

## Characteristics of Isopentanol as a Fuel for HCCI Engines

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Yi Yang, John Dec and Nicolas Dronniou  
Sandia National Laboratories

Blake Simmons  
Sandia NL and Joint BioEnergy Institute

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### ABSTRACT

Long chain alcohols possess major advantages over the currently used ethanol as bio-components for gasoline, including higher energy content, better engine compatibility, and less water solubility. The rapid developments in biofuel technology have made it possible to produce C<sub>4</sub>-C<sub>5</sub> alcohols cost effectively. These higher alcohols could significantly expand the biofuel content and potentially substitute ethanol in future gasoline mixtures.

This study characterizes some fundamental properties of a C<sub>5</sub> alcohol, isopentanol, as a fuel for HCCI engines. Wide ranges of engine speed, intake temperature, intake pressure, and equivalence ratio are investigated. Results are presented in comparison with gasoline or ethanol data previously reported. 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. Our 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.

### INTRODUCTION

Homogeneous charge compression ignition (HCCI) has been studied extensively in the past decade as an alternative internal combustion (IC) engine process to the conventional premixed spark-ignition (SI) gasoline engine and non-premixed compression-ignition (CI) diesel engine. HCCI possesses the potential for diesel-like efficiency without the problematic NO<sub>x</sub> and soot emissions, but has the problems of inadequate combustion control and limited load range. Major progress have been made in the recent years to expand the HCCI operating range from idle [1] to near full load [2] using conventional gasoline fuels. However, future fuels could be significantly different from those used today. This is largely due to the booming efforts in biofuel technology that are expected in the near future to not only expand the feedstocks for fuel production, but to change the composition of the transportation fuels.

One potential change is to replace the currently used ethanol with longer chain alcohols. Higher alcohols, containing four or more carbons, are more favorable gasoline constituents than ethanol. With longer alkyl chain, the polarity of alcohols rapidly decreases, and their physiochemical properties become more like those of the hydrocarbons in gasoline. For example, higher alcohols are less hygroscopic [3] and less susceptible to separation in the presence of water when blending with hydrocarbon fuels. This is in sharp contrast with ethanol, and it makes higher alcohols more compatible with the existing fuel infrastructure. Material compatibility issues such as elastomer swelling are also much improved with higher alcohols. Additionally, in many cases, blending ethanol into gasoline enhances the vapor pressure of the gasoline, which causes high evaporative emissions and potential operational problems such as vapor lock. This is due to the formation of minimum-boiling azeotropes (by ethanol and some hydrocarbons in gasoline) whose boiling points are lower than either component. However, the azeotropes formed by higher alcohols and gasoline compounds barely increase the mixture vapor pressure [4], but instead enhance the vaporization of these alcohols in engine operation since they usually have high boiling temperatures and high heats of vaporization. Another clear advantage of higher alcohols is their higher energy content, which would significantly improve fuel economy over ethanol. One potential drawback could be the increased fuel reactivity with the longer chain which diminishes the potential for improved antiknock performance for SI combustion. However the octane ratings of C<sub>4</sub>-C<sub>5</sub> alcohols are still sufficient for gasoline SI engines, and they could work well for advanced HCCI or other low-temperature combustion engines, since these engines have different requirements for fuel autoignition quality.

Recent years have seen great advancements in synthetic biology that engineer metabolic pathways in organisms to produce C<sub>4</sub>-C<sub>5</sub> alcohols from sugar [5,6,7]. These advanced biochemical production routes for next-generation biofuels hold great promise in terms of generating a significant volume of fungible fuels that are more compatible with the existing fuel distribution and combustion infrastructure. Although still at the early stages of technical maturity, commercial production of these second-generation biofuels is being highly anticipated, and there are already several start-up companies around these new conversion technologies. Meanwhile, combustion of higher alcohols, mostly butanols blended in conventional fuels, has been studied in gasoline engines [8,9,10,11,12,13,14,15,16,17] and in diesel engines [18,19,20], as well as in more fundamental experiments [21,22,23,24,25]. However, few studies have been reported in HCCI engines. With both HCCI engines and second-generation biofuels on the horizon, it is imperative to understand the performance of these new fuels in these advanced IC engines.

Two papers were found in the literature that studied HCCI combustion of higher alcohols. Weiskirch et al. [20] studied HCCI combustion of n-butanol blended with a diesel fuel at 15 and 30 vol% in a diesel engine. The butanol fuels were compared against a conventional diesel fuel, and a mixture of the diesel fuel with ethanol and a biodiesel fuel. They reported that in HCCI combustion (achieved by multiple fuel injections during 80-40°C<sub>CA</sub> BTDC) the butanol/diesel blends retard the combustion timing of both low-temperature heat release (LTHR) and high-temperature heat release (HTHR), and produced less soot and NO<sub>x</sub> than the other fuels. The indicated specific fuel consumption (ISFC) was also lower with butanol blends when normalized by net heating value. Saisirirat et al. [26] studied HCCI combustion in a diesel engine using binary mixtures of n-heptane with either n-butanol, ethanol, or isooctane mixed at the same molar percent. They found that as the blending level increased from 0 to 57 mol% the timings of both LTHR and HTHR were delayed for all three compounds. At the same blending level, n-butanol and ethanol delay LTHR more than isooctane does, but the three compounds delay HTHR to similar extents. The two alcohols also showed higher heat release rates (HRR) during the main combustion.

The objective of the current work is to investigate the HCCI combustion fundamentals of a C<sub>5</sub> branched alcohol, isopentanol or 3-methyl-1-butanol, which is an attractive candidate biofuel that has a greater similarity to gasoline in physiochemical properties than ethanol or butanol. Isopentanol has much lower miscibility in water (2.5 g/100 ml), compared to ethanol (fully miscible) and n-butanol (7.7 g/100 ml) [3]. The volumetric energy density of isopentanol is over 30% higher than that of ethanol and 2% higher than that of n-butanol [27]. Recent advances in synthetic biology have opened up new approaches to the production of a wide range of fungible fuels, such as isopentanol [6]. This branched carbon chain can be produced through the fermentative conversion of sugars and is currently the target of several ongoing research projects, including those underway at the DOE Joint BioEnergy Institute.

In this work, HCCI engine experiments are first conducted to examine the reactivity of isopentanol and compare it with other fuels in terms of the intake temperature required to maintain a constant combustion phasing over a wide range of engine speeds. The potential for high-load HCCI is then studied by examining the early stages of heat release as a function of intake temperature ( $T_{in}$ ) and pressure ( $P_{in}$ ). Since these early stages of heat release, and the chemical reactions associated with them, occur prior to the main hot ignition they will be referred to by the term “pre-ignition” in this paper. This includes both the LTHR (if present) and the intermediate temperature heat release (ITHR). The current study shows that isopentanol does not exhibit LTHR but has relatively strong ITHR. Since ITHR has been found

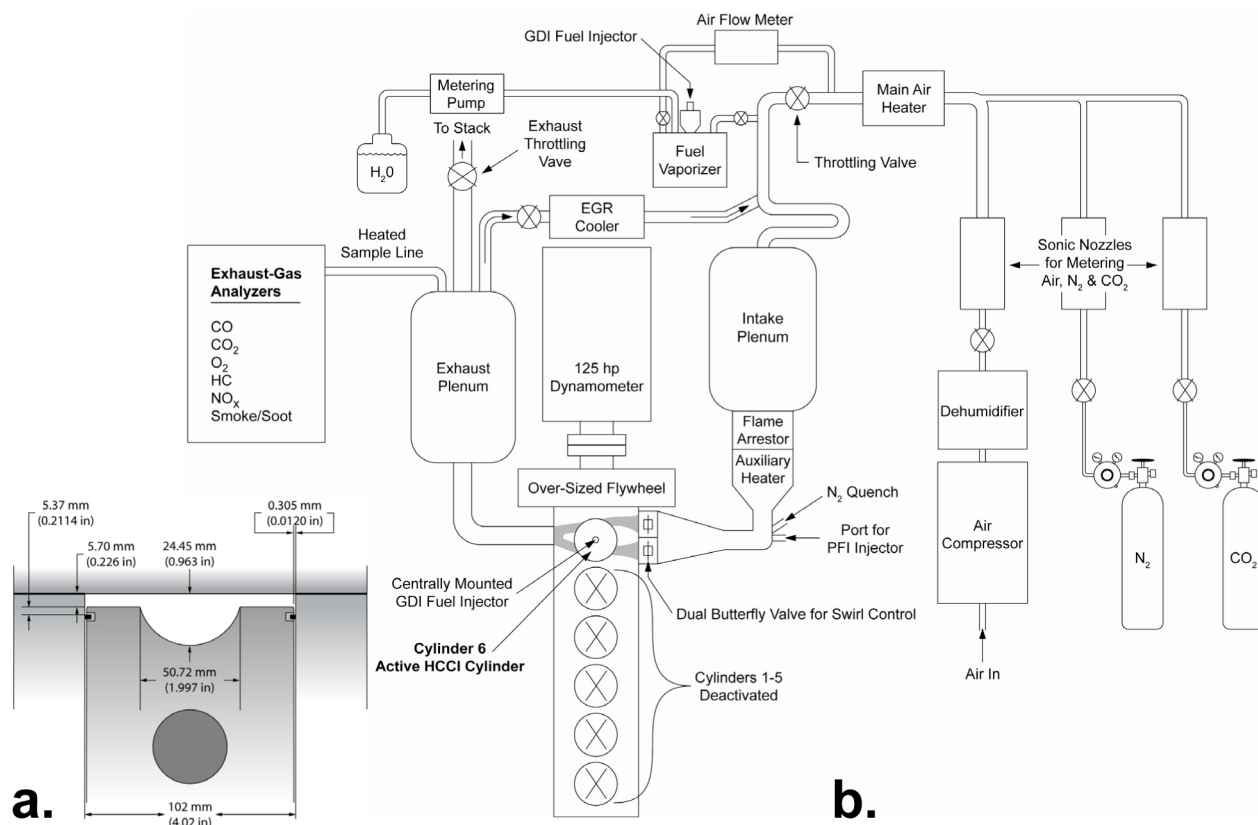


**Fig. 1. Schematic of the HCCI engine facility (b), and combustion chamber geometry of the CR = 14 piston, at TDC (a).**

advantageous for maintaining combustion stability with combustion phasing retard [28], as well as for extending HCCI to high-load boosted operation [2], the load limits of isopentanol are determined at  $P_{in} = 100$  and 200 kPa to allow comparison with other fuels. Finally, the potential for further high-load extension is tested by measuring the dependence of ignition timing on the equivalence ratio, otherwise known as  $\phi$ -sensitivity. Since isopentanol is a new fuel, these results are presented in comparison with gasoline and ethanol data, the majority of which have been reported in Ref. [2, 29].

## EXPERIMENTAL

### ENGINE FACILITY

The HCCI research engine used for this study was derived from a Cummins B-series six-cylinder diesel engine, which is a typical medium-duty diesel engine with a displacement of 0.98 liters/cylinder. Figure 1 shows a schematic of the engine, which has been converted for single-cylinder operation by deactivating cylinders 1-5. The active HCCI cylinder is fitted with a compression-ratio (CR) = 14 custom piston, as shown in Fig. 1a, which provides an open combustion chamber with a large squish clearance and a quasi-hemispherical bowl. The engine specifications and operating conditions are listed in Table 1. The configuration of the engine and facility is

identical to previous studies with gasoline [2] and ethanol [29].

The engine facility is equipped with a cooled EGR loop which introduces the EGR well upstream of the intake plenum to insure that the intake charge is well mixed. This system requires the back pressure to be higher than the intake pressure and was achieved by throttling the exhaust flow using the valve shown in Fig. 1b.

The intake air was supplied by an air compressor and precisely metered by a sonic nozzle. For operation without EGR, the air flow was adjusted to achieve the desired intake pressure, as measured by a pressure transducer on the intake runner. For operation with EGR, the air flow was reduced and the valve on the EGR line was opened. The exhaust back-pressure throttle valve was then adjusted to produce enough EGR flow to reach the desired intake pressure. This typically resulted in the exhaust pressure being about 2 kPa greater than the intake pressure. For consistency, the back pressure was maintained at 2 kPa above the intake pressure, even when EGR was not used.

For this study, the intake charge was fully premixed using the fueling system shown at the top of the schematic in Fig. 1b, except for the  $\phi$ -sensitivity test. This premixed fueling system consists of a gasoline direct injector (GDI) mounted in an

**TABLE 1. Engine Specifications and Operating Conditions**

|                                      |                                   |
|--------------------------------------|-----------------------------------|
| Displacement (single-cylinder) ..... | 0.981 liters                      |
| Bore .....                           | 102 mm                            |
| Stroke.....                          | 120 mm                            |
| Connecting Rod Length .....          | 192 mm                            |
| Geometric Compression Ratio .....    | 14:1                              |
| No. of Valves .....                  | 4                                 |
| IVO.....                             | 0° CA <sup>a</sup>                |
| IVC.....                             | 202° CA <sup>a</sup>              |
| EVO .....                            | 482° CA <sup>a</sup>              |
| EVC.....                             | 8° CA <sup>a</sup>                |
| Swirl Ratio.....                     | 0.9                               |
| Fueling system.....                  | Fully Premixed / GDI <sup>b</sup> |
| Coolant Temperature.....             | 100°C                             |

<sup>a</sup>0° CA is taken to be TDC intake. The valve-event timings correspond to 0.1 mm lift.

<sup>b</sup>GDI is only used in  $\phi$ -sensitivity test.

electrically heated fuel vaporizing chamber and appropriate plumbing to ensure thorough premixing with the air and EGR upstream of the intake plenum. A different GDI injector was mounted centrally in the cylinder head to enable direct injection in the  $\phi$ -sensitivity test. A positive displacement fuel flow meter was used to determine the amount of fuel supplied.

When EGR is used, an equivalence ratio based on total charge mass, rather than air alone, is used, which is called  $\phi_m$

$$\phi_m = \frac{(F/C)}{(F/A)_{stoich}}$$

and is defined as  $(F/A)_{stoich}$ , where  $F/C$  is the mass ratio of fuel and total inducted charge gas (i.e. fresh air and EGR), and  $(F/A)_{stoich}$  is the mass ratio of stoichiometric fuel/air mixture for complete combustion. This provides a convenient and consistent way to compare data with the same supplied energy content per unit charge mass (i.e., the same dilution level) for operating conditions with different fuels and different EGR levels. Note that  $\phi_m$  is the same as conventional air-based  $\phi$  when no EGR is used. It should also be noted that the air-based  $\phi$  is  $< 1$  for all conditions presented, so combustion is never oxygen limited.

The intake tank and plumbing were preheated to 50 - 60°C to avoid condensation of the fuel or water from the EGR gases. The intake temperature was precisely controlled by an auxiliary heater mounted close to the engine. The cooling water and lubricating oil were maintained at 100°C during the tests. All data were taken at an engine speed of 1200 rpm except for the speed sweep test.

## DATA ACQUISITION

Cylinder pressure measurements were made with a transducer (AVL QC33C) mounted in the cylinder head approximately 42 mm off center. The pressure transducer signals were

digitized and recorded at ¼° crank angle (CA) increments for 100 consecutive cycles. The cylinder-pressure transducer was pegged to the intake pressure near bottom dead center (BDC) where the cylinder pressure reading was virtually constant for several degrees. Intake temperatures were monitored using thermocouples mounted in the two intake runners close to the cylinder head. Firedeck temperatures were monitored with a thermocouple embedded in the cylinder head so that its junction was about 44 mm off the cylinder center and 2.5 mm beneath the surface. Surface temperatures were estimated by extrapolating the thermocouple reading to the surface, using the thickness of the firedeck and assuming that its back surface was at the 100°C cooling-water temperature. For all data presented, 0°CA is defined as TDC intake (so TDC compression is at 360°). This eliminates the need to use negative crank angles or combined bTDC, aTDC notation.

The crank angle of the 50% burn point (CA50) was used to monitor the combustion phasing. CA50 was determined from the cumulative apparent heat-release rate (AHRR), computed from the cylinder-pressure data (after applying a 2.5 kHz low-pass filter [30]). Computations were performed for each individual cycle, disregarding heat transfer and assuming a constant ratio of specific heats [31]. The average of 100 consecutive individual-cycle CA50 values was then used to monitor CA50 and for the CA50 values reported. The pressure-rise rates and ringing intensities (as defined in Ref. [32]) are computed from the same low-pass-filtered pressure data. For each cycle, the maximum pressure-rise rate was analyzed separately with a linear fit over a moving  $\pm 0.5^\circ$  CA window. Similar to CA50, these individual-cycle values were then averaged over the 100-cycle data set.

A second method of computing the HRR was used for detailed HRR-curve analysis. Here, the heat release was computed in a more refined way from the ensemble-averaged pressure trace (with the 2.5 kHz low-pass filter applied),

using the Woschni correlation for heat transfer [31]. Using the ensemble-averaged pressure trace has benefits from the standpoint of reduced noise on the heat-release traces. On the other hand, it can lead to overestimated burn durations if the cycle-to-cycle variations are large. However, for the condition where this was applied, the phasing was fairly stable with the standard deviation of CA50 over 100 fired cycles averaging  $< 1.3^\circ\text{CA}$ . Moreover, the results of this detailed HRR analysis are mainly used for comparisons of the early part of the heat release, leading up to hot ignition. Since these early autoignition reactions persist for  $15^\circ - 25^\circ\text{CA}$ , the relatively small cycle-to-cycle variation in CA50 will have little effect. Finally, it should be noted that applying the heat transfer correction only changed CA50 by about  $0.05^\circ\text{CA}$  compared to the AHRR method described above. Since this is less than the typical tolerance of  $\pm 0.1^\circ\text{CA}$  for combustion phasing control, no correction was applied to the CA50 values reported.

Although these detailed HRR curves appear quite smooth when plotted on a scale showing the entire combustion event, small quasi-periodic fluctuations were evident when viewed on the highly amplified scale used for comparisons of the early heat release. This is believed to be an artifact of the HRR being based on the derivative of the pressure trace (which amplifies noise in the pressure data) and the low-pass filtering process [30]. To mitigate these fluctuations, the HRR data were further filtered using a piecewise smoothing function, as described in Ref. [2], with care taken to ensure that the filtering does not alter the HRR trends.

Charge temperatures during the closed part of the cycle (*i.e.* compression/expansion) are computed using the ideal-gas law in combination with the measured pressure (ensemble-averaged over 100 cycles), the known cylinder volume, and the trapped mass. The trapped mass equals the sum of the supplied air, fuel, EGR, and residuals. The residual mass is computed by applying the ideal gas law to the clearance volume at TDC-valve-overlap, a pressure at the same timing determined from cycle-simulation modeling (using Ricardo's WAVE program), and an estimated residual temperature based on exhaust blowdown to this pressure. The average molecular weight used for the calculation of the charge temperature during the compression stroke corresponds to that of the trapped gases - including fresh air, EGR, retained residuals, and fuel. During the combustion event, and in proportion to the mass fraction burned, the molecular weight in the calculations is gradually changed to that of the measured exhaust composition (dissociation of the combustion products is neglected since it is expected to be small due to the relatively low peak combustion temperatures). This exhaust molecular weight is then used for the remainder of the expansion stroke and for computing the residual mass.

Exhaust emissions data were also acquired, with the sample being drawn just downstream of the exhaust plenum using a heated sample line (see Fig. 1b). CO, CO<sub>2</sub>, HC, NO<sub>x</sub>, and O<sub>2</sub> levels were measured using standard exhaust-gas analysis equipment. Particulate matter emissions were measured with an AVL smoke meter. In addition, a second CO<sub>2</sub> meter monitored the intake gases just prior to induction into the engine. This allowed the EGR fraction of the intake gases to be computed from the ratio of the intake and exhaust CO<sub>2</sub> concentrations.

## ISOPENTANOL AND TESTS CONDUCTED

Isopentanol is clear colorless liquid at room temperature. Although it has a disagreeable odor, isopentanol is rated similarly to gasoline in the Material Safety Data Sheet. The isopentanol used in this study was obtained from Sigma-Aldrich ( $> 98.5\%$ ), and relevant physiochemical properties are shown in Table 2 along with gasoline and ethanol. The data for isopentanol and ethanol are compiled from the CRC Handbook of Chemistry and Physics [27] and NIST Chemistry WebBook [33]. The data for gasoline is based on an analysis provided by the supplier, Chevron-Phillips.

Table 2 shows that most of the isopentanol properties are in between those of gasoline and ethanol. One notable exception is the viscosity which is higher for isopentanol than for gasoline (data for isooctane) and ethanol, by a factor of 8 and 3, respectively. The octane rating of isopentanol is unknown but is probably similar to that of n-butanol (RON/MON = 96/78) considering the longer but branched alkyl chain.

Isopentanol was studied in a number of operating parameter sweeps in which wide ranges of engine speed, intake pressure, intake temperature, combustion phasing, and equivalence ratio were examined. Details of each of these sweeps are presented below in the Results and Discussion. It should be pointed out that although the performance data are not reported in each case, all data were collected under the conditions where the HCCI combustion was clean ( $\text{ISNO}_x < 0.1 \text{ g/kWh}$ , no soot), efficient (combustion efficiency  $> 96\%$ ), stable ( $\text{COV}_{\text{IMEP}} < 2\%$ ), and non-knocking (ringing intensity  $< 5 \text{ MW/m}^2$ ), unless otherwise noted. It should also be noted that the boiling point of isopentanol is well above that of ethanol and toward the upper end of the gasoline boiling range. Therefore condensation of the fuel between the vaporizer and engine intake (see Fig. 1b) can occur more easily than for gasoline and ethanol. However, care was taken to maintain sufficient high temperature throughout this part of the intake system so that fuel did not condense even at the lowest  $T_{\text{in}}$  examined ( $60^\circ\text{C}$ ).

**TABLE 2. Fuel Properties Related to HCCI Combustion**

|                                                               | Gasoline                                         | Isopentanol  | Ethanol   |
|---------------------------------------------------------------|--------------------------------------------------|--------------|-----------|
| Formula                                                       | $C_{6.83}H_{13.7}^a$                             | $C_5H_{12}O$ | $C_2H_6O$ |
| Molecular Weight, g/mol                                       | 95.2                                             | 88.1         | 46.1      |
| Boiling Point, °C                                             | $T_{10} = 59$<br>$T_{50} = 93$<br>$T_{90} = 145$ | 131          | 78.3      |
| Density at 20°C, g/cm <sup>3</sup>                            | 0.7460                                           | 0.8014       | 0.7893    |
| Viscosity at 25°C, mPa-s                                      | 0.473 <sup>b,c</sup>                             | 3.69         | 1.074     |
| Specific heat ( $c_{p,g}$ ) at 500 K, J/(g•K)                 | 2.569 <sup>b</sup>                               | 2.277        | 2.079     |
| A/F stoichiometric                                            | 14.8                                             | 11.76        | 9.00      |
| Lower Heating Value, gas, MJ/kg                               | 43.47                                            | 35.37        | 27.75     |
| LHV for stoichiometric charge, MJ/kg                          | 2.734                                            | 2.722        | 2.683     |
| Heat of Vaporization at 25°C, kJ/kg                           | 324 <sup>b</sup>                                 | 631          | 920       |
| $\Delta H_{vap, 25^\circ C}$ for stoichiometric charge, kJ/kg | 20.1 <sup>b</sup>                                | 49.4         | 92.0      |
| RON                                                           | 90.8                                             | -            | 107       |
| MON                                                           | 83.2                                             | -            | 89        |
| Antiknock Index                                               | 87.0                                             | -            | 98        |

<sup>a</sup>Estimated from fuel hydrocarbon composition.

<sup>b</sup>Data for isooctane.

<sup>c</sup>From Ref. [34].

## RESULTS AND DISCUSSION

### ENGINE SPEED SWEEP

The first interest for an unknown fuel is its overall reactivity in HCCI combustion. The HCCI reactivity can be characterized in terms of the combustion phasing under given engine operating conditions. Reactive fuels have more advanced combustion phasing than less reactive fuels. Alternatively, if combustion phasing is held constant for different fuels, operating conditions have to be varied to accommodate the differences in fuel reactivity. For example, reactive fuels require lower intake temperature or more EGR for a given combustion phasing, compared to a less reactive fuel. In this study, the HCCI reactivity is characterized by the intake temperature that is required to maintain a given combustion phasing, specifically as the engine is swept over a wide range of speed. EGR is not used during the speed sweep.

Fig. 2 shows the engine speed sweeps for isopentanol, gasoline, and ethanol and the corresponding  $T_{in}$  required to

maintain  $CA_{50} = 372^\circ CA$  with  $\phi = 0.38$ . The gasoline and ethanol results are the same as in Ref. [29]. Over the speed range studied, isopentanol consistently requires a lower  $T_{in}$  than both ethanol and gasoline, indicating a higher HCCI reactivity than the other two fuels. The overall trend of the three fuels is quite similar, with nearly constant  $T_{in}$  at high speeds and declining  $T_{in}$  at low speeds. For speeds < 1200 rpm, a lower  $T_{in}$  is required to maintain the  $CA_{50}$  with decreased engine speed, which is likely due to two effects. First, a constant  $CA_{50}$  corresponds to a greater real-time ignition delay at lower speeds than at higher speeds. Thus, a somewhat lower  $T_{in}$  would be required at lower speeds to slow the reactions even if the reaction pathways remained the same. Second, the lower speeds allow more time for pre-ignition reactions to build up reactive mixtures and/or release more heat to speed up the autoignition process, thus further reducing the  $T_{in}$  requirement. This is particularly true for gasoline in that LTHR starts to occur as speed is reduced below 400 rpm, which significantly reduces the required  $T_{in}$  as shown in Fig. 2. Isopentanol does not show LTHR over the engine speeds plotted in Fig. 2. A low engine speed of 350