On the Autoignition of Ethanol/Gasoline Blends in Spark-Ignition Engines

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Abstract

Ethanol shows significant potential for improving both the efficiency and emissions of spark-ignition engines. It can be made from renewable or waste sources, in which case its use can substantially reduce the emission of greenhouse gases. However, there is still some uncertainty as to the best use of ethanol in spark ignition engines. This uncertainty is largely related to its blending with gasoline, and the susceptibility of the resulting mixture to the onset of autoignition - a form of uncontrolled combustion that reduces engine performance and leads to engine damage.

This work studies the autoignition of ethanol blended with gasoline and its surrogates in three parts. The octane numbers and the blending behaviour of ethanol with gasoline and its surrogates are first presented. The effect of charge cooling of ethanol on the octane numbers is then examined. Finally, the key parameters and mechanisms leading to the autoignition of these fuel blends are identified and analysed using numerical simulations.

The presented work shows that both $n$-heptane, isooctane and their Primary Reference Fuels blend synergistically with ethanol, whilst toluene blends antagonistically. This finding appears to explain the different reported trends in the octane numbers of ethanol/gasoline blends, and also has implications for fuel design. Also, since the standard Research Octane Number (RON) test is influenced by both the fuel’s charge cooling and its autoignition chemistry, the proposed, ‘modified’ RON test appears to be a more practical means of examining the significance of the autoignition chemistry of various fuels. Finally, nitric oxide (NO) is shown to significantly affect the autoignition of these fuel blends. However, considerable uncertainty is present in the chemical interaction of ethanol with isooctane, $n$-heptane and toluene, and that of NO with different gasoline surrogates and ethanol, suggesting that further experiment and modelling are required.
Declaration

This is to certify that:

(i) the thesis comprises only my original work towards the PhD,

(ii) due acknowledgement has been made in the text to all other material used,

(iii) the thesis is fewer than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices.
I would like to thank the following people for their support throughout my study. This thesis would not have been possible without them.

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## Abbreviations

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<tr>
<td>API</td>
<td>American Petroleum Institute</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing Material</td>
</tr>
<tr>
<td>BDC</td>
<td>bottom dead centre</td>
</tr>
<tr>
<td>bMON</td>
<td>blending Motor Octane Number</td>
</tr>
<tr>
<td>bRON</td>
<td>blending Research Octane Number</td>
</tr>
<tr>
<td>CAD</td>
<td>crank angle degree</td>
</tr>
<tr>
<td>CFD</td>
<td>computational fluid dynamics</td>
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<td>CFR</td>
<td>Cooperative Fuel Research</td>
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<td>CO</td>
<td>carbon monoxide</td>
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<td>Coordinating Research Council</td>
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<td>hydroperoxyl radical</td>
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<td>HUCR</td>
<td>highest useful compression ratio</td>
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<td>intake air temperature</td>
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<td>IMEP</td>
<td>indicated mean effective pressure</td>
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<td>intake value opening</td>
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<td>KP</td>
<td>knock point</td>
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<td>MFB50</td>
<td>CAD at which 50% mass fraction burned due to flame is reached</td>
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<tr>
<td>MON</td>
<td>Motor Octane Number</td>
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<tr>
<td>MTBE</td>
<td>methyl tert-butyl ether</td>
</tr>
<tr>
<td>N₂</td>
<td>nitrogen</td>
</tr>
<tr>
<td>NO</td>
<td>nitric oxide</td>
</tr>
<tr>
<td>NTC</td>
<td>negative-temperature-coefficient</td>
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<td>O₂</td>
<td>oxygen</td>
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**O.N.** octane number  
**ODE** ordinary differential equation  
**OH** hydroxyl radical  
**OI** octane index  
**PP** peak in-cylinder pressure  
**PRFs** Primary Reference Fuels  
**RMSE** root mean squared error  
**RON** Research Octane Number  
**SAE** Society of Automotive Engineers  
**TDC** top dead centre  
**TEL** tetraethyl lead  
**TRFs** Toluene Reference Fuels

### Variables

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<td>$\dot{\omega}$</td>
<td>molar net production rate</td>
</tr>
<tr>
<td>$\dot{m}$</td>
<td>mass flow rate</td>
</tr>
<tr>
<td>$\dot{W}$</td>
<td>rate of work</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stefan-Boltzmann constant</td>
</tr>
<tr>
<td>$A$</td>
<td>area</td>
</tr>
<tr>
<td>$c_p$</td>
<td>constant-pressure specific heat</td>
</tr>
<tr>
<td>$c_v$</td>
<td>constant-pressure specific heat</td>
</tr>
<tr>
<td>$C_0$</td>
<td>multiplier factor to the heat transfer coefficient</td>
</tr>
<tr>
<td>$h$</td>
<td>specific enthalpy (Chapter 5)/ heat transfer coefficient (Chapter 6-7)</td>
</tr>
<tr>
<td>$h_{fg}$</td>
<td>enthalpy of vaporisation</td>
</tr>
<tr>
<td>$k$</td>
<td>weighting factor of the octane index</td>
</tr>
<tr>
<td>$p$</td>
<td>in-cylinder pressure</td>
</tr>
<tr>
<td>$R$</td>
<td>specific gas constant</td>
</tr>
<tr>
<td>$Q$</td>
<td>heat transfer</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$V$</td>
<td>volume</td>
</tr>
<tr>
<td>$v$</td>
<td>volume fraction</td>
</tr>
<tr>
<td>$W$</td>
<td>molecular weight</td>
</tr>
<tr>
<td>$x$</td>
<td>mole fraction</td>
</tr>
<tr>
<td>$Y$</td>
<td>mass fraction</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 Historical background

Alcohol fuels have been used in internal combustion engines for many decades. Indeed, ethanol powered some of the first internal combustion engines designed by Otto in the middle of the 19th century [1], and both ethanol and methanol have been often used as fuels ever since. Whilst other alcohols, and particularly butanol, are of more contemporary research interest [2–4], ethanol remains the dominant alcohol fuel used today.

Of course, the massive growth of affordable crude oil products in the late 19th century displaced ethanol as a fuel, just as it did several other fuels and products [5]. The first 60 or so years of the 20th century then saw the use of ethanol in primarily non-fuel applications, even though ethanol was known to be an effective octane enhancer of gasoline [5].

Indeed, since its introduction in the 1920s, tetraethyl lead (TEL) was in widespread use as an effective and inexpensive octane enhancer for nearly 50 years [6]. The use of TEL, however, raised serious concerns. Long-term exposure to lead from vehicle tailpipe emissions caused significant public health problems [6]. Further, vehicles fuelled with leaded gasoline could not be fitted with catalytic converters due to poisoning of the catalyst substrate, thereby causing greater emissions of other pollutants [6]. Consequently, in the early 1970s the United States Environmental Protection Agency (EPA) ruled to gradually phase out the use of lead in gasoline [7], and later banned the sale of any leaded gasoline beginning January 1, 1996 [8]. In Australia, the sale of leaded gasoline was prohibited in 2002 [9]. Many other jurisdictions have now done the same [10].

The demise of TEL prompted the industry to change production methods to make up for the loss in octane quality in gasoline [6]. Initially, refiners reacted by increasing the quantity of high-octane blendstocks, i.e. benzene and butane, in gasoline. As summarised in Figure 1.1, however, these alternative octane enhancers have their own issues and were soon discontinued. Alcohols and ethers, such as methyl tert-butyl ether (MTBE), later became viable options. MTBE was the more attractive option until the early 2000s, because it was affordable and has a relatively low vapour pressure [6]. Moreover, MTBE could be mixed with gasoline at the refinery and transported using the existing gasoline distribution infrastructure. The use of MTBE as a gasoline additive reached its peak in the early 2000s (Figure 1.2), after which its use fell quickly due to its link to ground water contamination [11].
## 1 Introduction

![Diagram](image.png)

<table>
<thead>
<tr>
<th>Date</th>
<th>Environmental Problem</th>
<th>Available Options for Octane</th>
<th>Regulatory Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>1973-1984</td>
<td>Lead Exposure</td>
<td>MMT</td>
<td>• MMT use denied</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aromatics</td>
<td>• Oxygenates must obtain EPA waiver</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Butane</td>
<td>• Hydrocarbon use unregulated</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alcohols</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>MTBE</td>
<td></td>
</tr>
<tr>
<td>1986-1990</td>
<td>Evaporative Emissions</td>
<td>Aromatics</td>
<td>• Butane use curtailed through RVP limits</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Butane</td>
<td>• Aromatic use unregulated</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alcohols</td>
<td>• Oxygenate use increases</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MTBE</td>
<td></td>
</tr>
<tr>
<td>1988-1995</td>
<td>Benzene Exposure</td>
<td>MTBE</td>
<td>• Benzene cap enacted by Clean Air Act</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alcohols</td>
<td>• Oxygenate use required</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alkylation</td>
<td></td>
</tr>
<tr>
<td>1997-2001</td>
<td>Water Pollution</td>
<td>Alkylation</td>
<td>• MTBE emerges as water pollution threat</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alcohols</td>
<td>• MMT allowed by court order</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MMT</td>
<td>• Regulation of sulfur content</td>
</tr>
</tbody>
</table>

**MMT** = methylcyclopentadienyl manganese tricarbonyl  
**MTBE** = methyl tert-butyl ether  
**RVP** = Reid Vapor Pressure

Figure 1.1: Links between different octane enhancers or gasoline production technologies and the associated environmental problems [6].
1.2 The emergence of ethanol as a transport fuel/fuel additive

With MTBE losing its appeal, the use of ethanol as a gasoline additive began to gain momentum quickly in the United States. As Figure 1.2 shows, there was a sharp increase in the use of ethanol to replace MTBE around 2002. At the same time, the role of ethanol as an oxygenate in gasoline has also become more widely recognised in other regions of the world due to increasingly stringent emission regulations [12].

A tremendous growth in ethanol use in transportation globally has been observed in recent years. In 2008, the percentage of ethanol blended with gasoline globally was estimated to be 5.5% [13]. Although biofuels, primarily bioethanol and biodiesel, constitute a small fraction of the global primary energy consumption (Figure 1.3), world ethanol production nearly doubled from approximately 50 billion litres in 2005 to more than 100 billion litres in 2010 (Figure 1.4), with the three major ethanol producers being the United States, Brazil and the European Union (Table 1.1) [14].

In the United States, the 2007 Renewable Fuel Standard requires that the use of biofuels be increased to a total of 136 billion litres per year by 2022 [16]. Ethanol is expected to supply the majority of this mandated target, and could displace up to approximately 20% of gasoline demand in the United States [16]. Likewise, the European Union has set a target of 10% of transport fuel from renewable sources by 2020 [13]. Further, ethanol constituted 57% by volume of all gasoline-type fuels used in Brazil during the period from 2009 to 2011 [14]. In Australia, the New South Wales state government requires a minimum ethanol content of 6% by volume in all gasoline sold since 2011 [17]. These changes in energy policies worldwide imply a continuing rapid growth in global ethanol production, which is projected by the United Nations...
1 Introduction

Figure 1.3: Global primary energy consumption in 2006 [15].

Figure 1.4: Development of the world ethanol market (billion litres per year) from 2005 to 2021 [14].
1.3 Production of ethanol

Table 1.1: Transport fuel use (gasoline-type, current and projected data) in major ethanol producing countries adapted from [14]. The unit of “bnl” refers to billion litres per year.

<table>
<thead>
<tr>
<th>Country</th>
<th>2009-2011</th>
<th>2021 (projected)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total (bnl)</td>
<td>Of which: ethanol (bnl)</td>
</tr>
<tr>
<td>Brazil</td>
<td>31</td>
<td>21.7</td>
</tr>
<tr>
<td>China</td>
<td>81</td>
<td>2.2</td>
</tr>
<tr>
<td>EU</td>
<td>137</td>
<td>5.5</td>
</tr>
<tr>
<td>USA</td>
<td>541</td>
<td>43.4</td>
</tr>
</tbody>
</table>

to further increase to 180 billion litres in 2021 (Figure 1.4) [14]. This is roughly 14% of current global gasoline consumption [18].

1.3 Production of ethanol

Ethanol is produced from three main feedstocks [19]: sugar-bearing materials (e.g. sugar cane, sugar beet and sweet sorghum), starch (e.g. corn, wheat, cassava and barley), and lignocellulosic biomass (e.g. wood, straw and grasses). Of these different feedstocks, sugar-bearing materials can be most easily converted to ethanol, since their carbohydrate content is already in a fermentable, simple sugar form [20]. With starch, it is necessary to break down the carbohydrate chains to simpler sugars, which are then converted to ethanol by yeasts [21]. This process is more costly and also requires another energy source [20]. Ethanol production using lignocellulosic biomass is the most technically complex, and is not yet commercially significant [20–22]. Importantly, the choice of both the feedstock and the production method has a significant impact on the environmental benefits of ethanol as a fuel, as discussed in the next section.

In the United States, ethanol is primarily produced from corn, while sugar cane is used in Brazil for almost all ethanol production [19]. Wheat and sugar beet are mainly used to produce ethanol in the European Union [19]. In Australia, there are currently three ethanol-producing facilities, with another five planned [23]. The main feedstocks used in Australia include wheat starch, red sorghum and molasses [23]. Of note is that the wheat starch is a residual from flour processing [24], and the molasses is a by-product from sugar cane used in the sugar milling process [25]. Production of ethanol from these feedstocks also creates useful by-products, e.g. protein-rich livestock feed [24] and liquid fertilisers sold to sugarcane growers [25].

1.4 Life-cycle analysis of ethanol

One of the most important aspects concerning ethanol use in transport is whether producing and using ethanol consumes more energy or produces more greenhouse gas (GHG) emissions than the fuel it displaces. This varies significantly depending on the
Table 1.2: Life-cycle GHG emission reductions of ethanol produced from different feedstocks relative to the gasoline baseline [29]. The range of values in the table represents the 10th and 90th percentiles respectively, while those in brackets are of the 50th percentile.

<table>
<thead>
<tr>
<th>Life-cycle GHG emission reductions (%)</th>
<th>Corn</th>
<th>Sugarcane</th>
<th>Switchgrass</th>
<th>Miscanthus</th>
</tr>
</thead>
<tbody>
<tr>
<td>With land use change emissions</td>
<td>19-48</td>
<td>40-62</td>
<td>77-97</td>
<td>101-115</td>
</tr>
<tr>
<td></td>
<td>(34)</td>
<td>(51)</td>
<td>(88)</td>
<td>(108)</td>
</tr>
<tr>
<td>Without land use change emissions</td>
<td>29-57</td>
<td>-6-71</td>
<td>79-98</td>
<td>88-102</td>
</tr>
<tr>
<td></td>
<td>(44)</td>
<td>(68)</td>
<td>(89)</td>
<td>(95)</td>
</tr>
</tbody>
</table>

Figure 1.5: Percentage change in the life-cycle GHG emissions of corn ethanol produced in a natural-gas dry mill plant in 2022 compared to the 2005 gasoline baseline based on the EPA’s studies [34]. The 20% reduction threshold is shown by the thick dashed line, while the two thin dashed lines represent the 95% confidence interval (between 7% and 32% reduction).

production methods as well as the feedstocks. In particular, the net GHG emissions of ethanol produced from corn over its life cycle remain controversial to date. Hill et al. [26] reported a saving of approximately 10% in net GHG emissions during production and combustion of corn ethanol compared to those of gasoline. More recently, researchers from Argonne National Laboratory, building on previous work [27, 28], showed that corn ethanol could reduce GHG emissions by an average of 34% relative to gasoline (Table 1.2) [29].

However, it was argued by others [30–33] that these studies may have overestimated the GHG emission benefits of corn ethanol by underestimating or excluding the indirect land use change, such as deforestation or conversion of grazing land to crop cultivation, as a result of increased demand in biofuels. In response to these arguments, extensive reviews and studies were conducted by the EPA. With indirect land use change (domestic and abroad) considered, the EPA estimated the corn ethanol produced from a natural-gas fuelled dry mill plant in 2022 would yield an average reduction of 21% in GHG emissions relative to gasoline (Figure 1.5) [34].
1.5 Towards intermediate-level blends of ethanol in gasoline

In contrast, most studies have shown that ethanol produced from sugarcane has the potential for significant net energy and GHG emissions benefits [29, 34, 35]. Wang et al. [29] reported that GHG emissions can be reduced by 51% relative to gasoline, even when land use change is accounted for (Table 1.2). Similarly, the EPA estimated an average reduction of 61% in GHG emissions when displacing gasoline with ethanol produced from sugarcane [34]. It was also found [36] that savings in GHG emissions resulting from ethanol produced from sorghum and wheat could be similar to those of sugarcane.

Likewise, cellulosic ethanol has been shown to yield potentially significant GHG emission reductions [29, 34, 37, 38]. Consequently, further savings of at least 60% in GHG emissions from cellulosic ethanol, relative to gasoline, are called for under the EPA’s final rule [34].

1.5 Towards intermediate-level blends of ethanol in gasoline

While the 2007 Renewable Fuel Standard mandates the quantity of ethanol to be consumed each year in the United States, it does not specify how that goal should be achieved. Prior to 2011, conventional gasoline vehicles in the United States were limited by the EPA to use gasoline containing a maximum of 10% (v/v) ethanol (E10) [14]. While flexible-fuel vehicles can run on blends containing up to 85% (v/v) ethanol (E85), they constituted only a very small fraction (approximately 10 million in 2011 [39]) of the total light passenger vehicles in the United States, and these vehicles were only fuelled with E10 most of the time [14]. As a result, the so-called “blend wall” for ethanol was created, where the maximum amount of ethanol that can be blended into gasoline is lower than that mandated (Figure 1.6) [40].

The EPA then ruled in 2011 that the maximum concentration of ethanol blended into
gasoline be increased to 15% (v/v) (E15) for light-duty vehicles of model years 2001 and later [14]. With the approval of E15, it is projected that ethanol use in the United States will not reach the blend wall until 2016 (Figure 1.6) [14, 40]. However, the EPA recognised that it is still challenging to increase the consumption of ethanol/gasoline blends above E10 to meet the mandated volume in the near future [22]. These challenges are in part due to “current infrastructure and market-based limitations” [22]. For instance, the total corn ethanol production capacity in the United States in 2013 increased by less than 1% compared to 2012 [41]. Also, consumers were cautioned that using E15 might void the warranty of their vehicles due to its possible damage on engines [14], although most studies [42, 43] showed no evidence of deterioration in engine durability with the use of E15.

Nonetheless, it was projected that gasoline blends in the United States should contain approximately 16% (v/v) ethanol by 2021 (Table 1.1) [14], and could potentially reach 24% (v/v) [44]. Stein et al. [45] reported that these intermediate-level ethanol blends may be optimal in increasing engine efficiency and reducing specific emissions by capitalising on their higher octane numbers. Nonetheless, as this thesis argues, the best use of ethanol in gasoline blends is still not fully understood, and remains a topic of significant research today [44–46].

1.6 Summary

Ethanol use in transportation has grown significantly in recent years. The reasons for this growth are several, and include environmental, economic and social considerations. The removal of lead from gasoline, and the possible link of its replacement methyl tert-butyl ether (MTBE) to drinking water contamination, have led to the increased use of ethanol as an oxygenate and octane enhancer. These are in addition to the potential greenhouse benefits of displacing gasoline with ethanol. Whilst variable, and strongly dependent on the feedstock, production route and the accounting of indirect land use change, these benefits appear significant in some cases [26, 34, 35, 37].

World ethanol production nearly doubled from 2005 to 2010 [14]. In the United States, the 2007 Renewable Fuel Standard further requires that the use of biofuels be increased to a total of 36 billion gallons per year by 2022. Ethanol is expected to supply the majority of this mandated fuel volume, and could displace approximately 20% of gasoline demand in the United States by this date [16]. These changes in energy policy imply a continuing growth in ethanol production and the use of intermediate-level ethanol blends in gasoline (particularly in the United States) in the near future. As a result, determination of the best use of ethanol in these blends is a problem of growing practical importance, and is the greater aim to which this thesis intends to contribute.
2 Literature Review

This chapter reviews the literature that is relevant to knock and autoignition of spark-ignition fuels, specifically ethanol/gasoline blends. The origin of knock is first reviewed, followed by the historical background on the standard methods for rating knock, e.g. the octane numbers. The relevance of the octane numbers to the performance of modern engines is further discussed. Next, an overview of the numerical methods used to model autoignition in spark-ignition engines is presented, followed by a discussion of the different chemical kinetic models of the oxidation of spark-ignition fuels. In addition, an assessment of the benefits and drawbacks of ethanol as a fuel or fuel additive is provided in terms of engine performance and emissions. Lastly, the research questions of this work in relation to the autoignition of ethanol/gasoline blends are presented.

2.1 Knock and autoignition

2.1.1 What is knock?

Knock is the sound associated with abnormal combustion in which the unburned air-fuel mixture, commonly known as the “end gas”, burns at a point or multiple points ahead of the propagating flame front [47]. This abnormal combustion usually results in steeper local pressure rise than normal, due to the rapid release of energy contained in the end gas. This steep pressure rise subsequently creates pressure waves that propagate across the combustion chamber at a high velocity. The pressure waves are not completely dissipated when they first contact the cylinder wall. Instead, the waves are reflected back across the chamber. The oscillations of the pressure waves tend to bring the entire combustion chamber to its resonant frequency, and this results in a loud metallic pinging noise that defines knock [47, 48]. Figure 2.1 shows the typical in-cylinder pressure trace of a knocking cycle [49]. Oscillations of the pressure could be observed after the onset of knock.

The study of knock began around 1882, a time when the Otto-cycle internal combustion engine was still in its early days [50]. During World War I, knock was widely known as the primary limiting factor of “power output and economy of the spark-ignition engine” [51, 52]. Numerous studies on knock emerged during that time, as various instruments, including those of carbon resistances, piezoelectric crystals and electromagnetic generators, had been successfully devised to measure the in-cylinder pressure [53]. At the same time, the introduction of high-speed photography of the in-cylinder combustion events provided a good opportunity to visualise and characterise
2.1.2 End-gas inhomogeneity

The temperature and gas compositions in the end gas are not uniform. Since autoignition will occur where the conditions are most favourable, the average properties of the end gas may not be a good indicator of where and when autoignition will take place. Bradley reported the possible causes of inhomogeneity in the end gas [54]:

- imperfect air-fuel mixing, and turbulence,
- mixing of hot residual gas from the previous cycle,
- desorption of reactive species from wall deposits,
2.1 Knock and autoignition

![Image of knocking cycle](image)

Figure 2.2: An LIF image of a knocking cycle. Note the presence of hot spots (dark spots) where autoignition took place [57].

- non-uniform cooling by the cylinder wall, or heating by the exhaust valve,
- dispersed particulates which might catalyse or inhibit reaction.

It is therefore difficult to determine the transient properties of the end gas, due to varying degrees that each possible cause could affect the uniformity of the charge. Temperature inhomogeneity plays an important role in determining the knock onset, as knock often originates from one or multiple local hot spots [55]. Numerous experiments indicated the presence of hot spots preceded knock. König and Sheppard [56] were able to show one or multiple local hot spots in knocking cycles using high-speed schlieren and natural-light photography. Through the use of laser-induced fluorescence (LIF), temperature fluctuations of more than 20 K were found in a nominally homogeneous end gas [57]. Figure 2.2 illustrates the hot spots in a knocking cycle.

It was further suggested that end-gas autoignition could propagate from the hot spots in three modes [58],

1. deflagration - steep temperature gradients; knock may be non-existent or moderate,
2. thermal explosion - small temperature gradients; moderate knock,
3. developing detonation - intermediate temperature gradients; violent knock.

In the deflagration mode, a weak pressure wave propagates immediately away from the exothermic centre. Combustion experiences a gradual transition to deflagration and “continues as a normal flame”. Thermal explosion occurs when the end gas is nearly isothermal, resulting in effectively simultaneous fuel oxidation. When the thermal gradient is below a certain critical value, a strong shock is created and intense chemical reactions will be sustained, leading to developing detonation. A later study reported that interaction between adjacent deflagrative autoignition events may change the temperature gradients, which could then lead to developing detonation [59]. Of the three autoignition modes, only the developing detonation is capable of generating extreme pressure rise and potentially damaging the engine [60].
2 Literature Review

2.2 RON/MON test methods and knock measurement

2.2.1 The CFR engine

History of the CFR engine
Recognising that knock was the limiting factor of engine performance, in 1922 the Co-operative Fuel Research (CFR) committee was established in the United States, with the aim to develop a means of measuring and defining gasoline combustion characteristics [61]. In 1928, a group of fuel refiners and engine builders gathered within the CFR committee and started developing the much needed engine test method for motor gasoline knock rating. By 1929, Waukesha Motor Company began shipping the first variable-compression-ratio engine meant for knock rating to the CFR for evaluation. Numerous studies were conducted on the effects of various parameters, such as the intake temperature and spark timings, on knock intensity using the Waukesha engine. As a result, a standardised testing procedure for fuel rating was established, and the 0-100 octane scale based on blends of isooctane and n-heptane was defined, culminating in the Research Method and the corresponding Research Octane Number (RON) as we know today. The Waukesha engine became the base testing unit as specified in the “Research Method”, and is now more commonly known as the “CFR engine” [62].

In 1932, a study was carried out to determine the correlation of fuel rating obtained using the Research Method and that from road tests. With over 2500 test runs using a number of different vehicles and fuels, it was found that the results from the Research Method had a positive bias of about 2.5 to 3.0 octane number when compared to those from the road tests. Consequently, three changes were made to the Research Method in an attempt to better correlate the test method to the on-road fuel rating [62],

- increase the speed from 600 to 900 rpm,
- increase the temperature of the air-fuel mixture to 149 °C,
- advance the spark timing according to the compression ratio.

The changes were necessary in order to simulate a testing condition which was harsher as well as better represented by engine designs at that time relative to the Research Method. These modifications to the Research Method were approved by the CFR committee in 1932 and were subsequently incorporated into a new fuel rating method known as the “Motor Method”, which rates a fuel for its Motor Octane Number (MON).

For over 70 years, both the Research Method and Motor Method have remained the primary fuel rating methods used throughout the world. They are also defined in the American Society for Testing Material (ASTM) standards [63, 64]

- ASTM D-2699, the CFR F-1 Research Method Octane Rating Unit,
- ASTM D-2700, the CFR F-2 Motor Method Octane Rating Unit.
2.2 RON/MON test methods and knock measurement

The test methods
Both the RON and MON are intended for measuring the propensity of a fuel to knock at a given compression ratio. To determine the octane number, the CFR engine is run with the test fuel, say, unleaded gasoline, at the specified conditions. Based on the reading of the “knock meter” (a standard part of the CFR engine), the compression ratio is increased until the meter reports a knock intensity of about 50. The test is repeated with two blends of Primary Reference Fuels (PRFs) having known octane numbers that will bracket the knock rating of the test fuel. The octane number is then obtained by interpolation based on the bracketing reference fuels [63, 64].

Yates and his colleagues [65, 66] did a careful study to unravel the fundamental working principles of the knock measurement system on the CFR engine. The system essentially consists of a magnetostrictive pickup sensor, a signal conditioning device known as the detonation meter, and the knock meter which displays the knocking intensity. They reported that the low-pass filter present in the detonation meter was incapable of processing high-frequency signals, i.e. the pressure oscillations caused by autoignition of the end gas. Instead, the detonation meter was designed to respond to the rate of pressure rise. This is different from many other methods used to define the knock intensity in the literature, as they are based on interpretations of the pressure oscillations. The authors suggested that one should exercise caution when relating the MON and RON with autoignition [65, 66]. They also successfully emulated the knock measurement system by appropriately filtering the rate of pressure rise obtained with an ordinary piezoelectric pressure transducer [67].

Questions have also been raised as to whether the RON and MON methods are appropriate for rating fuel blends with high ethanol content. Originally developed for rating gasoline, use of the standard CFR engine may be problematic for fuels with drastically different properties [68, 69]. The major hardware limitation is the fuel metering jet and the air-fuel mixture heater. The stock fuel metering jet, while providing a sufficient fuel flow rate of gasoline or PRFs, may limit the fuel supply when rating ethanol due to its low stoichiometric air-fuel ratio [70]. Hence, careful selection of an appropriate fuel metering jet is required in order to deliver a sufficient fuel flow rate. As a result, the ASTM standards recommend that both test methods may not be applicable to fuels with high oxygenate concentration, although no information about the upper limit of the oxygenate concentration that may be used is provided [63, 64].

2.2.2 Octane number

Earlier work, especially that of Sir Harry Ricardo, had shown that compression ratio was an appropriate engine parameter to indicate the threshold of knock [71]. Ricardo, after World War I, studied the correlation of compression ratio to knock, and coined the term “highest useful compression ratio” (HUCR) by which a gasoline engine was limited before knock became so intense that power no longer increased with compression ratio [71]. In the 1920s, recognising the close relationship between compression ratio
Table 2.1: Operating conditions of the Motor and the Research methods.

<table>
<thead>
<tr>
<th>Engine parameter</th>
<th>Research Method</th>
<th>Motor Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine speed (rpm)</td>
<td>600</td>
<td>900</td>
</tr>
<tr>
<td>Intake temperature (°C)</td>
<td>52</td>
<td>149</td>
</tr>
<tr>
<td>Spark timing (CAD bTDC)</td>
<td>13</td>
<td>14 - 26</td>
</tr>
</tbody>
</table>

and the onset of knock, the CFR committee began to look for an appropriate scale on which the knock rating could be based. In 1927, Graham Edgar introduced an octane rating scale that defined the knock-limited compression ratio with respect to the blend proportion of the two PRFs, namely isooctane and \( n \)-heptane [72]. For example, a blend of 20% of \( n \)-heptane and 80% of isooctane by volume would provide an octane number of 80. Any fuels that are tested to have an octane number of 80 is assumed to have identical knocking characteristics as the PRF blend under the same conditions. This scale provided a robust method for knock rating and was quickly accepted by the CFR committee as part of the testing method. Later, the octane scale was extended from 100 to 120 to accommodate fuels that were found to have an octane number greater than 100. Instead of using the blends of the PRFs, TEL was added to isooctane to establish the reference fuels [63, 64].

With the use of the octane scale, two different octane numbers were introduced. The RON was used with the Research method; the MON, on the other hand, was associated with the Motor method. The different conditions at which these test methods are conducted are listed in Table 2.1.

The difference between the RON and the MON of a given fuel is called the “fuel sensitivity” (Figure 2.3a and Figure 2.3b). The sensitivity of a PRF is zero by definition, and for most other paraffinic fuels the sensitivity is close to zero. Olefins and aromatics are sensitive fuels, with a positive sensitivity. The sensitivity of commercial gasoline is about 10 depending on the fuel composition [47, 54]. Leppard [73] conducted an extensive study on the sensitivity of different fuels, and suggested that the sensitivity of a fuel was attributed to the different autoignition chemistry exhibited by paraffins compared to olefins and aromatics. He reported that paraffinic fuels were less prone to autoignite under lower pressure, shorter reaction time, and higher temperature due to the negative-temperature-coefficient (NTC) behavior. On the other hand, olefins and aromatics did not exhibit any NTC characteristics at all. Since the Motor Method provided a condition of lower pressure and higher temperature compared to the Research Method, it was shown that paraffins generally had higher MONs than those of olefins and aromatics [73].

### 2.2.3 Synergistic blending and antagonistic blending

One of the major issues associated with the RON and MON is that the octane number of a fuel blend is not necessarily a linear interpolation of the octane numbers of the its pure constituents. Studies have shown that a blend of alkanes and alkenes tends to produce
2.2 RON/MON test methods and knock measurement

(a) Paraffins

![Graph showing MON as a function of RON for different a) paraffins and b) monoolefins](image)

Figure 2.3: MON as a function of RON for different a) paraffins and b) monoolefins [73]. Note that any fuel below the solid line is considered sensitive.

(b) Monoolefins.

an octane number that is higher than that obtained by linear interpolation from that of its pure constituents, and this is called “synergistic blending” [54]. Blending alkanes and aromatics, however, exhibits the opposite effect, where the resulting octane number can be lower than that obtained by linear interpolation from that of its pure constituents, i.e. antagonistic blending. Figure 2.4a and 2.4b show the non-linearity of octane numbers when blending fuels of different types [54]. To work around this problem, Leppard [74] introduced the blending octane number (bON) by “extrapolating the experimentally determined octane number to a hypothetical mixture” using a specific equation. This non-linear behavior of RONs and MONs is complicated, particularly for gasoline, which is a complex mixture of hundreds of different hydrocarbon species. Hence, a thorough understanding of the chemical interaction between different fuels is required in order to explain these reported synergism and antagonism in the octane numbers.

2.2.4 Relevance of RON and MON in modern engines

It is generally agreed that the RON and MON are unable to completely describe knocking characteristics of commercial gasoline in modern engines [47, 54]. Instead, the octane index (OI) is more commonly used to represent the anti-knock performance of a given fuel. The OI is defined to be a weighted average of the RON and MON,

\[ OI = kMON + (1 - k)RON, \]

where \( k \) is the weighting factor. When \( k \) is equal to one, the octane index is entirely dependent on the MON; when \( k \) is zero, it simply becomes the RON. Presently, \( k \) is taken to be 0.5 in the United States, translating into an octane index equal to the average of the RON and MON at the petrol pump [75].

The CFR Research method was first established in the early 1930s, in an attempt
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(a) Antagonistic blending

(b) Synergistic blending

Figure 2.4: a) Antagonistic (the octane number of the mixture is lower than either of the pure components) and b) synergistic blending (the octane number of the mixture is higher than the pure components) of different fuels [54].

To characterise knock in spark-ignition engines for a given fuel. Numerous road tests, however, indicated poor correlation of the test method with the knocking characteristics of the actual vehicles. The CFR committee thus brought in the Motor Method, which had more severe rating conditions, in 1932 to better represent the knocking behavior of the engines of that time. By then, the octane index was equal to one, with $k = 1$. Nonetheless, by the end of the 1930s, the Motor method began to show degrading correlation with the road rating characteristics, with $k = 0.65$ [76]. It was found that improvements in engine designs had made vehicle engines cooler, and the more severe testing conditions of the Motor Method became less representative [62]. This trend continued as new engine designs were introduced over time, and $k$ had dropped to 0.5 by 1946 [77]. The Coordinating Research Council (CRC), which superseded the CFR committee, conducted annual surveys of the octane requirement of the road vehicles in the United States from 1947 to 1996 [78]. $k$ was found to decrease from an average of about 0.27 in 1951 to approximately 0.10 in 1991 (Figure 2.5). The on-the-road knock rating thus appears to correlate better with the Research Method than the more severe Motor Method.

In 2001, Kalghatgi [75] performed a study to determine the octane index of 21 different fuels in a single-cylinder engine, and reported that $k$ is a function of engine operating conditions. In some of the test cases, $k$ even became negative, suggesting that a fuel with a lower MON could result in better anti-knock performance at a given operating point of the engine. Indeed, in a companion paper, Kalghatgi concluded from tests of 23 modern vehicles that $k$ was generally negative, and that the octane index
2.2 RON/MON test methods and knock measurement

at the fuel pump in the United States, i.e. \((\text{RON} + \text{MON})/2\), was no longer appropriate to describe the anti-knock performance of a given fuel in modern vehicles [79]. In another study by Bradley et al. [80], \(k\) was found to be between -0.05 and -1.52 for lean homogeneous charge compression ignition (HCCI) combustion using a quasidimensional combustion model. It was further suggested that “it was not possible a priori to predict the engine performances on the basis of either the RON and MON tests”. More recently, Mittal and Heywood [78, 81] reported a \(k\) value of approximately zero for modern engines, and predicted that \(k\) should further decrease to -0.25 with the use of direct injection and turbocharging. This decline of \(k\) is likely a result of better cooling and breathing of modern engines [78].

2.2.5 Other knock quantification methods

In addition to the RON and MON, many different methods of characterising knock have been developed and put into practical use. In contrast to a proprietary measurement hardware such as the detonation meter on the CFR engine, these knock quantification methods rely on the use of an ordinary in-cylinder pressure transducer. Although convenient, knock characterisation based on in-cylinder pressure varies a lot, depending on the location of the pressure transducer, the geometry of the combustion chamber, etc. A good review of different knock measurement methods can be found in [82] and [83], and they are summarised below.

1. The maximum amplitude of the pressure oscillation was used to define the knock intensity by Chun and Heywood [84], as well as Benson [85]. A band pass filter was applied to the pressure signal with a window period from 30° before top dead centre (TDC) to 70° before TDC.

2. The difference between the maximum and the minimum values of the pressure oscillation was used by Yates [66]. Similarly, a band pass filter was applied to
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the pressure signal over a range of 5 to 25 kHz. The resulting knock intensity is double that of the above approach.

3. The third derivative of the pressure signal with respect to time was introduced by Checkel and Dale [86]. Although they claimed this method produced a much higher absolute value when knock occurred, the knock intensity obtained actually depended on the sampling frequency [82].

4. The magnitude of the pressure oscillations averaged over a 20-crank-angle-degree window, also known as KI20, was used by Konig and Sheppard [56]. KI20 was found to correlate well with the crank angle of knock onset.

5. The summation of the peak corrected pressure signal over a number of cycles was used by Brunt [87].

6. Energy methods, involving fast Fourier transform (FFT) and power spectral density (PSD), have commonly been used in characterising knock [82, 87]. The knock frequency calculated using these method may be compared to the theoretical estimation of the resonant mode frequencies in the cylinder cavity, as described below.

The pressure waves induced by the occurrence of knock can be modelled by fitting a solution of the wave equation for sound to the geometrical boundaries of the combustion chamber [53]. The estimated resonant frequency (Hz) for mode $m$ and $n$ is given by [87],

$$f_{m,n} = \frac{C \rho_{m,n}}{\pi B}$$

(2.2)

where $C$ is the acoustic velocity (m/s), $\rho_{m,n}$ is the resonant mode factor, $B$ is the cylinder bore (m), $m$ is the circumferential oscillation mode number and $n$ is the radial oscillation mode number. Using the above equation and assuming the acoustic velocity to be 950 m/s, the first circumferential resonant frequency of the CFR engine is approximately 6.7 kHz. Nonetheless, the knock frequency in modern engines should differ from that in the CFR engine, since this frequency is dependent on the combustion chamber geometries.

2.3 Modelling of spark-ignition engines

A fundamental understanding of knock and autoignition in spark-ignition engines can be obtained using an engine model with chemical kinetics. This section first reviews the different numerical methods used to simulate spark-ignition engine combustion, and then discusses previous work on the fuel oxidation chemistry, e.g. the underlying chemical models and various published kinetic mechanisms for ethanol/gasoline-surrogate blends.
2.3 Modelling of spark-ignition engines

2.3.1 Single-zone, multi-zone, and multi-dimensional models

Different model frameworks exist for simulating spark-ignition engine cycles, and they are typically classified as thermodynamic (single- and multi-zone) and multi-dimensional models [88]. Generally known as thermodynamic models, the single-zone and multi-zone models are based on the conservation of mass and energy. Since the implementation is time-dependent only, these models require solving ordinary differential equations (ODEs). A multi-zone model differs from a single-zone model in that certain geometrical constraints are imposed in the combustion submodel. Because of this, the single-zone model is sometimes referred to as a zero-dimensional model, while the multi-zone model is considered quasi-dimensional.

In the single-zone model, combustion is dictated by a predefined mass burning rate. The burning rate is commonly approximated using the Wiebe function [88]. This mass burning rate, however, needs to be determined for each operating condition of the engine, and is normally determined from the in-cylinder pressure traces. Therefore, when one specific mass burning rate is used, extrapolation to other operating conditions will be questionable.

The multi-zone model can avoid this particular problem with the use of a flame propagation model to estimate the mass burning rate. In the most basic formulation of a multi-zone model, at the instant of ignition the combustion chamber is divided into a burned zone and an unburned zone, separated by a propagating flame front of negligible thickness [89]. Patterson and Van Wylen first introduced the two-zone thermodynamic model in 1963 [90]. The first implementation of this model with ordinary differential equations was then published by Krieger and Borman in 1966 [91]. In 1976, the “quasi-dimensional” concept was introduced by Lancaster et al., who, from the burned volume, calculated the position of a spherical flame front propagating from the spark plug [92]. This formulation, however, was restricted to disc-shaped combustion chambers. Mattavi et al. [93] from General Motors Research Lab successfully extended the two-zone quasi-dimensional model to combustion chambers of different shapes in 1980. Poulos and Heywood [94] later presented a computational method to deal with the implementation of a two-zone model in a combustion chamber that could be of any shape. In the years that followed, the two-zone model was expanded to multi-zonal formulations, and many submodels were included to improve the model. The framework of the model, however, remained essentially the same.

As opposed to quasi-dimensional models, a multi-dimensional model attempts to numerically simulate the complex phenomena of combustion, some of which are listed below [95],

- compressible fluid dynamics,
- chemical equilibrium and kinetics,
- spray droplet interactions, as in a direct-injection engine,
- turbulence effects.
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The problem becomes increasingly complex due to the coupling of different systems of equations that model the phenomena above. In general, the model is governed by the Navier-Stokes equations in addition to the conservation of mass and energy. The governing equations are both temporally and spatially dependent, and therefore the model normally involves solving partial differential equations using the computational fluid dynamics (CFD) method, e.g. the code “KIVA” [95, 96]. Multi-dimensional models can be very computationally intensive, e.g. when introducing even a small number of species to simulate chemical kinetics (see Section 2.4).

2.3.2 Modelling of the end gas

There are generally three approaches to model the end gas in order to predict the onset of autoignition [97]. Different from typical combustion modelling where chemical equilibrium is assumed, these approaches incorporate at least some degree of chemical kinetics (to be described in Section 2.4.2) into the governing equations.

The first approach treats the end gas as a single zone, which is spatially homogeneous in temperature, pressure and compositions [49, 98, 99]. While incapable of addressing end-gas inhomogeneity, this single-zone approach can predict autoignition onset relatively well [49, 98, 99]. Further, this method is the least computationally intensive, and therefore permits the use of comprehensive kinetic mechanisms. However, models used in these studies [49, 98, 99] lacked blowby as well as accurate residual gas modelling, and the predictions were highly sensitive to the initial conditions. Hirst and Kirsch [99] used this approach along with the “Shell” kinetic model to simulate autoignition in a CFR engine. The knock intensity was found to correlate to some degree with the proportion of unburned fuel at the onset of autoignition. They also noted that the knock intensity was highly sensitive to the initial pressure and temperature, the heat transfer in the unburned gas, and the mass burning rate.

To improve the single-zone end-gas model, the end gas can be assumed to be the core, usually adiabatic, that is surrounded by a quench boundary layer near the cylinder wall [84]. Hajireza et al. [100] developed a quasi-dimensional multi-zone model which treats the end gas as having a thermal boundary layer of varying thickness (Figure 2.6). Heat transfer and mass transport could occur between the boundary layer and the hotter core. They also studied the effects of different thicknesses of the boundary layer on autoignition, and found that by reducing the thickness from 0.2 mm to 0.01 mm, autoignition was delayed by as much as 7.5 crank angle degrees (CAD). It was suggested that the thickness of the thermal boundary layer was critical in modelling autoignition.

In another model by Perumal and Floweday [101], the end gas was divided into multiple zones by volume, in addition to a thermal boundary layer. Each zone was assigned a unique value of temperature at intake valve closure (IVC) in an attempt to describe the temperature inhomogeneity (gradient = 20 K) in the end gas. This model successfully reproduced similar temporal pressure development for isoctane under RON conditions to that observed experimentally with the use of a formal structure (see Section 2.4.2.1),
2.4 Chemical kinetics

Chemical kinetics is the study of the rates of chemical reactions. Typically, these reactions are complex pathways from reactants to products. The complete oxidation or combustion process can involve many different elementary reactions [106, 107]. Chemical kinetics has been widely used to model autoignition and knock of hydrocarbon fuels since the 1970s [54]. The early work focused on modelling the kinetics of simple fuels, such as hydrogen and methane, and recent developments have resulted in comprehensive kinetic mechanisms of more complex fuels, including \( n \)-heptane and isoctane [108].

2.4.1 Stiff ODEs

Modelling of chemical kinetics often involves solving a system of first-order ordinary differential equations (ODEs) that describes how the chemical reactions proceed from given initial conditions. This system of ODEs is normally considered stiff, where the...
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time scale of certain chemical species, especially radicals, could be of several orders of magnitude smaller than that of the rest of the species. Stiff ODEs are normally solved using an implicit method even though it is more computationally intensive, because an explicit method will normally result in numerical instability for problems with a wide range of time scales. In fact, an implicit method can assume all values of the time step for linear first-order ODEs [109]. Solving these ODEs, therefore, require special computing algorithms, and several general-purpose software packages, e.g. Chemkin, are available for this purpose. Because Chemkin is widely used for kinetic computations, most reaction mechanisms have been developed in Chemkin format [52].

2.4.2 Kinetic models

Different kinetic models have been proposed in the last few decades to simulate the oxidation chemistry of different fuels. Generally these models can be categorised into two main groups - formal structures and comprehensive mechanisms, which will be discussed in the following sections.

2.4.2.1 Formal structures

Formal structures aim to represent certain experimental features or data by “establishing the minimum kinetic criteria” needed [110]. In formal structures, the thermokinetic analysis associated with the oxidation of hydrocarbons attempts to identify and model the key chemical interactions, including the cool-flame oscillations, two-stage ignitions as well as the NTC behaviours. These ‘lumped’ models are generalised in that the kinetics of all species is represented by only a few generic equations. The heat release is not calculated for every reaction, since it is hard to assign the heat of reaction for a given generic species. Instead, only the total chemical heat release is calculated for the reaction system as a whole. To be sufficiently accurate, the parameters of the generalised models involved have to be obtained and validated against experimental data. Of all the formal structures developed for hydrocarbons, the widely cited ones are as follows [110],

1. Gray and Yang,
2. Wang and Mou,
3. Griffiths,
4. Shell Model.

The “Shell” model is perhaps the most widely used formal structure in the simulations of autoignition of hydrocarbons since its introduction by Halstead et al. in 1975 [111], and will be examined in more detail here. Based on a degenerately branched chain mechanism, the Shell model is a mathematical model constructed to capture the essential features of autoignition of hydrocarbons under the physical conditions similar to
those of the end gas in an internal combustion engine. In fact, the pattern of behaviour that is observed in autoignition of a wide range of fuels bears numerous similarities and generality, implying a common basic mechanism. For example, the differences in the autoignition characteristics of gasoline, when compared to those of propane, are “of degree rather than of kind” [99]. Therefore, a generalised model, in which there is no specific identification of chemical reactions and intermediate species, should provide an adequate kinetic framework in simulating the various autoignition characteristics of hydrocarbons. The generalised kinetic reactions of the Shell model are listed below [111, 112],

- primary initiation: \( RH + O_2 \rightarrow 2\mathcal{R} \) (rate coefficient \( k_q \)),
- propagation cycle: \( \mathcal{R} \rightarrow \mathcal{R} + \text{products and heat} \) (rate coefficient \( k_p \)),
- propagation forming B: \( \mathcal{R} \rightarrow \mathcal{R} + B \) (rate coefficient \( f_1 k_p \)),
- propagation forming B: \( \mathcal{R} + Q \rightarrow \mathcal{R} + B \) (rate coefficient \( f_2 k_p \)),
- linear termination: \( \mathcal{R} \rightarrow \text{stable species} \) (rate coefficient \( f_3 k_p \)),
- propagation forming Q: \( \mathcal{R} \rightarrow \mathcal{R} + Q \) (rate coefficient \( f_4 k_p \)),
- quadratic termination: \( 2\mathcal{R} \rightarrow \text{stable species} \) (rate coefficient \( k_t \)),
- degenerate branching: \( B \rightarrow 2\mathcal{R} \) (rate coefficient \( k_B \)).

These result in a set of ordinary differential equations that can describe the kinetic interactions of autoignition,

\[
\frac{1}{V} \frac{dn_R}{dt} = 2 \left\{ \frac{k_q[RH][O_2] + k_B[B] - k_t[\mathcal{R}]^2}{n_{\text{tot}}} \right\} - f_3 k_p[\mathcal{R}],
\]

\[
\frac{1}{V} \frac{dn_B}{dt} = f_1 k_p[\mathcal{R}] + f_2 k_p[Q][\mathcal{R}] - k_B[B],
\]

\[
\frac{1}{V} \frac{dn_Q}{dt} = f_4 k_p[\mathcal{R}] - f_2 k_p[Q][\mathcal{R}],
\]

\[
\frac{1}{V} \frac{dn_{O_2}}{dt} = -pk_p[\mathcal{R}],
\]

\[
n_{RH} = \left( n_{O_2} - n_{O_2}(t = 0) \right) + n_{RH}(t = 0),
\]

\[
\frac{dT}{dt} = \frac{1}{c_v n_{\text{tot}}} \left[ Q_k - Q_L - \frac{n_{\text{tot}}RT}{V} \frac{dV}{dt} \right],
\]

where \([i]\) indicates the concentration of species \( i \), \( \mathcal{R} \) is the radical, \( RH \) is the fuel, \( B \) is the degenerate branching agent, \( Q \) is the labile intermediate, \( k_q, k_p, k_B, k_t, f_1 k_p, f_2 k_p, f_3 k_p, f_4 k_p \) are the rate coefficients for the corresponding reactions, \( V \) is the system
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volume, $T$ is the system temperature, $R$ is the universal gas constant, $c_v$ is the constant-volume specific heat, $n_{tot}$ is the total number of moles, $Q_L$ is the heat loss rate obtained by fitting experimental pressure traces, and $Q_k$ is the chemical heat release given by,

$$Q_k = k_p q V [R], \quad (2.9)$$

where $q$ is the exothermicity per cycle. Assuming two hydrogen atoms are generally abstracted when each carbon atom is consumed to form new products during a single propagation cycle, $a$ and $m$ can be determined from the overall stoichiometry,

$$\frac{1}{m} C_n H_{2m} + a O_2 \rightarrow z \left( \frac{n}{m} \right) CO + (1 - z) \left( \frac{n}{m} \right) CO_2 + H_2O, \quad (2.10)$$

where $z$ is assumed to be a constant of 0.67, and $a$ is defined as

$$a = \frac{n(2 - z) + m}{2m}. \quad (2.11)$$

The Shell model, in its preliminary form, was able to generally predict the cool flame effects, two-stage ignitions as well as the NTC regions of low-temperature oxidation of hydrocarbons. In 1977, the original authors extended and fitted the mathematical model (which is governed by 26 parameters in the aforementioned six equations) with autoignition data of common fuels in a rapid compression machine [112]. The fit was mainly on optimising the prediction of induction periods, and most weight was given to the total induction period. The six fuels used included PRFs of RON 70, 90 and 100 as well as two Toluene Reference Fuels (TRFs), which are a mixture of isooctane, $n$-heptane and toluene. They were able to obtain a good fit of the model with the available experimental data over a wide range of temperatures and pressures. In 1980, the Shell model was first used in simulating knock in SI engines using a two-zone thermodynamic model [99]. Even though the model made no attempt to predict the knock amplitude or peak pressure, it could still predict the number of moles of unburned fuel left in the end gas, and the predicted onset of autoignition was within an error of two crank angle degrees when compared to experimental data under RON testing. However, it was also found that the model was fairly sensitive to the empirical input parameters, including the heat transfer rate as well as the burning rate. A good simulation of knock therefore, required very carefully chosen and accurately calibrated input parameters.

The Shell model is widely used in multi-dimensional CFD models of SI engine modelling due to its simplicity with only five species and eight reactions. Full chemical kinetic mechanisms are substantially more complicated and simply impractical for implementation in CFD because of the enormous computational resource involved [113, 114].

### 2.4.2.2 Comprehensive kinetic mechanisms

While the formal structure is meant to capture the kinetics of a reacting system based on only a few key chemical reactions with lumped parameters, a comprehensive kinetic
2.4 Chemical kinetics

mechanism aims to include all elementary steps that are involved [110].

Constructing a comprehensive mechanism requires accurate reaction rate, thermodynamic, and transport data for each species, many of which have never been determined experimentally. Theoretical methods, therefore, have been used in many cases to determine the reaction rates. For example, the THERM code developed by Ritter and Bozzelli proved to be a useful tool to estimate the reaction rate and thermodynamic data for species without experimental data [52]. In general, the structures of the kinetic model for hydrocarbon are hierarchical, where the reaction mechanism of a given fuel is made up by the mechanisms of all of the possible smaller molecule fuels [115]. This hierarchical structure allows the reaction mechanism of more complex fuels to be built upon those of the simpler fuels of similar kinds, substantially reducing the time and effort in mechanism development.

Since the first kinetic mechanisms for hydrogen and methane fuels were introduced in the 1970s, the development of comprehensive reaction mechanisms for other practical hydrocarbon fuels have come a long way. In an attempt to model the combustion of natural gas, the GRI mechanism was developed by a team of kinetics experts [116], and has since been widely used in the research community [52]. The mechanism is, however, limited to applications of high-temperature oxidation specifically for methane and ethane [52]. In the years that followed, the reaction mechanisms of other fuels, including methanol, ethene, and propane, quickly emerged. In 1998, the comprehensive mechanism of \( n \)-heptane oxidation was presented by Curran et al. [108]. Consisting of 2450 reactions and 550 species, the mechanism was able to describe both low-temperature and high-temperature combustion of \( n \)-heptane. Coupled with the comprehensive mechanism of isoctane developed in 2002 [117], this provided a great opportunity to better understand engine knock and autoignition of PRFs, and to correlate the octane rating with fuel chemistry through detailed modelling. It is worth noting that while the early mechanism, such as that of hydrogen, comprises no more than 20 reactions, the comprehensive mechanism of isoctane alone is made up of 3600 elementary reactions among 860 chemical species [117].

2.4.2.3 Reduced kinetic mechanisms

Multi-dimensional engine modelling, when coupled with chemical kinetics, requires enormous computing resources during implementation. Using comprehensive kinetic mechanisms, therefore, often becomes infeasible in CFD models. In light of this issue, reduced kinetic schemes have usually been used in multi-dimensional modelling. Reduced kinetic mechanisms are derived from the comprehensive mechanisms by means of sensitivity analysis, as well as steady-state and partial equilibrium assumptions [54]. During oxidation and combustion, many of the intermediate species are present only in low concentrations. By assuming that these species are unimportant and/or they are at steady state, the number of reactions and species can significantly be reduced, resulting in a simplified system of ODEs to be solved. For comparison, the detailed ki-
Table 2.2: Recent kinetic mechanisms developed for ethanol oxidation [120, 121, 123–127].

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Type</th>
<th>Number of reactions, species</th>
<th>Temperature range (K)</th>
<th>Pressure range</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dunphy et al. [120]</td>
<td>semi-detailed</td>
<td>97, 30</td>
<td>1080 - 1660</td>
<td>1.8 - 4.6 bar</td>
<td>1991</td>
</tr>
<tr>
<td>Norton et al. [121]</td>
<td>detailed</td>
<td>142, -</td>
<td>≈ 1100</td>
<td>1 atm</td>
<td>1992</td>
</tr>
<tr>
<td>Marinov [123]</td>
<td>detailed</td>
<td>383, 57</td>
<td>1000 - 1700</td>
<td>1.0 - 4.5 atm</td>
<td>1999</td>
</tr>
<tr>
<td>Saxena et al. [124]</td>
<td>detailed</td>
<td>288, 57</td>
<td>≈ 1000</td>
<td>&lt; 100 bar</td>
<td>2007</td>
</tr>
<tr>
<td>Li et al. [125]</td>
<td>detailed</td>
<td>238, 39</td>
<td>1100 - 1700</td>
<td>1 - 12 atm</td>
<td>2007</td>
</tr>
<tr>
<td>Curran et al. [126]</td>
<td>detailed</td>
<td>310, 58</td>
<td>-</td>
<td>-</td>
<td>2009</td>
</tr>
<tr>
<td>Cancino et al. [127]</td>
<td>detailed</td>
<td>1349, 136</td>
<td>700 - 1600</td>
<td>10 - 50 bar</td>
<td>2010</td>
</tr>
</tbody>
</table>

The increasing use of ethanol as a blend in commercial gasoline has generated much interest in the kinetic modelling of ethanol/gasoline blends. Gasoline, however, is a complex mixture of hundreds of different hydrocarbons, such as paraffins, olefins and aromatics [128], and as a result its detailed kinetic modelling is difficult. To work around this problem, a combination of selected gasoline surrogates were proposed to represent the chemistry of gasoline. Popular choices of gasoline surrogates include isooctane, \( n \)-heptane, toluene, and 1-hexene [129]. With the emergence of detailed
2.4 Chemical kinetics

Table 2.3: Different kinetic mechanisms of ethanol/gasoline-surrogates that were developed recently [130–137].

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Type</th>
<th>Number of reactions, species</th>
<th>Gasoline surrogates</th>
<th>Origin of ethanol mechanism</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andrae [130]</td>
<td>detailed</td>
<td>8270, 1121</td>
<td>PRFs</td>
<td>Toluene, Diisobutylene</td>
<td>2007</td>
</tr>
<tr>
<td>Dagaut et al. [131]</td>
<td>semi-detailed</td>
<td>1866, 235</td>
<td>PRFs</td>
<td>Toluene</td>
<td>2008</td>
</tr>
<tr>
<td>Cancino et al. [132]</td>
<td>detailed</td>
<td>4748, -</td>
<td>PRFs</td>
<td>Toluene</td>
<td>2009</td>
</tr>
<tr>
<td>Haas et al. [133]</td>
<td>semi-detailed</td>
<td>1221, 469</td>
<td>PRFs</td>
<td>Li et al. [125]</td>
<td>2009</td>
</tr>
<tr>
<td>Jerzembeck et al. [134]</td>
<td>reduced</td>
<td>374, 107</td>
<td>PRFs</td>
<td>Marinov [123]</td>
<td>2009</td>
</tr>
<tr>
<td>Huang et al. [135]</td>
<td>semi-detailed</td>
<td>677, 120</td>
<td>PRFs</td>
<td>Marinov [123]</td>
<td>2010</td>
</tr>
<tr>
<td>Cancino et al. [136]</td>
<td>detailed</td>
<td>8280, 1130</td>
<td>PRFs</td>
<td>Marinov [123]</td>
<td>2011</td>
</tr>
<tr>
<td>Ranzi et al. [137]</td>
<td>detailed</td>
<td>13532, 435</td>
<td>C1-C16 hydrocarbons</td>
<td>Saxena et al. [124]</td>
<td>2012</td>
</tr>
</tbody>
</table>

models of these gasoline surrogates, a number of reaction mechanisms of the oxidation of ethanol/gasoline-surrogate blends were proposed in recent years. These reaction mechanisms commonly include submechanisms of TRFs. Meanwhile, the embedded submechanisms for ethanol oxidation in these models are largely based on that by Marinov [123]. Due to the inclusion of many different species and reactions, the size of such comprehensive mechanisms can be enormous. For example, more than 8,000 reactions and 1,000 chemical species can be found in the comprehensive mechanisms by Andrae [130]. A summary of recently proposed reaction mechanisms for different ethanol/gasoline-surrogate blends is shown in Table 2.3.

2.4.2.5 The effect of residual gas on end-gas kinetics

It has been reported [138–142] that the residual gas from a previous engine cycle may, in addition to thermal (specific heats) and dilution (lambda) effects, impact the oxidation of the fresh air-fuel mixture chemically. In particular, a very low concentration of nitric oxide (NO) in residual gas was shown to affect autoignition in HCCI engine combustion [142], while other chemically active species such as formaldehyde and partially oxidised hydrocarbons may have similar effects [138]. Before discussing the kinetics of these residual species in detail, a review of the formation of these species, specifically the hydrocarbons, in the residual gas is necessary.
2 Literature Review

Unburned hydrocarbons in the residual gas
There are four major mechanisms for the formation of unburned hydrocarbons (HC) in spark-ignition engines, e.g. flame quenching, crevice volumes, oil absorption and incomplete combustion [47, 143]. Of these mechanisms, crevice volumes were reported to have the largest contribution (ranges from 40% to as much as 74%) to HC emissions [47, 143, 144]. As the in-cylinder pressure rises during compression and prior to flame arrival, the unburned air-fuel mixture flows into the crevice regions. During combustion, the flame can either propagate into these crevices and fully or partially burn the unburned air-fuel mixture or it can quench at the crevice entrance [47]. At peak cylinder pressure, approximately 5 to 10% of the total cylinder charge can be trapped in the crevice regions. While this amount also includes burned gases, well above 50% of the trapped mass can be the unburned air-fuel mixture [47].

Of particular interest is the fate of these unburned HC, which escaped the primary combustion event as well as blowby, during expansion and the exhaust process. As the cylinder pressure drops below the crevice pressure during expansion, some of the unburned HC will flow out of the crevices into the hot bulk gases. These unburned HC will fully oxidise upon mixing with the bulk gases, since the bulk gas temperature generally exceeds 1250 K prior to the exhaust blowdown [47]. On the other hand, the rest of the unburned HC will remain near the wall and survive with little oxidation, and a majority of them will likely be purged out of the cylinder via two transport mechanisms [47]. The first mechanism occurs during the exhaust blowdown, where the unburned HC adjacent to the wall will be entrained by the rapid gas flow out of the cylinder. Approximately half of the total exhausted HC mass originates from this process (see Figure 2.7). The other half is transported out of the cylinder by the second mechanism at the end of the exhaust stroke, where the upward piston motion will scrape the boundary-layer gases off the wall, and roll them up into a vortex [47]. As the piston approaches the TDC, this vortex, which possesses a substantial fraction of HC, detaches itself from the wall and leaves the cylinder.

Experiments showed that approximately 50% of all unburned HC formed via these mechanisms will oxidise in the cylinder [47]. At full load, approximately two-thirds of the remaining unburned HC will be transported out of the cylinder via entrainment and the vortex flow [47], and they will undergo further oxidation in the exhaust port and the runner [145]. The remaining HC in the cylinder will eventually become part of the residual gas. The HC concentration in the residual gas was reported to be as much as 11 times that of the average exhaust level, and this is likely a result of the high HC concentration in the vortex flow at the end of the exhaust stroke [47].

Drobot [145] reported that of all cylinder-exit HC emissions for propane, n-butane and isooctane, approximately 60% would be the unburned fuel with the remaining being partially oxidised hydrocarbons (Figure 2.8). In the case of methane and toluene, the fraction of unburned fuel in HC emissions approached approximately 90% [145]. It is therefore believed that the fraction of unburned fuel(s) in the HC content in the residual gas would be of a similar magnitude. Of course, post-flame oxidation of HC is
2.4 Chemical kinetics

Figure 2.7: Variation in HC concentration and HC mass flow rate at the exhaust valve during the exhaust process [47].

Figure 2.8: Fuel species concentration as a percentage of the total HC emissions at the cylinder, port and runner exits for different fuels [145].

unsteady and inhomogeneous, and hence highly dependent on the cylinder geometry, crevice volumes, fuel type and operating conditions.

Chemical effects of NO
Autoignition of hydrocarbons is found to be sensitive to the concentration of NO, although the effect of NO is complicated. Amano and Dryer [146] reported that NO had a significant promoting effect on the oxidation of methane at temperatures below 1200 K. Likewise, through kinetic modelling Faravelli et al. [147] showed that the addition of NO to hydrocarbons (C1 through C4 molecules) enhanced the oxidation of hydrocarbons at low concentrations of NO. As the NO content is further increased, however, autoignition of hydrocarbons may be inhibited due to the scavenging of OH radicals [147]. A similar observation was reported by Machrafi et al. [138], in which the presence of NO at 45 ppm would advance the ignition delay for an HCCI engine.
2 Literature Review

Figure 2.9: Experimental and simulation (labelled as ‘TDAC’ in the figure) results for the pressure and the heat release rate using different initial concentrations of NO under HCCI conditions. [142]

fuelled with PRF40, while autoignition was delayed at higher concentrations of NO. More recently, it was reported [142] that under HCCI conditions the autoignition of isooctane would monotonically be advanced with increasing NO content (up to 500 ppm), as shown in Figure 2.9.

2.5 Ethanol as a fuel

2.5.1 Combustion and emissions of ethanol-fuelled spark-ignition engines

Alcohol, especially ethanol, has been used as a transport fuel since the 19th century, and was well-known as an effective octane enhancer [148]. Advocacy of alcohol fuels surged in the 1906 - 1908 periods and again in the 1930s, but was dampened by the discovery and later widespread use of TEL as an anti-knock agent [148]. In the years that followed, use of ethanol as a fuel dwindled and was displaced by leaded gasoline, which became cheaper and easier to produce in light of new oil discoveries [148]. However, ethanol has generated a renewed interest in the last two decades as an oxygenated fuel additive [12]. Numerous studies of ethanol-fuelled SI engines have since been conducted, and in most studies favourable results in emissions and engine efficiency were reported [45, 149–151].

Hsieh et al. [149] conducted a study on the combustion and emissions of ethanol/gasoline blends ranging from E0 to E30, where E0 represents neat gasoline, and E30 is 30% of ethanol blended with 70% of gasoline by volume. A dramatic reduction in carbon monoxide (CO) and unburned HC emissions was reported for a modern port-fuel-injection engine fuelled with ethanol/gasoline blends. Particularly in the case of E30, the CO emission was reduced by as much as 65% at wide open throttle, while that of HC was approximately halved. They suggested that the decrease in CO and HC emissions was primarily due to the “leaning effect” by the extra oxygen molecules in the fuel, although it was found later [43] that some vehicles could run leaner with
ethanol addition relative to E0 at wide open throttle and hence the reduced specific emissions. In another study, Yüksel [150] reported similar findings that the CO and HC emissions were reduced by about 80% and 50% respectively when using E30 - E60. On the other hand, particulate matter emissions were shown to decrease with increasing ethanol content in gasoline, since the extra oxygen molecules in the fuel inhibits the formation of soot precursors [45]. While the emissions of acetaldehyde and formaldehyde generally increase with increasing ethanol content, studies showed lower emissions of benzene and 1,3-butadiene (both classified as toxic compounds, as are acetaldehyde and formaldehyde) as ethanol content is increased [45]. Since the toxicity weighting factors for benzene and 1,3-butadiene are much higher relative to acetaldehyde and formaldehyde, the overall toxic emissions are improved with increased ethanol content in gasoline [45].

On the other hand, the numerical simulation using detailed kinetic mechanisms by Nakama et al. [152] showed that the presence of ethanol increased the laminar burning velocity. Bayraktar [153] reported that E20 was able to reduce the combustion duration by 22% in a two-zone model. Experimental studies further confirmed that the mass burning rate increased with increasing ethanol content in the fuel [154].

In terms of knock suppression, the higher octane number of ethanol permits further increase of compression ratio before the onset of knock when engines are fuelled with gasoline-ethanol blends. Experiments by Al-Baghdadi [151] showed that the HUCR was extended from 8:1 to 9.2:1 when E30 was used in place of neat gasoline, although that also resulted in a small penalty in the specific fuel consumption. Kar and Cheng [155] reported that the spark timing could be advanced by 5.6% for every 10% increase of ethanol volume in the blend, and this significantly increased the knock resistance. Similar observations showing improved engine efficiency through the use of ethanol or ethanol/gasoline blends could also be found in [2, 45, 156], and such efficiency increase may completely offset the degrading volumetric fuel economy (due to the lower energy content of ethanol relative to gasoline) in some cases [45].

### 2.5.2 The octane numbers of ethanol/gasoline blends

While it is generally agreed that ethanol has a higher octane number than gasoline, the exact octane numbers for different blends of gasoline and ethanol are inconsistent in the literature. The difficulty in determining the true octane numbers is attributed to the limitations of the CFR engine [68]. The different stoichiometry of ethanol requires the modification of the carburettor fuel jet, which was designed to handle stoichiometry of about 15:1, while that of ethanol is around 9:1. Second, the higher enthalpy of vaporisation of ethanol renders the mixture heater on the CFR engine unable to heat the mixture to the specified 149 °C.

According to the SAE Alternative Automotive Fuels Standard J1297 [157], the RON and MON of pure ethanol were 129 and 102, respectively. In another study [130], the RON and MON of ethanol were reported to be 128 and 90, respectively. Yates et al. [68],
however, argued that these values were unusually high and could be inferred from the blending octane number, and that the actual RON and MON should be approximately 109 and 90 respectively. These lower RON and MON numbers were taken from the standard tests carefully performed by Hunwartzen in 1982 [70], where modifications to the CFR engine were made by enlarging the diameter of the carburettor fuel jet, and installing additional heating elements around the intake manifold. More recently, Anderson et al. [158] from Ford revisited the same problem and reported very similar RON (108.7) and MON (90.5) values for neat ethanol.

Gasoline, on the other hand, typically has a RON of at least 90 for regular and up to 100 for premium gasoline. As one would expect, blending ethanol with regular gasoline increases the RON of a given blend [70, 158], although the extent of RON improvement varies from one study to another. Hunwartzen [70] measured the RON of premium gasoline (RON = 99) blended with ethanol in a 50:50 volumetric ratio, and reported an approximately linear increase in RON with the volumetric concentration of ethanol (Figure 2.10). Measurements reported by the American Petroleum Institute (API) [159] on various gasoline blendstocks blended with ethanol showed a non-linear dependence of the RONs on the ethanol content on a volume basis, but an almost linear relationship on a mole basis. However, non-linearity in RONs was observed both on a mole and a volume basis in data from Anderson et al. [158]. With respect to MONs, antagonistic blending has been reported [70] for ethanol/gasoline blends, where the MON of the blend was lower than the MON of either neat component (Figure 2.10). More recent studies [158, 159], however, showed the opposite trend. Such differences in trends are likely a result of different gasoline compositions, although it appears that at present little is understood as to the source(s) of such effects. Thus, clarification of the autoignition behaviour of these blends appears required.
2.5 Ethanol as a fuel

2.5.3 Charge cooling effects

Ethanol has an enthalpy of vaporisation that is approximately three times higher than gasoline [160]. Therefore, when ethanol is injected directly into the engine cylinder in liquid phase, its vaporisation results in increased evaporative cooling of the air-fuel mixture. This reduction in the in-cylinder temperature has been found to be one of the major factors of the superior anti-knock quality of ethanol [156, 161]. In the MON tests, the intake air has to be heated to 149 °C, and by doing this the ethanol fuel is fully vaporised before it enters the cylinder, making the charge cooling effect negligible. On the other hand, the charge cooling effect is considerably more significant in the RON tests given the intake temperature is set at 52 °C. The fact that this intake temperature is measured upstream of the carburettor means that the actual temperature of the charge entering the cylinder should be significantly lower when ethanol is used due to its higher enthalpy of vaporisation. It is therefore unsurprising when comparing the relatively large difference (~20) between the MON and RON of ethanol. Ethanol/gasoline blends is expected to exhibit greater charge cooling effects than neat gasoline due to the higher enthalpy of vaporisation, as shown in Figure 2.11 [160].

2.5.4 Cold starting

At room temperature, the Reid vapour pressure of pure ethanol is approximately one third that of gasoline [162], and its enthalpy of vaporisation approximately three times greater [160]. As these properties are associated with difficulties in engine start-up, particularly in cooler conditions, ethanol as a neat fuel may be impractical in some climates [163]. However, ethanol/gasoline blends up to about E50 have a higher vapour pressure than that of gasoline, reaching a maximum at around E10 (Figure 2.12). For this reason, the ethanol content in gasoline blends is reduced during winter in
2 Literature Review

Figure 2.12: Reid vapour pressures of different alcohol/gasoline blends from [162].

some locations [164]. Direct injection also appears capable of improving the cold start performance of high ethanol-content fuels, with Stein et al. [45] reporting significant improvement in fuel vaporisation over port fuel injection.

2.6 Summary and research questions

Knock is an abnormal combustion phenomenon that is defined by a loud pinging noise. The origin of knock is widely associated with autoignition in the end gas, which is generally inhomogeneous in temperature and composition. Knock is commonly rated using the RON and MON methods, which indicate the knocking propensity of a fuel with respect to blends of isoctane and n-heptane. Autoignition in the end gas can be modelled using chemical kinetics. With the development of comprehensive kinetic mechanisms for many hydrocarbon fuels in recent years, several good numerical simulations of end-gas autoignition in spark-ignition engines have been reported using either quasi- or multi-dimensional combustion models.

It is already well known that, relative to gasoline, ethanol can raise spark ignition engine efficiency while reducing specific emissions. Because of its higher octane numbers and a higher enthalpy of vaporisation relative to gasoline, ethanol exhibits great potential for enabling higher compression ratios and hence increasing engine efficiency. However, the knock limits of ethanol when blended with gasoline in spark-ignition engines are not thoroughly understood at present.

This work therefore aims to investigate the autoignition and the knocking characteristics of ethanol blended with gasoline and its surrogates. The following research questions are proposed.

1. What are the Research (RON) and Motor (MON) Octane Numbers of ethanol blended with gasoline and its surrogates?

As shown in the Literature Review, only a few studies in the public domain
have examined the effect of ethanol on the RON and MON of gasoline and its surrogates. Further, since gasoline was used in most of these studies, these results are unlikely to be general since gasoline composition varies significantly with both location and the date of production. Thus, experimental determination of both the MON and RON of ethanol blended with gasoline and its surrogates is important.

2. How does charge cooling affect the RON of ethanol blended with gasoline and its surrogates?
Ethanol has a lower stoichiometric air-fuel ratio and a significantly higher enthalpy of vaporisation than gasoline. Previous studies [69, 158] have argued that the standard RON test is unable to determine the relative significance of the charge cooling and the autoignition chemistry of ethanol blended with gasoline and its surrogates. Further, no systematic quantification of the significance of charge cooling on the RON of these blends appears to have been undertaken. This work therefore examines experimentally and numerically the effect of charge cooling of ethanol blended with gasoline and its surrogates on the RON.

3. What are the mechanisms leading to the autoignition of ethanol blended with gasoline and its surrogates in spark-ignition engines?
The Literature Review also discussed the several physical mechanisms that interact to initiate autoignition in spark ignition engines. Whilst the fuel chemistry is of course one important mechanism, it is not the only important mechanism. Others include the engine heat transfer, blowby and residual gases. Importantly, the Literature Review discussed how there are key uncertainties in several of these mechanisms. Thus, systematic investigation of these mechanisms, and how they might combine to drive the autoignition of ethanol blended with gasoline and its surrogates, is therefore important.
2 Literature Review
3 Experimental Methods

This chapter presents the experimental methods, particularly the RON and the MON methods, and the hardware used in this work. Modifications required to rate fuels of high-ethanol content are discussed in detail, followed by an introduction of the ‘modified RON’ test method, which is further discussed in Chapter 5. Lastly, an overview of the instrumentation used for both combustion and autoignition modelling is presented.

3.1 The CFR engine

The RON and MON values were measured on a standard Waukesha CFR F1/F2 engine (Figure 3.1). Standard knock rating instruments, including the detonation meter and the knock meter, were used in this study. An air dehumidifier (made by Lawler Manufacturing Corp) was installed upstream of the carburettor to control the humidity of the intake air. Critical engine parameters were monitored and maintained during the tests within the accepted limits as defined in the ASTM D2699 [63] and D2700 [64] standards.

Since the standards [63, 64] provide only a correlation between the critical cylinder height (dial indicator reading) and the octane number, the compression ratio at standard knock intensity has to be determined separately. Standard knock intensity is defined as the level of knock established when a fuel is introduced at an air-fuel ratio which yields maximum knock intensity, with the cylinder height set to the prescribed guide table value (Table A4.3) in the standards [63, 64]. The detonation meter is further adjusted to produce a knock meter reading of 50 for these conditions [63, 64].

Using the equation adapted from [165], the corresponding compression ratio for a given cylinder height is then given by,

\[ CR = \frac{DI + 0.3 + 4.5}{DI + 0.3}, \]

(3.1)

where \( DI \) is the dial indicator reading (inch) at standard knock intensity, and is a function of the octane number as listed in Table A4.3 in both standards [63, 64]. The complete tabulation of the compression ratio as a function of the RON and MON can be found in Appendix A.1. Figure 3.2 shows a non-linear relationship between the critical compression ratio and the RON or MON. Of interest is that the critical compression ratio for a given RON is, except for a small range of octane numbers at around 95, always higher than that for a given MON. Further, significant non-linearity is observed at octane numbers around 100. This is possibly a result of the change in the reference
fuels from PRFs to a mixture of isooctane and tetraethyl lead above a RON of 100.

Figure 3.3 shows the measured lift profiles of the intake and the exhaust valves, with the corresponding valve timings as specified in [63, 64]. The complete lift profile data can be found in Appendix A.2. A small valve overlap of approximately 5 CAD is present between the intake valve opening (IVO) and the exhaust valve closure (EVC) (although it is noted that both IVO and EVC are subject to a tolerance of ±2.5 CAD). As a result of this, the residual gas fraction is likely to be low. On the other hand, the late IVC timing, coupled with a low engine speed (600 - 900 rpm), suggests that a reverse flow may occur across the intake valve as the piston moves upward from the bottom dead centre (BDC). One-dimensional modelling using GT-Power indicates that this is indeed the case (see Figure 3.4). Right after BDC, the upward piston motion pushes the air-fuel-residual charge out of the cylinder, and hence the negative mass flow rate across the intake valve. This reverse flow may have an effect on the heat transfer in the intake system as well as the volumetric efficiency, and will be discussed in more detail in Chapter 5.

3.1.1 Engine control

A new 22-kW Siemens variable frequency electric dynamometer was installed to start and drive the engine at constant speeds, e.g. 600 rpm for the RON method and 900 rpm for the MON method. This dynamometer is fully controlled from a computer using Siemens’ software.
3.1 The CFR engine

Figure 3.2: Critical compression ratio versus RON/MON [165].

Figure 3.3: Measured intake and exhaust valve lift profiles of the CFR F1/F2 engine. The valve timings are obtained from the standards [63, 64].
3 Experimental Methods

The original ignition control system was replaced by a new digital system, which consists of a shaft encoder with a resolution of 0.10 CAD, National Instruments data acquisition devices and a Labview program. This new ignition system is deemed to perform as well as the original system, as the ‘Fit-for-Use Procedure’ (see Section 3.2.1) confirmed that all measurements were within rating tolerances.

3.2 The RON/MON test methods

The RONs and MONs in this study were determined using the Equilibrium Fuel Level Bracketing procedure. This method involves linear interpolation of the knock intensity of two PRFs of known octane numbers which ‘bracket’ the sample fuel. During the rating of a fuel, the air-fuel ratio was adjusted such that maximum knock intensity could be attained, as measured by the knock meter. As defined in the standards, the difference between two test results under repeatable conditions would exceed an octane number (O.N.) of 0.2 only in one case out of twenty for fuels having RON values between 90 and 100 [63], and MON values between 80 and 90 [64]. Outside of these O.N. ranges less repeatability is expected due to increasing experimental uncertainties.

3.2.1 Engine compliance tests

Toluene standardisation fuels were utilised to verify engine compliance in accordance with the ‘Fit-for-Use Procedure’ in the ASTM standards [63, 64]. By this procedure, the engine was deemed fit for rating any sample fuel with a RON or MON between 40 and 120 inclusive.
### 3.2 Fuels

Regular unleaded gasoline was obtained from a service station in Melbourne, Australia. Its composition was analysed by Intertek Testing Services using ASTM D6730 (gas chromatography method), and the results are listed in Table 4.5. The density of gasoline was estimated to be 0.73 g/cm$^3$ at 25 °C through simple volume-mass measurements, and its molecular weight was assumed to be 100 g/mol, which is consistent with values found in the literature [69, 158]. Isooctane (reference fuel grade) was obtained from Haltermann GmbH. Neat ethanol (anhydrous, not denatured) was at least 99.5% pure and obtained from Chem-Supply. The dilute TEL, required for rating fuels with RONs and MONs above 100, was obtained from Innospec. The typical composition of the dilute TEL is listed in Table 3.1. All other chemicals used in the experiments were analytical grade and at least 99% pure.

Blending of all fuels was done gravimetrically using a precision balance with a repeatability of 0.001 g, based on densities of the individual components. This is well within the blending tolerance limits of ±0.2% for a 500-ml sample, as specified in [63, 64].

### 3.2.3 RON measurement drifts

The RON measurements were done in two separate batches. Ethanol and its blends with PRFs (except for PRF91) were first rated. The rating of all other fuels was not performed until three months later. A repeatability test was performed on neat ethanol at the end of the second batch of measurements to verify data consistency. A measurement drift was observed, where the average RON (out of five tests) of neat ethanol has decreased from 108.5 in the first batch of measurements to 108.0 in the latter. It is believed that the measurement drift was a result of increasing combustion chamber deposits, as suggested by [166]. Deposit build-up in the engine hinders heat transfer and promotes the formation of hot spots [47], and hence likely to cause earlier autoignition, and consequently a lower O.N. It is emphasised that while a measurement drift was present, the ‘Fit-for-Use Procedure’ (see Section 3.2.1) that was performed for each operating period confirmed that the CFR engine was compliant with the standard throughout the tests, and that all measurements were within rating tolerances [63]. Therefore, no corrections were deemed necessary and the different RONs of ethanol...
were reported accordingly in this study. Furthermore, engine compliance tests indicated that the O.N. drift within a given batch of measurements was negligible.

3.3 Modifications for rating fuels of high ethanol content

3.3.1 Fuel metering jet

Measurements showed that while the required air-fuel ratio for maximum knock intensity varies from fuel to fuel, overall it was slightly rich in all cases. However, rating neat ethanol requires a considerably higher fuel flow rate, since its stoichiometric air-fuel ratio (9:1) is significantly lower than that of gasoline (15:1). Hence, the stock fuel metering jet in the present CFR engine fails to provide an adequate fuel flow rate in this case. In order to handle the increased fuel flow, the original jet in the carburettor was replaced by an adjustable orifice jet, following the recommendations detailed in the standards [63, 64, 167].

3.3.2 MON heater

While in a previous study [70] an auxiliary heater was required in the MON test to attain the mixture temperature of 149 °C when rating fuels with high ethanol concentrations, it was found that the stock MON heater alone was sufficient to achieve that for all fuels, including neat ethanol, studied in this study. A similar observation was reported in recent study by Anderson et al. [158].

3.3.3 Mixture temperature monitoring

In the standard RON rating, the intake air temperature (IAT) is set depending on the barometric pressure at the time of rating; at sea level, the IAT is generally required to be at 52±2 °C. In order to investigate the charge cooling effects of ethanol in the RON test (see Chapter 5), the temperature of the air-fuel mixture entering the engine was measured by a T-type thermocouple with an accuracy of ±1 K. The thermocouple was installed at the intake port, with the junction in the middle of the gas path and approximately 10 cm downstream of the carburettor, as shown in Figure 3.5. This temperature will be referred to as the ‘mixture temperature’ in this work.

3.4 The ‘modified RON’ test method

Since only the IAT upstream of the carburettor is regulated in the standard RON test, variation in the mixture temperature may exist due to different enthalpies of vaporisation. In an attempt to minimise the additional charge cooling provided with increasing ethanol content, a modification was made to the standard test by fixing the mixture temperature for all fuels. The modified RON tests were then performed with the following procedure.
3.4 The ‘modified RON’ test method

1. Calibrate the detonation meter system with a reference fuel having a RON close to that of the sample fuel.

2. Run the engine with the sample fuel, with the IAT adjusted such that the mixture temperature is 36 °C. This is the average mixture temperature for the PRF-only cases.

3. Adjust the air-fuel ratio and compression ratio to attain a knock meter reading of 50±2, at which standard knock intensity occurs.

4. The modified RON is obtained from the compression ratio at which this occurs, by referring to Table A4.3 in [63]. This table relates the dial indicator reading (compression ratio) to the RON at standard knock intensity.

5. If the RON of the sample fuel is more than ±1.5 octane numbers different from that of the calibration fuel (step 1), a new calibration fuel with a closer RON to that of the sample fuel has to be chosen, and steps 2 - 4 have to be repeated.

The modified tests were performed without the bracketing fuels, due to the long running times (up to 30 minutes for a single run) required to obtain an IAT up to 165 °C when rating ethanol/gasoline blends, and then to subsequently cool the IAT down to 52 °C again for rating the bracketing fuels. While the omission of the bracketing procedure may reduce the precision of the RON measurements, a deviation of no more than ±0.5 O.N. is normally expected compared to that obtained using bracketing fuels. The significance of the modified RON test method will be discussed in detail in Chapter 5.
3 Experimental Methods

3.5 In-cylinder pressure measurement

A Kistler piezoelectric pressure transducer (model 6125C) was used to acquire the in-cylinder pressure under knocking and non-knocking combustion. The transducer was mounted into an adapter, which has a 7/8”-18 threaded end that screws into the detonation pickup hole in the CFR engine. The diaphragm of the transducer was recessed by approximately 1 mm relative to the cylinder head, so that a thin layer of silicone rubber could be applied to the diaphragm in an attempt to reduce thermal stress and drift. A charge amplifier was used to convert the transducer signal into a voltage which was subsequently fed into the data acquisition card in a computer. A combustion analysis suite, developed in-house [168] in the Thermodynamics Laboratory at the University of Melbourne, was used to log and condition the transducer signals.

The raw transducer signal was referenced at the manifold absolute pressure acquired and averaged for 10 CAD before BDC at the end of the intake stroke. A shaft encoder with a resolution of 0.10 CAD was mounted to the end of the crank shaft, and was used to synchronise the transducer signal with the instantaneous volume of the combustion chamber.

3.6 Lambda measurement

A Bosch LSU 4.9 wide-band oxygen sensor was installed on the exhaust system (approximately 30 cm downstream of the exhaust port) to measure the lambda (\(\lambda\)) of the air-fuel mixture. The sensor signal was conditioned and logged using a MoTeC lambda meter.

\(\lambda\) was recorded for each standard octane rating that was performed, and it was found that under most conditions standard knock intensity occurred when the air-fuel mixture was slightly richer than stoichiometry. In the case of PRFs, \(\lambda\) was found to be approximately 0.88 at standard knock intensity under the RON conditions.

3.7 Fuel flow measurement

The volumetric fuel flow rate was obtained by measuring the time taken to consume a given volume of fuel. Each measured fuel flow rate was averaged from more than 1000 cycles. The volume of the fuel bowl was calibrated using a burette. However, there is an uncertainty of up to 2% due to tolerance in volume calibration as well as in reading the volume from the sight glass during measurements.

3.8 Exhaust gas analysers

HC emissions

Cambustion HFR400 fast flame ionisation detector (FFID) was used to measure the HC emissions. The analyser was mounted to the exhaust surge tank to in an attempt
3.8 Exhaust gas analysers

to avoid pulsations in the exhaust flow. It was calibrated using nitrogen gas containing 1020-ppm propane. Further detail of how to calibrate the analyser can be found in [169].

CO and NO emissions

Autodiagnostics ADS9000, a compact gas analyser, was used to measure the CO and NO emissions. It sampled at a rate of approximately 1.4 Hz with time constants on the order of a few seconds, and hence reported time-averaged measurements.
3 Experimental Methods
4 The Octane Numbers of Ethanol Blended with Gasoline and Its Surrogate Fuels

The content of this work has already appeared in [170]. This chapter reports the RON and MON values of ethanol blended with production gasoline, four gasoline surrogates, \( n \)-heptane, isooctane and toluene. The ethanol concentration was varied from zero to 100%, resulting in a clear picture of the variations of the RONs and MONs in all cases. Of initial interest is the almost linear variation of the RON and MON with ethanol content of blends with an Australian production gasoline. This is in contrast with other recent studies [158, 159] which have demonstrated varying synergism between US production gasolines and ethanol. These observed differences then prompt a systematic study of the variation in the RONs and MONs of ethanol blended with four gasoline surrogates, as well as with \( n \)-heptane, isooctane and toluene. Both \( n \)-heptane, isooctane and their PRFs are shown to blend synergistically with ethanol, whilst toluene blends antagonistically. Consistent with these trends, a progressive increase in the toluene content in TRFs of a constant RON results in increasingly linear ethanol/TRF blending. Together, these results show that the antagonism of ethanol’s blending with toluene acts against its synergism with isooctane and \( n \)-heptane, and more broadly suggest that the antagonism of ethanol’s blending with aromatics may act against its synergism with paraffins. If correct, this explains trends observed both in the literature and in this study, and has implications for fuel design.

4.1 Neat ethanol

The RON of neat ethanol is measured here as being in the range of 108.0 to 108.5, due to measurement drift as detailed in the Experimental Methods (note that both values are themselves the average of five standard test ratings). This RON variability, however, is well within the rating tolerance of ±1.4 ON in the ‘Fit-for-Use Procedure’ that applies to any fuel having a RON between 105.2 and 110.6 [63]. The measured MON of ethanol is 90.7.

Table 4.1 shows the RON and MON data of ethanol from the literature and this study. While several other octane number data for ethanol are readily found in the literature, it is believed that the measurements obtained by Hunwartzen [70] and Anderson et al. [158] are the most reliable, since they comply with the ASTM and DIN standards
4 The Octane Numbers of Ethanol Blended with Gasoline and Its Surrogate Fuels

4.1 Neat Ethanol

Table 4.1: Reported RON and MON for neat ethanol.

<table>
<thead>
<tr>
<th>RON</th>
<th>MON</th>
<th>Year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>108.6 ± 0.4\textsuperscript{a}</td>
<td>89.7 ± 0.3\textsuperscript{a}</td>
<td>1982</td>
<td>[70]</td>
</tr>
<tr>
<td>108.6 - 108.8</td>
<td>89.5 - 91.4</td>
<td>2012</td>
<td>[158]</td>
</tr>
<tr>
<td>108.0 - 108.5</td>
<td>90.7</td>
<td>2013</td>
<td>This study</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Average ± 95\% confidence interval.

concerning the proper configuration of the CFR engine to handle the high fuel flow rate of ethanol.

In comparison, both the RON and MON values of ethanol obtained in this study are in good agreement with those reported previously [70, 158]. Considering that the standard specifies a rating tolerance of ±1.4 ON, the variability in the different reported RON values of ethanol is within the limits of the test method [63]. Nonetheless, the MON measured in this study is similar to the average value reported by Anderson et al. [158] (90.7 vs. 90.5), but is 1.0 ON greater than that from Hunwartzen [70].

4.2 Ethanol/gasoline blends

Research Octane Number (RON)

Figure 4.1a shows the RON values of different ethanol/gasoline blends on a volume basis. The RON clearly shows a non-linear relationship with the volumetric concentration of ethanol. The RON values reported by the API [159] in 2010 for ethanol/gasoline blends up to approximately 30\% (v/v) ethanol are very similar to those measured in this study. However, the RONs of ethanol/gasoline blends (base gasoline with an average RON = 92.2 and MON = 84.7) reported by Anderson et al. [158] are more synergistic. These differing degrees of synergism are an inevitable consequence of the different gasoline compositions.

Also shown in Figure 4.1a are the calculated volumetric blending RON (bRON) values of ethanol in gasoline, each of which is defined by,

$$bRON_e = \frac{RON_{blend} - (1 - v_e)RON_g}{v_e},$$

(4.1)

where $RON_{blend}$ is the RON of any ethanol/gasoline blend, $RON_g$ is the RON of gasoline and $v_e$ is the volume fraction of ethanol in the blend. The bRON signifies the effectiveness of ethanol in increasing the RON of a given blend. Since the bRON of ethanol is greater than its RON in all cases, blending ethanol with gasoline is synergistic on a volume basis. The bRON of ethanol at 10\% (v/v) in gasoline is 128.5, which is sometimes mistakenly reported to be the RON of ethanol despite significant differences between the two [130, 157].

It has been suggested that the ON of ethanol/gasoline blends can be better interpreted on a mole basis, as chemical reaction rates scale in proportion with the molar
Figure 4.1: Measured RONs of ethanol/gasoline blends and the calculated blending RONs of ethanol versus ethanol content. Recent literature data from [159] and [158] are included for reference.
composition of the air-fuel mixture [69]. The volumetric and molar concentrations of these blends will differ significantly, since the molecular weight of ethanol is significantly lower than that of gasoline. Figure 4.1b shows the RON values of ethanol/gasoline blends plotted against the mole fraction of ethanol. In contrast to Figure 4.1a, the RON values now show an almost linear relationship with the molar concentration of ethanol. In light of this, Anderson et al. [69] suggested the use of a molar weighted ON to estimate the ON of any ethanol/gasoline blend. For the present study, this can be written as

\[ RON_{est} = (1 - x_e)RON_g + (x_e)RON_e, \] (4.2)

where \( x_e \) is the mole fraction of ethanol in the blend, \( RON_{est} \), \( RON_g \) and \( RON_e \) are the estimated blend’s RON and the measured RON of gasoline and ethanol respectively. As shown in Figure 4.1b, there is good agreement between this study’s estimated RONs and the measured values, with an average difference of approximately 0.4 ON. The maximum deviation is 0.7 ON, and that corresponds to the blend with 20% \((v/v)\) ethanol. Of all the parameters used in calculating the mole fraction of each ethanol/gasoline blend, the largest uncertainty lies in the molecular weight of gasoline, which is assumed to be 100 g/mol. A sensitivity analysis of the molecular weight of gasoline within a reasonable range of 90 to 110 g/mol however showed that the mole fraction of the blends was only weakly dependent on these variations in the molecular weight of gasoline.

**Motor Octane Number (MON)**

The MON values of ethanol/gasoline blends exhibit trends that are very similar to those observed in the RONs of these blends. Figure 4.2a shows the non-linear relationship between the MON and the volumetric concentration of ethanol. On the other hand, an almost linear relationship can be observed in the MONs of ethanol/gasoline blends when plotted against the molar concentration of ethanol (Figure 4.2b). This study’s measured MON values closely match the linear estimated MONs, with a maximum deviation of only 0.4 ON. The MON values of ethanol/gasoline blends reported by the API [159] agree well with those from this study when plotted against both the volumetric and the molar concentration of ethanol. For ease of comparison, data from Anderson et al. [158] for a different base gasoline (average RON = 88.2 and MON = 81.7) were plotted in Figure 4.2 instead of those discussed in the previous section. Even with a similar MON in the base gasoline, the ethanol blending of Anderson et al. [158] results in MONs that are significantly more non-linear with ethanol content.

Also shown in Figure 4.2a are the blending MON (bMON) values of ethanol in different blends. The bMON of ethanol for a given blend can be calculated using in Eq. 4.1, provided that MON is used in the equation instead of RON. Again, the bMON values of ethanol suggest synergism between ethanol and gasoline volumetrically. The bMON of ethanol evaluated from gasoline-E10 in this study is 103.1, which is similar to the value (bMON = 102) reported in the SAE Alternative Automotive Fuels Standard J1297 [157].
4.2 Ethanol/gasoline blends

Figure 4.2: Measured MONs of ethanol/gasoline blends and the calculated blending MONs of ethanol versus ethanol content. Recent literature data from [159] and [158] are included for reference.
4.3 Blending behaviour of ethanol with \( n \)-heptane, isoctane and toluene

The previous section has shown that different gasoline blendstocks when blended with ethanol exhibit varying degrees of non-linearity in octane numbers with respect to ethanol content. A parametric study of the potential interactions among major gasoline components is thus necessary in an attempt to understand the associated blending characteristics.

To simplify this analysis, three components representative of gasoline, namely toluene, isoctane and \( n \)-heptane, were blended with ethanol. Isooctane and \( n \)-heptane are branched and linear alkanes respectively, which act as surrogates for the major paraffinic fraction of gasoline. Toluene is a commonly used surrogate for the aromatic fraction of gasoline. Aromatics are important in this context since, like ethanol, they are used to increase the octane number of gasoline, despite having a relatively high cost to produce (and significant value as commodity chemicals) as well as generally accepted negative environmental effects [171].

Among these four components, a total of six first-order interaction pairs are present, namely

1. ethanol/isoctane,
2. ethanol/\( n \)-heptane,
3. ethanol/toluene,
4. isoctane/\( n \)-heptane,
5. isoctane/toluene, and
6. \( n \)-heptane/toluene blends.

Of these six interaction pairs, that of isoctane/\( n \)-heptane is linear by volume, as defined by the octane scale [63, 64]. Similarly, blending toluene with either isoctane or \( n \)-heptane was previously found to yield an approximately linear change in ON with respect to toluene content [172]. Figures 4.3 and 4.4 show the predicted RON and MON values of four different PRFs with respect to the volumetric concentration of toluene. On first sight the octane numbers of these blends exhibit some degree of non-linearity with the presence of a significant change in gradient at a toluene concentration of approximately 90% (v/v). This is believed to be a result of shortcomings in fitting the model at high toluene concentrations, and a further optimised model is likely to yield octane numbers that are more linear with toluene content. In this study, the toluene content of all gasoline surrogates is capped at 45% (v/v), in accordance with the Australian standard [9]. In light of this, the RON or MON of any TRF blend containing up to 45% (v/v) toluene is approximately linear even with the current model, as can be seen in Figures 4.3 and 4.4. This observation is in agreement with a recent study,
4.3 Blending behaviour of ethanol with n-heptane, isoctane and toluene

Figure 4.3: Predicted RONs of different PRFs blended with toluene using the model from Morgan et al. [172]. The dashed line indicates the 45% cap of aromatic content in Australian gasoline.

Table 4.2: Reported RON and MON for neat toluene.

<table>
<thead>
<tr>
<th>RON</th>
<th>MON</th>
<th>Year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>103.5</td>
<td>1958</td>
<td>[174]</td>
</tr>
<tr>
<td>120</td>
<td>109</td>
<td>1988</td>
<td>[47]</td>
</tr>
<tr>
<td>-</td>
<td>107</td>
<td>2013</td>
<td>This study</td>
</tr>
</tbody>
</table>

which proposed the use of a linear molar-weighted model to predict the octane numbers of any TRF blend [173]. A study was thus conducted on blends of ethanol/isoctane, ethanol/n-heptane and ethanol/toluene, as detailed below.

Due to the difficulty in measuring the high RON of neat toluene, which approaches the upper limit of the test method (valid working range = 40 - 120 ON [63, 64]), its RON value of 120 was obtained from a report published by the American Society for Testing Materials (ASTM) [174]. As shown in Table 4.2, a similar RON value of neat toluene was reported by Heywood [47], suggesting that the RON measurement from the ASTM report [174] is repeatable. Different MON values of toluene, however, were reported in the literature. Data from the ASTM [174] reported a MON of 103.5 for neat toluene, while according to Heywood [47] it is 109. Since there is a significant spread in the MON data, a MON measurement was performed on neat toluene. Its MON was found to be 107, which is bracketed by the values reported previously in the literature.
Research Octane Number (RON)

Figures 4.5a and 4.5b show the RON values of isooctane, n-heptane and toluene with respect to the volumetric and molar concentration of ethanol respectively. Blends of ethanol and isooctane are of particular interest. While a survey of the limited literature on ethanol/PRF blends has revealed no detailed information on the blending characteristics of these fuels, the RON values of blends with 20% to 80% (v/v) ethanol concentration exceed that of neat ethanol (the RON peaks at 110.2 with 40% ethanol). Such a significant relative RON improvement, particularly at a low ethanol concentration, is not observed in other PRF blends, suggesting the presence of some significant synergism between ethanol and isooctane.

Likewise, the addition of ethanol to n-heptane results in a significant non-linear increase in ON. This is likely due to the effectiveness of ethanol in suppressing the low-temperature chemistry of n-heptane [133].

While blending isooctane and n-heptane with ethanol results in synergism, ethanol/toluene blends clearly exhibit an antagonistic blending effect. The antagonistic effect is so significant that beyond 40% (v/v) ethanol, the difference between the RON of a blend and that of neat ethanol is negligible. Of all blends, toluene-E80 has the lowest RON of 107.9, which is effectively the same as that of neat ethanol.

Motor Octane Number (MON)

Figure 4.6 shows the MON values of blends of ethanol/n-heptane, ethanol/isoctane and ethanol/toluene. As expected, n-heptane blends synergistically with ethanol in the MONs both on a volume and a mole basis. For ethanol/isoctane blends, some
4.3 Blending behaviour of ethanol with n-heptane, isoctane and toluene

Figure 4.5: Measured RONs of blends of ethanol/isoctane, ethanol/n-heptane and ethanol/toluene versus ethanol content. The RON of neat toluene was obtained from [174].
synergism (on a volume basis) is found at low ethanol content of up to 20% (v/v), beyond which almost linear blending is observed. This is in contrast to the more significant synergism of these blends when evaluated on a mole basis. On the other hand, antagonistic blending in the MON can be observed in ethanol/toluene blends. On a volume basis, the antagonistic effect of the blends is more pronounced, amounting to a significant reduction in the MON even with a small amount of ethanol present in the blend. Nonetheless, analysis based on molar fractions is argued to be of greater significance, since reaction rates scale with the molar composition, as previously discussed.

Overall, these results demonstrate that ethanol blends synergistically with isooctane and n-heptane to increase the RONs and MONs, and antagonistically decreases the octane numbers when blended with toluene. At 20% (v/v) or greater ethanol content, blends of ethanol/isoctane and ethanol/toluene have RONs that differ by less than 3 ON, and are within 3 ON of the RON of neat ethanol. This is despite a full 20-point difference in the RONs of neat isoctane and toluene.

### 4.4 Formulation of gasoline surrogates

Various gasoline surrogates have been proposed in the literature. PRFs are a popular choice, given their well validated chemistry \[108, 117\] and defined octane numbers \[63, 64\]. However, previous studies \[172, 175\] showed that the autoignition characteristics of PRFs are significantly different from those of full-boiling-range gasoline. Several recent studies instead propose the use of TRFs - which are ternary mixtures of isooctane, n-heptane and toluene - as a gasoline surrogate \[132, 133, 135\]. A fourth component, such as 2-pentene \[175\] and 1-hexene \[131, 176\], has also been included in surrogates to represent olefins. Surrogates with more than 4 components have also been proposed \[177\], but are less common due to the complexity of the chemical model.

In this study, one PRF blend and three different TRF blends were selected as the gasoline surrogate fuels. PRF91, a mixture of 91% isooctane and 9% n-heptane (v/v), was chosen as a surrogate, since it has a similar RON to that of the commercial gasoline (91.5 in this study). The formulation of the TRF compositions, on the other hand, was based on the following constraints, which were adapted from other works \[173, 178\],

1. \( \text{RON} \approx 91 \),
2. \( \sum_{i=1}^{n} x_i H_i / \sum_{i=1}^{n} x_i C_i = 1.85 \),

where \( n \) is the number of compounds in the surrogate, \( x_i \) is the molar fraction of species \( i \), \( H_i \) is the number of hydrogen atoms in species \( i \) and \( C_i \) is the number of carbon atoms in species \( i \).

Matching both the RON and MON of commercial gasoline would be preferable \[173\]. Implementing this approach, however, would over-constrain the formulation of a 3-component (TRF) surrogate based on the RON-MON model of Morgan et al. \[172\].
Figure 4.6: Measured MONs of blends of ethanol/isoctane, ethanol/n-heptane and ethanol/toluene versus ethanol content.
While the RON test conditions differ considerably from the regime in which modern spark-ignition engines are usually operated, RON is still arguably the better representative test method for determining knock propensity compared to MON [75, 79]. Hence, MON is not taken into account in the formulation of gasoline surrogates in this study, although the MONs of these fuels will be reported.

The hydrogen to carbon (H/C) ratio is an equally important criterion in formulating a gasoline surrogate. The H/C ratio determines the stoichiometric air-fuel ratio, and affects the adiabatic flame temperature and the lower heating value of a fuel, and thus affects flame propagation and the heat release during combustion [173]. An H/C ratio of 1.85 was chosen to be consistent with what is specified in the Australian Standard AS2877 [179] for commercial gasoline in Australia.

The TRF gasoline surrogates were formulated in two steps. First, the composition of a TRF blend which satisfies the aforementioned constraints was estimated based on the modified linear by volume model (RON) by Morgan et al. [172],

\[
RON = a_p v + a_{tol} v_{tol} + a_{tol^2} v_{tol}^2 + a_{tol,p} v_{tol}^p,
\]

(4.3)

where \(v\) is the volume fraction, \(a\) are the model coefficients, and the subscripts \(tol\) and \(p\) refer to toluene and PRF respectively. The variable \(p\) is defined by,

\[
p = \frac{v_{iO}}{v_{iO} + v_{nH}},
\]

(4.4)

in which the subscripts \(iO\) and \(nH\) refer to isooctane and n-heptane respectively. The values of the model coefficients are listed in Table 4.3. Next, a standard test was performed to determine the RON of that particular TRF blend. The model yielded very good agreement (within ±1.0 ON) between the estimated (from Eq. 4.3) and the measured RONs. The composition of the blend was then fine-tuned such that the measured RON yielded approximately 91. In order to explore the effect of aromatic content on gasoline performance, TRFs were prepared with 15% (v/v), 30% (v/v) and 45% (v/v) toluene, which represent the range of total aromatics content typically encountered in gasoline [9]. These TRF blends are referred to as ‘TRF91-15’, ‘TRF91-30’ and ‘TRF91-45’ respectively. Note that by varying the toluene content in these TRFs, the H/C ratio (except for that of TRF91-30) no longer conforms to that of typical gasoline (the same applies to PRFs where there is already one less degree of freedom). Table 4.4 lists the properties of all gasoline surrogates used in this study.
Table 4.4: Properties of this study’s gasoline and its surrogates.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>RON&lt;sup&gt;a&lt;/sup&gt;</th>
<th>MON&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Toluene</th>
<th>Isooctane</th>
<th>n-Heptane</th>
<th>H/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>91.5</td>
<td>82.1</td>
<td>See Table 4.5</td>
<td>1.85&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PRF91</td>
<td>91.0</td>
<td>91.0</td>
<td>0</td>
<td>91.0</td>
<td>9.0</td>
<td>2.25</td>
</tr>
<tr>
<td>TRF91-15</td>
<td>91.0</td>
<td>88.4</td>
<td>15.0</td>
<td>72.6</td>
<td>12.4</td>
<td>2.04</td>
</tr>
<tr>
<td>TRF91-30</td>
<td>91.3</td>
<td>86.1</td>
<td>29.8</td>
<td>53.2</td>
<td>17.0</td>
<td>1.85</td>
</tr>
<tr>
<td>TRF91-45</td>
<td>91.1</td>
<td>83.5</td>
<td>45.0</td>
<td>34.7</td>
<td>20.3</td>
<td>1.67</td>
</tr>
</tbody>
</table>

<sup>a</sup>As measured in the present study using the standard RON and MON tests.

<sup>b</sup>This H/C value is in accordance with AS2877 [179].

4.5 Ethanol/PRF91 blends

Research Octane Number (RON)

Having established the ON relationships in different binary blends, it is interesting to determine if such relationships remain important in the blends of gasoline surrogates and ethanol. Hence, the octane numbers of gasoline surrogates blended with ethanol were measured, starting with the simple binary mixture PRF91 (91% isoctane and 9% n-heptane (v/v)).

Figure 4.7a shows the RONs of different ethanol/PRF91 blends plotted against the volumetric concentration of ethanol. Although similarly non-linear in RONs with respect to ethanol content, the non-linearity is significantly more pronounced compared to that observed in ethanol/gasoline blends. A blend with 40% (v/v) ethanol would yield a similar RON to that of neat ethanol. Of interest is that the RON values of these blends at 60% and 80% (v/v) ethanol concentration would exceed that of neat ethanol, which possesses a greater charge cooling effect than either of the blends. This suggests significant synergism between ethanol and PRF91, as has been observed in the binary blends of ethanol/isoctane and ethanol/n-heptane.

Figure 4.7b illustrates the RON values of ethanol/PRF91 blends with respect to the molar concentration of ethanol. In contrast to the almost linear relationship observed in ethanol/gasoline blends, significant non-linearity is observed for ethanol/PRF91 blends. Again this suggests that, although having very similar RONs, the autoignition chemistry of gasoline can be significantly different from that of PRF91 when blended with ethanol. The use of binary mixtures of n-heptane and isoctane to capture the autoignition behaviour of a gasoline blendstock, therefore, is deemed insufficient. This observation agrees with what has been reported in a recent study [172].

Further tests were conducted on other PRFs to confirm their synergistic blending with ethanol. Figure 4.8 shows the measured RON values of ethanol/PRF blends versus ethanol content. As expected, all ethanol/PRF blends are significantly synergistic. A small amount of ethanol added to any PRF blend increases the RON of the blends.
Figure 4.7: Measured RONs of ethanol/PRF91 blends versus ethanol content.
4.6 Ethanol/TRF91 blends

Motor Octane Number (MON)

Figure 4.9 shows the MON values of different ethanol/PRF91 blends with respect to the volumetric and the molar concentration of ethanol. It is again clear that the non-linearity in the MONs of these blends is significantly more pronounced compared to that of ethanol/gasoline blends, and significant synergism due to ethanol blending is present. Of note is that the RON and MON of gasoline in this study differ by approximately 9 ON, while PRF91 has the same RON and MON values by definition.

4.6 Ethanol/TRF91 blends

Research Octane Number (RON)

Prior results in this study have shown that aromatic content may have a significant role in the autoignition of blends of ethanol and gasoline or gasoline surrogates. Figure 4.10a shows the measured RON values of different ethanol/TRF blends with respect to the volumetric concentration of ethanol. The RONs of these blends do not scale linearly with ethanol content. The extent of non-linearity, however, differs for each TRF surrogate. TRF91-15 exhibits the greatest blending synergism in RONs with ethanol, followed by TRF91-30 and lastly TRF91-45 with the highest toluene content. This is consistent with earlier results, where ethanol/PRF91 blends possess the greatest non-linearity in RONs. These results suggest that increasing the toluene content and hence lowering the isooctane content in a surrogate, while maintaining a constant RON, reduces the octane enhancing effect of ethanol.

In comparison with gasoline, the TRF surrogates exhibit a more significant non-linear relationship in RONs when blended with ethanol. For example, adding 40% (v/v) ethanol to TRF91-30 would yield a RON of 106, which is a significant increase of approximately 4 ON over that of gasoline-E40. Increasing the toluene content or decreasing the PRF content helps narrow this gap, where the RON of TRF91-45-E40 differs from that of gasoline-E40 by only 2.5 ON.

Figure 4.10b shows the RON values of different ethanol/TRF blends on a mole basis. Similar to Figure 4.10a, significant non-linearity is found for ethanol/TRF blends, and ethanol/TRF91-45 blends exhibit the least synergism when blended with ethanol.

Motor Octane Number (MON)

Figure 4.11 illustrates the MON values of different ethanol/TRF blends with respect to the volumetric and the molar concentration of ethanol. While every surrogate in this study has a RON similar to that of gasoline, the MONs of these surrogates differ considerably from one to another. Of all surrogates, PRF91 has the highest MON (91 ON), followed by TRF91-15 (88.4 ON), TRF91-30 (86.1 ON), and lastly TRF91-45 (83.5 ON). This decrease in MONs is consistent with increasing toluene content in the surrogates. The results again clearly show a non-linear relationship between MONs and
Figure 4.8: Measured RONs for different ethanol/PRF blends versus ethanol content.
4.6 Ethanol/TRF91 blends

Figure 4.9: Measured MONs of ethanol/PRF91 blends versus ethanol content.
Figure 4.10: Measured RONs for different ethanol/TRF blends versus ethanol content. Recent literature data from Anderson et al. [158] are included for reference.
4.7 Octane sensitivity

The ethanol content. Blending ethanol with these surrogates results in synergism, with the greatest gain in ON usually observed with 20%-40% (v/v) of ethanol in a given blend.

4.7 Octane sensitivity

Figure 4.12 shows the blends’ octane sensitivity, which can be defined by the following,

\[ \text{octane sensitivity} = RON - MON. \]  

(4.5)

Of all base fuels, gasoline is the most sensitive fuel with an octane sensitivity of approximately 9 ON. On the other hand, PRF91, by definition, has no octane sensitivity. It is clear that the octane sensitivity increases with the toluene concentration in a blend.

Adding a small amount of ethanol to gasoline and its surrogates also raises the octane sensitivity significantly. Beyond 40% (v/v) ethanol, however, the octane sensitivity of a blend becomes almost independent of gasoline/surrogate content. This suggests that, even at a low concentration, ethanol has a significant impact on the chemistry of a blend.

4.8 Gasoline vs. its surrogates

In light of ethanol blending, the results in this study suggest that TRF91 may not be an ideal gasoline surrogate, despite having a similar RON and hydrogen-to-carbon ratio. Compared to gasoline, the use of a TRF surrogate results in more significant synergism in RONs when blended with ethanol.

The reasons for this difference in the octane numbers are several. First, the use of three components in formulating a gasoline surrogate may be inadequate to capture the autoignition characteristics of full-boiling-range gasoline. Increasing the number of components by including an olefin component and a naphthene component in a gasoline surrogate may improve the results, although little is understood regarding how these various components interact with each other. On the other hand, the use of isooctane to represent branched paraffins may not be justified due to its low concentration (1.4% v/v) in the gasoline used in this study. A recent study [173] suggested that isopentane (12.3% v/v in this study’s gasoline) be a more representative branched paraffin. Also, while a total of 8.37% (v/v) xylenes are present, toluene was chosen to be the only representative aromatic component.

It is important to point out that this observation corresponds to the specific type of gasoline used in this study, and by no means applies to all other types of gasoline fuels. In comparison, the ethanol/gasoline data (base gasoline with an average RON = 92.2 and MON = 84.7) reported by [158] exhibit a more non-linear relationship between the octane numbers and the ethanol content.
Figure 4.11: Measured MONs for different ethanol/TRF blends versus ethanol content. Recent literature data from Anderson et al. [158] are included for reference.
4.9 Implications on the RONs and MONs of ethanol/ gasoline blends

Earlier results showed clearly that the octane numbers of the production gasoline of Anderson et al. [158] blended with ethanol were significantly different to those of the present study. These differences of course arise from these studies’ differing gasoline compositions. Gasoline is a complex mixture of hydrocarbons, which are commonly grouped into five major classes, i.e. linear paraffins, branched paraffins, naphthenes, olefins and aromatics. Interactions between these different classes of hydrocarbons have been studied in the past [180]. For example, it is well established that hydrocarbons of the same class interact linearly with one another with regards to the ON, while significant non-linearity is readily found in blends of paraffins and olefins [74, 180, 181]. However, the blending behaviour of ethanol with gasoline remains less clear, especially at high concentrations.

In this present study, blends of both ethanol/isooctane and ethanol/\(n\)-heptane were shown to exhibit significant synergism in their RONs. In contrast, blends of ethanol/toluene were antagonistic in their RONs. Consistent with these trends, a progressive increase in the toluene content in TRFs of a constant RON resulted in increasingly linear TRF/ethanol blending. These results show that the antagonism of ethanol’s blending with toluene acts against its synergism with isooctane and \(n\)-heptane.

Further, the greater synergism in the RONs of ethanol/gasoline blends reported in Anderson et al. [158] compared to that observed in this study (Figure 1a) coincides with their higher paraffin content (64.3\% vs. 48.9\%) and lower aromatic content (26.0\% vs. 31.7\%) in their base gasolines (Table 4.5). A similar observation was reported by Livshits et al. [182] , who investigated the effect of methanol and ethanol addition on
Table 4.5: Composition of this study’s gasoline as determined by ASTM D6730, and of gasoline (‘B92E0’) studied by Anderson et al. [158].

<table>
<thead>
<tr>
<th>Component</th>
<th>This study (% volume)</th>
<th>Anderson et al. [158] (% volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Paraffins</td>
<td>48.9</td>
<td>64.3</td>
</tr>
<tr>
<td>iso-Paraffins</td>
<td>35.3</td>
<td>48.3</td>
</tr>
<tr>
<td>n-Paraffins</td>
<td>13.7</td>
<td>15.9</td>
</tr>
<tr>
<td>Aromatics</td>
<td>31.7</td>
<td>26.0</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>11.4</td>
<td>3.9</td>
</tr>
<tr>
<td>Olefins</td>
<td>8.0</td>
<td>5.8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>&lt; 0.01</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>MTBE</td>
<td>&lt; 0.01</td>
<td>N/A</td>
</tr>
</tbody>
</table>

the octane ratings of PRFs and toluene/n-heptane blends of similar MON values. They showed that methanol and ethanol were more effective in increasing the MONs of PRFs compared to those of toluene/n-heptane (Figure 4.13) [182]. This is consistent with a later study [183], which showed that the greatest increase in ON due to alcohol addition was found in mixtures containing the least amount of aromatics. More recently, it was also reported in [184] that between two base gasolines (one with 38.5% aromatics and 46.8% paraffins; the other with 26.9% aromatics and 59.8% paraffins), the addition of ethanol increases the ON of the latter more effectively. Likewise, da Silva et al. [185] measured the ON of two gasoline blendstocks blended with 25% (v/v) ethanol, and found that the blending RON of ethanol is significantly higher for the blendstock with lower aromatic content (9% vs. 33%). If the individual surrogate components (n-heptane, isooctane and toluene) grossly represent the blending behaviours of the respective paraffin and aromatic classes of hydrocarbons in gasoline, such results for the blending of production gasolines with ethanol are consistent with those observed for the blending of PRFs/TRFs (and their pure components) with ethanol, i.e. the antagonism of ethanol’s blending with aromatics may act against its synergism with paraffins. While the interaction between ethanol and olefins, as well as that between ethanol and naphthenes, is unclear, the small amount of olefins and naphthenes present in gasoline suggests that these interactions would be of secondary importance.

If correct, these findings have implications for fuel design. Exploitation of the synergism between ethanol and paraffins may enable a given octane number to be achieved with lower aromatic and lower ethanol content, i.e. it makes more effective use of the ethanol. Whilst the design of optimal gasoline/ethanol blends depends on many factors, both technical and non-technical, the observations reported in this study may nonetheless have environmental and/or economic benefits. In particular, if ethanol production for fuel use is likely to remain small relative to gasoline, it may make greater economic and/or environmental sense to blend this ethanol more uniformly through all production gasolines, and exploit the observations in this study, rather than burn this ethanol
at higher concentrations such as E85 or hydrous ethanol. Of course, quantification of these potential benefits can only be determined through further study, and is outside the scope of this present work.

4.10 Summary

This chapter reported the RONs and MONs of ethanol blended with production gasoline, four gasoline surrogates, \( n \)-heptane, isoctane and toluene. The ethanol concentration was varied from zero to 100\%, resulting in a clear picture of the variations of the RONs and MONs in all cases. Of initial interest was the almost linear variation of the RON and MON with ethanol content of blends with an Australian production gasoline. This was in contrast with other recent studies which demonstrated varying synergism between US production gasolines and ethanol [158, 159]. Such differences arose from differing gasoline compositions among the various studies, each with notably different aromatic content but similar RON and MON.

This, in turn, prompted a systematic study of the variation in the RONs and MONs of ethanol blended with four gasoline surrogates, as well as with \( n \)-heptane, isoctane and toluene. Both \( n \)-heptane, isoctane and their PRFs blended synergistically with ethanol, whilst toluene blended antagonistically. Of particular note was that the RON of some blends of isoctane and ethanol exceeded that of neat ethanol. Consistent with these trends, a progressive increase in the toluene content in TRFs of a constant RON resulted in increasingly linear ethanol/TRF blending. Together, these results show that the antagonism of ethanol’s blending with toluene acts against its synergism with isoctane and \( n \)-heptane, and more broadly suggest that the antagonism of ethanol’s blending with aromatics may act against its synergism with paraffins.

If correct, this explains the different trends in the octane numbers of ethanol/gasoline
blends in the literature and in this study, and also has implications for fuel design. In particular, exploitation of this synergism of ethanol and paraffins may enable a given octane number to be achieved with lower aromatic and lower ethanol content, i.e. it makes more effective use of the ethanol. Whilst the design of optimal gasoline/ethanol blends depends on many factors, both technical and non-technical, the observations reported in this study may nonetheless have environmental and/or economic benefits. Quantification of these potential benefits can only be determined through further study building on the present work.
5 The Effects of Charge Cooling and the Modified RON

The content of this work has already appeared in [170, 186]. This chapter examines the effect of charge cooling on the RON of ethanol/gasoline blends. While gasoline is fully vaporised prior to entry into the engine in a standard RON test, significant charge cooling is observed for blends with high ethanol content, with the presence of a near-saturated and potentially two-phase air-fuel mixture during induction. Thus, the relative significance of the charge cooling and the autoignition chemistry cannot be determined from the standard RON test.

In order to better delineate the effects of charge cooling and autoignition chemistry, a so-called ‘modified RON’ test is therefore devised in which the temperature of the air-fuel mixture entering the engine is fixed and representative of that observed for primary reference fuels. Thermodynamic modelling of this modified RON test suggests the mixture is always fully vaporised prior to compression, and that the modified RON test maintains much more constant temperatures during compression, regardless of the enthalpy of vaporisation. The modified RON test thus appears to be a more practical means of examining the significance of autoignition chemistry of various fuels, particularly gasoline blends with significant alcohol content.

5.1 The CFR intake system

Defined in the ASTM standards D2699 and D2700, the RON and MON test methods quantify the propensity of a fuel to knock in a standardized single-cylinder spark-ignition CFR engine [63, 64]. One of the key differences between these two test methods is the charge temperature. In the MON method, the intake air temperature (IAT), which is monitored upstream of the carburettor, is specified to be 38 °C, and the air-fuel mixture temperature entering the engine to be 149 °C [64].

The RON method, however, specifies only the IAT, leaving the air-fuel mixture temperature entering the engine to vary [63]. Figure 3.5 illustrates the cross section of the intake system in the CFR engine under the RON configuration. During a standard test, the IAT is regulated to 52±1 °C (for operation at standard barometric pressure of 101.0 kPa) through a thermocouple or thermometer, which is located downstream of the air heater. As the heated air passes through the venturi, liquid fuel is drawn from the carburettor via the vertical jet, cooling the air as it vaporises in the intake manifold. While this charge cooling effect may be similar for many non-oxygenated gasolines, fu-
The Effects of Charge Cooling and the Modified RON

eels blended with alcohols, e.g. methanol and ethanol, may have significantly greater charge cooling effect. Indeed, as this chapter discusses, the charge cooling effect of ethanol/gasoline blends varies significantly with ethanol content. Hence, the standard RON test itself is sensitive to the fuel’s charge cooling and not just its autoignition chemistry.

5.2 Mixture temperatures and dew points

Several studies have shown that ethanol can significantly cool the air-fuel charge as it evaporates, e.g. [160, 187]. The two factors that contribute to this charge cooling of ethanol are the enthalpy of vaporisation and the fuel stoichiometry. The enthalpy of vaporisation, \( h_{fg} \), of ethanol (per unit fuel mass) is approximately three times that of gasoline at 25 °C and 1 atm. On the other hand, while the stoichiometric air-fuel ratio by mass of gasoline is approximately 15:1, that of neat ethanol is approximately 9:1. Hence, taking into account both the higher enthalpy of vaporisation and greater fuel mass required to reach stoichiometry, Figure 5.1 shows an approximately five-fold increase in the evaporative cooling of the air in a stoichiometric mixture when the fuel is switched from gasoline to neat ethanol. Figure 5.1 also shows a representative variation of \( h_{fg} \) of gasoline/ethanol mixtures when an ideal mixture is assumed. Whilst there is evidence that vaporisation of gasoline/ethanol blends may not be closely approximated assuming an ideal mixture [160, 188], the value of \( h_{fg} \) for a given gasoline/ethanol mixture depends on the specific composition of the gasoline in question, which can of course vary significantly. Nonetheless, as Figure 5.1 shows, it is always the case that increasing ethanol content results in a reduced air-fuel ratio which infers a larger relative change in the charge cooling per unit mass of air-fuel mixture.

Given this large variation in the charge cooling of the fuel, it is reasonable to expect that the temperature of the air-fuel mixture entering the engine should vary. Figure 5.2 shows that this is indeed the case for the standard RON test, even though the air temperature upstream of the carburettor (the IAT defined previously) was controlled to be approximately 52 °C (depending on the barometric pressure) for all tests. Of note is that these measured mixture temperatures do not vary monotonically with increasing ethanol content, in contrast with the enthalpies of vaporisation shown in Figure 5.1. In the case of gasoline, the mixture temperature is approximately 38 °C. As ethanol is added to gasoline, the mixture temperature drops, with the lowest mixture temperature being approximately 20 °C for blends containing 40% (v/v) ethanol. Further addition of ethanol beyond 40% (v/v) increases the mixture temperature, eventually reaching approximately 22 °C for neat ethanol. For ethanol/isooctane blends, the mixture temperatures are very similar to those of ethanol/gasoline blends. Likewise, a similar trend can be observed in blends of ethanol/n-heptane, ethanol/toluene and ethanol/TRF91-30 (Figure 5.3), although the mixture temperatures of these blends at low and intermediate ethanol content are slightly lower than the others due to their higher enthalpies of vaporisation. However, it is worth noting that beyond approxi-
5.2 Mixture temperatures and dew points

Figure 5.1: Estimated enthalpy of vaporisation, $h_{fg}$, for ethanol/gasoline blends at 25 °C and 1 atm, where $h_{fg}$ is defined both per kg of fuel and per kg of air-fuel mixture assuming stoichiometric mixtures. The gasoline data was obtained from [47].

Approximately 40% (v/v) ethanol content, the mixture temperatures measured for all blends are almost identical (within the measurement tolerance of the thermocouple).

On the other hand, the mixture temperatures measured for gaseous fuels, e.g. propane and butane, approach 60 °C, as shown in Figure 5.4. It is clear then the charge cooling provided by liquid fuels is significant in the RON test, capable of lowering the mixture temperature by as much as approximately 20 °C even in the case of neat gasoline. Also of interest is that the mixture temperatures of these gaseous fuels are actually higher than the IAT (regulated to 52 °C). This suggests that some heat is transferred to the air-fuel mixture and is likely a result of the reverse flow of the hot residual gas (see Section 3.1 for more detail).

It was speculated that these variations in the mixture temperatures were in part due to saturation of the air-fuel mixture entering the engine. To investigate this further, the dew point of each blend in air was calculated [189, 190]. Calculations were performed on ethanol blends with PRFs, not gasoline, as gasoline is a complex mixture of hydrocarbons.

Figure 5.5a shows the saturated and stoichiometric mass fractions for isoctane and $n$-heptane in air at different temperatures. A stoichiometric mixture of air/isoctane saturates at approximately -1 °C, while that of air/$n$-heptane is saturated at approximately 4 °C. These calculated temperatures are significantly lower than the equivalent measured mixture temperatures (approximately 38 °C) entering the engine (Figure 5.2), strongly suggesting that the fuel entering the engine is fully vaporised and the air is unsaturated for the low ethanol content blends. This is not a surprising result given that the standard RON test is designed for such fuels.
Figure 5.2: Measured mixture temperatures for ethanol/\textit{n}-heptane, ethanol/isooctane and ethanol/gasoline blends in standard RON tests, estimated dew points (1 atm) for stoichiometric ideal mixtures of ethanol/isooctane/oxygen/nitrogen (solid line), and ethanol/\textit{n}-heptane/oxygen/nitrogen (- - -) [189]. Estimated dew points (1 atm) for stoichiometric mixtures of ethanol/\textit{n}-heptane/oxygen/nitrogen (- . -) from [190] based on the Peng-Robinson equation of state are also included.

Figure 5.3: Measured mixture temperatures for ethanol/TRF91-30 and ethanol/toluene blends in standard RON tests, estimated dew points (1 atm) for stoichiometric ideal mixtures of ethanol/TRF91-30/oxygen/nitrogen (solid line), and ethanol/toluene/oxygen/nitrogen (- - -) [189].
5.2 Mixture temperatures and dew points

With 50% (v/v) of ethanol in the blends, ethanol saturates at a considerably higher temperature compared to \( n \)-heptane and isoctane, as shown in Figure 5.5b. Once again, these temperatures are all lower than that measured at this condition (Figure 5.2), suggesting that vaporisation is complete and the air is unsaturated.

In contrast, Figure 5.5c shows the resulting saturated and stoichiometric mass fractions for neat ethanol in air at different temperatures. Given that the measured mixture temperature is approximately 22 °C for neat ethanol (Figure 5.2), it is therefore likely that the air-fuel mixture in this case has been cooled to its saturated condition by ethanol evaporation, and that some liquid fuel may even be entering the engine during the RON rating of ethanol. It therefore appears that the standard RON test does not guarantee a fully vaporised mixture entering the engine.

The dew points obtained using the same approach for ideal mixtures of ethanol/isoctane/air and ethanol/\( n \)-heptane/air are plotted in Figure 5.2. In general, the dew point decreases when ethanol is first added, reaching a minimum between 20% and 30% (v/v) ethanol for the two mixtures. Up to these minima, the isoctane and \( n \)-heptane are the condensates formed at progressively lower dew points as their partial pressures decrease. With further addition of ethanol, both lines show that the dew point rises with the ethanol now the condensate (Figure 5.5b). The dew points of ethanol/\( n \)-heptane/air mixtures were also estimated using the Peng-Robinson equation of state [190] to account for the non-ideal behavior of these blends. As shown in Figure 5.2, although having a different profile at low ethanol content, these dew points match those predicted using the ideal mixture assumption beyond roughly 40% (v/v) ethanol.

Thus, it appears likely that the standard RON test procedure features a transition from fully vaporised, unsaturated air-fuel mixtures at lower ethanol content, to near-
5 The Effects of Charge Cooling and the Modified RON

Figure 5.5: Saturated and stoichiometric mass fractions of a) isooctane, \textit{n}-heptane, b) isooctane/E50, \textit{n}-heptane/E50 and c) ethanol in air at different temperatures assuming ideal mixtures [189].
saturated mixtures at high ethanol content. The measured temperature variations in Figure 5.2 therefore suggest that the standard RON test does not examine only the autoignition chemistry of these blends.

5.3 Modified RON

A variation to the standard RON test is proposed, in which the temperature of the air-fuel mixture entering the engine is fixed at a representative temperature of the PRF-only mixtures from the standard RON test. The average mixture temperature for the PRF-only cases (ranging from PRF40 to PRF100) was measured to be 36 °C (Figure 5.4). This temperature is therefore chosen as the set temperature in this ‘modified RON’ test. The test method has been discussed in detail in Section 3.4. As Figures 5.2 and 5.3 showed, use of this fixed temperature should guarantee that the air-fuel mixture is unsaturated when entering the engine, regardless of the ethanol content. Variations in the ‘modified RON’ should then not be due to intake charge cooling effects, providing a truer picture of autoignition chemistry effects from ethanol/fuel blending.

Significant differences between the standard and modified test results can be observed for the blends with high ethanol content (Figure 5.6 and Table C.1). The modified RONs of these blends are lower than the standard RONs, as expected. However, up to approximately 20% (v/v) ethanol content (except for ethanol/toluene blends), the standard and modified RONs are similar. This suggests that the autoignition chemistry dominates the charge cooling effects for these blends initially, while the charge cooling of ethanol starts to have a greater effect on RONs as ethanol content is further increased. The ‘modified RON’ of neat ethanol is 103.5, suggesting that the charge cooling of ethanol alone contributes significantly to the standard RON of neat ethanol. This demonstrates the importance of the charge cooling effect relative to that from differing autoignition chemistry of these blends. It is also noteworthy that the modified RON of gasoline is identical to its standard RON (Figure 5.6a). This is not a surprising result, since the modified test is intended to create gasoline-like intake mixture temperatures for all fuels.

The ethanol/isoctane blends (10% - 80% v/v ethanol), shown earlier in Figure 4.5a as having a similar RON to ethanol, now show a higher RON than that of ethanol in all cases (Figure 5.6b). This demonstrates the importance of the autoignition chemistry of these blends. It is clear that relatively small quantities of ethanol have a profound effect on the autoignition chemistry of isoctane. Further work will be required to identify the source of this interesting phenomenon.

Similarly, Figure 5.6c presents the modified RON values for ethanol/n-heptane blends. The results suggest that the autoignition chemistry dominates the charge cooling effects for these blends initially, while the charge cooling of ethanol starts to have a greater effect on RONs as ethanol is further increased.

Likewise, Figure 5.6d compares the standard and the modified RON values of different ethanol/toluene blends. Antagonistic blending is found in the modified RONs of these blends.
Figure 5.6: Measured RON values, and the associated IATs for different ethanol blends with gasoline, isooctane, \(n\)-heptane, toluene and TRF91-30 under standard and modified conditions.
blends, although the modified RONs are found to decrease at a greater rate than their standard RONs with increasing ethanol content. These results suggest that both charge cooling and the autoignition chemistry are important in describing the complex way in which ethanol affects the octane numbers of gasoline-like fuels.

Figure 5.6 also shows how the intake air temperature (IAT) measured upstream of the carburettor varies with ethanol content for these modified RON tests. The IAT for the neat ethanol is now approximately 165 °C (versus 52 °C in the standard RON test), which is testimony to the strong charge cooling that ethanol provides.

5.4 Energy balance

Relative to the standard test method, the modified RON test appears better posed to examine the impact of fuel chemistry on autoignition, as it attempts to compensate for the significant charge cooling from vaporising fuel blends with a high enthalpy of vaporisation. This is achieved by fixing the mixture temperature to 36 °C in all cases, on the assumption that this achieves complete vaporisation. An energy balance is now performed on the intake system shown in Figure 3.5 to test this.

The energy exchange between the heated intake air and the fuel drawn out of the carburettor, together with the heat transfer to and from the surroundings, can be described by,

\[ \dot{m}_a h_{a,1}(T_{a,1}) + \dot{m}_f h_{f,1}(T_{f,1}) = \dot{m}_a h_{a,2}(T_{a,2}) + \dot{m}_f h_{f,2}(T_{f,2}) + Q, \]

where \( \dot{m}_a \) is the mass flow rate of air, \( \dot{m}_f \) is the mass flow rate of fuel, \( h_a \) is the specific enthalpy of air, \( h_f \) is the specific enthalpy of fuel, \( T_a \) is the air temperature, \( T_f \) is the fuel temperature, and \( Q \) is the heat transfer. Subscripts 1 and 2 represent the locations of measurement of the IAT and the mixture temperature respectively (Figure 3.5). The enthalpy of each species was obtained from the Third Millennium Ideal Gas and Condensed Phase Thermochemical Database [191]. The heat transfer (\( Q > 0 \) when heat is transferred from the fluid to the surroundings) includes both heat addition, \( Q_{in} \), and heat loss, \( Q_{out} \). The heat addition is defined to be the heat transferred from a heat source to the fluid, which is justified based on the experimental observation that the measured mixture temperature is always higher than the IAT at the instant the fuel flow was stopped. It was believed that the heat source may be due to the reverse flow of the hot residual gas into the inlet port, where the mixture temperatures were measured. Simulations done in GT-Power suggested that this is indeed the case (Section 3.1). In this model, this heat addition is assumed to be constant for all blends, since the valve timings are constant in all tests.

The heat loss from the external surface of the intake system to the environment comprises both convection and radiation,

\[ Q_{out} = h_e A_e(T_w - T_\infty) + \sigma A_e(T_w^4 - T_\infty^4), \]
Table 5.1: Parameters used in energy balance calculations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{f,1}$</td>
<td>25 °C</td>
</tr>
<tr>
<td>$T_{f,2}$</td>
<td>36 °C</td>
</tr>
<tr>
<td>$T_{a,2}$</td>
<td>36 °C</td>
</tr>
<tr>
<td>$T_{\infty}$</td>
<td>15 °C</td>
</tr>
<tr>
<td>$h_i$</td>
<td>96.8 W/m²·K</td>
</tr>
<tr>
<td>$h_e$</td>
<td>79.1 W/m²·K</td>
</tr>
<tr>
<td>$Q_{in}$</td>
<td>22.5 J/g air</td>
</tr>
<tr>
<td>$A_i$</td>
<td>0.028 m²</td>
</tr>
<tr>
<td>$A_e$</td>
<td>0.04 m²</td>
</tr>
</tbody>
</table>

where $h_e$ is the external convective heat transfer coefficient, $A_e$ is the external area of the pipe at which heat transfer occurs, $T_w$ is the average wall temperature, $T_{\infty}$ is the ambient temperature, and $\sigma$ is the Stefan-Boltzmann constant. The wall temperature, $T_w$, was assumed to be uniform, and determined from an energy balance between the inside and the outside surfaces of the intake system,

$$h_i A_i (T_g - T_w) = h_e A_e (T_w - T_{\infty}) + \sigma A_e (T_w^4 - T_{\infty}^4), \quad (5.3)$$

where $h_i$ is the internal convective heat transfer coefficient, $A_i$ is the internal area of the pipe at which heat transfer occurs, and $T_g$ is the average fluid temperature,

$$T_g = \frac{1}{2} (T_{a,1} + T_{a,2}). \quad (5.4)$$

In this model, $T_{a,1}$ is the IAT and of particular interest. The measured mixture temperature was used for the $T_{a,2}$ and $T_{f,2}$ (after vaporisation) values, which were both at 36 °C. The two remaining unknowns were $T_{a,1}$ and $T_w$, which could be obtained by simultaneously solving Eq. 5.1 - 5.4. The values of $h_i$, $h_e$ and $Q_{in}$ were optimised such that the sum of squared errors (SSE) between the measured IAT and the calculated IAT ($T_{a,1}$) was minimised for the ethanol/isooctane runs. The optimised values were then applied to all other cases. Table 5.1 lists the value of each parameter used in the calculations. These optimised values are within a reasonable range, as would be expected for an air-fuel mixture of a low flow rate and with forced external convection.

Figure 5.7 shows the modelling results for the modelled IAT, the wall temperature and the mean fluid temperature for ethanol blended with isooctane, n-heptane, toluene and TRF91-30. The close agreement between the measured and modelled IATs, and therefore the air/fuel charge energy balance, demonstrates that the modified RON test does indeed achieve complete vaporisation of the fuel prior to entry into the engine in all cases, since Eq. 5.1 assumes this condition.

A further calculation was performed to determine the minimum IAT required to fully vaporise the fuel. The same parameters, as listed in Table 5.1, were used in
Figure 5.7: Measured and modelled IATs, with the associated modelled fluid and wall temperatures for a) ethanol/isooctane, b) ethanol/n-heptane, c) ethanol/toluene and d) ethanol/TRF91-30 blends.
Figure 5.8: Measured IATs and the calculated minimum IATs required to fully vaporise the fuel for a) ethanol/isooctane, b) ethanol/n-heptane c) ethanol/toluene and d) ethanol/TRF91-30 blends.

the model, with the exception that $T_{a,2}$ and $T_{f,2}$ were set to the calculated dew point (see Figure 5.2) of a given blend. This model therefore estimates the IAT required to heat the air-fuel mixture, such that the resulting mixture temperature is at the dew point. Figure 5.8 compares the calculated minimum IATs and the measured IATs for different ethanol blends isooctane, n-heptane, toluene and TRF91-30. It is clear that the required IATs are significantly lower than the measured values in all cases. The biggest deviation could be observed for neat isooctane and n-heptane, in which the required and the measured IATs could differ by as much as 70 °C. This is in part due to the very low dew points calculated for these fuels, and also because the heat loss is significantly less pronounced at a low IAT as a result of a low wall temperature (see Eq. 5.2). For neat ethanol, there is a difference of approximately 25 °C between the calculated and the measured values, further confirming that fuel would be fully vaporised in the modified RON test.
5.5 In-cylinder temperatures

Since both the air-fuel ratios and specific heat ratios of all these fuels vary, a constant temperature entering the engine does not guarantee a constant temperature at some crank angle prior to spark ignition. A simulation was therefore performed to investigate the effect of charge cooling on the temperature of the unburned air-fuel mixture at spark ignition both in the standard and the modified RON tests. The temperature was modelled assuming adiabatic compression of the air-fuel mixture. The simulation started at IVC and stopped at 13° before TDC, which is the spark timing specified in the RON test. No blowby was modelled, and the air-fuel mixture was assumed to be homogeneous and uniform throughout the compressed volume. The specific heats of the air-fuel mixtures were a function of composition and temperature, and were obtained from [191].

A key parameter that affects the temperature at the end of compression is of course the mixture temperature at IVC. Determination of this temperature is not straightforward, since it depends on several factors, particularly the temperature and composition of the fresh charge mixture and residual gases as well as the in-cylinder heat transfer during induction, e.g. [47]. A study by Perumal and Flowday [101] modelled this temperature as 127 °C (or 400 K) for a standard RON test of isooctane. This value of temperature is therefore assumed for all modified RON tests in this study. This assumption is justified since the enthalpy of the fresh mixture entering the engine is almost constant due to air’s large mass fraction in all cases.

For the standard RON tests, the mixture temperature at IVC, $T_{std,IVC}$, is estimated using a First Law argument. Assuming constant specific heats and no change to the residual gases, an enthalpy balance results in,

$$T_{std,IVC} (^{\circ}C) = 127 - (T_{mod,mix} - T_{std,mix}),$$

where $T_{mod,mix}$ is the measured mixture temperature in the modified RON test (constant at 36 °C) and $T_{std,mix}$ is the measured mixture temperature in the standard RON test (see Figure 5.2). Of note is that due to the lower limit of the RON test method [63], only $T_{std,mix}$ of ethanol/$n$-heptane blends with greater than 30% (v/v) ethanol was measured. With Eq. 5.5, it is assumed that the air-fuel mixture at $T_{std,mix}$ is at most saturated and no liquid fuel is present. This is a rather conservative estimate, since the fuel may be two-phase at a high ethanol content, as has been discussed previously. The liquid fuel would evaporate in the cylinder during compression, further decreasing the charge temperature at spark ignition. Table 5.2 lists the parameters used in the simulation.

Figure 5.9 shows the compression ratios measured at standard knock intensity for ethanol/gasoline, ethanol/isoctane and ethanol/$n$-heptane blends under the standard and the modified RON conditions. As expected, the compression ratio of a blend in the modified RON test is similar to that in a standard test at low ethanol content. Further
5 The Effects of Charge Cooling and the Modified RON

Table 5.2: Simulation parameters used in the model to estimate the temperature of the unburned air-fuel mixture at spark.

<table>
<thead>
<tr>
<th></th>
<th>Standard RON</th>
<th>Modified RON</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk temperature @ IVC</td>
<td>as estimated by Eq 5.5</td>
<td>400 K</td>
</tr>
<tr>
<td>Pressure @ IVC</td>
<td>1 atm</td>
<td>1 atm</td>
</tr>
<tr>
<td>Lambda</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

increase of ethanol content, however, results in a significant deviation in the compression ratio between the two tests. For example, in the case of neat ethanol, the compression ratio measured at standard knock intensity in the modified RON test is approximately 1 unit lower than that in the standard test. As discussed previously, this result further supports that the charge cooling effect of ethanol is compensated for in the modified test. Of note is that the critical compression ratio for each ethanol/isooctane blend is greater than that of either neat fuel under standard and modified RON condition (discussed previously in Section 5.3).

The modelled temperatures at spark ignition for ethanol/isooctane and ethanol/\textit{n}-heptane blends are shown in Figure 5.10. For certain blends, the temperature modelled for the modified test is higher than that in the standard test, despite a lower compression ratio (Figure 5.9). This result is due to a lower mixture temperature at IVC in the standard test. With further addition of ethanol, the charge temperature in the standard test becomes higher than that in the modified test due to a considerably higher compression ratio (Figure 5.9). For neat ethanol, the temperature at spark ignition in the standard test is higher than that in the modified test by approximately 40 °C.

It is, however, difficult to examine the charge cooling effect of ethanol alone on the charge temperature at spark ignition from Figure 5.10, since the compression ratio (as well as RON) varies from one blend to the other. Hence, Figure 5.11 shows the modelled temperature of different stoichiometric air-fuel mixtures at spark ignition, with the compression ratio set to 7.818 (the critical compression ratio for isooctane in a RON test), regardless of the fuel used. The temperature at spark ignition varies by only approximately 1 °C from neat isooctane to neat ethanol, as shown in Figure 5.11a. However, a large variation of as much as 30 °C could be observed in the temperature in the standard RON test. The temperature reaches its minima at an ethanol concentration of 40% (v/v), beyond which it rises slowly despite the increase in the charge cooling of the fuel. As mentioned above, this is due to the assumption of a saturated air-fuel mixture (i.e. no liquid fuel). The actual temperature at spark is likely to be lower than the modelled value for any fuel with high ethanol content as a result of liquid fuel vaporisation in the cylinder. Likewise, the modelled temperature of stoichiometric air/ethanol/\textit{n}-heptane mixtures at spark exhibits similar trends (Figure 5.11b). In practice, this suggests that when rating fuels of similar knocking propensity but of significantly different enthalpies of vaporisation, the modified RON test would maintain much more constant temperatures after the in-cylinder compression, and so appears
5.5 In-cylinder temperatures

Figure 5.9: The measured compression ratios at standard knock intensity for a) ethanol/gasoline, b) ethanol/isoctane and c) ethanol/n-heptane blends under standard and modified RON conditions.
Figure 5.10: The modelled temperatures of stoichiometric air-fuel mixtures for a) ethanol/isooctane and b) ethanol/\textit{n}-heptane blends at spark ignition under standard and modified RON conditions.

Figure 5.11: The modelled temperatures of stoichiometric air-fuel mixtures for a) ethanol/isooctane and b) ethanol/\textit{n}-heptane blends at spark ignition under standard and modified RON conditions but with a fixed compression ratio of 7.818 in all cases.
to be a practical means of testing the significance of variations in the autoignition chemistry of various fuels.

5.6 Summary

This chapter examined the effect of charge cooling on the RON of ethanol blended with several hydrocarbon fuels, particularly gasoline. Particular attention was paid to the effect of charge cooling, using experimental data obtained from a CFR engine and modelling of this engine’s intake system. In a standard RON test, the temperature of the air-fuel mixture entering the engine depends on the enthalpy of vaporisation of the fuel because the intake temperature is prescribed upstream of the carburettor. For gasoline, measurements of this temperature suggest that a fully vaporised, unsaturated mixture was achieved prior to entry into the engine, as is expected. However, for neat ethanol, these temperature measurements suggested that the mixture entering the engine was saturated and potentially two-phase. This is due to ethanol’s high enthalpy of vaporisation and its low stoichiometric air-fuel ratio.

As such, a so-called ‘modified RON’ test was proposed in which the temperature of the mixture entering the engine was fixed to that measured for PRFs in the standard RON test. In this modified test, the mixture appeared to be unsaturated and fully vaporised prior to entering the engine, regardless of the ethanol content. Modelling also showed that the modified RON test maintained much more constant temperatures after the in-cylinder compression for fuels with very different enthalpies of vaporisation. It was therefore argued that the modified RON test is better posed to examine the impact of the fuel chemistry. Further, the relative contribution of the fuel chemistry and the charge cooling could be determined by comparing the standard and modified RON test results; such a comparison suggests that both the charge cooling and fuel chemistry effects of ethanol were significant. Thus, the proposed, modified RON test appeared to be useful, particularly for gasoline blends with significant alcohol content.
5 The Effects of Charge Cooling and the Modified RON
6 Modelling of Premixed Combustion

In a spark ignited, reciprocating engine, the flame propagates across the combustion chamber. Prior to the arrival of the flame, significant reactivity may occur in the end gas, potentially leading to autoignition. The composition of the end gas is not only the ingested air-fuel mixture, but also contains residual gases of uncertain composition from the previous cycle. Further, during the entire cycle, the gas inside the cylinder is exchanging heat with the head, piston, valves and bore. Clearly, this overall process is complex, and it is impractical to model all of these simultaneously, particularly if detailed chemistry is required to simulate autoignition.

This and the subsequent chapters therefore take a different route. This chapter first details the modelling of premixed combustion for several blends of ethanol with iso-octane, PRF91, and TRF91-30, as well as their base fuels under RON conditions. The goal is to estimate several key parameters from non-autoigniting, in-cylinder pressure measurements for use in the next chapter’s modelling of autoignition. This modelling approach is of course heavily empirical, and allows study of the detailed autoignition chemistry in a far less computationally demanding way.

The methodology used to acquire the in-cylinder pressure traces is first discussed. This method obtains pressure traces without autoignition, while maintaining the engine operating conditions at standard knock intensity. The representative non-autoigniting pressure trace for each fuel is then passed into a premixed combustion model in GT-Power [192]. Particular attention is paid to estimating the residual gas fraction and calibrating the in-cylinder heat transfer such that the modelled pressure traces agree with experiment. The mass fraction burned, the unburned gas temperature and the laminar and turbulent flame speeds are then determined, and appear to be reasonable relative to other studies in the literature. The key results from this investigation - the residual gas fraction, the heat transfer and the crank-angle-resolved mass fraction burned - are then used in the next chapter in modelling the end-gas autoignition.

6.1 Fuel selection

It has been demonstrated previously in this thesis that a small amount of ethanol can change the octane number of a fuel significantly (e.g. Figure 4.5a). Further, most blends of ethanol/gasoline used as transportation fuels are of lower ethanol concentrations, typically 5-15% (v/v) ethanol [14]. Hence, it is of particular interest to study the combustion of blends with low-to-intermediate ethanol content. Thirteen fuels in total, twelve of which have up to 20% (v/v) ethanol content, were chosen for combustion
6 Modelling of Premixed Combustion

Table 6.1: Fuels selected for combustion analysis

<table>
<thead>
<tr>
<th>No.</th>
<th>Fuel</th>
<th>RON</th>
<th>Lambda^a</th>
<th>Compression ratio^a</th>
<th>Fuel mass flow (g/cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PRF100</td>
<td>100^b</td>
<td>0.88</td>
<td>7.82</td>
<td>0.042</td>
</tr>
<tr>
<td>2</td>
<td>PRF100-E10</td>
<td>106.8</td>
<td>0.93</td>
<td>9.43</td>
<td>0.041</td>
</tr>
<tr>
<td>3</td>
<td>PRF100-E20</td>
<td>109.4</td>
<td>1</td>
<td>9.89</td>
<td>0.040</td>
</tr>
<tr>
<td>4</td>
<td>PRF91</td>
<td>91^b</td>
<td>0.88</td>
<td>6.72</td>
<td>0.044</td>
</tr>
<tr>
<td>5</td>
<td>PRF91-E10</td>
<td>98.7</td>
<td>0.92</td>
<td>7.58</td>
<td>0.043</td>
</tr>
<tr>
<td>6</td>
<td>PRF91-E20</td>
<td>103.8</td>
<td>0.97</td>
<td>8.77</td>
<td>0.040</td>
</tr>
<tr>
<td>7</td>
<td>TRF91-30</td>
<td>91.3</td>
<td>0.91</td>
<td>6.74</td>
<td>0.044</td>
</tr>
<tr>
<td>8</td>
<td>TRF91-30-E10</td>
<td>97.0</td>
<td>0.93</td>
<td>7.31</td>
<td>0.043</td>
</tr>
<tr>
<td>9</td>
<td>TRF91-30-E20</td>
<td>101.4</td>
<td>0.97</td>
<td>8.17</td>
<td>0.042</td>
</tr>
<tr>
<td>10</td>
<td>Toluene</td>
<td>120.0</td>
<td>1</td>
<td>12.25</td>
<td>0.042</td>
</tr>
<tr>
<td>11</td>
<td>Toluene-E10</td>
<td>112.8</td>
<td>1</td>
<td>10.49</td>
<td>0.042</td>
</tr>
<tr>
<td>12</td>
<td>Toluene-E20</td>
<td>110.9</td>
<td>1</td>
<td>10.15</td>
<td>0.044</td>
</tr>
<tr>
<td>13</td>
<td>Ethanol</td>
<td>108.0-108.5</td>
<td>0.97</td>
<td>9.64</td>
<td>0.063</td>
</tr>
</tbody>
</table>

^a The compression ratio and lambda were obtained at standard knock intensity.
^b The RON of a PRF are by definition [63, 64].
^c The RON of neat toluene was obtained from [174].

The composition of each multi-component gasoline surrogate, e.g. PRF91 and TRF91-30, can be found in Table 4.4.

Raw pressure traces were obtained for each fuel at standard knock intensity under RON conditions. Figure 6.1 shows some of the resulting pressure-volume diagrams of these different fuel blends. Since the use of a piezoelectric in-cylinder pressure transducer precludes simultaneous knock reading by a detonation meter, standard knock intensity was assumed by setting the critical cylinder height and lambda for a given fuel to the critical values measured previously (Table A4.3 in [63]).

6.1.1 Adding TEL to fuels

It is important to know the turbulent flame propagation at standard knock intensity in order to quantify its effects on the end gas. However, pressure traces obtained at standard knock intensity are accompanied by autoignition and significant pressure fluctuations, which complicate post-processing and analysis of flame propagation. Further, the mass fraction burned derived from a knocking pressure trace is a function of both the heat release from the flame propagation and reactivity in the end gas. Therefore, it is clearly desirable to obtain non-knocking pressure data that represents flame propagation prior to and during autoignition or knock.

Such non-knocking pressure data can, for example, be obtained by lowering the compression ratio and/or retarding the spark timing, albeit with some drawbacks. In these cases, the engine geometry as well as the temperature and pressure development inside the cylinder could be significantly different from those of the knocking cases, resulting in potentially different turbulence and thus flame propagation.
6.1 Fuel selection

Figure 6.1: Pressure-volume diagrams of different fuel blends at standard knock intensity under RON conditions.
Table 6.2: The concentration of the dilute TEL used to suppress autoignition of different fuel blends at the ‘standard knock intensity’ conditions, as defined in the RON test method [63]. Note that the concentrations of the dilute TEL listed below are not the minimum amount required to suppress autoignition.

<table>
<thead>
<tr>
<th>No.</th>
<th>Fuel</th>
<th>Dilute TEL (% vol.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PRF100</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>PRF100-E10</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>PRF100-E20</td>
<td>1.5</td>
</tr>
<tr>
<td>4</td>
<td>PRF91</td>
<td>0.8</td>
</tr>
<tr>
<td>5</td>
<td>PRF91-E10</td>
<td>1.3</td>
</tr>
<tr>
<td>6</td>
<td>PRF91-E20</td>
<td>1.5</td>
</tr>
<tr>
<td>7</td>
<td>TRF91-30</td>
<td>0.9</td>
</tr>
<tr>
<td>8</td>
<td>TRF91-30-E10</td>
<td>1.1</td>
</tr>
<tr>
<td>9</td>
<td>TRF91-30-E20</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>Toluene</td>
<td>&gt;&gt; 3.0&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>11</td>
<td>Toluene-E10</td>
<td>&gt;&gt; 3.0&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>12</td>
<td>Toluene-E20</td>
<td>&gt;&gt; 3.0&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>13</td>
<td>Ethanol</td>
<td>N/A&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>More than 3% (v/v) dilute TEL was required to suppress autoignition.

<sup>b</sup>The presence of 3% (v/v) dilute TEL appeared to have no noticeable effect on autoignition.

One way to circumvent this issue is to add a small amount of tetraethyl lead (TEL) to the fuel in order to suppress autoignition, without having to change the standard operating conditions, in particular the compression ratio and/or the spark timing. Table 6.2 lists the concentration of the dilute TEL that was added to different fuel blends such that autoignition no longer occurred. Of note is that the dilute TEL contains only approximately 18% of TEL by mass (see Table 3.1 for the detailed composition of the dilute TEL). While TEL is very effective in suppressing autoignition of PRFs and TRFs at standard knock intensity, the TEL response of neat toluene is rather weak, and that of neat ethanol is negligible. Even with 3% (v/v) dilute TEL present in the fuel, the knock intensity was only mildly reduced in the case of toluene and toluene/ethanol blends, and appeared unchanged in the case of neat ethanol. Also, the amount of the dilute TEL required to suppress autoignition increased with increasing ethanol content in all other fuel blends.

This observation is consistent with what has been reported in the literature. A comprehensive study by the ASTM showed that the effect of TEL on aromatics was considerably less pronounced than that on paraffins [174]. In the case of ethanol, a study [193] reported that the MON of neat ethanol decreased from approximately 90 to 85 when 1 ml of TEL was added to a U.S. gallon of ethanol, and the MON remained at 85 even when the amount of TEL was increased to 3 ml. Later, Salooja [194, 195] showed that lead monoxides, which TEL decomposes to, actually promoted the
oxidation of methanol, or in general, any hydrocarbon with one or more hydroxyl groups. Thus, since it was found that TEL had little effect on fuels containing a large fraction of ethanol or toluene, only nine were selected out of the thirteen fuels for further combustion analysis using GT-Power.

6.1.2 Effects of TEL on non-knocking combustion

By using TEL to acquire non-knocking pressure traces suitable for combustion analysis, it is assumed that TEL has negligible effect on the pressure and temperature development, and thus flame propagation, prior to autoignition. A test was devised to justify this assumption. Additional pressure traces were acquired for isooctane with and without TEL added but at a much retarded spark timing. A spark timing at TDC, as opposed to 13 CAD before TDC in the standard RON tests, was chosen to ensure that autoignition did not occur even when no TEL was added, while all other operating parameters were set to those at standard knock intensity. For each case, one representative raw pressure trace which minimises the cost function was selected out of 300 cycles. This cost function is given by

\[
\text{Cost} = \left( \frac{\text{IMEP}_i - \text{IMEP}_{avg}}{\text{IMEP}_{avg}} \right)^2 + \left( \frac{\text{PP}_i - \text{PP}_{avg}}{\text{PP}_{avg}} \right)^2 , \tag{6.1}
\]

where IMEP is the indicated mean effective pressure, PP is the peak in-cylinder pressure, and the subscripts \(i\) and \(avg\) denote the \(i^{th}\) cycle and the average quantity (evaluated from all cycles) respectively.

Figure 6.2 shows the effects of TEL on representative in-cylinder pressure and mass fraction burned traces. Only minor deviation can be observed between the traces, suggesting that TEL indeed has little impact on the flame propagation. This is in part due to the very low concentration of the TEL (~0.7% vol.) added to isooctane. A similar observation was reported by Curry [196], who remarked that TEL “does not appear to affect flame propagation rates under non-knocking engine condition.”

6.1.3 Representative cycles with autoignition

In-cylinder pressure traces are typically measured for a number of engine cycles during experiments, and it is often desirable to select one representative cycle for post-processing. For non-knocking combustion, criteria that have been widely used for this purpose are the IMEP, the peak pressure and the location of the peak pressure [197], as has been shown previously using Eq. 6.1.

However, when autoignition occurs, the aforementioned criteria are no longer justified due to significant variance in the peak pressure as well as its location, and more difficult estimate of the IMEP using common methods. As a result, a new set of criteria were established to select the representative knocking cycle out of 900 cycles. Any cycle which minimises the cost function is deemed the representative cycle, with the cost function now defined as
6 Modelling of Premixed Combustion

Figure 6.2: Effects of TEL on a) the in-cylinder pressure and b) the mass fraction burned for isoctane at retarded spark (0 instead of 13 CAD before TDC under RON conditions).

\[
\text{Cost} = \left[ (\text{MFB50}_i - \text{MFB50}_{avg})^2 + (\text{KP}_i - \text{KP}_{avg})^2 \right],
\]

(6.2)

where MFB50 is the crank angle at which 50% mass fraction burned is reached, and KP is the ‘knock point’. Again, the subscripts \(i\) and \(avg\) denote the \(i^{th}\) cycle and the average quantity (evaluated from all cycles) respectively. The mass fraction burned was evaluated using the method developed by Rassweiler and Withrow [198]. In these calculations, the polytropic index of the compression stroke was used up to the firing TDC, beyond which the polytropic index of the expansion stroke was used instead. It is noted that while such a method is less accurate than using GT-Power (discussed in Section 6.3.1), it can be used on raw data with pressure oscillations and is sufficiently accurate for this purpose.

The ‘knock point’ is the crank angle at which there is a distinctive change in the slope of the in-cylinder pressure development under knocking conditions in a CFR engine [199] (Figure 6.3). This is the crank angle at which the pressure rise due to autoignition dominates that due to flame propagation, although significant end-gas reactions may have already occurred prior to this point, as will be discussed in Chapter 7. To estimate the knock point, the second derivative of the in-cylinder pressure with respect to CAD was evaluated. The knock point was then assumed to occur at the instant where the absolute value of the second derivative is greater than a threshold (2000 kPa/deg²). Figure 6.3 shows selected in-cylinder pressure traces with the corresponding MFB50 and knock points labelled. Considerable cycle-to-cycle variations can be observed, although a large number of the knock points fall in a narrow range of CAD, with a standard deviation of 0.98 CAD.

Once the representative knocking cycle for each fuel blend was identified, the corresponding non-knocking cycle was selected out of 900 cycles. This was done by matching the pressure development of the representative knocking trace prior to the knock point.
6.2 GT-Power simulations

The representative non-knocking pressure data were imported into GT-Power (version 7.3) for combustion analysis. A so-called ‘reverse-run’ simulation was first performed. The reverse-run model works by iterating within each time step the amount of fuel that...
6 Modelling of Premixed Combustion

Figure 6.4: Representative knocking pressure trace (at standard knock intensity under RON conditions), and the associated non-knocking trace (with added TEL) for selected fuel blends.
Figure 6.5: The representative in-cylinder pressure trace measured for isoctane at standard knock intensity under RON conditions, with the calculated a) mean and b) median traces.

Figure 6.6: The knock point of the representative trace versus that of the calculated median trace for different fuel blends at standard knock intensity under RON conditions.
is transferred from the unburned to the burned zone until the estimated in-cylinder pressure matches the measured data. A quasi-dimensional two-zone combustion submodel and full chemical equilibrium for 11 species (N$_2$, O$_2$, H$_2$O, CO$_2$, CO, H$_2$, N, O, H, NO, OH) are assumed [192]. The reverse-run simulation requires several parameters to be estimated,

1. the residual gas fraction,

2. the multiplier factor, $C_0$, of the heat transfer coefficient, $h$, and

3. the combustion chamber wall temperatures (bore, head and piston).

These will be discussed in detail in the following sections.

### 6.2.1 Estimating the residual gas fraction

A full-flow GT-Power model (Figure 6.7) of the standard CFR engine was built. The intake and exhaust systems representative of the actual engine were modelled, and particular attention was paid to modelling the venturi and the fuel delivery system. The charge coefficients of the intake (shrouded) and exhaust valves were obtained from [200], as listed in Tables A.4 and A.5.

The calculated residual gas fraction (Table 6.3) ranges from 5% to 7% when the engine is fuelled with different fuel blends at standard knock intensity under RON conditions. Since the engine speed, throttle and camshaft timings are constant, the residual gas fraction appears primarily a function of the compression ratio (see Tables 6.1 and 6.3), and is only weakly dependent on lambda and the fuel type. This is consistent with what has been reported in the literature [47].
Table 6.3: The residual gas fraction modelled by GT-Power for different fuel blends at standard knock intensity under RON conditions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Fuel</th>
<th>Residual gas fraction (% mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PRF100</td>
<td>6.3</td>
</tr>
<tr>
<td>2</td>
<td>PRF100-E10</td>
<td>5.3</td>
</tr>
<tr>
<td>3</td>
<td>PRF100-E20</td>
<td>5.1</td>
</tr>
<tr>
<td>4</td>
<td>PRF91</td>
<td>7.3</td>
</tr>
<tr>
<td>5</td>
<td>PRF91-E10</td>
<td>6.3</td>
</tr>
<tr>
<td>6</td>
<td>PRF91-E20</td>
<td>5.6</td>
</tr>
<tr>
<td>7</td>
<td>TRF91-30</td>
<td>7.3</td>
</tr>
<tr>
<td>8</td>
<td>TRF91-30-E10</td>
<td>6.7</td>
</tr>
<tr>
<td>9</td>
<td>TRF91-30-E20</td>
<td>6.1</td>
</tr>
</tbody>
</table>

6.2.2 Calibrating the heat transfer and wall temperatures

Once the residual gas fraction is known from the full-flow model, the heat transfer needs to be calibrated in order to yield close agreement between the simulated and the measured data. The heat transfer model in GT-Power is based on Woschni’s correlation [192]. The only difference is in the treatment of the heat transfer coefficient during valve opening, where the heat transfer is enhanced by the inflow through the intake valve(s) as well as the backflow through the exhaust valve(s) [192]. At all other times, the heat transfer coefficient \((W/m^2 \cdot K)\) is given by

\[
h = 3.26B^{-0.2}p^{0.8}T^{-0.55}w^{0.8},
\]

where \(B\) is the bore (m), \(p\) the in-cylinder pressure (kPa), \(T\) the charge temperature (K) and \(w\) the average cylinder gas velocity (m/s), which is given by

\[
w = \left[ C_1 \bar{S}_p + C_2 \frac{V_d T_{IVC}}{p_{IVC} V_{IVC}} (p - p_m) \right],
\]

where \(\bar{S}_p\) is the mean piston speed, \(V_d\) is the displaced volume, \(p_{IVC}, T_{IVC}, V_{IVC}\) are the in-cylinder pressure, temperature and volume at IVC respectively and \(p_m\) is the motored in-cylinder pressure at the same crank angle as \(p\). During compression, \(C_1\) and \(C_2\) are 2.28 and 0 respectively. During combustion and expansion, their values are 2.28 and 0.00324 respectively.

The resulting heat flux is then expressed as

\[
\dot{q} = C_0 h (T - T_w),
\]

where \(T_w\) is the wall temperature (either the bore, head or piston temperature) and \(C_0\) is a calibration constant (also called ‘heat transfer multiplier factor’) used to calibrate the heat transfer such that that the predicted in-cylinder pressure agrees more closely
Table 6.4: Heat transfer multiplier factors for different fuels assuming a bore temperature of 127 °C, and a head/piston temperature of 165 °C.

<table>
<thead>
<tr>
<th>No.</th>
<th>Fuel</th>
<th>Multiplier factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PRF100</td>
<td>0.9</td>
</tr>
<tr>
<td>2</td>
<td>PRF100-E10</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>PRF100-E20</td>
<td>0.8</td>
</tr>
<tr>
<td>4</td>
<td>PRF91</td>
<td>1.0</td>
</tr>
<tr>
<td>5</td>
<td>PRF91-E10</td>
<td>0.9</td>
</tr>
<tr>
<td>6</td>
<td>PRF91-E20</td>
<td>0.9</td>
</tr>
<tr>
<td>7</td>
<td>TRF91-30</td>
<td>1.0</td>
</tr>
<tr>
<td>8</td>
<td>TRF91-30-E10</td>
<td>0.9</td>
</tr>
<tr>
<td>9</td>
<td>TRF91-30-E20</td>
<td>0.9</td>
</tr>
</tbody>
</table>

with the experimental data.

The bore temperature was assumed to be 127 °C (or 400 K), which is similar to that used in a recent study [101] to model the combustion of isoctane in the CFR engine under RON conditions. The head and piston temperatures were both assumed to be 165 °C. Measurements of these temperatures in a CFR engine have been performed previously [201, 202], although surprisingly not at the standard RON and MON conditions. Wittmann and Smith [202] conducted a careful measurement of the piston temperature in a CFR engine running at different operating conditions. They reported a piston temperature of approximately 165 °C with the water jacket temperature set to 99 °C, the fuel-air ratio to 0.08, and the engine speed to 800 rpm. These operating conditions closely resembled those in a standard RON test. Hence, their measured value is believed to be reasonable. As a result, calibrating the heat transfer then required only $C_0$ to be varied.

Figure 6.8 shows the normalised root mean squared error (RMSE) of the simulated in-cylinder pressure relative to measurement resulting from different values of $C_0$. The RSME is normalised by the IMEP, and is given by

$$\text{Normalised RMSE} = \frac{\sqrt{\sum (p_{\text{meas}} - p_{\text{sim}})^2 / n}}{\text{IMEP}}$$

where $p_{\text{meas}}$ is the measured in-cylinder pressure, $p_{\text{sim}}$ is the simulated in-cylinder pressure and $n$ is the number of crank angles (i.e. from -120 to 80 CAD after TDC). In all cases, there is a narrow range of $C_0$, typically between 0.8 and 1, where the smallest SSE is obtained. Table 6.4 lists the selected values for the heat transfer multiplier factors. These values result in good agreement between the measured and the simulated in-cylinder pressure traces (Figure 6.9), and so will be further used in the modelling of the end-gas autoignition in Chapter 7.
6.2 GT-Power simulations

Figure 6.8: The normalised root mean squared error (RMSE) of the measured and the simulated in-cylinder pressure evaluated from -120 to 80 CAD after TDC. The bore and piston/head temperatures were fixed to 127 °C and 165 °C respectively. The multiplier factor, $C_0$, to Woschni’s heat transfer coefficient was varied from 0.5 to 1.5.
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Figure 6.9: Measured and simulated in-cylinder pressure traces from -120 to 80 CAD after TDC for selected fuels. The simulated results were based on the calibrated heat transfer multiplier factors as listed in Table 6.4.
Table 6.5: The concentrations of the unburned HC and CO measured in the exhaust for different fuel blends under RON conditions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Fuel</th>
<th>Unburned HC (ppm mole)</th>
<th>CO (% mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PRF100</td>
<td>2500</td>
<td>4.0</td>
</tr>
<tr>
<td>2</td>
<td>PRF100-E10</td>
<td>2400</td>
<td>2.2</td>
</tr>
<tr>
<td>3</td>
<td>PRF100-E20</td>
<td>1800</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>PRF91</td>
<td>2000</td>
<td>4.0</td>
</tr>
<tr>
<td>5</td>
<td>PRF91-E10</td>
<td>2000</td>
<td>2.6</td>
</tr>
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<td>6</td>
<td>PRF91-E20</td>
<td>1950</td>
<td>0.9</td>
</tr>
<tr>
<td>7</td>
<td>TRF91-30</td>
<td>2000</td>
<td>3.2</td>
</tr>
<tr>
<td>8</td>
<td>TRF91-30-E10</td>
<td>2000</td>
<td>2.5</td>
</tr>
<tr>
<td>9</td>
<td>TRF91-30-E20</td>
<td>1950</td>
<td>0.9</td>
</tr>
</tbody>
</table>

6.3 Modelling results and discussion

6.3.1 Mass fraction burned

Figure 6.10 shows the estimated mass fraction burned profile for each fuel using GT-Power. This mass fraction burned is defined as the fraction of the fuel mass that has been consumed by the flame,

\[
MFB = 1 - \frac{m_{f,i}}{m_{f,0}},
\]

(6.7)

where \(m_f\) is the fuel mass and the subscripts \(i\) and \(0\) represent the \(i^{th}\) and the initial time step respectively. As previously discussed, the mass fraction burned is approximated from the measured non-knocking pressure data in the reverse-run model. The residual gas fraction was first estimated using a full-flow GT-Power model, and the heat transfer was calibrated such that the simulated pressure trace matches the measured trace.

As shown in Figure 6.10, the fuel is not fully consumed at the end of combustion in all cases, i.e. the burned mass fraction never reaches one. For all the fuels studied, the final burned mass fraction ranges from approximately 97% to 99%. This is primarily due to the unburned HC, which escape the main combustion event and remain in the crevices until further oxidation during expansion and exhaust. Table 6.5 shows the concentrations of the unburned HC and CO in the exhaust measured for different fuels. While the CO emission clearly decreases with increasing lambda and/or ethanol content, the measured concentration of the unburned HC decreases only slightly, and in some cases remains similar as lambda and ethanol content are increased. Whether this is a fuel or lambda effect is unclear and outside the scope of this investigation.

It is also interesting to note that under RON conditions combustion starts off slowly, but proceeds rapidly after around 20% of the fuel mass has been burned. Closer scrutiny of the mass fraction burned profile reveals that it can take more than 30% of the total combustion duration to only burn the first 10% of the fuel, regardless of the fuel type. This suggests slow flame propagation early into combustion. The mass burning rate
Figure 6.10: Mass fraction burned versus CAD of different fuels (with TEL added) under RON conditions estimated using GT-Power’s reverse-run and predictive models respectively.
also slows significantly towards the end of combustion in all cases. It appears that such mass burning profiles are characteristic of the CFR engine under RON conditions, and are little influenced by the fuel type.

### 6.3.2 Unburned gas temperature

Of particular interest is the unburned gas temperature since this temperature has a major impact on autoignition onset of a given fuel. Figure 6.11 shows the unburned temperature modelled by GT-Power for different fuels, in which autoignition has been suppressed through the addition of TEL. Similar to the mass fraction burned profile, the unburned temperature rises slowly following spark ignition. In all cases, the temperature rise is less than 50 K in the first 10 CAD after spark ignition. On the other hand, a rapid rise in the unburned temperature can be observed after TDC, in conjunction with the high mass burning rate at this point (see Figure 6.10). The unburned gas temperature of these non-autoigniting cases peaks at around 12 CAD after TDC, beyond which it drops quickly as the piston moves downwards.

In the case of neat isooctane, the unburned temperature peaks at approximately 920 K. This value matches the estimated peak unburned temperature for isooctane under RON conditions in the study by Leppard [73]. The peak unburned temperature increases with increasing ethanol content, which is a result of the increased compression ratio as the RON of the fuel becomes higher. Indeed, the highest peak unburned temperature is found in the case of isooctane-E20, which also has the highest RON of all fuels studied.

The knock point estimated from the equivalent, representative knocking pressure trace for each fuel is also shown in Figure 6.11. It is interesting that the peak unburned temperature is found at or very near the knock point in most cases. This is not a surprising result, as autoignition should occur near the highest temperature in the end gas under RON conditions. Indeed, these results are likely linked to how the RON test is conducted for a given fuel. At the sub-critical compression ratio, autoignition of course does not occur. Increasing the compression ratio to criticality raises the unburned temperature, resulting in greater end-gas reactivity. At the critical compression ratio, the unburned temperature should approach this peak with just enough reactive radicals in the end gas, and so leading to autoignition. Nonetheless, as discussed in Chapter 7, heat release due to chemical reactivity in the end gas can raise the unburned temperature by more than 100 K near autoignition onset, and so this argument is only approximate.

### 6.3.3 Flame speeds

Although autoignition is primarily a consequence of end-gas chemistry, it is also influenced by the speed at which the flame propagates [54]. This is because the pressure and the temperature in the end gas depend not only on the piston motion but also on the flame speed, which determines the rate at which the end gas is compressed due to
Figure 6.11: Modelled unburned temperatures versus CAD of different fuels (with TEL added) under RON conditions.
6.3 Modelling results and discussion

Expansion of the burned gas. Studies showed that generally autoignition is more likely to occur as the flame speed is further increased relative to the piston speed [54].

Hence, the so-called ‘predictive’ simulation in GT-Power was used to estimate the laminar and the turbulent flame speeds. This simulation is based on the study by Blizard and Keck [203], in which the mass entrainment rate is modelled as

\[
\frac{dm_e}{dt} = \rho_u A_f S_T, \tag{6.8}
\]

where \( \rho_u \) is the density of the unburned gas, \( A_f \) is the entrainment area at the edge of the flame front and \( S_T \) is the turbulent flame speed. The mass burning rate is then given by

\[
\frac{dm_b}{dt} = \frac{m_e - m_b}{\tau}, \tag{6.9}
\]

where \( \tau \) is a time constant,

\[
\tau = \frac{\lambda}{S_L}, \tag{6.10}
\]

in which \( \lambda \) is the Taylor microscale length and \( S_L \) is the laminar flame speed.

To match the mass burning profile as generated by the reverse-run model, the flame propagation model has to be adjusted. This is done by calibrating three multipliers which independently affect the flame kernel development time, the effects of turbulence intensity on the turbulent flame speed, and the Taylor microscale length [192]. Figure 6.10 shows good agreement between the mass fraction burned estimated by the predictive model and that by the reverse-run model in all cases.

Figure 6.12 shows the laminar flame speed estimated using GT-Power for different fuels (with TEL added) under RON conditions. The addition of ethanol content appears to increase the laminar flame speed. This is consistent with the literature, which reports that ethanol has a higher laminar flame speed relative to isooctane, \( n \)-heptane and toluene [204, 205]. In all cases, the laminar flame speed peaks at around 12 CAD after TDC and drops rapidly after that, consistent with the trend observed in the unburned temperature (see Figure 6.11).

The turbulent flame speed is shown in Figure 6.13. Following spark ignition, the flame speed rises rapidly. The maximum flame speed is attained at around TDC, and this coincides with the rapid mass burning rate as seen in Figure 6.10 at this point. The turbulent flame speed remains relatively constant after this before diminishing slightly at the end of combustion. Similar to the laminar flame speeds, the turbulent flame speed increases with increasing ethanol content.

Nonetheless, caution should be exercised when interpreting these results, which were extrapolated from the flame model of the neat fuels in GT-Power. Indeed, the laminar and the turbulent flame speeds of these different ethanol/gasoline-surrogate blends under engine conditions remain unclear and are not validated experimentally to date.
Figure 6.12: Modelled laminar flame speeds versus CAD of different fuel blends (with TEL added) under RON conditions.
6.3 Modelling results and discussion

![Graphs showing turbulent flame speeds versus CAD for different fuel blends](image)

(a) Ethanol/isoctane blends  
(b) Ethanol/PRF91 blends  
(c) Ethanol/TRF91-30 blends

Figure 6.13: Modelled turbulent flame speeds versus CAD of different fuel blends (with TEL added) under RON conditions.
6 Modelling of Premixed Combustion

6.4 Summary

This chapter presented an analysis of combustion occurring under RON conditions on several blends of ethanol with isooctane, PRF91 and TRF91-30, as well as their base fuels. A method to acquire the non-knocking pressure traces by adding the dilute TEL to these fuel blends was introduced, and was shown to have negligible effect on flame propagation under non-knocking conditions. This ensured that the flame propagation would be similar to those in knocking conditions prior to autoignition, since the operating conditions such as compression ratio, spark timing and air-fuel ratio were the same.

In order to further understand the combustion characteristics of each fuel, representative non-autoigniting pressure traces were then passed into GT-Power for further analysis. The residual gas fraction was estimated using a full-flow model, and was found to be primarily dependent on the compression ratio and relatively low under RON conditions. The heat transfer model was also calibrated against in-cylinder pressure measurement. Overall, the modelled pressure trace agreed well with measurement. Results showed a relatively slow mass burning rate in the beginning of combustion that was typical of the CFR engine under RON conditions, regardless of the fuel type. This was supported by analysis of the calculated laminar and turbulent flame speeds.

Importantly, the modelled peak unburned temperature was close to the measured knock point for most fuels, suggesting that autoignition occurred where the temperature in the end gas was highest. This was a reasonable result given the nature of the RON test, but should be interpreted with caution due to the absence of end-gas kinetics and the associated temperature rise. As a result, the key results from this chapter - the residual gas fraction, the heat transfer calibration constant \( C_0 \) and the crank-angle-resolved mass fraction burned - can be used with some confidence in modelling the end-gas autoignition, as will be presented in Chapter 7.
7 Modelling of Autoignition

This chapter presents the development and use of a quasi-dimensional engine model with full chemical kinetics to simulate end-gas autoignition under RON conditions for several blends of ethanol with isooctane, PRF91, and TRF91-30. An overview of the model is first presented. A parametric study on autoignition onset then shows that NO in the residual gas can significantly enhance end-gas kinetics. In addition, end-gas chemistry is sensitive to heat transfer and the mixture temperature at IVC. Different kinetic mechanisms developed for ethanol/gasoline-surrogate blends are evaluated next, and one mechanism is chosen for further use. Finally, the modelling results are analysed in relation to the pressure and temperature development, along with fuel decomposition, in the end gas. Comparisons with experimental results are made, followed by a discussion of the model uncertainty and implications.

7.1 Quasi-dimensional SI engine model with full chemical kinetics

7.1.1 Model overview and assumptions

A quasi-dimensional engine model is developed to simulate combustion and autoignition in the CFR engine under RON conditions. The goal is to estimate the temporal evolution of the end gas using chemical kinetics, and hence to generate a better understanding of the underlying processes leading up to and including autoignition. Of interest are the temperature, pressure and species concentrations in the end gas. Due to compression by both the moving piston and the propagating flame front, autoignition could occur spontaneously in the end gas under certain conditions (commonly associated with high pressure and temperature) prior to the arrival of the flame. The assumption of frozen chemistry or chemical equilibrium is, therefore, no longer valid, and chemical kinetics has to be simulated. Although numerous quasi-dimensional approaches have been reported in the literature previously, these models appear lacking in some aspects, as discussed in Section 2.3.2. For example, many studies exclude modelling of the residual gas, although it has been shown to have a significant effect on the burning rate and autoignition [142, 147].

Appendix D presents the derivation of the present model. While this model is based on the work in [49, 98, 100], further refinements have been included. Unlike previous models, chemical kinetics can be modelled throughout the simulation, i.e. during compression, combustion and expansion. Further, a blowby model is included to sim-
ulate mass loss through the crevices. Since it has been discussed in Chapter 2 that autoignition onset is sensitive to certain species even at very low concentrations, the composition of the residual gas is also modelled.

In this modelling, the mass burning rate is prescribed during combustion, while the heat transfer coefficient and cylinder temperatures are also imposed. These parameters were estimated using GT-Power in Chapter 6 using the representative non-autoigniting pressure traces acquired under RON conditions. As such, whether autoignition occurs is solely dictated by the chemical kinetics simulated in the end gas. Where autoignition does not occur, the simulated in-cylinder pressure should follow the measured pressure trace closely.

Figure 7.1 illustrates the solution flowchart of this engine model. The simulation is divided into compression, combustion, and expansion. The composition, temperature and pressure of the gas at intake valve closure (IVC) are first estimated, and then compression commences. Following the start of combustion at spark ignition, the mass burning rate from GT-Power is prescribed. Combustion ends as soon as either of the following conditions is fulfilled,

1. the end of combustion is reached, as determined from the pressure traces in the absence of autoignition (Section 6.3.1),

2. the fuel in the end gas (unburned zone) is fully consumed by autoignition.

When combustion is not occurring, the entire charge is assumed to be spatially homogeneous in a single zone, and can therefore be modelled using the same set of governing equations. Combustion starts at spark ignition, separating the burned gas and the unburned gas into two zones. Several assumptions are made with regards to the combustion model,

- the air-fuel mixture is spatially homogeneous in temperature and in composition within both the unburned and the burned zones,

- chemical kinetics is modelled in both zones during combustion,

- the mass burning rate is prescribed using the two-zone modelling of the experimental pressure traces obtained under RON conditions but without autoignition, as detailed in the last chapter,

- the flame front has negligible volume,

- mass and energy is transported from the unburned zone to the flame front, and instantaneously from the flame front to the burned zone,

- the flame front is at chemical equilibrium,

- there is no heat transfer between the two zones.
7.1 Quasi-dimensional SI engine model with full chemical kinetics

Figure 7.1: Solution procedure flowchart for the quasi-dimensional model in this study. The associated inputs and outputs are also listed. The variables $p$, $T$, $Y$, $m$ and $V$ represent the pressure, temperature, species mass fraction, mass and volume respectively. The subscripts $u$ and $b$ denote the unburned and the burned zone respectively.
Figure 7.2: Comparison of the ignition delay times of different fuels calculated using Chemkin (version II) and Cantera (version 1.8) assuming a constant-volume reactor (initial pressure = 30 atm, stoichiometric and adiabatic). The mechanisms of ethanol, \( n \)-heptane and isooctane were from Marinov [123], Curran et al. [108] and Curran et al. [117] respectively.

Also, chemical kinetics is simulated during compression so that any fuel reactivity prior to ignition can be incorporated. Of note is that although the reactivity of modern gasoline may be negligible during compression in a standard RON/MON test, it still exhibits significant influence on subsequent fuel oxidation, and fuels with a low ON may decompose well before ignition.

With the use of Cantera (version 1.8), the fuel oxidation chemistry can be incorporated even with full kinetics [206]. Cantera was called and run in Matlab, which served as the front end for all simulations. To validate Cantera’s performance, the ignition delay times in a constant-volume reactor were simulated for ethanol, \( n \)-heptane and isooctane at different initial temperatures. It is clear from Figure 7.2 that the results obtained using Cantera and Chemkin agree very well. This suggests that Cantera is able to produce reliable results for kinetics simulations.

### 7.1.2 Initial conditions

The gas exchange processes during intake and exhaust are not accounted for. Compression starts at IVC, and expansion stops at the end of the expansion stroke at BDC. At IVC, the initial state of the charge is determined from the ideal gas law based on the following.

1. The measured in-cylinder pressure at IVC.
2. The cylinder volume at IVC.
3. The measured mass of the fuel and that of air calculated using the measured \( \lambda \) on the engine.
4. The estimated residual gas fraction from GT-Power (Table 6.3).

Of note is that the temperature at IVC calculated using this method is sensitive to the mass of the fuel and, to a lesser degree, the estimated residual gas fraction. Hence, some uncertainty is expected for the calculated temperature at IVC due to the uncertainty in the fuel flow measurement and the residual gas model. This will be discussed further in the following section.

7.1.3 Flame front chemical equilibrium

The combustion model requires calculation of the flame temperature, its enthalpy and species distribution, as shown in the governing equations (Appendix D). The assumption that the flame front is in chemical equilibrium throughout its propagation is justified in spark-ignition engine combustion [88, 207], regardless of whether chemical kinetics is modelled in the burned and the unburned zones.

In Cantera, chemical equilibrium in the flame front can be calculated by two different algorithms: the element potential method, which is similar to that used in STANJAN [208] and by minimising the Gibbs free energy of the system [206]. Although widely used in modelling combustion in the literature, these calculations can be computationally relatively intensive. Thus, chemical equilibrium in the flame was interpolated linearly from solutions that were tabulated prior to the start of the simulation. Interpolations were based on the pressure and the temperature of the unburned air-fuel mixture in a given time step. The composition of the unburned air-fuel mixture is assumed to be constant over time. The tabulated solutions were obtained from Cantera’s constant-pressure equilibrium solver by varying the pressure and the temperature. As a check, three tables with different resolutions were generated for the data range of $1 \text{ MPa} \leq p \leq 4.5 \text{ MPa}$ and $700 \text{ K} \leq T \leq 1200 \text{ K}$. The first table has a coarse resolution, where solutions were generated in grids of $\Delta T = 25 \text{ K}$ and $\Delta p = 0.5 \text{ MPa}$. The solutions in the second table are of a medium resolution ($\Delta T = 10 \text{ K}$ and $\Delta p = 0.25 \text{ MPa}$), while the third table has the finest resolution ($\Delta T = 2 \text{ K}$ and $\Delta p = 0.1 \text{ MPa}$).

Figure 7.3 shows the simulation results that were obtained using the full solution of flame equilibrium using the element potential method as well as the tabulated method, with all other model parameters being identical. Using the tabulated method, the temperature in the burned zone is approximately 20 K higher near autoignition than that calculated from the full solution. Most importantly, the calculated unburned temperature (Figure 7.3a) shows that the differences arising from different flame equilibrium solutions are small. To maintain both modelling accuracy and computational efficiency, therefore, the coarse tabulated data was chosen.

7.1.4 Blowby

Blowby is defined as the gas that flows from the combustion chamber past the piston rings and into the crankcase [47]. While approximately 5% to 10% of the total cylinder
Figure 7.3: Effects of different methods of solving chemical equilibrium in the flame front on a) unburned temperature, b) burned temperature and c) in-cylinder pressure.
7.1 Quasi-dimensional SI engine model with full chemical kinetics

![Graph showing cumulative blowby versus CAD for isoctane, as modelled by the two-zone adiabatic combustion model. Autoignition onset occurs at approximately 14 CAD.](image)

Figure 7.4: Cumulative blowby versus CAD for isoctane, as modelled by the two-zone adiabatic combustion model. Autoignition onset occurs at approximately 14 CAD.

Charge is trapped in the crevice region at peak pressure, most of the trapped mass returns to the cylinder during expansion (likely to be further oxidised) and about 1% escapes to the crankcase as blowby [47].

In this model, the time rate of change of the total blowby is a simple function of the instantaneous in-cylinder pressure \( p(t) \) as well as the trapped mass \( m(t) \),

\[
\frac{dm_l}{dt} = C_b m(t)p(t),
\]

(7.1)

where \( C_b \) is the blowby multiplier, which is merely a tuning parameter used to attain a required blowby rate (see Section 7.3.1). During combustion, the total blowby is given by,

\[
\frac{dm_l}{dt} = \frac{dm_{l,b}}{dt} + \frac{dm_{l,u}}{dt},
\]

(7.2)

in which \( m_{l,b} \) and \( m_{l,u} \) are the blowby masses in the burned zone and the unburned zone respectively.

As expected, the blowby rate in this model peaks at the peak pressure, and this is consistent with the literature [47]. Simulations based on this model show that only approximately 30% of the total blowby occurs prior to autoignition onset (Figure 7.4). Therefore, the effect of blowby on the end-gas kinetics and the unburned temperature is relatively small, as shown in Figure 7.5. The increase in blowby from 0% to 7% in mass (relative to the total trapped mass at IVC) only slightly delays autoignition onset, and reduces the unburned temperature at that point by only approximately 3 K.
7 Modelling of Autoignition

![Graph showing effects of blowby (% mass relative to the trapped mass at IVC) on autoignition onset (solid) and the unburned temperature (dashed) at autoignition for isooctane, as modelled by the two-zone adiabatic combustion model.]

Figure 7.5: Effects of blowby (% mass relative to the trapped mass at IVC) on autoignition onset (solid) and the unburned temperature (dashed) at autoignition for isooctane, as modelled by the two-zone adiabatic combustion model. The detailed PRF mechanism from Curran et al. [108, 117] was used.

7.1.5 Residual gas

As discussed in the literature review, certain species in the residual gas can have a significant impact on autoignition. Nitric oxide (NO), for example, was shown to advance autoignition onset in different studies at a very low concentration [142, 147]. On the other hand, the effects of other species in the residual gas, including partially oxidised hydrocarbons (HC), remain unclear. Therefore, these complex relationships between autoignition and the composition as well as the amount of the residual gas warranted a parametric study.

The following four different cases were investigated,

- Case 1: The residual gas consists of N₂, O₂, H₂, CO, CO₂ and H₂O only,
- Case 2: The residual gas consists of N₂, O₂, H₂, CO, CO₂, H₂O and unburned HC, where the unburned HC comprise only the neat fuel,
- Case 3: The residual gas consists of N₂, O₂, H₂, CO, CO₂, H₂O and unburned HC, where the unburned HC comprise both the neat fuel and partially oxidised HC in a 50:50 mass ratio, and
- Case 4: The residual gas consists of N₂, O₂, H₂, CO, CO₂, H₂O and unburned HC, where the unburned HC comprise only partially oxidised HC.

Except for the unburned HC, the concentrations of all residual gas species were determined from the combustion products at equilibrium based on the initial unburned air-fuel mixture composition at 298 K and 1 atm [47]. These calculated concentrations agreed to within approximately 15% with the measured data for O₂, CO, CO₂ and H₂O in the case of isooctane under RON conditions.
7.1 Quasi-dimensional SI engine model with full chemical kinetics

Figure 7.6: Effects of different unburned HC compositions on in-cylinder pressure of isooctane at standard knock intensity under RON conditions, as modelled by the two-zone combustion model. The unburned HC concentration was assumed to be 10 times that measured in the exhaust. The residual gas fraction is 6.3%. The PRF mechanism from [108, 117] was used.

The composition of the partially oxidised HC was estimated from simulating the oxidation of the fresh air-fuel mixture in a constant-volume chamber. The speciation profile at the instant where the fuel had already decomposed by 50% was extracted to represent partially oxidised HC. An initial temperature of 700 K was used in the simulation to approximate the charge temperature at the end of the exhaust stroke, at which most of the unburned HC in the residual gas are estimated to form [47]. It was further assumed that any radical, such as OH and H, is short-lived and should not survive in the residual gas, especially after mixing with the fresh air-fuel mixture.

Figure 7.6 shows the resulting pressure traces with residuals modelled as per cases 1 to 4 above, as well as a case without any residual. Even when the HC concentration is ten times the measured value, the resulting autoignition onset for different cases differs only by approximately 0.1 CAD. Thus, the presence of any HC appears to have a weak effect at engine representative conditions.

Effects of NO on autoignition

Nitric oxide (NO) was then added to the residual gas. To simplify the analysis, it was further assumed that the unburned HC contained only the neat fuel, and its fraction in the residual gas was as measured in the exhaust. The PRF kinetic mechanism from Curran et al. [108, 117] was used for the baseline case without NO, while those from Contino et al. [142] and Ranzi et al. [137] were used where NO was present.

Figure 7.7 shows that Curran et al.’s [108, 117] and Contino et al.’s [142] models agree closely in the absence of NO, and that autoignition onset is always advanced with the addition of NO content in the models of Contino et al. [142] and Ranzi et al. [137]. Of note is that the NO concentration in the trapped mass at IVC for isooctane under RON
Modelling of Autoignition

conditions was estimated to be 50 ppm based on exhaust measurement. This suggests that the presence of NO should significantly influence autoignition onset under RON conditions.

Nonetheless, as with the case of unburned HC, uncertainty remains regarding the accuracy of these different kinetic mechanisms. The mechanism from Contino et al. [142] models only interactions between NO and hydrocarbons up to ethane. While Ranzi’s mechanism includes reactions between NO and longer-chain hydrocarbons, these reactions are not fully validated especially under spark-ignition engine conditions. Thus, caution should be exercised when interpreting the results, although it is likely that the general trend with increasing NO content is correct. A very small concentration of NO (in the order of tens of ppm) appears sufficient to shift autoignition onset significantly. While the absolute magnitude of such effects can only be determined and validated through further study, and is highly dependent on the kinetic mechanism used, it should nonetheless remain as a feature of this model.

7.1.6 Heat transfer

The heat transfer coefficient \( (W/m^2K) \) is modelled using Woschni’s correlation [209], and is given by

\[
h = 3.26B^{-0.2}p^{0.8}T^{-0.55}w^{0.8},
\]

where \( B \) is the bore \((m)\), \( p \) the in-cylinder pressure \((kPa)\), \( T \) the temperature \((K)\) and \( w \) the average cylinder gas velocity \((m/s)\), which is given by

\[
w = \left[ C_1\bar{S}_p + C_2\frac{V_dT_{IVC}}{p_{IVC}V_{IVC}}(p - p_m) \right],
\]

where \( \bar{S}_p \) is the mean piston speed, \( V_d \) is the displaced volume, \( p_{IVC}, T_{IVC}, V_{IVC} \) are the in-cylinder pressure, temperature and volume at IVC respectively, \( p \) is the in-cylinder pressure and \( p_m \) is the motored in-cylinder pressure at the same crank angle as \( p \).

During compression, \( C_1 \) and \( C_2 \) are 2.28 and 0 respectively. During combustion and expansion, their values are 2.28 and 0.00324 respectively.

The resulting heat flux in the model is then expressed as

\[
\dot{q} = C_0h(T - T_w),
\]

where \( T_w \) is the wall temperature and \( C_0 \) is a calibration constant (also called ‘heat transfer multiplier factor’) used to calibrate the heat transfer, both of which were discussed and determined earlier in Chapter 6.

Figure 7.8 shows the effects of heat transfer on the in-cylinder pressure development, the end-gas temperatures and autoignition onset. As expected, increasing the heat transfer reduces the end-gas temperature significantly at spark ignition, and more so at MFB50. From the adiabatic case \( (C_0 = 0) \) to the case where heat transfer is doubled \( (C_0 = 2) \), the end-gas temperature at MFB50 decreases by more than 100 K. As a result,
7.1 Quasi-dimensional SI engine model with full chemical kinetics

Figure 7.7: Effects of increasing NO concentration on a) in-cylinder pressure and b) autoignition onset of isooctane at standard knock intensity under RON conditions, as modelled by the two-zone combustion model. The NO concentration in the trapped mass at IVC was varied from 0 to 400 ppm (mole fraction). The reference case without NO was based on the mechanism from [108, 117]. Mechanisms from Contino et al. [142] and Ranzi et al. (Version 1212) [137] were used where NO was present.
a significant delay to autoignition onset can be observed. This shows that autoignition is strongly dependent on heat transfer in the CFR engine under RON conditions.

### 7.1.7 Temperature at IVC

Lastly, the effect of the charge temperature at IVC was investigated. Figure 7.9 shows that a given change in the temperature at IVC leads to a slightly larger change in the end-gas temperature during combustion. More importantly, varying the temperature at IVC significantly affects autoignition onset. For example, autoignition onset can be advanced by 1 CAD when the temperature at IVC is increased by approximately 8 °C.

Further, it is difficult to accurately determine the temperature at IVC experimentally. This uncertainty in the temperature at IVC will be further discussed later.

### 7.2 Choosing the kinetic mechanism

As discussed in Section 2.4.2, several kinetic mechanisms for the purpose of simulating the oxidation or combustion of ethanol/gasoline-surrogate blends under engine conditions are available in the literature (see Table 2.3). Of these published mechanisms, only the detailed models were considered in this study,

1. ethanol/TRF/diisobutylene mechanism from Andrae [130],
2. ethanol/TRF/diisobutylene mechanism from Cancino et al. [136], and
3. ethanol/C1-C16-hydrocarbon mechanism (version 1212) from Ranzi et al. [137].

#### 7.2.1 Ignition delay in a constant-volume chamber

**Neat fuels**

The ignition delay times of isooctane, n-heptane, ethanol and toluene in a constant-volume chamber were simulated using these three mechanisms. The initial temperature was swept from 700 K to 1200 K, effectively covering the low-temperature (below 800 K) and the intermediate-temperature (850 K - 1200 K) regions in fuel oxidation. The initial pressure was set to 30 atm to represent typical engine conditions.

Figure 7.10a shows the ignition delay times predicted at different temperatures for isooctane using different mechanisms. An additional simulation was done using the mechanism from Curran et al. [108, 117] as comparison. This model has been extensively validated and is in wide use. Andrae’s mechanism [130] agrees very well with that of Curran et al. This is not surprising given Andrae’s isooctane submechanism is based on Curran et al.’s. A similar trend is found with Cancino et al.’s mechanism [136], although a difference can be seen as the temperature is increased above 1000 K. The ignition delay time calculated with Ranzi et al.’s mechanism [137] differs considerably from the others in most cases.
7.2 Choosing the kinetic mechanism

Figure 7.8: Effects of heat transfer on a) in-cylinder pressure, b) end-gas temperatures and c) autoignition onset of isooctane at standard knock intensity under RON conditions, as modelled by the two-zone combustion model. The heat transfer multiplier, $C_0$, was varied from 0 (i.e. adiabatic) to 2. The detailed PRF mechanism from Curran et al. [108, 117] was used. Note that autoignition did not occur when $C_0$ was set to 1.5 and 2.
Figure 7.9: Effects of different charge temperatures at IVC on a) end-gas temperatures at spark and at MFB50 (without NO) and b) autoignition onset for isoctane, as modelled by the two-zone combustion model. All other parameters were kept constant except for the in-cylinder pressure at IVC (changed to yield different IVC temperatures). The baseline temperature at IVC was approximately 425 K. The mechanism from Contino et al. [142] was used where NO was present. In all other cases the detailed PRF mechanism from Curran et al. [108, 117] was used.
7.2 Choosing the kinetic mechanism

Figure 7.10: Ignition delay times versus the inverse of the initial temperature for a) isooctane and b) n-heptane, as calculated using different mechanisms in a constant-volume reactor (initial pressure = 30 atm, stoichiometric and adiabatic). Mechanisms from Andrae [130], Cancino et al. [136], Ranzi et al. (Version 1212) [137] and Curran et al. (PRF mechanism) [108, 117] were used.

For n-heptane, Andrae’s and Cancino et al.’s mechanisms perform very similarly to that of Curran et al. in terms of ignition delay times at the low-temperature region (Figure 7.10b). Again, Ranzi et al.’s is the exception, where the ignition delay is consistently underpredicted.

Figure 7.11a shows the ignition delay times calculated using these same mechanisms for ethanol, as well as the detailed mechanism for neat ethanol only by Marinov [123], which is validated at temperatures greater than 1000 K only. Nonetheless, most ethanol submechanisms embedded in the mechanisms of gasoline surrogates have their origin in Marinov, as shown in Table 2.3. Results clearly indicate two different trends in the ignition delay of ethanol as calculated using different mechanisms. It is believed that such differences arise from the additional validation and fitting against low-intermediate-temperature shock tube data in Cancino et al.’s mechanism, as shown in Figure 7.12. However, a recent study [210] showed that any shock tube data of ethanol acquired at below 1000 K was prone to pre-ignition effects, which resulted in much shorter ignition delay. Therefore, further experimental study appears to be required to fully determine the oxidation characteristics of ethanol at low temperatures.

In the case of toluene, both Andrae’s and Cancino et al.’s mechanisms yield very similar ignition delay times at all temperatures (Figure 7.11b). In comparison, Ranzi et al.’s shows a significant difference in the ignition delay of toluene.

Binary fuel mixtures

In addition to the individual neat fuels, a check was also performed on the oxidation of different ethanol/isoctane binary mixtures using these mechanisms. As expected, the simulation results are consistent with what has been observed previously for the neat
Figure 7.11: Ignition delay times versus the inverse of the initial temperature for a) ethanol and b) toluene, as calculated using different mechanisms in a constant-volume reactor (initial pressure = 30 atm, stoichiometric and adiabatic). Mechanisms from Andrae [130], Cancino et al. [136], Ranzi et al. (Version 1212) [137] and Marinov [123] were used.

Figure 7.12: Measured and calculated low- and high-temperature ignition delay times for ethanol/air stoichiometric mixture from Cancino et al. [127]. The calculated values are represented by the solid lines using the mechanism from [127, 136].
7.2 Choosing the kinetic mechanism

fuels. For Andrae’s and Ranzi et al.’s mechanisms, isooctane oxidises much more easily compared with ethanol at low temperatures (Figure 7.13). When the temperature becomes sufficiently high, isooctane can take a longer time to fully oxidise relative to ethanol. In contrast, the ignition delay times of ethanol are consistently calculated to be shorter than those of isooctane according to Cancino et al.’s mechanism. Finally, Ranzi et al.’s suggests that the ethanol chemistry in ethanol/isooctane blends has a significantly larger effect on ignition delay than isooctane.

7.2.2 Autoignition onset in an engine

Having compared the ignition delay times in a constant-volume chamber using different mechanisms, further evaluation of these mechanisms was conducted using the quasi-dimensional engine model in this study. Simulations were run based on the operating conditions at standard knock intensity under RON conditions. In the case of isooctane, none of the mechanisms (without NO in the residual gas) predicts autoignition onset that is similar to measurement (Figure 7.14a). A closer look at the results indicates that Ranzi et al.’s mechanism [137] results in more end-gas reactivity after spark ignition than the other mechanisms. This is consistent with the calculated ignition delay times in Figure 7.10a, where earlier ignition of isooctane can be observed below 900 K when using Ranzi et al.’s mechanism.

Figure 7.14b shows the simulated in-cylinder pressure for isooctane-E10 using different mechanisms. All mechanisms predict earlier autoignition onset relative to the measured data. Cancino et al.’s mechanism [136] results in the most advanced autoignition onset, approximately 5 CAD earlier than that in the measured trace, which is consistent with Figure 7.13.

Based on these observations, Andrae’s mechanism [130] will therefore be used to model the combustion and autoignition of ethanol/gasoline-surrogate blends in the rest of this work.

7.2.3 NO submechanism

As discussed in Section 7.1.5, the presence of NO even at a very low concentration can have a significant impact on the autoignition of isooctane. Therefore, the NO submechanism from Contino et al. [142] was incorporated into Andrae’s mechanism [130] in an attempt to capture the NO sensitisation on the oxidation of these ethanol/gasoline-surrogate blends. In doing so, it is assumed that this NO submechanism, while developed only for isooctane, should yield similar trends for other blends. A more detailed kinetic model capable of describing the interactions between NO and other hydrocarbons and ethanol is of course a better alternative, but developing a new NO submechanism is beyond the scope of this work. The final kinetic mechanism, as a result of combining Andrae’s mechanism and the NO submechanism from Contino et al. [142], consists of 1150 species and 8525 reactions.
Figure 7.13: Ignition delay times versus the inverse of the initial temperature for binary ethanol/isooctane blends, as calculated using different mechanisms in a constant-volume reactor (initial pressure = 30 atm, stoichiometric and adiabatic).
7.3 Modelling results for SI combustion

7.3.1 Determination of model parameters and initial conditions

Earlier results have shown that several model parameters can have a major impact on autoignition under RON conditions, namely the heat transfer, NO content in the residual gas and the temperature at IVC. Thus, attention was given to determining these model parameters or initial conditions in an attempt to match experimental data as closely as possible. Where a parameter is impossible to be precisely determined, its uncertainty will be considered and discussed.

**Blowby**

Autoignition onset was found to be relatively insensitive to blowby (up to 7% by mass), as established in the parametric study in Section 7.1.4. Therefore, in all cases the total blowby from IVC to the end of expansion was fixed at approximately 1% of the total trapped mass at IVC in accordance with what was reported in the literature [47].

**Residual gas fraction and composition**

Similarly, the residual gas fraction was determined using GT-Power’s simulation (see Table 6.3) based on the measured valve lift profile (Section A.2) and the measured discharge coefficients of the valves (Section A.3). In all cases, the composition of residual gas was assumed to be N₂, O₂, H₂, CO, CO₂, H₂O, NO and HC, where the concentrations of N₂, O₂, H₂, CO, CO₂ and H₂O were obtained from chemical equilibrium of these species assuming an initial temperature of 298 K, an initial pressure of 1 atm and the measured λ. The HC concentration for each fuel blend was obtained from the measured exhaust data, with the unburned HC consisting of only the neat fuel(s) without any partially oxidised HC species, which has been found to have little impact
on autoignition onset.

Recognising that autoignition can be very sensitive to the presence of NO and that there is uncertainty in the exhaust measurements, cases were run without any NO, the measured NO concentration and twice this value.

**Heat transfer**

As discussed in Section 6.2.2, the heat transfer multiplier constant was calibrated using GT-Power, with the results shown in Table 6.4.

**Temperature at IVC**

Since it is difficult to measure the temperature at IVC experimentally, it was determined using the ideal gas law,

\[
T_{IVC} = \frac{p_{IVC} V_{IVC}}{m_{total} R}, \tag{7.6}
\]

where \( p_{IVC} \) is the in-cylinder pressure at IVC, \( V_{IVC} \) the cylinder volume at IVC, and \( R \) the specific gas constant. The term \( m_{total} \) is the total mass trapped in the cylinder at IVC, which can be defined by,

\[
m_{total} = m_{fuel} + m_{air} + m_{residual}, \tag{7.7}
\]

where \( m_{fuel} \) is the measured fuel mass per cycle, \( m_{air} \) is the inferred air mass based on the measured \( \lambda \) and \( m_{residual} \) is the residual gas mass estimated from GT-Power.

However, it is noteworthy that the temperature at IVC estimated using this method is sensitive to the trapped mass at IVC. For example, a 5% error in the mass could lead to a change in the estimated temperature at IVC by approximately 20 K, which is significant given its influence on autoignition. In this study, the uncertainty in the measured fuel flow/mass, \( \lambda \) reading and the calculated residual gas fraction from GT-Power should contribute to some error in the estimated temperature at IVC.

Table 7.1 lists the estimated charge temperature at IVC for different fuels. In the case of isooctane, the estimated temperature at IVC is 420 K. However, this value appears higher than what was reported in the literature. Perumal and Floweday [101] estimated the temperature to be 400 K for isooctane under RON conditions, and their modelling results based on this temperature showed good agreement with the experiments. A more recent numerical study by Thiart et al. [211] found that there was a large spatial variation in the temperature at IVC under RON conditions. In the case of isooctane, a large fraction of the charge fell within 360-380 K, while near the piston/wall the temperature could be as high as 400 K. However, the low head or piston temperature used in their model (400 K vs. 438 K in this study) suggests that their overall temperature at IVC could be underestimated.

Therefore, acknowledging the uncertainty in the estimated temperature at IVC, two different values of this temperature were proposed and used. The first value was that estimated from Eq. 7.6. This temperature was then modified based on the literature data for isooctane and the fuel’s charge cooling. For example, the addition of 10%
ethanol has been shown in Figures 5.2 and 5.3 to reduce the mixture temperature at the inlet port by approximately 5 K relative to isooctane. Hence, a similar decrease in the temperature at IVC due to ethanol addition was assumed. These modified charge temperatures at IVC can be found in Table 7.1.

**Chemical kinetics prior to spark ignition**
A survey of the literature indicates that chemical kinetics prior to spark ignition is rarely simulated in many studies, e.g. [49, 98, 100]. To justify this assumption, a simple validation test was conducted where simulations were run with and without kinetics modelled prior to spark ignition under RON conditions.

Figure 7.15 shows that the chemical kinetics prior to spark ignition is significant. The pre-spark chemical reactivity in the end gas can advance fuel decomposition, consume NO sooner and lead to an earlier build-up of HO$_2$ and OH radicals. Consequently, autoignition onset is advanced, as illustrated in Figure 7.16. Of further note is that this activity occurs whilst having a small effect on the rate of oxidation of the unreacted fuel. Hence, chemical kinetics was simulated from IVC through the end of combustion in this study.

### 7.3.2 Results - ethanol/isoctane blends

**In-cylinder pressure and end-gas temperature**
Combustion of ethanol/isoctane blends of up to 20% ethanol content by volume and under RON conditions was modelled with full chemical kinetics using the quasi-dimensional engine model in this study. Figure 7.17 shows the modelled and measured in-cylinder pressure for these fuels, and Figure 7.18 shows the fuel decomposition profiles. Three different concentrations of NO were investigated for each fuel. For isoctane, agreement between the simulated and the measured pressure traces improves
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Figure 7.15: The effects of kinetics prior to spark ignition on the mass fraction of a) isooctane, b) NO, c) \( \text{HO}_2 \) and d) OH for isooctane at standard knock intensity under RON conditions (with NO present in the residual gas). The detailed mechanisms from [130, 142] were used.

Figure 7.16: The effects of chemical kinetics prior to spark ignition on the estimated burned mass fraction for isooctane at standard knock intensity under RON conditions (with NO present in the residual gas). The detailed mechanisms from [130, 142] were used.
7.3 Modelling results for SI combustion

with increasing NO concentration. For isoctane-E10 and isoctane-E20, the modelled autoignition onset is more advanced than experiment.

Clearly, the presence of NO increases the end-gas temperature at a given crank angle. Figure 7.17 shows that at MFB50, the end-gas temperature with NO present can differ from that without NO by approximately 50 K in the case of isoctane, and this difference is magnified with the addition of ethanol. For isoctane-E20, autoignition occurs prior to MFB50 with the presence of NO, and thus it is more relevant to compare the end-gas temperature attained when 50% of the fuel species has decomposed (Figure 7.17). For all fuels, the end-gas temperature at this instant is around 1000 - 1050 K, and remains relatively unchanged by different NO concentrations. Importantly, NO considerably shortens the time required to reach this temperature.

Such results are likely due to the ability of NO to form more OH radicals by reacting with HO$_2$ [138, 146] (a product of fuel decomposition) via

\[
\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}. \quad (7.8)
\]

NO is further formed through the H atom assisted destruction of NO$_2$,

\[
\text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{OH}, \quad (7.9)
\]

which is typically a much faster process than reaction 7.8 [138]. Combining these two reactions yields

\[
\text{HO}_2 + \text{H} \rightarrow 2\text{OH}. \quad (7.10)
\]

In the absence of NO and at low temperatures, HO$_2$ reacts with H predominantly via the recombination process,

\[
\text{HO}_2 + \text{H} \rightarrow \text{H}_2\text{O}_2, \quad (7.11)
\]

whereas at high temperatures H$_2$O$_2$ formed in reaction 7.11 would have sufficient energy to directly dissociate to two OH radicals, equivalent to reaction 7.10 [138]. However, consistent with the trends found in the in-cylinder pressure and temperature previously, the effects of NO diminish with further increases in its concentration. This may be linked to the scavenging of the reactive OH radicals by the overall reaction

\[
\text{NO} + 2\text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O}, \quad (7.12)
\]

which could be more effective than reaction 7.8 as the amount of NO increases [138]. Further, Faravelli et al. [147] reported that the promoting effects of NO in oxidation of hydrocarbons diminish at very high temperatures. Of course, such arguments cannot be confirmed without more fundamental study.

In addition to advancing autoignition onset of these fuels, NO also advances fuel decomposition. This is especially evident when ethanol is added to the fuel, suggesting
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Figure 7.17: The in-cylinder pressure and the end-gas temperature with respect to CAD for a) isooctane, b) isooctane-E10 and c) isooctane-E20 under RON conditions. The crosses denote the CAD at which 50% of the major fuel species has decomposed in the end gas.
Figure 7.18: Modelled fuel decomposition and the mass fraction burned with respect to CAD for a) isooctane, b) isooctane-E10 and c) isooctane-E20 under RON conditions. The NO concentration used in modelling the mass fraction burned was as measured.
higher reactivity between NO and ethanol (Figure 7.18). However, whether or not this is representative of the actual chemistry between NO and ethanol is unclear, as there exists considerable uncertainty in the kinetic mechanism used. This will be discussed further in Section 7.3.5.

7.3.3 Results - ethanol/PRF91 blends

In-cylinder pressure and end-gas temperature

Figure 7.19 shows the modelled in-cylinder pressure and the end-gas temperature for ethanol/PRF91 blends under RON conditions. In all cases, autoignition is observed, although the onset again lags that observed in experiments.

Similarly, NO again significantly advances autoignition onset, and the effects of NO diminish when its concentration is further increased. Likewise, NO also increases the rate of the end-gas temperature rise for these fuel blends. Overall, these results suggest that the autoignition kinetics of ethanol/PRF91 is similar to that of ethanol/iso-octane.

Regardless of NO content, two-stage ignition is modelled for PRF91 under RON conditions. While this is expected for $n$-heptane, it is interesting that both iso-octane and $n$-heptane decompose in two stages (Figure 7.20). This is contrary to the single-stage decomposition profile previously observed for iso-octane in Figure 7.18. It is thus believed that the two-stage heat release from $n$-heptane affects the way iso-octane decomposes, and hence the oxidation chemistry of these two species is coupled.

The presence of ethanol appears to remove such two-stage characteristics. A recent study by Haas et al. [133] reported that the decomposition of $n$-heptane at low temperatures generates radicals that will subsequently react with ethanol to form potentially more stable species. Such chemistry is initiated by

$$nC_7H_{16} + O_2 \rightarrow C_7H_{15} + HO_2,$$  \hspace{1cm} (7.13)

which is followed by the reaction between ethanol and HO$_2$ to form $\alpha$-hydroxyethyl,

$$C_2H_5OH + HO_2 \rightarrow CH_3CHOH + H_2O_2.$$  \hspace{1cm} (7.14)

$\alpha$-Hydroxyethyl then rapidly reacts with O$_2$ to form acetaldehyde and thus regenerate HO$_2$,

$$CH_3CHOH + O_2 \rightarrow CH_3CHO + HO_2.$$  \hspace{1cm} (7.15)

Overall, reactions 7.14 and 7.15 when combined result in stable acetaldehyde and H$_2$O$_2$ as products [133]. Haas et al. [133] suggested that these specific reactions are responsible for the lack of the negative-temperature-coefficient (NTC) or two-stage behaviour as observed in blending ethanol with fuels like $n$-heptane. Specifically, the competition for HO$_2$ and OH radicals between ethanol and $n$-heptane leads to slower regeneration of OH. This subsequently reduces the reactive radical pool that would
otherwise be growing when \(n\)-heptane alone is oxidised. Hence, ethanol can suppress the low-temperature reactivity of \(n\)-heptane and yield a single-stage fuel decomposition profile as shown in Figure 7.20.

### 7.3.4 Results - ethanol/TRF91-30 blends

**In-cylinder pressure and end-gas temperature**

Similar to that observed for ethanol/PRF91 blends, NO is predicted to significantly advance autoignition onset for ethanol/TRF91-30 blends under RON conditions (Figure 7.21). It is however interesting that the NO effect on the in-cylinder pressure development is smaller in the case of TRF91-30 compared with other fuels. It appears that the oxidation of toluene (when ethanol is not present) is less sensitive to NO, although such interaction is not validated experimentally and requires further study.

Figure 7.22 shows the fuel decomposition and mass fraction burned profiles for different ethanol/TRF91-30 blends. Of all fuels, toluene decomposes at the slowest rate, followed by ethanol, isoctane and lastly \(n\)-heptane. In the case of TRF91-30, each fuel species appears to decompose in two stages, regardless of NO content. This again suggests that although \(n\)-heptane is the only fuel with apparent two-stage ignition, the chemistry of isoctane and toluene may be coupled with that of \(n\)-heptane. Adding ethanol again effectively eliminates this two-stage decomposition profile. As previously discussed, this is likely a result of ethanol’s ability to suppress the low-temperature reactivity of \(n\)-heptane via reactions 7.14 and 7.15. Once again, NO significantly advances fuel decomposition. This leads to earlier autoignition onset, and is consistent with all the other fuels studied thus far.

### 7.3.5 Model uncertainty and implications

Having previously discussed the modelling results for specific fuel blends, this section now reviews the overall model performance as well as its uncertainty. Figure 7.23 compares the modelled and measured autoignition onset under RON conditions for all fuels. The following general trends are observed.

1. The presence of NO is modelled to significantly advance autoignition onset, though such effects diminish when its concentration increases.

2. Where the fuel contains 10% (v/v) or less ethanol, the presence of NO can improve agreement between the modelled and measured autoignition onset. For fuels containing 20% (v/v) ethanol, autoignition onset with NO is modelled to be earlier than in experiment.

However, caution should be exercised when interpreting these results, as there is considerable uncertainty in several aspects of this problem. First, the NO submechanism used was originally developed only for the oxidation of isoctane [142]. The chemical interaction between NO and \(n\)-heptane, toluene and ethanol has not yet been validated.
Figure 7.19: The in-cylinder pressure and the end-gas temperature with respect to CAD for a) PRF91, b) PRF91-E10 and c) PRF91-E20 under RON conditions. The crosses denote the CAD at which 50% of the major fuel species has decomposed in the end gas.
7.3 Modelling results for SI combustion

Figure 7.20: Modelled fuel decomposition and the mass fraction burned with respect to CAD for a) PRF91, b) PRF91-E10 and c) PRF91-E20 under RON conditions. The NO concentration used in modelling the mass fraction burned was as measured.
Figure 7.21: The simulated in-cylinder pressure and the end-gas temperature with respect to CAD for a) TRF91-30, b) TRF91-30-E10 and c) TRF91-30-E20 under RON conditions. The crosses denote the CAD at which 50% of the major fuel species has decomposed in the end gas.
Figure 7.22: Modelled fuel decomposition and the mass fraction burned with respect to CAD for a) TRF91-30, b) TRF91-30-E10 and c) TRF91-30-E20 under RON conditions. The NO concentration used in modelling the mass fraction burned was as measured.
7 Modelling of Autoignition

(a) Using the temperature at IVC as estimated from Eq. 7.6

(b) Using the modified temperature at IVC

Figure 7.23: Modelled autoignition onset for different fuels with and without NO based on different temperatures at IVC - a) as estimated from Eq. 7.6 and b) as modified (see Table 7.1). The measured autoignition onset is also included for reference.
Further, although the chemistry of neat ethanol is reasonably well understood, few studies in the literature have explored the oxidation of ethanol blended with different gasoline surrogates. Complicating the problem further, different published mechanisms predict different trends in the low-temperature reactivity of ethanol (Section 7.2).

Figure 7.23 also shows the modelled autoignition onset based on the modified temperature at IVC. It was established earlier that autoignition is sensitive to this temperature (Figure 7.9). Agreement between the modelled and measured autoignition onset is now significantly better. Indeed, Figure 7.23 indicates that it is possible for the modelled autoignition onset to match the measured data by tuning of the temperature at IVC to within ±5% of its original value.

Based on these observations, implications for future kinetic model development include the following.

1. A validated kinetic model of NO interaction with common gasoline surrogates and ethanol at engine representative conditions is required.

2. The chemical interaction of ethanol with isooctane, n-heptane and toluene needs further modelling work. In particular, the modelled autoignition onset (Figure 7.23) of these fuel blends is not consistent with the observed synergism and antagonism in the engine experiments reported in Chapter 4.

3. Whilst accurate kinetic models are challenging to obtain, so too is the modelling of several other phenomena that also affect autoignition significantly. There is little point in solving computationally more demanding, full chemical models if the flame propagation, the engine heat transfer or the mixture temperature at IVC cannot be measured or modelled with a similar degree of accuracy. Thus, the reliable prediction of autoignition and knock does not only involve work on the fuel chemistry, but also work on all aspects of the modelling of fluid motion through an engine.

With respect to points 1 and 2 above, these kinetic studies should focus on temperatures between 600 K and 1200 K, since these span the end-gas temperatures observed in the engine, such as those in Figures 7.17, 7.19 and 7.21. Studies of autoignition chemistry at temperatures higher than 1200 K appear to be less relevant to modern, spark ignition engines, such as those undertaken in the majority of shock tube experiments reported in the literature, e.g. [119, 123]. Also, the pressures examined in these proposed studies should range from 20 to 100 bar, since this encompasses the pressures likely to be observed due to cylinder compression and boosting.

### 7.4 Summary

This chapter presented the development and use of a quasi-dimensional engine model with full chemical kinetics to simulate end-gas autoignition under RON conditions for several blends of ethanol with isooctane, PRF91, and TRF91-30. A parametric study
on autoignition onset was first conducted for iso-octane. These results showed that NO in the residual gas could significantly enhance end-gas kinetics even at a very low concentration, while unburned HC exhibited negligible effect. Unsurprisingly, end-gas chemistry was also sensitive to heat transfer and the temperature at IVC.

Different kinetic mechanisms developed for ethanol/gasoline-surrogate blends were then evaluated. Calculated ignition delay times in a constant-volume reactor and modelled autoignition onset in an engine suggested that the mechanism from Andrae [130] was best suited for modelling the fuels of interest. Nonetheless, none of these simulation results showed a trend that was consistent with the previously observed RON/MON synergism between ethanol and iso-octane or n-heptane, or the antagonistic blending of ethanol and toluene.

Finally, the modelling results were analysed in relation to the pressure and temperature development, along with fuel decomposition and burned mass fraction in the end gas. In some cases, autoignition onset was accurately modelled when NO was included. Importantly, NO was modelled to advance autoignition onset considerably for all the fuels in this study, but its effects diminished when its concentration was further increased. Also, simulations showed that ethanol effectively suppressed low-temperature reactivity of n-heptane, consistent with previous studies. These observations, however, should be interpreted with caution due to uncertainty in the underlying chemistry of ethanol’s interaction with common gasoline surrogates, as well as NO’s interaction with common gasoline surrogates and ethanol. This suggests that further experiment and modelling are required.
8 Conclusions and Recommendations for Future Work

In reference to the research questions listed in Section 2.6, this thesis makes the following conclusions.

1. **What are the Research (RON) and Motor (MON) Octane Numbers of ethanol blended with gasoline and its surrogates?**

   The RON and MON of ethanol/gasoline blends are strongly dependent on the composition of gasoline. While recent studies reported varying RON/MON synergism between US production gasolines and ethanol [158, 159], an almost linear variation of the octane number with ethanol content was found in this study for blends with an Australian production gasoline. Further, n-heptane, isooctane and their PRFs were found to blend synergistically with ethanol, whilst toluene blended antagonistically. Consistent with these trends, a progressive increase in the toluene content in TRFs of a constant RON resulted in increasingly linear ethanol/TRF blending.

   These trends in ethanol blending with PRFs and TRFs suggest how different types of gasoline blend differently with ethanol. Specifically, these observations suggest that the antagonism of ethanol’s blending with aromatics may act against its synergism with paraffins. If correct, this has implications for fuel design. In particular, exploitation of this synergism of ethanol and paraffins may enable a given octane number to be achieved with lower aromatic and lower ethanol content, and thus makes more effective use of the ethanol.

2. **How does charge cooling affect the RON of ethanol blended with gasoline and its surrogates?**

   In a standard RON test, the temperature of the air-fuel mixture entering the engine depends on the enthalpy of vaporisation of the fuel because the intake temperature is prescribed upstream of the carburettor. For gasoline, measurements of this temperature suggested that a fully vaporised, unsaturated mixture was achieved prior to entry into the engine. For neat ethanol, however, these temperature measurements suggested that the mixture entering the engine was saturated and potentially two-phase due to ethanol’s high enthalpy of vaporisation and its lower stoichiometric air-fuel ratio. Hence, the standard RON test is significantly influenced by a fuel’s charge cooling.
To better delineate the effect of charge cooling and autoignition chemistry, a so-called ‘modified’ RON test was therefore proposed. The temperature of the mixture entering the engine was fixed to that measured for PRFs in the standard RON test, so that any additional charge cooling due to ethanol was compensated for. In this modified test, the mixture appeared to be unsaturated and fully vaporised prior to entering the engine, regardless of the ethanol content. Modelling also showed that the modified RON test maintained much more constant temperatures after in-cylinder compression for fuels with very different enthalpies of vaporisation. This modified RON test thus appeared to be better posed to examine the impact of fuel chemistry, particularly for fuel blends with significant alcohol content. Results suggested that both the charge cooling and fuel chemistry effects were significant in the RONs of the ethanol/gasoline blends.

3. **What are the mechanisms leading to autoignition of ethanol blended with gasoline and its surrogates in spark-ignition engines?**

The reliable prediction of autoignition and knock does not only involve accurate chemical models, but also accurate modelling of fluid motion through an engine. Engine parameters, in particular the engine heat transfer, the mixture temperature at IVC and the residual gas composition, should be carefully estimated or calibrated against measurement prior to modelling of autoignition.

Specifically, a parametric study on autoignition onset of isoctane suggested that NO in the residual gas could significantly enhance end-gas kinetics even at a very low concentration, while unburned HC exhibited negligible effect. In addition, end-gas chemistry was highly sensitive to heat transfer and the mixture temperature at IVC. Different kinetic mechanisms developed for ethanol/gasoline-surrogate blends were also evaluated, and Andrae’s mechanism [130] appeared best suited for modelling the chemistry of these fuels. Nonetheless, simulation results did not show a trend that was consistent with the RON/MON synergism between ethanol and isoctane or n-heptane, or the antagonistic blending of ethanol and toluene.

Integrating these mechanisms into a single simulation approach showed that NO advanced autoignition onset considerably for all the fuels in this study. Also, ethanol was found to suppress the low-temperature reactivity of n-heptane. However, these observations should be interpreted with caution due to the considerable uncertainty in the chemical interaction of ethanol with isoctane, n-heptane and toluene, and that of NO’s interaction with different gasoline surrogates and ethanol.

### 8.1 Recommendations for future work

Recommendations for future work include the following.
8.1 Recommendations for future work

1. **Octane number measurements of ethanol blended with other hydrocarbons**

   Whilst paraffins (both linear and branched) and aromatics are the major constituents in gasoline, other classes of hydrocarbons, e.g. naphthenes and olefins, could make up 5 - 15% of regular gasoline. Thus, it is of interest to study the blending behaviour of ethanol with these hydrocarbons. Experimental determination of the RONs and MONs of ethanol blended with naphthenes and olefins, combined with that already undertaken in this work, may provide more insights into how ethanol blends with gasoline.

2. **Detailed modelling of the charge cooling effect of ethanol**

   It has been shown in this work that the charge cooling of ethanol is significant in the RON test, and that the mixture entering the engine is likely two-phase at high ethanol content. The use of a CFD model on the intake mixture and the gas exchange processes in the engine should determine the spatial and temporal variation in the state of the mixture, and be used to estimate the average mixture temperature at IVC. This temperature has been shown to be an important parameter which affects autoignition.

3. **Development of a quasi-dimensional combustion model with multiple zones in the end gas**

   As discussed in Chapter 7, the model in this work considers the end gas to be entirely homogeneous in composition and temperature. An improvement to this combustion model can be made by implementing multiple zones in the end gas. Such an approach is useful in modelling the temperature inhomogeneity in the combustion chamber that is typical of normal engine operating conditions. As shown in the Literature Review, temperature inhomogeneity may have a significant influence on autoignition.

4. **Development and validation of a kinetic model for ethanol’s interaction with n-heptane, isoctane and toluene**

   This work showed that the published kinetic mechanisms of ethanol/TRF blends differ significantly at engine representative conditions. In particular, the chemical interaction of ethanol with n-heptane, isoctane and toluene remains unclear. Also, limited experimental data exists for model validation. Whilst this is a large undertaking, developing accurate kinetic models is required in order to have truly predictive tools.

5. **Development and validation of a kinetic model for NO’s interaction with common gasoline surrogates and ethanol**

   It appears that NO can significantly affect the autoignition of ethanol blended with different gasoline surrogates. However, the mechanisms used are mostly
8 Conclusions and Recommendations for Future Work

validated against experiments performed under HCCI (lean) conditions, and also lack the modelling of NO’s interaction with longer-chain hydrocarbons. Hence, the chemical interaction of NO with common gasoline surrogates and ethanol within the spark-ignition engine operation regimes remains unclear. A validated kinetic model for these interactions is therefore as important practically as the validated models for the fuels themselves.
Bibliography


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A Engine

A.1 Compression ratio as a function of RON/MON

Table A.1: The compression ratio of the CFR engine as a function of the RON at standard knock intensity [63].

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## A.1 Compression ratio as a function of RON/MON

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| 90 | 6.76 | 6.77 | 6.78 | 6.79 | 6.81 | 6.81 | 6.83 | 6.84 | 6.86 |
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A.2 Camshaft timing and valve lift profile of the CFR engine

Table A.3: Measured camshaft timing and valve lift profile of the F1/F2 CFR engine.

The camshaft timing is relative to the intake TDC. The valve lift is zero outside of the camshaft timings specified in the table.

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### A.2 Camshaft timing and valve lift profile of the CFR engine

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<td>0.520</td>
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<tr>
<td>210</td>
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<td>0.445</td>
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*continue on next page*
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</tr>
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<tr>
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<td>228  -2    0.225  1.355</td>
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<td>236    6    0.200  0.660</td>
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<td>238    8    0.190  0.520</td>
</tr>
<tr>
<td>240   10    0.180  0.420</td>
</tr>
<tr>
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<td>244   14    0.150  0.305</td>
</tr>
<tr>
<td>246   16    0.130  0.270</td>
</tr>
<tr>
<td>248   18    0.120  0.250</td>
</tr>
<tr>
<td>250   20    0.100  0.235</td>
</tr>
<tr>
<td>252   22    0.080  0.225</td>
</tr>
<tr>
<td>254   24    0.065  0.210</td>
</tr>
<tr>
<td>256   26    0.050  0.205</td>
</tr>
<tr>
<td>258   28    0.040  0.200</td>
</tr>
<tr>
<td>260   30    0.030  0.195</td>
</tr>
<tr>
<td>262   32    0.020  0.190</td>
</tr>
<tr>
<td>264   34    0.020  0.185</td>
</tr>
<tr>
<td>266   36    0.010  0.175</td>
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<tr>
<td>268   38    0.010  0.165</td>
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<td>270   40    0.005  0.150</td>
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<td>272   42    0.020  0.135</td>
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<td>276   46    0.010  0.110</td>
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<td>278   48    0.010  0.095</td>
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<td>280   50    0.005  0.080</td>
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<tr>
<td>282   52    -      0.060</td>
</tr>
<tr>
<td>284   54    -      0.035</td>
</tr>
<tr>
<td>286   56    -      0.030</td>
</tr>
<tr>
<td>288   58    -      0.020</td>
</tr>
<tr>
<td>290   60    -      0.010</td>
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</table>
A.3 Discharge coefficient of the CFR intake and exhaust valves

Table A.4: Measured forward and reverse discharge coefficients of the intake valve in the CFR engine from [200].

<table>
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<tr>
<th>Valve lift (mm)</th>
<th>Discharge coefficient forward</th>
<th>Discharge coefficient reverse</th>
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</thead>
<tbody>
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<td>0.05</td>
<td>0.351</td>
<td>0.166</td>
</tr>
<tr>
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<td>0.375</td>
<td>0.360</td>
</tr>
<tr>
<td>0.2</td>
<td>0.434</td>
<td>0.447</td>
</tr>
<tr>
<td>0.3</td>
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<tr>
<td>0.4</td>
<td>0.451</td>
<td>0.503</td>
</tr>
<tr>
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<td>0.446</td>
<td>0.495</td>
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<td>0.402</td>
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<tr>
<td>1.1</td>
<td>0.375</td>
<td>0.451</td>
</tr>
<tr>
<td>1.2</td>
<td>0.361</td>
<td>0.444</td>
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Table A.5: Measured forward and reverse discharge coefficients of the exhaust valve in the CFR engine from [200].

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<th>Valve lift (mm)</th>
<th>Discharge coefficient forward</th>
<th>Discharge coefficient reverse</th>
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<td>0.05</td>
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<td>0.329</td>
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## B Standard RON and MON data

Table B.1: Measured RONs and MONs of toluene blended with ethanol, and the associated volume and mole fractions of ethanol.

<table>
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<th>Fuel</th>
<th>RON</th>
<th>MON</th>
<th>x_{ethanol}</th>
<th>(v_{ethanol})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>120 (^a)</td>
<td>107</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Toluene-E10</td>
<td>112.8</td>
<td>101</td>
<td>0.1</td>
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<td>Toluene-E20</td>
<td>110.9</td>
<td>97</td>
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<td>0.368</td>
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<td>Toluene-E40</td>
<td>108.6</td>
<td>93.3</td>
<td>0.4</td>
<td>0.608</td>
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<td>Toluene-E60</td>
<td>108.1</td>
<td>91.9</td>
<td>0.6</td>
<td>0.778</td>
</tr>
<tr>
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<td>108.0 (^b)</td>
<td>90.7</td>
<td>1</td>
<td>1</td>
</tr>
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</table>

\(^a\) The RON of toluene was obtained from \([174]\).  

\(^b\) The RON of ethanol measured for this specific batch of measurements.  

See Experimental Methods for more details.
### B Standard RON and MON data

Table B.2: Measured RONs and MONs of gasoline and its surrogates blended with ethanol, and the associated volume fractions of ethanol.

<table>
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<th>Fuel</th>
<th>RON</th>
<th>MON</th>
<th>v_{ethanol}</th>
<th>x_{ethanol}</th>
</tr>
</thead>
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<td>82.1</td>
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<td>0</td>
</tr>
<tr>
<td>Gasoline-E10</td>
<td>95.2</td>
<td>84.2</td>
<td>0.1</td>
<td>0.206</td>
</tr>
<tr>
<td>Gasoline-E20</td>
<td>98.3</td>
<td>85.5</td>
<td>0.2</td>
<td>0.368</td>
</tr>
<tr>
<td>Gasoline-E40</td>
<td>102.1</td>
<td>87.7</td>
<td>0.4</td>
<td>0.608</td>
</tr>
<tr>
<td>Gasoline-E60</td>
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<td>89</td>
<td>0.6</td>
<td>0.778</td>
</tr>
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<td>Gasoline-E80</td>
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<td>0.903</td>
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*a The RON and MON of a PRF are by definition [63, 64].

*b The RON of ethanol measured for this specific batch of measurements. See Experimental Methods for more details.
Table B.3: Measured RONs and MONs of different PRFs blended with ethanol, and the associated volume fractions of ethanol.

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continued on next page
### B Standard RON and MON data

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<sup>a</sup>The RON and MON of a PRF are by definition [63, 64].

<sup>b</sup>The RON of ethanol measured for this specific batch of measurements. See Experimental Methods for more details.
# C The modified RON data

Table C.1: Measured RON values, and the associated IATs for blends of ethanol/\textit{n}-heptane, ethanol/isooctane and ethanol/toluene blends under standard and modified conditions.

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<td>107.5</td>
<td>103.5</td>
<td>51.7</td>
<td>143</td>
</tr>
<tr>
<td>Ethanol</td>
<td>108.0(^b)</td>
<td>103.5</td>
<td>51.7</td>
<td>168</td>
</tr>
</tbody>
</table>

---

\(^a\) The modified IATs were adjusted such that the mixture temperature became approximately 36 °C. See Section 3.4 for more details.

\(^b\) The RON of ethanol measured for this specific batch of measurements. See Experimental Methods for more details.
C The modified RON data
D Two-zone spark-ignition engine modelling with chemical kinetics

This Appendix presents a derivation of equations for a two-zone model of a reciprocating, internal combustion engine. This model is similar to several of those already in the literature (e.g. [49, 98, 100]), but also has the following features that are important for examining autoignition.

1. It permits kinetic activity to occur in the unburned and burned gases throughout the compression, combustion and expansion processes. Kinetic activity during compression and combustion in particular are shown to be significant in this study.

2. It includes the rate of change of the specific gas constant \( R \). This rate is usually and legitimately assumed to be zero in normal combustion. However, this study shows that this assumption it is not permissible when examining autoignition.

D.1 Conservation of energy

The conservation of energy for an open control volume with low Mach numbers throughout can be stated as

\[
\frac{dE_{cv}}{dt} = \frac{dQ}{dt} - \dot{W} + \sum \dot{m}_{in}h_{in} - \sum \dot{m}_{out}h_{out},
\]  

(D.1)

where \( E_{cv} \) is the internal energy over the control volume, \( Q \) is the heat transfer into the control volume, \( \dot{W} \) is the rate of work done on the gas, \( \dot{m} \) is the mass flow rate, \( h \) is the specific enthalpy, and the subscripts \( in \) and \( out \) represent the in-flow and out-flow respectively. The term \( \frac{dE_{cv}}{dt} \) can also be written as,

\[
\frac{dE_{cv}}{dt} = \frac{d(me)}{dt} = \frac{d(mh - pV)}{dt},
\]  

(D.2)

where \( m \) is the mass in the control volume, \( e \) is the specific internal energy, \( p \) is the pressure and \( V \) is the volume. The enthalpy \( h \) can be written as,

\[
h = \sum_{i}^{N} h_{i}Y_{i},
\]  

(D.3)

where \( h_{i} \) is the enthalpy and \( Y_{i} \) is the mass fraction of species \( i \) in a system of \( N \) species. Combining Eq. D.1, D.2 and D.3, the rate of change of internal energy becomes,
Two-zone spark-ignition engine modelling with chemical kinetics

\[
\frac{d(m \sum_{i=1}^{N} h_i Y_i - pV)}{dt} = \frac{dQ}{dt} - \dot{W} + \sum \dot{m}_{in} h_{in} - \sum \dot{m}_{out} h_{out}. \tag{D.4}
\]

### D.2 Conservation of species

The conservation of species \(i\) can be expressed in the following way,

\[
\frac{d(m Y_i)}{dt} = VW_i \dot{\omega}_i + \dot{m}_{in} Y_{i,in} - \dot{m}_{out} Y_{i,out}, \tag{D.5}
\]

where \(W\) is the molecular weight and \(\dot{\omega}\) is the molar net production rate (\(kmol/m^3 \cdot s\)).

### D.3 Governing equations for compression and expansion

Assuming some mass is lost due to blowby, the energy transport across the control volume is described by,

\[
\sum \dot{m}_{in} h_{in} = 0, \tag{D.6}
\]

\[
\sum \dot{m}_{out} h_{out} = h \frac{dm_l}{dt}, \tag{D.7}
\]

where \(dm_l/dt\) is the rate of mass blowby during compression and expansion (\(dm_l/dt > 0\) when mass is transferred from the cylinder to the crankcase/crevices). Substituting these into Eq. D.4 and since \(\dot{W} = pdV/dt\),

\[
\frac{d(m \sum_{i=1}^{N} h_i Y_i - pV)}{dt} = \frac{dQ}{dt} - p \frac{dV}{dt} - h \frac{dm_l}{dt}. \tag{D.8}
\]

The species transport in to and out of the control volume is given by,

\[
\dot{m}_{in} Y_{i,in} = 0, \tag{D.9}
\]

\[
\dot{m}_{out} Y_{i,out} = Y_i \frac{dm_l}{dt}, \tag{D.10}
\]

The conservation of species is then

\[
\frac{d(m Y_i)}{dt} = VW_i \dot{\omega}_i - Y_i \frac{dm_l}{dt}. \tag{D.11}
\]

Expanding the LHS of Eq. D.11,

\[
m \frac{dY_i}{dt} + Y_i \frac{dm}{dt} = VW_i \dot{\omega}_i - Y_i \frac{dm_l}{dt}. \tag{D.12}
\]

Since the rate of change of the mass in the control volume is

\[
\frac{dm}{dt} = - \frac{dm_l}{dt}, \tag{D.13}
\]
D.3 Governing equations for compression and expansion

by rewriting Eq. D.12, the rate of change of the mass fraction of species $i$ can be expressed,

$$\frac{dY_i}{dt} = \frac{W_i \dot{\omega}_i}{\rho}. \quad (D.14)$$

Expanding the LHS of Eq. D.8,

$$\frac{d}{dt} \left( m \sum_i^N h_i Y_i - pV \right) = \begin{align*}
m \left( \sum_i^N h_i \frac{dY_i}{dt} + \sum_i^N Y_i \frac{d}{dt} \frac{dh_i}{dt} \right) \\
+ \sum_i^N (h_i Y_i) \frac{dm}{dt} - p \frac{dV}{dt} - V \frac{dp}{dt}. \quad (D.15)
\end{align*}$$

Since $\frac{\partial h}{\partial T} = c_p(T)$ for an ideal gas that is weakly dependent on the pressure, substituting Eq. D.13 and D.14 into Eq. D.15 results in

$$\frac{d}{dt} \left( m \sum_i^N h_i Y_i - pV \right) = \begin{align*}
m \left( \sum_i^N h_i W_i \frac{\dot{\omega}_i}{\rho} + c_p \frac{dT}{dt} \right) \\
- h \frac{dm}{dt} - p \frac{dV}{dt} - V \frac{dp}{dt}. \quad (D.16)
\end{align*}$$

Equating this with the RHS of Eq. D.8,

$$m \left( \sum_i^N h_i W_i \frac{\dot{\omega}_i}{\rho} + c_p \frac{dT}{dt} \right) - V \frac{dp}{dt} = \frac{dQ}{dt}. \quad (D.17)$$

Finally, the rate of change of the temperature can be obtained by rearranging Eq. D.17,

$$mc_p \frac{dT}{dt} = \frac{dQ}{dt} + V \frac{dp}{dt} - V \sum_i^N h_i W_i \dot{\omega}_i. \quad (D.18)$$

Differentiating the ideal gas law $pV = mRT$,

$$p \frac{dV}{dt} + V \frac{dp}{dt} = mR \frac{dT}{dt} - RT \frac{dm}{dt} + mT \frac{dR}{dt}, \quad (D.19)$$

where $dR/dt$ is the rate of change of the specific gas constant, which will be discussed in a later section. The rate of change of pressure is then given by rearranging Eq. D.19,

$$\frac{dp}{dt} = \frac{1}{V} \left( mR \frac{dT}{dt} - RT \frac{dm}{dt} + mT \frac{dR}{dt} - p \frac{dV}{dt} \right). \quad (D.20)$$

Substituting this equation into Eq. D.18, the rate of change of temperature becomes,
D Two-zone spark-ignition engine modelling with chemical kinetics

\[ \frac{m c_p}{dt} \frac{dT}{dt} = \frac{dQ}{dt} + \left( m R \frac{dT}{dt} - R T \frac{dm_l}{dt} + m T \frac{dR}{dt} - p \frac{dV}{dt} \right) - V \sum_{i=1}^{N} h_i W_i \omega_i. \]  

(D.21)

Simplifying Eq. D.21 by recognising that \( c_p(T) - R = c_v(T) \),

\[ \frac{dT}{dt} = \frac{1}{mc_v(T)} \left( \frac{dQ}{dt} - R T \frac{dm_l}{dt} + m T \frac{dR}{dt} - p \frac{dV}{dt} - V \sum_{i=1}^{N} h_i W_i \omega_i \right). \]  

(D.22)

\[ \frac{dT}{dt} = \frac{1}{mc_v(T)} \left( \frac{dQ}{dt} - R T \frac{dm_l}{dt} + m T \frac{dR}{dt} - p \frac{dV}{dt} - V \sum_{i=1}^{N} h_i W_i \omega_i \right). \]  

(D.23)

D.4 Governing equations for combustion

D.4.1 Burned zone

Assuming mass is transported from the flame front into the burned zone, and at the same time some mass in the burned zone is lost due to blowby, the energy transport into and out of the burned zone is

\[ \sum (m_{in} h_{in})_b = h_f \frac{dm_x}{dt}, \]  

(D.24)

\[ \sum (m_{out} h_{out})_b = h_b \frac{dm_{lb}}{dt}, \]  

(D.25)

in which \( dm_x/dt \) is the mass burning rate, \( dm_l/dt \) is the rate of mass blowby, while \( h_f \) and \( h_b \) are the specific enthalpy of the burned products in the flame front, and of the products in the burned zone respectively. From Eq. D.4, the conservation of energy becomes,

\[ \frac{d(m \sum_{i=1}^{N} h_i Y_i - pV)_b}{dt} = \frac{dQ_b}{dt} - p \frac{dV_b}{dt} + h_f \frac{dm_x}{dt} - h_b \frac{dm_{lb}}{dt}. \]  

(D.26)

The species transport into and out of the burned zone is

\[ (m_{in} Y_{i,in})_b = Y_{i,f} \frac{dm_x}{dt}, \]  

(D.27)

\[ (m_{out} Y_{i,out})_b = Y_{i,b} \frac{dm_{lb}}{dt}, \]  

(D.28)

where \( Y_{i,f} \) and \( Y_{i,b} \) are the mass fraction of species \( i \) in the flame front and in the burned zone respectively. The conservation of species can be described by,

\[ \frac{d(m_b Y_{i,b})}{dt} = V_b W_{i,b} \omega_i b + Y_{i,f} \frac{dm_x}{dt} - Y_{i,b} \frac{dm_{lb}}{dt}. \]  

(D.29)
Expanding the LHS of Eq. D.29,

\[
\frac{m_b}{dt} \frac{dY_{i,b}}{dt} + Y_{i,b} \frac{dm_b}{dt} = V_b W_{i,b} \dot{\omega}_{i,b} + Y_{i,f} \frac{dm_x}{dt} - Y_{i,b} \frac{dm_{l,b}}{dt}.
\]  \hspace{20mm} (D.30)

Since the rate of change of the mass in the burned zone is defined as,

\[
\frac{dm_b}{dt} = \frac{dm_x}{dt} - \frac{dm_{l,b}}{dt},
\]  \hspace{20mm} (D.31)

by rewriting Eq. D.30, the rate of change of the mass fraction of species \(i\) in the burned zone can be expressed

\[
\frac{dY_{i,b}}{dt} = \frac{W_{i,b} \dot{\omega}_{i,b}}{\rho_b} + \frac{1}{m_b} \frac{dm_x}{dt} (Y_{i,f} - Y_{i,b}).
\]  \hspace{20mm} (D.32)

Expanding the LHS of Eq. D.26,

\[
\frac{d(m \sum_i^N h_i Y_i - pV)_b}{dt} = m_b \sum_i^N h_{i,b} \frac{dY_{i,b}}{dt} + m_b \sum_i^N Y_{i,b} \frac{dh_{i,b}}{dt} + \sum_i^N (h_i Y_i)_b \frac{dm_b}{dt} - p \frac{dV_b}{dt} - V_b \frac{dp}{dt}.
\]  \hspace{20mm} (D.33)

Recognising that \(\partial u/\partial T = c_v(T)\) and \(\sum_i^N h_i Y_i = h\), substituting Eq. D.32 into Eq. D.33,

\[
\frac{d(m \sum_i^N h_i Y_i - pV)_b}{dt} = m_b \sum_i^N h_{i,b} \left[ W_{i,b} \dot{\omega}_{i,b} + \frac{1}{m_b} \frac{dm_x}{dt} (Y_{i,f} - Y_{i,b}) \right] + m_b c_p h_b \frac{dT_b}{dt} + h_b \left( \frac{dm_x}{dt} - \frac{dm_{l,b}}{dt} \right) - p \frac{dV_b}{dt} - V_b \frac{dp}{dt}.
\]  \hspace{20mm} (D.34)

Equating this with the RHS of Eq. D.26,

\[
\frac{dQ_b}{dt} - \frac{dV_b}{dt} + m_x h_f - m_{l,b} h_b = m_b \sum_i^N h_{i,b} \left[ W_{i,b} \dot{\omega}_{i,b} + \frac{1}{m_b} \frac{dm_x}{dt} (Y_{i,f} - Y_{i,b}) \right] + m_b c_p h_b \frac{dT_b}{dt} + h_b \left( \frac{dm_x}{dt} - \frac{dm_{l,b}}{dt} \right) - p \frac{dV_b}{dt} - V_b \frac{dp}{dt}.
\]  \hspace{20mm} (D.35)

Finally, the rate of change of the temperature in the burned zone can be obtained by rearranging Eq. D.35,

\[
\frac{dT_b}{dt} = \frac{1}{m_b c_p h_b} \left[ \frac{dQ_b}{dt} + \frac{dV_b}{dt} \right] + V_b \frac{dp}{dt} - \left[ V_b \sum_i^N h_{i,b} W_{i,b} \dot{\omega}_{i,b} + \frac{dm_x}{dt} \sum_i^N Y_{i,f} (h_{i,f} - h_{i,b}) \right].
\]  \hspace{20mm} (D.36)
D Two-zone spark-ignition engine modelling with chemical kinetics

D.4.2 Unburned zone

Assuming mass is transported from the unburned zone to both the flame front and the cylinder crevices due to blowby, the energy transport into and out of the unburned zone is given by,

\[ \sum (m_{in} h_{in})_u = 0, \]  

\[ \sum (m_{out} h_{out})_u = h_u \frac{dm_x}{dt} + h_u \frac{dm_{l,u}}{dt}, \]  

where \( h_u \) is the specific enthalpy of the unburned air-fuel mixture, and the subscript \( u \) represents the unburned zone. From Eq. D.4, the conservation of energy becomes,

\[ \frac{d(m \sum_i h_i Y_i - pV)}{dt} = \frac{dQ_u}{dt} - p \frac{dV_u}{dt} - h_u \frac{dm_x}{dt} - h_u \frac{dm_{l,u}}{dt}. \]  

Similarly, the species transport into and out of the unburned zone is given by,

\[ (m_{in} Y_{i,in})_u = 0, \]  

\[ (m_{out} Y_{i,out})_u = Y_{i,u} \frac{dm_x}{dt} + Y_{i,u} \frac{dm_{l,u}}{dt}, \]  

where \( Y_{i,u} \) is the mass fraction of species \( i \) in the unburned zone. The conservation of species in the unburned zone is described by

\[ \frac{d(m_u Y_{i,u})}{dt} = V_u W_{i,u} \omega_{i,u} - Y_{i,u} \frac{dm_x}{dt} - Y_{i,u} \frac{dm_{l,u}}{dt}. \]  

Expanding the LHS of Eq. D.43,

\[ m_u \frac{dY_{i,u}}{dt} + Y_{i,u} \frac{dm_u}{dt} = V_u W_{i,u} \omega_{i,u} - Y_{i,u} \frac{dm_x}{dt} - Y_{i,u} \frac{dm_{l,u}}{dt}. \]  

Since the rate of change of the mass in the unburned zone is defined as,

\[ \frac{dm_u}{dt} = \frac{dm_x}{dt} - \frac{dm_{l,u}}{dt}. \]  

Substituting Eq. D.45 into Eq. D.44, the rate of change of the mass fraction of species \( i \) in the unburned zone becomes,

\[ \frac{dY_{i,u}}{dt} = \frac{W_{i,u} \omega_{i,u}}{\rho_u}. \]
Expanding the LHS of Eq. D.40,
\[
\frac{d}{dt}\left(m\sum_i h_i Y_i - pV\right) = m_u \frac{d}{dt}\left(\sum_i h_i Y_i\right) + \sum_i (h_i Y_i) \frac{dm_u}{dt} - p \frac{dV_u}{dt} - V_u \frac{dp}{dt} = m_u \sum_i h_i \frac{dY_i}{dt} + m_u \sum_i Y_i \frac{dh_i}{dt} + \sum_i (h_i Y_i) \frac{dm_u}{dt} - p \frac{dV_u}{dt} - V_u \frac{dp}{dt}.
\]
\[(D.47)\]

Recognising that \(\frac{\partial u}{\partial T} = c_v(T)\) and \(\sum_i^N h_i Y_i = h\), and substituting Eq. D.46 into Eq. D.47,
\[
\frac{d}{dt}\left(m\sum_i h_i Y_i - pV\right) = m_u \sum_i h_i \frac{dY_i}{dt} + m_u c_p \frac{dT_u}{dt} + h_u \left(\frac{dm_x}{dt} - \frac{dm_{l,b}}{dt}\right) - p \frac{dV_u}{dt} - V_u \frac{dp}{dt}.
\]
\[(D.48)\]

Equating this with the RHS of Eq. D.40,
\[
\frac{dQ_u}{dt} - p \frac{dV_u}{dt} - h_u \frac{dm_x}{dt} - h_u \frac{dm_{l,b}}{dt} = m_u \sum_i h_i \frac{dY_i}{dt} + m_u c_p \frac{dT_u}{dt} + h_u \left(\frac{dm_x}{dt} - \frac{dm_{l,b}}{dt}\right) - p \frac{dV_u}{dt} - V_u \frac{dp}{dt}.
\]
\[(D.49)\]

Finally, the rate of change of the temperature in the unburned zone can be obtained by rearranging Eq. D.49,
\[
\frac{dT_u}{dt} = \frac{1}{m_u c_p} \left[\frac{dQ_u}{dt} + V_u \frac{dp}{dt} - m_u \sum_i h_i \frac{dY_i}{dt} + m_u c_p \frac{dT_u}{dt} + h_u \left(\frac{dm_x}{dt} - \frac{dm_{l,b}}{dt}\right) - p \frac{dV_u}{dt} - V_u \frac{dp}{dt}\right].
\]
\[(D.50)\]

**D.4.3 Conservation of volume and the ideal gas law**

Using the conservation of volume and \(pV = mRT\), the following can be obtained,
\[
\frac{dV}{dt} = \frac{dV_b}{dt} + \frac{dV_u}{dt} = \frac{1}{p} \left( R_b \frac{dm_b}{dt} + m_b \frac{dR_b}{dt} + m_b R_b \frac{dT_b}{dt} - V_b \frac{dp}{dt}\right) + \frac{1}{p} \left( R_u \frac{dm_u}{dt} + m_u \frac{dR_u}{dt} + m_u R_u \frac{dT_u}{dt} - V_u \frac{dp}{dt}\right).
\]
\[(D.51)\]
where \( R \) is the specific gas constant. The term \( dR/dt \) is usually assumed to be zero in combustion modelling, since there is insignificant variation in the composition of either the burned or unburned zone with respect to time. During autoignition, however, this assumption is not justified due to the rapid change in gas composition in the unburned zone, which results in a rapid change in the specific gas constant (see Figure D.1b). Therefore, the \( dR/dt \) term must be evaluated.

To start,

\[
R = \frac{\mathcal{R}}{\mathbb{W}}, \tag{D.52}
\]

where \( \mathcal{R} \) is the universal gas constant and \( \mathbb{W} \) is the mean molecular weight of the mixture. Differentiating this,

\[
\frac{dR}{dt} = \frac{\mathcal{R}}{\mathbb{W}} \frac{d(1/\mathbb{W})}{dt}. \tag{D.53}
\]

Recall the definition of \( \mathbb{W} \),

\[
\frac{1}{\mathbb{W}} = \sum_{i}^{N} \frac{Y_i}{W_i}, \tag{D.54}
\]

thus,

\[
\frac{dR}{dt} = \mathcal{R} \sum_{i}^{N} \frac{1}{W_i} \frac{dY_i}{dt}. \tag{D.55}
\]

Substituting Eq. D.55 into Eq. D.51,

\[
\frac{dV}{dt} = \frac{1}{p} \left[ R_b T_b \frac{dm_b}{dt} + m_b T_b \left( \mathcal{R} \sum_{i}^{N} \frac{1}{W_{i,b}} \frac{dY_{i,b}}{dt} \right) \right. \\
+ \left. m_b R_b \frac{dT_b}{dt} - V_b \frac{dp}{dt} \right] \\
+ \frac{1}{p} \left[ R_u T_u \frac{dm_u}{dt} + m_u T_u \left( \mathcal{R} \sum_{i}^{N} \frac{1}{W_{i,u}} \frac{dY_{i,u}}{dt} \right) \right. \\
+ \left. m_u R_u \frac{dT_u}{dt} - V_u \frac{dp}{dt} \right]. \tag{D.56}
\]
Substituting Eq. D.37 and D.50 into Eq. D.56, and rearranging yields,

\[
\frac{dp}{dt} = \left( V - \frac{R_b V_b}{c_p b} - \frac{R_a V_u}{c_p u} \right)^{-1} \left\{ -p \frac{dV}{dt} + \frac{R_b}{c_p b} \frac{dQ_b}{dt} + \frac{R_a}{c_p u} \frac{dQ_u}{dt} \right\} + \left( R_b T_b - R_u T_u + \frac{R_b}{c_p b} \sum_i Y_{i,f} (h_{i,f} - h_{i,b}) \right) \frac{dm_x}{dt} \\
- \left( R_b T_b \frac{dm_{l,b}}{dt} + R_u T_u \frac{dm_{l,u}}{dt} \right) + m_b T_b \left( R \sum_i \frac{1}{W_{i,b}} dY_{i,b} \right) + m_u T_u \left( R \sum_i \frac{1}{W_{i,u}} dY_{i,u} \right) \\
- \left( R_b V_b \sum_i h_{i,b} \dot{w}_{i,b} + R_a V_u \sum_i h_{i,u} \dot{w}_{i,u} \right) \right\} .
\]

(D.57)

\[
\frac{dp}{dt} = \left( V - \frac{R_b V_b}{c_p b} - \frac{R_a V_u}{c_p u} \right)^{-1} \left\{ -p \frac{dV}{dt} + \frac{R_b}{c_p b} \frac{dQ_b}{dt} + \frac{R_a}{c_p u} \frac{dQ_u}{dt} \right\} + \left( R_b T_b - R_u T_u + \frac{R_b}{c_p b} \sum_i Y_{i,f} (h_{i,f} - h_{i,b}) \right) \frac{dm_x}{dt} \\
- \left( R_b T_b \frac{dm_{l,b}}{dt} + R_u T_u \frac{dm_{l,u}}{dt} \right) + R \left[ V_b T_b \sum_i \dot{w}_{i,b} + V_u T_u \sum_i \dot{w}_{i,u} + T_b \frac{dm_x}{dt} \sum_i \left( \frac{Y_{i,f} - Y_{i,b}}{W_{i,b}} \right) \right] \\
- \left( R_b V_b \sum_i h_{i,b} \dot{w}_{i,b} + R_a V_u \sum_i h_{i,u} \dot{w}_{i,u} \right) \right\} .
\]

(D.58)

Finally, using the definitions of \( dY_{i,b}/dt \) and \( dY_{i,u}/dt \) from Eq. D.30 and D.46, Eq. D.57 can be rewritten,
Figure D.1: Modelled a) temperature and b) mean molecular weight versus time for the oxidation of isooctane in a constant-volume reactor (initial temperature = 900 K, initial pressure = 30 atm, adiabatic and stoichiometric). The sharp decrease of the mean molecular weight at approximately 0.006 second into the simulation is a result of autoignition. The kinetic mechanism from [117] (Version 3) was used.
Author/s: FOONG, TIEN MUN

Title: On the autoignition of ethanol/gasoline blends in spark-ignition engines

Date: 2013


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