

The Effect of HCHO Addition on Combustion in an Optically Accessible Diesel Engine Fueled with JP-8

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ABSTRACT

Under the borderline autoignition conditions experienced during cold-starting of diesel engines, the amount and composition of residual gases may play a deterministic role. Among the intermediate species produced by misfiring and partially firing cycles, formaldehyde (HCHO) is produced in significant enough amounts and is sufficiently stable to persist through the exhaust and intake strokes to kinetically affect autoignition of the following engine cycle. In this work, the effect of HCHO addition at various phases of autoignition of n-heptane-air mixtures is kinetically modeled. Results show that HCHO has a retarding effect on the earliest low-temperature heat release (LTHR) phase, largely by competition for hydroxyl (OH) radicals which inhibits fuel decomposition. Conversely, post-LTHR, the presence of HCHO accelerates the occurrence of high-temperature ignition. Experimentally, these effects are observed by high-speed imaging of combustion in an optically-accessible diesel engine run in skip-fire mode and fueled with JP-8, whose intake is doped with HCHO. The occurrence of LTHR is both retarded and reduced in magnitude, peak heat release rates are strongly attenuated and combustion efficiency decreases as intake HCHO fractions increase. The addition of HCHO results in a dramatic degree of yellow-orange luminous emission characteristic of soot production. Increases in swirl level and advances in injection timing were unable to compensate for the changes in heat release rates, combustion efficiency and sooty burning observed to result from HCHO addition.

INTRODUCTION

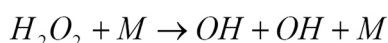
In the quest for greater efficiency and the simultaneous reduction in engine-out emissions, current trends are pushing compression-ignition engine design towards lower compression ratios and into unstable combustion regimes. An

unavoidable consequence of reduced compression ratio is more difficulty in cold-starting as compression temperatures are depressed. While ultra-lean combustion and aggressive degrees of exhaust gas recirculation (EGR) may provide emissions benefits, such techniques often require a fine degree of control over valve timing, intake temperature, swirl levels or charge stratification. Common to both trends is a need to understand the autoignition process and the factors that influence its occurrence.

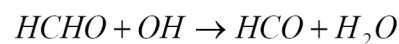
Autoignition has classically been considered to be a function of temperature, mixture density, induction duration, and mixture composition. While ignition delay periods have been quantified by modified Arrhenius forms fit to empirical data [1,2,3], the more subtle and less understood role of minor species influencing the kinetic process have more recently been acknowledged. Comparing the effects of real EGR against synthetic EGR mixtures comprising carbon dioxide, water vapor and nitrogen mixtures on combustion phasing in a Homogeneous Charge Compression Ignition (HCCI) engine, Sjöberg *et al* [4] attribute differences to the presence of trace partially-oxidized hydrocarbons. Such species were observed to enhance autoignition for iso-octane and gasoline fuels, but to have a retarding effect on a primary reference fuel (PRF) blend containing iso-octane and 20% n-heptane. Fitzgerald and Steeper [5] have performed kinetic modeling to substantiate a split-injection HCCI process with negative valve overlap (NVO) and iso-octane fuel. Variations in heat release were observed to result from a change in injection timing during the NVO period, and attributed to formyl radical oxidation and reactions involving ethylene (C₂H₄) and formaldehyde (HCHO).

The influence of aldehydes on the different oxidation stages of combustion has been known for some time. In a constant-temperature reaction chamber, Salooja compared the effect of nine different saturated, branched-chain and unsaturated

aldehydes on the characteristics of hexane combustion. While the aldehydes were found to be largely ignition promoting, formaldehyde was uniquely found to strongly inhibit all pre-flame stages and raise the ignition temperature. Acetaldehyde was deemed to be the best promoter. The combustion-inhibiting effect of HCHO was concluded to occur over the entire temperature range studied (170-500 °C) [6]. Karim *et al* [7] have examined the role of intermediate oxidation products such as formaldehyde on the ignition delay period of a dual-fuel compression ignition engine. Atomizing an aqueous HCHO solution in the intake of the engine operated in conventional diesel mode, and accounting for the presence of H₂O, the HCHO addition was observed to extend the ignition delay period over a range of equivalence ratios from 0.2 to 0.4, although peak pressures were judged to remain unchanged. Similar, retarding effects of HCHO were observed with the engine operated in dual-fuel mode with gaseous methane and propane fuels and ignited by a pilot injection of diesel fuel. The effect of formaldehyde as a controlling agent of autoignition has been more recently investigated by Furutani *et al.* [8]. An HCCI engine of compression ratio 18 was run on gaseous fuel blends of n-butane and methane, with greater fraction of the former resulting in a monotonic advance of the ignition timing. However, the addition of 1350 ppm HCHO resulted in stable ignition timing that was invariant with respect to the fuel blend; advancing the autoignition of the mixtures with least n-butane composition, yet retarding the timing of the mixtures with greater n-butane fraction. Experiments at HCHO fractions of 2100 ppm again suppressed the effect of n-butane/methane ratio on autoignition timing, but advanced this ratio-invariant value by approximately two crank-angle degrees. In a subsequent work [9], the effect of HCHO addition was examined in both spark-ignited and compression-ignited engines fueled with gasoline and a distillate fuel oil of cetane index 52, respectively. By varying intake temperature and compression ratios, the interaction of HCHO with the autoignition process at different top-dead center (TDC) temperatures was observed. The authors conclude that when low-temperature heat release (LTHR) begins at temperatures above 900 °K, HCHO addition advances autoignition through the conversion of HCHO to H₂O₂. The subsequent breakdown of the latter species through reaction (1) serves as a radical generator and advances the process. However below 900 °K, HCHO is reported to have a strong retarding effect due to the OH scavenging effect of HCHO, through reaction (2). Moreover, OH radical light emission as recorded through spectral measurements is observed to be eliminated by the HCHO addition below 900 °K.



1)



2)

The behavior of HCHO as a reaction controller when mixed with intake air in a di-methyl ether (DME)-fueled HCCI engine has been investigated experimentally and numerically by Konno *et al* [10]. The findings corroborate the retarding effect of this species on the LTHR, through its consumption of hydroxyl (OH) radicals which otherwise would contribute to the dehydrogenation of fuel. The formyl radical (HCO) formed by reaction (2) goes on to form hydrogen peroxide (H₂O₂), which accumulates to greater levels in the presence of HCHO. The high temperature heat release (HTHR), on the other hand, largely tracks the rate of OH production, which is predominantly formed from the dissociation of H₂O₂. Since H₂O₂ is accumulated to greater concentrations in the presence of HCHO, this HTHR process is enhanced. A comparison of kinetic modeling results to measurements from a cylinder gas sampling valve, found the kinetic modeling results to over-predict the measured values of HCHO mole fraction by a factor of twenty. The experimental, peak heat release rate was found to gradually decline with HCHO addition.

The presence of chemically reacting species NO, CO and HCHO in EGR gases of a low-compression ratio (10.2) HCCI engine fueled by n-heptane and PRF40, has been investigated by Machrafi *et al* [11]. These results support the earlier findings that the addition of HCHO retards autoignition. Moreover, the total heat release was found to decrease by 6% as a result of adding HCHO at a mole fraction of 1400ppm. The work also concluded that there was no significant effect on autoignition by CO addition in amounts up to 1000 ppm, and at magnitudes likely to be encountered in an engine. NO, on the other hand, was determined to play a promoting role in amounts up to 45 ppm, beyond which its role becomes inhibitive. The constant volume kinetic modeling work of Subramanian *et al* shows that the presence of CO in an n-heptane-air mixture extends ignition delay at an initial temperature of 600 °K, but decreases this value when the temperature is 1000 °K. In both temperature regimes the effect of the additive becomes less pronounced as the mixture becomes rich.

Investigating combustion stability during cold-starting of a diesel engine, earlier work in this Wayne State University laboratory measured pre-injection chemiluminescence from the combustion chamber of an optical engine at the end of the compression stroke. Over a range of engine cycles during the unstable, warm-up phase, a strong correlation was observed between the intensity of this chemiluminescence and the combustion phasing of the subsequent engine cycle as measured by the location of the peak of the premixed-phase combustion (LPPC) [12]. The spectrum of this emission closely resembled that of Emeleus' formaldehyde cool flame

lines [13]. Further, exhaust gas analysis of this diesel-fueled engine during unstable combustion identified HCHO on the order of 300ppm, as well as similar amounts of CO and ethane (C_2H_6). This relationship in a later work was determined to be a function of both swirl level and engine temperature, suggesting the role of wall fuel-film evaporation [14]. Numerical simulations have also been conducted to quantify the relative effects of engine wall temperature and HCHO concentration on autoignition [15].

The kinetics of HCHO in hydrocarbon combustion also plays a role in small-bore, high speed diesel engines. In such devices, fuel wall impingement is commonplace and particularly during engine starting, results in ongoing wall-film evaporation during the compression stroke. The formaldehyde formed by the fuel decomposition during this process is then present and free to interact with the fuel subsequently injected near TDC.

In this work, the effect of HCHO on the hydrocarbon combustion process is investigated. The role of this specie during the various phases of combustion is numerically simulated using a detailed n-heptane mechanism and constant-volume and single-zone HCCI models. The results of experiments from a diesel engine fueled with JP-8 and inlet air doped with HCHO are then presented.

EXPERIMENTAL SETUP

ENGINE

The engine used in this investigation is a naturally-aspirated, single-cylinder, direct-injection AVL Model 5402 optical-access research engine with a bore of 85 mm, stroke 90 mm and resulting displacement of 510 cm³. The geometric compression ratio has been measured to be 15:1. The intake ports are equipped with a swirl control valve, allowing the control of swirl ratios between 2.0 and 4.5. This engine is equipped with a Bosch CR CP1 common-rail fuel injection system rated to 1350 bar injection pressures. Engine and injection system specifications are shown in [Tables A1](#) and [A2](#) of the [Appendix](#).

Optical access is provided via a classic Bowditch extended piston in which is mounted a 20 mm-thick fused-silica (quartz) window, as shown in [Figure 1](#). The placement of a mirror inside the piston assembly at 45° relative to the cylinder axis provides a view of the entire 40 mm-diameter combustion bowl. The combustion bowl is of rectangular cross-section, and the flat surface geometry of the combustion chamber is interrupted only by valve pockets placed in the piston bowl rim and valve seat chamfers in the cylinder head. Oil-less lubrication is provided by slotted graphite rings and the sealing by uninterrupted bronze-teflon rings. Compressed air directed at the underside of the piston window provides cooling of this assembly during operation.

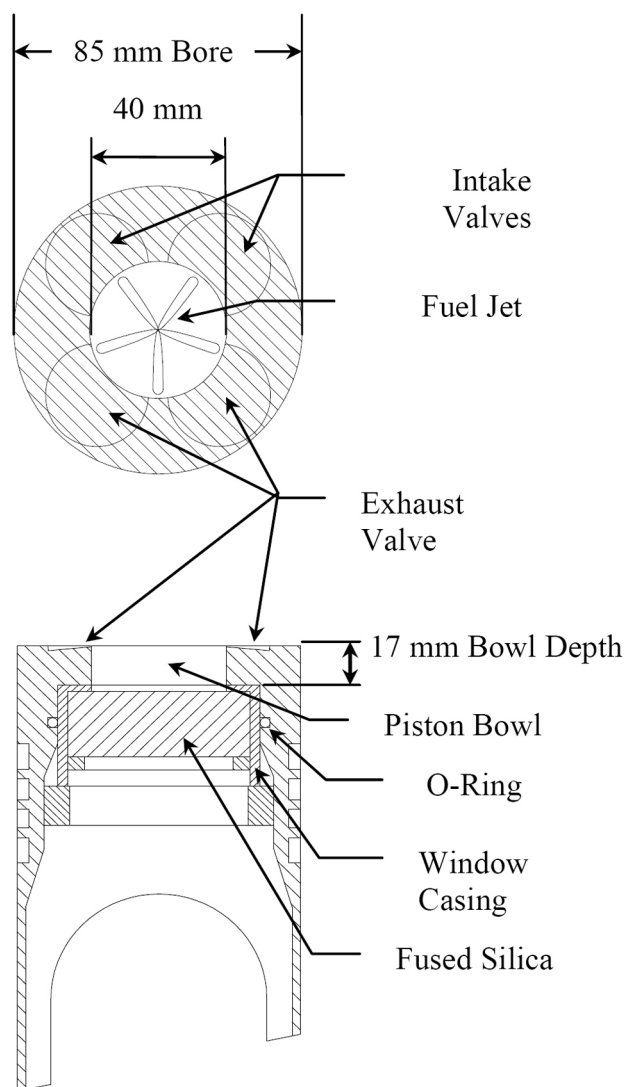


Figure 1. Extended piston and combustion bowl geometry.

ENGINE INSTRUMENTATION

To measure cylinder pressures, an un-cooled piezo-electric pressure transducer (AVL GH 12 D) is mounted through an opening in the cylinder head. A needle lift sensor (MicroEpsilon) is installed in the fuel injector to detect the displacement of the injector needle. An additional pressure transducer measures the pressure in the line between the fuel rail and injector. Sensor signals are recorded by a high-speed data acquisition system triggered by an optical encoder wheel mounted on the engine crankshaft. This instrumentation is used to calculate the Apparent Rate of Heat Release (ARHR) using the analysis provided by Heywood [1], and is shown normalized by the engine displacement. A more detailed description about the engine and instrumentation has been reported earlier [16].

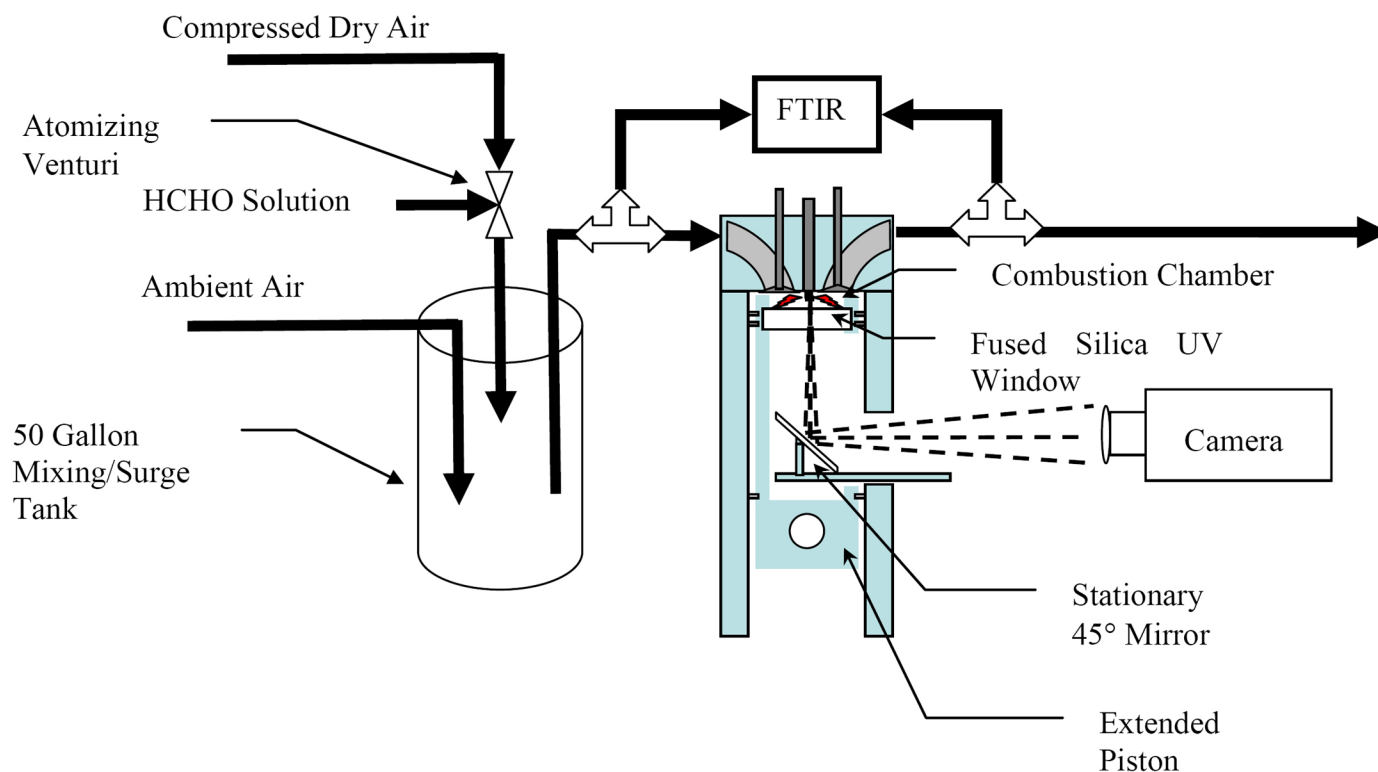


Figure 2. Experimental setup, optical access via Bowditch piston and HCHO metering system.

Chemiluminescent images of the combustion chamber were captured through the piston window using an intensified charge-coupled device camera (ICCD), (Princeton Instruments PI-MAX2) optimized for operation in the ultraviolet spectrum. The intensifier has a multi-alkali photocathode whose nominal sensitivity spans the range from 125 to 900 nm. This range effectively covers the chemiluminescence spectrum of species such as HCHO, OH, CH, C₂ and CO₂ [13] that occurs in the early stages of diesel autoignition [17], as well as the yellow-orange thermal emission of sooty combustion. A visible range color camera (Vision Research Phantom 7.3) was used to obtain high speed cycle-resolved images. Frames were triggered at 0.5 CAD intervals and synchronized to the crankshaft position through a field-programmable gate array (National Instruments) and optical-encoder compatible input module (DRIVEN).

Figure 2 shows the experimental layout with the ICCD aligned with the axis of the extended piston through the 45° mirror. In such a configuration, the camera field of view, as represented by the circle in Figure 3, covers the 40 mm-diameter combustion bowl. Swirl motion is in the clockwise direction.

Formaldehyde in an aqueous solution of 37% (vol/vol), was kept in a stainless steel vessel that was pressurized by nitrogen to a value of 30 psi. A commercial port-fuel injector was then electronically controlled to meter the solution into the throat of an atomizing venturi, which was connected to a

supply of dry, compressed air. The outlet of this venturi delivered the spray into a 50-gallon mixing drum, which doubled as a surge tank and had a second inlet that was open to the ambient pressure of the laboratory. The amount of HCHO thus added was continually monitored by a fast Fourier Transform Infrared spectrometer (FTIR). After optimizing the HCHO injection pulse duration and injection pressure, a reasonable degree of control over the mole fraction of the dopant in the intake air could be achieved. Moreover, by adjusting the flow rate of the dry, compressed air running through the atomizing venturi, humidity levels in the engine inlet could be controlled independently of the HCHO, as the moisture-free compressed air could compensate for the water injected along with the HCHO.

ENGINE OPERATING CONDITIONS

Experimental results reported here are taken from the optical engine that had been pre-heated to a temperature of 60 °C. In a typical experimental sequence, the engine was motored while HCHO solution injection duration and compressed air flow rates were adjusted to achieve steady, desired formaldehyde and water vapor concentrations. The engine was then continually fired to warm up surfaces to values more closely resembling engine operating conditions. In an attempt to control for varying degrees of cylinder sealing by the oil-less rings, the cylinder pressure prior to fuel injection was monitored. When a predetermined value was reached, engine operation was switched to a 3/9 injection/skip pattern.

The engine was operated in skip mode until the cylinder pressure prior to fuel injection was deemed steady, and then data collection was begun. The work reported here consists of measurements taken from the engine operated at speed of 1000 RPM at swirl ratios of 2.0 and 4.5. For all experiments, the fuel was administered in a single injection at an injection pressure of 800 bar. The injector command signal was constant at 430 μsec , corresponding to an estimated fuel delivery rate of 6 mm^3/cycle . Only the third firing cycles of each sequence are considered in the ARHR calculations presented, as the third firing cycle is believed to more closely represent operating engine conditions in terms of surface temperatures and residual composition. Inlet temperatures and pressures were at ambient levels.

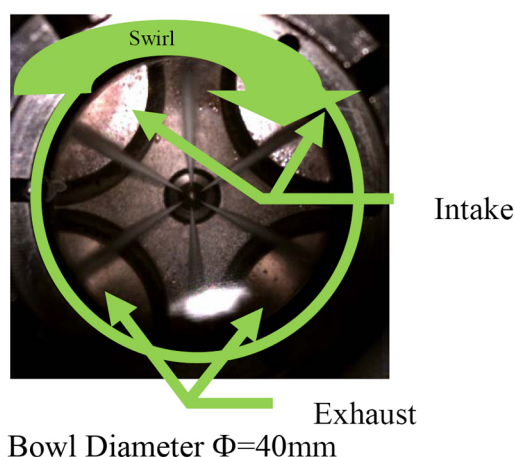


Figure 3. Camera field of view relative to combustion chamber, swirl direction (clockwise) and spray orientation.

FUEL

Jet Propulsion fuel (JP-8) was used during experiments. The atmospheric pressure distillation curve of this fuel, as provided by the supplier, is shown in Figure 4. JP-8 fuel is used by the US Military for powering both gas turbine and reciprocating powerplants, and was chosen to further characterize its performance in the latter type of engine. Noteworthy features of this fuel are its low aromatic content (14% by volume) and a 50% distillation point of 206 $^{\circ}\text{C}$, a temperature that is nearly 50 $^{\circ}\text{C}$ lower than for ultra-low sulfur diesel (ULSD) fuel typically used in this laboratory. This fuel can then be considered more volatile and with less soot-forming tendency than ULSD.

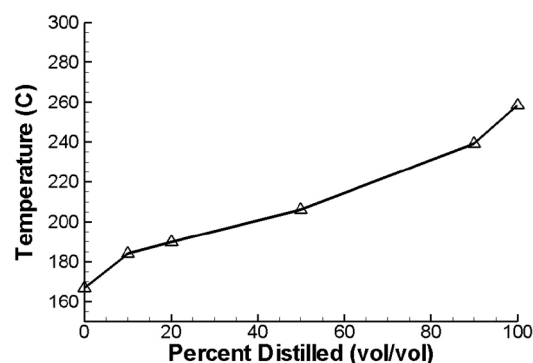


Figure 4. Atmospheric pressure distillation curve for JP-8 fuel used during experiments.

CHEMICAL KINETIC MODELLING

Although limited shock tube validations of various kinetic mechanisms and JP-8 surrogates have been performed [18], these results show appreciable deviation between experimental and modeled results of JP-8 autoignition at lower temperatures. In addition, the maximum pressure at which JP-8 was tested in this work was 30.9 atm, below pressures encountered in engines. To gain insight to the role of HCHO in the kinetic processes of normal alkane autoignition, then, the latest (v3) detailed n-heptane mechanism available from Lawrence Livermore National Laboratories (LLNL) [19,20] was chosen for modeling.

The LLNL v3 n-heptane mechanism was first applied to a single-zone, adiabatic HCCI model to qualify the results of fuel decomposition experienced within an engine cylinder during misfiring conditions. The compression ratio was chosen to be 15, the connecting rod length-to-stroke ratio was 1.65, and inlet temperature conditions 298K and 1 bar pressure. The cycle was simulated at an equivalence ratio of 1.0, with an n-heptane fuel and 1:3.76 ratio of oxygen to nitrogen. The calculations were run over a range of engine speeds from 600 to 1800 RPM, to examine the effect of the time-temperature-pressure history on the autoignition of the mixture. The simulated compositions, in terms of cumulative mole fractions, at bottom dead center (BDC), or 180 crank-angle degrees (CAD) after top dead center (TDC), are shown in Figure 5. At the lowest engine speeds, there is ample time for autoignition to occur, and the fuel is readily oxidized to carbon dioxide and water vapor. At the highest speeds, the piston expansion interrupts the autoignition process before the thermal ignition point is reached, and the composition is largely the same as at the beginning of the cycle, fuel and air. In between is a range of speeds, however, where fuel decomposition occurs, and partial oxidation products are formed and subsequently frozen. A detail of this engine speed range is shown in Figure 6. Between engine speeds of 1450 and 1600 RPM, evident is the presence of aldehydes in mole fractions on the order of 1,000 parts-per-million (ppm).

Strikingly, the pressure-temperature history where aldehyde formation occurs, yet does not lead to its consumption, lies within an engine speed range of 150 RPM. Engine speed fluctuations of this magnitude are readily encountered during both engine cranking periods and the unstable, after-start phase characteristic of diesel engine cold-starts [21,22]. A comparison of the mole fraction ratios between HCHO and the major intermediates CO, C₂H₂ and H₂O₂ are shown in Figure 7. These ratios vary greatly over the engine speed range shown, with the HCHO/CO ratio extending from a negligible value to six, and the HCHO/H₂O₂ and HCHO/C₂H₄ ratios varying by two orders of magnitude. While the autoignition-advancing effect of hydrogen peroxide is generally established [23], the role of CO and HCHO is contradictory [15,24] and therefore the overall effect on autoignition of a residual mixture of partially oxidized hydrocarbons is not convincingly defined.

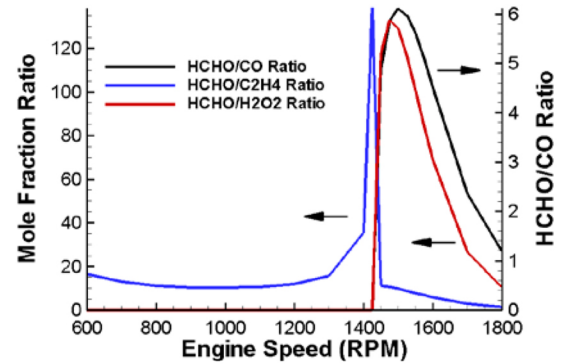


Figure 7. Modeled HCHO/CO, HCHO/C₂H₄ and HCHO/H₂O₂ mole fraction ratios at BDC as a function of engine speed. Variation of these ratios result from various degrees of fuel decomposition.

To remove the heating effects by piston compression and expansion, an adiabatic, homogeneous, constant volume reactor was used to model the autoignition process. Applying the same LLNL v3 mechanism with an n-heptane-air equivalence ratio of 0.3, the process was examined under 725 °K and 40 bar initial conditions. Such a state is expected to occur in the experimental engine. Shown in Figure 8 are the modeled results.

The autoignition process is divided into four phases as per the analysis of Ando and Kuwahara [25,26]; Low-Temperature Oxidation (LTO), Negative Temperature Coefficient (NTC), Thermal Ignition Preparation (Thermal Prep) leading to thermal ignition and the Post Ignition phase. Shown in Figure 8 are the modeled results, showing both the temperature-time history, as well as the heat release rate as a function of the temperature. Fuel breakdown occurs, leading to a rise in temperature and HCHO mole fraction in the LTO period. At a temperature of 823 °K, a local maximum in the heat release rate is reached, and the NTC phase begins, as an increase in temperature leads to reduced reaction rates. When the temperature reaches 929 °K, the third phase of the process begins, the so-called Thermal Prep or H₂O₂-Loop period, which is dominated by reactions 3-6 [25,26] :

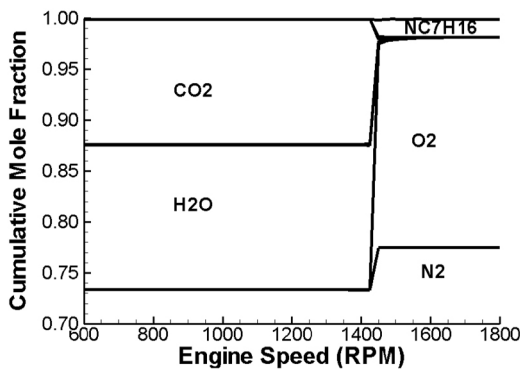
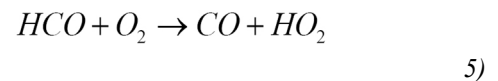
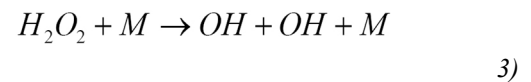


Figure 5. Modeled HCCI reactor mixture composition at BDC, after compression and expansion process. N-heptane/air mixture, equivalence ratio $\Phi = 1.0$, $T_{initial} = 298K$, $P_{initial} = 1$ bar, compression ratio = 15, LLNLv3 mechanism. Higher speeds allow insufficient time for autoignition.

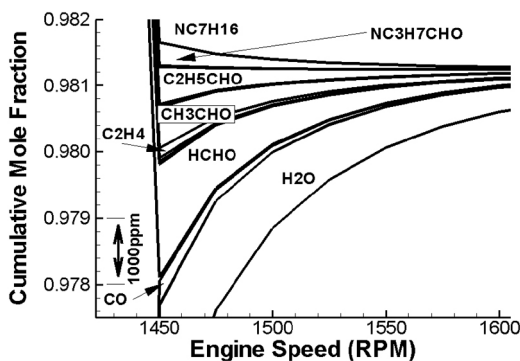


Figure 6. Modeled HCCI reactor mixture composition at BDC, after compression and expansion process, detail of Fig. 5. Varying degrees of fuel decomposition occur over a narrow range of engine speeds.