octane mixture diluted with CO₂.

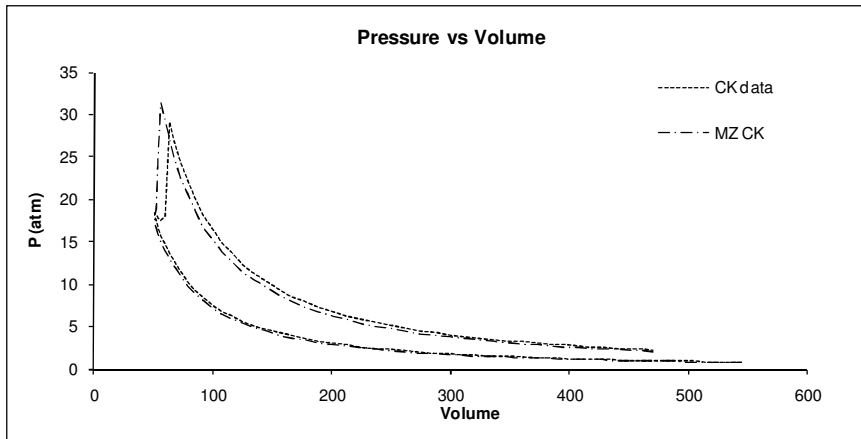


Figure A4.66 – Pressure vs volume comparison between simulations for 100% iso-octane mixture diluted with CO₂.

Iso-Octane Fuelled HCCI – 95% iso-Octane

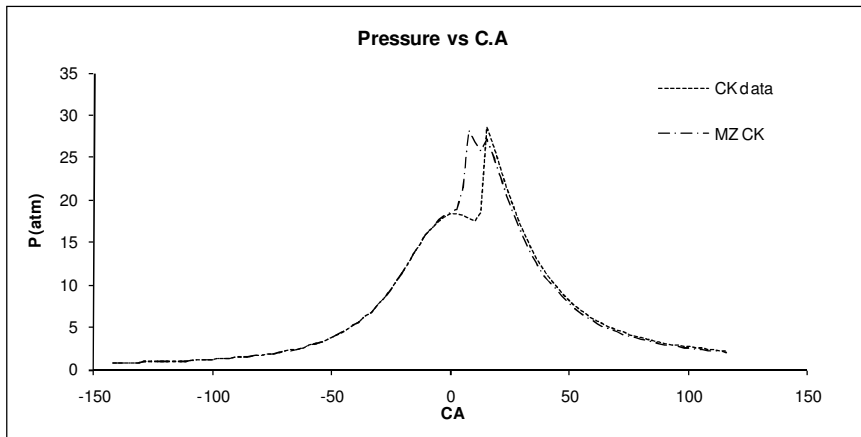


Figure A4.67 – Pressure vs crank angle comparison between simulations for 95% iso-octane/water mixture diluted with CO₂.

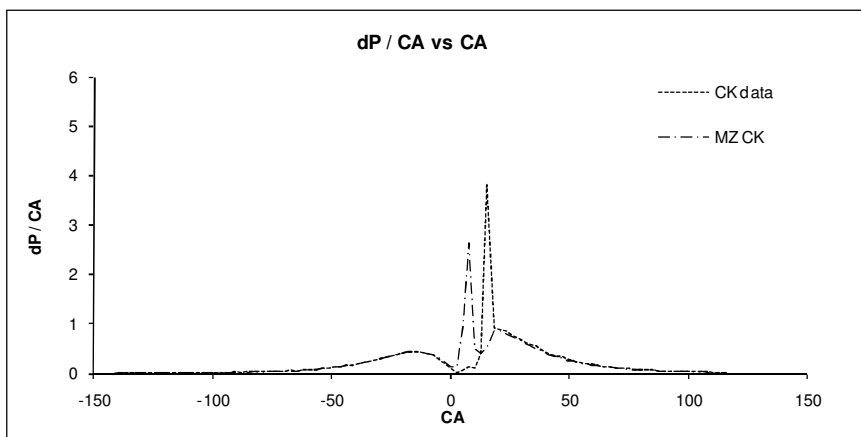


Figure A4.68 – Pressure release per crank angle vs crank angle comparison between simulations for 95% iso-octane/water mixture diluted with CO₂.

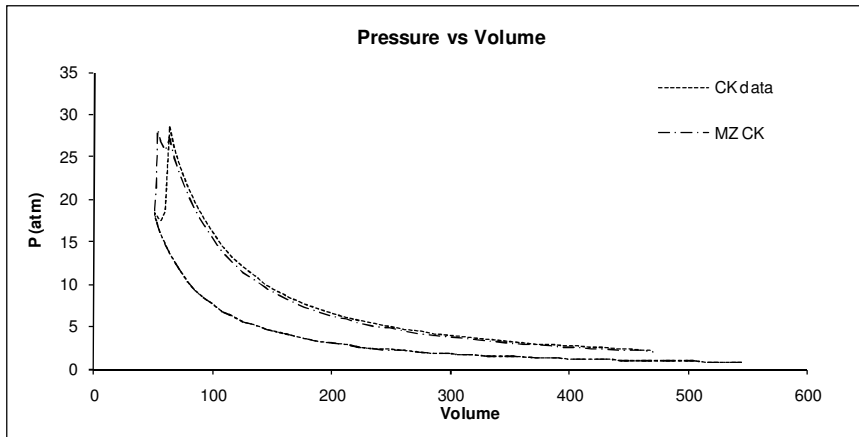


Figure A4.69 – Pressure vs volume comparison between simulations for 95% iso-octane/water mixture diluted with CO₂.

Iso-Octane Fuelled HCCI – 90% iso-Octane

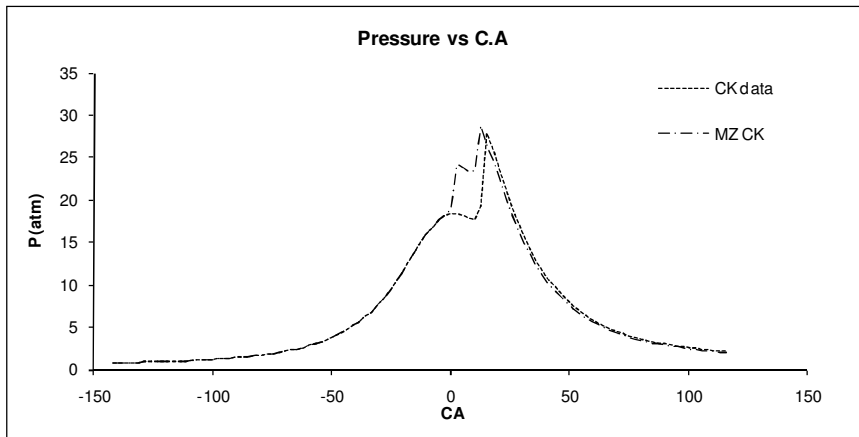


Figure A4.70 – Pressure vs crank angle comparison between simulations for 90% iso-octane/water mixture diluted with CO₂.

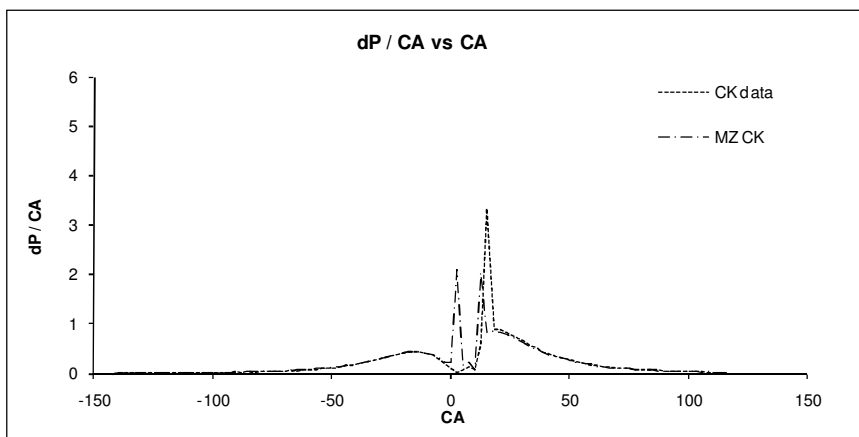


Figure A4.71 – Pressure release per crank angle vs crank angle comparison between simulations for 90% iso-octane/water mixture diluted with CO₂.

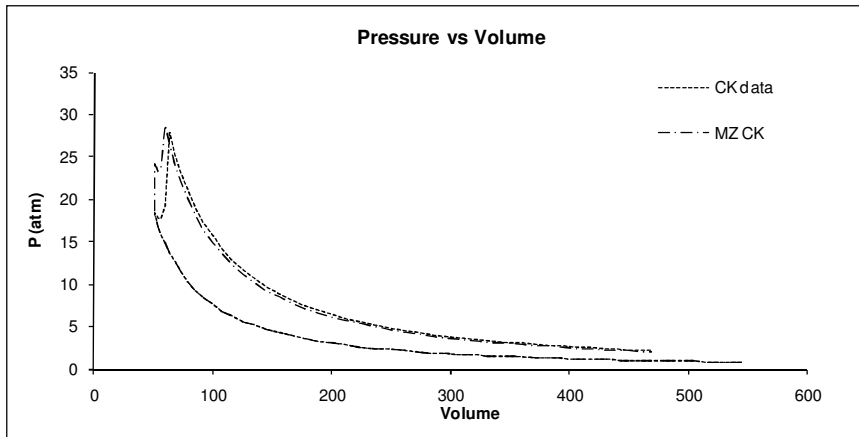


Figure A4.72 – Pressure vs volume comparison between simulations for 90% iso-octane/water mixture diluted with CO₂.

Iso-Octane Fuelled HCCI – 85% iso-Octane

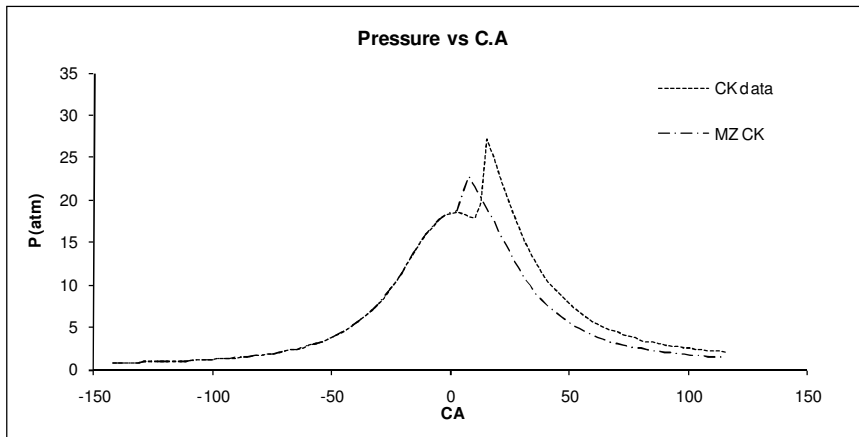


Figure A4.73 – Pressure vs crank angle comparison between simulations for 85% iso-octane/water mixture diluted with CO₂.

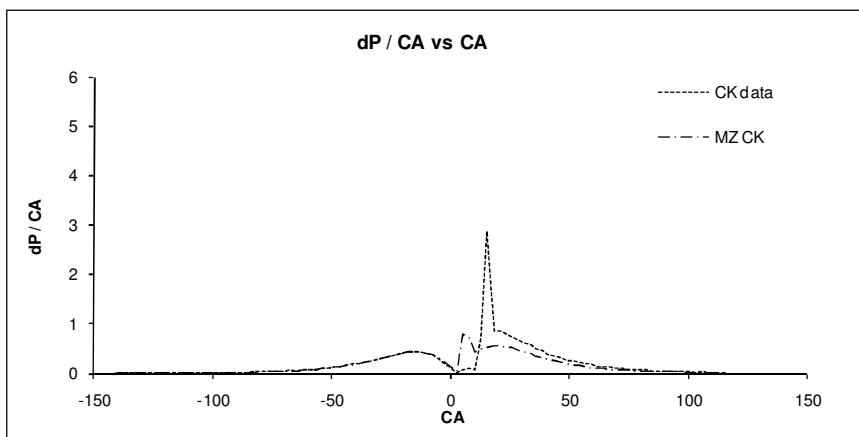


Figure A4.74 – Pressure release per crank angle vs crank angle comparison between simulations for 85% iso-octane/water mixture diluted with CO₂.

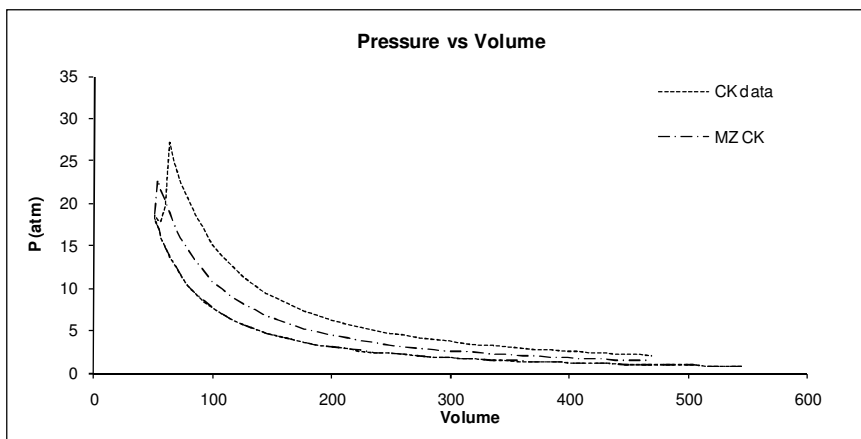


Figure A4.75 – Pressure vs volume comparison between simulations for 85% iso-octane/water mixture diluted with CO₂.