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## **Analysis of Advanced Biofuels**

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# Analysis of Advanced Biofuels

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## Abstract

Long chain alcohols possess major advantages over ethanol as bio-components for gasoline, including higher energy content, better engine compatibility, and less water solubility. Rapid developments in biofuel technology have made it possible to produce  $C_4$ - $C_5$  alcohols efficiently. These higher alcohols could significantly expand the biofuel content and potentially replace ethanol in future gasoline mixtures. This study characterizes some fundamental properties of a  $C_5$  alcohol, isopentanol, as a fuel for homogeneous-charge compression-ignition (HCCI) engines. Wide ranges of engine speed, intake temperature, intake pressure, and equivalence ratio are investigated. The elementary autoignition reactions of isopentanol is investigated by analyzing product formation from laser-photolytic Cl-initiated isopentanol oxidation. Carbon-carbon bond-scission reactions in the low-temperature oxidation chemistry may provide an explanation for the intermediate-temperature heat release observed in the engine experiments. Overall, the results indicate that isopentanol has a good potential as a HCCI fuel, either in neat form or in blend with gasoline.

## **ACKNOWLEDGMENTS**

Nicolas Dronniou (8362) is acknowledged for his contributions to the HCCI engine experiments, and Judit Zádor and John D. Savee (both 8353), and Giovanni Meloni (University of San Francisco) are acknowledged for their contributions to the experiments at the Advanced Light Source. Ravi X. Fernandes (8353, now RWTH Aachen University) is also acknowledged for his participation in early OH LIF experiments.

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## NOMENCLATURE

|                   |   |
|-------------------|---|
| CA                | Crank Angle   |
| CA10              | Crank Angle at 10% of total combustion heat release |
| DOE               | Department of Energy                                |
| HCCI              | Homogeneous-Charge Compression-Ignition             |
| IMEP <sub>g</sub> | Gross Indicated Mean Effective Pressure             |
| ITHR              | Intermediate-Temperature Heat Release               |
| LDRD              | Laboratory-Directed Research and Development        |
| LIF               | Laser-Induced Fluorescence                          |
| SNL               | Sandia National Laboratories                        |
| TDC               | Top Dead Center                                     |

## 1. INTRODUCTION

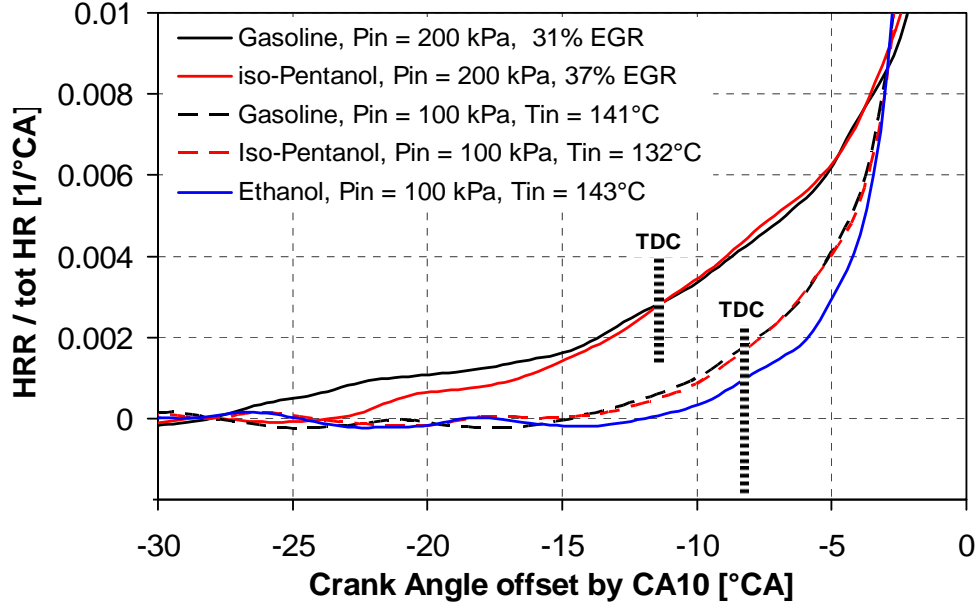
The development of new liquid fuels that can readily be derived from cellulosic biomass is one key strategy for reducing the greenhouse-gas intensity of the transportation sector and for improving the nation's energy security. Furthermore, new clean, high-efficiency combustion strategies that rely on compression ignition may be facilitated by chemical characteristics of new fuels. This LDRD analyzes the combustion characteristics of one particular candidate, isopentanol (3-methyl-butan-1-ol). A potentially high-efficiency pathway has been identified for isopentanol production from biomass, but its combustion characteristics have never been explored. Preliminary measurements both in a research homogeneous-charge compression-ignition (HCCI) engine and in the fundamental chemistry laboratory had suggested that isopentanol may be a high-performing HCCI fuel and that this performance may be related to its intermediate-temperature heat release properties.

This project combines measurements of the engine performance of isopentanol, carried out in the HCCI engine, with investigations of the fundamental chemistry that governs the low-temperature initiation reactions for autoignition. These reactions are key to the two-stage ignition behavior that can improve the control strategies for HCCI. The fundamental chemistry studies are built on laser-photolytic Cl-initiated oxidation with synchrotron-ionization mass-spectrometric detection of key products. The coupling of elementary chemistry and engine performance couples into a broader effort in the biofuel research community to determine how molecular structure is related to desired combustion characteristics for advanced engines and to begin to provide feedback to the development of fuel biosynthesis strategies.

## 2. HCCI ENGINE EXPERIMENTS

The results on HCCI combustion of isopentanol are reported in a peer-reviewed publication (Yang, Dec et al. 2010), and only a short synopsis is given here. For a given combustion phasing, isopentanol requires lower intake temperatures than gasoline or ethanol at all tested speeds, indicating a higher HCCI reactivity. Similar to ethanol but unlike gasoline, isopentanol does not show two-stage ignition even at very low engine speed (350 rpm) or with considerable intake pressure boost (200 kPa abs.). However, isopentanol does show considerable intermediate temperature heat release (ITHR) that is comparable to gasoline. Previous work has found that ITHR is critical for maintaining combustion stability at the retarded combustion phasings required to achieve high loads without knock. The stronger ITHR causes the combustion phasing of isopentanol to be less sensitive to intake temperature variations than ethanol. With the capability to retard combustion phasing, a maximum IMEP<sub>g</sub> of 5.4 and 11.6 bar was achieved with isopentanol at 100 and 200 kPa intake pressure, respectively. These loads are even slightly higher than those achieved with gasoline. The ITHR of isopentanol depends on operating conditions and is enhanced by simultaneously increasing pressures and reducing temperatures. However, increasing the temperature seems to have little effect on ITHR at atmospheric pressure, but it does promote hot ignition. Finally, the dependence of ignition timing on equivalence ratio, here called  $\phi$ -sensitivity, is measured at atmospheric intake pressure, showing that the ignition of isopentanol is nearly insensitive to equivalence ratio when thermal effects are

removed. This suggests that partial fuel stratification, which has been found effective to control the HRR with two-stage ignition fuels, may not work well with isopentanol at these conditions. Overall, these results indicate that isopentanol has a good potential as a HCCI fuel, either in neat form or in blend with gasoline.



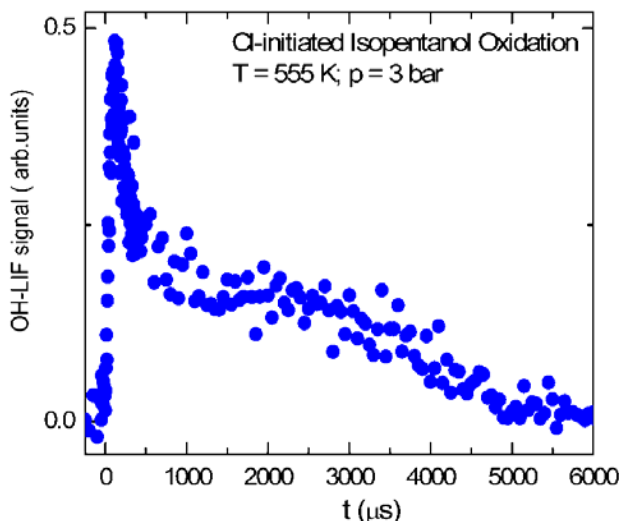
**Figure 1. Comparison of ITHR of isopentanol, ethanol, and gasoline at 100 and 200 kPa.  $T_{in}=60^{\circ}\text{C}$ ,  $\phi_m = 0.38$ , 1200 rpm.  $CA_{10} = 368.4^{\circ}\text{CA}$  at 100 kPa,  $371.5^{\circ}\text{CA}$  at 200 kPa. The width of TDC bar indicates the range of  $CA_{10}$  variation.**

### 3. FUNDAMENTAL CHEMISTRY EXPERIMENTS

The autoignition process that is central to successful operation of an HCCI or similar advanced compression-ignition engine is sensitive to the initial steps of oxidation, where the fuel molecule is attacked by an initiating radical, typically OH, losing a hydrogen atom. The subsequent fuel radical, “R”, can then react with molecular oxygen. The details of this reaction, and in particular the branching among the possible product channels, is the basis of most of the fuel effects in autoignition (Zádor, Taatjes et al. 2010). The formation of an OH radical in the  $R + O_2$  reaction is particularly important, both because OH is an excellent chain carrier and because OH production is kinetically linked to the formation of hydroperoxyalkyl radicals, whose reactions are responsible for low-temperature chain branching (Battin-Leclerc, Herbinet et al. 2010). The fundamental chemistry experiments in this project employed the technique of Cl-initiated oxidation, where a chlorine atom reacts with the fuel molecule to produce the fuel radical R and initiate the oxidation. The Cl atom is produced by pulsed-laser photolysis of a suitable precursor, and the course of the reaction is monitored by either optical (e.g., laser-induced fluorescence) or mass-spectrometric detection of products.

### 3.1. Laser-Induced Fluorescence Probing of OH Formation

Preliminary measurements of OH formation from Cl-initiated isopentanol oxidation were carried out in experiments associated with an earlier LDRD (Taatjes, Miller et al. 2009). The formation of OH at elevated pressure showed two timescales at low temperature. This has been associated in other systems with the presence of alkylperoxy and hydroperoxyalkyl chemistry that can lead to low-temperature and intermediate-temperature heat release in real combustion applications.

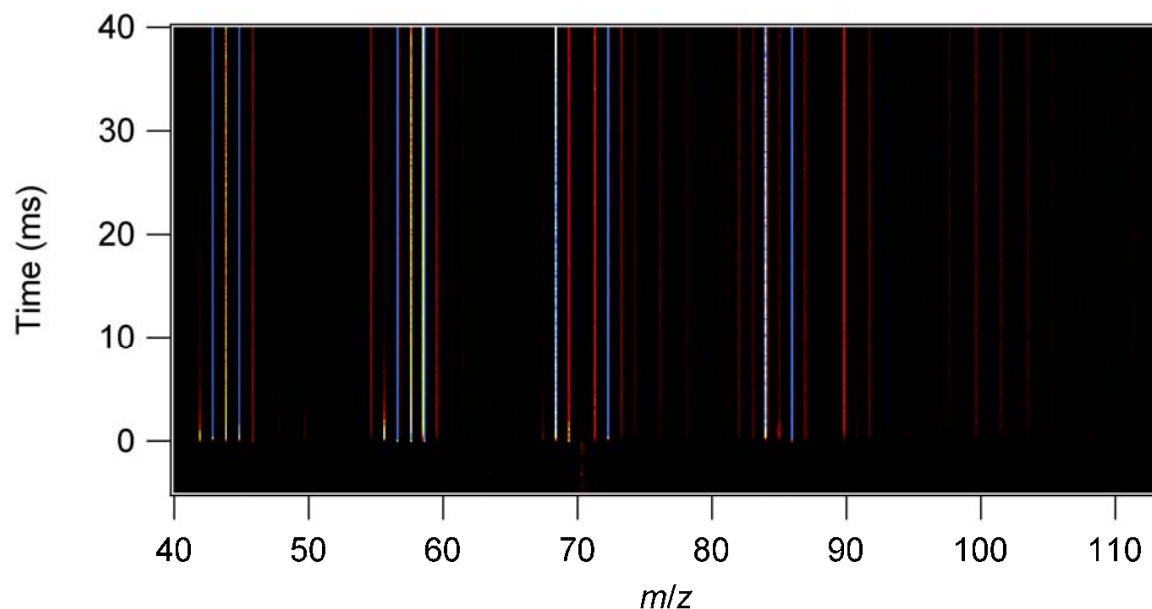


**Figure 2. Time-resolved OH LIF in pulsed-photolytic Cl-initiated isopentanol oxidation. The photolysis laser fires at  $t = 0$ .**

The details of the chemistry for isopentanol oxidation have not yet been explored; the mass-spectrometric experiments described in the following section will provide some more framework for future computational investigations that will analyze the molecular pathways. However, the qualitative behavior of isopentanol is “between” alkanes, for which a dramatic separation of prompt OH (from formally direct channels) and a longer-time alkylperoxy- and hydroperoxyalkyl-mediated OH production is noted, and ethanol, for which a single timescale of OH formation is observed (Taatjes, Miller et al. 2009).

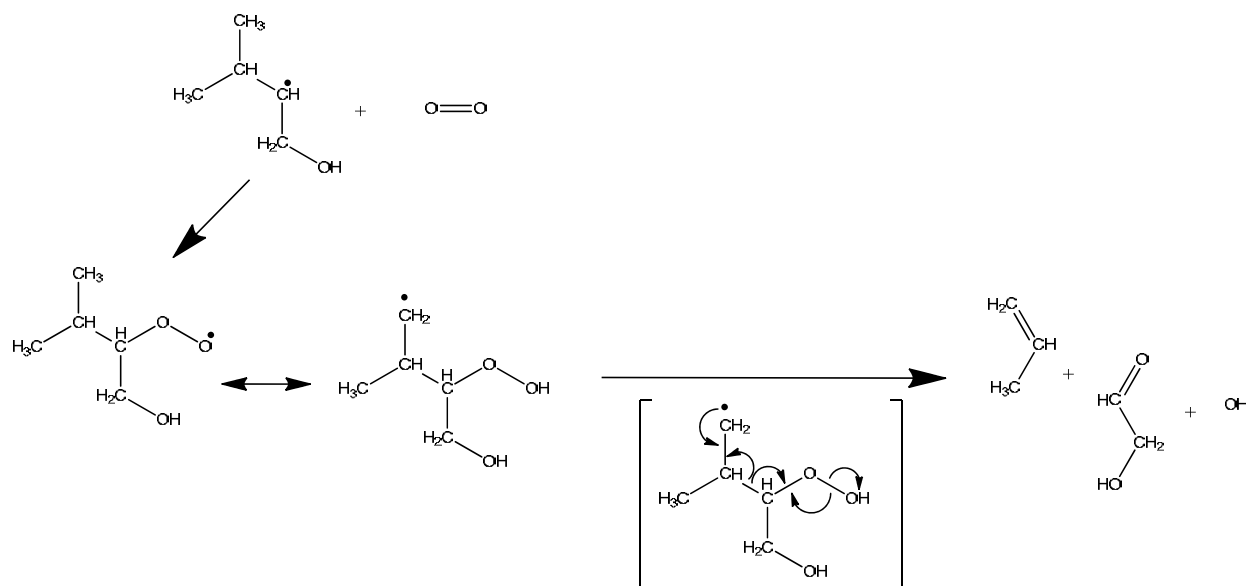
### 3.2. Synchrotron Photoionization Mass Spectrometry

The technique of multiplexed tunable synchrotron mass spectrometry (Osborn, Zou et al. 2008; Taatjes, Hansen et al. 2008) is a powerful means for isomer-resolved probing of chemical kinetics. In such experiments, a chemical reaction is initiated by pulsed laser photolysis, and the composition of the reacting mixture is continuously analyzed by time-of-flight or dual-sector mass spectrometry. The ionization step is accomplished by tunable synchrotron radiation; the dependence of the signal on the ionization photon energy allows discrimination of individual isomers (Taatjes, Hansen et al. 2005). In the Cl-initiated oxidation of isopentanol, a very rich chemistry is observed, with multiple product channels evident in the mass spectrum (Figure 3).



**Figure 3. Time-resolved photoionization mass spectrum for pulsed-photolytic Cl-initiated isopentanol oxidation. The photolysis laser fires at Time = 0.**

Of specific interest is the presence of many bond-fission channels, appearing at lower mass than the isopentanol parent ( $m/z = 88$ ). Whereas in alkane oxidation the formation of OH is linked with the production of cyclic ether products, which have higher mass than the alkane parent, in ethanol oxidation (Zádor, Fernandes et al. 2009) and evidently also in isopentanol oxidation, C-C bond cleavage from hydroperoxyalkyl radicals can dominate OH production. A representative C-C fission pathway (not the most favored one) is depicted schematically in Figure 4.



**Figure 4. Schematic depiction of one C-C fission channel in isopentanol oxidation that is coupled with OH production.**

Such channels are relatively underexplored; the transition state for the similar channel in  $\beta$ -hydroxyethyl radical reaction with  $O_2$  has considerable multireference character, implying that theoretical characterization may not be completely straightforward. Nevertheless, the prominence of such channels in the isopentanol oxidation suggests that they may be a general feature of larger alcohol autoignition chemistry.

## 4. CONCLUSIONS

This work introduces isopentanol for the first time as a new biofuel to the automotive and fuels industries. Isopentanol performs well, indicating that it has many advantages over the currently used ethanol and some over butanol, which is already being widely considered as a second generation biofuel for SI engines. Furthermore, the initial pathways of its oxidation chemistry have been at least qualitatively outlined, laying the groundwork for detailed chemical kinetic modeling. These are critical first steps toward the potential implementation of this fuel.

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