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Homogeneous Charge Compression Ignition

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The Effect of the Di-Tertiary Butyl Peroxide (DTBP) additive on HCCI Combustion of Fuel Blends of Ethanol and Diethyl Ether

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ABSTRACT

The influence of the small amounts (1-3%) of the additive di-tertiary butyl peroxide (DTBP) on the combustion event of Homogeneous Charge Compression Ignition (HCCI) engines was investigated using engine experiments, numerical modeling, and carbon-14 isotope tracing. DTBP was added to neat ethanol and diethyl ether (DEE) in ethanol fuel blends for a range of combustion timings and engine loads. The addition of DTBP to the fuel advanced combustion timing in each instance, with the DEE-in-ethanol mixture advancing more than the ethanol alone. A numerical model reproduced the experimental results. Carbon-14 isotope tracing showed that more ethanol burns to completion in DEE-in-ethanol blends with a DTBP additive when compared to results for DEE-in-ethanol without the additive. However, the addition of DTBP did not elongate the heat release in either case. The additive advances combustion timing for both pure ethanol and for DEE-in-ethanol mixtures, but the additive results in more of an advance in timing for the DEE-in-ethanol mixture. This suggests that although there are both thermal and kinetic influences from the addition of DTBP, the thermal effects are more important.

INTRODUCTION AND BACKGROUND

CARBON 14 TRACING

Chemical pathways of combustion can be identified through tracing and measurement of unusual isotopes. Radioisotopes are specific and distinctive because they are extremely rare in natural materials. A radioisotope-labeled compound has a very high abundance-to-background ratio, but poor detection efficiency may obscure this property. Using a long-lived radioisotope (e.g., ^{14}C half life = 5730 years) can eliminate issues associated with radioactivity if the detector measures mass rather than radioactive decays. Accelerator mass spectrometry (AMS), an isotope-ratio measurement method developed in the late 1970s for radiocarbon

dating is ideally suited to measure variations from the natural level of $^{14}\text{C} / \text{C}$ ratios $\approx 10\text{E-}12$ against a petroleum background $^{14}\text{C} / \text{C}$ ratios $< 10\text{E-}15$ [2]. Accordingly, components of bio-derived fuels contain elevated ^{14}C as compared to fossil fuels. This isotopic elevation is sufficient to trace the fate of bio-derived fuel components (ethanol) in emission products without the use of radioactive materials.

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 [3-6], the techniques for measuring the ^{14}C concentrations of PM and CO_2 by AMS are straightforward and routine.

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 [7]. HCCI engines have features of both spark ignited (SI) engines and Diesel engines. HCCI engines, like SI engines, are generally premixed and significantly lean at $\Phi < 0.5$, thus they produce very low nitrous oxides (NO_x) and particulate matter (PM) emissions. Yet, HCCI engines typically have high compression ratios and thus high efficiencies similar to that found in Diesel engines. In an SI engine, the combustion event is initiated by a spark and 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. 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 (around 1-3 milliseconds).

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 (i.e. different autoignition times). The goal is that each fuel would burn in succession and thus spread out the HCCI combustion duration, termed heat release elongation (HRE). Examples of this HRE strategy include using dimethyl ether (easy to autoignite) mixed with methane (difficult to autoignite) [8], naphtha with methane [9], and octane with n-heptane [10].

Furthermore, addition of fuel with a low autoignition temperature lowers the intake temperature required for HCCI operation. Intake temperature is typically a slowly responding parameter, with lags associated with heating a flowing gas. Small changes in temperature can dramatically affect CA50, so overshooting a target temperature can push the combustion into an unstable regime [11-13]. In this paper, the combustion event (CA50) is defined as time when 50% of the cumulative heat release has occurred [14].

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. Fuel Characteristics

	DEE	EtOH	DTBP
Flash Point (Celsius)	-45	13	6
Vapor Pressure @ 298K	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 lead EtOH in blends, but not as much as expected [15]. There was no significant elongation of the combustion event with DEE-EtOH blends [15]. 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 [16]. DTBP is widely used as a catalyst of polymerization for olefin copolymers and crosslinking agent for unsaturated polyesters. It is also used as an ignition improver for increasing cetane number in diesel engines [17-19]. Our intention was to use the exothermic decomposition DTBP to elongate the combustion event by igniting the DEE earlier.

We anticipate that DEE will autoignite first followed by autoignition of EtOH. Determining the source of CO₂ produced by each fuel requires a means of distinguishing the sources of the carbon. Since bio-derived EtOH has a natural carbon-14 (¹⁴C) level and petroleum-derived DEE and DTBP are free of ¹⁴C, we could distinguish the contribution of EtOH to CO₂ by measuring its isotopic content.

The single cylinder engine used in these experiments is a Caterpillar 3401. See Table 2 for engine specifications.

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 engine was maintained at constant speed of ~1800 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 meter upstream to insure complete vaporization of the fuel, controlled the equivalence ratio.

EXPERIMENTAL PROCEDURE

The equivalence ratio was maintained at $\Phi=0.3$ throughout the course of 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 at a constant $P=1.7$ bar. Grain ethanol (EtOH) served as the tracer (bio-derived, contains ¹⁴C) fuel while diethyl ether (DEE) and DTBP are petroleum-derived fuels (¹⁴C free). The isotopic level of the lubrication oil and DEE was at instrument background (¹⁴C /C ratios <10E-15). Since the ethanol is bio-derived, it is uniformly labeled; each carbon atom in the ethanol molecule is equally labeled with ¹⁴C.

The fuel blends containing 25% DEE-in-EtOH were defined on a volume percent basis (e.g. 250 mL DEE for every 750 mL EtOH at 25%). With the addition of DTBP, the volume of DEE was maintained while the balance was EtOH.

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

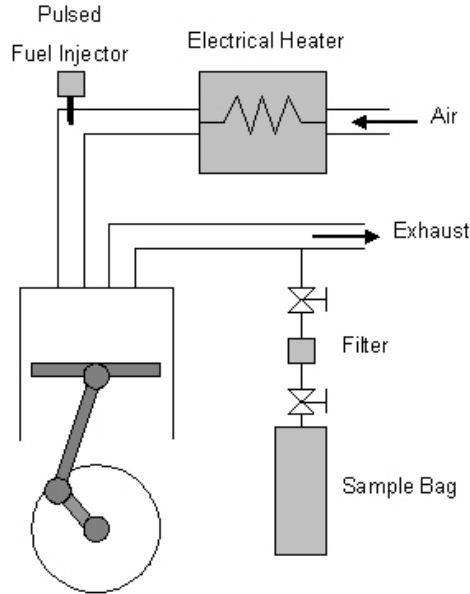


Figure 1. Experimental set-up for exhaust collection from the single cylinder CAT3401 engine. Note that the fuel is introduced after the intake heater and well upstream (~1m) of the engine so as to insure mixing and evaporation.

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 CO₂. All gas molecules except N₂ 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 CO₂. A valve between the traps was closed and non-condensable gases were evacuated. The CO₂ was then cryogenically transferred to a quartz sample tube which was sealed with a H₂/O₂ torch. Each purified CO₂ 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 CO₂ pressure in a small fixed volume before transfer to an individual reactor and reduction to graphite in the presence of iron catalyst [20]. All graphite targets were measured at the Center for AMS at LLNL

[21]. A general description of how AMS works is available in the literature [2].

AMS is an isotope ratio mass spectrometry technique where ¹⁴C / C ratios of the unknowns are normalized to measurements of 4-6 identically prepared standards of known isotope concentration. The isotope ratio of the sample, R_s , is calculated from the measured isotope ratios of the sample, $R_{s(meas)}$, the average of the measured standards, $R_{stand(meas)}$, and the known isotope ratio of the standard, R_{stand} , shown in Eq.1.

$$R_s = \frac{R_{s(meas)}}{R_{stand(meas)}} R_{stand} \quad (1)$$

Only the ethanol contains a significant ¹⁴C signal in this system. Backgrounds associated with sample prep are known and the contribution of intake air to the exhaust CO₂ is subtracted. Expanding the ¹⁴C / 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.2).

$$R_s = \frac{{}^{14}C_E}{C_E + C_D} = \frac{C_E(R_E)}{C_E + C_D} \quad (2)$$

The denominator of Eq.2 is an expression for the total carbon mass of the sample. By manipulating Eq.2 we solve for the fraction of ethanol-derived carbon F_E in the sample (Eq.3).

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

NUMERICAL MODELING

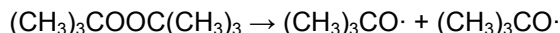
Simulations of HCCI combustion of the diethyl-ether-in-ethanol blend have been conducted using a “single-zone” numerical model of the engine. This single-zone in time model treats the cylindrical combustion chamber as a uniform reactor with uniform temperature, pressure, and composition throughout. The reactor volume changes based on slider-crank relations that determine the motion of the piston in the 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.

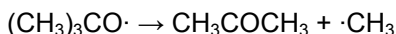
The DEE/EtOH chemical mechanism contains an extension of that for dimethyl ether [22] with diethyl ether chemistry provided by Curran [23] and a mechanism of EtOH [24]. The combined mechanism contains 112 species and 484 reactions. Additional reactions for the

adiabatic decomposition of DTBP were added into the mechanism, following the work of Iizuka et al [25].

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 ($\cdot CH_3$).



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 $\cdot CH_3$ attacking the main fuels and commencing radical chain reactions, including chain branching. However, close examination of the simulation shows that $\cdot CH_3$ rapidly reacts to form relatively stable species rather than species that lead to chain propagation and chain branching. 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 resulting slight increase in the temperature is amplified by further compression of the mixture. For this thermal reason (as opposed to kinetic reasons) addition of DTBP leads to advancement of SOC timing at constant input temperature; or equivalently, a reduction of input temperature if the same SOC 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 [1,8,26-27], 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 gases 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 [28].

Heat transfer [29-32] and trapped residuals are also included in the model. Simulations were conducted using the geometric and operating parameters for the engine specified in Table 1.

EXPERIMENTAL RESULTS

The addition of DTBP to DEE in EtOH blends significantly advanced CA50 at fixed intake temperature. DTBP also enabled ignition at much lower intake temperatures. There was an advance in CA50 with an

increase in %DTBP due to the exothermic decomposition of DTBP which raised the temperature of the intake charge sufficiently to initiate ignition. Figure 2 shows the dependence of CA50 on intake temperature for different concentrations of DTBP in 25%DEE-in-EtOH blends.

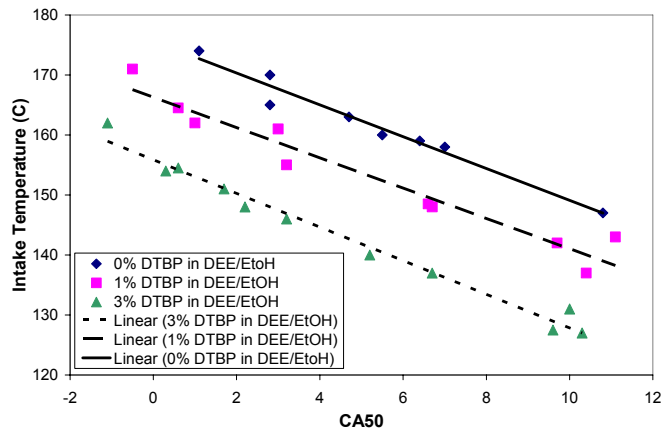


Figure 2. The addition of DTBP to 25%DEE-in-EtOH fuel blends significantly affects the dependence between intake temperature and CA50

More Ethanol burns to completion with the addition of DTBP. Without DTBP, DEE burned more completely than EtOH for the entire range of CA50 measured. Addition of DTBP eliminated differences in the completeness of combustion between EtOH and DEE for early ignition points. The drop off in EtOH combustion for later CA50 can be attributed to the lower in-cylinder temperatures (i.e. more of the charge is too cool for the ethanol to ignite). Figure 3 shows the fraction of exhaust CO₂ that comes from EtOH normalized to the fuel EtOH concentration (designated zeta (ζ)) at different CA50. Thus, when $\zeta=0$, none of the EtOH in the fuel is burning to CO₂. When $\zeta=1$, EtOH and DEE are combusting equally. Since it is unlikely that both EtOH and DEE will only partially combust due to differences in auto-ignition properties, $\zeta=1$ implies complete combustion aside from small and equal amounts of fuel retained in crevices or cold boundary layers. The sudden drop off in EtOH-derived CO₂ for later CA50 is similar but greater than the decrease seen in the total CO₂ (Figure 8).

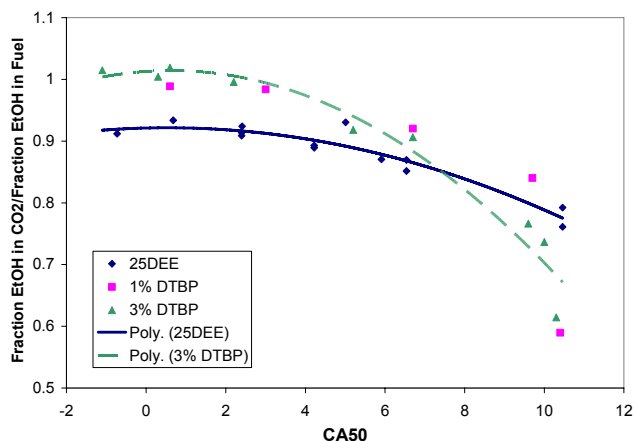


Figure 3. The addition of DTBP to DEE/EtOH blends causes more EtOH to burn to completion

The addition of DTBP to DEE/EtOH blends advanced the timing (CA50) more than the addition of DTBP to pure EtOH at a constant equivalence ratio. However, it did not make later combustion timings easier to obtain. Figure 4 shows that for a given intake temperature the DTBP/DEE/EtOH blend advanced CA50 more than the DTBP/EtOH blend at $\Phi=0.3$. It also shows that misfire occurs when combustion timing approaches a CA50 of 11 degrees after TDC, regardless of blend composition.

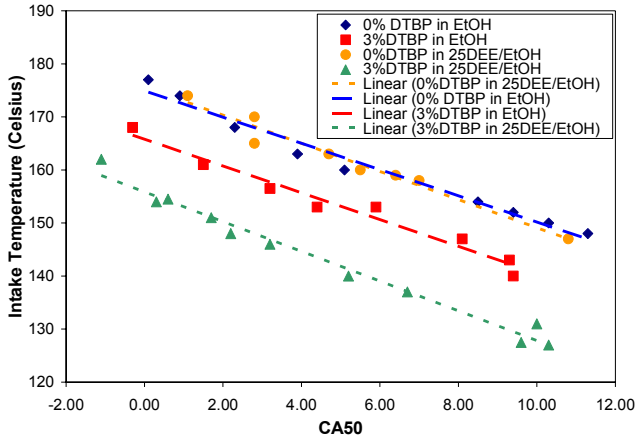


Figure 4. CA50 advances more at a constant intake temperature for blends of DTBP/DEE/EtOH than for blends of DTBP/EtOH or DEE/EtOH

Figure 5 compares the pressure traces for blends of 1% DTBP in 25DEE/EtOH and 3% DTBP in EtOH. The motor trace included shows the change in pressure due to movement of the piston alone (no fuel included).

At a constant equivalence ratio the CA50 for both blends is approximately equal. This suggests that blends of DTBP and EtOH can generally behave like blends of DTBP, DEE, and EtOH.

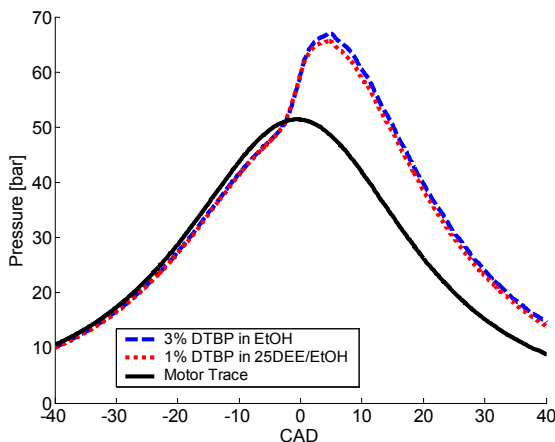


Figure 5. Comparison of blends of 1% DTBP in 25DEE/EtOH and 3% DTBP in EtOH

Figures 6, 7, and 8 show the emissions taken for 100% EtOH, a 3% DTBP in EtOH blend, and a 3% DTBP in a 25% DEE-in-EtOH blend.

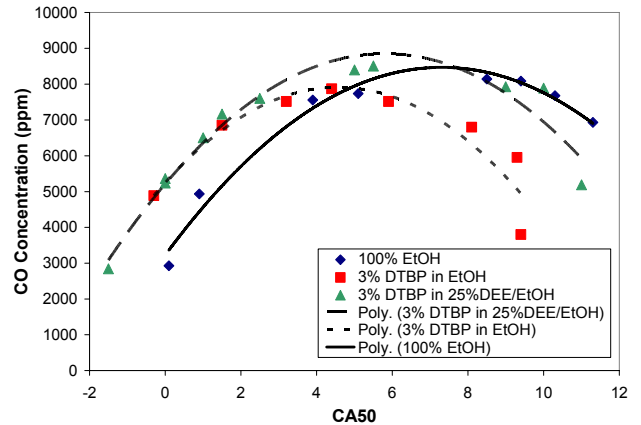


Figure 6. CO emissions for different fuel blends. Colder temperatures occur earlier for fuel blends containing DTBP, thus inhibiting the production of CO.

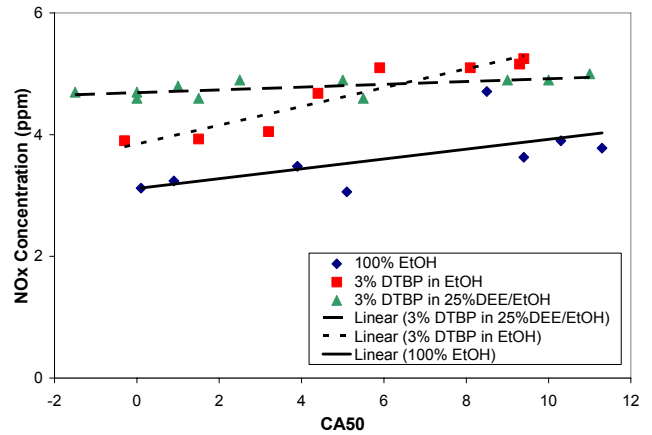


Figure 7. NOx emissions for different fuel blends. The low NOx emissions seen here are typical for HCCI engines.

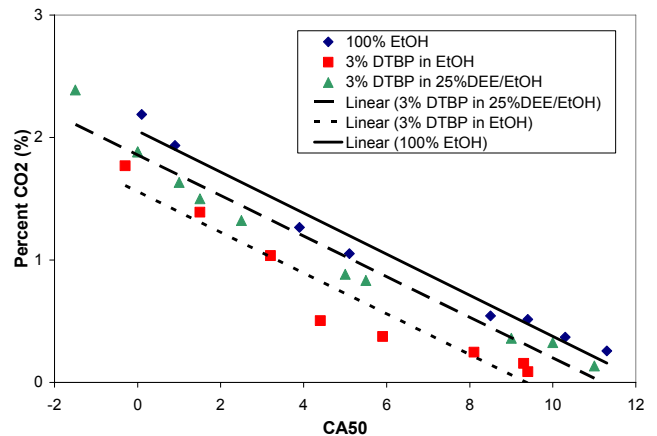


Figure 8. CO2 emissions for different fuel blends

Heat release calculations indicate the 10% to 90% duration of cumulative heat release [14]. Figure 9 shows the heat release duration for multiple fuel blends. The

correlation between heat release duration and CA50 for different fuel blends is seen to be weak.

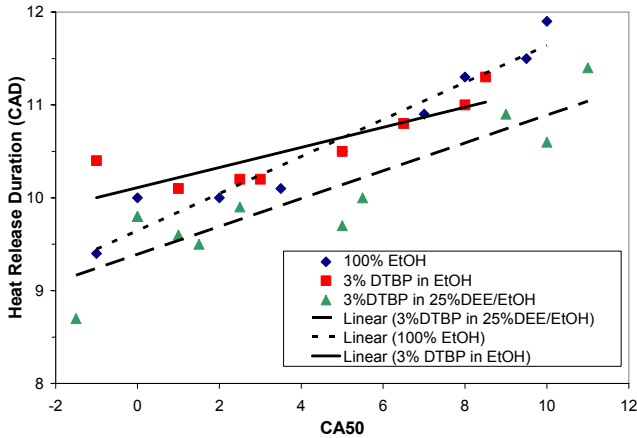


Figure 9. The correlation between heat release duration and CA50 for different fuel blends.

MODELING RESULTS

The modeling results show similar trends to those found in the experiments. While using fuel of 100% EtOH, the latest combustion timings occurred at a constant intake temperature followed by blends of 25% DEE in EtOH (25DEE/EtOH), 1% DTBP in EtOH, 1% DTBP in 25DEE/EtOH, 3% DTBP in EtOH, and 3% DTBP in 25DEE/EtOH.

Figure 10 compares blends of DTBP and 25DEE/EtOH and is analogous to the experimental results shown in Figure 2. The addition of DTBP to 25DEE/EtOH blends advances the timing of the engine.

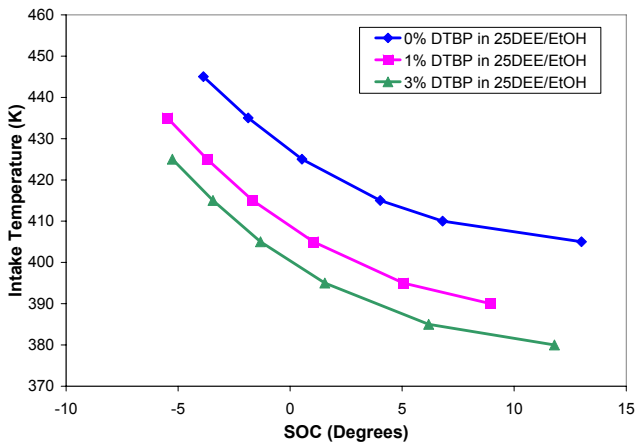


Figure 10. Modeling results showing advancement in combustion timing with the addition of DTBP to 25DEE/EtOH fuel blends.

Comparisons were also drawn between blends of DTBP with 100% EtOH and blends of DTBP and 25DEE/EtOH. The modeling results seen in Figure 11 are analogous to the experimental results of Figure 4.

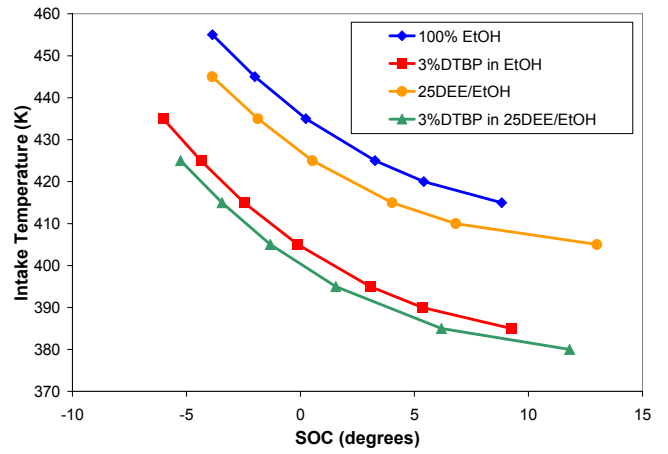


Figure 11. Numerical modeling results showing the advancement of combustion timing for fuel blends of DTBP in both EtOH and 25DEE/EtOH.

The advancement in combustion timing for 25DEE/EtOH blends with the addition of DTBP in the numerical modeling results is not as large as the advancement seen in the experiments. This is most likely due to an insufficient mechanism for DTBP and its' interaction with the different fuel blends.

The crank angle at 90% consumption of each fuel component in the 25DEE/EtOH blend was also investigated. Note that the point of 90% consumption will occur very early in the heat release process, well ahead of the CA50. Figure 12 shows that the DEE is consumed earlier with the addition of DTBP.

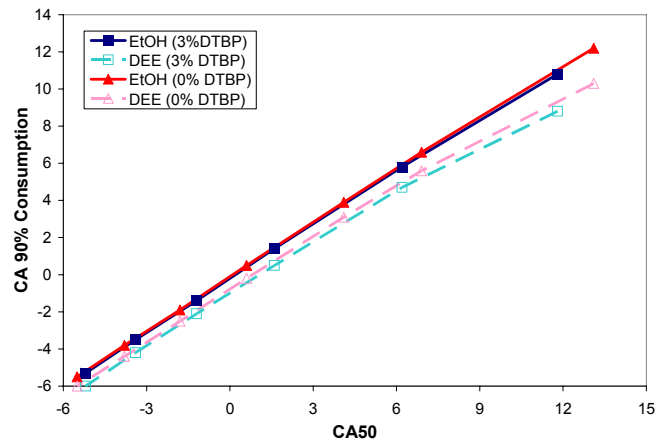


Figure 12. The addition of DTBP to 25DEE/EtOH causes the DEE to burn earlier in the cycle, especially at later combustion timings.

CONCLUSION

It was observed the addition of DTBP did not elongate the combustion event, as defined by duration of heat release.

A possible benefit with regards to HCCI engines is that the decreased inlet temperature makes control easier since most HCCI engines control combustion timing through fueling rate and temperature. However, the

addition of DTBP to fuel blends of DEE and EtOH did not make later combustion timings easier to obtain.

In the experiments, when DTBP was added to mixtures of DEE and EtOH, it had a greater effect on combustion timing than when DTBP was added to EtOH alone. The addition of DTBP to fuel mixtures enabled complete combustion of EtOH ($\zeta=1$, not including crevice effects) for earlier combustion timings, which was not achieved for fuel mixtures without DTBP.

Numerical modeling suggests that the decomposition of DTBP and subsequent formation of acetone is exothermic and raises the mixture temperature slightly as the decomposition occurs. Although the addition of DTBP also has potential kinetic influences, this temperature increase is the significant contributor to the advance in combustion timing seen with DTBP addition.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

25DEE/EtOH: 25% Diethyl Ether in Ethanol (by volume)

AMS: Atomic Mass Spectrometry

CA: Crank Angle

CA50: Crank Angle at 50% Heat Release

DEE: Diethyl Ether

DTBP: Di-tertiary Butyl Peroxide

ECU: Electronic Control Unit

EtOH: Ethanol

HCCI: Homogeneous Charge Compression Ignition

HRE: Heat Release Elongation

LHV: Latent Heat of Vaporization

PHI (Φ): Equivalence Ratio

PM: Particulate Matter

TDC: Top Dead Center

SOC: Start of Combustion

Zeta (ζ): Fraction of exhaust CO₂ that comes from EtOH normalized to the fuel EtOH concentration