

Towards the understanding of 1-, 2-, and 3-pentanol oxidation at high temperatures

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Abstract

A reaction mechanism for three pentanol isomers has been investigated in this work. These alcohols have similar C₅-alkane structure with difference in the location of hydroxyl group and thereby different reactivity. A reaction kinetic mechanism is developed using the open-source rule-based generation software “RMG” developed at W.H. Green’s group at MIT. Though a number of studies for 1-pentanol are available in literature, no reaction mechanisms are available so far for 2- and 3-pentanol. The mechanism for all the three pentanols studied here is validated against global parameters of ignition delay time and flame speed experiments from literature over a wide range of conditions. The initial reaction mechanism developed in this work will provide insight towards the understanding of pentanol chemistry.

Introduction

Among the EU’s total emission of main greenhouse gas, carbon dioxide (CO₂), road transports adds about one-fifth whereas aviation accounts for 3% of total emission. An annual growth of 3-5% (passenger transport) and 9-10% (freight) is foreseen over the next 20 years. Radical changes experienced in road transport i.e. e-mobility, hydrogen based cars has been initiated due to societal push. Technological solutions to shift transport towards non-carbon cycles based fuels have different degrees of maturity, complexity, and requirements depending on the sector. Yet all sectors at the world scale acknowledge that they will still heavily rely on carbon fuels and that a short-term solution needs to be implemented. For 2020, EU legislation has committed to cut the overall greenhouse gas emission to 20% of 1990 level. These very ambitious goals in terms of CO₂ emissions from the transport industry - road, aviation, maritime - can only be met with a substantial contribution of low carbon alternative (non-petroleum) fuels: Fuels that are clean, renewable, sustainable, and more importantly compatible with current engine designs.

In this context, alcohol based fuels or blend stocks have been considered to be promising alternatives to conventional fossil fuels since renewable production pathways already exist, e.g. fermentation of sugars, starches, and lignocellulosic residues obtained from agricultural and forest feedstock or are target of intense investigations. Moreover, alcohols tend to produce less soot due to additional oxygen atoms in the fuel molecule and they practically contain no sulfur, which eliminates sulfur oxides emissions and are better suited for the catalyst used in the exhaust systems of automobiles. Ethanol has been used as a fuel or as blend stock to gasoline fuel since its inception as sustainable alternative fuel around 1980s. However, compared to

gasoline, it possesses certain disadvantages such as lower energy density, mixing instability in blends, or solubility in water. Fuels with high ethanol content are only used in fuel-flex vehicles, which experience problems under certain conditions. During startup in cold weather conditions the fuel’s lower vapor pressure (with respect to gasoline) is detrimental to the vaporization thus to the ignition which follows the spark.

The last decade saw a great focus on the combustion research of alcohols as an alternative bio-fuel. Since then, various research groups have published works at a wide variety of conditions. The combustion chemistry of larger alcohols has gained growing attention as its suitability in various transportation means such as road transport [1], aviation [2], and as liquid fuels in stationary power generation [3,4] has been investigated. Such alcohols include butanol, pentanol, and hexanol. Larger alcohols provide certain advantages over ethanol as they have a higher energy content; similar to gasoline or diesel (butanol, pentanol) or aviation fuel (hexanol, as potential blendstock yet non drop-in) and have better compatibility with piston engines. Among these are pentanol isomers whose combustion characteristics are the current topic of interest.

Pentanol Chemistry

The pentanols possess eight structural isomers depending on the position of the hydroxyl group on the alkane chain length. At low pressure flame conditions, major species of fuel, oxidizer, and combustion products display identical global behavior with respect to different isomers but vary in intermediates such as carbonyl compounds, hydrocarbon intermediates, soot precursors, etc. which are all responsible for pollutant emissions. Therefore, this study of isomers is important and provides information on selection criteria for the

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suitability in practical use of one isomer over another [5].

Within the last two years, a few studies have been dedicated to explore fundamental combustion properties of various pentanol isomers. These studies are mainly focused on determining the combustion characteristic of pentanol as fuel for different engine types [6–8]. They demonstrated its suitability of as an engine fuel, e.g. Gautam et al. [6] studied higher alcohol-gasoline blends and found that the alcohol blended gasoline showed better resistance to knock and tend to have faster flame speeds compared to neat gasoline. In addition to the findings reported in [6], Christensen et al. [8] showed that compared to *iso*-pentanol (3-methyl-1-butanol), *n*-pentanol is less suitable since it has a lower octane number whereas *iso*-pentanol had similar knocking properties as *n*-butanol. In their Homogeneous Charge Compression Ignition (HCCI) engine study, Yang et al. [7] found that *iso*-pentanol possesses properties closer to gasoline, in particular a higher energy density and lower miscibility in water compared to ethanol and butanol and similar HCCI combustion properties as gasoline. They discussed the benefits of *iso*-pentanol as HCCI fuel either in neat form or as blend with gasoline.

Despite engine studies, a comprehensive chemical kinetics study of pentanols remains open, and therefore in order to optimize its performance at engine condition and to get insight into emissions its reaction mechanism is strongly needed. Recent studies on *n*-pentanol [9–13], *iso*-pentanol [13–17] and 2-methylbutanol [13,18–21] involve investigations at a variety of combustion conditions. Only studies on 2- and 3-pentanol include flame speed measurement from Li et al. [11]. Other pentanol isomers are not studied in the literature so far.

Initially, Togbe et al. [9] and Dayma et al. [14] studied 1-pentanol and *iso*-pentanol respectively. In both studies, various stable species profiles are measured in a jet-stirred reactor (JSR) at 10 bar and over a wide range of equivalence ratios and the results are compared to modeling.

Heufer et al. [10,12] extended their *n*-butanol model to 1-pentanol [10] and presented low temperature, high pressure ignition characteristics of 1-pentanol measured in RCM and in shock-tubes [12]. Furthermore, Tang et al. [13] measured high temperature ignition delay times of three pentanol isomers namely, 1-, *iso*-pentanol and of 2-methylbutanol. To estimate the autoignition characteristics at engine conditions, Tsujimura et al. [15] reported a reaction mechanism of *iso*-pentanol to predict autoignition characteristics at low- and high-temperature. Similarly, Welz et al. [16] investigated and provided insight into the low temperature autoignition chemistry of *iso*-pentanol. To our knowledge, there is no ignition delay time measurement of 2- and 3-pentanol reported so far.

Li et al. measured laminar flame speeds of 1-, 2-, and 3-pentanol and 2-methylbutanol [11,19]. Among very recent investigations, the only study on flame structure is by Lucassen et al. [20] who presented experimental and modeled species profiles in

stoichiometric low pressure flame (25 torr), high pressure JSR studies by Serinyel et al. [21] and low and atmospheric pressure pyrolysis study in flow reactor measured by mass spectroscopy and supported by modeling [18]: All these studies focused to investigate 2-methylbutanol. Thus the investigations on pentanol are limited to a few isomers.

Reaction mechanism

Traditionally kinetic models have been constructed by hand, which for the case of smaller to medium size species is a very time-consuming, tedious, and sometimes error-prone work, yielding very inflexible models. The complexity of larger molecules limits this method. In case of pentanol, the mechanism has to contain many isomers, which will lead to a large and complicated kinetic scheme. Therefore rule based generation tools have become more important. In the present work the reaction mechanism for all the three pentanols is constructed using the RMG developed at MIT [22] The RMG (Reaction Mechanism Generator), is a computer-aided kinetic model construction tool which builds mechanism iteratively using the rate-based algorithm by Susnow et al. [23]. As an input, for mechanism generation, one is required to specify initial conditions of temperature, pressure, and species concentration. Based on its chemistry database and a set of rules and parameters, RMG generates a mechanism. The thermochemical information, for the species where information is unavailable is supplied using the group-additivity method [24]. It has been successfully applied to various combustion systems e.g. the oxidation of butanol isomers [25], pyrolysis of *n*-butanol [26].

The reaction mechanism of the present work considered USC-II as base mechanism to represent C₁-C₄ chemistry [27].

Mechanism Validation

The mechanism generated in this work is compared to the limited experiments (as described above) of ignition delay time and flame speed available in the literature. The simulations of which are performed using Chemical WorkBench [28].

Ignition delay times

Fuel reactivity, reflected by ignition characteristics, is an important parameter in fuel design. For the sake of safety considerations and to understand ignition process in engines, a wide range of conditions of *T*, *p*, and fuel-air ratio at which the fuel will ignite is necessary to investigate. Among all reported studies on measured ignition delay times, the high temperature measurements of Tang et al. [13] are suitable for high temperature mechanism validation. Unfortunately, there are no reported ignition delay times measurements for validation of the reaction scheme for 2- and 3-pentanol. Therefore, in this work the ignition delay time study is restricted to 1-pentanol.

Tang et al. reported ignition delay time of 1-pentanol for five test conditions. They measured them behind

reflected shock waves at two pressures, 1.0 and 2.6 atm. The conditions at which the simulations are compared with experiments are summarized in Table 1.

Table 1: Experimental conditions, Tang et al. [13].

p (atm)	1.0			2.6	
X_{fuel}	50%			25%	
ϕ	0.25	0.5	1.0	0.5	0.5

The atmospheric measurement of the ignition delay time is compared for three different fuel stoichiometry, i.e. 0.25, 0.5, and 1.0. These three test cases are compared in Fig. 1-3 respectively where the fuel composition is 50% in all cases (Argon dilution varies). The simulated ignition delay times are determined from the maximum slope of the temperature profile. The ignition delay time is measured in the range of 1100-1500 K and is very well reproduced by the simulations in all three cases. With increase in fuel stoichiometry, the ignition delay time of the test mixtures increases. At temperature lower than 1100 K, there is a small over prediction of the simulated profiles compared to the experiments which is apparent as the mechanism does not contain reactions for low temperature chemistry. Any variations in the temperature or pressure profiles measured due to gas dynamic effects are not considered in the modeling.

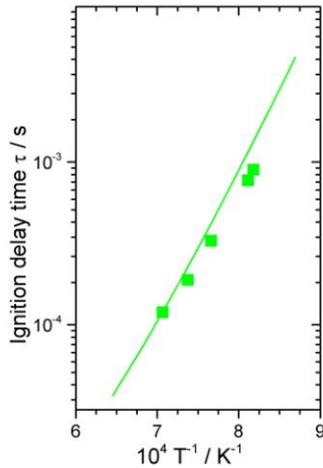


Fig. 1: Measured (symbol) and predicted (line) ignition delay time of *I*-pentanol/O₂/Ar mixture. Experiments are from Tang et al. [13]. Mixture composition: fuel = 0.5%, O₂ = 15%, in argon, $\phi = 0.25$, $p = 1$ atm.

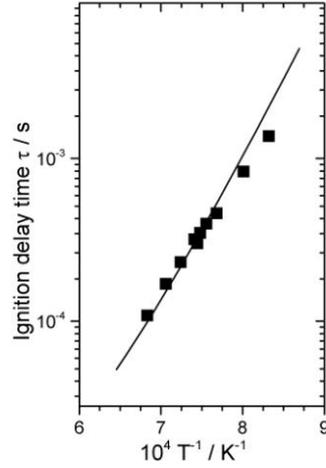


Fig. 2: Measured (symbol) and predicted (line) ignition delay time of *I*-pentanol/O₂/Ar mixture. Experiments are from Tang et al. [13]. Mixture composition: fuel = 0.5%, O₂ = 7.5%, in argon, $\phi = 0.5$, $p = 1$ atm.

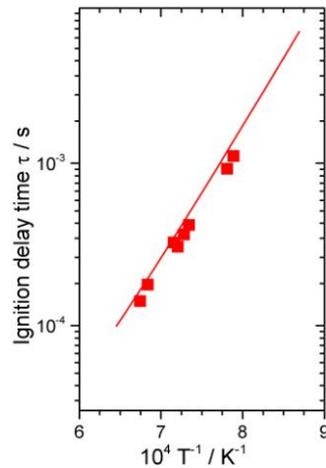


Fig. 3: Measured (symbol) and predicted (line) ignition delay time of *I*-pentanol/O₂/Ar mixture. Experiments are from Tang et al. [13]. Mixture composition: fuel = 0.5%, O₂ = 3.75%, in argon, $\phi = 1.0$, $p = 1$ atm.

Figures 4 and 5 show results of ignition delay times at fixed fuel stoichiometry of 0.5 but at two different pressures 1.0 and 2.6 atm. With increase in pressure, the ignition delay time decreases which is well predicted by model. In general, the model shows excellent agreement with the ignition delay times measured by Tang et al. [13].

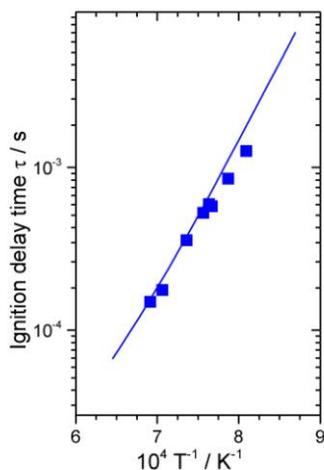


Fig. 4: Measured (symbol) and predicted (line) ignition delay time of *1*-pentanol/ O_2 /Ar mixture. Experiments are from Tang et al. [13]. Mixture composition: fuel = 0.25%, O_2 = 3.75%, in argon, $\phi = 0.5$, $p = 1$ atm.

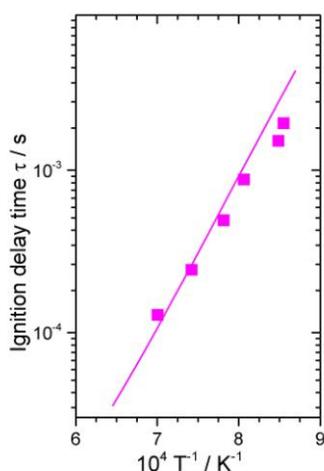


Fig. 5: Measured (symbol) and predicted (line) ignition delay time of *1*-pentanol/ O_2 /Ar mixture. Experiments are from Tang et al. [13]. Mixture composition: fuel = 0.25%, O_2 = 3.75%, in argon, $\phi = 0.5$, $p = 2.6$ atm.

Laminar flame speed

Flame studies are important as these give information on the fuel's heat release linked with the flame speeds and on the reactivity of different intermediates through measurement of species profiles. The chemistry of the isomers differs from each other. One can see such differences from the flame speed experiments of various isomers of C3-C5 alcohols in the studies in [11,29,30]. The position of hydroxyl radical on main carbon chain determines the different structure of its isomers. Studies have shown that structural difference can lead to different chemical properties even if their transport and thermodynamic properties are very close [11]. In case of alcohols, butanol isomers showed different flame speed, studied by Sarathy et al. [29]. The degree of branching

determines the flame speed. The least branched *n*-butanol has the fastest flame speed whereas most branched *tert*-butanols have the slowest flame speeds. As pointed out by Sarathy et al. [29], the differences in flame speed are due to the formation of different radical intermediates, which further leads to unreactive or resonantly stabilized products.

So far there are only two flame studies on pentanol, from Togbe et al. [9] and Li et al. [11]. The flame speed of Togbe et al. involves *1*-pentanol at 423 K whereas Li et al. measured *1*-, *2*-, and *3*-pentanol air mixtures at a variety of pressures and initial temperatures. In this report we present results for 433 K and 1 atm. Figures 6-8 show a comparison of flame speeds in the stoichiometry range of 0.6 to 1.8 for *1*-, *2*-, and *3*-pentanol, respectively. The predicted laminar flame speeds are in excellent agreement with the experimental results.

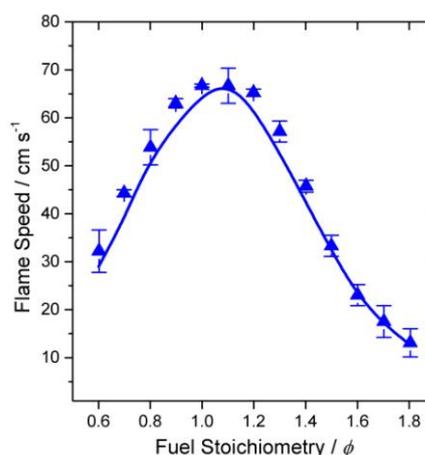


Fig. 6: Measured (symbol) and predicted (line) laminar flame speed of *1*-pentanol/air mixture at various fuel stoichiometries. Experiments are from Li et al. [11]. Flame speeds are at an initial temperature of 433 K and $p = 1$ atm.

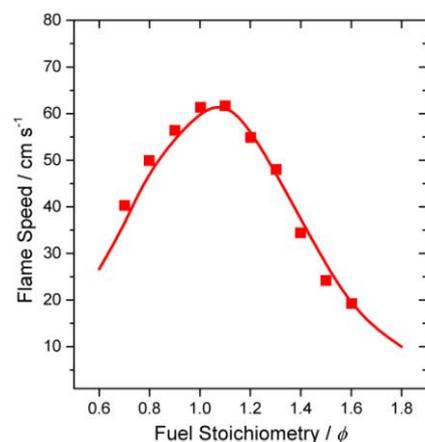


Fig. 7: Measured (symbol) and predicted (line) laminar flame speed of a *2*-pentanol/air mixture at various fuel stoichiometries. Experiments are from Li et al. [11]. Initial conditions are $T = 433$ K and $p = 1$ atm.

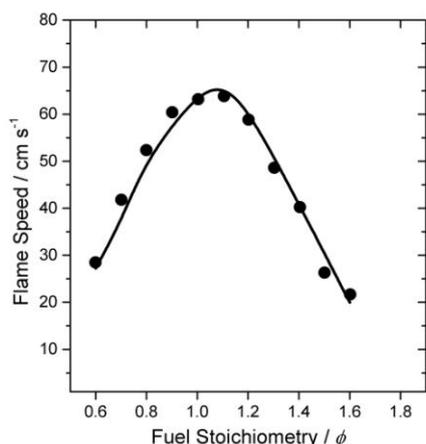


Fig. 8: Measured (symbol) and predicted (line) laminar flame speed of a 3-pentanol/air mixture at various fuel stoichiometries. Experiments are from Li et al. [11]. Flame speeds are at initial temperature of 433 K and $p = 1$ atm.

Conclusions

A detailed reaction mechanism describing oxidation of 1-, 2-, and 3-pentanol has been constructed using RMG. The mechanism is generated for high temperature conditions. The predictions of this mechanism are compared with ignition delay time and flame speed experiments from literature. The results show that the ignition delay times available for 1-pentanol in literature is excellently reproduced by the model at all three fuel stoichiometries, namely, $\phi = 0.25$, 0.5 and 1.0. In addition, the calculated flame speed compared with those measured by Li et al. [11] over wide range of stoichiometry and at atmospheric condition are in excellent agreement. Thus, this reaction model for all three pentanol isomers predicts excellent global combustion behavior.

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