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Using Biofuel Tracers to Study Alternative Combustion Regimes

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1.0 Abstract

Interest in the use of alternative fuels and combustion regimes is increasing as the price of petroleum climbs. The inherently higher efficiency of Diesel engines has led to increased adoption of Diesels in Europe, capturing approximately 40% of the new passenger car market. Unfortunately, lower CO₂ emissions are countered with higher nitrogen oxides (NO_x) and particulate matter (PM) emissions, and higher noise. Noise and PM have traditionally been the obstacles toward consumer acceptance of Diesel passenger cars in North America, while NO_x (a key component in photochemical smog) has been more of an engineering challenge. Diesels are lean burning (combustion with excess oxygen) and reducing NO_x to N₂ in an oxygen rich environment is difficult. Adding oxygenated compounds to the fuel helps reduce PM emissions, but relying on fuel alone to reduce PM is unrealistic. Keeping peak combustion temperature below 1700 K prevents NO_x formation. Altering the combustion regime to burn at temperatures below the NO_x threshold and accept a wide variety of fuels seems like a promising alternative for future engines. Homogeneous Charge Compression Ignition (HCCI) is a possible solution. Fuel and air are well mixed prior to intake into a cylinder (*homogeneous charge*) and *ignition* occurs by *compression* of the fuel-air mixture by the piston. HCCI is rapid and relatively cool, producing little NO_x and PM. Unfortunately, it is hard to control since HCCI is initiated by temperature and pressure instead of a spark or direct fuel injection. We investigate biofuel HCCI combustion, and use intrinsically labeled biofuels as tracers of HCCI combustion. Data from tracer experiments are used to validate combustion modeling.

2.0 Keywords

Biofuels, Tracers, Combustion, HCCI, 14C

3.0 Introduction

3.1 Historical use of Tracers in Internal Combustion Engines

The methods described below for tracing fuel component carbon in the emissions can be applied to any combustion system. Any molecule containing carbon can be labeled with ^{14}C . Although only recently applied to studies of engine combustion processes [1-5], the techniques for measuring the ^{14}C concentrations of PM and CO_2 by AMS are straightforward and routine.

The use of ^{14}C tracers in combustion engines provides insight into a number of different processes. There has been a significant amount of interest in Diesel engines, and ^{14}C -radiolabelled experiments have been used to study the relative contributions of parent and alkyl-PAC to diesel exhaust emissions [6-7]. Soot formation by labeled components in Diesel fuel have been examined using decay counting methods [8,9].

In addition to looking at exhaust contributions from fuel components, there has been research on the contributions of engine oils to exhaust emissions [1]. Other studies focused on applying isotope tracing techniques to the study of engine wear and damage [10].

Recent applications have explored the use of isotope tracers in Homogeneous Charge Compression Ignition (HCCI) engines, which is explained further below [11].

3.2 Homogeneous Charge Compression Ignition

The Homogeneous Charge Compression Ignition (HCCI) engine has received renewed interest in recent years. In the past decade, several hundred papers have been published, largely in the literature of the Society of Automotive Engineers. A recent text reviews much of this literature [12]. HCCI engines have some features of both spark ignited (SI) engines and Diesel engines. HCCI engines, like SI engines, are generally premixed and very lean at fuel-air equivalence ratio, Φ , <0.5 ; thus they produce very low NO_x and particulate matter (PM) emissions. Yet, HCCI engines typically have high compression ratios, leading to high efficiency similar to that found in Diesel engines. In an SI engine, the combustion event is initiated by a spark, and the timing of the spark is routinely adjusted by an onboard computer called an electronic control unit (ECU). Similarly, the combustion event in a Diesel engine is initiated by injection of the Diesel fuel and the injection time and duration is variable. However, the HCCI engine does not have a spark plug or direct fuel injection; the combustion event occurs when the cylinder contents are hot enough (approximately 1000-1200 K) for a long enough time (order ~ 1 millisecond).

Many challenges remain to practical HCCI engines. One of the major challenges of HCCI is controlling the combustion timing. Combustion timing is defined as the crank angle at which 50% heat release occurs, often called CA50. Each stroke of the piston in the cylinder occurs over 360 crank angle degrees. The point of peak compression is called top dead center (TDC) and engine timings are referred to in times of degrees after top dead center (ATDC).

Another issue for HCCI engines is that pressure rise occurs very rapidly, because autoignition occurs nearly simultaneously throughout the combustion chamber. This rapid pressure rise can lead to noise, and potentially damaging knocking conditions within the engine. Avoiding detrimental effects of rapid pressure rise can limit the power output of HCCI engines.

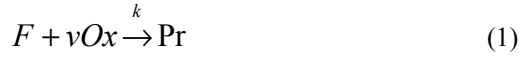
3.3 Approach and Motivations

Better understanding of the HCCI combustion process can be greatly aided by evaluation of the chemical processes occurring in the combustion process, such as the effect of chemistry on combustion timing. It is possible to observe combustion characteristics of the fuel-in-air charge by collecting exhaust samples at different combustion timing.

Combustion timing is determined by a number of different parameters, such as equivalence ratio, intake manifold pressure, and intake manifold temperature. The primary influence of combustion timing is the intake manifold temperature (T_{in}) of the fuel-in-air mixture inducted into the engine combustion chamber.

Devices such as electrical heaters, heat exchangers, and exhaust gas recirculation (EGR) control the HCCI engine intake temperature.

The composition of the fuel also plays a major part in the ignition process, as different fuels possess different autoignition characteristics. Autoignition is controlled by the rate of reaction between the fuel and oxidizer components. For a general reaction of



where F is the fuel component, Ox is the oxidizer component, Pr is the products, and k is the rate of reaction, which can be expressed as

$$k = AT^n \exp\left(\frac{-E_A}{RT}\right) \quad (2)$$

where E_A is activation energy, A is the pre-exponential constant, and n is the temperature dependence. Each of these parameters can be associated with the autoignition properties of the fuel. Therefore, the autoignition properties of the fuel-in-air charge inside the engine combustion chamber can be manipulated through the use of different fuels. With this in mind, blending fuels with different properties can yield small changes in combustion timing. Using fuel components with different ¹⁴C isotope ratios, we can see differences in the source of exhaust carbon dioxide composition, that is how much of each fuel component is converted to the CO₂, which varies based on the fuel component characteristics and the combustion history of the fuel blend-in-air mixture.

3.4 Experimental Objectives

The rapid combustion event in HCCI presents a major engineering challenge, resulting in a pressure rise rate that can exceed 10 bar/ms, which exceeds the material limits of the rings on a piston engine (J. Hiltner and S. Fiveland, personal communication, June 2003). One strategy to spread out the combustion event is to use a blend of two or more fuels that have different autoignition characteristics. The goal is that each fuel would burn in succession and thus spread out the combustion event duration, termed heat release elongation (HRE), which would help overcome the problem of too rapid rate of pressure rise. Examples of this fuel blending strategy include using dimethyl ether (easy to autoignite) mixed with methane (difficult to autoignite) [13], naphtha with methane [14], and octane with n-heptane [15].

Furthermore, addition of fuel more prone to autoignition (low autoignition temperature) lowers the intake temperature required for HCCI operation. Intake temperature is typically a slowly responding parameter, with lags associated with thermal inertia of the intake system used for heating the flowing gas. Small changes in temperature can dramatically affect CA₅₀, so overshooting a target temperature can push the combustion into an unstable regime [16-18], which may be difficult to respond to quickly enough with an intake temperature control scheme. Combustion timing is considered the most important combustion controlled parameter to achieve safe and stable operation. The combustion event is typically defined as CA₅₀, the time when 50% of the cumulative heat release has occurred [19].

In this paper, we explore the HCCI combustion of blends of diethyl ether (DEE, sometimes written as EtOEt) in ethanol (EtOH) with small amounts of the additive Di-Tertiary Butyl Peroxide (DTBP). Volatility and flammability properties of the fuel components from Material Data Safety Sheets (MSDS) at 1 atmosphere are listed in Table 1.

Table 1. Properties of the fuels used in the experimental blends

Property at T=298K, P=1atm	DEE	EtOH	DTBP
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Flash Point (Celsius)	-45	13	6
Vapor Pressure (mm Hg)	58.9	5.8	2.6
Boiling Point (Celsius)	35	79	110
Autoignition Temperature (Celsius)	160	363	165
Specific Gravity	0.789	0.71	0.79

DEE autoignites more readily than ethanol. In earlier research, we observed that the autoignition of DEE leads EtOH in blends, but not as much as expected [20]. There was no significant elongation of the combustion event with DEE-EtOH blends [20]. The autoignition temperature of DTBP is similar to DEE, but DTBP experiences self accelerating (exothermic) decomposition at 80C. The exothermic decomposition of DTBP is a common property of organic peroxides.

The addition of DTBP to gasoline reduces the ignition delay time in HCCI Engines operating near idle [21]. DTBP is widely used as a catalyst for polymerization of olefin copolymers and crosslinking agent for unsaturated polyesters. It is also used as an ignition improver for increasing cetane number in diesel engines [22-24]. Our intention was to use the exothermic decomposition DTBP to elongate the combustion event by igniting the DEE earlier.

Because of the greater reactivity of DEE, we anticipated that DEE would autoignite first followed by autoignition of EtOH, which might be determined if the contribution of each fuel component to the CO₂ in the engine exhaust could be measured. Determining the source of CO₂ produced by each fuel requires a means of distinguishing the sources of the carbon. Using bio-derived EtOH that has a natural carbon-14 (14C) level and petroleum-derived DEE and DTBP that are free of 14C, we could distinguish the contribution of EtOH to CO₂ by measuring its isotopic content.

Table 2. Caterpillar 3401 Engine Specifications

Configuration	Single Cylinder
Valves	4 (2 int., 2 exh.)
Compression Ratio	16.25
Displacement	2.44 L
Camshaft Lobe Lift (Exhaust)	8.796 mm
Camshaft Lobe Lift (Intake)	8.113 mm

The experiments were conducted in a single cylinder Caterpillar 3401 engine, the specifications of which are in Table 2. The engine was maintained at constant speed of 1800 RPM (+/- 10 rpm) by an induction motor/generator. Intake temperatures were changed using an electrical heater located 1 meter upstream of the engine. Liquid fuel injectors, mounted 0.75 meters upstream to insure complete vaporization of the fuel, controlled the equivalence ratio.

4.0 Experimental Procedure

Experiments were conducted for HCCI engine operation conducted with mixtures of ethanol with DEE and DTBP. The equivalence ratios, Φ , of 0.3 and 0.4 were used in the experiment. High loads were not investigated due to the nature of HCCI engines and previous research done on DTBP which points to more effectiveness at lower loads [16]. The intake pressure was held at a constant $P=1.7$ bar. Grain ethanol

(EtOH) served as the tracer (bio-derived, contains ^{14}C) fuel while diethyl ether (DEE) and DTBP are petroleum-derived fuels (^{14}C free). The isotopic level of the lubrication oil and DEE was at instrument background ($^{14}\text{C}/\text{C}$ ratios $<10\text{E}-15$). Since the ethanol is bio-derived, it is uniformly labeled with ^{14}C ; each of the two carbon atoms in the ethanol molecule is equally likely to be ^{14}C .

The fuel blends containing DEE-in-EtOH were defined on a volume percent basis (for example, 250 mL DEE for every 750 mL EtOH for the 25% DEE-in ethanol blend). With the addition of DTBP, the volume of DEE was maintained while the EtOH was reduced to accommodate the volume of DTBP.

Figure 1 shows the experimental set-up. Exhaust gas samples were collected at varying combustion timing for each fuel mixture. CA50 was controlled by adjusting the intake temperature. Exhaust gas routed from the exhaust manifold through a particulate filter and then collected in 3-L or 10-L Tedlar bags, which filled in less than a minute. No particulate matter was observed on the particulate filter.

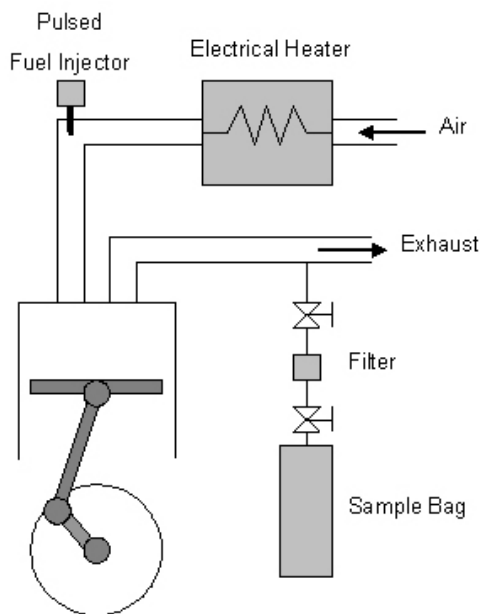


Figure 1. Experimental set-up for exhaust collection from the single cylinder CAT3401 engine. Note that the fuel is introduced after the intake heater and well upstream (~1m) of the engine so as to insure thorough mixing and evaporation.

The gas sample bags were maintained at temperatures between 290-300 K and processed within several days of collection. Bags were equilibrated with an evacuated ~60 mL volume to obtain AMS samples containing 0.2-1.1 mg C from separated CO_2 . All gas molecules except N_2 and CO were initially condensed with a liquid nitrogen (LN) cold trap. This first cold trap was then switched to dry ice-isopropanol so water, sulfur dioxide, and unburned fuel were retained and second cold trap with LN was placed in series to condense CO_2 . A valve between the traps was closed and non-condensable gases were evacuated. The CO_2 was then cryogenically transferred to a quartz sample tube which was sealed with a H_2/O_2 torch. Each purified CO_2 sample was then transferred to our graphitization rig where it passed through another dry ice-isopropanol cold trap and was condensed again with LN. Carbon mass was determined from CO_2 pressure in a small fixed volume before transfer to an individual reactor and reduction to graphite in the presence of iron catalyst [25]. All graphite targets were measured at the center for AMS at LLNL using 6 identically prepared oxalic acid standards for normalization [26].

Only the ethanol contains a significant ^{14}C signal in this system. Backgrounds associated with sample prep are known and the contribution of intake air to the exhaust CO_2 is subtracted. Expanding the $^{14}\text{C}/\text{C}$ ratio to show the remaining terms for each sample produces a simple expression where C and R denote carbon mass and isotope ratio and the subscripts E and D denote ethanol and DEE+DTBP, respectively (Eq.3).

$$R_s = \frac{C_E^{14}}{C_E + C_D} = \frac{C_E(R_E)}{C_E + C_D} \quad (3)$$

The fraction of ethanol-derived carbon F_E in the sample is given in Equation 4.

$$F_E = \frac{C_E}{C_E + C_D} = \frac{R_S}{R_E} \quad (4)$$

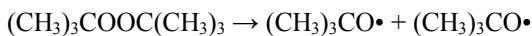
5.0 Numerical Modeling Approach

Simulations of HCCI combustion of the diethyl-ether-in-ethanol blend have been conducted using a “single-zone” numerical model of the engine. This single-zone model treats the cylindrical combustion chamber as a spatially uniform reactor with uniform temperature, pressure, and composition throughout. The reactor volume changes based on slider-crank relations that determine the motion of the piston in an engine cylinder. The simulation handles only the closed part of the cycle; intake and exhaust processes are not considered.

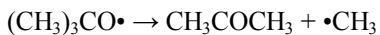
In the single zone, conservation of energy and chemical kinetic relations based on a gas-phase detailed kinetic mechanism for diethyl-ether and ethanol combustion are solved to determine temperature and species histories for the engine cycle.

The DEE/EtOH chemical mechanism contains an extension of that for dimethyl ether [27] with diethyl ether chemistry provided by Curran [28] and a mechanism of EtOH [29]. The combined mechanism contains 112 species and 484 reactions. Additional reactions for the adiabatic decomposition of DTBP were added into the mechanism, following the work of Iizuka et al [30].

In the simulation, DTBP is seen to thermally decompose into two t-butoxy radicals, in the 600-650K temperature range.



These radicals internally rearrange very quickly; primarily forming acetone (CH_3COCH_3) and a methyl radical ($\cdot\text{CH}_3$).



The acetone is stable and lingers in the cycle until the main ignition promoting reactions commencing at temperatures of approximately 1100K. It is tempting to assign the advance in combustion timing to the presence of $\cdot\text{CH}_3$ attacking the main fuels and commencing radical chain reactions, including chain branching. However, close examination of the simulation shows that the $\cdot\text{CH}_3$ radicals formed remain relatively stable species do not significantly contribute to the chain propagation and chain branching reactions that lead to ignition. After the formation of these relatively stable species, little chemistry is taking place; the temperature is still too cold. Importantly, the formation of these relatively stable species is exothermic. The more important effect on ignition resulting from these “low-temperature reactions” associated with decomposition of DTBP is a slight increase in the temperature that is amplified by further compression of the mixture. For this thermal reason (as opposed to direct kinetic reasons) addition of DTBP leads to advancement of CA50 timing at constant input temperature; or equivalently, a reduction of input temperature if the same CA50 timing is desired.

The single-zone model is a highly idealized representation of the actual processes occurring in the combustion chamber. Models exist, e.g. KIVA, that have thousands of zones and thus capture in more detail the three-dimensional processes occurring in the combustion chamber [13,31-32], such as crevice and

boundary layer effects. Still, single-zone models can give insight into the processes occurring in the combustion chamber, especially processes that occur in the hottest central core gasses of the combustion chamber away from the crevice and boundary layers. It has been shown in the literature that a single zone model is effective in predicting engine behavior versus experimental data for HCCI engines [33].

A multiple-zone model would provide more detailed results but at a high computational cost. In this case, a single-zone model is effective in predicting system behavior primarily due to the homogeneous mixture found in HCCI engines. Diesel and SI engines are inherently more difficult to model due to the inhomogeneities found in the combustion chamber, and would not be well simulated with this type of model. In contrast, HCCI engine combustion can be well represented by this single-zone approach.

Important to accurate prediction with a single-zone model is inclusion of heat transfer [34-37] and trapped residuals in the model. Simulations were conducted using the geometric and operating parameters for the engine specified in Table 1.

6.0 Results

When analyzing the results provided by the isotope tracing, parameter called zeta (ζ) was defined. Zeta, defined in Equation 5, is the fraction of ^{14}C in exhaust CO_2 normalized to the ^{14}C fraction of the fuel.

$$\zeta = \frac{(F_{\text{EtOH}})_{\text{CO}_2}}{(F_{\text{EtOH}})_{\text{FUEL}}} \quad (5)$$

When zeta equals 1, all of the EtOH in the fuel blend is burning to completion. Likewise, when the value of zeta is zero, none of the EtOH in the fuel blend is burning to completion.

Figure 2 shows variation of zeta for three different fuel blends of varying amounts of the DEE blended with EtOH, with respect to the combustion timing.

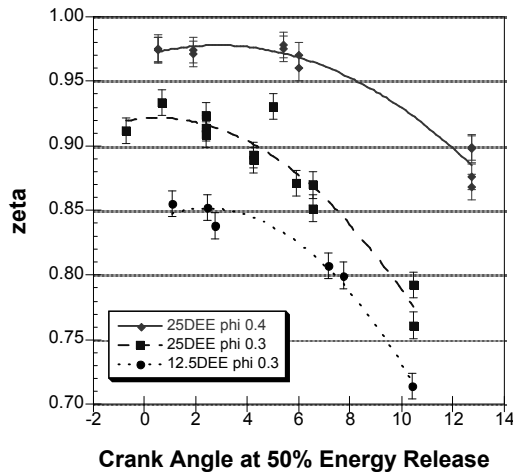


Figure 2. Zeta, the mass fraction EtOH in CO_2 normalized to fuel, for three fuels mixtures. Error bars assume 1% uncertainty in fuel concentration. The uncertainty in the fuel shifts the whole series up or down (the accuracy). However, the precision is unchanged.

Figure 2 shows that as the amount of DEE in the fuel blend is increased, more of the EtOH burns to completion. The top two lines show data for two different loads (phi equal to 0.3 and 0.4) but with the same blend composition. As more fuel is added to the mixture (higher values of phi), the overall heat

release is greater and the combustion event provides more power. The limiting factor in adding fuel to gain power is mechanical considerations (risk of engine damage).

Figure 3 shows variation of zeta for fuel blends containing the additive DTBP in 25% DEE in EtOH blends (25DEE) with respect to combustion timing.

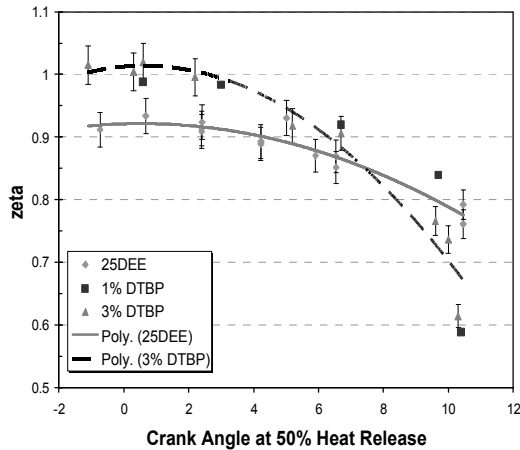


Figure 3. The addition of DTBP to DEE/EtOH blends causes more EtOH to burn to completion

The addition of DTBP causes the EtOH in the fuel blend to burn even further to completion. Experimental data sets for fuel blends containing DTBP approach zeta values of 1 while the 25DEE blend by itself does not approach complete combustion.

Figure 4 shows exhaust gas emissions data for the base fuel blend of 25DEE. The increase of carbon monoxide (CO) and unburned hydrocarbons (HC) at later combustion timings confirms less complete combustion. Data for exhaust nitric oxide emissions is not shown in the figure but was extremely low (~5 ppm) as expected with HCCI combustion.

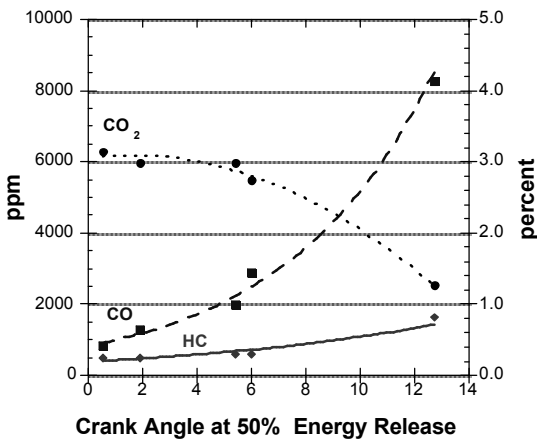


Figure 4. Gas analyzer data for 25% DEE in EtOH at $\Phi=0.4$; CO₂ (in percent), decreases as CA50 is delayed, while CO and HC (in ppm) increases.

Figure 5 shows the numerical modeling results for fuel blends (25DEE), with and without the DTBP additive. The crank angle for 90% combustion (CA90) of a fuel component remains unchanged for EtOH

in both cases (1% and 3% DTBP) but the CA90 for DEE is slightly earlier, especially for later combustion timings.

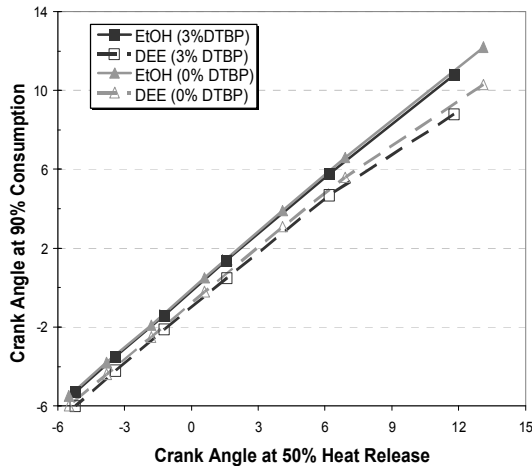


Figure 5. The addition of DTBP to 25DEE/EtOH causes the DEE to burn earlier in the cycle, especially at later combustion timings.

The two-stage combustion event discussed in the motivations would show a drastic difference in CA90 for the fuel blend components but the difference seen in Fig.5 is around 1 CAD. Not until the latest combustion timings (after 9 CAD) does the CA90 of DEE significantly precede the EtOH CA90. Experimentally, we are unable to obtain these latest combustion timings due to the increased sensitivity to heat transfer.

Figures 6 and 7 show the intake temperature (in Kelvin) versus the combustion timings (CA50, crank angle for 50% heat release) for experimental and numerical results, respectively.

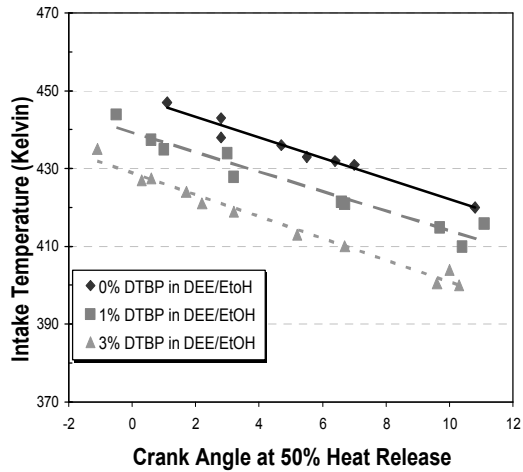


Figure 6. Experimental results for the Intake Temperature (Kelvin) versus the Crank Angle at 50% Heat Release (CA50)

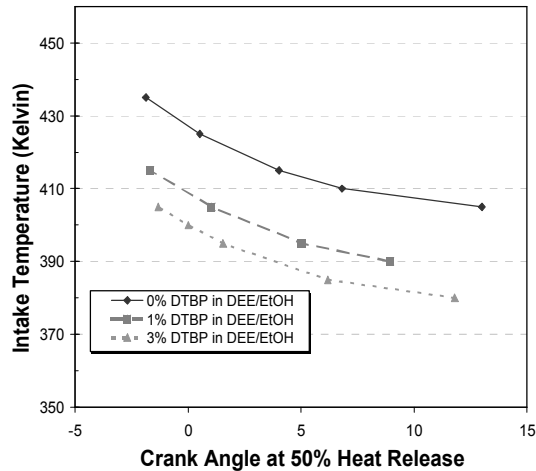


Figure 7. Numerical Modeling results for the Intake Temperature (Kelvin) versus the Crank Angle at 50% Heat Release (CA50)

One of the major advantages for HCCI combustion when using DTBP is the decrease in required intake temperature for start of combustion. This is shown in both the experimental and numerical modeling figures. As the amount of DTBP is increased, the required intake temperature at a given CA50 is significantly reduced.

7.0 Conclusions

HCCI presents many advantages (i.e. low NO_x, low PM, and high efficiency) not seen in the traditional engine, but there are still many obstacles to overcome before it is a commercially viable alternative. Through the use of ¹⁴C isotope tracers, we are able to gain further insight into the combustion characteristics of fuel blends inside the engine. In this set of experiments, the data shows that Ethanol burns further to completion with addition of Diethyl Ether and Di-tert-butyl Peroxide. Through the use of a single-zone model, numerical results provided additional information on the behavior of the fuel blends during combustion.

The intake temperature required for start of combustion (as defined by CA50, the crank angle of 50% heat release) was observed to decrease dramatically with the addition of DTBP to all fuel blends. Numerical modeling was able to show this trend for all operating conditions.

Although an elongation of the heat release was not observed for these particular fuel blends, it is possible that through the use of isotope tracing we will be able to identify fuel blends that display the kind of behavior that will help in balancing out the barriers to practical deployment of HCCI engine technology.

8.0 Acknowledgements

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