
Autoignition of Alcohols and Ethers in a Rapid Compression Machine

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Abstract

The autoignition characteristics of methanol, ethanol and MTBE (methyl tert-butyl ether) have been investigated in a rapid compression machine at pressures in the range 20-40 atm and temperatures within 750-1000 K. All three oxygenated fuels tested show higher autoignition temperatures than paraffins, a trend consistent with the high octane number of these fuels. The autoignition delay time for methanol was slightly lower than predicted values using reported reaction mechanisms. However, the experimental and measured values for the activation energy are in very good agreement around 44 kcal/mol. The measured activation energy for ethanol autoignition is in good agreement with previous shock tube results (31 kcal/mol), although ignition times predicted by the shock tube correlation are a factor of three lower than the measured values. The measured activation energy for MTBE, 41.4 kcal/mol, was significantly higher than the value previously observed in shock tubes (28.1 kcal/mol). The onset of preignition, characterized by a slow energy release prior to early ignition was observed in some instances. Possible reasons for these occurrences are discussed.

1. Introduction

Methanol, ethanol and MTBE have received particular attention as emissions-reducing [1,2] and octane-enhancing additives [3,4] for automotive fuels. Whereas the effect of these oxygenated fuels in retarding autoignition is well documented, the chemical mechanisms leading to this result are still under discussion and development [3-5]. The gas phase oxidation chemistries of methanol, ethanol and MTBE have been experimentally investigated at low pressures in flow reactors [6-7], shock tubes [8-10] and static

reactors [11, 12]. Other researchers have investigated the chemistry of oxygenated fuels relevant to autoignition by sampling from motored engines [3,4]. Whereas all of these experiments contribute to construct a comprehensive picture of the combustion chemistry of oxygenated fuels, only motored engine experiments have been performed at realistic pressures (30-40 atm) and temperatures (800-1200 K) encountered in the pre-flame region of a spark-ignition engine prior to knock.

The present experiments in a rapid compression machine provide a well-characterized high pressure (20-50 atm), low temperature (750-1000 K) environment that can be directly related to the pure gas-phase oxidation chemistry occurring prior to autoignition. Further advantages are the fact that induction times can be directly observed and the experiment is undisturbed by residual gases and fluid mechanical effects. Drawbacks of the current experiment are the inability to sample or observe individual species, and the limited observation time due to heat transfer effects. The current experiments provide pressure histories during the constant volume, nearly adiabatic oxidation process of the mixture. These profiles can be used as the basis for comparison to chemical kinetic models to be developed in parallel with the present experiments.

2. Experimental

The Rapid Compression Machine (RCM) consists of a hydraulically operated piston-cylinder assembly that can compress gas mixtures within 5-30 milliseconds to pressures around 30 atmospheres or more. The cylinder has a 5.08 cm bore. The stroke and the clearance height can be adjusted to fit final conditions. The cylinder head was designed with a special crevice that can swallow the thermal boundary layer generated during compression, to avoid a generation of a corner vortex around the piston head and therefore to minimize non-uniformity effects in the

core gas [13]. Temperatures and pressures after compression can be varied by changing the relative amounts of inert diluent gases nitrogen and argon. Peak pressures are in general 80 to 90 percent of the ideal isentropic pressure, where the difference is accounted for by heat losses during compression. Heat losses also account for the drop in pressure from the peak, as shown in Fig. 1 for the same initial pressure and temperature but different Ar/N₂ ratios.

The temperature of the core gas is calculated by iterative numerical integration of the pressure-time profile throughout compression, assuming the existence of an adiabatic core:

$$\ln \left(\frac{T}{T_0} \right) = \int_{P_0}^P \frac{\gamma(T) - 1}{\gamma(T)} d(\ln P)$$

where P₀ and T₀ are the initial conditions and $\gamma(T)$ is the ratio of specific heats of the mixture. This assumption is adequate provided that (a) the thermal boundary layer is thin and (b) there is negligible energy release due to reaction. CFD simulations performed in a rapid compression studies showed that core gas has an almost adiabatic temperature at the end of the compression process [14].

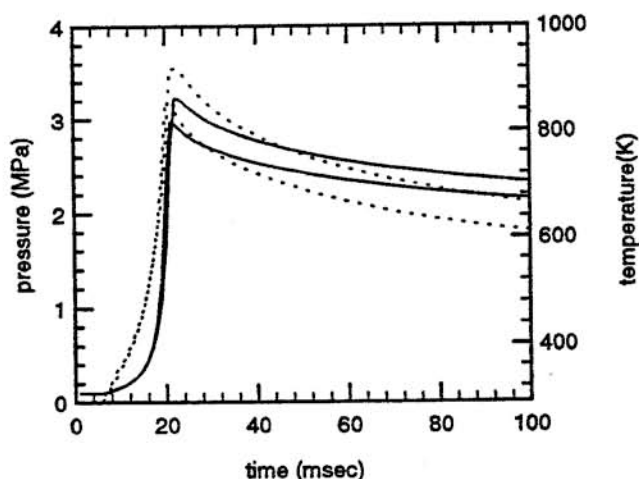


Fig.1 Calculated temperature of core gas from measured pressure. P_i=96.06kPa, T_i=298.5K, CR=15.8,
 ——— pressure, - - - - - temperature,
 upper curve : Ar/N₂=0.6/0.4, lower : Ar/N₂=0.5/0.5

The growth of the thermal boundary layer limits the maximum observation time to about 100 ms, beyond which the boundary layer thickness becomes larger than 10 percent of the clearance height and the assumption of a well characterized uniform temperature core breaks down.

The assumption of negligible heat release breaks down prior to ignition. In order to obtain the

temperature for chemical kinetic calculations, one can use a constant volume assumption, which yields the average chamber temperature during reaction (which is somewhat lower than the actual core temperature). For a more accurate temperature determination, the volume occupied by the thermal boundary layer can be obtained using non-reacting pressure profiles, thus yielding the volume of the adiabatic core as a function of time and the corresponding temperature. For short induction times, pressure and temperature differences are small, so that the uncertainties in the core temperature are negligible. For long induction times, one must be more careful in evaluating the core temperature, which can be 40 or 50 K higher than the average temperature.

The experimental conditions used in the present series were selected to span temperatures and pressures in the range where autoignition occurs in engines, and an equivalence ratio of 1.0.

Fuels and gases used had research grade purity or maximum available (MTBE: Aldrich, 98%, methanol: Mallinckrodt, 99%+, ethanol: Aaper alcohol). The mixture composition was determined by measuring partial pressures with an MKS 122A diaphragm pressure gage with an accuracy of 0.1 torr. Dynamic pressures were measured using a calibrated Kistler 6123 piezoelectric transducer with an accuracy of 1%, the voltage-time signal being stored in a standard data acquisition software for PCs.

A purge sequence with inert gas, followed by a dummy run with pure oxygen, was performed between two consecutive experiments, in order to ensure repeatability by avoiding transport of fuel and other reactive substances absorbed on oil layers, viton O-rings and other surfaces to the subsequent experiment. Since the piston is hydraulically driven, it proved very difficult to completely eliminate oil layers from the cylinder walls. Hydrocarbons are very strongly absorbed on by the oil, whereas oxygenated species are not. The purge sequence was effective in providing reproducible results.

3. Chemical Kinetic Model

The experimental results for the autoignition of methanol have been compared with model calculations using the proposed chemical kinetic mechanisms by Norton and Dryer [6], Egolfopoulos, Du and Law [15]. The chemical kinetic equations were integrated using Chemkin [16], under the assumptions of adiabatic reaction and constant volume. As discussed above, the assumption of adiabatic conditions is only good for very short induction times. For longer induction times, heat transfer leading to an expansion of the adiabatic core must be taken into account. For comparisons with the model in this first phase of the analysis, the results were compared to the experiment by adopting the average core temperature prior to ignition, and adopting conservative error bars on the estimated temperatures, ranging from the minimum to the maximum adiabatic core temperature before ignition.

4. Results and Discussion

A typical pressure trace during compression and ignition is shown in Fig. 2 for the autoignition of the primary reference fuels heptane and isooctane, previously studied in the same facility by Park [13]. Compression times range from 5 to 20 ms depending on the initial and final pressure desired. Modeling results show that negligible reaction takes place during the compression period. Therefore, a suitable choice for the initial reaction time is the upper inflection point of the pressure signal, which is better defined than the peak pressure point. The uncertainty in the chosen zero time is no larger than a millisecond. The ignition point is defined as the the inflection point in the pressure rise during ignition. From consecutive runs with the same initial experimental conditions, the error range of measured ignition delay times was within 10 percent.

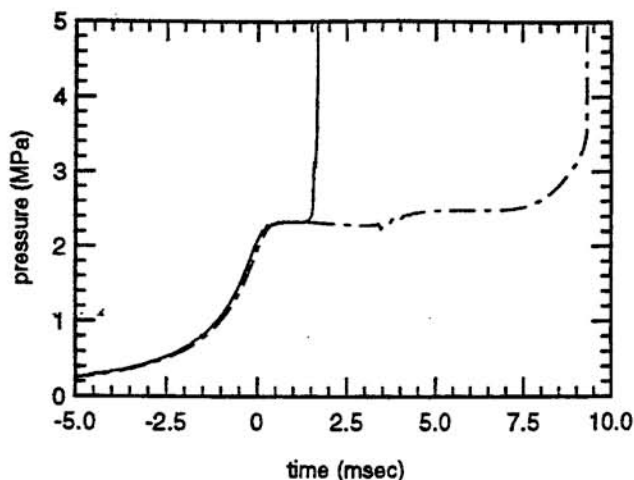


Fig.2 Pressure vs. time curve for autoignition of primary reference fuels. — n-heptane, --- i-octane, $P_i=66.66\text{kPa}$, $T_i=770\text{K}$, $\phi=1.0$, $CR=15.8$, $(N_2+Ar)/O_2=3.77$, $N_2/(N_2+Ar)=0.5$

Ignition delay times within a relatively narrow temperature range can be represented as a simple function of fuel and oxygen concentration, and temperature: $\tau = A (c_f)^\alpha (c_{O_2})^\beta \exp(E/RT)$, where A is a collision factor, c_f and c_{O_2} the molar concentrations of fuel and oxygen, respectively, E the activation energy, R the is the gas constant and T the temperature; α and β are coefficients that represent the sensitivity of the delay time to the concentrations. The expression can be written as a function of the pre-compression conditions using mass conservation, such that $\tau = A(X_{O_2} c_0 r)^{\alpha+\beta} (\phi S)^\alpha \exp(E/RT)$, where X_{O_2} is the oxygen molar fraction, c_0 the total molar concentration prior to compression, r the compression ratio, ϕ the equivalence ratio and S the stoichiometric coefficient in moles of fuel per moles of oxygen. Therefore, by keeping the initial concentration of oxygen, compression ratio and equivalence ratio constant, an overall

activation energy can be obtained. The experimental results can therefore be summarized as a function of initial conditions and $1/T$, as described further below.

4.1. Methanol

Figure 3 shows pressure traces for methanol for different initial conditions generated by varying the relative amounts of N_2/Ar in the mixture, with the oxygen to diluent (N_2+Ar) ratio kept constant. The traces are typical for three oxygenated fuels tested: no two-stage ignition behavior. Note that for longer ignition times, the pressure decreases due to heat losses. The observed fluctuations of the pressure signal area associated with movement of hydraulic oil slapping inside the RCM during sudden deceleration. Although these vibrations translate as fluctuations on the pressure signal, the core gas pressure and temperature are not expected to be significantly affected.

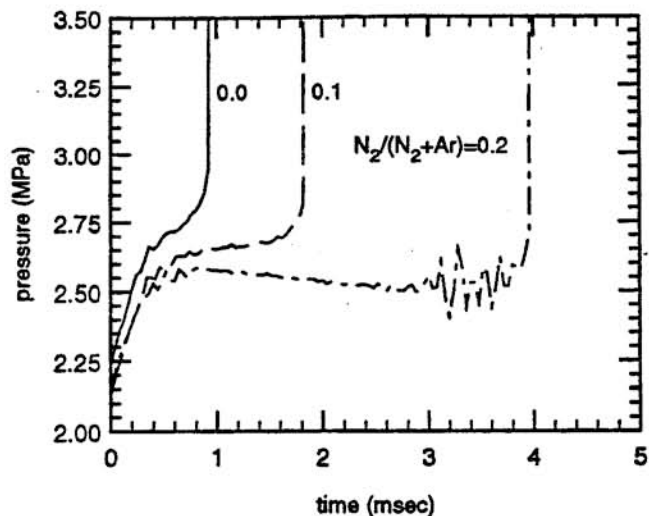


Fig.3 Unfiltered pressure signal for autoignition of methanol.

Oscillations between 3–4msec are a result of vibration caused by hydraulic oil slapping.

$P_i=53.33\text{kPa}$, $T_i=295\pm 1\text{K}$, $T_f=886\sim 942\text{K}$, $\phi=1.0$, $CR=18$, $CH_3OH/O_2/(N_2+Ar)=0.1/0.15/0.75$

Measured and calculated ignition delay times for methanol are shown in Fig. 4. Time error bars correspond to the uncertainty in determining the point where reaction effectively starts. Temperature error bars represent the minimum temperature of the adiabatic core (which occurs just prior to ignition) and the maximum (peak) temperature before ignition (which occurs at the end of compression). Open symbols are calculated ignition times, using a constant volume assumption at the average experimental temperature and pressure, and the chemical kinetic mechanisms proposed in [6] and [15].

The measured activation energy for the autoignition of methanol is 43.9 kcal/mol. The predicted activation energies clearly compare favorably with the measured value, although the predicted ignition delay times are rather long compared to the experimental values. Since the model does not take heat losses into account, calculated ignition delays for longer times

(lower temperatures) may be slightly underestimated. More accurate comparison with models requires programming of the compression process to include any potential effects of pre-reaction before the end of compression and the corresponding pressure and temperature decreases due to heat losses.

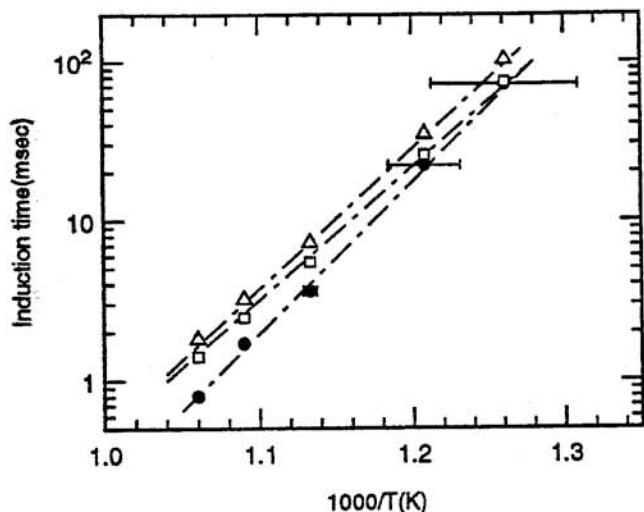


Fig.4 Arrhenius plot for methanol autoignition. $P_i=66.7\text{kPa}$, $T_i=298\pm 1\text{ K}$, $P_f=2.42\pm 0.24\text{ MPa}$, $\phi=1.0$, $CR=18$,
 ● this study, $\text{CH}_3\text{OH}/\text{O}_2/(\text{N}_2+\text{Ar})=1/0.15/75$
 □ calculated using chemical kinetic model from [15]
 △ calculated from [9]

The open symbols are calculated ignition times using constant volume assumption at the average core temperature and pressure, and the chemical kinetic mechanism proposed in [6] and [15]. The calculated activation energy is seen to compare favorably to the measured value, although the predicted induction times are rather long compared to the experiment.

Occasional preignition was observed in some of the experiments during repeatability tests, as shown in Fig. 5, for methanol. Preignition only occurred in the lower temperature range, around $850 \pm 10\text{ K}$. The slow initial energy release that typically accompanied these events resembles "thermal ignition" characteristics, as suggested in classical explosion theories [18], as opposed to the sharp energy release characteristics of kinetically controlled ignition. Similar "weak" explosion phenomena have been observed in shock tube oxidation studies with hydrogen [20,21]. In addition, in spite of its high octane number, methanol is known to display undesirable preignition behavior in spark ignition engines [22]. A plausible explanation for this phenomenon might be that at the low temperatures and high pressures prevalent in RCM experiments, the sensitivity to small changes in temperature and pressure is very high, so that non-uniformities in the state of the mixture could lead to local instead of uniform ignition. However, it is worthwhile noting that whereas such behavior has been observed in RCM experiments with

methanol, ethanol and hydrogen, no such behavior has been observed in experiments with primary reference fuels in our laboratory.

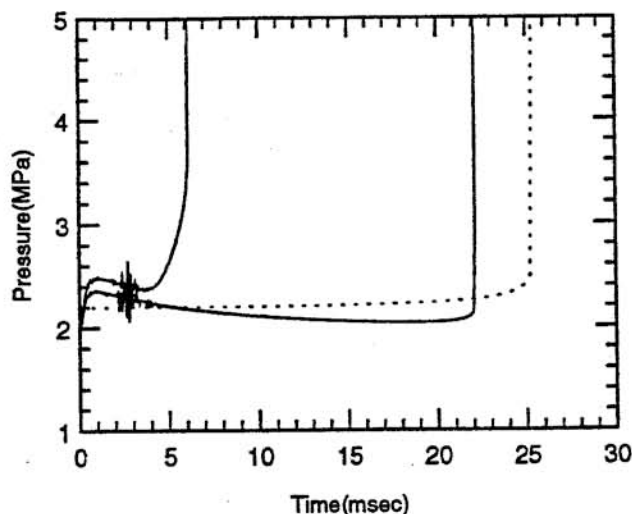


Fig.5 Measured and calculated pressure vs. time curve for methanol. $T_i=850\text{K}$, $P_i=66.13\text{kPa}$, $\phi=1.0$, $CR=18$,
 — measured, $\text{CH}_3\text{OH}/\text{O}_2/(\text{N}_2+\text{Ar})=1/0.15/75$
 - - - calculated from [15]

4.2. Ethanol

Ethanol displays similar autoignition characteristics as methanol, although its measured activation energy is slightly lower, 31.0 kcal/mol . Figure 6 shows measured induction times for ethanol autoignition in the rapid compression machine, and values extrapolated using a proposed correlation by Curran et al. [17]. The two lower temperature experimental points in Fig. 6 showed incipient "preignition" behavior as discussed above for the case of methanol, i.e., a slight pressure rise prior to full ignition, and may not entirely represent the purely kinetic behavior of the mixture. If these points are excluded and only the higher temperature experiments considered, the activation energy would be in perfect agreement with previous experiments. However, the actual ignition delay times are almost one order of magnitude larger than the extrapolated correlation by Curran et al. Notice that the shock tube correlation was obtained in the temperature range $1100\text{-}1900\text{ K}$ and pressure range $0.2\text{-}0.45\text{ MPa}$, and therefore does not extend to the present concentration range, at pressures around 3.2 MPa and temperatures down to 800 K . In addition, a secondary effect might be the effect of nitrogen as a diluent, since the shock tube experiments were done using argon only. The current results would imply a much higher sensitivity to concentration than obtained from the shock tube experiments.

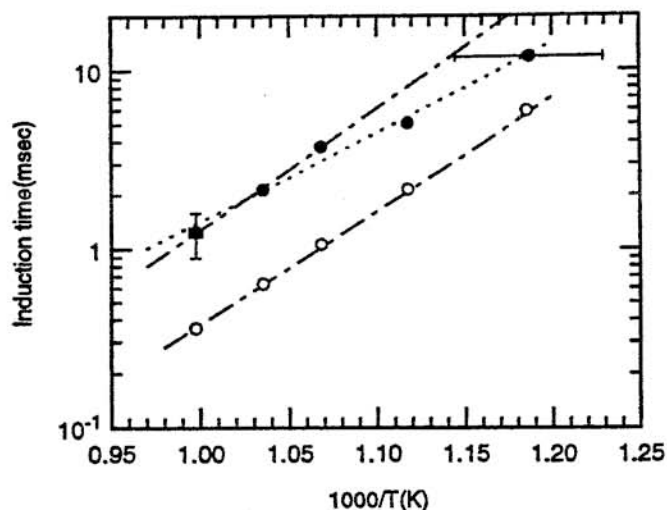


Fig.6 Arrhenius plot for ethanol autoignition. $T_f=292\pm 1K$, $\phi=1.0$,
 $CR=17.1$, $P_i=66.6kPa$, $P_f=3.22\pm 0.19MPa$,
 ● measured, $C_2H_5OH/O_2/(N_2+Ar)=0.053/0.158/0.789$
 ○ global expression by Curran, *et al.* [17]
 $\tau=10^{-14.0}\exp(15500/T)[C_2H_5OH]^{-0.315}[O_2]^{0.78}[N_2+Ar]^{0.259}$

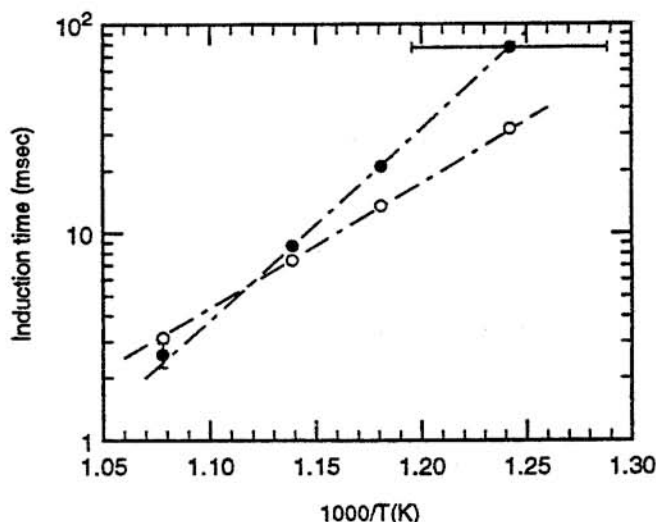


Fig.7 Arrhenius plot for MTBE autoignition. $T_f=300\pm 1K$, $\phi=1.0$,
 $CR=16.7$, $P_i=66.7kPa$, $P_f=2.43\pm 0.08MPa$,
 ● measured, $MTBE/O_2/(N_2+Ar)=0.022/0.163/0.815$
 ○ global expression by Curran, *et al.* [17]
 $\tau=10^{-12.4}\exp(14140/T)[MTBE]^{0.097}[O_2]^{-1.036}[N_2+Ar]^{0.188}$

4.3. MTBE

Measured induction times for MTBE are shown in Fig. 7. The measured activation energy of 41.4 kcal/mol is larger than the previously reported [17] value of 28.1 kcal/mole. Interestingly, such a high activation energy would be comparable to the predictions of the proposed full kinetic models [17], which did not agree very well with the reported shock

tube experiments. Clearly, further experimentation at intermediate concentrations between shock tube and the present results would be desirable in order to understand the chemical kinetic behavior of these fuels.

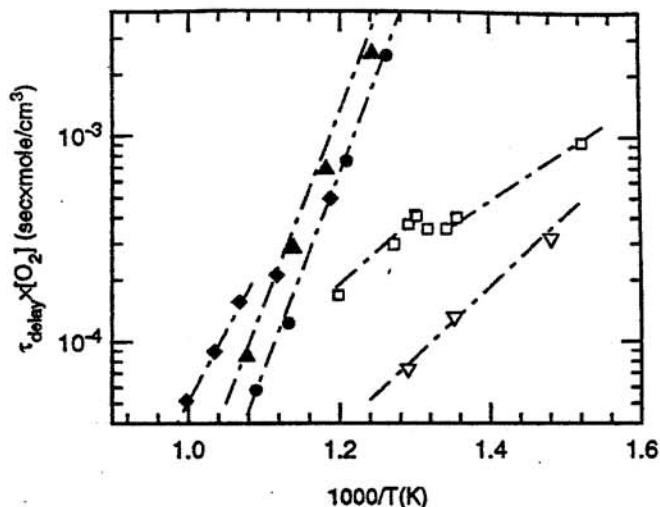


Fig.8 Comparison of ignition delay times for methanol, ethanol, MTBE, i-octane, and n-heptane. $\phi=1.0$,
 $O_2/diluent=5.0$: ● methanol, ◆ ethanol, ▲ MTBE,
 $O_2/diluent=3.77$: □ i-octane, ▽ n-heptane

Figure 8 summarizes the present results for the ignition delay times multiplied by the oxygen concentration, along with previous results obtained with primary reference fuels for similar pressure and oxygen concentrations. From the figure, it is clear that oxygenated fuels display an intrinsically high resistance to autoignition compared to primary reference fuels. This is consistent with previous results by Leppard [3] in motored engine experiments.

5. Conclusions

The present experiments represent direct measurements of autoignition characteristics of methanol, ethanol and MTBE at the low temperatures and high pressures encountered in the early pre-flame region in spark ignition engines. The present experiments confirm the intrinsic resistance to autoignition of oxygenated fuels relative to reference fuels.

Preliminary chemical kinetic simulations for pure methanol have been made, and the comparison with experiment is encouraging. An extension of the current study to a wider temperature and pressure range is currently being produced.

The observed phenomenon of preignition with slow energy release deserves more careful investigation. Experimentally, it is possible to utilize ionization probes and visualization to detect the onset of ignition. Complementary modeling of the effect of local temperature and pressure perturbation should permit the interpretation of the experimental results based on the

computed stability, overall heat release and effect of perturbations on the overall ignition delay time.

Finally, a thorough investigation of the discrepancies between extrapolated shock tube correlations and the present experiments for ethanol and MTBE must be made if chemical kinetic models are to be developed based on these observations.

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