

Methyl and ethyl esters as biodiesel surrogates: observations on trends in ignition behavior

Benjamin Akih-Kumgeh, Jeffrey M. Bergthorson

Department of Mechanical Engineering, McGill University, Montreal, H3A 2K6, Canada

1 Introduction

A sustainable energy future will likely involve increased use of biofuels such as biodiesel. On the other hand, concerns about the associated costs and environmental neutrality, prompts a closer look at biofuel production methods with the goal of improving the sustainability of the process. While biodiesel is mainly produced by methanol-based transesterification of fatty acid triglycerides in acidic or alkaline media, the possibility of using other alcohols are being explored with increasing interest [1, 2]. Successful system level tests of ethyl ester as biodiesel have been reported [3, 2]. The possibility of using mixtures of methanol and ethanol in the transesterification of soy bean oil have been explored by Joshi et al. [4] concluding that the resulting methyl and ethyl ester mix can offer improved physical properties.

Further use of various alkyl esters beside methyl esters in combustion engines can be guided by understanding their relative combustion and physico-chemical properties through systematic experimental studies. Previous studies by Metcalfe et al. [5] explored the relative ignition of the ester isomers, ethyl propanoate (EP), and methyl butanoate (MB), concluding that the EP is more readily ignited than MB under the same conditions. In a recent study of the ignition of selected C3 oxygenated hydrocarbons, the current authors showed that ethyl formate (EF) is more reactive than its ester isomer, methyl acetate (MA) [6].

In this study new experimental data for EP and ethyl acetate (EA) are reported. Together with literature data for methyl formate (MF), EF, MA, and MP, their ignition behavior is explored to reveal the effect of methyl and ethyl ester groups on the same carboxylic acid. This relative behavior is further put into perspective by considering the effect of ester isomers as exemplified by the three surrogates, MP, EP and MB. These comparisons are done for mixtures of fuel, oxygen and argon under conditions of constant equivalence ratios, ϕ , oxygen/argon ratios, D and nominal pressures, p , over a range of post-reflected shock temperatures, T .

2 Experimental technique

Ignition delay times are obtained using a 5 cm inner diameter shock tube described previously [7]. Test mixtures are prepared in a 90 L mixing tank and allowed to mix for approximately 24 hours. In the course of preparing the test mixtures, volumes of the injected liquid fuel are chosen such that the resulting partial pressure after complete evaporation is less than 50% of its vapor pressure at room temperature in order to avoid fuel condensation. The purities of EP and EA are 99+% and 99.5%, respectively. Those of the other fuels are reported in their earlier studies [7, 10, 6]. The shock tube is helium driven and the shock velocity is obtained from pressure signals of four fast-response pressure transducers mounted

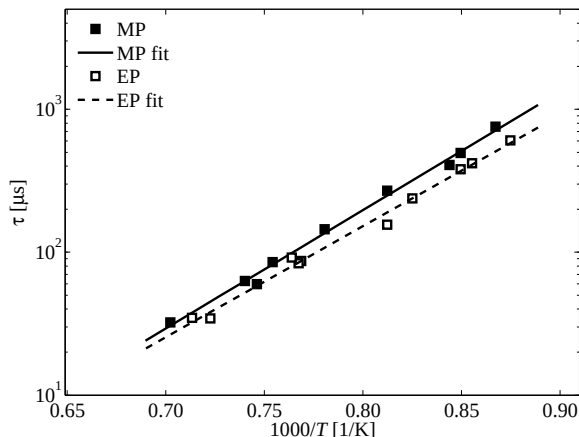


Figure 1: Methyl propanoate (MP) and ethyl propanoate (EP) ignition trends for stoichiometric mixtures with argon/oxygen ratios, D , of 14.2 at 10 atm.

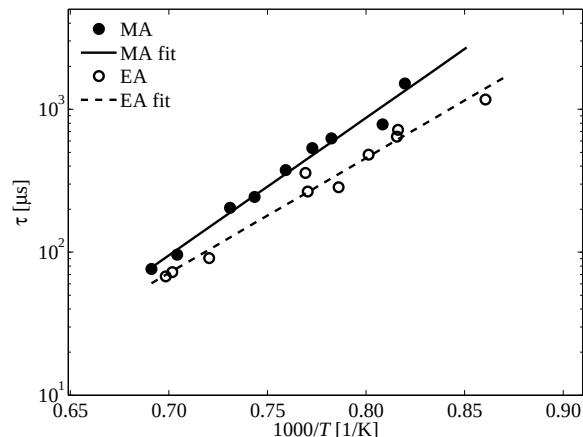


Figure 2: Comparison of methyl acetate (MA) and ethyl acetate (EA) - isomer and alkyl ester effects for rich mixtures ($\phi = 2.0$) with argon/oxygen ratios, D , of 24 at 10 atm.

50 cm apart close to the end wall. The post-reflected shock temperature is calculated using the one-dimensional shock equations in the GasEq software package [8]. Ignition delay times are determined from CH emission profiles obtained using a photodiode with a filter centered at 430 ± 10 nm. Uncertainty in the calculated temperature results from the uncertainties in the shock velocity and composition of the combustible gas. It is estimated that the average temperature uncertainty in this work is between 10 K and 25 K. In this study, ignition delay times are obtained for EA and EP while the other data are obtained from previous work in our laboratory on alkyl ester ignition [7, 9, 10, 6].

3 Results and discussion

The results of the relative behavior are presented as ignition delay times plotted against inverse temperatures for test mixtures with the same equivalence ratio, ϕ , argon/oxygen ratio, D , and nominal pressures, p . Variations in the post-reflected shock pressure are corrected by a power-law based on the known dependence of ignition delay times on pressure:

$$\tau \propto p^\gamma \quad (1)$$

where γ is determined from correlating ignition delay times at various pressures.

Figure 1 shows the ignition delay times of methyl propanoate, MP, and ethyl propanoate at an average pressure of 10 atm for stoichiometric mixtures with argon/oxygen ratio of 14.2. The data for MP are obtained from Ref. [10] while the EP data are from this study. The ignition delay times of MP are approximately 20% longer than those of EP. The increased reactivity of EP is thought to be associated with the presence of the ethyl group bonded to the carboxylic acid part of the ester. The ethyl group, with a secondary C-H bond site offers a more vulnerable site for attack by H-abstrating radicals such as H, OH, HO_2 and CH_3 . Further, as shown by El Nahas et al. [11], the concerted elimination of ethene and propionic acid in EP is more favorable than other unimolecular reactions that these esters can undergo. This leads to increased reactivity especially at reaction onset when the radical pool is not high in concentration. The analogue reaction is not possible for MP.

The same trend is observed for methyl and ethyl esters of acetic acid, MA and EA as shown in Fig. 2. The MA data are from Ref. [10]. In this case, the ignition delay times of MA are approximately

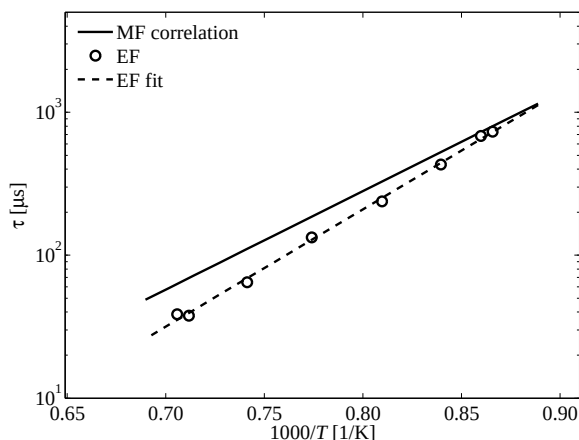


Figure 3: Methyl and ethyl formate ignition trends for stoichiometric mixtures with argon/oxygen ratios, D , of 18.8 at 12 atm. The methyl formate correlation is based on a previous study [7].

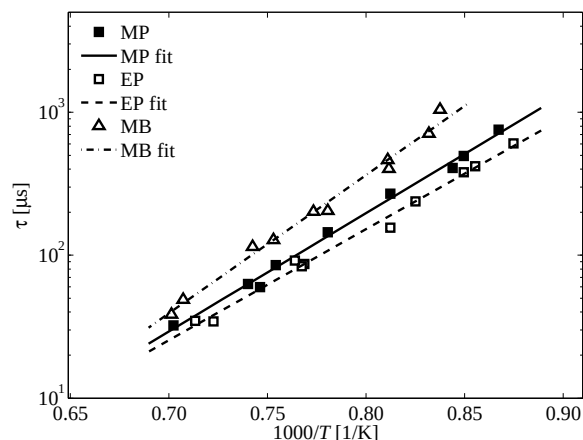


Figure 4: Comparison of MB, MP and EF - isomer and alkyl ester effects for stoichiometric mixtures with argon/oxygen ratios, D , of 14.2 at 10 atm.

40% longer those observed for EA, especially at lower temperatures. In Ref. [10], it was observed that MA has the longest ignition delay times compared to other methyl esters of C1-C4 alkanolic acids. The increased effect of the ethyl group here seems to emphasize the significance of non-terminal C-H bonds in enhancing the reactivity of these esters.

In Fig. 3 a correlation developed for MF ignition [7] has been used to compare to ignition data for EF from Ref. [6]. Consistently, the ethyl ester, EF is found to be more reactive than the methyl ester, MF. The ignition delay times of MF are longer by approximately 25%. It is possible that the absence of C-H bonds in the formate group modifies the methyl/ethyl ester trends in these formates. It is also worth noting that the global activation energy of MF was found to be lower than other methyl esters in Ref. [10].

The methyl/ethyl effect as well as isomer effects are illustrated in Fig. 4, where ignition data for MB from Ref. [9] have been used to compare with MP and EP. Similar to observations by Metcalfe et al. [5] at lower pressures of 1 atm and 4 atm, EP ignites more readily than its ester isomer, MB under the conditions investigated. With respect to MP, MB shows longer ignition delay times. The reason for this behavior is not completely understood.

Extension of this work to other combustion properties is required for better understanding of the role the alkyl group has in the oxidation of alkyl esters. The investigation of combustion properties can complement the evaluation of alternative alcohols for transesterification of fatty acid into biodiesel. However, the gas phase combustion properties must also be considered along with the physical properties of the resulting esters. Properties such as fuel viscosity and vapor pressures will affect injection, atomization and droplet evaporation. It seems possible that ethyl ester oxidation will be accompanied by higher concentrations of intermediate organic acid species which may present increased demands on material compatibility. These issues need to be addressed as progress is made towards a more sustainable biodiesel energy economy.

4 Conclusion

The relative ignition behavior of a series of short-chain methyl and ethyl esters is presented based on new shock tube ignition data and published ignition delay times by the current authors. Comparison

is based on the shock ignition of homogeneous gas-phase mixtures of esters, oxygen and argon under the constraint of constant equivalence ratio, argon/oxygen ratio and nominal pressure over a range of temperatures. It is observed that ethyl esters generally have shorter ignition delay times than the methyl esters of the same carboxylic acid. This increased reactivity of the ethyl esters is thought to be linked to the presence of the ethyl group which provides a weaker C–H site for H abstraction reactions as well as further reactivity enhancement through the more favorable elimination of ethene by concerted unimolecular reaction to yield the corresponding carboxylic acid. In the case of methyl and ethyl ester isomers, ethyl esters have shorter ignition delay times for reasons similar to the aforementioned.

5 Acknowledgements

Support by the Natural Sciences and Engineering Research Council of Canada is acknowledged. Useful discussions with the other members of the Shock Wave Physics Group at McGill University are gratefully acknowledged.

References

- [1] A. Demirbas. Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey. *Energ Convers. Manag.*, 44(13):2093–2109, 2003.
- [2] B. Baiju, M.K. Naik, and L.M. Das. A comparative evaluation of compression ignition engine characteristics using methyl and ethyl esters of karanja oil. *Renewable Energy*, 34(6):1616–1621, 2009.
- [3] C.L. Peterson, D.L. Reece, J.C. Thompson, S.M. Beck, and C. Chase. Ethyl ester of rapeseed used as a biodiesel fuel—a case study. *Biomass and Bioenergy*, 10(5-6):331 – 336, 1996.
- [4] H. Joshi, B.R. Moser, J. Toler, and T. Walker. Preparation and fuel properties of mixtures of soybean oil methyl and ethyl esters. *Biomass and Bioenergy*, 34(1):14–20, 2010.
- [5] W.K. Metcalfe, S. Dooley, H.J. Curran, J.M. Simmie, A.M. El-Nahas, and M.V. Navarro. Experimental and modeling study of C₅H₁₀O₂ ethyl and methyl esters. *J. Phys. Chem. A*, 111:4001–4014, 2007.
- [6] B. Akih-Kumgeh and Jeffrey M. Bergthorson. Ignition of C3 oxygenated hydrocarbons and chemical kinetic modeling of propanal oxidation. *Combust. Flame*, 2011. in press.
- [7] B. Akih-Kumgeh and Jeffrey M. Bergthorson. Shock tube study of methyl formate ignition. *Energy Fuels*, 24:396–403, 2010.
- [8] B. Akih-Kumgeh and Jeffrey M. Bergthorson. Comparative high temperature ignition study of C1-C4 alkanic acid methyl esters. *Combust. Flame*, 2011. in press.
- [9] C. Morley. *A Chemical Equilibrium Program for Windows*. <http://www.arcl02.dsl.pipex.com>. Accessed 22 June, 2009.
- [10] B. Akih-Kumgeh and Jeffrey M. Bergthorson. Comparative study of methyl butanoate and *n*-heptane high temperature autoignition. *Energy Fuels*, 24:2439–2448, 2010.
- [11] A.M. El-Nahas, M.V. Navarro, J.M. Simmie, J.W. Bozzelli, H.J. Curran, S. Dooley, and W. Metcalfe. Enthalpies of formation, bond dissociation energies and reaction paths for the decomposition of model biofuels: Ethyl propanoate and methyl butanoate. *J. Phys. Chem. A*, 111:3727–3739, 2007.