

Bio-Ketones: Autoignition Characteristics and Their Potential as Fuels for HCCI Engines

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ABSTRACT

This paper studies autoignition characteristics and HCCI engine combustion of ketone fuels, which are important constituents of recently discovered fungi-derived biofuels. Two ketone compounds, 2,4-dimethyl-3-pentanone (DMPN) and cyclopentanone (CPN), are systematically investigated in the Sandia HCCI engine, and the results are compared with conventional gasoline and neat ethanol. It is found that CPN has the lowest autoignition reactivity of all the biofuels and gasoline blends tested in this HCCI engine. The combustion timing of CPN is also the most sensitive to intake-temperature (T_{in}) variations, and it is almost insensitive to intake-pressure (P_{in}) variations. These characteristics and the overall HCCI performance of CPN are similar to those of ethanol. In contrast, DMPN shows multi-faceted autoignition characteristics. On the one hand, DMPN has strong temperature-sensitivity, even at boosted P_{in} , which is similar to the low-reactivity ethanol and CPN. On the other hand, DMPN shows much stronger pressure-sensitivity than ethanol and CPN. This pressure-sensitivity reduces the T_{in} requirement for DMPN as P_{in} increases, in a manner similar to gasoline, and it allows the same $T_{in} = 60^{\circ}\text{C}$ for DMPN as for gasoline at $P_{in} = 2.4$ bar. At this P_{in} , DMPN reaches a maximum HCCI load similar to gasoline, ~ 14 bar IMEP. Unlike gasoline, which requires significant combustion-timing retard to prevent knock at this maximum load, DMPN allows a more advanced combustion timing because its high temperature-sensitivity causes a lower heat release rate. As a result, DMPN yields a higher thermal efficiency than gasoline at comparable loads.

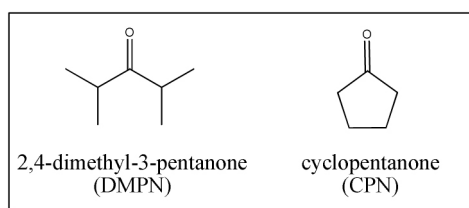
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INTRODUCTION

Biofuels are being increasingly used to supplement conventional petroleum-derived fuels for transportation. As a renewable energy source, biofuels help to reduce dependence on foreign-oil, mitigate greenhouse-gases emissions, and in some cases, improve air quality. Mandates for biofuels have been established around the world [1], requiring an even larger increase in biofuel usage in the future. Second-generation biofuels, using non-food-crop feedstocks, will contribute the major part of these increases. For example, US EPA has mandated that by 2022, 21 out of 36 billion gallons of biofuels ($\sim 20\%$ of total projected fuel demands) must be advanced biofuels produced from cellulosic or other non-food feedstocks [2].

With respect to the development of practical strategies for producing second-generation biofuels, the current practice involves feedstock pretreatment (breaking down biomass), separation of cellulose, conversion of cellulose to simple sugars, and fermentation of sugars to alcohols. A major area of difficulty in this process is the recalcitrance of lignocellulosic biomass, which requires extensive pretreatment of the feedstock and consequently reduces energy efficiency and increases the cost of production. One potential means of addressing this difficulty is the exploitation of natural biological mechanisms for breaking down biomass. For example, certain fungi, endophytes, naturally consume cellulose and excrete volatile organic compounds (VOC) -hydrocarbons and hydrocarbon derivatives - that may have utility as fuels [3, 4, 5, 6, 7].

Ketones are prominent in the VOC streams from several different fungi [3-4], but their combustion chemistry and application in engines are not well understood. The suitability of a fuel for combustion applications depends on many properties. The present study investigates ketone autoignition characteristics under engine conditions, which are critical for many emerging clean and efficient combustion strategies, including homogeneous charge compression ignition (HCCI) engines, as well as for conventional spark-ignition engines. Two ketones, 2,4-dimethyl-3-pentanone (DMPN), also called di-isopropyl ketone) and cyclopentanone (CPN), were chosen to represent branched ketones and cyclic ketones, respectively, which were observed in ketone products of fungi [4, 8]. Molecular structures of the two ketones are shown below.



A comprehensive literature survey on the topic of ketone combustion revealed few results relevant to this work. Most of these studies have focused on a single ketone compound, 3-pentanone, which is a commonly used fuel tracer for laser induced fluorescence (LIF) experiments. Ignition delays have been reported for 3-pentanone in shock tube experiments [9-10] for its impact on the autoignition of the doped fuels. In addition, combustion of a C6 cyclic ketone, cyclohexanone, was reported in a diesel engine and a significant reduction in engine-out soot emissions was observed, primarily due to the low cetane number of this ketone (CN = 10) [11]. However, we are not aware of comprehensive engine autoignition and combustion results for any ketone compounds.

In this paper, the autoignition characteristics of DMPN and CPN are studied in an HCCI engine. The approach is similar to that used recently in the same facility to study a C5 alcohol (3-methyl-1-butanol, or isopentanol) [12]. Fundamental engine experiments are conducted over a wide range of operating conditions to characterize the autoignition reactivity of the two fuels, and their autoignition sensitivity to variations in temperature and pressure. These characteristics are compared with ethanol and conventional-gasoline results from the same facility, some of which were reported in [12-13]. HCCI engine performance is tested for the maximum loads at naturally aspirated and boosted intake pressures. Partially stratified HCCI combustion is also investigated to determine the potential of utilizing the unique autoignition properties of these fuels to improve the performance of HCCI engines. The fuel autoignition characteristics here obtained from fundamental HCCI experiments are not only useful for HCCI engines, but can also be applied to understand the autoignition behavior in conventional engines, for example,

to understand the effects of charge temperature and pressure on fuel antiknock characteristics in spark-ignition engines.

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 1a 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. 1b, which provides an open combustion chamber with a large squish clearance and a quasi-hemispherical bowl. The engine specifications and some operating conditions are listed in Table 1. The configuration of the engine and facility is identical to recent studies with gasoline [14], ethanol [13], and isopentanol [12].

Table 1. Engine Specifications

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 ^a
IVC	202° CA ^a
EVO	482° CA ^a
EVC	8° CA ^a
Swirl Ratio	0.9
Fueling System	Fully Premixed / GDI
DI Injector.....	Bosch, 8-hole
Included Angle.....	70°
Hole Size.....	Stepped-hole, min. hole dia. = 0.125 mm
Injection Pressure.....	120 bar
Coolant/Oil Temperature	100°C

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

The engine is set up to allow both premixed fueling and direct fuel injection (DI). The premixed fueling system, shown at the top of the schematic in Fig. 1a, consists of a gasoline direct injector (GDI) mounted in an electrically heated fuel-vaporizing chamber and appropriate plumbing to ensure thorough premixing with the air and EGR upstream of the intake plenum. This system supplies all the fuel for the fully premixed combustion and ≥ 60% of fuel for the partially stratified combustion. The DI fueling is via another GDI injector (Bosch, 8-hole) mounted centrally in the cylinder head. DI fueling supplies ≤ 40% of fuel for partially stratified

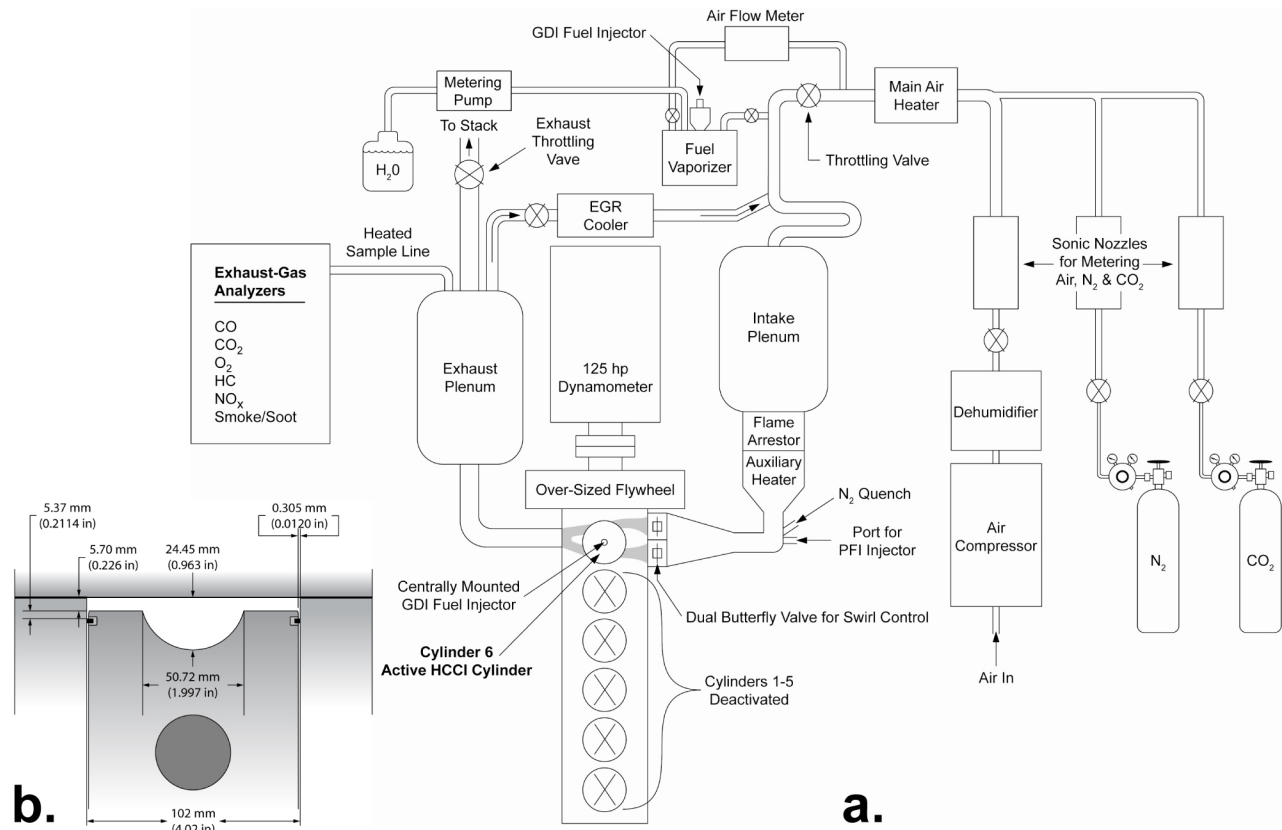


Fig.1. (a) Schematic of the HCCI engine facility and (b) combustion chamber geometry of the CR = 14 piston at TDC.

combustion. A positive displacement fuel flow meter was used to determine the total amount of fuel supplied.

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.

When EGR is used, an equivalence ratio based on total charge mass, rather than air alone, is used, which is called ϕ_m .

It is defined as $\phi_m = \frac{(F/C)}{(F/A)_{stoich}}$, 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 ϕ_m is the same as the conventional air-based ϕ when no EGR is used. For all

conditions presented, the air-based ϕ is < 1 , 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 was measured with a piezoelectric transducer (AVL QC33C) mounted in the cylinder head approximately 42 mm off center. The pressure transducer signals were recorded at $\frac{1}{4}^\circ$ 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. 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 on the fly during the experiment. CA50 was determined from the cumulative

Table 2. Fuel Properties Related to HCCI Combustion

	2,4-Dimethyl-3-pentanone	Cyclopentanone	Ethanol	Gasoline
Formula	C ₇ H ₁₄ O	C ₅ H ₈ O	C ₂ H ₆ O	C _{6.83} H _{13.7} ^a
Molecular Weight, g/mol	114.2	84.1	46.1	95.2
Boiling Point, °C	125.4	130.5	78.3	T ₁₀ = 59 T ₅₀ = 93 T ₉₀ = 145
Density at 20°C, g/cm ³	0.8108	0.9487	0.7893	0.7460
Lower Heating Value (LHV), gas, MJ/kg	36.22	32.60	27.75	43.47
A/F stoichiometric (kg/kg)	12.02	10.61	9.00	14.8
LHV for stoichiometric charge, MJ/kg	2.782	2.808	2.683	2.734
Heat of Vaporization at 25°C, kJ/kg	363.5	507.9	920	324 ^b
ΔH _{vap, 25°C} for stoichiometric charge, kJ/kg	27.7	43.5	92.0	20.1 ^b
Research octane number (RON)	-	-	107	90.8
Motor octane number (MON)	-	-	89	83.2
Antiknock Index, (RON + MON)/2	-	-	98	87.0

^a Estimated from fuel hydrocarbon composition.^b Data for isooctane.

apparent heat-release rate (AHRR), computed from the cylinder-pressure data (after applying a 2.5 kHz low-pass filter [15]). The start of heat release is set at the minimum point on the AHRR curve before the main heat release peak. Computations of CA50 were performed for each individual cycle, disregarding heat transfer and assuming a constant ratio of specific heats ($\gamma = c_p / c_v$) [16]. The average of 100 consecutive individual-cycle CA50 values was then used to monitor CA50 and for the CA50 values reported. For cases where the pre-ignition heat release rates were of particular interest, the 10% burn point (CA10) instead was monitored. The individual-cycle based method was also used to analyze the maximum pressure rise rates from combustion and to calculate ringing intensity as described by Eng in [17]. As with other works from our laboratory, the ringing intensity was kept $\leq 5 \text{ MW/m}^2$ to prevent engine knock [18].

A second method of computing the heat release rate (HRR) was used for detailed HRR-curve analysis. Here, the heat release rate 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 [16] and a variable γ which updates as a function of burn fraction. In using the Woschni correlation, the main coefficient, C , and a coefficient in the gas velocity term, C_2 , were adjusted for each combustion condition so that the heat release rate is zero before and after the combustion. Consistent values for the C and C_2 were used at comparable operating conditions. 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 HRR analysis was applied, the phasing was fairly stable with the standard deviation of CA10 over 100 fired cycles averaging $< 1.2^\circ\text{CA}$ and the standard deviation of the gross indicated mean effective pressure (IMEP_g) $< 2\%$.

Exhaust emissions data were acquired with the sample being drawn just downstream of the exhaust plenum using a heated sample line (see Fig. 1a). CO, CO₂, HC, NO_x, and O₂ levels were measured using standard exhaust-gas analysis equipment [15]. Smoke measurements were also made with an automated smoke meter for partial stratified combustions.

Fuel Properties and Test Conditions

The ketone compounds used in this study were obtained from Sigma-Aldrich (purities: CPN $\geq 99\%$, DMPN = 98%). The relevant physiochemical properties are shown in Table 2, along with those of gasoline and ethanol. Both ketones are clear colorless liquids at room temperature. The data for the ketones and ethanol are compiled from the CRC Handbook of Chemistry and Physics [19] and NIST Chemistry WebBook [20]. The data for gasoline is based on an analysis provided by the supplier, Chevron-Phillips.

Autoignition of the two ketone compounds were 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 (ISNO_x $< 0.1 \text{ g/kWh}$, no soot).



Documents

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efficient (combustion efficiency > 96%, based on CO and hydrocarbon emissions), stable ($COV_{IMEP} < 2\%$), and non-knocking (ringing intensity $\leq 5 \text{ MW/m}^2$), unless otherwise noted.

RESULTS AND DISCUSSION

HCCI Reactivity - Engine Speed vs. T_{in} Sweep

HCCI combustion is initiated by the early autoignition reactions at low and intermediate temperatures, which trigger the main heat-release event. A fuel with higher autoignition reactivity will reach hot ignition sooner than a fuel with lower reactivity, for otherwise equal conditions. Therefore, combustion timing is often used to compare autoignition reactivity of different fuels in HCCI engines. Alternatively, autoignition reactivity can be compared based on the adjustments that are required to reach a prescribed combustion timing. For example, a fuel with lower autoignition reactivity would need a higher intake temperature, a higher intake pressure, or less EGR, etc., in order to give a same combustion timing as a more reactive fuel, since the autoignition kinetics are accelerated by increasing reaction temperature, pressure, and oxygen concentration, etc.

The HCCI autoignition reactivity of the two ketone fuels, DMPN and CPN, is compared in an engine speed vs. intake temperature (T_{in}) sweep. The results are shown in Fig. 2, together with those for gasoline and ethanol. During this test, the combustion timing, equivalence ratio, and intake pressure (P_{in}) were kept constant, so that $CA_{50} = 372^\circ CA$ ($12^\circ CA$ after TDC compression), $\phi = 0.38$, and $P_{in} = 1 \text{ bar}$. No EGR was used at these naturally aspirated conditions, and T_{in} was adjusted to maintain the constant CA_{50} . At the low speed range (< about 1200 rpm), a higher T_{in} is typically required with increasing speed (Fig. 2). This is because higher temperatures accelerate the reaction rate, which compensates for the reduced time available for autoignition reactions as speed increases. At the high speed range (> about 1200 rpm), however, more pumping work is required to induct the charge in a shorter amount of time, which causes a stronger dynamic heating effect [21] that raises the temperature of the charge mixture significantly more than at lower speeds. Also, higher engine speeds allow less time for heat transfer. As a result of these two effects, less external heating is required, even though the charge temperature must continue to increase with engine speed to maintain the same CA_{50} [21]. Therefore, the required T_{in} hardly changes or even drops slightly with increasing speed.

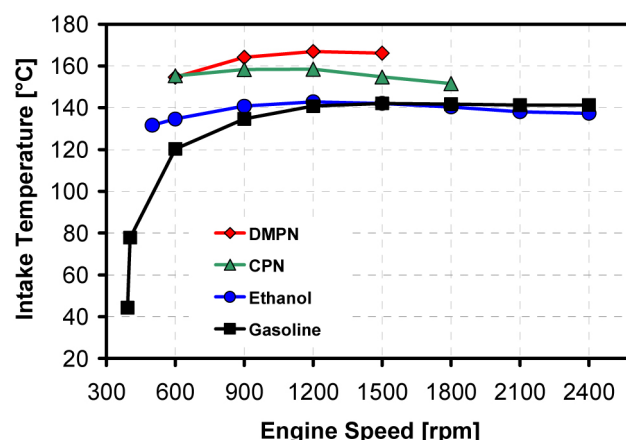


Fig. 2. Comparison of HCCI reactivity: engine speed vs. T_{in} sweeps. Constant $CA_{50}=372^\circ CA$, $P_{in}=1 \text{ bar}$, $\phi=0.38$, fully premixed charge, no EGR.

At a given engine speed, Fig. 2 shows that the intake temperatures required for the two ketones to reach a given CA_{50} are consistently higher than those of gasoline and ethanol, indicating a lower HCCI reactivity for the ketone compounds at these conditions. Unlike gasoline, neither ketone could achieve successful HCCI combustion at the desired combustion timing with engine speed less than 600 rpm. The steep T_{in} drop with gasoline at < 600 rpm is due to the onset of two-stage ignition at these speeds, and the low-temperature heat release (LTHR) significantly reduces the T_{in} requirement. On the other hand, the two ketones and ethanol show single-stage ignition throughout the speeds tested. Attempts to operate at lower speeds and lower T_{in} with these fuels were not successful (fuel failed to autoignite). Between the two ketones, the open-chain ketone (DMPN) requires a higher T_{in} , but the cyclic ketone (CPN) shows a steeper T_{in} drop for engine speeds $\geq 1200 \text{ rpm}$. The latter suggests that the autoignition of CPN is more sensitive to the temperature increase resulting from dynamic heating, which is confirmed in the next section by the temperature sensitivity test.

Autoignition Sensitivity to Temperature - T_{in} Sweep

As one of the most important parameters to reaction kinetics, temperature can affect the autoignition process and HCCI combustion in different ways due to the non-linear, and for some cases, non-monotonic effects of temperature on autoignition kinetics. For example, from Fig. 2 one would expect very different temperature effects on gasoline autoignition at 400 rpm and at 1200 rpm. Since 1200 rpm is our de facto standard speed for this study, a T_{in} sweep is conducted at this speed to determine the sensitivity of hot-ignition timing, as indicated by 10% burn point (CA_{10}), to variations in T_{in} (i.e. the T_{in} sensitivity) for the different fuels. An engine speed of 1200 rpm is also used for the rest of the experiments reported in this work.