NRC Publications Archive Archives des publications du CNRC

The NO_x and N₂O emission characteristics of an HCCI engine operated with n-Heptane

Li, Hailin; Neill, W. Stuart; Guo, Hongshen; Chippior, Wally

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/10.1115/1.4005243>

Journal of Energy Resources Technology, 134, 1, pp. 011101-1-011101-9, 2011-12-23

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

<https://nrc-publications.canada.ca/eng/view/object/?id=276127f7-0354-4ec7-baea-810b682b02d2>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=276127f7-0354-4ec7-baea-810b682b02d2>

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.

The NO_x and N₂O Emission Characteristics of an HCCI Engine Operated With n-Heptane

Hailin Li

Department of Mechanical and
Aerospace Engineering,
West Virginia University,
Morgantown, WV 26506

W. Stuart Neill

Hongsheng Guo

Wally Chippior

Institute for Chemical Process and
Environmental Technology,
National Research Council Canada,
Ottawa, ON, Canada

This paper presents the oxides of nitrogen (NO_x) and nitrous oxide (N₂O) emission characteristics of a Cooperative Fuel Research (CFR) engine modified to operate in homogeneous charge compression ignition (HCCI) combustion mode. N-heptane was used as the fuel in this research. Several parameters were varied, including intake air temperature and pressure, air/fuel ratio (AFR), compression ratio (CR), and exhaust gas recirculation (EGR) rate, to alter the HCCI combustion phasing from an overly advanced condition where knocking occurred to an overly retarded condition where incomplete combustion occurred with excessive emissions of unburned hydrocarbons (UHC) and carbon monoxide (CO). NO_x emissions below 5 ppm were obtained over a fairly wide range of operating conditions, except when knocking or incomplete combustion occurred. The NO_x emissions were relatively constant when the combustion phasing was within the acceptable range. NO_x emissions increased substantially when the HCCI combustion phasing was retarded beyond the optimal phasing even though lower combustion temperatures were expected. The increased N₂O and UHC emissions observed with retarded combustion phasing may contribute to this unexpected increase in NO_x emissions. N₂O emissions were generally less than 0.5 ppm; however, they increased substantially with excessively retarded and incomplete combustion. The highest measured N₂O emissions were 1.7 ppm, which occurred when the combustion efficiency was approximately 70%.

[DOI: 10.1115/1.4005243]

Keywords: HCCI engine, n-heptane, NO_x emissions, N₂O emissions, combustion efficiency, combustion phasing

Introduction

Diesel engines are widely used in on- and off-road vehicles due to their high power density and fuel-conversion efficiency. The application of diesel engines to light-duty vehicles is expected to grow in the coming decade, especially in North America. However, significant technical challenges must be overcome for this to occur. For example, fundamental changes to the combustion system of diesel engines and exhaust emission control devices are needed to satisfy future emission regulations, which are becoming increasingly stringent and aimed at near zero emissions. The driving forces behind these changes are the difficult and often contradictory objectives of simultaneously improving fuel economy and reducing the two problematic pollutants associated with diesel combustion: oxides of nitrogen (NO_x) and particulate matter (PM). Historically, fuel economy improvements have usually been obtained through the enhancement of the conventional diesel combustion process, which often increases NO_x formation. The application of cooled exhaust gas recirculation (EGR) has been demonstrated to be effective in reducing NO_x emissions, but usually result in higher fuel consumption and PM emissions. It has been demonstrated that innovative emission control devices, such as the diesel particulate filter, must be employed to reduce PM emissions. However, the application of these devices increases vehicle cost, deteriorates fuel economy, and requires extra maintenance. Correspondingly, engine technologies with the potential to significantly reduce engine-out NO_x and PM emissions with minimal penalties in fuel economy have become the subject of increasing research. This has led to investigations of innovative combustion concepts aiming to simultaneously enhance fuel-conversion efficiency and reduce the forma-

tion of these pollutants [1,2]. In principle, lowering the combustion temperature and eliminating the presence of fuel-rich mixture regions will reduce thermal NO_x and PM formation, respectively. On the other hand, the rapid burning of a fuel-air mixture near top dead center (TDC) maintains high thermodynamic and fuel-conversion efficiency, but this is normally deteriorated when the combustion temperature is reduced using EGR and retarded injection timing to lower NO_x formation.

Homogeneous charge compression ignition (HCCI) is an advanced low temperature combustion technology being increasingly considered for internal combustion (IC) engines. In its simplest form, HCCI combustion involves the auto-ignition of a homogeneous mixture of fuel, air, and diluents at low to moderate temperatures and high pressure. This approach enables the engine designer to have a high compression ratio (CR), minimize air throttling losses, and rapidly burn the fuel-air-diluents mixture near TDC, which contributes to high fuel-conversion efficiency. Meanwhile, burning a homogeneous fuel lean mixture at a relatively low temperature suppresses the formation of both PM and NO_x. These desirable combustion characteristics make HCCI a potential alternative combustion mode for IC engines, especially diesel engines [3,4].

Although much progress has been made in the past decade, there are still many challenges and technical issues to be solved before the HCCI concept can be widely adopted in production engines. Most of these are associated with the short combustion duration, effective control of combustion phasing during transient operation, transition between HCCI and traditional combustion modes, extension of HCCI engine operational range, and development of suitable fuels that can be applied to both HCCI and traditional IC engines [1]. Currently, HCCI combustion is typically used under low load operating conditions. HCCI combustion is challenged by the high peak in-cylinder pressures, pressure rise rates, the onset of knock, and unacceptable NO_x emissions [1,3] at high load operating conditions.

Contributed by the IC Engine Division of ASME for publication in the JOURNAL OF ENERGY RESOURCES TECHNOLOGY. Manuscript received August 13, 2010; final manuscript received August 5, 2011; published online December 23, 2011. Assoc. Editor: Prof. Nesrin Ozalp.

This material is declared a work of the Government of Canada and is not subject to copyright protection in Canada. Approved for public release; distribution is unlimited.

Over the years, there has been increasing interest in examining the NO_x emission characteristics of an HCCI engine. Optimization approaches and fuels which produce lower NO_x emissions under high load operating conditions need to be investigated. For example, Oakley et al. [5] examined the combustion and emissions characteristics of the controlled auto-ignition (CAI) combustion of hydrocarbon and alcohol fuels. NO_x emissions were generally much lower compared to traditional gasoline and diesel engines, and were shown to be load dependent. Among the fuels examined, methanol exhibited the lowest NO_x emissions. As expected, relatively high NO_x emissions were observed at high fuel flow rates when the engine operated close to the knocking region. However, specific NO_x emissions were reported to increase at leaner conditions when operated around the low load limit. This phenomenon was not observed in similar research conducted by Xie et al. [6]. HCCI combustion of E100 (pure ethanol), E50 (50% gasoline and 50% ethanol) and M100 (pure methanol) were found to produce lower NO_x emissions compared to gasoline.

Numerical simulations have also been used to investigate the NO_x emission characteristics of HCCI engines. For example, Amnéus et al. [7] presented a single zone numerical simulation with detailed NO_x formation chemistry. NO_x formation chemistries derived from GRI-mech 3.0, Lawrence Livermore National Laboratory's NO_x -mechanism and another mechanism developed by Heidelberg were compared. The numerical simulation demonstrated the importance of N_2O to the formation of NO_x . The prediction of bulk gas temperature history was shown to be very important in predicting NO_x emissions under the operating conditions examined. The numerical results were only validated against very limited experimental data with EGR. The application of EGR was shown to increase NO_x emissions when operated at a fixed combustion phasing and constant fuel flow rate. This is not consistent with common IC engine practice, whereby EGR has been demonstrated as an effective approach to reduce the peak combustion temperatures and NO_x emissions [8]. Therefore, it is necessary to further examine the NO_x emission characteristics of HCCI engines. At this stage, a brief review of the NO_x formation mechanisms is appropriate.

NO_x Formation Mechanisms. During the combustion of fuels that do not contain nitrogen, NO_x is formed when oxygen (O_2) and nitrogen (N_2) are present at elevated temperatures. Traditionally, it is believed that NO_x is formed mainly through three mechanisms denoted as the thermal, prompt, and N_2O -intermediate mechanisms [8–10]. Although there is also growing evidence of a fourth mechanism involving NNH [10,11], it will not be reviewed in this paper.

Thermal NO_x Mechanism. The thermal mechanism is based on what is known as the extended Zeldovich mechanism. The three main reactions are $\text{O} + \text{N}_2 \leftrightarrow \text{NO} + \text{N}$, $\text{N} + \text{O}_2 \leftrightarrow \text{NO} + \text{O}$, and $\text{N} + \text{OH} \leftrightarrow \text{NO} + \text{H}$ [8–10]. This mechanism has very strong temperature dependence. The threshold temperature for NO_x formation from this mechanism is about 1800 K. Thermal NO_x is generally considered to be formed in the post flame gases in spark ignition (SI) engines where high temperatures exist for an extended period of time. Due to the lower combustion temperatures associated with HCCI combustion, it is believed that HCCI engines produce less NO_x through this mechanism than both gasoline and diesel engines.

Prompt NO_x Mechanism. The prompt NO_x formation in hydrocarbon–air mixtures is initiated by the reactions of hydrocarbon radicals with molecular nitrogen to form atomic nitrogen and species containing nitrogen elements, which are finally converted to nitrogen oxide (NO) through a sequence of reactions [7–10]. The prompt NO_x mechanism was traditionally considered to be important for fuel-rich mixtures. Since the formation of prompt NO_x requires the presence of hydrocarbon radicals, prompt NO_x is usually formed in the initial stages of combustion and is reduced with decreasing hydrocarbon content in a mixture. This

mechanism may play an important role in the initial stages of HCCI combustion. Some prompt NO_x may also be formed after HCCI combustion is finished when hydrocarbons emitted from the crevice region mix with combustion products, which are not hot enough to oxidize the hydrocarbons completely but can form NO_x through the prompt NO_x mechanism.

N_2O Intermediate Mechanism. As described in the literature [8–12], the nitrous oxide (N_2O) intermediate route is initiated mainly by the reactions $\text{O} + \text{N}_2 + \text{M} \leftrightarrow \text{N}_2\text{O} + \text{M}$, $\text{N}_2\text{O} + \text{H} \leftrightarrow \text{N}_2 + \text{OH}$, $\text{N}_2\text{O} + \text{O} \leftrightarrow \text{N}_2 + \text{O}_2$, and $\text{N}_2\text{O} + \text{OH} \leftrightarrow \text{N}_2 + \text{HO}_2$. These initiation reactions convert molecular nitrogen to N_2O , which is then partially converted to NO . It was demonstrated that this mechanism plays an important role in NO production under extremely lean and low temperature combustion processes, such as in the lean operation of SI engines and low load operation of gas turbines. For example, Lentini [12] demonstrated the importance of N_2O intermediate mechanism in gas turbine combustion. The numerical simulations conducted by Amnéus et al. [7] showed that the N_2O intermediate route plays an important role for NO_x formation in HCCI engines at moderate NO_x levels.

N_2O Emissions. N_2O is a very stable compound with a lifetime of about 120 years in the troposphere [13,14]. It is a relatively inert chemically but is a strong infrared absorber and radiator. The global warming potential of N_2O is 296 times that of carbon dioxide (CO_2), which makes N_2O a problematic greenhouse gas for global warming [15]. In addition, since the conversion of N_2O to NO with consumption of O_3 is the major source of NO in the stratosphere, an increase in N_2O emissions will enhance ozone depletion [14,16]. It is accepted that N_2O is normally formed at relatively low combustion temperatures. It was reported that current diesel engines emit low levels of N_2O [17–19]. However, the N_2O emissions of HCCI engines have not been reported extensively.

As described before, N_2O may play an important role in NO_x formation within an HCCI engine. One numerical study suggested that N_2O was highly likely to be formed in HCCI engines [7]; however, the numerical results were not validated with experimental data. Correspondingly, there is a need to examine experimentally the N_2O emission characteristics of HCCI engines. The correlation between N_2O and NO_x emissions also needs to be established, which may help to explain the specific NO_x emissions characteristics of HCCI engines especially when the combustion temperature is lower than the threshold value for the formation of NO_x by the thermal mechanism.

This research investigates the NO_x and N_2O emission characteristics of an HCCI engine operated with n-heptane. The effects of operational parameters on NO_x and N_2O emissions were experimentally examined. The parameters examined include intake temperature and pressure, air/fuel ratio (AFR), compression ratio, and EGR rate. The experimental results were analyzed to show the strong dependence of NO_x emissions on combustion phasing as well as conditions where NO_x emissions were elevated. This provides valuable guidelines for the optimization of HCCI engines.

Experimental Apparatus and Procedure

Cooperative Fuel Research (CFR) Engine. A CFR engine was used. It is a single-cylinder, variable compression ratio, four-stroke engine commonly used to evaluate the knock resistance of gasoline fuels. Table 1 provides the manufacturer's basic dimensional specifications of this engine. Figure 1 is a schematic diagram of the research engine facility. An air flow bypass valve was installed immediately downstream of the air heater, so the intake and exhaust systems could be warmed up without motoring or running the engine. When the engine was running or motoring, this valve was closed.

The engine was modified from the standard ASTM setup by the addition of a port fuel injection system and the other hardware and

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	36 deg CA ABDC
Exhaust valve open	40 deg CA BBDC
Exhaust valve close	5 deg CA ATDC
Fuel system	Air-assist port fuel injection

software needed for the control of critical engine parameters such as intake air temperature, air/fuel ratio, EGR, and intake and exhaust pressure. The engine was coupled to an eddy current dynamometer/variable speed AC motor combination for starting the engine and controlling engine speed (N). The combination of the variable speed AC motor coupled with an overdrive clutch was used to motor the engine before HCCI combustion was initiated and to maintain engine speed when HCCI combustion was unstable.

Port Fuel Injector. A port fuel injector for flexible fuel vehicles was modified to provide air-assist atomization of liquid fuels. A similar injector was shown to be able to finely atomize liquid fuels with an appropriate blast air pressure [20]. For this study, the fuel system and air-assist pressures were maintained at 500 kPa and 200 kPa, respectively. The experimental data indicates that the fuel injector produces droplets with a Sauter mean diameter less than 15 μ m for both gasoline and diesel fuels.

For this study, n-heptane was injected into the intake manifold at 25 deg CA after top dead center (ATDC) during the intake

stroke. The injection process lasted about 10–30 deg CA depending on fuel flow rate and intake pressure and was finished well before intake valve closure. The finely atomized fuel droplets mixed with the intake air in the inlet manifold and entered the engine during the intake stroke of the same working cycle.

Intake, Exhaust, and EGR Systems. Clean, compressed air was supplied to the intake system of the engine. The intake pressure was controlled using two electronically controlled pressure regulators. An intake surge tank was installed to minimize the pressure pulsation of the intake air, thereby improving engine operational stability, airflow measurement, and charge pressure control. The temperature of the intake air and EGR mixture was maintained constant by precisely controlling the power supplied to a 1.5 kW electrical heater installed after the intake surge tank.

The exhaust surge tank was installed to reduce pressure pulsations and provides complete mixing of the exhaust gases prior to sampling the exhaust gases for emissions measurement and recirculating the exhaust gases into the intake manifold. An EGR system was produced by connecting the exhaust and intake surge tanks. The exhaust back pressure valve was installed at exit of the exhaust surge tank and used to raise the exhaust pressure above that of the intake air to initiate exhaust gas recirculation. The EGR rate was controlled using an EGR valve. In this research, the pressure differential between the exhaust and intake surge tanks was maintained at 15 kPa for all experiments, except when this pressure differential was not sufficient to provide the desired EGR rate with a fully open EGR valve.

The air flow rate to the engine was measured using a mass flow meter (Sierra, model 780 Series Flat-Trak™). The amount of fuel injected was measured using a Coriolis-effect mass flow meter and controlled by adjusting the fuel injection pulse width to obtain the fuel flow rate and air/fuel ratio required. In this research, the fuel was injected to the intake manifold during the intake stroke, just after intake valve opening. The instrumentation used to measure the pressure and temperature of the intake mixture was installed well before the fuel injector to avoid fuel vaporization effects on temperature measurement. The exhaust pressure and temperature were measured before the exhaust surge tank. Another thermocouple was installed after the surge tank at the location where exhaust gases were sampled.

Data Acquisition and Combustion Analysis. The in-cylinder pressure was measured with a high frequency-response piezoelectric pressure transducer (Kistler, model 6121) mounted flush with the cylinder surface using the detonation transducer access port. The transducer was connected to a dual mode charge amplifier (Kistler, model 5010). An encoder fitted to the cam shaft provided a resolution of 0.1 deg camshaft (0.2 deg crankshaft), which was used as the data acquisition clock to acquire the pressure data and also served as an input to the fuel injection controlling hardware/software. The resultant pressure and crank angle signals were routed to a high-speed data acquisition system.

The onset of knock tends to be encountered at richer fuel–air mixture conditions with advanced combustion phasing, especially when a higher compression ratio and intake temperature are employed. In this research, the onset of knock was determined by a combination of the appearance of rapid pressure oscillations and an audible knocking noise. The detailed knock characterization of an HCCI engine can be done by examining the knock intensity and knock frequency of each combustion cycle but this analysis was not conducted in this research. The experimental matrix was designed to avoid severe engine knocking conditions.

Exhaust Gas Sampling and Analysis. A heated probe was installed downstream of the exhaust surge tank to sample the exhaust gases. The exhaust gases supplied to the total hydrocarbon (THC) analyzer were maintained at a constant temperature of

Fig. 1 Schematic diagram of HCCI engine setup

Table 2 Experimental matrix

Test	Experiment	AFR (mass)	CR	T _{in, air} (°C)	P _{in} (kPa)	P _{exh} (kPa)	EGR rate (%)	$\dot{m}_{\text{fuel}}$ (kg/h)
1	AFR1	38–65	10	30	100	106	0	0.268–0.456
2	AFR2	34–60	10	30	95	106	0	0.274–0.464
3	CR1	50	9–16	30	95	106	0	0.319–0.328
4	CR2	40	7.9–13	40	95	106	0	0.395
5	T _{in}	50	10	25–116	95	106	0	0.276–0.331
6	P _{in}	22.5	10	65–72	95–200	P _{in} + 15	45	0.309–0.721
7	EGR1	14–40	10	40–62	95	110	0–62	0.395
8	EGR2	40	10	50	95	110	0–43	0.241–0.386

190°C, while those sent to the NO_x analyzer were kept at 75°C. The portion of the exhaust gases sampled for carbon monoxide (CO), CO₂, and O₂ analyses was cooled to 4°C to remove moisture before being analyzed. The regulated emissions instrumentation (CAI, model 600) consisted of a chemiluminescent analyzer for NO_x, a flame ionization THC analyzer, a nondispersive infrared CO analyzer, and a paramagnetic oxygen (O₂) analyzer. Nondispersive infrared CO₂ analyzers were used to measure CO₂ concentrations in the engine intake and exhaust streams (CAI, model 600), and the ratio of the two quantities was used to infer the EGR rate. The minimum range of the NO_x analyzer was 10 ppm and the noise specification was $\pm 1.0\%$ full scale. In NO_x mode, the exhaust sample was passed through an internal converter in the NO_x analyzer, which converted any NO₂ present in the exhaust to NO. Before entering the reaction chamber for NO_x measurement, the exhaust gas sample was cooled to 4°C to remove the moisture. The N₂O emissions were measured using a gas filter correlation analyzer (TEI, model 46C), which utilized the principle of N₂O absorption of infrared radiation. It should be noted that the ambient concentration of N₂O is approximately 0.3 ppm. The N₂O concentrations reported in this paper were the raw data measured after both water vapor and CO₂ had been completely removed from the exhaust gases.

The analyzers were calibrated prior to and after each set of tests and had good repeatability. The fuel flow rate obtained through a carbon balance was consistent with the intake fuel flow rate measured using a Coriolis-effect mass flow meter. The emissions of THC, CO, and CO₂ were used to calculate the combustion efficiency, defined as the molar percentage of CO₂ formed relative to the total carbon in the fuel.

Experimental Procedure. Prior to each experiment, the lubrication oil and coolant systems were preheated by electric heaters installed in external loops until their temperatures reached 82°C. At the same time, the intake and exhaust systems were warmed up by flowing heated air through the intake system, bypass valve, and exhaust systems without motoring or running the engine. HCCI combustion was easily initiated when the coolant, lubrication oil, and fuel/air mixture temperatures reached their prescribed values.

At each operating condition, the engine was run for 5 min or longer (if required to stabilize engine operation) before collecting any experimental data. Brake power, brake specific fuel consumption, and exhaust emissions were continuously monitored to ensure that steady state conditions prevailed. In each experiment, engine performance data and key operating parameters were recorded for approximately 4 min. at a frequency of 1 Hz and averaged prior to analysis. During the same time period, cylinder pressure traces for 500 engine working cycles were acquired and saved for later processing. The average cylinder pressure was analyzed to obtain the peak cylinder pressure, pressure rise rate, indicated power, heat release rate, mass fraction burned as well as a complete set of combustion phasing parameters. The crank angle location where 50% of the fuel chemical energy has been released, defined as CA50, was used to quantify HCCI combustion phasing.

At each experiment, a single engine operating parameter was varied over a wide operational range at a time, while other

parameters were kept constant. A detailed description of the operating conditions can be found in Table 2. The experiments were conducted at an engine speed of 900 rpm. NO_x emissions are reported on a wet volume basis in this paper since the concentrations tend to be extremely low compared to traditional diesel and gasoline engines. However, it is important to remember that the emission regulations limit the specific mass emission rates (i.e., g/hp-hr). It should be noted that the brake power produced by this research engine is relatively low due to its high friction losses and the low fuel flow rates.

Results and Discussion

Our previous research has demonstrated the capability of the experimental facility for obtaining stable and repeatable HCCI combustion [21]. Table 3 compares the NO_x emissions measured over the period of this research at a typical operating condition. This data show that the repeatability of the NO_x emission measurements was reasonable. This was further demonstrated in Figs. 2 and 3, which shows the data obtained in three set of experiments over the period of this research especially when operated at extremely lean fuel–air mixtures.

As shown in Fig. 2, relatively high NO_x emissions (30 ppm) were observed under heavy knocking conditions. Gradually leaning the fuel–air mixture suppressed the onset of knock and substantially reduced NO_x emissions. This was due to the reduced combustion temperature resulting from a leaner fuel–air mixture and a retarded combustion phasing beyond TDC [21]. Extremely low NO_x concentrations (<5 ppm) were obtained over a wide range of air/fuel ratios, with a minimum concentration of 1.4 ppm observed at an air/fuel ratio of 50. This reflects one of the desirable features of HCCI combustion. However, further leaning of the fuel–air mixture increased NO_x emissions, despite the fact that the mean combustion temperature was expected to decrease further as a combined result of the leaner mixture, retarded combustion phasing [21], and increasingly incomplete combustion represented by low combustion efficiency, as shown in Fig. 3. Such a phenomenon is not consistent with the traditional belief that NO_x formation is primarily dominated by the temperature of the combustion products [8,9,22]. Peng et al. [23] reported similar results with high EGR levels but did not give a detailed explanation.

The presence of N₂O has been shown to enhance NO_x formation through the N₂O intermediate mechanism under fuel lean conditions [8,9,12]. As shown in Fig. 4, the N₂O emissions were fairly constant at 0.45 ppm for air/fuel ratios between 35 and 45. For leaner mixtures, N₂O emissions increased dramatically and were accompanied by increased NO_x emissions. It is possible that the higher levels of N₂O enhanced the formation of NO_x. Peak N₂O emissions of 1.7 ppm were observed at an air/fuel ratio of

Table 3 Repeatability of NO_x emission measurements (CR = 10, T_{in} = 30°C, P_{in} = 95 kPa, AFR = 50)

Test number	1	2	3	4
NO _x emissions (ppm)	1.33	1.37	1.38	1.49

Fig. 2 Effect of air/fuel ratio on the emissions of NO_x , CO, and THC. CR = 10, $T_{\text{in}} = 30^\circ\text{C}$, $P_{\text{in}} = 95 \text{ kPa}$, $P_{\text{exh}} = 105 \text{ kPa}$, no EGR.

54. As the mixture was further leaned, N_2O decreased substantially though NO_x emissions continued to increase. Also, the N_2O emissions obtained in this research were comparable to the numerical simulation data reported in the literature [7].

Similar phenomena were also observed when the compression ratio and EGR rates were varied to optimize HCCI combustion. Figure 5 shows the NO_x and N_2O emissions for compression ratios ranging from 8 to 16 at a constant air/fuel ratio of 50. NO_x emissions decreased from approximately 3 to 1.2 ppm as the compression ratio decreased from 16 to 11, reflecting the relatively weak effect of compression ratio on NO_x emissions when the engine was operated with extremely lean mixtures. As shown in Fig. 5, the N_2O emissions were approximately constant when the compression ratio was over 11. Decreasing the compression ratio below 10, both NO_x and N_2O emissions were found to increase substantially. Peak NO_x (15.8 ppm) and N_2O (1.7 ppm) emissions were observed at compression ratios of 9.0 and 9.3, respectively. Reducing the compression ratio further, both NO_x and N_2O concentrations dropped quickly. At compression ratios below 9.0, the NO_x emissions decreased rapidly as the combustion efficiency dropped off sharply, as shown in Fig. 6. The sudden drop in combustion temperature resulting from the incomplete combustion contributed to the dramatic drop in NO_x and N_2O emissions.

Figure 7 shows the effect of EGR on NO_x and N_2O emissions at a constant air/fuel ratio of 40. With increasing EGR rate, the fuel and intake air flow rates decreased. The application of EGR was found to reduce NO_x emissions until its minimum value was observed at an EGR rate of 27.0%. Meanwhile, the N_2O emissions were also reduced slightly from 0.4 ppm to a minimum value of 0.3 ppm. Further increasing the EGR rate, NO_x emissions were found to increase even though the mean combustion temperature

Fig. 3 Effect of air/fuel ratio on combustion efficiency and NO_x emissions. CR = 10, $T_{\text{in}} = 30^\circ\text{C}$, $P_{\text{in}} = 95 \text{ kPa}$, $P_{\text{exh}} = 105 \text{ kPa}$, no EGR.

Fig. 4 Effect of air/fuel ratio on NO_x and N_2O emissions. CR = 10, $T_{\text{in}} = 30^\circ\text{C}$, $P_{\text{in}} = 95 \text{ kPa}$, $P_{\text{exh}} = 106 \text{ kPa}$, no EGR.

was expected to decrease further due to the reduced fuel flow rate, increased diluents, retarded combustion phasing, and significantly deteriorated combustion efficiency, as shown in Fig. 8. At the same time, N_2O emissions were found to increase significantly with its peak value of 1.4 ppm observed at an EGR rate of 31.8%. Further increasing the amount of exhaust gas recirculation lowered the N_2O emissions but continued to increase the NO_x emissions.

Figure 9 shows the effect of EGR rate on NO_x and N_2O emissions when fuel flow rate was maintained at 0.4 kg/h. Since the intake pressure was held constant, the air/fuel ratio decreased due to the reduced intake air flow rate as EGR increased. The application of EGR was demonstrated to reduce both NO_x and N_2O emissions. The minimum NO_x and N_2O emissions were observed with an EGR rate of approximately 50%. This is much higher than the EGR rate (27%) obtained under constant air/fuel ratio operation, as shown in Fig. 7. Both N_2O and NO_x emissions increased significantly as combustion became increasingly incomplete when the EGR rate increased beyond 50%, which is illustrated in Fig. 10 as deteriorated combustion efficiency at higher EGR rates. Peak N_2O and NO_x concentrations were not measured as data were not collected after HCCI combustion became unstable.

Figure 11 shows the effect of intake pressure boosting on NO_x emissions when the EGR rate and intake air/fuel ratio were maintained at 45% and 22.5, respectively. For these conditions, boosting the intake pressure was shown to increase NO_x concentrations. Our previous study [21] showed that turbocharging advanced the HCCI combustion phasing for n-heptane, which increased the temperature of the combustion products and enhanced NO_x formation. Additionally, the relatively larger mass of combustion products per

Fig. 5 Effect of compression ratio on NO_x and N_2O emissions. $P_{\text{in}} = 95 \text{ kPa}$, $T_{\text{in}} = 30^\circ\text{C}$, AFR = 50, no EGR.

Fig. 6 Effect of compression ratio on combustion efficiency and NO_x emissions. $P_{\text{in}} = 95 \text{ kPa}$, $T_{\text{in}} = 30^\circ\text{C}$, $\text{AFR} = 50$, no EGR.

Fig. 9 Effect of EGR rate on NO_x and N_2O emissions at constant fuel flow rate. $\text{CR} = 10$, $T_{\text{in}} = 40\text{--}62^\circ\text{C}$. $P_{\text{in}} = 95 \text{ kPa}$, $\dot{m}_{\text{fuel}} = 0.395 \text{ kg/h}$.

Fig. 7 Effect of EGR rate on NO_x and N_2O emissions at constant air/fuel ratio. $\text{CR} = 10$, $\text{AFR} = 40$, $T_{\text{in}} = 50^\circ\text{C}$, $P_{\text{in}} = 95 \text{ kPa}$.

Fig. 10 Effect of EGR rate on NO_x emissions and combustion efficiency at constant fuel flow rate. $\text{CR} = 10$, $T_{\text{in}} = 40\text{--}62^\circ\text{C}$, $P_{\text{in}} = 95 \text{ kPa}$, $\dot{m}_{\text{fuel}} = 0.395 \text{ kg/h}$.

Fig. 8 Effect of EGR rate on combustion efficiency and NO_x emissions at constant air/fuel ratio. $\text{CR} = 10$, $\text{AFR} = 40$, $T_{\text{in}} = 50^\circ\text{C}$, $P_{\text{in}} = 95 \text{ kPa}$.

Fig. 11 Effect of intake pressure on NO_x emissions. $\text{CR} = 10$, $T_{\text{in}} = 65\text{--}72^\circ\text{C}$, $\text{AFR} = 22.5$, $\text{EGR rate} = 45\%$, $P_{\text{exh}} = P_{\text{in}} + 15 \text{ kPa}$, $\dot{m}_{\text{fuel}} = 0.309\text{--}0.721 \text{ kg/h}$.

heat transfer area reduced the specific heat transfer from the bulk mixture to the engine coolant. This increased the combustion temperature, which also contributed to the increased NO_x emissions.

Figure 12 shows the effects of compression ratio on NO_x emissions for two different air/fuel ratios. Much higher NO_x emissions were observed with a richer fuel-air mixture even at lower com-

pression ratios compared to operation with a leaner mixture. This was due to the much higher combustion temperatures resulting from burning more fuel at an advanced combustion phasing [21], which tended to increase the temperature of the combustion products and enhance NO_x formation. This was further clarified in Fig.

Fig. 12 Effects of air/fuel ratio and compression ratio on NO_x emissions. $P_{\text{in}} = 95$ kPa, no EGR, $T_{\text{in}} = 30^\circ\text{C}$ for AFR = 50; $T_{\text{in}} = 50^\circ\text{C}$ for AFR = 40.

Fig. 14 Variations of combustion efficiency with changes in combustion phasing. $P_{\text{in}} = 95$ kPa, no EGR. $T_{\text{in}} = 30^\circ\text{C}$ for AFR = 50, $T_{\text{in}} = 50^\circ\text{C}$ for AFR = 40.

Fig. 13 Variations of NO_x emissions with changes in combustion phasing. $P_{\text{in}} = 95$ kPa, no EGR. $T_{\text{in}} = 30^\circ\text{C}$ for AFR = 50, $T_{\text{in}} = 50^\circ\text{C}$ for AFR = 40.

Fig. 15 Variations of NO_x emissions with changes in combustion phasing. AFR = 50; CR experiment: CR = 9–16, $T_{\text{in}} = 30^\circ\text{C}$. Intake temperature experiment: CR = 10, $T_{\text{in}} = 25$ – 116°C .

13, where NO_x emissions are plotted as a function of combustion phasing. Higher NO_x emissions were observed with a richer mixture at the same combustion phasing, reflecting the influence of fuel flow rate on NO_x emissions. The effects of combustion phasing and compression ratio on NO_x emissions were found to be more problematic for richer mixtures, especially with overly advanced combustion phasing. However, extremely low NO_x emissions with high combustion efficiency were obtained with richer fuel–air mixtures when the combustion phasing was retarded as shown in Figs. 13 and 14, respectively. Retarding the combustion phasing appears to be a good approach for maintaining low NO_x emissions as engine load increases, while achieving acceptable combustion efficiency.

Figure 15 shows that NO_x emissions are correlated strongly with the combustion phasing. The approach used to control the combustion phasing tends to have a very mild effect on NO_x emissions. Extremely low NO_x emissions (less than 2 ppm) were obtained over a wide range of combustion phasing (CA50) from -14 to 10 deg CA ATDC. Retarding the combustion phasing beyond 10 deg CA ATDC led to increased NO_x emissions due to deteriorated combustion efficiency as described above. This phenomenon is further demonstrated by constant fuel flow rate operation while the EGR rate and compression ratio were varied to minimize NO_x emissions. As shown in Fig. 16, low NO_x emissions (<5 ppm) were observed with CA50 ranging from -7 to 17 deg CA ATDC, a more retarded phasing compared to that shown

Fig. 16 Variations of NO_x emissions with change in combustion phasing obtained by varying EGR rate or compression ratio. $P_{\text{in}} = 95$ kPa, $\dot{m}_{\text{fuel}} = 0.395$ kg/h. EGR experiment: $T_{\text{in}} = 40$ – 62°C , CR = 10. CR experiment: $T_{\text{in}} = 50^\circ\text{C}$, no EGR.

in Fig. 15. This is mainly due to the relatively high fuel flow rate, which makes it possible to achieve stable HCCI combustion with a more retarded combustion phasing. As mentioned before, NO_x emissions increased significantly when the combustion phasing was retarded excessively.

Fig. 17 Comparison of NO_x emission variations with change in combustion phasing obtained by different approaches. Operating conditions as described in Table 2.

Fig. 18 Correlation of NO_x emissions with THC emissions. Operating conditions described in Table 2.

Figure 17 shows how NO_x emissions vary with changes in combustion phasing achieved using numerous approaches. Engine operation with overly advanced combustion phasing resulted in engine knock, which dramatically increased NO_x emissions. Extremely low (less than 5 ppm) NO_x emissions were obtained over a wide range of combustion phasing. The increased NO_x emissions obtained with excessively retarded combustion phasing shown in Fig. 17 have not been reported extensively in the literature. Further research is required to explain this phenomenon.

When retarded combustion and increased NO_x emissions were observed with excessively low intake temperatures, leaner mixtures, lower compression ratios, or excessive amounts of EGR, the combustion efficiency dropped quickly. For these cases, large quantities of unburned hydrocarbons were present under relatively high temperature conditions, which may enhance NO_x formation through some mechanism. For example, the increased NO_x emissions under retarded and incomplete combustion conditions were accompanied by increased THC emissions and deteriorated combustion efficiency, as shown in Figs. 2 and 3, respectively. Figure 18 illustrates the correlation between NO_x and THC emissions for all the experiments examined in this research. The NO_x emissions obtained under conditions of incomplete combustion were found to increase almost linearly with THC emissions. Considering the significant variation in the operating conditions, a strong correlation between NO_x formation and THC emissions is evident when

Fig. 19 Correlation of NO_x emissions with combustion efficiency. Operating conditions described in Table 2.

Fig. 20 Correlation of N_2O emissions with combustion efficiency. Operating conditions described in Table 2.

retarded and incomplete combustion occurred. As shown in Fig. 19, the NO_x emissions observed with incomplete combustion were also a function of the combustion efficiency. The deteriorated combustion efficiency (below 90%) was accompanied by excessive NO_x emissions. For these experiments, NO_x emissions increased at a substantially higher rate when EGR was applied at a constant fuel flow rate (EGR1), even though the combustion efficiency was still relatively high.

Figure 20 shows the correlation between combustion efficiency and N_2O emissions. N_2O emissions observed were found to be extremely low (lower than 0.5 ppm) when the combustion efficiency was over 95%. As combustion efficiency decreased, N_2O emissions increased substantially up to a peak value of 1.7 ppm when the combustion efficiency was approximately 70%. Finally, N_2O emissions were found to drop gradually toward that observed in ambient air with a further reduction in combustion efficiency.

Conclusions

The NO_x and N_2O emission characteristics of a single-cylinder HCCI engine fueled with n-heptane were experimentally investigated. The parameters examined include intake temperature and pressure, compression ratio, air/fuel ratio, and EGR rate. Correlations between NO_x and N_2O emissions and fuel flow rate, combustion phasing, THC emissions, and combustion efficiency were presented and discussed. A new NO_x emission phenomenon associated with incomplete HCCI combustion was presented. N_2O emissions from HCCI combustion were measured and discussed.

The correlation between unexpected NO_x emissions and excessive THC emissions associated with overly retarded HCCI combustion was established. Based on the experimental data obtained in this research, the following conclusions can be drawn:

- HCCI combustion produces extremely low NO_x emissions (<5 ppm) over a wide range of operating conditions, with the exception of conditions of excessively advanced combustion phasing where knocking occurred or overly retarded combustion phasing where incomplete combustion was observed.
- Under normal operation, the combustion phasing and fuel flow rate are the major factors affecting NO_x emissions from HCCI engines. NO_x emissions are relatively independent of the approach used to obtain the desired HCCI combustion phasing.
- NO_x emissions increase significantly when incomplete and retarded combustion occurs, despite the expectation for reduced combustion temperatures. Increased N₂O and THC emissions under these conditions may contribute to increased NO_x formation in these cases.
- N₂O emissions are very low (<0.5 ppm) for normal HCCI combustion. However, they increase significantly when incomplete combustion occurs. A peak value of 1.7 ppm was observed when the combustion efficiency dropped to approximately 70%.

Acknowledgment

Funding for this work was provided by Natural Resources Canada through the Program of Energy Research and Development (PERD/AFTER) Program, Project C22.001, and the ecoENERGY Technology Initiative, Project C21.002.

References

- [1] Zhao, F., Asmus, T., Assanis, D., Dec, J., Eng, J., and Najt, P., 2003, *Homogeneous Charge Compression Ignition (HCCI) Engines: Key Research and Development Issues*, SAE PT-94, Society of Automotive Engineers, Inc., Warrendale, PA.
- [2] Sun, R. N., Thomas, R., and Gray, C. L., 2004, "An HCCI Engine: Power Plant for a Hybrid Vehicle," SAE Paper No. 2004-01-0933.
- [3] Chen, R., and Milovanovic, N., 2001, "A Review of Experimental and Simulation Studies on Controlled Auto-Ignition Combustion," SAE Paper No. 2001-01-1890.
- [4] Epping, K., Aceves, S. M., Bechtold, R. L., and Dec, J. E., 2002, "The Potential of HCCI Combustion for High Efficiency and Low Emissions," SAE Paper No. 2002-01-1923.
- [5] Oakley, A., Zhao, H., Ladmatos, N., and Ma, T., 2001, "Dilution Effects on the Controlled Auto-Ignition (CAI) Combustion of Hydrocarbon and Alcohol Fuels," SAE Paper No. 2001-01-3606.
- [6] Xie, H., Wei, Z. P., He, B. Q., and Zhao, H., 2006, "Comparison of HCCI Combustion Respectively Fuelled With Gasoline, Ethanol and Methanol Through the Trapped Residual Gas Strategy," SAE Paper No. 2006-01-0635.
- [7] Amnéus, P., Mauss, F., Kraft, M., Vressner, A., and Johansson, B., 2005, "NO_x and N₂O Formation in HCCI Engine," SAE Paper No. 2005-01-0126.
- [8] Glassman, I., 1987, *Combustion*, Academic, New York.
- [9] Turns, S. R., 1996, *An Introduction to Combustion: Concepts and Applications*, McGraw-Hill, New York.
- [10] Guo, H., Liu, F., and Smallwood, G., 2005, "A Numerical Study on NO_x Formation in Laminar Counterflow CH₄/Air Triple Flame," *Combust. Flame*, **143**, pp. 282–298.
- [11] Tomeczek, J., and Gradon, B., 2003, "The Role of N₂O and NNH in the Formation of NO via HCN in Hydrocarbon Flames," *Combust. Flame*, **133**, pp. 311–322.
- [12] Lentini, D., 2003, "Prediction of NO_x Emissions in Gas Turbine Combustors Inclusive of the N₂O Contribution," *Proc. Inst. Mech. Eng., Part A*, **217**, pp. 83–90.
- [13] Wuebbles, D. J., 2009, "Nitrous Oxide: No Laughing Matter," *Science*, **326**, pp. 56–57.
- [14] Prather, M. J., and Hsu, J., 2010, "Coupling of Nitrous Oxide and Methane by Global Atmospheric Chemistry," *Science*, **330**, pp. 952–954.
- [15] Robertson, G. P., and Grace, P. R., 2004, "Greenhouse Gas Fluxes in Tropical and Temperate Agriculture: The Need for a Full-Cost Accounting of Global Warming Potentials," *Environ., Dev. Sustainability*, **6**, pp. 51–63.
- [16] Sloss, L. L., 1991, *NO_x Emissions From Coal Combustion*, IEACR/36 IEA Coal Research, Lexington, KY.
- [17] Dasch, J. M., 1992, "Nitrous Oxide Emissions From Vehicles," *J. Air Waste Manage. Assoc.*, **42**, pp. 63–67.
- [18] Koike, N., and Odaka, M., 1996, "Methane and Nitrous Oxide (N₂O) Emissions Characteristics From Automobiles," SAE Technical Paper No. 960061.
- [19] Meffert, M. W., Lenane, D. L., Openshaw, M., and Roos, J. W., 2000, "Analysis of Nitrous Oxide Emissions From Light Duty Passenger Cars," SAE Technical Paper No. 2000-01-1952.
- [20] Amann, M., Ryan, T. W., and Kono, N., 2005, "HCCI Fuels Evaluations-Gasoline Boiling Range Fuels," SAE Paper No. 2005-01-3727.
- [21] Li, H., Guo, H., Neill, W. S., Chippior, W., and Taylor, J. D., 2010, "An Experimental and Modeling Study of HCCI Combustion Using n-Heptane," *ASME J. Eng. Gas Turbines Power*, **132**, p. 022801.
- [22] Heywood, J. B., 1988, *Internal Combustion Engine Fundamentals*, McGraw-Hill, New York.
- [23] Peng, Z., Zhao, H., and Ladommatos, N., 2003, "Effect of Air/Fuel Ratios and EGR Rates on HCCI Combustion of n-Heptane, a Diesel Type Fuel," SAE Paper No. 2003-01-0747.