

Unregulated Emissions of an HCCI Engine Operating on N-Heptane / *Iso*-Octane Blends

Cosmin E. Dumitrescu^{a*}, Vahid Hosseini^a, W. Stuart Neill^a, Wallace L. Chippior^a, Trevor Connolly^b, Lisa Graham^{b,c}, Hailin Li^d

^a National Research Council, Ottawa, Ontario K1A 0R6

^b Environment Canada, Ottawa, Ontario K1A 0H3

^c University of Canterbury, Christchurch, New Zealand

^d West Virginia University, Morgantown, West Virginia, USA 26506-6106

1. Introduction

Homogeneous Charge Compression ignition (HCCI) is an advanced combustion technology being considered for use in internal combustion (IC) engines to improve fuel economy and reduce NO_x and soot emissions. Similar to a spark-ignition (SI) engine, an HCCI engine may be operated by injecting fuel into the intake manifold. The resulting homogeneous mixture of air, fuel and diluents may be compressed until spontaneous autoignition occurs. The advantage of a pure HCCI engine over an SI engine is better fuel economy due to its higher part-load efficiency. Compared to diesel engines, the low to moderate combustion temperatures in HCCI engines results in lower NO_x and soot emissions while maintaining diesel-like efficiency. HCCI combustion relies on mixture auto-ignition, which strongly depends on fuel chemistry and can be controlled only indirectly by adjusting the engine operating parameters (intake temperature and pressure, compression ratio, air/fuel ratio, EGR rate).

For practical combustion applications, HCCI and traditional combustion modes may coexist throughout the engine operational range, for maximum combustion efficiency and reduced emissions. Therefore, it is critical to find suitable fuels which can be used for both HCCI and traditional combustion modes [1]. In HCCI mode, the shorter combustion duration and lower combustion temperature leads to lower NO_x and soot emissions, but higher unburned hydrocarbon (HC) and carbon monoxide (CO) emissions compared with standard diesel engines when regular fuels are used [2].

The major engine pollutants (CO, NO_x, HC, and soot) are reported in IC engine studies for different engine operating conditions and combustion chamber configurations, but there is little information about unregulated emissions. For example, polycyclic aromatic hydrocarbons (PAH) are potentially carcinogenic, while oxygenated hydrocarbons (OHC), as aldehydes or ketones, act as ozone precursors [3]. For HCCI operation using *i*-octane, Dec [4] showed that at low and very-low engine loads, for various intake temperatures, engine speeds, and compression ratios, the CO emissions increased substantially due to the low combustion efficiency, with large emissions of OHC indicated by a single-zone model. In a later work the same group [5] performed a detailed analysis of exhaust samples for different air/*i*-octane mixtures, with equivalence ratios from 0.08 to 0.28 and fixed compression ratio (CR) of 14. Large fractions of HC (mostly *i*-octane) and OHC were identified as the mixture equivalence ratio decreased. They concluded that a stratified-charge mixture technique which reduces the ultra-lean zones inside the combustion chamber can be employed to reduce the HC and OHC emissions and improve combustion efficiency. Merritt et al. [6] studied the unregulated emissions from a diesel engine operating in alternate modes similar to HCCI: premixed charge compression ignition (PCCI), and low-temperature combustion (LTC). The engine-out emissions of carbonyl compounds were significantly increased for all LTC modes and for PCCI-Lean conditions as compared to diesel operation using diesel fuel. Kaiser et al. [7] measured detailed emissions of a surrogate gasoline, direct-injection, HCCI engine. A significant change was found in the combustion

* Corresponding author: Cosmin.Dumitrescu@nrc-cnrc.gc.ca

process at low engine loads (A/F ratio over 70), which resulted in sharp increases of HC and OHC emissions.

Differences in the composition of commercially available fuels make it difficult to detail HCCI chemical reactions. Therefore unregulated emissions data of fuels with known chemistry are necessary in the search of the “ideal” fuel or “ideal” combustion strategy. One direction is to look at the fuels generally used to characterize CI or SI engines: n-heptane and *i*-octane. Our research group investigated characteristics of an HCCI engine using n-heptane [8], and reported both regulated and unregulated emissions, while Dec [5] reported results of HCCI operation using *i*-octane. Considering that n-heptane and *i*-octane are extreme points on the octane rating scale, and that detailed mechanism describing their oxidation in air are available [9, 10], it is of interest to analyze low engine load HCCI combustion for blends having different n-heptane/*i*-octane ratios. This study can help to better understand the combining fuel characteristics / engine operating conditions effect on HCCI combustion mode and indicate directions for further process improvement.

2. Experimental setup and procedure

The experimental setup and procedure are described in detail in a previous paper [8]. Only a short description will be provided here.

2.1. CFR engine

The study was performed on a single cylinder, variable compression, four-stroke, air-assist port fuel injection CFR engine, coupled to a dynamometer. The critical engine parameters (intake temperature, air/fuel ratio, intake and exhaust pressure) are controlled by a DynoLab controller using National Instruments hardware. Engine specifications are presented in Table 1.

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 °CA ATDC
Intake valve close	36 °CA ABDC
Exhaust valve open	40 °CA BBDC
Exhaust valve close	5 °CA ATDC
Fuel System	Air assist atomization port fuel injection

A high frequency pressure transducer (Kistler Corp., model 6121) measured the cylinder pressure, which was routed together with the crank angle to a high-speed data acquisition system (Optimum Power Technology PTrAc). The intake air temperature and both intake and exhaust pressures were kept constant throughout the experiments. A Sierra model 780 FlatTrack mass flow meter measured the intake airflow. A Micro Motion D6, Coriolis-effect, mass flow meter measured the fuel flow rate. The injection pulse width controlled the amount of fuel injected.

2.2. Exhaust gas analysis

CAI 600 gas analyzers determined the regulated emissions (CO, CO₂, O₂, NO_x, and THC). The unregulated emissions were collected from the exhaust gas using a Dekati two stage ejector diluter, with an overall dilution ratio of 59.4. SUMMA stainless steel electro-polished containers (1.8L vol.) collected the diluted exhaust samples. A Hewlett Packard 6890 gas chromatograph equipped with a flame ionization detector or with a 5973 mass selective detector (MSD) and an Agilent 1100 liquid chromatograph measured the unregulated emissions.

2.3. Experimental Procedure

Table 2 presents the experimental conditions. The HCCI engine was operated with no EGR on 4 different Primary Reference Fuels (PRF), from pure heptane (PRF 0) to PRF 50, where the number represents the *i*-octane percentage in the n-heptane / *i*-octane blends. The blend chemical composition influenced the minimum compression ratio for stable HCCI combustion. The maximum compression ratio was limited at

16. Previous work [8] on the same engine found that CO and THC emissions sharply increased and combustion efficiency decreased for $A/F > 50$, with the NO_x minimum at $A/F = 50$. Also, an intake temperature around 30 - 40°C minimized the NO_x emissions. Therefore the measurements were taken at a fixed $T_{air, in} = 30^\circ C$ and $A/F = 50$. Two hundred engine cycles were averaged at each operating condition.

Table 2. Experimental Matrix

Parameter	Value
Air/Fuel Ratio	50
Intake Air Temperature	30°C
Compression Ratio	9.5~16

3. Results and discussion

3.1. Blend composition influence on the overall engine performance

Figures 1.a and 1.b show the combustion efficiency and CA50 (defined as the crank angle where 50% energy has been released) as a function of the fuel blend and engine compression ratio. The combustion efficiency decreases and the minimum CR at which there is efficient HCCI combustion increases with increasing *i*-octane ratio in the blend. A larger *n*-heptane ratio in the fuel advances the autoignition timing, which results in a higher combustion temperature, therefore higher combustion efficiency. For *i*-octane blends greater than 10%, the start of combustion is delayed and a higher compression ratio is needed to achieve acceptable levels of combustion efficiency. There is a small increase in the indicated specific fuel consumption (isfc) for PRF 0 (Fig. 1.c) with increasing CR. *I*-octane addition increased the optimal isfc by 25% for PRF 10, 30 and 50. The CR also had a larger influence on isfc at lower and higher ends of the CR sweep for *i*-octane fuel blends.

3.2. Regulated emissions

The CO emissions are plotted in Figure 1.d. *I*-octane addition sharply increased CO emissions at lower compression ratio, which indicates incomplete combustion at these regimes. The minimum is found at CR = 13 for PRF 0, 10 and 30 and at CR = 14 for PRF 50, and it increased 100% from PRF 0 to 50. The increase in CO emissions is a result of a reduction in the combustion temperature with *i*-octane addition due to incomplete combustion due to the 5°CA delay in the CA50 combustion phasing (Fig. 1.b) from PRF 0 to PRF 50. It is known that CO oxidation is problematic when the combustion temperature is below 1500K [11]. The THC and NO_x emissions (Fig. 1.e and 1.f) are influenced by both the compression ratio and fuel blend. The minimum values of isHC and is NO_x are found at CR = 11 for PRF 0, 10 and 30 and at CR = 12 for PRF 50. Comparing PRF 50 to PRF 0, the minimum isHC and is NO_x emissions increased by 100% and 65%, respectively. The isHC and is NO_x emissions dependence on CR is very similar for all four fuel blends. There is a sharp increase in their levels, particularly at lower CR, when CR values depart from the optimal values where isHC and is NO_x are minimized. The slight increase in NO_x emissions is caused by the prompt and NNH intermediate mechanisms [12]. Overall, *i*-octane addition reduces the compression ratio range for low HC and NO_x emissions in the present engine configuration.

3.3. Unregulated emissions

A detailed chemical characterization of the exhaust emissions was conducted using similar methods described previously [8]. It was shown in the previous section that fuel chemistry and engine compression ratio influenced the regulated emissions. The engine operating point of minimum NO_x emissions was chosen to compare the fuel chemistry influence on unregulated emissions. The combustion efficiency of this operating point was close to 94% for all four fuel blends, and the CO and HC emissions were also close to their minimum values (see Figure 2). The compression ratios were CR = 11 for the PRF 0, PRF 10 and PRF 30, and CR = 12 for PRF 50.

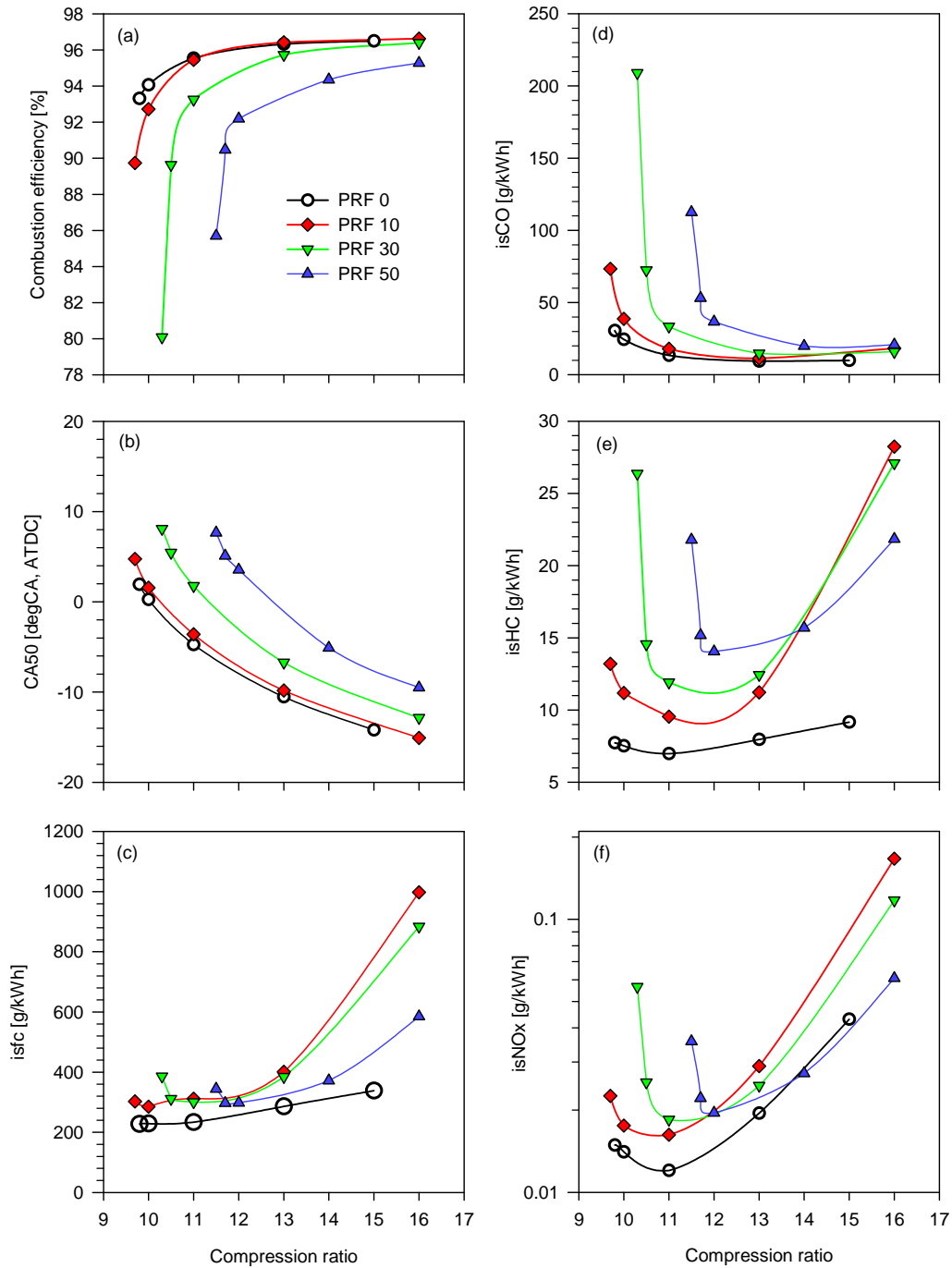


Figure 1. Combustion efficiency (a), CA50 (b), indicated specific fuel consumption (c), CO indicated specific emission (d), HC indicated specific emission (e), and NO_x indicated specific emission (f) function of fuel composition and compression ratio ($T_{in, air} = 30^{\circ}\text{C}$, $P_{in} = 95 \text{ kPa}$, $P_{exh} = 105 \text{ kPa}$, no EGR)

More than 150 species were identified. The exhaust included mainly alkanes, alkenes, carbonyl compounds and alkynes. No concentration of cycloalkanes and aromatics was detected when the engine was operating on pure n-heptane, but they appeared with increasing *i*-octane in the fuel. Only some of the most important species will be discussed next.

Table 3 presents both the total mass in milligrams per kilogram of fuel and the percentage of different species categories in the total HC emissions. The average fuel mass flow rate was constant throughout the experiments. Oxygenates in Table 3 are propylene oxide, furan, 2-propenol, 2-methyl furan,

tetrahydrofuran, and butyltetrahydrofuran. Two other large peaks indicating oxygenated compounds could not be precisely identified by the MS library search.

Table 3. Total HC emissions mass in milligrams per kilogram of fuel and the percentage of different species categories in the total HC emissions ($T_{in, air} = 30^{\circ}C$, $P_{in} = 95$ KPa, $P_{exh} = 105$ KPa, no EGR, CR = 11 for the PRF 0, PRF 10 and PRF 30, and CR = 12 for PRF 50)

PRF	50		30		10		0	
HC	mg/	%THC	mg/	%THC	mg/	%THC	mg/	%THC
alkanes	23744	63%	20915	64%	17225	67%	5598	72%
alkenes	4394	12%	3794	12%	2966	12%	1069	14%
alkynes	103	0%	92	0%	78	0%	22	0%
cycloalkanes	437	1%	357	1%	101	0%	0	0%
aromatic	382	1%	470	1%	10	0%	3	0%
carbonyls	8660	23%	6857	21%	5035	20%	1103	14%
oxygenates	265	1%	240	1%	198	1%	0	0%
Total HC	37985	100%	32726	100%	25613	100%	7796	100%

The total mass of hydrocarbons in the exhaust increased by 400% from PRF 0 to PRF 50. This indicates that with *i*-octane addition in the blend the combustion process was incomplete for a larger fraction of the fuel entering the cylinder.

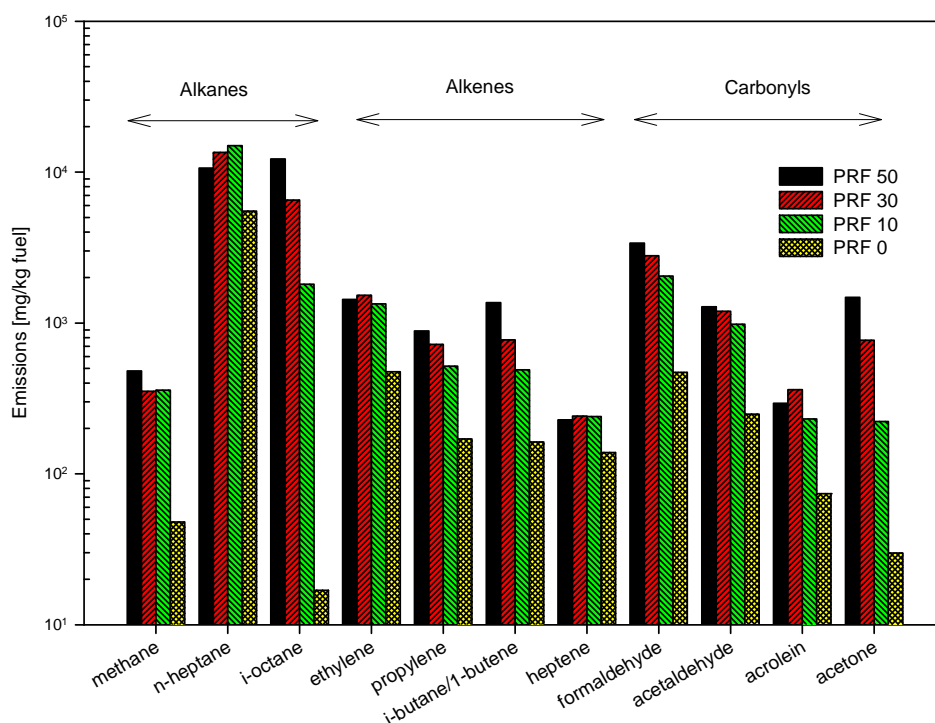


Figure 2. Fuel blend influence on alkanes, alkenes, and carbonyls emissions ($T_{in, air} = 30^{\circ}C$, $P_{in} = 95$ KPa, $P_{exh} = 105$ KPa, no EGR, CR = 11 for the PRF 0, PRF 10 and PRF 30, and CR = 12 for PRF 50)

Figure 2 shows the influence of fuel blend on the largest alkane, alkene and carbonyl emissions. Alkanes are the dominant unregulated species. The *i*-octane fraction in the emissions increased proportional with the fuel *i*-octane content. The alkane emissions increased 400% from PRF 0 to PRF 50. This increase is attributed to a reduction in the bulk combustion chamber temperature associated with the 10°C combustion delay increase from PRF 0 to PRF 50. The retarding in the start of combustion with *i*-octane addition in the fuel resulted in temperatures below those required for starting the combustion process for a

larger fraction of fuel from the crevices and engine boundary layer and delayed the combustion further into the expansion stroke. The methane concentration was relatively small, but more than doubled when *i*-octane was added in the blend, and remained constant from PRF 10 to PRF 50. But even if the total mass of alkanes increased four times from PRF 0 to PRF 50, their percentage in the total HC decreased from 72% to 63%.

The carbonyls and oxygenates percentage in HC increased from 14% for PRF 0 to 23% for PRF 50. There were no cycloalkanes and aromatics detected in the exhaust of pure n-heptane, but once the *i*-octane fraction increased more than 30% in the blend, cycloalkanes and aromatics were detected (2% of total HC). Two processes are considered responsible for oxygenated compounds production in an HCCI engine fueled with *i*-octane [5, 13]. In the first, the oxidation is quenched as partial combustion products travel from the hot zones in the center of the combustion chamber towards the colder ones close to the engine boundary layers. In the second, the carbonyls are the result of the low temperature oxidation of the fuel trapped in the crevices and engine boundary layer. *I*-octane addition increased the combustion delay, both decreasing the temperature and the time available for completing the oxidation process.

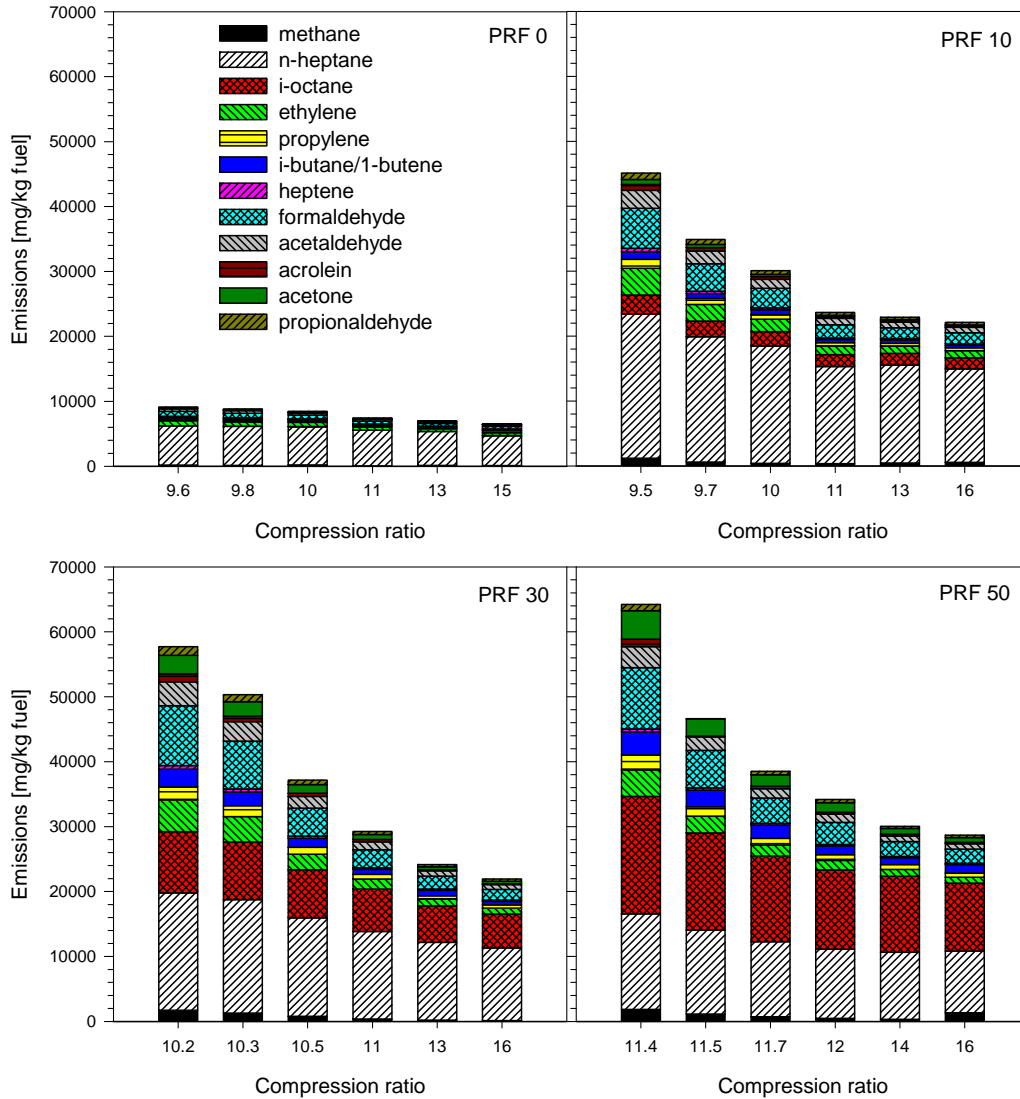


Figure 3. Compression ratio influence on alkanes, alkenes, and carbonyls emissions ($T_{in, air} = 30^{\circ}C$, $P_{in} = 95$ KPa, $P_{exh} = 105$ KPa, no EGR)

Figure 3 shows the compression ratio influence on the most important alkane, alkene and carbonyl emissions. There was a decrease in the total HC emissions with increasing CR, and it was more important at larger *i*-octane fraction in the fuel. As expected, the alkene and carbonyl emissions had the largest decrease with increasing CR for all fuel blends. Similar to NO_x, CO and HC emissions, both alkenes and

carbonyls decreased rapidly with increasing compression ratio until $CR \approx 12$, and continued decreasing slowly to their minimum values at the maximum observed compression ratio.

4. Conclusion

A detailed exhaust speciation study was performed on a HCCI engine fueled with four different n-heptane/*i*-octane blends, ranging from pure n-heptane to a 50/50 blend by volume (PRF 0 to PRF 50). The air to fuel ratio, engine speed and intake conditions were kept constant, while compression ratio sweeps were performed. For each fuel blend, unregulated emissions were measured at the compression ratio (CR) having the lowest NO_x emissions. These engine operating conditions corresponded to a CR of 11 for PRF 0, PRF 10 and PRF 30 and a slightly larger CR of 12 for PRF 50.

i-octane addition resulted in retarded combustion phasing, leading to lower combustion temperatures and reduced combustion efficiency. Significant increases in the CO, HC and NO_x emissions were detected for blends containing *i*-octane.

The detailed exhaust speciation identified more than 150 species. The exhaust included mainly alkanes, alkenes, carbonyl compounds and alkynes. The major findings are summarized below.

- Alkanes were the dominant species. Their content increased 400% from PRF 0 to PRF 50. This increase is attributed to a reduction in the bulk combustion chamber temperature associated with the 10°C combustion delay going from PRF 0 to PRF 50. The methane concentration more than doubled when *i*-octane was added in the blend. Overall, the alkanes percentage in the total HC decreases from 72% to 63%.
- The carbonyls and oxygenates percentage in HC increased from 14% for PRF 0 to 23% for the PRF 50
- No cycloalkanes and aromatics were found in the exhaust of PRF 0, but once the *i*-octane fraction increased to more than 30% in the blend, cycloalkanes and aromatics were detected (2% of total HC).
- Both alkenes and carbonyls decreased quickly with increasing compression ratio until $CR \approx 12$, and continued decreasing slowly to their minimum values at the maximum compression ratio investigated.

The unregulated emissions are a result of partial oxidation due to retarded and incomplete combustion. There was a reduction in the combustion temperature with *i*-octane addition, shown by the increase in combustion delay, and the 100% increase in the isCO and isHC emissions from PRF 0 to PRF 50. The 65% increase in is NO_x emissions is believed to be caused by the prompt and NNH intermediate mechanisms.

Acknowledgements

The authors would like to acknowledge the financial support of the Government of Canada's PERD/AFTER program.

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