Experimental Measurements of Ignition Delay Times of *Iso*-octane/*n*-Butanol Blend Mixtures in Rapid Compression Machine (RCM)

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Abstract

Among oxygenated alternative fuels, *n*-butanol is considered as a promising alternative biofuel which can partially (or fully) replace conventional transportation fuels currently in use. However, before *n*-butanol can be commercially utilised, its fundamental combustion characteristics need to be fully understood. In this work, the effect of adding *n*-butanol on autoignition property of *iso*-octane was studied. Measurements of ignition delay times for the two blends of *n*-butanol proportions of 30% and 50% by mole weight were made in a Rapid Compression Machine for stoichiometric mixtures at 2.0 MPa and temperature range 651-918 K. *n*-butanol increased ignition delay times of *iso*-octane at lower temperatures and hence acted as an octane enhancer, while at higher temperatures delay times were reduced. In the intermediate temperatures there was visually no difference in delay times between the two blends. Throughout the temperature range studied, the delay times of both blends were much closer to those of pure *n*-butanol which suggests that the combustion chemistry of *n*-butanol was dominant over that of *iso*-octane. These results have shown that *n*-butanol can enhance fuel octane rating and therefore can potentially improve thermal efficiency of SI engines, whilst CI engines can benefit from the reduced delay times at higher temperatures

Keywords: Ignition delay times, *iso*-octane, *n*-butanol, Rapid Compression Machine, Blending.

Introduction

Fossil fuels are still dominant sources of current world energy demands, with approximately 82% of world's energy consumption coming from fossil fuels (BP 2022), with approximately 40% used in the transportation sector (IEA 2021). However, heavy dependency of fossil fuels has increasingly come under scrutiny due to their associated negative effects on the climate change and due to their known viable sources becoming depleted at a faster rate than new ones being made.

This has led to an increase in research to find alternative methods to mitigate these effects. The two most viable options currently explored include development of new and efficient engine technologies such as controlled autoignition (CA) and Homogeneous Compression Charge Ignition (HCCI), and introduction of new alternative fuels which can partially or fully substitute the petroleum-based ones. Bio-derived alcohols such as ethanol and *n*-butanol have generated great interest as alternative fuels, due to their similarity in physical and chemical properties with conventional fuels,

making a possibility of being used in the current engines without modifications. Currently in the US, all gasoline engine vehicles can use a gasoline fuel blended with 10% by volume of ethanol (E10), with the likelihood of increasing proportions in the future (U.S. Energy Information Administration 2022). *n*-butanol on the other hand has properties even more closely matched to those of gasoline and thus offering a possibility of higher blending ratios without any adjustment in operating conditions. However, its uses have been less popular due to the high costs associated with its production. A few years back, new production techniques were introduced by Tashiro et al. (2013) which led to increased *n*-butanol production yields, using the same raw materials and hence lowered its production costs.

Characterisation of combustion properties of new alternative fuels is of vital importance before they can be commercially available. This will help to fully understand their behaviour at various conditions of pressure, temperature and concentration and therefore optimize their use in modern engines. One of the important fundamental fuel combustion property is autoignition.

Autoignition plays a vital role in combustion efficiency. It is a sudden exothermic heat release from the fuel, occurring without an application of external source after a delay time. It critically depends on pressure, temperature and mixture concentration. The phenomenon of "knock" in SI engines arises from the autoignition of the end gas, accompanied with a rapid rise and oscillatory pressures which can be very detrimental to the engine. Compression ratio in SI engines is knock limited, constraining fuel efficiency and reduction of CO_2 emissions. In controlled autoignition (CA) engines, the autoignition influences the smooth operation and drivability, especially under high load. Autoignition is usually characterised using the ignition delay time τ_i which is the time lapsed before the onset of the main combustion explosion.

Measurements of τ_i in engines or turbines would be very complex due to the continually changing conditions and the complex flow fields. Thus, to enhance fundamental understanding and interpretation, measurements are conducted under controllable conditions in relatively simple devices. Low pressure constant volume vessels, combustion bombs, and flow reactors have all been used. For the high-pressure engine condition, the most suitable devices are Rapid Compression Machine (RCM) and Shock Tubes (ST).

Even though interest in *n*-butanol as a viable alternative fuel is on the rise, fundamental experimental studies of ignition delay times in its pure state and blends is still scarce. Weber et al. (2011) measured τ_i of pure *n*-butanol in RCM for a temperature range of 675-925 K at pressures of 1.5 and 3.0 MPa and found that τ_i values decreased as temperature and pressure increased with lack of a negative temperature coefficient (NTC) and two stages ignition. Similar results were obtained by Heufer et al. (2011) who measured τ_i values of a stoichiometric mixture at higher pressures of 4.0 MPa in a temperature range of 770-1250 K. Black et al. (2010) used a shock tube at low pressures (0.1 MPa, 0.26 MPa and 0.8 MPa), high temperatures (1100 K-1800 K) and varying equivalence ratios (0.5, 1.0 and 2.0) which showed a decrease of τ_i values with increase in equivalence ratio and temperature for all compression pressures studied. Other researchers confirmed the trends explained above with expanded experimental conditions, including Zhu et al. (2015) using shock tube and Karwat et al. (2011) using RCM.

Studies of ignition delay times for simple *n*-butanol binary blends have been conducted by Zhang et al. (2011), Yang et al. (2013) and Zhang et al. (2013) who measured τ_i values of *n*-butanol/*n*-heptane mixtures at various conditions of pressures, temperatures and concentrations. Karwat et al. (2011) conducted speciation study and measured the intermediate species generated during combustion of *n*-butanol/*n*-heptane blends at 700 K and at 0.9 MPa. Kumar et al. (2015) also measured τ_i values of *n*-butanol blends with primary reference fuels.

Moreover, there have been several studies investigating the effects of *n*-butanol addition to the autoignition property of conventional commercial transportation fuels and surrogates in RCM from Agbro et al. (2017) and Gorbatenko et al. (2019).

To gain good fundamental understanding of the effect of adding *n*-butanol on ignition delay times of commercial gasoline, it is preferred to start with simple surrogates such as those conducted by Zhang et al. (2011), Kumar et al. (2013), Zhang et al. (2013), Zheng et al. (2013) and Xu et al. (2018). To the authors' knowledge these are the only existing studies of such blends. Commercial gasoline comprises approximately 25%-40% by volume *iso*-paraffins and thus in this work, measurement of ignition delay times for blends of *n*-butanol and *iso*-octane was studied using an RCM.

Materials and Methods
Rapid compression machine

A Rapid Compression Machine (RCM) is, essentially, a piston inside a cylinder. Its purpose is to rapidly compress a combustible mixture to a higher temperature and pressure at which its autoignition characteristics can be studied. As in the present work, such machines find application in the study of engine fuels because they are a reasonable representation of a single stroke compression ignited engine. Detailed information can be found in Bradley et al. (2015) and Agbro et al. (2017).

Mixture preparation

Fuel-air mixtures were prepared in a separate mixing chamber. The mixing chamber was first heated to a pre-determined temperature to ensure a test fuel would be fully vapourised. For most fuels tested in this work this temperature was typically 80 °C. This was followed by a purging of the mixing chamber to remove all residuals by flushing it with pressurised laboratory air for about 2 minutes. The chamber was then filled with laboratory air up to 0.2 MPa and finally evacuated to less than 0.002 MPa. This process was repeated twice using dry air to ensure that there was less than 0.01% residual gas from the previous mixture. The temperature within the chamber and volume of liquid fuel injected was pre-determined so that fuel partial pressure was less than its vapour pressure; this was done to ensure that the liquid fuel would fully vapourized.

The pre-determined liquid volume of fuel was injected into the mixing chamber under partial vacuum through a stainless steel Luer-lok inlet. After fuel injection, the increase in pressure (the fuel partial pressure) was measured and was typically found to be within +/- 0.0001 MPa of that expected from a partial pressure calculation. After fuel injection, the gaseous components, usually comprising various amount of N_2, CO_2, Ar and O_2 were carefully introduced into the mixing chamber using the high precision needle valves and the fuel mixture was left in the chamber for about 2 hours for thorough mixing before it was used.

Experimental conditions

Autoignition measurements for all fuels presented in this work were conducted at stoichiometric conditions with the end of compression pressure of 2.0 MPa and temperature range of 640 K to 941 K. For each condition tested, 3 to 5 repeats of experiments were performed. Measurements of total spread between maximum and minimum measured ignition delay times were made and presented by error bars, the standard deviation from mean value for each test was less than 10%. Dry air purging in the combustion chamber was made after every experimental run to ensure no residual gases from the previous experiment are present, the chamber was also cleaned with acetone after every mixture change to avoid soot deposition on the chamber walls.

Fuel blending was done by mole basis where 30% and 50% by mole of *n*-butanol was added to *iso*-octane and designated as I70 and I50 respectively. Table 1 summarize compositions of the blends and the conditions under which they were tested.

Table 1: Fuel composition and test conditions

	Constituents fuels		Fuel		Conditions	
	iso-octane	*n-butanol*	Designation	Ø	Pressure (MPa)	Temperature (K)
Fuel mole fraction	0.7	0.3	I70	1.0	2.0	650-926
Fuel mole fraction	0.5	0.5	I50	1.0	2.0	650-893

Definition of ignition delay time

In RCMs, ignition delay time τ is obtained from pressure records and it is defined as the duration from the end of compression (t = 0) when the piston reached top dead centre (TDC), to the point of maximum rate of pressure rise (i.e., maximum dP/dt) (Gallagher et al. 2008, and Gersen et al. 2010). Figure 1 illustrates the definition of ignition delay (τ) used in this study.
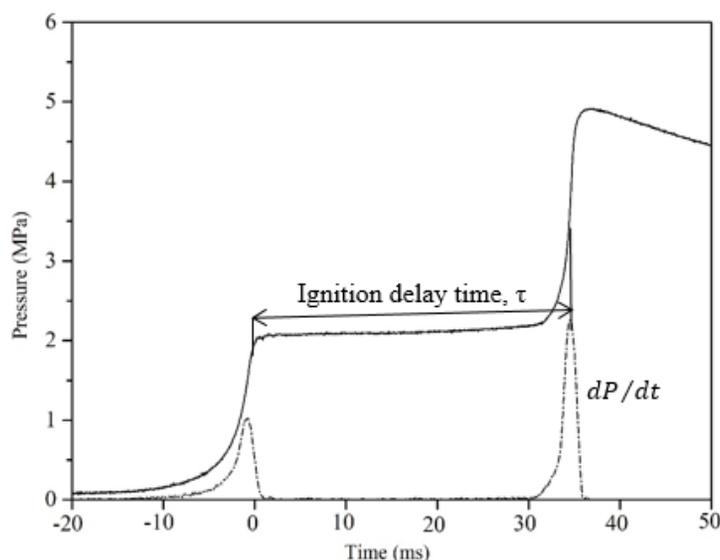
Figure 1: Definition of ignition delay time.

Results and Discussion
n-butanol

Figures 2 and 3 show the pressure records of *n*-butanol for stoichiometric (Ø = 1) and lean (Ø = 0.5) mixtures at different end of compression temperatures. For both equivalence ratios *n*-butanol shows only single stage ignition, with a near-linear change in τ, with no NTC, throughout the temperature range. The ignition delay time generally decreases with increase of temperature, while the leaner mixture has longer ignition delay times throughout the temperature range. A monotonic change in the slope of ln t is clear in Figure 4 for a stoichiometric mixture in the temperature range (705 K-725 K). This finding is similar to that obtained by Weber et al. (2011) and Heufer et al. (2011) and the results were also compared with a numerical and chemical kinetic model in our previous work in Agbro et al. (2015) and found to be in good agreement, particularly in the intermediate temperature range of 735 K-793 K. No ignition measurements were possible for the lean mixture at temperatures lower than 730 K due to difficulty in *n*-butanol evaporation.

Iso-octane

Shown in Figure 5 are measured RCM pressure records for stoichiometric *iso*-octane when compressed to a pressure of 2.0 MPa at different end of compression temperatures. Unlike *n*-butanol, at low to medium temperatures (650 K-802 K), the occurrence of two stages of ignition is evident in Figure 5, where the first stage is usually attributed to the occurrence of cool flames and the second stage to the main exothermic ignition. At higher temperatures (>900 K) a non- cool flame, single stage, main ignition is obtained. Figure 6 shows the corresponding ignition delay times derived directly from these pressure traces. The negative temperature coefficient (NTC) behaviour, where the reaction rates decrease with the increase of temperature, is seen in the medium temperature range (725 K-833 K). These results agree fairly well with those obtained by Griffiths et al. (1993), Fieweger et al. (1997), Westbrook et al. (1998) and Davidson et al. (2005)
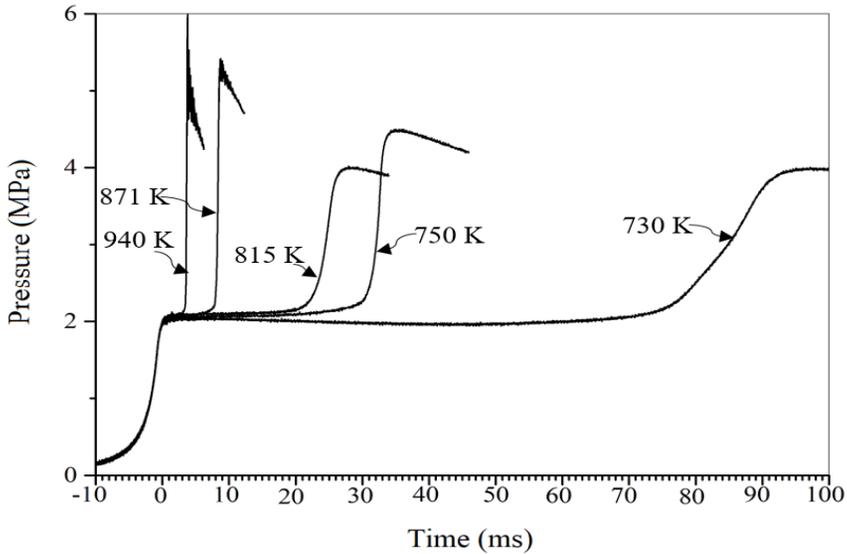
Figure 2: Pressure records for lean ($\emptyset = 0.5$) *n*-butanol at a compressed pressure of 2.0 MPa.
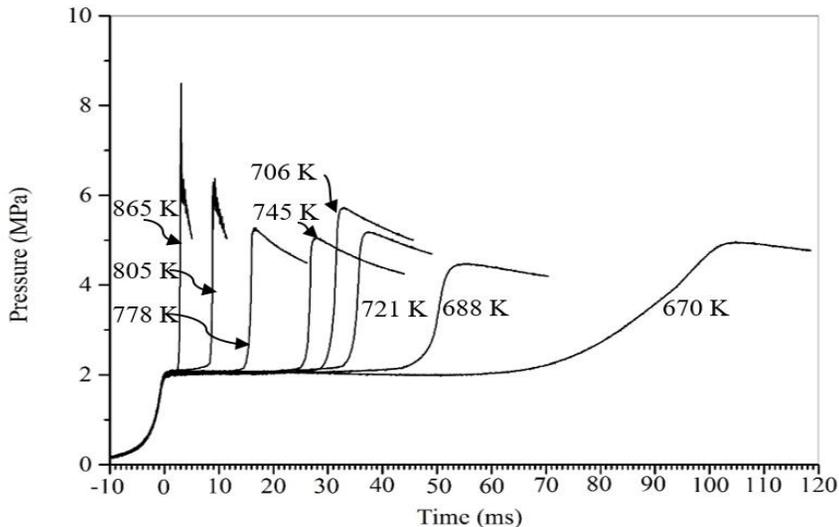
Figure 3: Pressure records for stoichiometric ($\emptyset = 1$) n-butanol at a compressed pressure of 2.0 MPa.
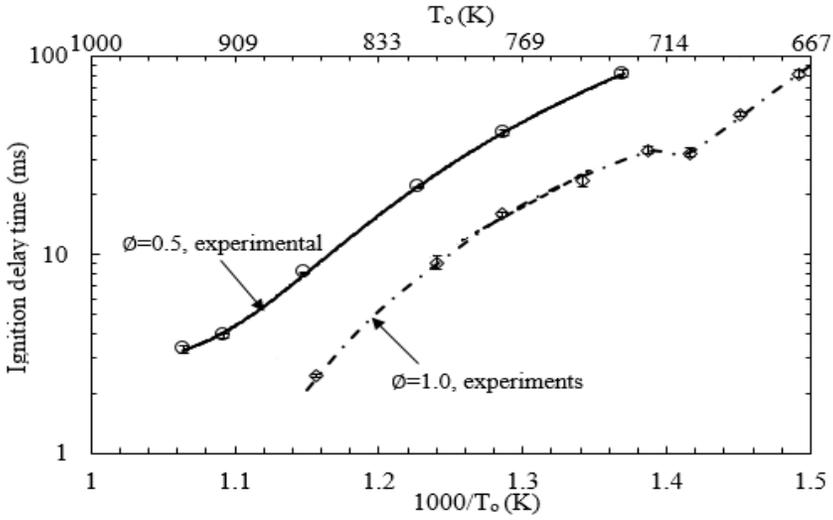
Figure 4: Ignition delay times vs inverse of temperature for pure *n*-butanol for stoichiometric and lean mixtures.
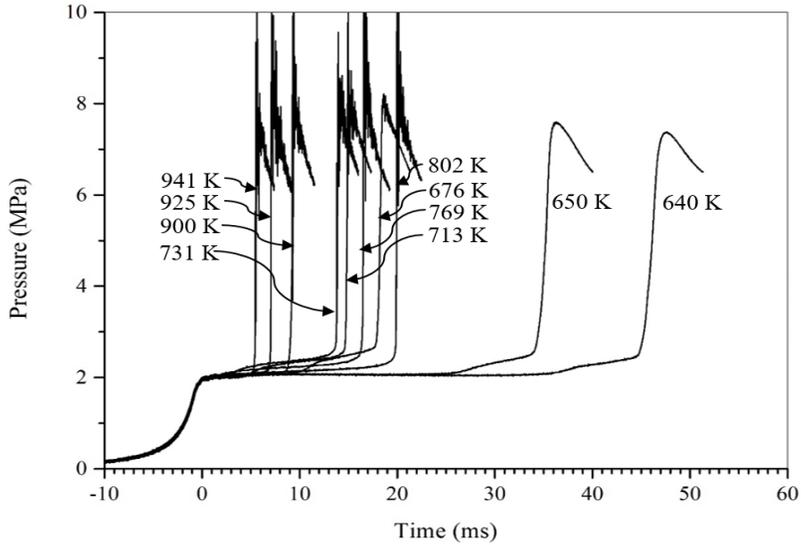
Figure 5: Pressure records for stoichiometric ($\emptyset = 1$) iso-octane at the end of compression pressure 2.0 MPa.
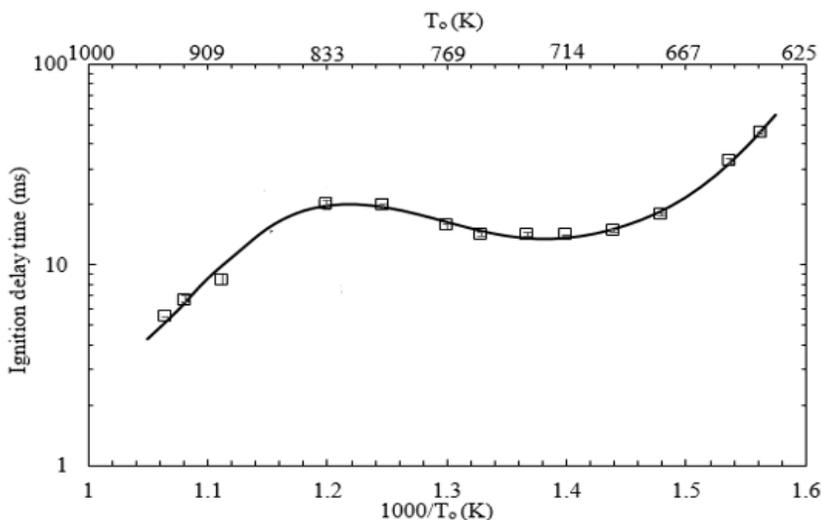
Figure 6: Ignition delay times for stoichiometric ($\emptyset = 1$) iso-octane at compressed pressure of 2.0 MPa.

n-butanol/iso-octane blends

Figures 7-9 show the experimental results for the *iso*-octane/*n*-butanol blends, all conducted at stoichiometric concentrations and a pressure of 2.0 MPa. The pressure traces show the occurrence of two stage ignition in the temperature range 685-835 K for I50 and 687-715 K for I70 and for both blends; the NTC strength of *iso*-octane is weakened with the addition of *n*-butanol. In general, at the higher temperatures the addition of *n*-butanol in the *iso*-octane mixture decreases the overall ignition delay time, while, at the lower temperatures it increases. This is due to the *n*-butanol delay times being lower than those of *iso*-octane at the higher temperatures, while they are higher at lower temperatures. The change of delay time due to the addition of *n*-butanol is not linear, Figures 10-12 summarise the changes in delay time, as a function of the proportions of *n*-butanol in the blend mixture, at different temperatures.

At the higher temperatures (>760 K), the addition of *n*-butanol decreases the delay time, and the trend can be presented by a second order function, as seen in Figures 10-11. The middle temperature range, between 750 K-660 K in Figure 11, shows an interesting behaviour where the addition of *n*-butanol increases the delay time but there is visually no difference in τ values between I50 and I70, whereas at the lowest temperature (660 K) there is a significant increase.

Non-linearity of ignition delay times in these blends can be attributed by the interactions between the fuels and the small radical pool of OH, H and HO_2 formed as intermediate species during fuel oxidation. The reactions of these radicals with the constituent fuels in the blends control the rates at which fuel is consumed at various conditions. At different temperatures, different reactions become dominant and therefore controls the main ignition reaction within the mixture. Brute force sensitivity analysis is usually conducted to assess the dominant reactions at different temperatures, the studies by Weber et al. (2011), Zhang et al. (2013), Kumar et al. (2015), Agbro et al (2017) and Gorbatenko et al. (2019) of pure *n*-butanol and different *n*-butanol based blends have shown that at the lowest temperatures, *n*-butanol reaction in the blends was dominant even when it has lower concentration. At lower temperatures, the main reaction is the H-abstraction via OH from the α-carbon site:

$$CH_3CH_2CH_2CH_2OH + \cdot OH \rightarrow$$
$$CH_3CH_2CH_2C^{\cdot}HOH + H_2O \qquad (1\alpha)$$
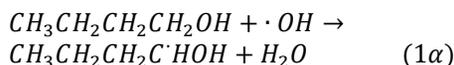
This reaction has ignition inhibiting role. The importance of H abstraction by OH from the α-site at low temperatures leads to the octane enhancing influence of *n*-butanol under these conditions as seen in Figure 12. At higher temperatures the overall rate of reaction is more sensitive to the concentration of *n*-butanol in the blend, with higher *n*-butanol concentration reduce ignition delay times and hence does not enhance octane rating of *iso*-octane. In these conditions the dominant reaction suggested in Kumar et al. (2015) for *n*-butanol/*iso*-octane blends and Gorbatenko et al. (2019) for *n*-butanol/gasoline blends as the H abstraction from the α-site by HO_2, a reaction which promotes reactivity because the H_2O_2 formed decomposes to form OH radicals.

The low temperature range in this study is within the same range of the operating temperatures of Spark Ignition (SI) engines and since one of the performance limitation of the SI engines is the occurrence of knock, then adding *n*-butanol to the conventional fuels will be beneficial by increasing the fuel knock temperature and hence enable the engine to potentially run safely with increased power at higher temperatures and pressures. As where for compression engines, whose operating temperatures is within the high temperature range of this study, the reduced ignition delay times resulted from *n*-butanol addition will be beneficial in enabling the engines to potentially attain similar power at a reduced pressure and/or temperature, this means the engines can use reduced compression ratio to attain the same power using conventional diesel fuel.
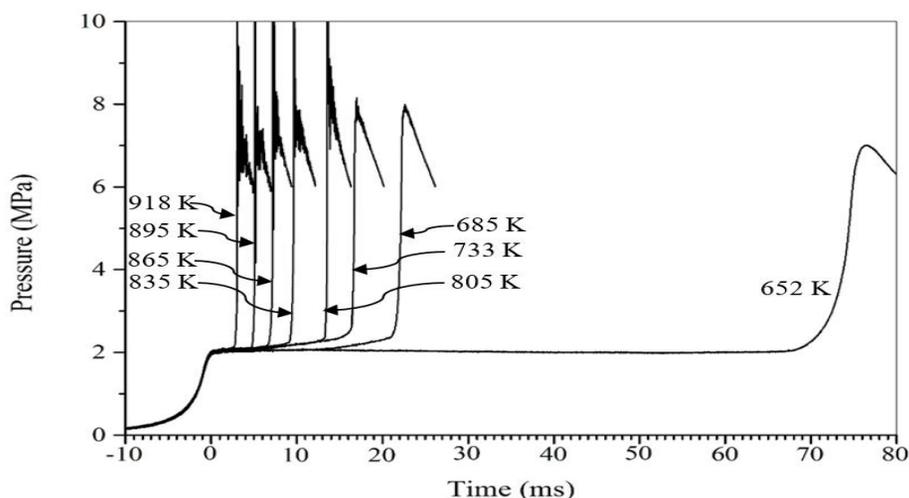
Figure 7: Pressure records for stoichiometric I70 blend at a compressed pressure of 2.0 MPa.
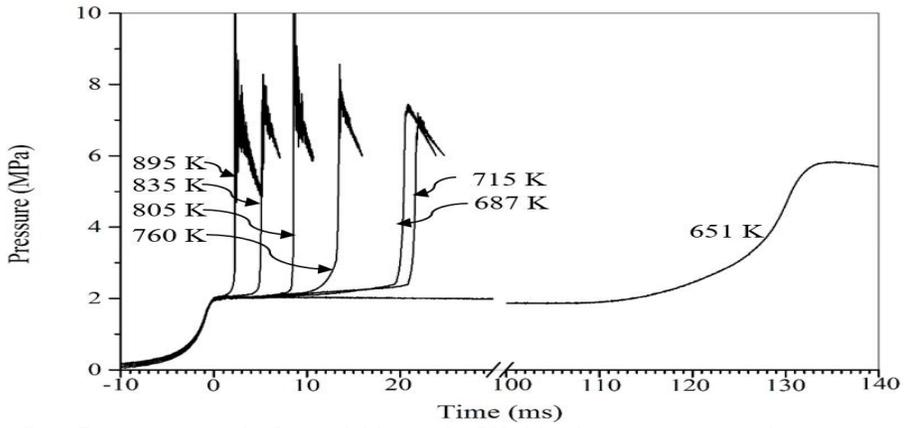
Figure **8**:   Pressure records for stoichiometric I50 blend at a compressed pressure of 2.0 MPa.
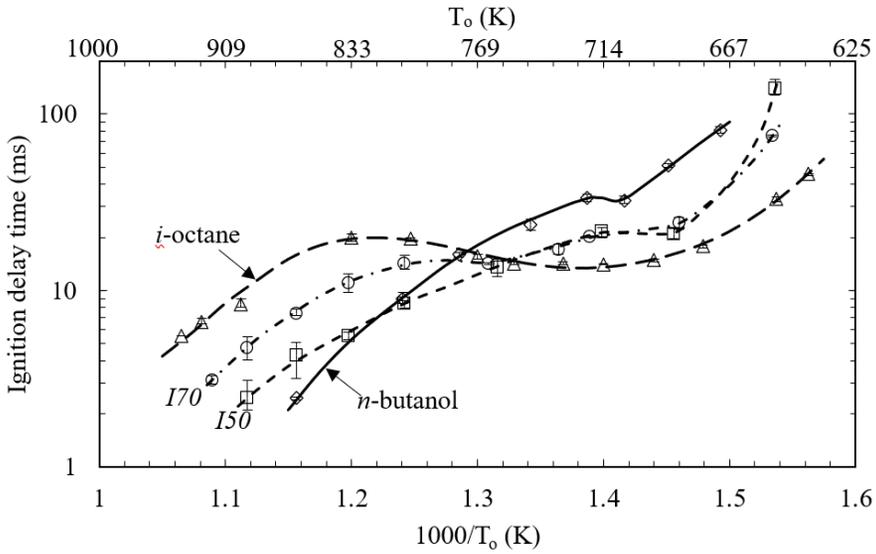
Figure 9:   Ignition delay times for stoichiometric pure iso-octane, n-butanol and their blends I70, I50 at a compressed pressure of 2.0 MPa.
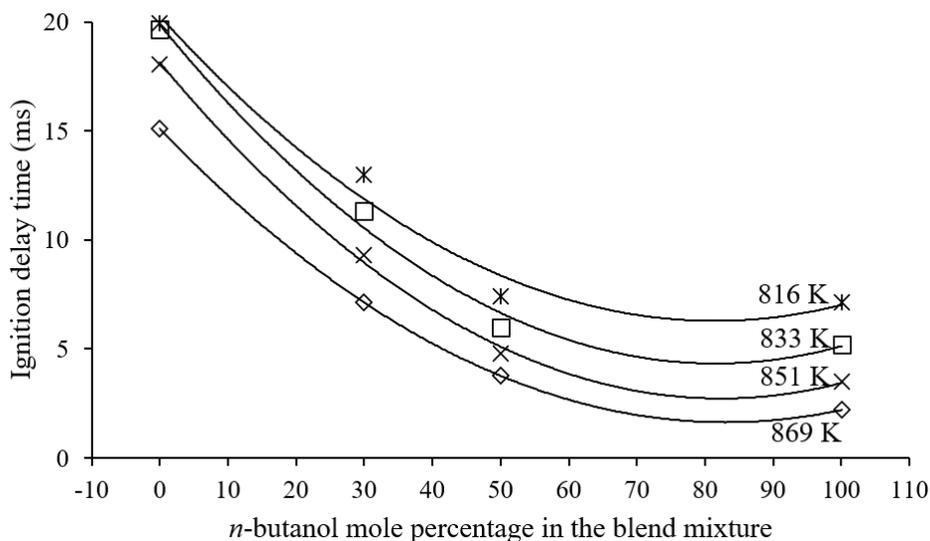
Figure 10: Ignition delay times of iso-octane/n-butanol at Ø = 1.0 as a mole % of n-butanol in the blend mixture, at a compressed pressure of 2.0 MPa, in the temperature range (816 K-869 K).
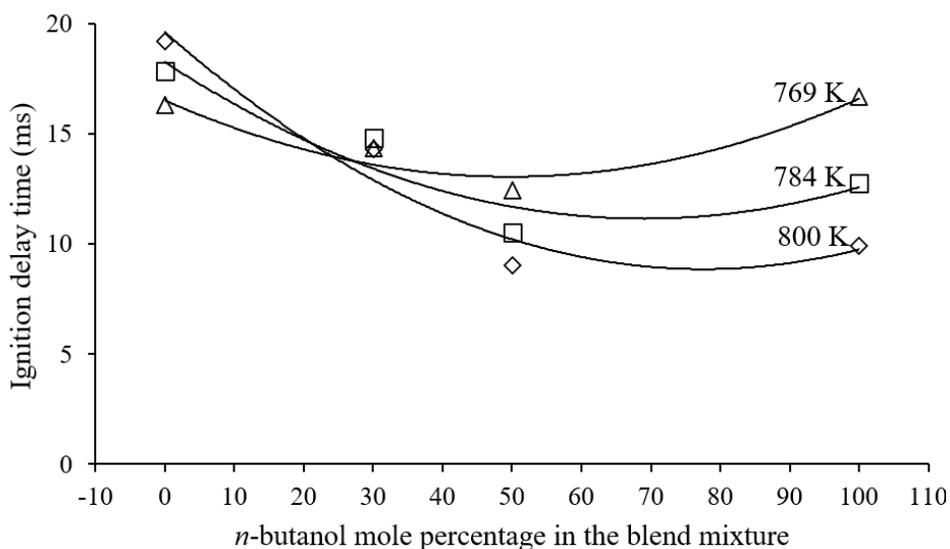
Figure 11: Ignition delay times of iso-octane/n-butanol at Ø = 1.0 as a mole % of n-butanol in the blend mixture, at a compressed pressure of 2.0 MPa, in the temperature range (769 K-800 K).
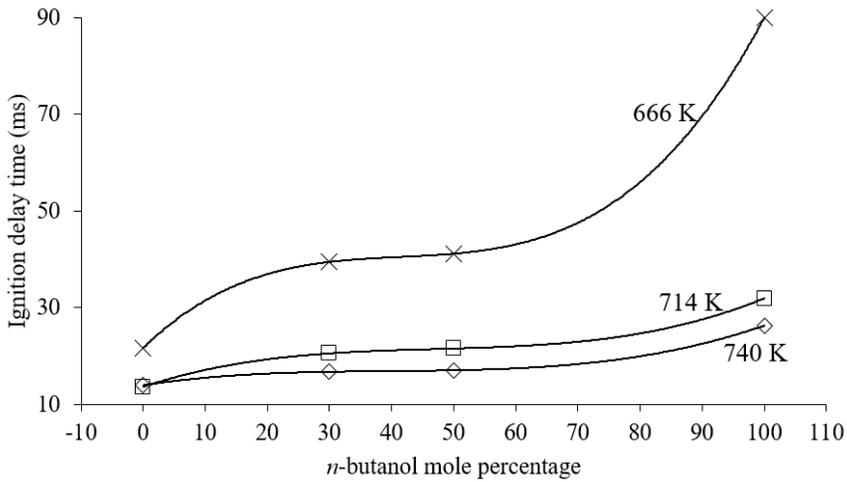
Figure 12: Ignition delay times of iso-octane/n-butanol at $\emptyset = 1.0$ as a mole % of *n*-butanol in the blend mixture, at a compressed pressure of 2.0 MPa, in the temperature range (666 K-740 K).

The effect of pressure on I50 and I70 blends was also investigated using University of Cape Town (UCT) RCM. Measurements were made at 2.0 MPa and 4.0 MPa and results presented in Figures 13 and 14. For both blends, pressure increase results in shorter τ values. The NTC strength is also reduced with pressure increase. Using these results, pressure exponent, *n*, was calculated, for each blend, based on the relation $\tau \alpha P^{-n}$, and it was found that *n* values changes with temperature, with higher values of *n* obtained in the intermediate range and fairly constant values at higher and lower temperatures, as shown in Figure 15.
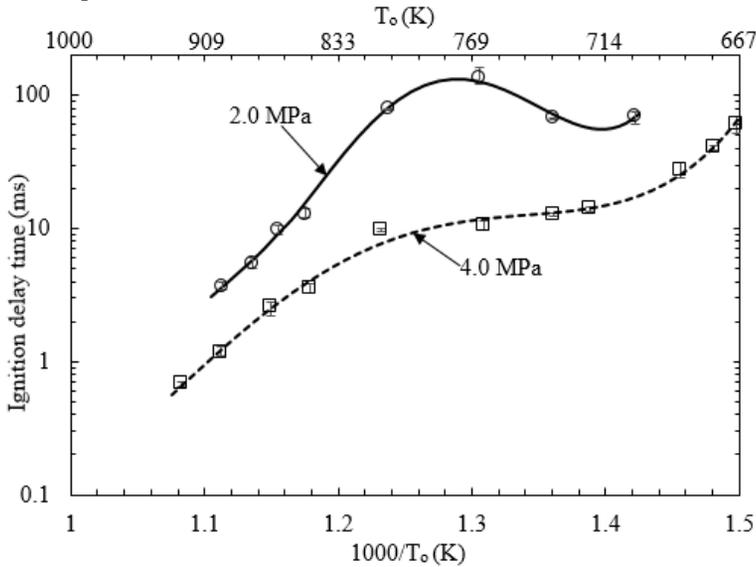
Figure 13: Ignition delay times for stoichiometric blend I70, at a compressed pressure of 2.0 MPa and 4.0 MPa.
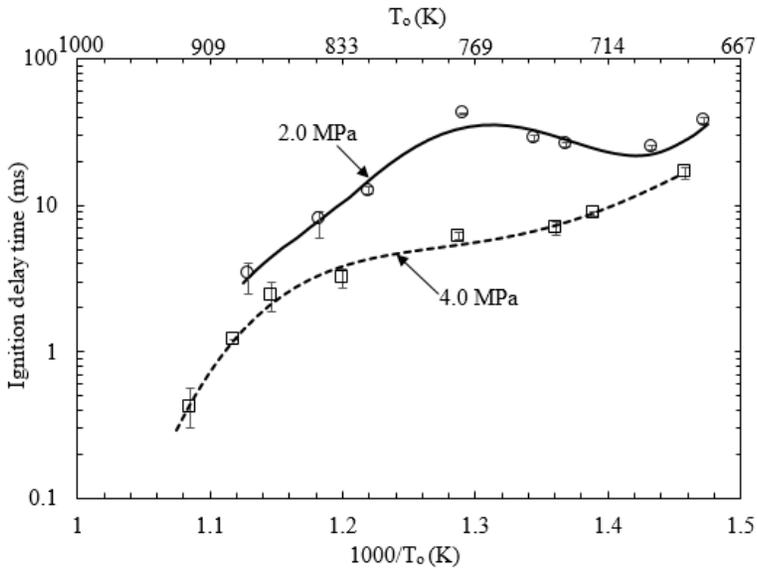
Figure 14: Ignition delay times for stoichiometric blend I50, at a compressed pressure of 2.0 MPa and 4.0 MPa.
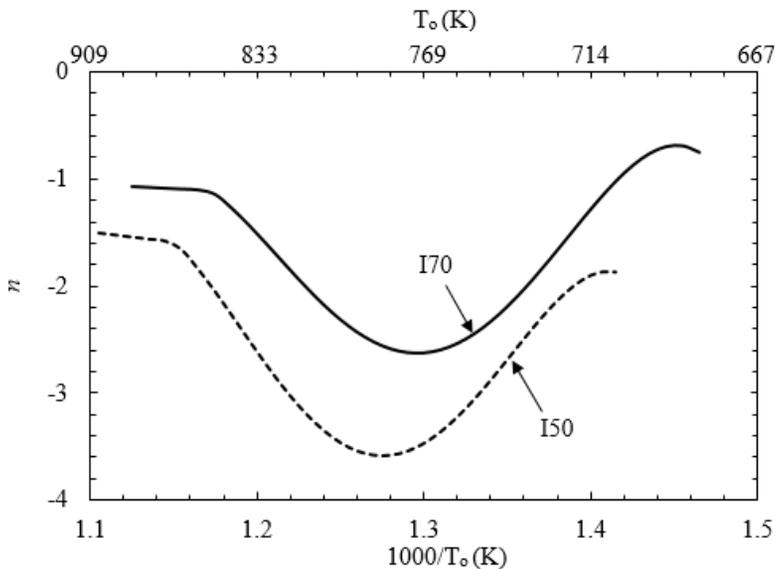
Figure 15: Values of pressure exponent, n, for stoichiometric blends I70 and I50 and different compression temperatures.

Conclusion

The two constituent fuels have different autoignition behaviours at different temperatures. *iso*-octane has 2 stages ignition at the intermediate temperature range with a characteristic NTC region, whilst *n*-butanol has a more Arrhenius like behaviour with slight drop in slope in the lower temperature region. At lower temperatures n-butanol acted as octane booster increasing ignition delay times of iso-octane while at high temperatures the effect was reversed. Even though two stage ignition was noted for both blends at the intermediate temperature range, their NTC regions were weaker compared to that of *iso*-octane. This effect was more pronounced with the increase in pressure. Almost no effect on ignition delay times was

seen for different *n*-butanol proportions in the low to intermediate temperature range.

Further investigation is warranted with more variety of experimental conditions to check if the observed trends will prevail.

Acknowledgements

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