Some Observations on the Effects of EGR, Oxygen Concentration, and Engine Speed on the Homogeneous Charge Combustion of n-Heptane

Jincai Zheng, David L. Miller* and Nicholas P. Cernansky
Mechanical Engineering Department, Drexel University

Dexin Liu and Xinshun Zhao
National Engine Combustion Laboratory, Tianjin University, Tianjin, PRC

Mingxian Zhang
College of Chemical Engineering, Beijing Union University, Beijing, PRC

ABSTRACT

NOx and soot emissions remain critical issues in diesel engines. One method to address these problems is to achieve homogeneous combustion at lower peak temperatures – the goal of research on controlled autoignition. In this paper n-heptane is used to represent a large hydrocarbon fuel and some of the effects of internal and external EGR, oxygen concentration, and engine speed on its combustion have been examined through simulation and experiment. Simulations were conducted using our existing skeletal chemical kinetic model, which combines the chemistry of the low, intermediate, and high temperature regimes. Experiments were carried out in a single cylinder, four-stroke, air cooled engine and a single cylinder, two stroke, water cooled engine.

In the four-stroke engine experiments the effects of EGR were examined using heated N_2 addition as a surrogate for external EGR and engine modifications to increase internal EGR. Two-stage ignition was observed in both the simulations and experiments. The modeling results indicate that the ignition times were sensitive to EGR through both thermal and chemical effects. High levels of EGR completely suppressed autoignition. The most apparent effect of oxygen concentration is a shortening of the time between the first stage and second stage ignition. The modeling shows that EGR or extra air are key factors in eliminating knock during mid-load conditions. For higher load operation knock is serious and the only way to avoid it is to control reaction timing through the use of spark ignition. The experimental and modeling results from the two-stroke engine show that autoignition can be avoided by increasing the engine speed. This appears to result from shortened reaction time at lower temperatures thereby reducing the extent of the low and intermediate temperature chemical reactivity. The two-stroke engine experiments indicate that high levels of internal EGR (obtained by increasing the engine back pressure) can enable spark ignition at lean/dilute conditions. Based on the similarity between two-stoke and four-stroke engines, spark ignition may be possible at higher load conditions using internal EGR (simultaneously keeping peak temperature lower) for four-stroke engines.

INTRODUCTION

Diesel engines have been faced with increasingly stringent emissions legislation for more than a decade. The new standards in 2007-2010 are challenging and will likely require development of advanced combustion systems to reduce the emissions. New engine technologies for lower emissions and higher efficiency are developing very rapidly. The Homogeneous Charge Compression Ignition (HCCI) engine concept is a developing technology that has the potential to overcome the current fundamental NOx and particulate emission limitations of IC engines while simultaneously providing high diesel-like efficiency. This is possible because HCCI operates with overall very lean or dilute mixtures with lower temperatures. HCCI engines have developed from initial experiments in Controlled Auto-Ignition (CAI) systems. CAI technology was first applied successfully to two-stroke gasoline engines [1, 2], where stable combustion was achieved with lean mixtures at part-throttle operation and fuel consumption and emissions were improved remarkably. The HCCI concept was extended to the diesel fuelled four-stroke process by Najt and Foster [3], and major efforts to investigate the potential for diesel-fueled HCCI have been underway since the mid-1990s. Since the engine was operated without the benefit of internal residuals like a two-stroke engine, the intake air had to be heated in order to obtain HCCI combustion. Subsequently, experiments have been conducted in four-stroke engines operating on fuels as diverse as gasoline,

*Corresponding author: dmiller@coe.drexel.edu

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diesel, ethanol, and natural gas. A variety of physical control methods (e.g., inlet temperature and EGR, etc.) have been examined in an effort to obtain stable combustion over ever broader operating conditions [4-10].

Unfortunately, HCCI is not without its problems. HCCI engines operate at low combustion temperatures, so more unburned hydrocarbons (UHC) and CO emissions are generated than in traditional engines. Also knock is a serious problem at higher load conditions, and therefore, HCCI engines usually operate with lower Indicated Mean Effective Pressure (IMEP) [7, 11, 12]. Additionally, at idle and near-idle loads HCCI cannot be achieved because the compression temperature is too low. In general, there is an inability to control the initiation and rate of combustion over the required speed and load range [5]. These factors presently are limiting the commercialization of the HCCI concept.

The HCCI combustion of diesel type fuels can be more easily achieved than with gasoline type fuels because of diesel fuels' lower autoignition temperature. However, there is a problem getting diesel fuel to vaporize and premix with the air due to the low volatility of the diesel fuel [13, 14]. n-Heptane, with a cetane number (CN) of 56, is often used as an "autoignition" surrogate for diesel fuel. Therefore, it was selected for use in this study that focuses on autoignition chemistry.

To achieve HCCI combustion at idle or near-idle load levels, several technologies and solutions have been suggested: modifying the fuel to change its reaction kinetics, using variable compression ratio, or utilizing a hybrid powertrain to avoid the problems of low load operation, etc. For the higher load condition, premixed HCCI is not likely to be developed into a practical technique for production, diesel-fueled engines. Other strategies have been developed, for example, early direct-injection HCCI [15], late direct-injection HCCI [16], "dual mode" engines [12], or water injection for HCCI control [17]. While strategies that produce in-cylinder gradients in fuel concentration and/or temperature do not strictly follow the HCCI concept, they do have potential for spreading out the reaction zone thereby producing favorable combustion phasing and duration behavior.

There are several critical issues to be addressed with HCCI engines, and many of these issues, especially those related to combustion initiation, are associated with the fact that HCCI combustion is mainly chemically controlled with initiation triggered by the low and intermediate temperature preignition chemistry. The structure of the low and intermediate temperature kinetic mechanism is based on degenerate chain branching. At low temperature the branching reaction of OOQOOH•,

$$OOQOOH• => 2RCHO + RCO• + OH• + OH•,$$
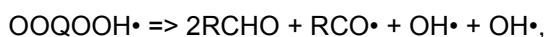
where OOQOOH• is produced via RO_2• isomerization and O_2 addition reactions, will dominate the reaction process leading to the first-stage ignition. When temperature increases, the reverse of the oxygen addition to the alkyl radical reaction,

$$R• + O_2 \Leftrightarrow RO_2•,$$
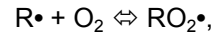
becomes more important and the reaction follows,

$$R• + O_2 => C=C + HO_2•,$$
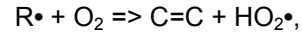
to form C=C and HO_2•. This mechanistic switch retards the chain branching reactions and is the primary mechanism necessary for explaining the first-stage ignition and Negative Temperature Coefficient (NTC) behavior. The HO_2• is converted to HOOH via

$$HO2• + HO2• => HOOH + O_2,$$
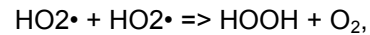
and, as the temperature is further increased, the HOOH thermally decomposes to two OH• radicals leading to the second-stage ignition. For larger HC's, the alternative fates of RO_2•, QOOH•, etc. are also important for reproducing the temperature dependence of the NTC behavior. When temperature increases, the chain propagation reactions of QOOH• will accelerate and affect the NTC behavior [18]. Further, the major preignition oxidation behavior of the fuel components at low and intermediate temperatures releases heat. This raises the mixture temperature thereby increasing the rate of reaction. Such positive feedback makes prediction of ignition very difficult.

If autoignition can be controlled and a homogeneous lean or dilute mixture tailored to produce an appropriate combustion rate and low combustion temperature, then low NOx and negligible soot are produced. The key issues are how to control the timing of the onset of ignition especially under idle and near-idle loads, and how to achieve high load operation with appropriate combustion rates. While several methodologies have been investigated, spark ignition with subsequent flame propagation is still the most practical control method for both combustion initiation and combustion rate.

In this study, experiments were conducted on two engines using n-heptane as a surrogate diesel fuel. Our existing chemical kinetic model [19] with 69 reactions and 45 active species was used to explore the chemistry. The model combines the chemistry of the low, intermediate, and high temperature regions with conservation of energy and atoms. All of the chemical reaction rate parameters come from published data. Simulations were compared with measured and calculated data from the engines. The simulations are generally in good agreement with the experimental data including temperature, pressure, ignition delay, and heat release. At first the NTC behavior of n-heptane was studied in both experimental and modeling studies. We then investigated a special combustion phenomenon, low temperature, late cycle autoignition, to try to determine its origins. Finally, we used

simulations and experiments to explore techniques to achieve stable and acceptable combustion processes at lower and higher load conditions.

EXPERIMENTAL APPARATUS AND PROCEDURES

The data used in this study were collected from both four-stroke and two-stroke engine experiments. The four-stroke engine was a single cylinder, air cooled research engine which was originally modified at Sandia National Laboratory, with subsequent modifications at Drexel University [20]. In its present configuration, the engine has a 76.2 mm bore, a 82.6 mm stroke and a 8.2 compression ratio. An important characteristic of this engine test facility is the ability to control the manifold temperature and pressure independently. In this study, the inlet air temperature was varied between 393 – 560 K and the inlet manifold pressure was set at 100.0 kPa (1 atm). The n-heptane was injected into the air stream of the heated inlet manifold well upstream of the intake valve to assure complete vaporization and mixing. The equivalence ratio was held at either 0.2 or 0.3, and the engine was operated at a constant speed 600 or 750 rpm. Cylinder pressure data were collected via a wall mounted piezoelectric pressure transducer, and these data were transferred to a computer system for further analysis. The pressure data were averaged for 11 cycles and this average trace was used to calculate temperature and heat release using a standard Heat Release Model (HRM). The CO and fuel concentration were measured in the cylinder using a fast acting gas sampling system with subsequent gas chromatographic (GC) analysis. In order to obtain large enough gas samples for analysis, the sampling valve was opened for 1 ms on sequential engine cycles at the desired CAD for a period of approximate 3 minutes. To increase the internal EGR in the cylinder, the exhaust valve rod clearance was increased to shorten the opening period of the exhaust valve.

The two-stroke engine was a single cylinder, water-cooled engine located and operated at the National Engine Combustion Laboratory, Tianjin University, PRC. The engine has a 50.0 mm bore, a 50.6 mm stroke, and a geometric compression ratio of 14 (effective compression ratio of 13). Experiments with this engine focused primarily on stoichiometric operating conditions. As such, the fuel channel in the carburetor for idle operation was closed so that rich mixtures would be avoided at idle and the main fuel channel was partly closed in order to obtain mixtures leaner than the factory calibration. n-Heptane was used for these engine experiments, and the speed was varied from 1200 to about 10000 rpm. Pressure in the cylinder was measured using a piezoelectric pressure transducer mounted in the spark plug and the data were recorded and processed as noted above. CO and UHC emissions were measured in the exhaust line. In order to increase the internal EGR in the cylinder, the exhaust back pressure was increased using a valve installed in the exhaust pipe.

EXPERIMENTAL RESULTS AND DISCUSSION

A brief overview of our work is given prior to providing the detailed results. We first studied the two-stage ignition of n-heptane under HCCI conditions both experimentally and via simulations, and we analyzed the effect of EGR and oxygen concentration on the HCCI combustion process. Then, considering the limitations of HCCI at ideal or near-ideal conditions and based on our previous results with two-stroke engines [21], we investigated the spark ignition of very lean mixtures of n-heptane (low load) with high levels of internal EGR. At the same time, a new analysis/explanation was put forward to interpret our previous and present experimental results. This reinterpretation and new analysis suggests an approach for overcoming some of the current limitations on HCCI systems. Finally, we explored the possibility of operating in a homogeneous charge mode in a high compression ratio engine at higher loads using spark ignition.

TWO-STAGE IGNITION OF N-HEPTANE

Our initial experiments were conducted on the four-stroke engine using n-heptane and keeping the same air flow at equivalence ratio of 0.2 and 0.3 conditions. The experimental and simulated results [22] are presented in Figures 1 and 2. The simulation results (labeled SKM) are calculations of CO, fuel reacted, and heat release using the Skeletal Kinetic Model (SKM); the experimental results included measured CO and fuel reacted, from GC measurements, and cumulative heat release calculated from the in-cylinder pressure traces using a standard HRM. In Figure 1 an apparent two-stage ignition is observed, fuel is not completely consumed, and CO concentration, which represents the extent of reactivity, is higher than that in Figure 2. Since autoignition has not occurred at the condition of equivalence ratio of 0.2 in Figure 2, this shows that at lower load conditions HCCI cannot be achieved simply by compression and self-heating at our experimental conditions. Analysis and interpretation of these and later experimental results requires a more detailed understanding of the underlying chemical mechanism than that provided in the Introduction. Thus, a brief foray into the world of chemistry is appropriate at this point.

Two-stage ignition is a complex combustion phenomenon for hydrocarbons. The process is initiated by the reaction of fuel with oxygen

$$RH + O_2 \Leftrightarrow R\bullet + HO_2\bullet.$$
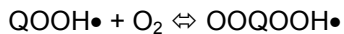
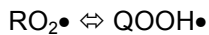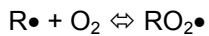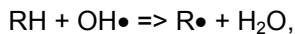The following mechanism causes the first-stage ignition,
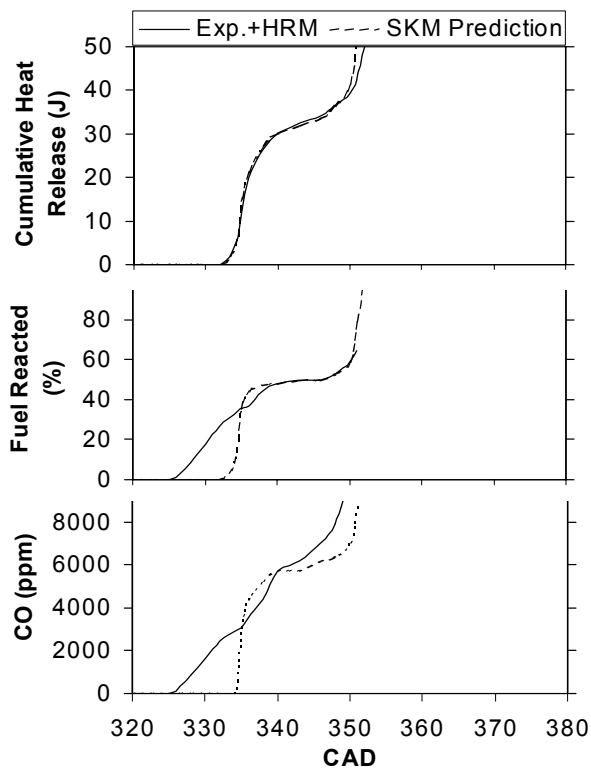
Figure 1. Comparison of measured and predicted cumulative heat release, fuel consumption and [CO] profiles in the four-stroke engine for n-heptane, 600 rpm, compression ratio of 8.2, Tin=376 K, Pin=108 kPa, and ϕ=0.3 [22]
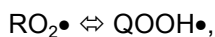
$$R\bullet + O_2 \Leftrightarrow RO_2\bullet$$

$$RO_2\bullet \Leftrightarrow QOOH\bullet$$

$$QOOH\bullet + O_2 \Leftrightarrow OOQOOH\bullet$$

$$OOQOOH\bullet => OQ'OOH + OH\bullet$$

$$OQ'OOH => OQ'O\bullet + OH\bullet.$$
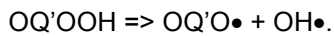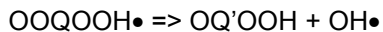
During this sequence,

$$RH + OH\bullet => R\bullet + H_2O,$$

dominates fuel consumption and alkyl radical, $R\bullet$, formation.

When the mixture temperature increases via compression and heat release, further reactions will lead into the Negative Temperature Coefficient (NTC) region. The reverse reactions,

$$R\bullet + O_2 \Leftrightarrow RO_2\bullet \text{ and}$$

$$RO_2\bullet \Leftrightarrow QOOH\bullet,$$

will be enhanced, and

$$R\bullet + O_2 => C=C + HO_2\bullet$$

Figure 2. Comparison of measured and predicted cumulative heat release, fuel consumption and [CO] profiles in the four-stroke engine for n-heptane, 600 rpm, compression ratio of 8.2, Tin=376 K, Pin=108 kPa, and ϕ=0.2 [22]
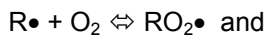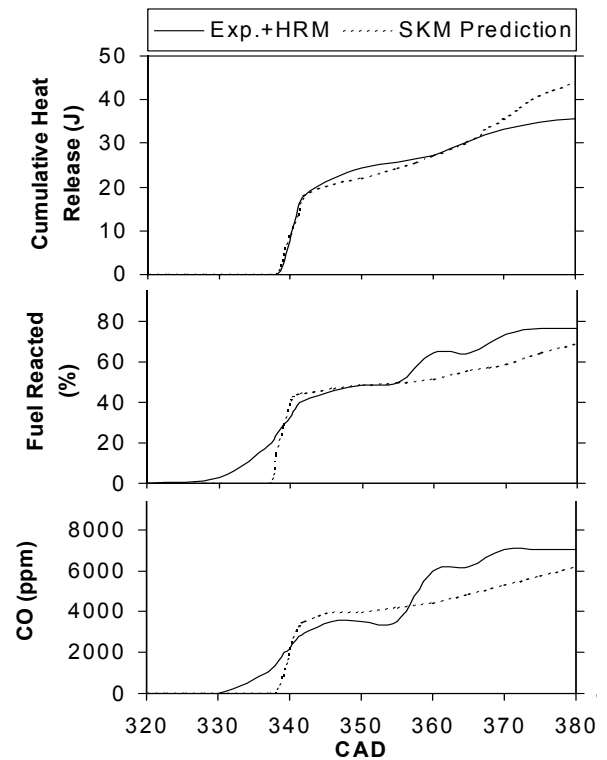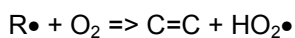
will be the dominating reaction.

Recent work in our laboratory [18] identified negative temperature coefficient behavior for neopentane. This requires an alternative to the traditional conjugate olefin pathway to NTC behavior, as neopentane does not have a conjugate olefin. Detailed modeling indicated that NTC behavior of neopentane is caused by the β-scission of the neopentyl radical reaction and the chain propagation reactions of the hydroperoxyl-neopentyl radical [18]. Therefore it is logical to include such reactions for all large alkanes. For n-heptane the chain propagation,

$$QOOH\bullet => C=C + RCHO + OH\bullet, \text{ and}$$

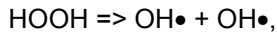$$RO_2\bullet => ether + OH\bullet, \text{ etc.}$$
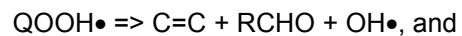
will affect NTC behavior. This is the chemical kinetic mechanism in the low and intermediate temperature regions based on degenerate chain branching.

HOOH is formed during the first-stage ignition process via

$$HO_2\bullet + HO_2\bullet => HOOH + O_2,$$
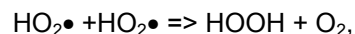
and, if temperature is further increased,

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$$HOOH => OH\bullet + OH\bullet,$$

takes over and the second-stage ignition (hot ignition) occurs.

The chemical kinetic mechanism reasonably explains chemical behaviors in the low and intermediate temperature regions. Our skeletal model follows this mechanism and the simulated results agree with the experimental results as shown in Figures 1 and 2. This mechanism indicates that the mixture temperature dominates the chemical process. The pre-ignition reactions of n-heptane release heat, the heat release raises the system temperature and control becomes more difficult.

AUTOIGNITION CONTROL WITH N-HEPTANE

As a first step, we progressively substituted N2 for air in the inlet mixture while keeping the same fueling rate and observed how the ignition behavior changed. At this point we used our model to study the cause of this change and, in the process, we defined several features and characteristic times that are derived from measured pressure data as illustrated in Figure 3. We defined the beginning of first-stage ignition, τ_{beg}, as the CAD where apparent heat release begins. Ignition time, τ_{ign}, is the CAD where the tangents to the pressure trace during the NTC region and during the rapid pressure rise intersect. The period between the first-stage ignition and the end of the NTC region, $\Delta\tau_{NTC}$, is the CAD duration between the first-stage ignition beginning time and the ignition time. In all of our data, we observed that the calculated heat release rate is approximately 5 J/CAD at the experimentally determined ignition time. The rapid combustion duration, $\Delta\tau_{rc}$, is the CAD duration between the ignition time and the point where the rate of heat r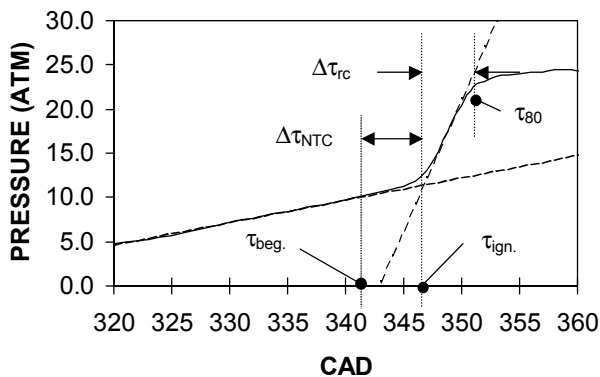elease begins to slow. Experimentally, reaction was observed to slow down at roughly 80% of the potential heat release, τ_{80}.

For comparison with the skeletal kinetic model, we used the point where the cumulative heat release is 0.1 of the available energy as the onset of first-stage ignition. Ignition was defined as the CAD where 5 J/CAD heat release was attained. We also calculated the CAD of the 80% heat release point to use in determining $\Delta\tau_{rc}$.

Calculated results for a four-stroke engine with residual gas fraction of 13% and an effective compression ratio of 13 are shown in Figure 4 and Tables 1 and 2. These calculations were intended to explore the effect of external EGR on the HCCI combustion process, and to separate the mixture heat capacity and O_2 concentration effects. When the equivalence ratio (fresh charge equivalence ratio) is 1.0, the external EGR consisted of 12.4% of CO_2, 14.2% of H_2O, and 73.4% of N_2. At lower fresh charge equivalence ratios, some O_2 was present in the external EGR which increased the O_2 concentration beyond what was present in the fresh charge. Table 1 shows the characteristic times obtained when the true mixture heat capacity is considered, and Table 2 shows comparable data obtained when the mixture heat capacity is fixed at the value appropriate for the $\Phi = 0.4$ case; therefore, investigating the O_2 chemical effect without changing the heat capacity of the mixture. As shown in Table 1, at modest levels of EGR (e.g., up to 30% at $\Phi = 0.6$), the combined effects of O_2 reactivity and specific heat are small with less than 2 CAD change in the characteristic times. As EGR increases the three characteristic times increase and the $\Delta\tau_{NTC}$ all increases. At the highest level the thermal effect completely suppresses hot ignition. The results from

Figure 3. Experimentally measured pressure profile, showing onset of heat release (τ_{beg}), the duration of first-stage ignition and NTC duration ($\Delta\tau_{NTC}$), ignition time (τ_{ign}), and rapid combustion duration ($\Delta\tau_{rc}$)

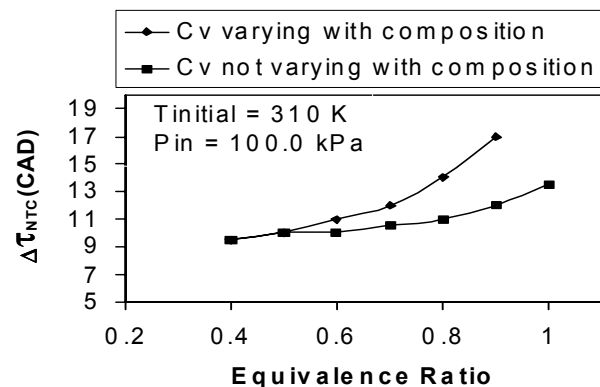

Figure 4. The simulated duration from the onset of the first-stage ignition to the end of the NTC regime, $\Delta\tau_{NTC}$, and its variation with equivalence ratio at an effective compression ratio of 13, keeping the fuel of every cycle constant while progressively substituting external EGR for air

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Table 1. The calculated heat release beginning time (τ_{beg}), ignition time (τ_{ign}), time for 80% potential heat released (τ_{80}), and rapid combustion duration ($\Delta\tau_{rc}$) in the four-stroke engine for Tinitial=310 K, Pin=100.0 kPa, engine speed of 750 rpm, effective compression ratio of 13, at specified fresh charge equivalence ratio and external EGR achieved by keeping the amount of fuel and total moles constant, where the mixture specific heat is varied for each condition

Fresh Charge Ratio	EGR Mole Fraction (%)	τ_{beg} (CAD)	τ_{ign} (CAD)	τ_{80} (CAD	$\Delta\tau_{rc}$ (CAD)
0.4	0.0	340.5	350	353	3
0.5	17.3	341	351	354	3
0.6	28.8	342	353	356	3
0.7	37.0	342	354	357	3
0.8	43.2	343	357	360	3
0.9	48.0	344	361	365	4
1.0	51.8	345	NO	NO	NO

Table 2. The calculated heat release beginning time (τ_{beg}), ignition time (τ_{ign}), time for 80% potential heat released (τ_{80}), and rapid combustion duration ($\Delta\tau_{rc}$) in the four-stroke engine for Tinitial=310 K, Pin=100.0 kPa, engine speed of 750 rpm, effective compression ratio of 13, at specified fresh charge equivalence ratio and external EGR achieved by keeping the amount of fuel and total moles constant, where the mixture specific heat is held constant at the ϕ=0.4 value

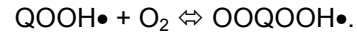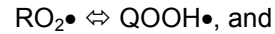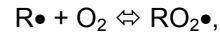| Fresh Charge Ratio	EGR Mole Fraction (%)	τ_{beg} (CAD)	τ_{ign} (CAD)	τ_{80} (CAD	$\Delta\tau_{rc}$ (CAD)
0.4	0.0	340.5	350	353	3
0.5	17.3	341	351	354	2.5
0.6	28.8	341	351	354	3
0.7	37.0	341	351.5	354	2.5
0.8	43.2	341	352	355	3
0.9	48.0	341	353	356	3
1.0	51.8	341.5	355	358	3

numerically decoupling the chemical effect of O_2 and thermal effect of EGR, shown in Table 2, show that while O_2 has little effect on τ_{beg} it significantly shortens the time from first stage ignition to hot ignition ($\Delta\tau_{NTC}$) and thereby τ_{ign}. Figure 4 also illustrates the relative effects of heat capacity and O_2. τ_{ign} was most sensitive to EGR level, with a smaller oxygen concentration effect.

These results can be explained by examining the chemical kinetic mechanism. The initiation of chemical reactions starts with the reaction of fuel with oxygen,

$$RH + O_2 \Leftrightarrow R\bullet + HO_2\bullet.$$
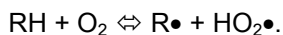
The activation energy of this process is high, 46 kcal/mole, which means that the initial reaction depends strongly on the mixture temperature. As such, at the same initial temperature, τ_{beg}, will not change very much and will primarily be impacted by changes in the mixture specific heat. However, the build-up of reactive intermediates following τ_{beg} and during the first-stage ignition processes will change significantly, because their concentrations are controlled by reactions, such as

$$R\bullet + O_2 \Leftrightarrow RO_2\bullet,$$

$$RO_2\bullet \Leftrightarrow QOOH\bullet, \text{ and}$$

$$QOOH\bullet + O_2 \Leftrightarrow OOQOOH\bullet.$$

Two of these reactions involve molecular oxygen, so if O_2 concentration increases, more OOQOOH$\bullet$ will be formed and more OH$\bullet$ will be produced from the OOQOOH$\bullet$ branching reaction. It is apparent that more fuel will be consumed and more heat will be released leading to increasing temperature. Further, the extent of the reaction will be accelerated leading to more HOOH. Since HOOH decomposition controls the second-stage ignition, this means that the second-stage ignition will occur more easily.

Lean and dilute mixtures can decrease the maximum combustion temperature, but O_2 is the active species during the reactions in the high temperature region. Using our existing skeletal model we calculated $\Delta\tau_{rc}$ under these conditions, holding fuel and total moles constant, but raising the equivalence ratio by increasing the proportion of external EGR. Note that $\Delta\tau_{rc}$ is almost the same for all conditions, as shown in Tables 1 and 2. In the high temperature region of rapid combustion the reaction rates depend mainly on temperature. This is also apparent from the high activation energy, 30 kcal/mole, of the single-step global reaction rate parameter for n-heptane decomposition. The more dilution and extra air, the lower the combustion temperature leading to the lower combustion rate in the high temperature region. So EGR or extra air is a key factor in reducing combustion rate in high temperature region during mid-load conditions and the effects of both are almost identical.

IDLE AND LOW LOAD CONDITIONS

The mixture temperature is a critical factor for HCCI operation. In experiments in our four-stroke engine operating on n-heptane, at the condition of equivalence ratio of 0.3 and the engine speed of 600 rpm, the autoignition temperature was about 950 K [22] (Figure 5). When the equivalence ratio was reduced to 0.2, autoignition did not occur since the temperature was not high enough. This is why HCCI cannot be achieved in four-stroke engines at lower load conditions, unless a high level EGR or some other method of charge heating is provided.

However, two-stroke engines can operate at these lower load conditions, and low UHC and CO emissions
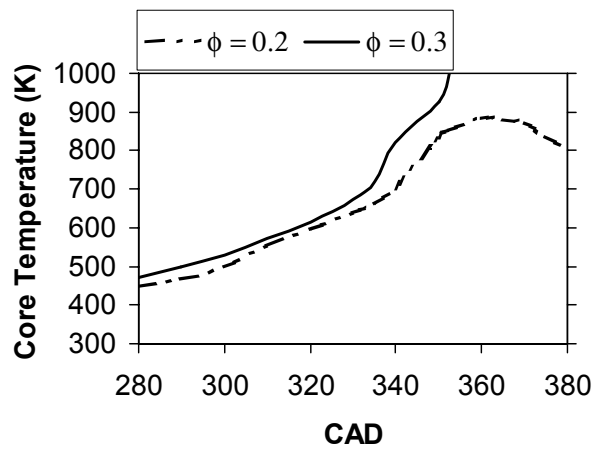
Figure 5. Temperature profiles derived from pressure data for 600 rpm, compression ratio of 8.2, Pin=108.2 kPa, and Tin=376 K in the four-stroke engine [22]
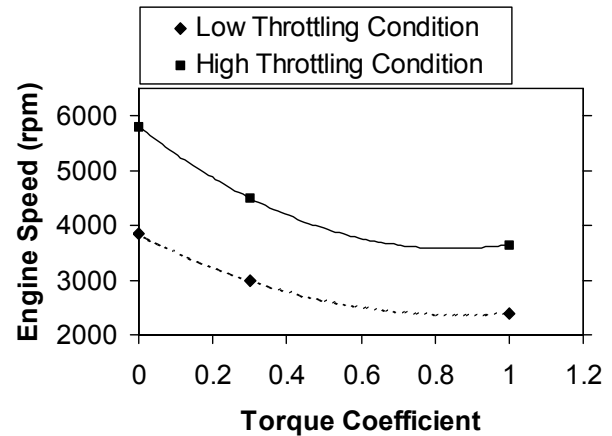
Figure 6. The variation of engine speed with load at two different throttling conditions with the same amount of fuel per cycle at each torque level on a two-stroke engine with equivalence ratio of 1.0 and effective compression ratio of 13

can even be achieved [1]. This is in fact what led to the initial interest in HCCI. Our experimental results on a two-stroke engine with a high level of internal EGR demonstrate that spark ignition can be realized and produce stable combustion with lower UHC and CO (as low as 0.3% CO) emissions [21]. These data indicate that the same positive results may be achievable at idle and near-idle conditions during HCCI operation.

In this study, n-heptane was run at low load conditions in the two-stroke engine with an effective compression ratio of 13. The experiments were conducted as follows. Using spark ignition at a selected fuel flow rate and external load the engine was allowed to reach a steady state speed at a high level of EGR (significant exhaust throttling). Then, the spark ignition was turned off and engine slowed to a new steady state speed. This new speed and the measured power dissipated by the dynamometer were used to calculate the torque coefficient (power/(k•speed), where k is a constant for a given dynamometer). The dynamometer load was increased and a new steady state speed achieved with a new torque coefficient. Then, the dynamometer load was reduced and a third steady state torque coefficient determined. This procedure was repeated for a low level of EGR (minimal exhaust throttling) starting at the same spark ignition steady state.

Figure 6 represents the stable engine speed for low and high throttling conditions as a function of torque as represented by the torque coefficient. As torque is proportional to fuel flow rate, a constant value of torque coefficient means the percentage of fresh mixture in the cylinder is constant.

When increasing the level of internal EGR, there are more residuals in the cylinder and, even though the initial temperature can be higher, the combustion temperature is lower. However, more stable combustion can be achieved with more internal EGR, because the engine can run at higher speed and higher power. In our four-stroke engine simulations, increasing dilution (external EGR or air) tends to degrade performance.

Why is there such a difference between two-stroke engines and four-stroke engines relative to their combustion stability and UHC and CO emissions behavior with increasing levels of EGR? Even accounting for the obvious thermal effects, current theory and models can not explain these phenomena. Following presentation of another relevant experimental observation, we will present our best explanation for the observed phenomena and differences.

In the course of our past autoignition studies, we observed a unique combustion phenomenon in our four-stroke engine that occurred for a variety of fuels including n-heptane, 87/13 mixture of isooctane/n-heptane, and n-hexane. At appropriate experimental conditions in our research engine, a second rise in pressure indicative of autoignition would occur very late in the cycle, with the maximum combustion pressure reaching the TDC compression pressure later in the cycle [23]. Figure 7 presents two motored, single cycle pressure traces recorded during a manifold temperature sweep with stoichiometric n-hexane at an engine speed of 600 rpm and supercharged manifold pressure of 165 kPa. At a stabilized manifold temperature of 389 K a typical motored trace was
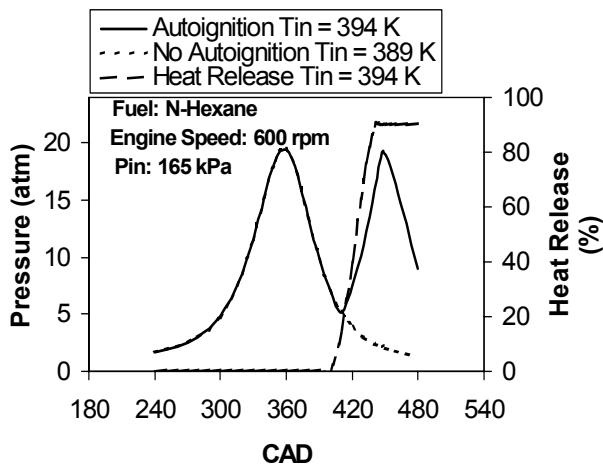
Figure 7. Pressure and heat release of late autoignition on a four-stroke engine with equivalence ratio of 1.0 and compression ratio of 8.2 [23]

recorded (the dotted trace); as the manifold temperature was increased to 394 K, an autoignition event began at approx. 55 CAD ATDC with the pressure reaching the compression pressure at 87 CAD ATDC. The observed late autoignition and combustion occurs at relatively low temperature and without significant early heating, as evidenced by the fact that the pressure trace prior to autoignition coincides with the lower non-autoigniting manifold temperature pressure trace. For the conditions of Figure 7, the mixture temperature at 55 CAD ATDC was 480 K. As stated earlier, similar late-cycle autoignitions occurred for stoichiometric mixtures of n-heptane and 87/13 mixtures of isooctane and n-heptane at equivalent conditions. So in these cases, some mixture of reactive intermediates was formed and they progressed to conditions that triggered rapid heat release beginning at low temperatures.

Previous explanations [e.g., 24] for such late autoignition have postulated the occurrence of cool flames, which carry the fuel-air mixture beyond the NTC region and into the intermediate temperature region where autoignition can occur. Such explanations are based on OQ'OOH accumulation and decomposition. However, decomposition of OQ'OOH,

$$OQ'OOH => OQ'O\bullet + OH\bullet,$$
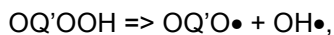
requires relatively higher temperature, since activation energies are typically E = 40.0 kcal/mole. Using our skeletal model (although not strictly applicable for n-hexane), if the equivalence ratio is 1 and the speed is 600 rpm, the temperature of the first-stage ignition is never lower than 600 K.

So how can autoignition occur at the lower temperature of 480 K? A revised explanation is that the preignition chemical reactions continue well after TDC

(chemical synthesis reactions and decomposition reactions can occur even at much lower temperatures) to form some small reactive species, which then drive the autoignition process. The process might occur as follows. The initiation step is the formation of alkyl radical, $R\bullet$, from a fuel molecule via reaction with a radical or any other active species present in the system. Then, at low temperature, the oxygen addition reactions,

$$R\bullet + O_2 \Leftrightarrow RO_2\bullet,$$
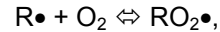
take over and are strongly biased in the forward direction, because $E^+ = 0.0$ and $E^- = 27.4$ kcal/mole. Then,

$$RO_2\bullet + RO_2\bullet => RO\bullet + RO\bullet + O_2$$
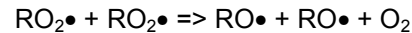
will be underway because it too has a small activation energy, E = 5.09 kcal/mol. Further, $RO\bullet$ is unstable and tends to decompose quite readily into small stable oxygenate species, primarily aldehydes or ketones, in addition to small alkyl species. Since aldehydes are also reactive and the small alkyl species lead to a smaller alkyl species following similar reaction paths, the decomposition of $RO\bullet$ accelerates the process [25]. In addition, the reactions of any alkyl radical with O_2 are strongly exothermic reactions. Therefore, we propose that the extent of these reactions is large enough to form many small reactive species and the late-autoignition can occur.

In the two-stroke engine, reactive species and/or their precursors in the internal EGR can readily survive to the following cycle and will react with fresh mixture. This results in a triggering of low temperature reactions prior to the first-stage ignition. Following the same mechanism of late-ignition, the content in the cylinder is ready to autoignite or to be ignited by a spark even at a high level of dilution. For a four-stroke engine, insufficient internal EGR is normally present to trigger these pre-first-stage reactions. Increasing synthetic or external EGR just produces dilution, which only inhibits the reactivity. Increasing internal EGR, with its potentially high levels of reactive species and/or their precursors, can initiate the chemical reactions prior to the first-stage ignition that are critical for spark ignition, stable flame propagation and lower emissions.

HIGHER LOAD CONDITION

To keep the HCCI advantages (low NOx emissions and high efficiency), dilution and high compression ratio are necessary. However, a HCCI engine cannot achieve such higher load operation, because rapid autoignition of the richer mixture produces destructive knock. The way to avoid this is to use spark ignition to initiate reaction for homogenous charge engines at dilute condition so knock does not occur easily. So two issues are emerging: how to avoid autoignition at high compression ratio conditions; and how to spark-ignite a dilute mixture.

Experiments were conducted using n-heptane in the two-stroke engine with a effective compression ratio of 13. The critical engine speeds for transition from HCCI operation (i.e., autoignition) to no autoignition as a function of engine load were measured and are shown in Figure 8. At 80% of full load (with almost an 80% fresh mixture fraction in the cylinder) the knock was excessive. The top of the piston was even burned off after several experiments. However, in general, autoignition could be avoided by increasing the engine speed. This results from the reduced reaction time at lower temperatures, which reduces the extent of the low and intermediate temperature chemistry. So the first question is answered – increasing engine speed will help to avoid unwanted autoignition in two stroke engines.

We used our existing skeletal chemical model to simulate the speeds and external EGR level over which knock can be avoided for a four-stroke engine with an effective compression ratio of 13 operating on n-heptane (Figure 9). The simulated results show that for higher load a higher engine speed is required to avoid autoignition. In these calculations load is varied by the amount of fuel per cycle (keeping total in-cylinder mass constant, equivalence ratio equal to 1.0, and varying the external EGR). As defined earlier, external EGR contains no active species. Therefore, no pre-first-stage reactions occur. Simulation shows that the higher load produces more heat from pre-ignition reactions so that a higher engine speed is required to avoid autoignition.

Although the general "increasing engine speed to avoid autoignition" conclusion is the same, the simulated results for the four-stroke engine show an opposite trend with engine load from the experimental results for the two-stroke engine. This is attributed to the fact that, in the two-stroke engine experiment, it is the initial temperature increase and the pre-first-stage reactions by internal EGR that makes the mixture with a

Figure 9. Simulated boundary between HCCI (AI – autoignition) and non-HCCI (NAI – non autoignition) operation as a function of speed and load for a four-stroke engine operating on n-heptane. Equivalence ratio and in-cylinder mass were kept constant, while varying the level of external EGR

high level of internal EGR easily autoignite at low load conditions.

Because the knock from autoignition at higher load conditions can be very serious, we want to use spark ignition to avoid it. Now if we turn on the spark ignition system in our 2-stroke experiments, stable operation of the engine could continue at engine speeds up 10000 rpm. This apparently answers the second question. But the mechanism is not very clear. We only apply the pre-first-stage reactions to interpret that the spark can ignite fuel and air mixture diluted by internal EGR. The pre-first-stage reactions are triggered by the initial radicals or precursors from the internal EGR, as soon as mixing occurs. The reactions are the same as those that control late-cycle autoigniton. The current skeletal chemical kinetic model does not include such reaction paths so that the pre-first-stage reactions cannot be simulated. The mechanism needs extension in order to handle this reaction regime.

For a four-stroke engine the method we employed to increase internal EGR was to adjust the exhaust valve rod clearance so that the exhaust period was shortened and more burned gases remained in the cylinder. Experimental results showed that spark ignition could still ignite the mixtures in consecutive cycles with even up to 50% internal EGR, although misfire occurred in some cycles [21]. This demonstrates that there is a similarity between the behavior of experimental two-stroke and four-stroke engines and we believe that this implies that pre-first-stage reactions are triggered by active species in the internal EGR. If the mechanism can be interpreted clearly and applied in the four-stroke engine, the homogeneous operation of a diesel engine fueled at
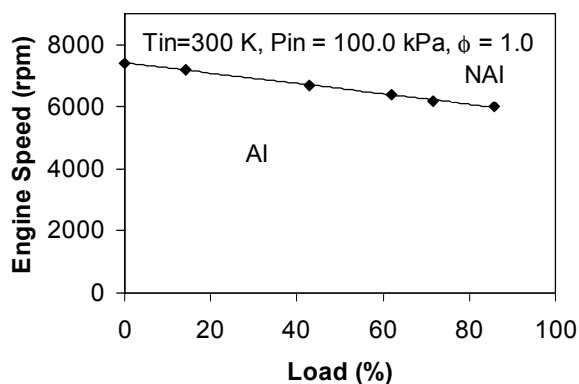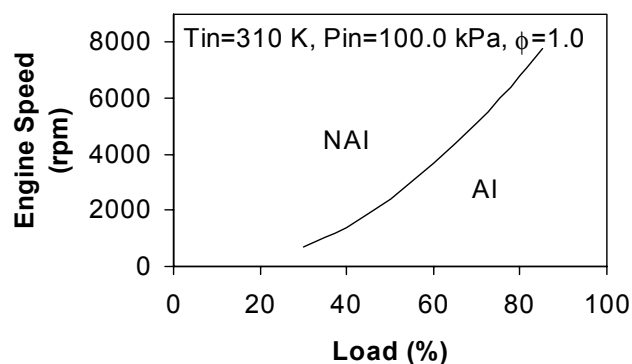

Figure 8. Measured boundary between HCCI (AI – autoignition) and non-HCCI operation (NAI – non autoignition) as a function of speed and load for a two-stroke engine operating on n-heptane

higher load conditions would be achievable with higher efficiency and lower emissions.

CONCLUSION

Two-stage ignition of n-heptane was examined and the mechanism was discussed. A special combustion phenomenon - late-cycle autoignition - was observed experimentally and interpreted. The relationship between spark ignition and pre-first-stage reactions was examined. The possible methods at lower and higher load conditions were provided using the fuel of n-heptane for a diesel homogenous charge engine. The following observations can be made about the experiments and the modeling results:

1. Two-stage ignition is very apparent for n-heptane. Both heat release (thermal theory) and chemical reactions of pre-ignition (reaction theory) are important for the autoignition.
2. The ignition times were very sensitive to external EGR through both thermal and chemical effects. The most apparent effect of oxygen concentration is a shortening of the time between the onset of the first-stage ignition and hot ignition. The main factor to affect combustion rate in the high temperature region is the mixture temperature, and extra air or EGR dilution is a key factor in eliminating knock during mid-load conditions.
3. The pre-first-stage reactions (low temperature) are critical for the late-cycle ignition and spark ignition of the high dilute mixture. The reactions paths of the pre-first-stage reactions require further study.
4. For a homogenous charge and high compression ratio engine using n-heptane, at lower load condition stable combustion can be achieved with help of internal EGR, especially, if coupled with spark ignition.
5. At higher load conditions increasing the engine speed is an effective method to control transition from HCCI operation to non-HCCI operation and successful spark ignition of a highly dilute mixture can avoid serious knock.

ACKNOWLEDGMENTS

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