NRC Publications Archive Archives des publications du CNRC

The effect of iso-octane addition on combustion and emission characteristics of a HCCI engine fueled with n-heptane

Dumitrescu, Cosmin E.; Guo, Hongsheng; Hosseini, Vahid; Neill, W. Stuart; Chippior, Wallace L.; Connolly, Trevor; Graham, Lisa; Li, Hailin

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1115/1.4003640>

Journal of Engineering for Gas Turbines and Power, 133, 11, pp. 112801-1-112801-7, 2011-11-01

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=b2a970e9-6158-4a46-9bd4-13b9065bfb69>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=b2a970e9-6158-4a46-9bd4-13b9065bfb69>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Cosmin E. Dumitrescu¹

e-mail: cosmin.dumitrescu@nrc-cnrc.gc.ca

Hongsheng Guo

Vahid Hosseini

W. Stuart Neill

Wallace L. Chippior

Institute for Chemical Process and Environmental
Technology,
National Research Council of Canada,
1200 Montreal Road,
Ottawa, ON, K1A 0R6, Canada

Trevor Connolly

Environment Canada,
Ottawa, ON, K1A 0H3, Canada

Lisa Graham

University of Canterbury,
Christchurch 8140, New Zealand

Hailin Li

West Virginia University,
Morgantown, WV 26506-6106

The Effect of Iso-Octane Addition on Combustion and Emission Characteristics of a HCCI Engine Fueled With n-Heptane

This paper investigates the effects of iso-octane addition on the combustion and emission characteristics of a single-cylinder, variable compression ratio, homogeneous charge compression ignition (HCCI) engine fueled with n-heptane. The engine was operated with four fuel blends containing up to 50% iso-octane by liquid volume at 900 rpm, 50:1 air-to-fuel ratio, no exhaust gas recirculation, and an intake mixture temperature of 30°C. A detailed analysis of the regulated and unregulated emissions was performed including validation of the experimental results using a multizone model with detailed fuel chemistry. The results show that iso-octane addition reduced HCCI combustion efficiency and retarded the combustion phasing. The range of engine compression ratios where satisfactory HCCI combustion occurred was found to narrow with increasing iso-octane percentage in the fuel. NO_x emissions increased with iso-octane addition at advanced combustion phasing, but the influence of iso-octane addition was negligible once CA50 (crank angle position at which 50% heat is released) was close to or after top dead center. The total unburned hydrocarbons (THC) in the exhaust consisted primarily of alkanes, alkenes, and oxygenated hydrocarbons. The percentage of alkanes, the dominant class of THC emissions, was found to be relatively constant. The alkanes were composed primarily of unburned fuel compounds, and iso-octane addition monotonically increased and decreased the iso-octane and n-heptane percentages in the THC emissions, respectively. The percentage of alkenes in the THC was not significantly affected by iso-octane addition. Iso-octane addition increased the percentage of oxygenated hydrocarbons. Small quantities of cycloalkanes and aromatics were detected when the iso-octane percentage was increased beyond 30%. [DOI: 10.1115/1.4003640]

Keywords: HCCI, n-heptane/iso-octane blends, regulated emissions, unregulated emissions

1 Introduction

Homogeneous charge compression ignition (HCCI) is a low temperature combustion strategy that offers the potential for relatively high fuel conversion efficiency and near-zero NO_x and soot emissions. In pure HCCI combustion, a volatile fuel is injected into the intake manifold in an effort to form a nearly homogeneous mixture inside the combustion chamber prior to the start of the compression stroke, similar to a spark-ignition (SI) engine. However, HCCI combustion is different because the process is initiated solely by compression, similar to a diesel engine. As a result, HCCI combustion offers the potential for diesel-like fuel conversion efficiency since higher compression ratios (CR) may be used as well as significantly lower oxides of nitrogen (NO_x) and soot emissions resulting from the lean, homogeneous fuel-air mixture.

The main challenge of HCCI combustion is to control the combustion phasing. In addition, HCCI combustion produces higher total unburned hydrocarbon (THC) and carbon monoxide (CO) emissions than conventional diesel combustion when conventional fuels are used [1]. Furthermore, HCCI combustion currently has a limited operational range and thus must coexist with traditional engine combustion modes. Therefore, it is possible that some fuel

reformulation may be beneficial to facilitate the adoption of HCCI combustion, although HCCI fuels must also remain compatible with existing internal combustion engines [2].

A detailed understanding of fundamental HCCI combustion characteristics is required for fuel effect investigations. The variation in the composition of commercially available fuels makes them relatively unattractive for studying details of the HCCI combustion process. Alternatively, an effective way to study fuel effects is to look at HCCI combustion of model fuel compounds. N-heptane and iso-octane are primary reference fuels (PRF) used to rate the autoignition resistance of gasoline. Although these two compounds have similar molecular sizes, n-heptane is a straight-chain alkane while iso-octane is a branched-chain alkane. They have widely different knocking tendencies, being at the opposite extremes of the octane rating scale. N-heptane exhibits two-stage autoignition behavior, while iso-octane's ignition is dominated by high temperature energy release. The detailed chemical kinetic mechanisms of these two fuels have been relatively well established [3,4] and are thus widely used by the combustion research community.

Emissions control is an important preoccupation of engine designers. Critical engine exhaust pollutants, such as NO_x, CO, THC, and particulate matter (PM), have been widely regulated. Numerous engine investigations have been conducted in an effort to understand the effects of combustion chamber configuration, operating condition, and fuel chemistry on regulated emissions. Other pollutants, typically present in smaller concentrations in engine exhaust, have not been studied extensively or restricted.

¹Corresponding author.

Contributed by the IC Engine Division of ASME for publication in the JOURNAL OF ENGINEERING FOR GAS TURBINES AND POWER. Manuscript received April 14, 2010; final manuscript received November 16, 2010; published online May 13, 2011. Assoc. Editor: Margaret Wooldridge.

On the other hand, the adverse effects of some unregulated emissions on human health and the environment may lead to additional regulations in the future. For example, polycyclic aromatic hydrocarbons (PAH) are known carcinogens, while oxygenated hydrocarbons (OHC), such as aldehydes or ketones, act as ozone precursors [5]. Therefore, investigation of both regulated and unregulated emissions is of great interest for engine researchers whenever possible.

Since understanding the mechanisms for production of unregulated emissions during the combustion of real fuels is formidable, numerous researchers have chosen to investigate HCCI combustion and emission characteristics using n-heptane and/or iso-octane. For example, Christensen et al. [6] used n-heptane and iso-octane fuel mixtures to explore the effects of fuel octane number, inlet temperature, and CR on HCCI combustion. They found that almost any fuel was suitable for HCCI combustion as long as an appropriate compression ratio was used. Olsson et al. [7] reported that the CO and THC emissions from a HCCI engine running on n-heptane/iso-octane blends were reduced if preheated inlet air was used at low loads. A higher intake temperature was needed as the iso-octane percentage increased to maintain the same combustion phasing and engine load. However, these two studies did not report unregulated emissions. Lemel et al. [8] reported the formaldehyde and OHC emissions from a HCCI engine with port fuel injection using n-heptane and iso-octane. Compression ratios of 11.5 and 18 were used for n-heptane and iso-octane, respectively. Dec and Sjöberg [9] studied HCCI combustion using iso-octane at various intake temperatures, engine speeds, and compression ratios. They showed that CO emissions were high due to the low combustion efficiency and that OHC emissions were significant. Later, Dec et al. [10] and Hessel et al. [11] performed more detailed analyses of exhaust samples from the same HCCI engine using iso-octane with equivalence ratios from 0.08 to 0.28 at a fixed compression ratio of 14. Increased THC (primarily iso-octane) and OHC emissions were reported as equivalence ratio decreased. In a rapid compression machine, Lim et al. [12] investigated the effect of n-heptane/iso-octane blends on low and high temperature combustion stages. They found that n-heptane had a lower ignition temperature for the low temperature ignition stage compared with iso-octane, but its main oxidation stage started at a higher temperature. Recently, regulated and unregulated emissions from a HCCI engine operated with n-heptane were reported by Li et al. [13]. However, to our knowledge, only a few studies have reported both the combustion behavior and regulated/unregulated emissions of HCCI engines using n-heptane and iso-octane fuel blends. Nowak et al. [14] performed a detailed exhaust analysis on a HCCI engine using a 60/40 n-heptane/iso-octane blend at one operating condition. Their analysis showed that total unburned hydrocarbons in the exhaust were composed of unburned fuel species, alkenes, and some light oxygenated compounds, but they did not directly specify formaldehyde. It is of great interest to further investigate how iso-octane and n-heptane fuel blends influence HCCI combustion and regulated/unregulated emission behavior over a wide range of operating conditions since n-heptane/iso-octane fuel blends have relatively well-known oxidation behavior and exhibit autoignition behavior between those of typical diesel and gasoline fuels.

This paper reports an experimental and numerical study on the effect of iso-octane addition on the combustion and emission characteristics of a HCCI engine fueled with n-heptane at constant speed and air/fuel ratio over a wide range of compression ratios. Both regulated and unregulated emissions were investigated. The results may assist engine designers to better understand the combined effect of fuel characteristics and engine operating conditions on HCCI combustion and indicate directions for further process improvement.

Table 1 Engine specifications

Cylinder bore	82.55 mm
Stroke	114.3 mm
Displacement	611.7 cc
Connecting rod length	254 mm
Compression ratio	4.6–16
Combustion chamber	Pancake shape
Intake valve open	10 deg CA ATDC
Intake valve close	34 deg CA ABDC
Exhaust valve open	40 deg CA BBDC
Exhaust valve close	5 deg CA ATDC
Fuel system	Air-assist atomization PFI

2 Experimental Setup and Numerical Model

The experimental setup and procedure have been described in detail in a previous study [13], so only brief descriptions will be provided here.

2.1 CFR Engine. The study was performed using a single-cylinder, variable compression ratio, four-stroke, air-assist port fuel injection Cooperative Fuel Research (CFR) engine coupled to a dynamometer. Engine specifications are presented in Table 1. The critical engine parameters are controlled by National Instruments hardware and Sakor Technologies' DYNOLAB™ test cell software.

A high frequency pressure transducer measured the cylinder pressure, which was routed together with the crank angle to a high-speed data acquisition system. The intake air temperature and pressure as well as the exhaust backpressure were maintained constant throughout the experiments. A Sierra Instruments (model 780) mass flow meter measured the intake air flow rate. A Micro Motion (model D6) mass flow meter measured the fuel flow rate. The fuel injection quantity was controlled by the injection pulse width.

2.2 Exhaust Gas Analysis. California Analytical Instruments (series 600) gas analyzers were used to measure CO, CO₂, O₂, NO_x, and THC emissions from the HCCI engine. Exhaust samples were also collected into SUMMA stainless steel electropolished canisters using a Dekati two-stage ejector diluter with an overall dilution ratio of 59.4. An Agilent (model 6890) gas chromatograph equipped with a flame ionization detector was used for quantitative analysis of all unburned hydrocarbons except for carbonyl compounds. For the carbonyl compounds, separate samples were collected using 2,4-dinitrophenylhydrazine coated cartridges, which were analyzed using an Agilent (model 1100) liquid chromatograph with an ultraviolet-visible light diode array detector. An Agilent (model 593) mass selective detector was used beforehand to identify the oxygenated compounds.

2.3 Experimental Procedure. Experimental conditions are presented in Table 2. The HCCI engine was operated at a speed of 900 rpm using different n-heptane/iso-octane blends. The composition of each blend is represented by PRF followed by the liquid volume percentage of iso-octane. For example, PRF0 represents pure n-heptane and PRF30 represents a blend of 30% iso-octane and 70% n-heptane by volume. In this paper, PRF0, PRF10, PRF30, and PRF50 fuel blends were investigated. Since engine compression ratio significantly influences the start of combustion, measurements were taken over a range of CR for each fuel blend.

Table 2 Experimental conditions

Engine speed	900 rpm
Compression ratio	10–16
AFR	50
T _{air,intake}	30°C
EGR	0%

The minimum CR corresponds to the onset of stable combustion. The maximum compression ratios were limited to 15 for PRF0 and 16 for the other blends because further CR increase resulted in unacceptable engine knocking. Li et al. [13] found that CO and THC emissions sharply increased and combustion efficiency decreased for air-to-fuel ratios (AFR) greater than 50 with this engine and that minimum NO_x emissions occurred around an AFR of 50 and 30°C intake temperature. Therefore, the HCCI engine was operated at AFR 50 and 30°C intake temperature for this study. The engine was operated without exhaust gas recirculation (EGR) to simplify the numerical simulation and data interpretation. The data from 200 cycles were averaged at each operating condition.

2.4 Numerical Model. A combined single- and multizone model was used to investigate the combustion and emission characteristics of the HCCI engine using n-heptane/iso-octane blends. The model assumes the working fluid to be an ideal gas and simulates a full cycle of engine operation starting from the top dead center (TDC) during the exhaust process. Details of the model have been presented elsewhere [15] and therefore only a brief description is provided below.

The simulation uses a single-zone model for the intake and exhaust gas exchange processes and a multizone model for simulating the combustion process from intake valve closing (IVC) to exhaust valve opening (EVO). An iterative calculation procedure is used, starting from an estimate of the initial conditions. Following the first engine cycle, the composition and temperature from the previous engine cycle are used as the input for the next engine cycle. The simulation stops when the differences in composition and temperature between two consecutive iterations are smaller than the specified tolerances.

Mass exchange between zones was neglected, but heat exchange was included in the calculation procedure. Heat transfer to the cylinder wall was calculated by the model proposed by Woschni [16]. In addition, radiation heat transfer from each zone to the cylinder wall was considered using an optically thin model in which the radiating species are CO₂, H₂O, and CO. The radiation heat loss from each zone was calculated by

$$\frac{dQ_{r,k}}{dt} = 4v_k \sigma k_p (T_k^4 - T_w^4) \quad (1)$$

where $Q_{r,k}$ is the heat loss of zone k , σ is the Stefan-Boltzmann constant, v_k is the volume of zone k , T_k is the temperature of zone k , T_w is the cylinder wall temperature, and k_p is the Planck mean absorption coefficient that is calculated by the method recommended by Tien et al. [17], considering the three aforementioned radiating species.

The gas exchange rate during intake and exhaust processes was calculated by a one-dimensional quasi-steady flow model. Further details of the model are provided in Refs. [15,18].

The chemical reaction scheme used for primary reference fuels was essentially the one developed at Lawrence Livermore National Laboratory [19] with the addition of NO_x formation chemistry from GRI-MECH3.0 [20]. In total, 1051 species and 4339 reactions were included in the reaction scheme. Since a large number of chemical species have been included in the chemistry employed for this investigation, only four zones (crevice, boundary, core, and hot zones) were used in the multizone model during the closed portion of the engine cycle to reduce the computational cost. The mass percentages of fuel-air mixture in the crevice, boundary, core, and hot zones were assumed to be 3%, 9.7%, 77.6%, and 9.7%, respectively. The use of only four zones in the model might lead to some quantitative errors, but this was deemed acceptable for the purpose of quantitatively understanding the combustion and emission characteristics.

Fig. 1 Combustion phasing (CA50) versus CR for four PRF blends

3 Results and Discussion

3.1 Overall Engine Performance. For HCCI combustion, the compression ratio influences the combustion phasing and efficiency. The combustion phasing, typically quantified in terms of the crank angle where 50% energy has been released (CA50), is plotted as a function of CR for the four fuel blends in Fig. 1.

The experimental data show that when CR increased from 10 to 15, CA50 advanced 14 deg CA for PRF0, while CA50 advanced 17 deg CA for PRF50 when CR increased from 11.5 to 16. This suggests that a blend with more iso-octane is more sensitive to CR. This feature has been qualitatively captured by the numerical simulation. Both the experimental and numerical simulation data show progressively retarded CA50 with increasing iso-octane percentage in the fuel blend [6,12]. However, quantitative differences exist between the experimental data and the numerical simulation, especially when the iso-octane percentage in the blend increases.

Figure 2 shows how the combustion efficiency varies as a function of CA50 for the different fuel blends. Combustion efficien-

Fig. 2 Combustion efficiency versus combustion phasing for four PRF blends

Fig. 3 Measured (EXP) and calculated (NS) cylinder pressure traces at CA50 $\approx$ -5 deg CA ATDC for four PRF blends

cies were not calculated based on the numerical simulation results due to the difficulty in modeling CO emissions. The general trend is that combustion efficiency increases as CA50 is advanced (i.e., increasing CR) until reaching a plateau around CA50 = -10 deg CA ATDC. This result is inconsistent with that reported by Christensen et al. [6], who showed that combustion efficiency decreased with increasing CR for n-heptane/iso-octane fuel blends. Differences in experimental conditions may have caused this disparity, as intake air temperature was adjusted for different CR in Ref. [6], while a constant intake air temperature was maintained for all CR in this study. Figure 2 also shows that combustion efficiency decreased as the iso-octane percentage in the fuel blend increased. This is consistent with the result obtained by Christensen et al. [6]. The difference in combustion efficiency between PRF0 and PRF10 was significant only when the CA50 took place after TDC.

Furthermore, Fig. 2 indicates that the combustion efficiency decreased quickly with increasing iso-octane in the fuel blend at retarded combustion phasing (CA50 after TDC) for the all higher iso-octane blends. Overall, the CA50 range for stable HCCI combustion with no engine knocking decreased with iso-octane addition.

Figure 3 shows the measured and predicted combustion pressure traces for all fuel blends at a similar combustion phasing (CA50 = -5 ± 1.5 deg CA, ATDC). The corresponding compression ratios were CR=11 for PRF0, CR=11.5 for PRF10, CR=13 for PRF30, and CR=14 for PRF50. Although there were quantitative differences between the experimental and numerical results, they were qualitatively in agreement. While the model predicted a more advanced phasing for low temperature heat release in the temperature range of 760–880 K for all PRF blends, it captured the phasing of the main combustion stage. The increased compression ratio required to obtain similar combustion phasing as iso-octane fraction increases is responsible for the differences in the maximum cylinder pressures shown in Fig. 3.

3.2 Regulated Emissions. The variations in CO, HC, and NO_x emissions as a function of combustion phasing (CA50) are plotted in Fig. 4. The experimental data show that CO emissions sharply increased with retarded combustion phasing (i.e., CA50 after TDC) because a larger fraction of the combustion process took place during the expansion stroke with correspondingly lower combustion temperatures. This would be expected to delay CO oxidation, which is greatly affected by combustion temperature [21]. Slightly lower CO emissions were observed as iso-octane addition increased due to the higher temperatures and pressures associated with the higher CR required to achieve similar combustion phasing, which provided more favorable conditions

for CO oxidation.

At higher compression ratios, CA50 always occurred before TDC for all blends. Consequently, the combustion efficiency was close to its maximum with CO emissions almost reaching a plateau at CA50 $\approx$ -5 deg CA, ATDC. Unfortunately, the CO emission trend was not captured by the numerical simulation. This may be due to the simplified assumptions made in the model.

The experiment and numerical models show a qualitatively consistent trend for THC emissions despite some quantitative differences. An increase in the iso-octane fraction in the fuel increased THC emissions in most cases. In addition, both the experimental and numerical results show that the THC emission curves almost overlap for PRF0 and PRF10. Furthermore, the THC emissions seem to reach a minimum with advanced combustion phasing for all PRF blends. The quantitative difference between the experimental and numerical results may be due to insufficient zones and some of the assumptions made in the numerical model.

The experimental results do not show significant differences in NO_x emissions among the different fuel blends when CA50 was retarded beyond -5 deg ATDC. The numerical simulation correctly captured the observed trend of increasing NO_x emissions with higher iso-octane fraction in the blend at advanced combustion phasing. This is due to increased combustion temperatures associated with increased CR at similar combustion phasing for the higher PRF blends. However, the slight increase in NO_x emissions that was experimentally observed at most retarded CA50 values was not captured by the model. The experimentally observed phenomenon is also inconsistent with the general knowledge that combustion temperature dominates NO_x formation in internal combustion engines since retarding the combustion phasing after TDC reduces the compression temperatures and pressures. It should be pointed out that the NO_x chemistry used in the model includes all the current known NO_x formation mechanisms, i.e., the thermal route, the prompt route, the N₂O, and the NNH intermediate routes. Therefore, it is not clear what caused the discrepancy in NO_x emissions between the experimental and numerical results for CA50 retarded after TDC, but it may be related to the experimentally observed increase in cycle-to-cycle variations for the most retarded CA50 values.

Overall, the results show that for the present engine configuration and experimental conditions, increasing the fraction of iso-octane in the blend reduced the CR range for low CO, HC, and NO_x emissions.

3.3 Unregulated Emissions. The effect of iso-octane addition on unregulated emissions was investigated at a combustion phasing of -5 ± 1.5 deg CA, ATDC. For all four fuel blends, the combustion efficiency was higher than 94%, NO_x emissions were at their minimum values, and CO and HC emissions were relatively close to their minimum values.

Table 3 provides the mass percentage of different classes of hydrocarbons that contribute to the THC emissions. More than 150 unregulated species were identified. The species were classified as alkanes, alkenes, oxygenates, cycloalkanes, and aromatics. The numerical simulation did not provide emission data for the last two classes. The OHC were primarily carbonyls. Other OHC, such as propylene oxide, furan, 2-propenol, 2-methyl furan, tetrahydrofuran, and butyltetrahydrofuran, represented less than 1% of the THC emissions.

Both the experimental and numerical simulation results indicate that alkanes are the predominant HC species, followed by oxygenates and alkenes. In addition, the experiment and model predictions show qualitatively consistent trends for alkanes and oxygenates when the iso-octane fraction increased from 0% to 30%, i.e., the percentages of alkanes decreased and oxygenates increased with increasing iso-octane fraction. However, differences exist between the experimental and predicted results when the iso-octane fraction increased to 50%. It is not clear what caused the differ-

Fig. 4 CO, THC, and NO_x emissions versus combustion phasing (CA50) for four PRF blends

ences, but it should be noted that the CR used for PRF50 was the largest (CR=14). As the majority of unburned fuel comes from the crevices, the CR difference may have altered the initial conditions. The predicted trend for alkenes was also not consistent with the measured data. The model does not take into account the changes in exhaust species composition during the exhaust process, which may contribute to qualitative or quantitative differences between the experimental and numerical results.

Cycloalkanes and aromatics are two hydrocarbon classes that were detected in the measured THC emissions, but they were not included in the reaction scheme employed in the numerical simu-

lation. Cycloalkanes and aromatics were found to comprise 2% and 1% of the THC emissions for PRF30 and PRF50, respectively, but were not detectable with the other two fuel blends.

Figure 5 compares the measured and predicted variations of several key hydrocarbon species in the THC emissions for the four PRF blends at the previously mentioned CR. Both the experimental and numerical simulation results show that the dominant alkane species in the exhaust were n-heptane and iso-octane. In addition, the iso-octane percentage in the THC emissions increased, while that of n-heptane decreased with increasing iso-octane addition. This implies that the largest source of THC emissions in HCCI combustion occurs due to the lack of fuel oxidation in the colder regions. The numerical simulation shows that almost all THC emissions originate from the crevice and boundary zones. Again, the differences between experimental and numerical simulations exist for PRF50 with a sharper decrease in n-heptane and no increase in iso-octane in the predicted results.

Methane is an important alkane in the engine exhaust. The experimental data show a relatively small and constant methane percentage for all blends. The numerical model overpredicted the methane percentage in the exhaust for PRF0 to PRF30 by a factor of about 3, but then predicted a sudden decrease in methane percentage for PRF50.

The alkenes primarily consisted of ethylene, propylene, and 1-butene (~80% of the total alkenes). Ethylene emissions were found to decrease linearly from PRF0 to PRF50 with good agreement between the experiment and the model. The model successfully captured the experimentally measured trend for both propylene and i-butene, but there were discrepancies in the quantitative

Table 3 Percentages of different classes in THC emissions

		PRF			
HC		0	10	30	50
Alkanes (%THC)	EXP	72	67	68	69
	NS	68	63	64	31
Oxygenates (%THC)	EXP	14	21	19	19
	NS	26	30	30	50
Alkenes (%THC)	EXP	14	12	11	11
	NS	5	6	5	18
Cycloalkanes (%THC)	EXP	0	0	1	1
	NS	NA	NA	NA	NA
Aromatic (%THC)	EXP	0	0	1	0
	NS	NA	NA	NA	NA
Other (%THC)	EXP	0	0	0	0
	NS	1	1	1	1

Fig. 5 Selected hydrocarbon percentages in THC emissions at CA50 $\approx$ -5 deg CA ATDC for four PRF blends

results.

The oxygenated compounds in a HCCI engine are mainly the result of quenched oxidation of partial combustion products as they travel from hotter regions to colder ones as well as from fuel trapped in the crevices and engine boundary layer. Experimentally, the addition of iso-octane was found to increase OHC production. Carbonyls were the major class of oxygenate species detected. Four species, namely formaldehyde, acetaldehyde, acrolein, and acetone, represented 70–75% of the carbonyls. The percentages of formaldehyde and acetone in the THC increased with increasing iso-octane fraction. Both acetaldehyde and acrolein emissions were nearly constant for all four PRFs. The numerical model correctly captured the trends for acetaldehyde and acetone, but under- and overpredicted the formaldehyde and ac-

rolein contributions, respectively.

There were no cycloalkanes and aromatics detected in the exhaust of PRF0 and PRF10. However, 1–2% aromatic and cycloalkane compounds were detected in THC emissions for PRF30 and PRF50, which is relatively surprising considering the lean fuel-air mixture used in this study. A literature survey did not provide a clear explanation for these findings. What is known is that there is almost an order of magnitude increase in single-ring aromatics production in rich iso-octane premixed combustion compared with n-heptane oxidation at similar conditions [22–25]. It is possible that some fuel-rich pockets existed in the combustion chamber in the current experiments even though best efforts were made to achieve a homogeneous fuel-air mixture. In addition, PRF30 and PRF50 required a higher compression ratio to achieve similar

combustion phasing. The higher surface area/volume ratio of the combustion chamber at higher compression ratios may have contributed to quenching the oxidation reactions of the aromatics and cycloparaffins that formed during the combustion process. However, the fact that small quantities of aromatics were detected for PRF30, but not for PRF50, shows that further investigation is needed to determine the exact cause of this phenomenon. The numerical simulation did not provide any insight because cycloalkanes and aromatics were not included in the reaction scheme employed by the numerical simulation.

Overall, the numerical simulation reproduced the qualitative trends for most unregulated species even though only four zones were employed in the numerical simulation to reduce the computational cost. The notable exception was for PRF50 where the iso-octane percentage in the engine exhaust was significantly underpredicted.

4 Conclusions

An experimental and numerical study was performed to determine the influence of iso-octane addition on the combustion and emission characteristics of a HCCI engine fueled with four different n-heptane/iso-octane blends, ranging from pure n-heptane to a 50/50 blend. The CR was varied from 10 to 16, while maintaining a constant engine speed of 900 rpm, AFR 50, 30°C intake temperature, and no EGR. The combustion efficiency and regulated emissions were compared based on the combustion phasing (CA50). The unregulated emissions were measured at optimum combustion phasing (CA50 = -5 ± 1.5 deg CA, ATDC).

Results show that for the operating conditions studied, iso-octane addition retarded the combustion phasing and reduced combustion efficiency. The operating compression ratio range narrowed with increasing iso-octane fraction in the fuel. The NO_x emissions at advanced CA50 increased with increasing iso-octane fraction, but the difference became negligible once CA50 approached TDC and beyond.

The primary components of the unburned hydrocarbons in the exhaust, in order of decreasing importance, were alkanes, oxygenated hydrocarbons (mainly carbonyls), and alkenes. The alkanes were composed almost exclusively of completely unburned fuel (i.e., n-heptane and iso-octane). The percentage of alkanes in the THC did not significantly change, with the n-heptane and iso-octane contributions decreasing and increasing monotonically, as the iso-octane fraction in the fuel increased. The addition of iso-octane was found to increase the percentage of OHC emissions in the THC emissions. The alkenes were primarily ethylene, propylene, and 1-butene (~80% of the alkene total), and their emissions were not significantly influenced by iso-octane addition. No cycloalkanes and aromatics were detected in the exhaust for PRF0 and PRF10, but they composed 1–2% of the THC emissions for PRF30 and PRF50.

The numerical predictions confirmed many of the experimental results with the obvious exceptions of overpredicting the percentage of oxygenates in the THC emissions and the failure to predict the CO emission trend. Simplified assumptions used in the model, including freezing the exhaust species composition at exhaust valve opening, may have contributed to the discrepancies between the experimental and numerical results, especially when the iso-octane percentage was increased over 30%.

Acknowledgment

The authors would like to acknowledge the financial support of the Government of Canada's PERD/AFTER Program, Project No. C22.001.

Nomenclature

ATDC = after top dead center
ABDC = after bottom dead center
BBDC = before bottom dead center

References

- [1] Stanglmaier, R. H., and Roberts, C. E., 1999, "Homogeneous Charge Compression Ignition (HCCI): Benefits, Compromises, and Future Engine Applications," SAE Technical Paper No. 1999-01-3682.
- [2] Zhao, F., Asmus, T., Assanis, D., Dec, J. E., Eng, J., and Najt, P., 2003, *Homogeneous Charge Compression Ignition (HCCI) Engines: Key Research and Development Issues*, Society of Automotive Engineers, Inc., Warrendale, PA.
- [3] Curran, H. J., Gaffuri, P., Pitz, W. J., and Westbrook, C. K., 1998, "A Comprehensive Modeling Study of n-Heptane Oxidation," *Combust. Flame*, **114**(1–2), pp. 149–177.
- [4] Curran, H. J., Gaffuri, P., Pitz, W. J., and Westbrook, C. K., 2002, "A Comprehensive Modeling Study of Iso-Octane Oxidation," *Combust. Flame*, **129**(3), pp. 253–280.
- [5] Cardone, M., Prati, M. V., Rocco, V., Seggiani, M., Senatore, A., and Vitolo, S., 2002, "Brassica Carinata as an Alternative Oil Crop for the Production of Biodiesel in Italy: Engine Performance and Regulated and Unregulated Exhaust Emissions," *Environ. Sci. Technol.*, **36**(21), pp. 4656–4662.
- [6] Christensen, M., Anders, H., and Johansson, B., 1999, "Demonstrating the Multi Fuel Capability of a Homogeneous Charge Compression Ignition Engine With Variable Compression Ratio," SAE Technical Paper No. 1999-01-3679.
- [7] Olsson, J.-O., Erlandsson, O., and Johansson, B., 2000, "Experiments and Simulation of a Six-Cylinder Homogeneous Charge Compression Ignition (HCCI) Engine," SAE Technical Paper No. 2000-01-2867.
- [8] Lemel, M., Hultqvist, A., Vressner, A., Nordgren, H., Persson, H., and Johansson, B., 2005, "Quantification of the Formaldehyde Emissions From Different HCCI Engines Running on a Range of Fuels," SAE Technical Paper No. 2005-01-3724.
- [9] Dec, J. E., and Sjöberg, M., 2003, "A Parametric Study of HCCI Combustion—The Sources of Emissions at Low Loads and the Effects of GDI Fuel Injection," SAE Technical Paper No. 2003-01-0752.
- [10] Dec, J. E., Davisson, M. L., Sjöberg, M., Leif, R. L., and Hwang, W., 2008, "Detailed HCCI Exhaust Speciation and the Sources of Hydrocarbon and Oxygenated Hydrocarbon Emissions," SAE Technical Paper No. 2008-01-0053.
- [11] Hessel, R. P., Foster, D. E., Aceves, S. M., Davisson, M. L., Espinosa-Loza, F., Flowers, D. L., Pitz, W. J., Dec, J. E., Sjöberg, M., and Babajimopoulos, A., 2008, "Modelling Iso-Octane HCCI Using CFD With Multi-Zone Detailed Chemistry: Comparison to Detailed Speciation Data Over a Range of Lean Equivalence Ratios," SAE Technical Paper No. 2008-01-0048.
- [12] Lim, O. T., Sendoh, N., and Iida, N., 2004, "Experimental Study on HCCI Combustion Characteristics of N-Heptane and Iso-Octane Fuel/Air Mixture by the Use of a Rapid Compression Machine," SAE Technical Paper No. 2004-01-1968.
- [13] Li, H., Neill, W. S., Chippior, W., Graham, L., Connolly, T., and Taylor, J. D., 2007, "An Experimental Investigation on the Emission Characteristics of HCCI Engine Operation Using N-Heptane," SAE Technical Paper No. 2007-01-1854.
- [14] Nowak, L., Guibert, P., Cavadias, S., Dupré, S., and Momique, J. C., 2008, "Methodology Development of a Time-Resolved In-Cylinder Fuel Oxidation Analysis: Homogeneous Charge Compression Ignition Combustion Study Application," *Combust. Flame*, **154**(3), pp. 462–472.
- [15] Guo, H., Li, H., and Neill, W. S., 2009, "A Study on the Performance of Combustion in a HCCI Engine Using N-Heptane by a Multi-Zone Model," ASME Paper No. ICEF2009-14117.
- [16] Woschni, G., 1967, "Universally Applicable Equation for the Instantaneous Heat Transfer Coefficient in the Internal Combustion Engine," SAE Technical Paper No. 670931.
- [17] Tien, C. L., Irvine, T. F., Jr., and James, P. H., 1969, "Thermal Radiation Properties of Gases," *Adv. Heat Transfer*, **5**, pp. 253–324.
- [18] Heywood, J. B., 1988, *Internal Combustion Engine Fundamentals*, McGraw-Hill, New York.
- [19] Lawrence Livermore National Laboratory' Primary Reference Fuels (PRF): Iso-Octane/N-Heptane Mixtures Detailed Chemical Kinetic Mechanism, Available Online at https://www-pls.llnl.gov/?url=science_and_technology-chemistry-combustion-prf.
- [20] Smith, G. P., Golden, D. M., Frenklach, M., Moriarty, N. W., Eiteneer, B., Goldenberg, M., Bowman, C. T., Hanson, R. K., Song, S., Gardiner, W. C., Jr., Lissianski, V. V., and Qin, Z., 2010, Available Online at http://www.me.berkeley.edu/gri_mech/.
- [21] Sjöberg, M., and Dec, J. E., 2005, "An Investigation Into Lowest Acceptable Combustion Temperatures for Hydrocarbon Fuels in HCCI Engines," *Proc. Combust. Inst.*, **30**(2), pp. 2719–2726.
- [22] El Bakali, A., Delfau, J.-L., and Vovelle, C., 1999, "Kinetic Modeling of a Rich, Atmospheric Pressure, Premixed n-Heptane/O₂/N₂ Flame," *Combust. Flame*, **118**(3), pp. 381–398.
- [23] Zhang, H. R., Eddings, E. G., and Sarofim, A. F., 2007, "Combustion Reactions of Paraffin Components in Liquid Transportation Fuels Using Generic Rates," *Combust. Sci. Technol.*, **179**(1&2), pp. 61–89.
- [24] Blanquart, G., Pepiot-Desjardins, P., and Pitsch, H., 2009, "Chemical Mechanism for High Temperature Combustion of Engine Relevant Fuels With Emphasis on Soot Precursors," *Combust. Flame*, **156**(3), pp. 588–607.
- [25] Marchal, C., Delfau, J.-L., Vovelle, C., Moréac, C., Mounaïm-Rousselle, C., and Mauss, F., 2009, "Modelling of Aromatics and Soot Formation From Large Fuel Molecules," *Proc. Combust. Inst.*, **32**(1), pp. 753–759.