

Detailed Kinetic Modeling of HCCI Combustion with Isopentanol

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ABSTRACT

Isopentanol is an advanced biofuel that can be produced by micro-organisms through genetically engineered metabolic pathways. Compared to the more frequently studied ethanol, isopentanol's molecular structure has a longer carbon chain and includes a methyl branch. Its volumetric energy density is over 30 % higher than ethanol, and it is less hygroscopic.

Some fundamental combustion properties of isopentanol in an HCCI engine have been characterized in a recent study by Yang and Dec (SAE 2010-01-2164). They found that for typical HCCI operating conditions, isopentanol lacks two-stage ignition properties, yet it has a higher HCCI reactivity than gasoline. The amount of intermediate temperature heat release (ITHR) is an important fuel property, and having sufficient ITHR is critical for HCCI operation without knock at high loads using intake-pressure boosting. Isopentanol shows considerable ITHR, and the amount of ITHR increases with boost, similar to gasoline. However, the individual effect of pressure and temperature on ITHR for isopentanol is still unclear. Also, the chemistry leading to ITHR for isopentanol in an HCCI engine needs to be explained.

To answer these key questions, a detailed chemical kinetic model for isopentanol has been developed and used to perform HCCI engine simulations. The isopentanol model consists of low- and high-temperature chemistry based on reaction models for butanol isomers and isooctane (an alkane which a branched molecular structure similar to isopentanol). The model includes a new reaction step for concerted

elimination of HO₂ from isopentanol, a process recently examined by da Silva and Bozzelli for ethanol (J. Phys. Chem. A, 113, 31, 2009). The isopentanol model was validated with rapid-compression-machine and shock-tube data over a wide range of temperatures, pressures and equivalence ratios (712 - 1205 K, 0.8 - 2.3 MPa, and 0.5 - 1.0, respectively). Excellent agreement between model predictions and experimental data was achieved. With regard to simulating HCCI combustion, the model reproduces the experimentally observed ITHR of isopentanol and its enhancement when simultaneously increasing pressure and decreasing temperature for a set combustion phasing. As seen in the HCCI experiments, the model shows that increasing the temperature for a fixed intake pressure promotes hot ignition, with little effect on ITHR.

INTRODUCTION

Stringent emission regulations have been enforced in the U.S., Europe and Japan to suppress local and global air pollution attributed to toxic emissions from vehicles. Drastic improvement in fuel economy of heavy duty vehicles as well as passenger cars will be required to reduce global warming and improve energy security. In particular, it has been greatly encouraged to use bio-derived fuels in some countries for a reduction in dependence of petroleum-derived fuels [1, 2, 3]. The most popularized bio-derived fuel is ethanol which is used as a gasoline substitute. Because of the high O/C ratio of ethanol, the volumetric energy density of ethanol is over 35 % lower than gasoline. Also, ethanol/gasoline mixtures at low blending levels (E3 or E10) have a considerably higher vapor

pressure, which would cause an increase in evaporative emissions and requires a decrease in vapor pressure of gasoline. Moreover, it's significantly easy to solve ethanol into water. Severe water separation would damage fuel lines of vehicles and infrastructures.

Other alcohols, which have more carbon atoms in their molecules than ethanol, have been produced from various bio-derived feedstocks either directly or via gasification. In addition, a recent method of production with micro-organisms through genetically engineered metabolic pathways has been developed, and this method can produce C₄-C₅ alcohols without the traditional fermentation route [4, 5, 6]. Such advanced biochemical production routes for next-generation biofuels offer the promise that a large amount of fungible fuels can be generated, and that those fuels can be more compatible with the existing fuel distribution and combustion infrastructure [7].

Compared to ethanol, higher alcohols have great advantages as gasoline substitutes because of their higher energy density, lower hygroscopicity, and lower vapor pressure. That would be significantly important in practical use when such new fuels are blended in existing fuels for wide distribution. A C₅ branched alcohol, isopentanol or 3-methyl-1-butanol, is one of the components in higher alcohols produced through the fermentative conversion of sugars and is the one of the targets at the Department of Energy (DOE) Joint BioEnergy Institute in the U.S. [5, 6]. Isopentanol can also be produced via the metabolic engineering approach using *Escherichia coli* from glucose, a renewable carbon source [4]. Therefore, isopentanol is a prospective next-generation biofuel. Other attractive characteristics of isopentanol are that isopentanol has a greater similarity to gasoline in physiochemical properties than ethanol or C₄ alcohols (butanols), and that it has much lower miscibility in water, and higher volumetric energy density (over 30 % higher than ethanol, 2 % higher than n-butanol).

Although the fundamental combustion characteristics of butanol isomers have been investigated by many researchers, there are few publications that describe combustion characteristics of isopentanol. One study is on an HCCI (Homogeneous Charge Compression Ignition) engine fueled with isopentanol conducted by Yang, Dec, et al. at Combustion Research Facility in Sandia National Laboratories [7]. They investigated some fundamental combustion properties of isopentanol in the HCCI engine, and found that isopentanol, like ethanol, lacks two-stage ignition for typical HCCI operating conditions but has a higher HCCI reactivity than gasoline or ethanol. The amount of intermediate temperature heat release (ITHR) is an important fuel property, and having sufficient ITHR is critical for HCCI operation without knock at high loads using intake-pressure boosting. Like gasoline, isopentanol shows

considerable ITHR and its amount increases with boosting. ITHR gives isopentanol the capability to retard combustion phasing and allows it to achieve a similar high load limit as gasoline under non-boosting and boosting conditions. The ITHR of isopentanol is dependent on intake pressure and temperature, and EGR (Exhaust Gas Recirculation) conditions. Also the ITHR can be enhanced by simultaneously increasing pressure and decreasing temperature. However, if only temperature is increased, little effect on the ITHR could be seen, while the increasing temperature promotes hot ignition. The individual effect of pressure and temperature on ITHR for isopentanol is still unclear. Furthermore, the chemistry leading to ITHR in an HCCI engine needs to be explained.

The objective of this study is to answer these key questions with a detailed chemical kinetic modeling approach. A reaction model for C₄ alcohols, butanol isomers, is the most likely basis for developing isopentanol chemical kinetic model. Although combustion modeling works for butanol isomers have been conducted [8, 9, 10, 11, 12, 13], most of them focused on combustion chemistry under relatively higher temperature compared to in-cylinder temperatures because butanol is expected as an alternative to jet fuel as well as to gasoline. It is necessary that a detailed chemical kinetic model for isopentanol be developed that is valid under the extended temperature and pressures ranges found HCCI in engines.

In this paper, it would be described that a structure of a newly developed chemical kinetic model for isopentanol and some typical combustion characteristics are shown. Regarding HCCI combustion, required temperatures for HCCI simulations are investigated to achieve similar combustion phasing observed in experiments under various engine speeds, boost, and EGR conditions. And also, ITHR behaviors observed in simulations and experiments are compared with individually or simultaneously varying intake temperatures, pressures, and EGR rates.

DETAILED CHEMICAL KINETIC MODEL

DEVELOPMENT OF ISOPENTANOL MECHANISM

As mentioned in the previous section, no chemical kinetic model for isopentanol has been found in literatures. Kinetic models for butanol isomers are helpful for developing an isopentanol model because butanol isomers have similar molecular structures to some parts of isopentanol. However, most of kinetic modeling and experimental work are focused on high temperature chemistry, and kinetic models for butanol isomers lack detailed low-temperature chemistry [9, 11, 13, 14]. Sung pointed out that these models predict much

longer auto-ignition delays for temperatures around 700 to 850 K. The predicted auto-ignition delays are about ten times longer than those measured in a rapid-compression-machine [15].

Figure 1 indicates a conceptual behavior for the ignition of alcohols and hydrocarbons. The symbols in Fig. 1 represent auto-ignition delay times measured in a shock-tube and a rapid-compression-machine. For comparison to the experiments, the ignition delay times from a reaction model developed on the basis of smaller alcohols (methanol or ethanol) is shown as a red dashed curve. It can precisely reproduce auto-ignition delays at high temperature, but gives much longer auto-ignition delays at low temperature because its lack of low-temperature chemistry. In order to improve the low temperature behavior, n-alkanes, which exhibit low-temperature chemistry, can be added into the alcohol mixture. Many useful models for C_8 to C_{16} n-alkanes are available [16]. The combined model still reproduce auto-ignition delays for high temperature conditions, but show to much reactivity at low temperatures as seen by strong negative temperature coefficient (NTC) ignition behavior. Therefore, it is necessary construct a new chemical kinetic model to predict ignition behaviors of higher alcohols.

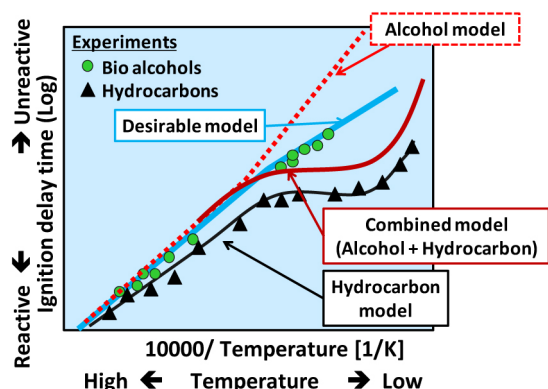


Figure 1. Schematic diagram indicating a concept of model development for higher alcohols

In addition to the overall chemical kinetic model, it is interesting to focus on a new reaction step for concerted elimination of HO_2 from isopentanol, a process recently examined by da Silva and Bozzelli et al. for the case of ethanol [17]. This new step begins with the isopentanol radical with the radical site at the carbon α from the OH group (Figure 2). This radical is called α -hydroxypentyl. It is easy to form α -hydroxypentyl because C-H bond dissociation energy at a site is a few kilocalorie less than those at other C-H sites on isopentanol. Therefore, a plenty of α -hydroxypentyl radical can be formed via H abstraction reactions from the fuel by OH, followed by O_2 addition reaction to α -hydroxypentyl radical which forms α -hydroxypentylperoxy radical. And as shown in Figure 2, there are two

possible pathways (referred to I and II) to make HO_2 and aldehyde. Pathway I is a concerted elimination reaction. This reaction pathway is analogous to the dominant addition-elimination pathway in the hydroxymethyl + O_2 reaction [18], and has much lower energy barrier than one for Pathway II, which is an intramolecular hydrogen shift from the hydroxyl group to the peroxy radical site. Pathway II is the first step of conventional low-temperature chemistry that leads chain branching and the appearance of NTC behavior. However, Pathway II is suppressed by the presence of Pathway I and almost no NTC like behavior is seen for isopentanol.

The isopentanol model developed in this study consists of low- and high-temperature chemistry based on reaction models for butanol isomers and isooctane (an alkane which a branched molecular structure similar to isopentanol) and the concerted HO_2 elimination mechanism based on an ethanol reaction model. The isopentanol model was validated with rapid-compression-machine and shock-tube data over a wide range of temperatures, pressures and equivalence ratios (712 - 1205 K, 0.8 - 2.3 MPa, and 0.5 - 1.0, respectively). The experimental data used for model validation in this study will be published soon [Paper is preparation, give reference]. Excellent agreement between model predictions and experimental data was achieved. Note that THERM software [19] was used to acquire thermochemical data for the species in the model, and also that the CHEMKIN-PRO software [20] was used for simulations of auto-ignition character in a constant volume zone and an HCCI engine.

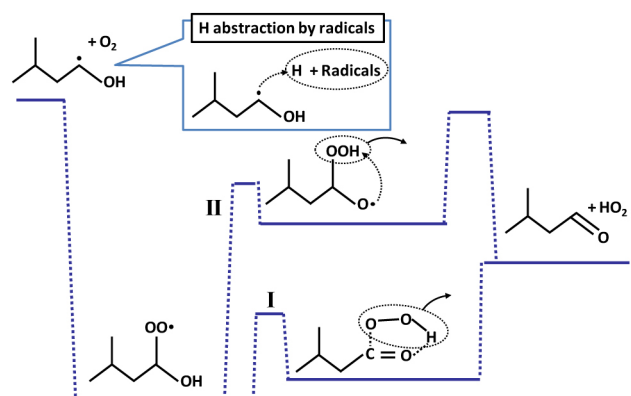


Figure 2. Schematic energy diagram for HO_2 elimination mechanism, α -hydroxypentyl is on the top left side and this figure roughly indicates an energy diagram for α -hydroxypentyl + O_2 reaction which eventually forms aldehyde and HO_2 on the right side in this figure. This figure is based on an energy diagram for ethanol proposed by da Silva and Bozzelli et al. [17]

RESULTS AND DISCUSSION

AUTO-IGNITION CHARACTER OF ISOPENTANOL

Auto-ignition delay times of isopentanol/air mixtures were calculated under various conditions of temperature, pressure, and equivalence ratio with assuming conservation of energy and species in an adiabatic constant volume zone. These auto-ignition times were compared with computed times for a representative constituent for gasoline, isooctane [16]. Isooctane has a branched molecular structure like isopentanol. Also, the auto-ignition times of isopentanol were compared to computed times for a gasoline surrogate fuel [21] which consists of four representative components (isooctane, n-heptane, toluene, and 2-pentene).

For all fuels, auto-ignition timing is defined as a time when temperature increases 500 K from a given initial temperature. This time corresponds to a steep increase in temperature associated with high temperature ignition. The isooctane model used here is distributed in [16], and has excellent agreement with several experimental data sets [21, 22]. Figure 3 shows a comparison of auto-ignition delay time calculated for isopentanol, isooctane, and gasoline surrogate for equivalence ratios Φ and initial pressures of 0.5 and 4.0 MPa, respectively. For isopentanol, auto-ignition delays were calculated for pressures of 2.0 and 8.0 MPa in order to investigate pressure dependence of isopentanol auto-ignition.

Regardless of the initial pressure, the auto-ignition character of isopentanol hardly shows a NTC-like trend, and it is supposed that auto-ignition delay times in a logarithmic scale are almost proportional to the inverse of temperatures. On the other hand, in case of isooctane for a temperature range of around 750 to 850 K ($10,000/T = 11.8$ to 13.3), NTC trend can be clearly seen, and many experiments also have shown NTC trends for isooctane [23, 24, 25]. Also, auto-ignition character of 87 octane gasoline surrogate shows slightly weaker NTC trend than isooctane. The degrees of NTC behavior of isooctane and gasoline surrogate are not so stronger than those of other alkanes [26, 27, 28] but are much stronger than isopentanol. Within this temperature range, auto-ignition delays for isooctane and gasoline surrogate seem to have less temperature sensitivity. However, for temperatures 850 K, auto-ignition delays for all fuels decrease significantly with an increase in temperature.

Fuel lean mixtures like $\Phi=0.5$ in Figure 3 allow HCCI operation without excessive pressure rise rates. It is important to compare the relative reactivities of the fuels at these fuel lean conditions. An interesting thing seen in Fig. 3 is that isopentanol is more reactive than isooctane and gasoline surrogate for temperatures over 850 K which is close to the experimentally measured mass averaged temperature at

around 340 deg.CA for an engine speed of 1200 rpm without boost and EGR [7, 29]. (Top dead center is 360 deg.C A).

It is also interesting to note the pressure dependence of isopentanol auto-ignition shown in Figure 3 and how it affects HCCI operation. Increasing pressure results in shorter auto-ignition delays for a wide range of temperature. This means that a combustion phasing in an HCCI engine would advance at a higher boost pressure.

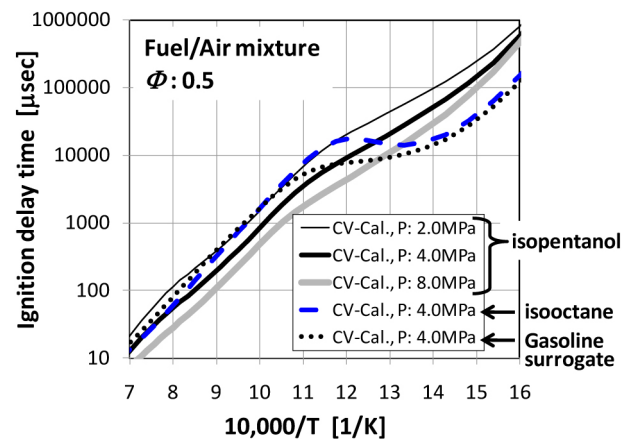


Figure 3. Auto-ignition delay times calculated for isopentanol, isooctane, and gasoline surrogate under various conditions of temperature. Constant volume combustion is assumed. For isopentanol, the calculated results are shown for several initial pressures (2, 4, and 8 MPa).

AUTO-IGNITION PROCESS OF ISOPENTANOL

As seen in Fig. 3, isopentanol, isooctane, and gasoline surrogate have significantly different auto-ignition characters particularly for lower temperature conditions, and by contrast, they show similar characters for higher temperature conditions. In this section, ignition processes will be compared in the cases that similar auto-ignition delay times are achieved for all fuels, which corresponds to aligning combustion phasing for each fuel. For this comparison, two different auto-ignition delay conditions were chosen (15 and 5 ms, respectively). The definition of auto-ignition delay time is the same as one defined in the previous section. Figure 4 indicates a comparison of the accumulated heat release which is normalized by total heat release. The shape of the accumulated heat release resembles the pressure history, since pressure rise in an adiabatic constant volume zone is directly associated with emitted heat by reactions.

In case of the 15 ms ignition delay, each fuel requires lower initial temperature T_{ini} to achieve longer ignition delays. And as shown in Fig. 3, to achieve these auto-ignition delays, each fuel was required different initial temperatures. The heat

release of isopentanol started earlier than others because the higher T_{ini} was required for isopentanol than those needed for the other fuels. However, the accumulated heat release for isopentanol is much less than those for the other fuels until the onset of hot-ignition. The other two fuels began to show two-stage heat release which began later than the onset of heat release of isopentanol. And even though the start of heat release for gasoline surrogate was the latest, the accumulated heat release increased much faster than others, and eventually all fuels could achieve the similar auto-ignition delay times.

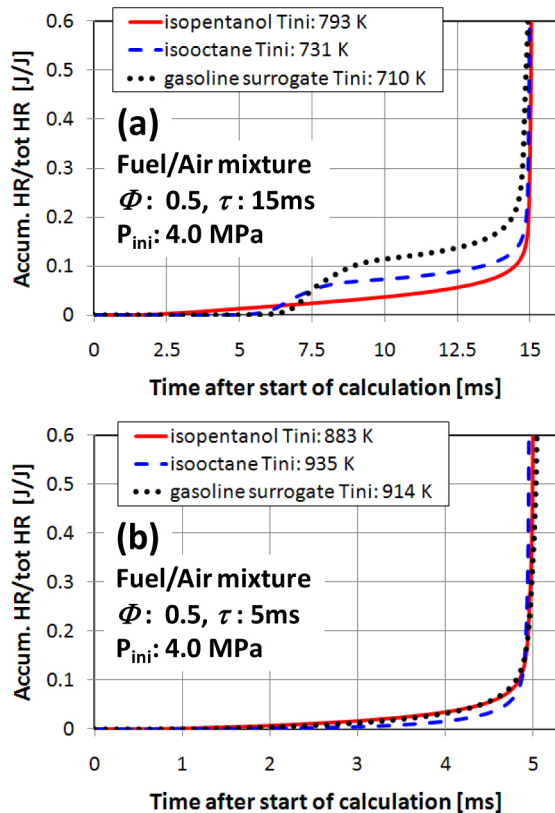


Figure 4. Comparisons of accumulated heat release of isopentanol with those of isooctane and gasoline surrogate, (a) for $\tau: 15\text{ms}$, and (b) for $\tau: 5\text{ms}$.

In case of the shorter ignition delay, 5ms, all fuels needed higher temperatures than those needed for 15ms ignition delay case. It is clearly different from the longer ignition delay case because no fuel indicates two-stage heat release. And, especially, isopentanol and gasoline surrogate show quite similar heat release processes, while the normalized pre-ignition heat release for isooctane was less than the others. In the HCCI engine experiments, each fuel used here has never indicated two-stage heat release as the engine was operated without boost and EGR at a moderate speed (e.g. 1200 rpm) [7, 29]. On the other hand, when the engine fueling gasoline was operated with boost and EGR and when the intake temperature was decreased to achieve an appropriate combustion phasing, low temperature heat release

(LTHR) appeared [29]. The reasons why the transition between single-stage and two-stage heat release occurs in an actual HCCI engine are supposed to be strongly associated with changes in intake temperature, pressure, amounts of fuel and residuals, and so on. Therefore, it is important to clarify a mechanism of the transition, and the chemistry leading to it in an HCCI engine needs to be explained.

CONDITIONS FOR HCCI ENGINE SIMULATION

Yang and Dec et al. have experimentally investigated fundamental combustion properties of isopentanol in an HCCI engine in a number of operating parameter sweeps in which wide ranges of engine speed, intake pressure, intake temperature, combustion phasing, and equivalence ratio, and all data were acquired with satisfying clean ($\text{ISNO}_x < 0.1\text{ g/kWh}$, no soot), efficient (combustion efficiency $> 96\%$), stable (coefficient of variation for indicated mean effective pressure (COV_{IMEP}) $< 2\%$), and non-knocking (ringing intensity $< 5\text{ MW/m}^2$) combustion [7]. Table 1 shows an engine and other parameters for HCCI engine experiments and simulations. As shown in Table 1, although a geometric compression ratio of the HCCI engine is 14.0, for HCCI engine simulations conducted in this study, an effective compression ratio, 13.3, was used, which was estimated with taking heat-loss analysis into account [30]. All simulations use a single-zone model that assumes homogeneous adiabatic combustion. Because of adiabatic conditions for the simulations, simulated in-cylinder pressures are likely to be higher than those measured. However, as measured in-cylinder pressures at a top dead center (TDC) during motored cycles and those simulated were compared, the pressure differences at TDCs for intake pressures of 100, 150, and 200 kPa were only 7.6 %, 4.9 %, and 4.2 %, respectively. Therefore, regarding initial conditions for intake pressure, the same pressure conditions as the experiments are used. Also, constituents of intake mixture and their fractions are the same as those measured in the experiments. It should be noted that unburned hydrocarbon in EGR gas is considered as isopentanol, because Hessel and Foster et al. showed in their CFD simulations and experiments that most of unburned hydrocarbon in exhaust gases is likely to be a fuel itself, if a mixture is not significantly lean (e.g. $\Phi < 0.2$) [31].

Because of the presence of EGR in some experiments, equivalence ratio is determined on the basis of total mass, rather than air alone. It is termed “Charge Mass Equivalence Ratio Φ_m ” which is defined as described below.

$$\Phi_m = \frac{(F/C)}{(F/A)_{stoic}} \quad (1)$$

(F/C) is the mass ratio of fuel and total inducted charge gas, and $(F/A)_{stoic}$ is the mass ratio of stoichiometric fuel/air