Formulation of a Reduced Chemical Kinetic Mechanism for the Combustion Modelling of Iso-Pentanol Fuel


Published in:
WCX SAE World Congress Experience 2022: Proceedings

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

Publisher rights
© 2022 SAE.
This work is made available online in accordance with the publisher’s policies. Please refer to any applicable terms of use of the publisher.

General rights
Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Open Access
This research has been made openly available by Queen's academics and its Open Research team. We would love to hear how access to this research benefits you. – Share your feedback with us: http://go.qub.ac.uk/oa-feedback
Formulation of a reduced chemical kinetic mechanism for the combustion modelling of iso-pentanol fuel

Author, co-author (Do NOT enter this information. It will be pulled from participant tab in MyTechZone)
Affiliation (Do NOT enter this information. It will be pulled from participant tab in MyTechZone)

Abstract

In this paper, the formulation of a reduced chemical kinetic mechanism for iso-pentanol fuel is presented. First, the main reaction pathway and pertinent key species for iso-pentanol oxidation were identified. Then, the detailed chemical kinetic mechanism for iso-pentanol was reduced using reduction techniques which included directed relation graph, isomer lumping and temperature sensitivity analysis, where a reduced mechanism of 92 species and 444 reactions was obtained. The reduced mechanism for iso-pentanol was validated against experimental data as well as detailed mechanism predictions under zero-dimensional shock tube auto-ignition and jet-stirred reactor (JSR) conditions, at initial temperatures from 650 K to 1350 K, initial pressures from 10.1 bar to 60 bar and equivalence ratios between 0.5 and 2. Under the shock tube auto-ignition conditions, more than 85% of the experimental measurements and detailed mechanism predictions for the ignition delay (ID) of iso-pentanol were replicated by the reduced mechanism. Similarly, species profiles under the JSR conditions which were related to the formation of oxidation, aldehyde and emissions for iso-pentanol were also reproduced. Furthermore, the rate of production analysis revealed that the elementary reactions associated to the oxidation of iso-pentanol in the detailed mechanism were successfully retained in the reduced mechanism. Meanwhile, the computational runtime was saved by three times when the reduced mechanism was implemented to model the simulations. These results therefore indicate that the reduced mechanism developed for iso-pentanol is sufficient and reasonable.

Introduction

In an effort to reduce the reliance on conventional fuels and also the associated greenhouse gas emissions, the demand for alternative fuels has been increasing. It has been reported that alcohol fuel is a suitable substitute for diesel and also gasoline fuels because of the lower production of nitrogen oxides emissions and anti-knocking properties [1–3]. Furthermore, several apparent advantages are obtained when alcohol fuel is blended with diesel fuel such as decreased exhaust of soot/particulate matter [2,4], carbon monoxide (CO) [5,6] and also lower life-cycle of carbon dioxide (CO2) [4,5,7] emissions. However, owing to the lower cetane number and enthalpy of vaporization, short-chain alcohol fuels such as ethanol (C2H5OH) exhibited low miscibility with diesel fuel [8–10] and thus caused retardation in ignition delay (ID) [10] and stability problems [8]. As a result, alcohol fuels with longer carbon chains for example butanol and pentanol are sought after for diesel engine operations. In comparison to those of the short-chain alcohol fuels, long-chain alcohol fuels demonstrated better compatibility with diesel and/or biodiesel due to the higher physicochemical properties i.e. lubricity, viscosity and energy density [3,11].

Current research effort focusses to characterize different variations of pentanol fuel such as n-pentanol and iso-pentanol for computational fluid dynamics (CFD) modelling. Earlier fundamental works have been concentrated on the formulation of detailed mechanism for pentanol fuel. According to Togbé et al. [12], the predictions of laminar flame speeds and jet-stirred reactor (JSR) species mole fractions such as ethylene (C2H4), CO and CO2 using the detailed mechanism proposed for 1-pentanol fuel with 261 species and 2099 reactions were reasonable when validated against the experimental measurements, at 1 bar of initial pressure and equivalence ratios (φ) of 0.7 to 1.4. Meanwhile, a detailed mechanism of 599 species and 3010 reactions for pentanol fuel was developed by Heufer et al. [13]. Good agreement was recorded when the detailed mechanism was validated against the experimental data, at an initial pressure range of 9 bar to 30 bar and stoichiometric condition for the predictions of auto-ignition, JSR and premixed laminar flame [13]. Similarly, based on Sarathy et al. [14], the measured ID periods, species mole fractions and laminar flame speeds at initial pressures ranging from 1 bar to 60 bar and initial temperatures of 650 K to 1500 K were reproduced by the iso-pentanol detailed mechanism, which consisted of 360 species with 2075 reactions.

Since these detailed mechanisms [12–14] are not suitable for practical CFD combustion modelling, several works have been conducted to formulate reduced mechanisms for pentanol fuel. Ma et al. [15] have successfully formulated a reduced combustion chemistry mechanism for diesel-biodiesel-n-pentanol blends with a size of 229 species and 902 reactions. The reduced mechanism was examined for zero-dimensional (0D) ID periods and one-dimensional laminar flame, at the initial pressures of 1 bar to 100 bar, initial temperatures from 650 K to 1000 K and φ between 0.5 and 2. Ma et al. [15] found that the addition of 20% pentanol (by vol.) into diesel-biodiesel blend elongated the ID periods at the initial pressure of 100 bar as compared to those of the diesel-biodiesel blends. On the other hand, a 47-species reduced mechanism for n-pentanol was formed using the decoupling methodology [16]. At initial pressures between 9 bar and 30 bar, temperature range of 640 K to 1220 K and φ between 0.35 to 2, the reduced mechanism predictions were comparable to the experimental data and detailed mechanism predictions for the ID periods in shock tube and rapid compression machine as well as the species concentrations in JSR [16]. More recently, a reduced mechanism with 161 species and 622 reactions for n-pentanol fuel was developed using rate of production (ROP) and isomer lumping by Liu et al. [3]. Despite the good agreement between the predicted JSR species mole fractions and experimental data, at stoichiometric...
condition with an initial pressure of 10.1 bar, a maximum discrepancy of approximately 2.5 times in the acetylene (C2H2) predictions of the reduced mechanism was reported.

Based on the aforementioned limitations and also the authors’ best knowledge, the reduced chemical kinetics for iso-pentanol fuel have yet to be established. Therefore, this study aims to formulate a reduced chemical kinetic mechanism for iso-pentanol fuel. This paper is structured such that the selection of suitable detailed mechanism and identification of main reaction pathway for iso-pentanol are first described. This is followed by the discussion on the reduction methodology of the chemical kinetic mechanism for iso-pentanol. Consequently, the validation and benchmarking studies of the reduced mechanism for iso-pentanol under shock tube auto-ignition and JSR conditions are presented. Key conclusions are drawn in the final section.

**Development of the reduced chemical kinetic mechanism for iso-pentanol**

In this work, the detailed mechanism for iso-pentanol (iC5H10O) developed by Tsujimura et al. [17] with 511 species and 3000 reactions is selected for reduction. Prior to the reduction process, the main reaction pathway for iso-pentanol is identified, as illustrated in Figure 1. This is performed to ensure that the original chemical comprehensiveness and reaction pathways of the detailed mechanism [17] are retained in the reduced mechanism. Meanwhile, the reduction steps to obtain the reduced mechanism for iso-pentanol are reported in Figure 2. As seen in Figure 2, the detailed iso-pentanol mechanism [17] is initially reduced using the directed relation graph (DRG) method [18] in ANSYS Reaction Workbench. The reduction process using the DRG method [18] is performed three times consecutively. In addition, target species including iC5H10O, C5H9OH, CO2, O2, hydroxyl (OH), hydroperoxyl (HO2) and hydrogen peroxide (H2O2) are specified to avoid the elimination of vital isomers in a single-step reduction process [19]. This produces a reduced mechanism of 155 species and 837 reactions. After that, species in the reduced mechanism are lumped together according to the isomer lumping method by Lu and Law [20]. It is noteworthy to mention that the isomers for iso-pentanol including iC5H10OH, jC5H11OH, kC5H10OH and lC5H10OH are excluded from isomer lumping, as demonstrated in Figure 1. This is because the authors discovered that the chemical comprehensiveness including auto-ignition and extinction characteristics of the detailed mechanism could not be accurately conserved in the reduced mechanism when these isomers are lumped together. Here, a reduced mechanism with 131 species and 789 reactions is obtained. In order to eliminate species which have lost their connection pathway due to isomer lumping, the relationship among the lumped species in the reduced mechanism is recalculated and subsequently removed using the DRG method [18]. The reduction process for iso-pentanol is concluded with a temperature sensitivity analysis using ANSYS Chemkin-Pro, where less significant elementary reactions are removed based on the normalized temperature sensitivity coefficient calculated for individual elementary reaction [21], as presented in Eq. 1. Finally, a reduced mechanism for iso-pentanol with 92 species and 444 reactions is formulated.

\[
\text{Normalized individual temperature sensitivity coefficient} = \frac{\text{Absolute individual temperature sensitivity coefficient}}{\text{Maximum individual temperature sensitivity coefficient}}
\]

(1)

At each reduction step, the capability of auto-ignition prediction by the reduced mechanism is selected as the basis of reduction. As such, the ID periods predicted by the reduced mechanism for iso-pentanol under the shock tube auto-ignition conditions [14] are constantly compared against the experimental measurements and also the detailed mechanism predictions. Here, the ID period is defined as the duration to increase the initial temperature of the air-fuel mixture by 400 K [21]. Due to the large size of the detailed mechanism, the maximum deviation for the predictions between the reduced and detailed mechanisms is set at 40% [19]. Besides, mole fractions of key species such as those related to fuel (iso-pentanol), soot
formation ($\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_4$) and emissions (CO and CO$_2$) under the JSR conditions [22] for the reduced mechanism are validated in order to replicate the steady-state extinction of a combustion process [21]. Table 1 presents the initial conditions of the shock tube auto-ignition [14] and JSR [22] experiments, where both the experiments are simulated using the 0D models of a closed homogenous reactor and a perfectly-stirred reactor (PSR) in ANSYS Chemkin-Pro, respectively.

Table 1 Initial conditions used in 0D closed homogenous reactor and PSR.

<table>
<thead>
<tr>
<th>Operating condition</th>
<th>Initial pressure [bar]</th>
<th>Initial temperature [K]</th>
<th>$\phi$ [-]</th>
<th>Residence time [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shock tube auto-ignition</td>
<td>40, 60$^a$, 60$^a$</td>
<td>650 – 1350</td>
<td>0.5, 1, 2</td>
<td>-</td>
</tr>
<tr>
<td>JSR</td>
<td>10.1$^b$</td>
<td>700 - 1200</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Selected operating conditions to replicate the shock tube auto-ignition experiment conducted by Sarathy et al. [14].

$^b$ Selected operating conditions to replicate the JSR experiment conducted by Dayma et al.’s work [22].

Due to the elimination of more than 400 species and 2500 reactions, the Arrhenius rate constants for selected elementary reactions are optimized to incorporate the influence of the removed reactions as well as to improve the predictions of ID periods and species concentrations for the 92-species reduced mechanism [21,23–26]. Relevant reactions for the optimization of Arrhenius rate constants are selected based on the sensitivity analysis conducted using ANSYS Chemkin-Pro, which is adopted according to the approach by Cheng et al. [21]. In addition, this optimization exercise is only restricted to the oxidation reactions of the fuel species i.e. iso-pentanol [21,27]. Based on the sensitivity analysis, only one reaction which is $\text{iC}_5\text{H}_{11}\text{OH} + \text{HO}_2 = \text{iC}_5\text{H}_{10}\text{OH} + \text{H}_2\text{O}_2$ is identified. As such, the associated Arrhenius rate constant for this reaction as summarized in Table 2 is carefully adjusted until reasonable predictions of ID periods and species mole fractions throughout all the tested conditions (less than the specified deviation of 40%) are obtained for the reduced mechanism.

Table 2 Original and optimized Arrhenius rate constants for the reduced iso-pentanol mechanism

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$A$ [mol cm s K]</th>
<th>$b$ [-]</th>
<th>$E_r$ [cal mol$^{-1}$]</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{iC}<em>5\text{H}</em>{11}\text{OH} + \text{HO}_2 = \text{iC}<em>5\text{H}</em>{10}\text{OH} + \text{H}_2\text{O}_2$</td>
<td>189.6</td>
<td>3.37</td>
<td>1.1746e+04</td>
<td>Original</td>
</tr>
<tr>
<td></td>
<td>696.0</td>
<td>3.37</td>
<td>1.1746e+04</td>
<td>Optimized</td>
</tr>
</tbody>
</table>

Validation of the reduced mechanism for iso-pentanol under 0D conditions

**Shock tube auto-ignition**

The 92-species reduced mechanism for iso-pentanol is validated under the shock tube auto-ignition conditions [14], at initial pressures of 40 bar and 60 bar and $\phi$ between 0.5 and 2, as shown in Table 1. Higher initial pressures are selected for the auto-ignition conditions in order to replicate those in a diesel engine. Figure 3(a) and (b) compare the ID period predictions of the reduced mechanism against the detailed mechanism predictions and experimental data, at both the initial pressures of 40 bar and 60 bar. Based on Figure 3, the measured ID periods [14] at all tested $\phi$ values are reproduced by the reduced mechanism, within a maximum deviation of 45%. This is identical to the findings by Tang et al. [28], where a 50% over-prediction is obtained when comparing the ID predictions of the iso-pentanol mechanism to the experimental data. Despite a 2-time deviation recorded for the reduced mechanism predictions at the initial pressure of 40 bar, initial temperature of 850 K and $\phi$ of 1 and 2, such deviation is similarly found between the detailed mechanism predictions and the experimental data [14]. The ID periods calculated for the detailed mechanism at the negative temperature coefficient region are deviated by approximately twice, as shown in Figure 3(a) and (b). On the other hand, a good agreement is obtained for the ID period predictions between the reduced and detailed mechanisms. The ID periods predicted by the reduced mechanism do not deviate more than a maximum difference of 33.8% as compared to those of the detailed mechanism. These results are thus considered reasonable since the induced deviations for the reduced mechanism predictions are within the specified deviation of 40% as compared to those of the detailed mechanism.
conditions are also validated against the measurements recorded by Dayma et al. [22]. The initial conditions of the JSR experiment [22] are compiled in Table 1. The species selected for validation include reactants, oxygenated products and fuel rich products such as iC\(_5\)H\(_{11}\)OH, CO, C\(_2\)H\(_2\) and formaldehyde (CH\(_2\)O). As illustrated in Figure 5(a), (d) and (g), the mole fractions and profiles for iC\(_5\)H\(_{11}\)OH, CO and CO\(_2\) estimated using the reduced mechanism are comparable to those of the detailed mechanism as well as the experimental data [22]. Although a larger discrepancy against the experimental data is found, the maximum deviation for the predictions between the reduced and detailed mechanisms excluding that for CO is recorded at approximately 10%.

Apart from those, additional species which are related to the fuel oxidation such as HO\(_2\), OH and O\(_3\) are also monitored for the reduced mechanism. Here, the mole fractions of these species computed for the reduced mechanism are benchmarked against those of the detailed mechanism since experimental data is unavailable. Figure 6(a) to (c) compares the predicted mole fractions of HO\(_2\), OH and O\(_3\) using the reduced mechanism against those of the detailed mechanism, where a reasonable agreement is obtained. However, a discrepancy is found in the OH mole fractions between the reduced and detailed mechanisms at the initial temperature of 1250 K and \(\phi\) of 0.5, as illustrated in Figure 6(a). This may be attributed to the elimination of intermediate reactions and isomer lumping performed during the reduction process, which leads to a lower formation of OH mole fractions. Nevertheless, this is in line with the findings by Luo et al. [29].

### Conclusions

A reduced mechanism with 92 species and 444 reactions for iso-pentanol fuel is developed using the calculation methods of DRG, isomer lumping and temperature sensitivity analysis. The formulated reduced mechanism has reasonably replicated the experimental measurements and detailed mechanism predictions under the conditions of shock tube auto-ignition and JSR. At the initial pressures of 40 bar and 60 bar, initial temperatures from 650 K to 1350 K and \(\phi\) of 0.5 to 2, the ID periods computed using the reduced mechanism excluding those at 850 K and \(\phi\) of 1 and 2 are deviated by 45% (maximum difference) as compared to the measurements. These predictions are also not more than 33.8% different from those of the detailed mechanism. In terms of the JSR species profiles and concentrations which included iC\(_5\)H\(_{11}\)OH, CO\(_2\) and C\(_2\)H\(_2\) at 10.1 bar pressure, temperatures of 700 K to 1200 K and \(\phi\) of 0.5 to 2, the reduced mechanism predictions are well within a 10% deviation as compared to those of the detailed mechanism. Although a maximum difference of 5.7 factor is found in the aldehyde related species, the reduced mechanism predictions are generally comparable to the experiment data. Based on the ROP analysis, vital reactions for iso-pentanol oxidation from the detailed mechanism i.e. the hydrogen abstraction reactions by OH radicals are successfully retained in the reduced mechanism. Here, the mole fractions of these species computed for \(\phi\) of 0.5 to 2 are deviated by approximately 10%.

It is worth to highlight that a maximum reduction of approximately three times in the computational runtime is achieved when the reduced mechanism is implemented to model the auto-ignition simulation cases under the shock tube conditions using a 3.5 GHz Intel Core i7-7800X workstation with 12 number of processors, as compared to that of the detailed mechanism.

### JSR conditions

Apart from that, pertinent combustion species profiles predicted using the reduced mechanism for iso-pentanol under the JSR conditions are also validated against the measurements recorded by Dayma et al. [22]. The initial conditions of the JSR experiment [22] are measured [14].

![Figure 3 Predicted ID periods for iso-pentanol using the detailed mechanism, reduced mechanism and combined diesel-iso-pentanol mechanism against experimental measurements [14], at initial pressures of (a) 40 bar and (b) 60 bar and \(\phi\) of 0.5, 1 and 2. * Only the ID periods at the initial pressure of 40 bar and \(\phi\) of 2 are measured [14].](image-url)
Figure 4 Comparisons of normalized ROPs calculated for the elementary reactions in the detailed and reduced mechanisms at ignition point, with an initial pressure of 40 bar, initial temperature of 850 K and φ of (a), (b) 0.5, (c), (d) 1 and (e), (f) 2.
Figure 5 Predicted mole fractions\(^a\) for the detailed and reduced mechanisms of iC\(_{5}\)H\(_{11}\)OH, CO\(_2\), CO, C\(_2\)H\(_2\), C\(_2\)H\(_4\), C\(_2\)H\(_6\), CH\(_3\)O, CH\(_3\)CHO and C\(_2\)H\(_3\)CHO against experimental measurements [22], under JSR conditions, with an initial pressure of 10.1 bar, \(\varphi\) of (a), (d), (g) 0.5, (b), (e), (h) 1 and (c), (f), (i) 2 and a residence time of 0.7 s.\(^a\) Mole fractions for iC\(_{5}\)H\(_{11}\)OH, C\(_2\)H\(_2\) and C\(_2\)H\(_4\) are increased by a factor of two.
Figure 6 Predicted mole fractions\textsuperscript{a} for the detailed and reduced mechanisms of O\textsubscript{2}, HO\textsubscript{2} and OH under JSR conditions\textsuperscript{[22]}, with an initial pressure of 10.1 bar, $\phi$ of (a) 0.5, (b) 1 and (c) 2 and a residence time of 0.7 s.

\textsuperscript{a} Mole fractions of O\textsubscript{2} are decreased by 3 orders, while those of OH are increased by 1 order.

References


Contact Information

Xinwei Cheng, x.cheng@qub.ac.uk.

Definitions/Abbreviations

0D zero-dimensional

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFD</td>
<td>computational fluid dynamics</td>
</tr>
<tr>
<td>C(_2)H(_2)</td>
<td>acetylene</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>ethylene</td>
</tr>
<tr>
<td>CH(_3)O</td>
<td>formaldehyde</td>
</tr>
<tr>
<td>CO</td>
<td>carbon monoxide</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>DRG</td>
<td>directed relation graph</td>
</tr>
<tr>
<td>HO(_2)</td>
<td>hydroperoxyl</td>
</tr>
<tr>
<td>H(_2)O(_2)</td>
<td>hydrogen peroxide</td>
</tr>
<tr>
<td>ID</td>
<td>ignition delay</td>
</tr>
<tr>
<td>JSR</td>
<td>jet-stirred reactor</td>
</tr>
<tr>
<td>O(_2)</td>
<td>oxygen</td>
</tr>
<tr>
<td>OH</td>
<td>hydroxyl</td>
</tr>
<tr>
<td>PSR</td>
<td>perfectly-stirred reactor</td>
</tr>
<tr>
<td>ROP</td>
<td>rate of production</td>
</tr>
<tr>
<td>(\phi)</td>
<td>equivalence ratio [-]</td>
</tr>
</tbody>
</table>