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Comparative investigation of ignition behavior of butanol isomers using constant volume combustion chamber under diesel-engine like conditions

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ABSTRACT

Butanol is a sustainable carbon-neutral fuel that can be derived from a variety of biomass resources. It can be potentially be used as an alternative fuel to blend with diesel to decrease greenhouse gas and pollutant emissions. In this paper, three butanol isomers (n-butanol, tert-butanol, and iso-butanol) are blended with diesel in various volume ratios. The combustion characteristics of butanol isomers are experimentally determined in a constant volume vessel under engine-like conditions. The effects of blend ratio, chamber temperature, and chamber pressure on ignition delay and combustion process are investigated. It is shown that the ignition delay decreases at high temperature and at low butanol blend ratio regardless of the isomer type. The combustion characteristics of butanol/diesel blends differ from neat butanol. Both low temperature heat release (LTHR) and high temperature heat release (HTHR) are observed for the three butanol isomers/diesel blends. Under current operating conditions, the ignition delay of three butanol isomer/diesel blends is ordered according to iso-butanol > n-butanol > tert-butanol. Notwithstanding its higher octane number, tert-butanol/diesel blends show the fastest LTHR and thereafter the shortest ignition delay. This is because of the absence of H atom on the alpha carbon of tert-butanol, which contributes to consumption of OH radicals. Consequently, oxidation of diesel is less suppressed. However, the HTHR of tert-butanol/diesel blends is much slower than that of n-butanol/diesel. At 80% blend ratio, a higher chamber pressure is required to improve the reactivity and ignition. Overall, the low reactivity of butanol is beneficial to be applied in diesel engines to increase the fuel/air mixing time so as to attenuate soot emissions.

1. Introduction

Carbon neutrality is a hot topic worldwide for the sake of reducing greenhouse gas and mitigating climate change. Many countries and associations have announced by the year 2060 or even earlier to become carbon neutral (or even carbon negative) [1]. To achieve these goals and implement sustainable development, renewable electricity, non-carbon-based fuels (hydrogen, ammonia), and carbon-neutral fuels are three major technical routes [2]. For road-transportation and shipping sectors, applying carbon-neutral fuel is a more applicable path to reduce the dependence on fossil fuel without tremendous modification on existing power generation devices and infrastructures. Hence, much research has been done regarding the production of bio-fuels via a variety of biomass sources (first, second, and third-generation biofuels) [3] and related costs [4].

Bio-derived butanol is one of the carbon-neutral fuels which could be potentially used in internal combustion (IC) engine. Due to its low reactivity and oxygenated chemical structure, butanol has been shown to contribute to an improved mixing of the fuel and air so that the local equivalence ratio is reduced and particulate matter emissions are expected to decrease [5,6]. Unlike ethanol, which due to its polarity does not blend well with diesel [7], butanol does. It can be used as a drop-in...
fuel to blend with diesel in a wide range of ratios and can be used as an alternative for a pure fossil fuel. Butanol has four isomers: the straight-chained n-butanol, sec-butanol, and the branched chained iso-butanol and tert-butanol. The two straight-chained isomers are reported to show higher reactivity than branch-chained isomers [8,9], where most literature and recent studies show that n-butanol is the most reactive isomer [10-12]. The reaction mechanism of neat n-butanol and n-butanol/n-heptane blends have been investigated in numerical studies as well [13]. Particularly, the combustion and emission characteristics when used in IC engines have drawn researchers’ interests. Compared with other oxygenated fuels, the simple fuel structure of butanol also reduces the formation of soot precursors [14]. Moreover, butanol is very suited for advanced combustion concepts such as homogeneous charge compression ignition (HCCI) [15], partially premixed combustion (PPC) [16], and reactivity controlled compression ignition (RCCI) [17,18] to achieve ultra-high efficiency and low emissions.

Butanol will likely serve as a component fuel and blended with fossil fuel instead of replacing fossil fuels completely in near future. Therefore, it is necessary to investigate the combustion property of butanol fuel blends. Li et al. [19] investigated the performance and emissions of a gasoline direct injection (GDI) engine fueled with gasoline/butanol blends. Each isomer was tested at a blend ratio from 10% to 50%. The tests were performed to achieve the maximum break torque (MBT). It was reported that both particle number concentration and mean particle diameter decreased at high butanol ratios. Tert-butanol and iso-butanol cases tended to show higher smoke emissions than n-butanol and iso-butanol cases. A published study conducted by Mack et al. [20] compared neat n-butanol and iso-butanol in an HCCI engine in a wide range of intake pressures and equivalence ratio. The results showed that both isomers presented single-stage ignition behavior and similar combustion stability. Also, the emissions of two butanol isomers were in the same range as gasoline. However, iso-butanol was reported to be more resistant to knock than n-butanol. The author claimed that butanol was suitable fuel in HCCI engines, either in neat form or blended with gasoline. The experiments conducted by Karabektas et al. illustrated the utilization of iso-butanol/diesel in a naturally aspirated four stroke direct injection diesel engine at full-load conditions at the speeds between 1200 and 2800 RPM in steps of 200 [21]. Up to 20 vol% iso-butanol blends were applied. Due to the lower energy density of iso-butanol, it was shown that both engine brake power and brake thermal efficiency decreased at high iso-butanol blend ratio. Though NOx and CO emissions decreased, HC emissions increased considerably compared to that of diesel. Xia et al. [22] investigated butanol isomers/diesel dual-fuel combustion in a compression-ignition (CI) engine. N-butanol, sec-butanol, and iso-butanol were port-injected into the intake manifold while diesel was directly into the cylinder. The tests were performed at 2250r/min, the loads were swept from 25%, 50%, 75%, and 100%. It was shown that n-butanol ignition was easier than that of sec-butanol and iso-butanol. Besides, it showed fast combustion, more isochoric, compared to the other isomers. Consequently n-butanol yielded higher NOx emissions but less HC and CO emissions compared to sec-butanol and iso-butanol. Han et al. [23] blended up to 70 vol% of n-butanol with n-heptane to achieve PPC combustion at medium loads on a heavy-duty (HD) diesel engine. Three injection strategies were compared in terms of engine efficiency, stability, and emissions. It was reported that the pilot/main injection strategy showed the highest efficiency and lowest emissions compared to the single and main/post injection strategy. In addition, the authors claimed that a higher blend ratio is necessary to reduce the mixing time and reduce the soot emissions further. Nevertheless, a tradeoff might occur since the high blend ratio tends to show too low reactivity for low load operation. Misfire and cold start can be crucial issues. Thus, inlet heating, inlet boosting, and double injection strategies were investigated to improve the load performance of a HD diesel engine [24]. The results indicated that double injection strategy showed clear advantages in decreasing pressure rise rate (PRR) and peak pressure. And up to 49% indicated efficiency can be achieved. Furthermore, butanol isomers have been used as port injection fuel in a RCCI approach. Han et al. [10] reported that butanol RCCI can be operated from 4 to 12 bar with higher than 50% indicated efficiency and Euro-VI complaint engine-out NOx/soot emissions relieving the need for an aftertreatment system. The load range was limited by PRR and ringing intensity. Therefore, double injection can be used without consuming extra energy from the engine itself. All these engine tests have proven that butanol shows great advantages in decreasing engine-out particulate matter (PM) and NOx emissions and achieving high efficiencies simultaneously.

Though, engine tests can be more intuitive to investigate butanol utilization in real-life applications. The combustion process cannot be explicitly described due to fact that the ambient conditions (temperature and pressure) in an engine are closely coupled and vary throughout the process. The constant volume combustion chamber (CVCC) technique on the other hand is an easier way to investigate the effects of ambient conditions on the combustion process. The chamber condition can be set to mimic the conditions of an engine after the compression stroke. So that the effects of parameters like (ambient pressure, temperature, injection pressure, oxygen concentration, etc.) on ignition delay (ID), can be isolated and both quantitatively and qualitatively investigated. In [25], n-butanol was blended with diesel in various ratios and tested in a CVCC. It was shown that ignition delay increases as the n-butanol content increases and decreases at high chamber temperature. Importantly, low temperature heat release (LTHR) becomes remarkable at high blend ratio cases and shortens the ignition delay. The effect of n-butanol replacement by iso, sec, or tert-butanol on the autoignition reactivity of diesel and biodiesel/butanol blends (the total alcohol content is 40 vol%) was analyzed by Hernandez et al. [26]. The study was performed in a CVCC under different initial temperatures (535 °C, 600 °C, and 650 °C) and n-butanol substitutions. Results showed that the partial substitution of n-butanol by tert-butanol improved the reactivity of blends while iso-butanol and sec-butanol decreased the reactivity of the blends. This trend was corroborated by chemical kinetic simulation and can be explained by the different consumption rates of active radicals from the butanol isomers. Further insights into the autoignition behavior of n-butanol in a Waukesha Fuel Ignition Tester (FIT) and a HCCI engine are provided by Baumgardner et al. [27]. In their experiments, n-butanol and iso-octane were blended with n-heptane up to 100 vol% respectively. The results further showed that n-butanol blends behaved differently than primary reference fuel (PRF) blends when comparing the autoignition behavior at different the blend ratios. The authors also compared the HCCI and FIT experimental results against single and multizone models with detailed chemical kinetic mechanisms. It was concluded that the FIT instrument was a valuable tool for analysis of high pressure, low temperature chemistry, and autoignition for future fuels in advanced combustion engines. In [28], butanol isomers were added to two gasoline surrogate fuels, primary reference fuels (PRF) and toluene primary references fuels (TPRF), and tested in a CVCC facility at various ambient temperatures (840–920 K). The study revealed that butanol addition extended the ignition delay and burn duration of two surrogate fuels. And the ignition delay changed according to the sequence iso-butanol > sec-butanol ~ n-butanol > tert-butanol. The authors attributed the shortest ignition delay of tert-butanol to the earliest first-stage combustion. Liang et al. [29] investigated autoignition of n-heptane and butanol isomers (n-butanol, sec-butanol, and iso-butanol) blends in a CVCC. It was reported that the autoignition tendency of binary fuel blends decreased at high butanol fraction. And the autoignition inhibition effects of butanol isomers on n-heptane were in the order of iso-butanol > sec-butanol > n-butanol. The results also showed that both high chamber temperature and high pressure shortened the ignition delay and combustion delay. In particular, the heat release peak at fuel-lean conditions increased at high temperature cases. The ignition delay, combustion delay, peak pressure, and peak heat release rate were monotonically promoted as the equivalence ratio increases from 0.17 to 0.9.
The above literature overview shows the potential utilization of butanol as an alternative fuel in IC engines. Although there is published work on the ignition delay and combustion process of butanol in CVCCs, they paid less attention to cover the heat release differences of neat n-butanol and n-butanol/diesel blends. And only limited number of papers focus on butanol isomers with high blend ratios. Thus, there is still need for a dedicated experimental investigation to bridge the gap and address the combustion characteristics and reactivity difference of butanol isomers/diesel blends. This paper deals with these blends' combustion process in a CVCC, named the combustion research unit (CRU [30]). Three butanol isomers (n-butanol, tert-butanol, and iso-butanol) are blended with diesel from low to high volume ratio and tested in various conditions. The effects of chamber temperature, and chamber pressure are compared for n-butanol, iso-butanol, and tert-butanol. More importantly, the effects of the butanol addition on the heat release mode are evaluated.

2. Methodology and apparatus

In this work, a combustion research unit (CRU) based on the well-established CVCC technology is used to test the combustion process of butanol isomers/diesel blends. Fig. 1 shows a schematic of CRU setup. The combustion chamber can be charged with a mixture of synthetic air and pure nitrogen. The two gases are supplied by two external pressured gas bottles. Therefore, the oxygen concentration can be regulated by the ratio of these two gases. In the CRU, the combustion chamber is heated by the electric heaters around the chamber wall and the injector is cooled by water. The chamber pressure and temperature can be adjusted from 10 to 55 bar and from 300 °C to 580 °C respectively. This setup has a flexible modular design, the CRU is built of components and sub-systems (injection system and optical accessibility) that can be adapted to the specific research requirements. It is equipped with an industry-standard common rail injection system. Specifically, a direct injector from Bosch (Type: CRIP2) is used for the direct injection. It has an umbrella angle of 158°, sac volume of 0.23 mm³, and 7 nozzle holes (nozzle hole diameter: 0.139 mm). More detailed information about the instrument can be found in [5,25]. Fuel pressure can be boosted up to 1700 bar by a high-pressure pump. The specific parameters and related accuracies can be found in Table 1. During the operation, fuel is directly injected into the pressurized and heated combustion chamber, where it mixes with the hot air and ignites. The pressure trace of the combustion chamber after injection is automatically recorded for 47 ms and saved by the software control system. A typical pressure trace is shown in Fig. 2. The start of combustion (SOC) is determined as the time when the pressure reaches a level of 0.2 bar above the initial chamber pressure, which is consistent with the definition in the ASTM D7668-17 standard. The end of combustion (EOC) is defined by the time when 95% of maximum pressure is reached. Accordingly, the ignition delay (ID) can be calculated as the period from the start of injection (SOI) to SOC. Burn duration (BD) can be calculated as the time interval between SOC and EOC. The rate of heat release (ROHR) can be

**Table 1**

CRU basic specifications.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Range</th>
<th>Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chamber volume</td>
<td>475 [cm³]</td>
<td>Ref ± 1 °C for 150 s</td>
</tr>
<tr>
<td>Chamber temperature</td>
<td>300-580 [°C]</td>
<td>Ref ± 3.0 bar</td>
</tr>
<tr>
<td>Chamber pressure</td>
<td>10-60 [bar]</td>
<td>Ref ± 3.0 bar</td>
</tr>
<tr>
<td>Injection duration</td>
<td>0-2 [ms]</td>
<td>Ref ± 3.0 bar</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic overview of the combustion chamber system (Reproduced with permission from Fueltech).
calculated by Equation (1) based on the first law of thermal dynamics, where $V$ is the volume of the combustion chamber and $dp/dt$ is pressure rise rate calculated from chamber pressure (0.02 ms). The specific heat ratio $\gamma$ can be estimated from the average composition and $T$. However, in the constant volume setup, the ROHR is nearly directly proportional to the pressure rise rate (in fact the pre-factor $\frac{1}{\gamma}$ varies only slightly since the total pressure rise is rather limited). Therefore, a ROHR is not included and only the pressure rise rate profiles are shown in the paper.

$$\text{ROHR} = \frac{1}{\gamma} \cdot V \cdot \frac{dp}{dt}$$

(1)

Of the fuels used in this study, n-butanol (purity > 99.5%) is supplied by JBC solutions, and iso-butanol (>99%) and tert-butanol (>99%) are from Sigma-Aldrich. Diesel is the commercially available EN590. Sec-butanol is excluded in this study for its similar reactivity as n-butanol [31]. The major properties of the tested fuels are shown in Table 2. The butanol isomers are blended with diesel in various volume ratios from 0 to 100% in steps of 20% respectively. Due to the reactivity difference, only neat n-butanol (DN100) can be tested at 580 °C from 30 to 50 bar while the tert-butanol and iso-butanol can only be tested up to 80 vol%.

The n-butanol/diesel blends are named DN20-DN100, tert-butanol/diesel blends are named DT20-DT80, and iso-butanol/diesel blends are named DI20-DI80. The number in the abbreviation refers to the volume percentage. To reduce personal error, all the binary fuel samples are splash blended by the same operator. They all show good stability after stored for >30 days, this has been illustrated by many studies [32,33].

![Fig. 2. Chamber pressure as a function of time. A graphical interpretation of ID and BD is included.](image1)

![Fig. 3. Samples of tert-butanol/diesel blends. State after 30 days.](image2)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>CN</th>
<th>RON</th>
<th>LHV[MJ/kg]</th>
<th>Melting point</th>
<th>Boiling point</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butanol</td>
<td>15.92</td>
<td>98</td>
<td>33.08</td>
<td>-90 °C</td>
<td>117.7 °C</td>
<td><img src="image3" alt="n-butanol structure" /></td>
</tr>
<tr>
<td>iso-butanol</td>
<td>NA</td>
<td>113</td>
<td>33.11</td>
<td>-108 °C</td>
<td>108 °C</td>
<td><img src="image4" alt="iso-butanol structure" /></td>
</tr>
<tr>
<td>tert-butanol</td>
<td>NA</td>
<td>105</td>
<td>32.57</td>
<td>25.7 °C</td>
<td>82.4 °C</td>
<td><img src="image5" alt="tert-butanol structure" /></td>
</tr>
<tr>
<td>EN590</td>
<td>51</td>
<td>NA</td>
<td>42.9</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

a [11].
No phase separation is noticed after the fuel blends are stored for 30 days. It is worth noting that the melting point of tert-butanol is 25.7 °C and it is a crystalline solid at room temperature. It was heated above the melting point so that it could be blended with diesel. Fig. 3 shows the examples of the thus acquired blends of tert-butanol/diesel and no phase separation or re-solidification is observed at room temperature.

The investigation starts with a chamber temperature sweep (460 °C to 580 °C), where all butanol isomers/diesel blends are tested at fixed chamber pressure (30 bar). For the blend ratio of 80 vol%, the reactivity of fuel blends is too low even at 580 °C (highest possible currently) and the chamber pressure was increased from 30 to 55 bar. These specifically selected chamber pressures and temperatures are to mimic the idle and low load engine conditions, where misfire and high cyclic variations tend to occur when fuel blends with moderately high research octane number (RON) are used in advanced more pre-mixed combustion concepts. During the tests, the fuel pressure was set as 1500 bar and a constant injection duration of 1.5 ms was applied throughout the tests. When a non-diesel fuel is to be tested, both the fuel line and injection system are flushed by diesel to prevent corrosion in the rubber parts and seal rings of CRU system by the end of the test day. When a new batch of fuel is to be measured, old fuel from the previous sample is bled off and up to 13 trial injections are performed to ensure only the new batch fuel is tested. Furthermore, each measurement consists of 8 injections where the first three injections are dummy tests and dismissed automatically by the CRU software, only the last 5 injections stored and analyzed. The results presented in Section 4 are the assembled average of each measurement. An error bar is added in the in the ignition delay curves. It can be seen that the error is minor, indicating good repeatability of the measurements. An error bar is not included in the pressure and pressure rise rate profiles for the sake of clarity.

3. Results and discussions

3.1. Effects of chamber temperature

Fig. 4 compares the ID of butanol isomers blends at various chamber temperatures and blend ratios. After discharged through injector nozzle hole, the liquid fuel breaks up into ligaments, small droplets and penetrates into the ambient hot air. The entrainment of ambient hot air leads to fuel evaporation such that it promotes the mixing process. This often termed ‘physical ignition delay’ decreases when the chamber temperature is higher. In addition, temperature is one of the most crucial factors in the combustion process as the chemical reactions depend exponentially on it. Therefore, the increased temperature enhances the evaporation and thus mixing (physical ignition delay) and the reaction rates (chemical ignition delay). It can be seen in Fig. 4 that ID decreases as
chamber temperature increases regardless of the butanol isomer type and blend ratio. And the slope of ID profiles decrease at elevated temperature, except for DI80 case. It is interesting to find that the decrease of the ID for all temperatures follows the ordering: iso-butanol > n-butanol > tert-butanol. Moreover, the ID differences between iso-butanol and n-butanol seem to be insignificant up to a 40 vol% blend ratio, after which a notable difference can be observed. Particularly, ID increases substantially at the blend ratio of 80 vol%, where DI80 reaches 22.8 ms, more than a factor of 5 longer than those of n-butanol and tert-butanol. Furthermore, the curvature of DI80 is opposite to that of the DN80 and DT80 and all blends at lower percentages. The burn duration of butanol/diesel blends are shown in Fig. 11 in Appendix. It shows that burn duration of butanol/diesel blends is generally longer than that of diesel, regardless of the isomer type. At 20 and 40 vol% cases, all three isomers present reduced burn duration at high chamber temperature. For the 60 vol% cases, the burn duration of DT60 and DI60 first increases then decreases while DN60 keeps decreasing as the enhancement of chamber temperature. For the case of 80 vol%, no consistent trend can be found among the three butanol isomers.

Note that the observed sequence of reactivity of the blends: tert-butanol > n-butanol > iso-butanol is inconsistent with the RON of the neat isomers. Still, this behavior can be explained by the distinct chemical reaction pathways for neat butanol and blends of butanol and alkane. Initial reactions of neat butanol isomers start with a unimolecular reaction followed by the H abstraction when the temperature is below 1000 K [13]. Due to lower bond dissociation energy (BDE), the alpha carbon is easier to experience H-abstraction reaction. For that reason, as is shown in Table 2, n-butanol shows the lowest BDE while tert-butanol (the most highly branched isomer) shows the highest BDE. However, the chemical kinetics of butanol/alkane blends differs from that of neat butanol isomers. Simulation work of n-butanol/n-heptane showed that both butanol and n-heptane are dominantly consumed by H-abstraction by OH radicals which are mainly produced by n-heptane through low temperature branching [13]. Apparently, this leads to the promotion of butanol consumption and suppression of n-heptane consumption. For high butanol substitution cases, the reduced production of OH radicals from diesel also explains the increased ID, irrespective of butanol type. Hence, the overall reactivity of butanol isomer/diesel blends depends on the competition of OH radicals instead of the reactivity of neat butanol isomers [30] and the ID is dominated by the suppression effects of butanol isomers on diesel oxidation. The results are in line with this observation as the C–H bond dissociation energy (BDE) of the alpha carbon from n-butanol and iso-butanol are 95.5 and 95.9 respectively whereas tert-butanol does not have C–H on alpha carbon and the beta carbon has a C–H BDE of 103.9. Consequently, n-butanol and iso-butanol are much more likely to compete for the OH

Fig. 5. Pressure and PRR profiles of DN100 and DN80 at different chamber pressure.
radical from diesel and tert-butanol will have a weaker suppression effects on the reactivity the alkane and shows the shortest ID among the blends. Overall, the results presented in Fig. 4 have illustrated that more than 40 vol% addition of butanol to diesel yields in an obvious extended ID, which might not be feasible for conventional CI engine (injection close to the top dead center) [16]. This holds for all three tested isomers. Nevertheless, high butanol addition cases are well suited for advanced combustion concepts like partially premixed compression ignition (PPCI) and homogeneous charge compression ignition (HCCI) [23], where early injection and long ID are required to create a relatively well-premixed charge, avoid local high equivalence ratio region, and mitigate the classical soot/NO\textsubscript{x} tradeoff [24].

Fig. 5 compares the combustion of neat n-butanol (DN100) and DN80. It can be seen that DN80 illustrates higher peak pressure after combustion than DN100 at all three tested conditions. This is because n-butanol has lower LHV than diesel does. After the start of injection, a negative dip in PRR caused by fuel vaporization is observed for both DN100 and DN80. For the case of DN80, the ignition reaction becomes exothermic to overcome the latent heat of vaporization so that PRR becomes positive again. This first stage of heat release is relatively small with a short duration and then falls back to almost zero. This period of heat release is generally termed as low temperature heat release (LTHR). Then the PRR increases rapidly in the second stage of heat release which is normally termed the high temperature heat release (HTHR). Note that the peak of HTHR is much higher than that of LTHR. However, for the case of neat n-butanol, DB100 presents only single stage heat release and no noticeable LTHR can be observed. This is in good agreement with published literature and studies that report that n-butanol doesn’t show two-stage heat release and negative temperature coefficient behavior [13]. In the work of Kumar et al. [34], both neat n-butanol and its blend with primary reference fuel were tested in a rapid compression machine. Neat n-heptane showed the presence of distinct two-stage behavior but n-butanol and iso-octane did not within the temperature and pressure range covered. Zhu et al. [35] utilized a new constrained-reaction-volume method in shock-tube to measure ignition delay time of n-butanol /O\textsubscript{2}/N\textsubscript{2} mixtures over temperatures between 716 and 1121 K.
and nominal pressures of 20 and 40 atm for equivalence ratios of 0.5/1.0/2.0. The reported ignition delay time didn’t show negative temperature coefficient behavior. Yet, a pre-ignition phenomenon was reported in their work, namely strong pressure rise before the final ignition event at temperatures of 809 K and 829 K. It is also mentioned that such pre-ignition effects are both temperature-dependent and pressure-dependent. High-temperature and high-pressure experiments illustrated a much lower pre-ignition pressure rise [36,37]. However, caution should be taken when interpreting the origin of these pressure rise before ignition. It could be caused by either non-ideal shock tube behavior or exothermic chemical reaction. In the work of Stranic et al. [38], n-butanol was tested with a shock tube facility and pre-ignition was reported at temperature below 1000 K. Stranic et al. further showed that the pre-ignition pressure rise was associated with heat release due to exothermic chemical reaction by the increased sidewall photodetector signal. To be conclusive, more experimental and simulation work is required to rationalize this pre-ignition behavior and two-stage heat release of neat n-butanol. The presented results in this work supports that neat butanol does not present two-stage heat release under engine-like conditions. The two-stage heat release of n-butanol/diesel fuel blends can be explained by the earlier mentioned chemical effect. Butanol in butanol/alkane experiences H-abstraction from OH radicals produced by the alkane low-temperature kinetics. Compared to neat butanol, butanol in butanol/alkane blends experiences higher concentration of OH radicals and its consumption is therefore also promoted in the first heat release stage.

As is illustrated in Fig. 6a-c, all three butanol-isomer/diesel blends show a two-stage heat release. Additionally, the peak HTHR of n-butanol is structurally higher than that of tert-butanol and iso-butanol cases, even for the cases where its ID is longer. Note that for all cases the injection has mostly ended before ignition starts which implies that most fuel burns in a premixed-dominant combustion regime. One can hypothesize that then the flame velocity is relevant to describe the duration of the combustion and the consequent heat release rate. Both experimental and modeling work have shown that flame velocity increases as the degree of branching decreases [11,39], so that n-butanol has the highest while tert-butanol has the lowest flame speed among butanol isomers. This is corroborated by the data. Especially for the cases with 80 vol% blend ratio, where ID time is much longer so that mixture becomes more and more homogeneous and leaner at the same time. These cases show the most pronounced difference between the isomers where the tert-butanol blend (DT80) with the lowest flame velocity indeed shows the lowest pressure rise rate even it occurs earlier than iso-butanol. However, numerical modeling work is needed to reveal the definite reasons for the slow second-stage heat release of tert-butanol as the flame-speed and the burn-duration in homogeneous reactors are probably close coupled

Fig. 7. Pressure rise rate profiles of butanol isomers/diesel blends and neat diesel at different temperatures.
phenomena. Both may drive the heat-release in these experiments. It is worth noting that tert-butanol/diesel fuel blends consistently show the earliest LTHR among the three isomers. This early LTHR also leads to the shorter ID of tert-butanol as is shown in chamber pressure profiles. This again corroborates the earlier explanation, namely the fact that C–H BDE of tert-butanol is higher than those of iso-butanol and n-butanol and the oxidation of diesel is less suppressed. Consequently, the LTHR is more prominent. This phenomenon is more obvious as the blend ratio increases. As is presented in Fig. 6c and Fig. 6d, both DT60 and DT80 exhibited an earlier LTHR. Nevertheless, the following HTHR is slower than that of DN60 and DN80 which was already addressed in the previous part. Among the isomers, iso-butanol presents both the latest LTHR and HTHR, thus the lowest reactivity. In fact, the LTHR of DI80 is barely visible. One possible reason could be that OH radicals produced from diesel via low temperature chain branching reactions might not suffice for iso-butanol to experience H abstraction at a high blend ratio.

Fig. 7 compares the pressure rise rate of 20 vol% and 40 vol% butanol isomers/diesel blends at different temperatures. The situation at other temperatures and blend ratios are similar and are not shown for clarity. It can be noticed from Fig. 7a-c that the PRR peaks decrease and the profiles widen when chamber temperature decreases. In addition, the PRR profile retards and PRR peak decreases as blend ratio increases. Both trends indicate a longer burn duration irrespective of the isomer. This is because of the specific combustion regime under current operation. Generally, combustion starts after the end of the injection event, which results in a premixed fuel/air mixture with its average equivalence decreasing as ID increases. Accordingly, it mainly consists of premixed combustion and a small fraction of burnout. Therefore, any condition (lower temperature or higher blend ratio) that prolongs the ID will result in over-mixing conditions and lower reaction rate. On the contrary, in the regime where ignition takes place during injection event, first an increased ID will promote the amount of pre-mixed fuel yielding a higher heat release peak up to a certain point after which over-mixing will become dominant. Neat diesel cases (Fig. 7d) clearly
Temperature decreases from 580 to 520 °C, illustrating this change of combustion regime when the chamber temperature decreases from 580 to 520 °C. First, the increased ID leads to more premixed combustion and as the temperature decreases further to 490 °C, combustion becomes premixed dominated and the increased mixing time results in a lower heat release. Interestingly, DT20 (solid blue line in Fig. 7a) is on the verge of becoming fully premixed as heat release slightly increases when temperature is increased to 520 °C and then decreases for 490 °C. All other (DT40, DI20-DI40 and DN20-DN40) are always in the regime of premixed dominated combustion and the ID is so long that over-mixing reduces the heat release rate when temperature is reduced.

Fig. 8 compares the pressure and PRR profiles of 80% butanol/diesel blends at different chamber temperatures. Both DT80 and DN80 show two-stage heat release. It can be seen from Fig. 8a that the LTHR of DT80 gradually becomes more prominent at low temperature cases, both the peak and width of LTHR in the PRR profile increase as temperature decrease. This so-called negative temperature coefficient (NTC) behavior is also validated in the zoomed pressure plots. The initial pressure enhancement (due to LTHR) of DT80 gets more remarkable at low temperature cases, indicating more heat is released in the first stage ignition. Therefore, it is expected less heat is released in the HTHR. This is confirmed by the PRR profiles of DT80 that the HTHR is delayed and the peak decreases as the chamber temperature decreases. Though NTC behavior is not remarkable for DN80, Fig. 8b presents delayed and slower HTHR at low temperature cases as well. A notable exception to the trend discussed above is observed for iso-butanol cases (Fig. 8c), where LTHR of DI80 is barely visible. Further to note, the extreme long ignition extends the mixing time between fuel and air, which yields an over-mixing charge and thus a low local equivalence ratio. It can be seen that the combustion is slow and not fully completed during the sampling period (47 ms) even at 580 °C (the highest achievable temperature for the current combustion chamber). As the temperature decreases below 565 °C, no ignition occurs evidenced by both the pressure and PRR in Fig. 8c.

3.2. Effects of chamber pressure

The previous section has illustrated that at an 80 vol% blend ratio, butanol/diesel blends (iso-butanol cases especially) show long ID even at the highest chamber temperature. In this section, the chamber pressure is enhanced to improve the combustion process. It can be seen from Fig. 9a that ID decreases with increasing chamber pressure for all three butanol blends. This can be attributed to the increased oxygen concentration (mole/cm³), and the improved vaporization and entrainment due to the higher density of the charge. So, both the physical ID and chemical ID decrease at elevated chamber pressure. Particularly, ID of DI80 decreases from 22.3 ms to 7.8 ms when the chamber pressure increases from 30 bar to 55 bar, 65% of reduction. Interestingly, the reduction of ID for DN80 and DT80 cases are lesser, 35.3% and 31% respectively. A correlation appears to exist between the fuel reactivity and ID reduction at elevated pressure. The results indicate that fuels with lower reactivity (i.e. DI80) tend to be more sensitive to the change of ambient conditions. Consequently, the ID reduction of DI80 is larger. Similar results can be found in [5] where it is shown that ethanol/n-heptane blends experience a greater decrease of ID than n-butanol/n-heptane blends at elevated chamber temperature as well. Comparing the results in Section 3.1, increasing temperature and pressure are both conductive to decrease ID. Nevertheless, their mechanisms are different. Temperature increases the kinetic energy and pressure enhances the collision frequency [40]. Despite the enormous ID reduction at high chamber pressure cases, the ID of 80 vol% butanol/diesel is still much too long and is not applicable in a conventional diesel engine. It is an excellent candidate for advanced combustion concepts, such as PPC and HCCI.

Fig. 9b illustrates the burn duration of butanol isomer/diesel blends. It can be seen that burn duration generally decreases as chamber pressure increases and n-butanol cases show the shortest burn duration at all pressure cases. Interestingly, though tert-butanol/diesel blends show the shortest ID, the burn duration is the longest among the three isomers between 30 and 50 bar. As the chamber pressure increases further to 55 bar, it is surpassed by iso-butanol which then yields the longest burn duration. This is due to the previously postulated different effect of the butanol isomers on the LTHR of the diesel. This is corroborated by the pressure and PRR profiles in Fig. 10. Both n-butanol and tert-butanol blends present a definite two-stage heat release which becomes more and more prominent as the chamber pressure increases (zoom-plots in Fig. 10a and Fig. 10b). While the iso-butanol cases barely shows an LTHR at 80 vol% blend ratio. For DN80 the LTHR gradually merges into the HTHR resulting in a single peak in the heat release at a 55 bar chamber pressure. This does not happen for DT80 due to the reactivity of the tert-butanol. DI80 consistently shows a single-stage heat release (the LTHR from zoom-plots in Fig. 10c is negligible), the PRR profile advances for an increase in chamber pressure whereas its burn-duration remains nearly constant.

4. Conclusion

In this work, three butanol isomers (n-butanol, iso-butanol, and tert-
butanol) are blended with diesel in various blend ratios and tested in CRU. The combustion characteristics of butanol isomers are compared at different chamber temperatures and pressures. The effects of temperature and pressure on the auto-ignition process of butanol isomers/diesel blends are experimentally investigated. More importantly, the heat release patterns for the different blends are analyzed. Based on the results, the following conclusions can be drawn:

1. The ignition delay of butanol isomers/diesel blends under current operation follows the sequence of iso-butanol > n-butanol > tert-butanol which is not according to their octane ratings. This is assumed to be driven by the lack of C–H bond in the alpha carbon of tert-butanol, such that the oxidation of diesel is less suppressed than with the other isomers. Consequently, tert-butanol/diesel presents the earliest LTHR, more heat released in the early stage, and therefore shortest ignition delay among the tested butanol isomers.

2. Ignition delay increases at high butanol blend ratio and low chamber temperature, regardless of the isomer type. Therefore, under these operating conditions, butanol isomers/diesel blends present premixed-dominant combustion and show decreased pressure rise rate. Whereas, diesel displays much less premixed-dominated combustion and pressure rise rate first increases then decreases as temperature decreases due to change of combustion regime.

3. Among the tested butanol/diesel blends, the cases with n-butanol and tert-butanol show both a LTHR and HTHR regardless of the blend ratio. Blends with iso-butanol only present two-stage heat release up to 60 vol% with the largest retardation of the LTHR and HTHR. Although the n-butanol’s LTHR is later than tert-butanol, the HTHR of n-butanol is the earliest. For neat n-butanol no LTHR was observed.

4. When chamber pressure increases from 30 to 55 bar at 80 vol% blend ratio, ID decreases 35.3%, 31%, and 65% for n-butanol, tert-butanol, and iso-butanol respectively. In addition, burn duration decreases.

Fig. 10. Chamber pressure and pressure rise rate of DT80, DN80, and DI80 at different chamber pressure (T\text{chamber} = 580 ^\circ \text{C}).
The presented results indicate that a large amount of butanol addition to diesel might not be applicable for conventional CI engines but are very good candidates for advanced combustion concepts like PPC and HCCI.

The analysis described in this paper can provide guidelines for implementing butanol as a component fuel in diesel engines. The addition of butanol in diesel substantially prolongs the ignition delay of fuel blends, especially for iso-butanol. The increased mixing time for fuel/air mixture can effectively reduce soot production. Therefore, butanol/diesel fuel blends can be formidable fuel candidate for low temperature combustion concepts. The unique LTHR pathway of tert-butanol resulting in its early ignition can be quite helpful and crucial for engine conditions like low load and idle condition. However, its HTHR is late leading to a more homogeneous combustion. Since it is a delicate balance whether it still leads to misfire engine experiments need to be conducted. This is part of a next study. Also, though only binary fuel blends are being applied in this work, it is the authors intention to perform ternary fuel blends with butanol fuel blends in the future to include the merits of tert-butanol and other butanol isomers. Simulation work is also required to understand the slow second stage heat release of tert-butanol. However, for that a mechanism is needed that both includes butanol isomers and a large alkane. To the authors knowledge this is not available yet.

**CRediT authorship contribution statement**

**Jinlin Han:** Conceptualization, Investigation, Methodology, Writing - original draft. **L.M.T. Somers:** Funding acquisition, Supervision, Writing - review & editing.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Appendix**

**Fig. 11.** Burn duration of butanol isomers/diesel blends as a function of chamber temperature.