

TRENDS AND SIMILARITIES IN C1-C4 PRIMARY ALCOHOL HIGH-TEMPERATURE IGNITION

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Abstract

A review of shock tube ignition of primary alcohols from methanol to *n*-butanol is presented. Most of these literature data were obtained in studies of individual alcohols. Recent work published by the current authors focused on the comparative study of these alcohols, showing similarity in their ignition behavior. This similarity is also observed when ignition delays obtained by other groups under the same conditions are compared. Further comparison is carried out using ignition correlations obtained in the previous study by the current authors. A similar approach in the study of flame propagation of methanol, ethanol and *n*-butanol was reported by Veloo et al. [Veloo et al., *Combust. Flame*, 157 (2010) 1989-2004], concluding that under lean conditions the flames of these alcohols propagate with the same velocity. The same trend was observed under rich conditions, apart from methanol flames which were found to propagate faster. However, the comparable behavior is not fully captured by the various literature mechanisms of these fuels. The observed similarity, which is not obvious from the analysis of individual alcohols, can be employed in the development, validation and optimization of their detailed and reduced chemical kinetic models. Furthermore, this similarity can be useful in the practical design and modification of engine systems for flexible alcohol-based fuels.

1. Introduction

Primary alcohols are among the emerging alternative fuels for transportation. Among these, ethanol has received much attention in the fundamental studies of its combustion properties as well as in practical combustion systems such as spark-ignition engine. Other alcohols have become of great interest, as alternative production methods and biomass sources are being investigated for improved sustainability. *n*-Butanol is of particular interest because of its higher energy content, a property which compares poorly relative to gasoline for the lower primary alcohols. The physical properties of *n*-butanol also compare favorably to those of conventional gasoline so that it can be used in existing gasoline engines with minimum modifications.

System-level tests are being carried out with these fuels in order to determine compatibility, proof of combustion concepts and to determine the relative emission levels. However, there is still need for fundamental research on the combustion properties of these fuels. Gas-phase combustion chemistry research in this area is aimed at constructing comprehensive chemical kinetic models which can enable numerical simulation of alcohol combustion with the goal of optimizing designs, predicting engine combustion dynamics and evaluating emission levels. This requires extensive validation of the developed models over a wide range of conditions. The task is further complicated by the wide variety of primary and branched-chain alcohols which could be present in practical fuels. There is therefore a need to investigate the relative combustion behavior of these fuels in order to use a wider range of experimental data to constrain the chemical kinetic models during development, validation and optimization.

One of the most important combustion properties relevant to engine combustion is the ignition behavior of the fuel. Knowledge of the ignition property is necessary for the proper design of the combustion chamber as well as associated combustion control systems. Ignition delay times are also used extensively in the development and validation of chemical kinetic models. In this light, a systematic comparison of the ignition properties of a series of fuels and fuel surrogates can benefit the overall model development effort, especially when similarity is suspected.

Advances in the combustion studies of biofuels, especially alcohols and biodiesel, have recently been reviewed by Kohse-Hoöinghaus et al. [1], highlighting the spectrum, level of success and persisting challenges in the mechanistic description of the combustion chemistry of these alternative fuel sources. In this work, the authors review the high-temperature ignition of primary alcohols from methanol to *n*-butanol. They seek to uncover trends and similarities in the ignition of these alcohols. Based on the results earlier reported by the same authors in Ref. [2], experimental correlations are used to compare with other data. Ignition studies of each of the alcohols is first reviewed, followed by a comparison of their ignition properties.

2. Literature Review

Methanol, the simplest of primary alcohols, has been investigated in shock tubes and flames. The shock ignition properties were investigated for various compositions at pressures up to 5 atmosphere in Refs. [3–5]. The shock tube data by Bowman [4] have been used in the development and optimization of chemical kinetic models for methanol combustion by Held et al. [6] and Li et al. [7]. However, these data were obtained at very dilute conditions, with over 90% Ar. Ignition data at higher pressures and for fuel/air mixtures have been reported by Fieweger et al [8]. Recent ignition delay times at pressures up to 10 atm and dilution levels of 85% and above have been reported by the current authors in the framework of a comparative study [2].

Ethanol ignition in shock tubes has also been studied by various authors as reviewed by Noorani et al. [2]. Early shock tube studies of ethanol were reported by Natarajan and Bhaskaran [9] and Dunphy and Simmie [10]. These data were useful targets in chemical kinetic model development such as by Marinov [11]. New data over a wider range of pressures and dilution have been reported [2, 12, 13]. In the study in Ref. [12], the modification of ethanol ignition by the additives, isopropyl nitrate and isopropyl formate, is also investigated.

The third alcohol, *n*-propanol has received relatively less attention in terms of its high temperature ignition. An experimental and modeling study of *n*-propanol, compared to iso-propanol, has been reported by Johnson et al. [14]. The ignition data in this study were obtained under atmospheric conditions under very dilute conditions. New data have been reported by the current authors [2]. A similar modeling study addressing the isomer effects of *n*-propanol and iso-propanol has been carried out by Frassoldati et al. [15]. These studies confirm the reduced reactivity of iso-propanol, compared to *n*-propanol. The difference in reactivity is linked to the structural differences in these two isomers.

The higher energy density of *n*-butanol has generated interest in the research of its combustion properties. Ignition data of *n*-butanol have been reported by Moss et al. [16], Black et al. [17], the current authors [2] and Heufer et al. [18]. Black et al. [17] also proposed a chemical kinetic model. Other chemical kinetic models by Sarathy et al. [19] and Harper et al. [20] have been suggested. As observed by Heufer et al. [18], predicted ignition delays by both models are generally longer than measured ignition delays at higher pressures. These trends have also been observed in the simulations presented in Ref. [2]. Some of the results

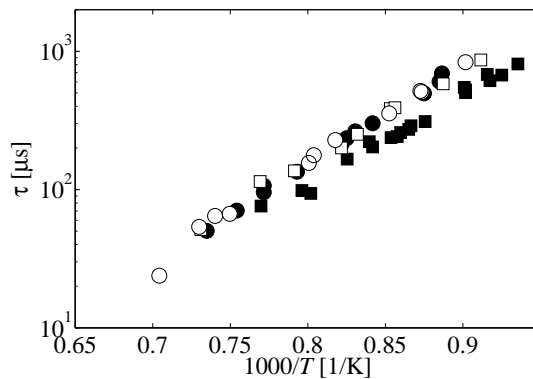


Fig. 1: Comparison of C1-C4 primary alcohol ignition for stoichiometric fuel in oxygen/argon mixtures with argon/oxygen ratio, D , of 10 at an average pressure of 10 atm (adapted from Noorani et al. [2]). Methanol (■), ethanol (●), n -propanol (□) and n -butanol (○).

reviewed above will be presented in the next section, beginning with the comparative study by the current authors [2].

3. Comparison of ignition behavior

Noorani et al. [2] carried out a systematic study of the relative ignition behavior of the first four primary alcohols from methanol to n -butanol. In their study, the equivalence ratio, ϕ , argon/oxygen ratio, D , and average pressure are maintained constant over a range of temperatures. These constraints also permit the comparison of trends in ignition behavior with trends in laminar burning velocity of fuel/air mixtures. The constraint, D , not only reflects the constant nitrogen/oxygen ratio in air but also sheds light on the relative importance of reactive oxygen and non-reactive collision partners in gas-phase combustion. Ignition correlations were also developed to facilitate comparison with data obtained under different conditions. In a study of methyl formate ignition, Akih-kumgeh and Bergthorson [21], showed that for the same post-reflected shock temperature, ignition delays with nitrogen as a bath gas are comparable with those of mixtures with argon as a bath gas. The correlations from their study can therefore be used to compare with ignition delays of fuel/air mixtures.

Figure 1 is adapted from Ref. [2] and shows the ignition delays of the four primary alcohols, methanol, ethanol, n -propanol and n -butanol at an average pressure of 10 atm for

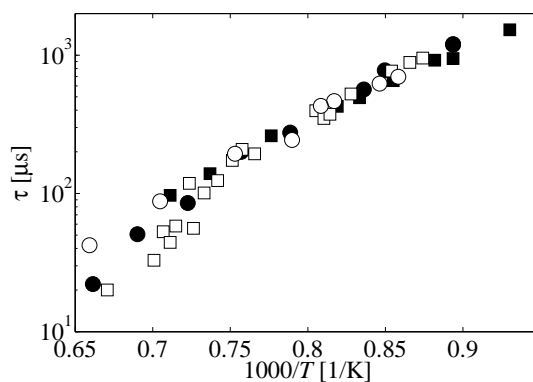


Fig. 2: Comparison of C1-C4 primary alcohol ignition for rich fuel in oxygen/argon mixtures ($\phi = 2.0$) with argon/oxygen ratio D , of 15 at an average pressure of 2 atm (adapted from Noorani et al. [2]). Methanol (■), ethanol (●), n -propanol (□) and n -butanol (○).

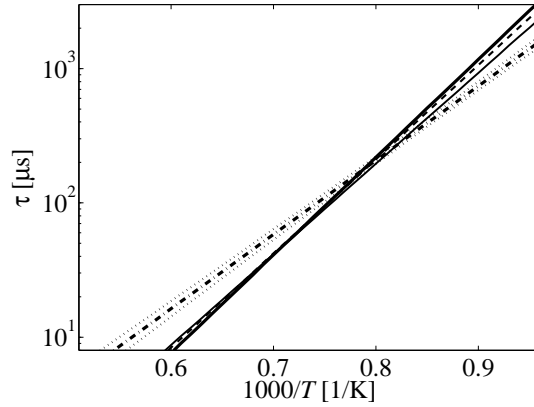


Fig. 3: Ignition delay correlations obtained by linear regression of ignition data for C1-C4 primary alcohols [2]. These are plotted here for the conditions, $\phi = 0.7$, $D = 12$, $p = 11$ atm. Methanol (dash-dotted line) and its 95% correlation prediction bounds (thin dotted lines), ethanol (dashed lines), *n*-propanol (thin solid line), and *n*-butanol (thick solid line).

stoichiometric mixtures of fuel, oxygen and argon with an argon/oxygen ratio, D , of 10. It is observed that ethanol, *n*-propanol and *n*-butanol show similar ignition behavior under these conditions. The ignition delays of methanol are also comparable, especially at higher temperature but a lower temperature sensitivity or activation energy is observed. In Fig. 2, the same trend is observed for a rich mixture with slightly higher dilution, at an average pressure of 2 atm. In this case, all four alcohols show strong similarities in ignition behavior.

In order to extend the results in their study to other conditions, Noorani et al. [2] developed ignition correlations for the four fuels. Figure 3 shows a comparison of the ignition delay correlations, together with the 95% prediction bounds for the methanol correlation. Unlike the other three alcohols, methanol is characterized by a weaker global activation energy. This makes the relative ignition behavior dependent on the temperature range. At lower temperatures, methanol is slightly more reactive, becomes closely similar at intermediate temperatures and at much higher temperatures, appear to be more slightly resistant to ignition.

The similarity observed in experiments is not quite reflected in the model predictions. Figure 4 shows an instance of comparing model predictions to the experimental data, using selected literature models for each of the fuels. It is observed that whereas the methanol mechanism by Li et al. [7] and the ethanol mechanism by Marinov [11] show reasonable agreement with the experimental data under these conditions, longer ignition delays are predicted for *n*-propanol and *n*-butanol. Experimental data for each of the fuels are usually limited during the development phase of a chemical kinetic model. It is therefore possible to take advantage of the comparable ignition and flame propagation to expand the dataset for development and validation of chemical kinetic models.

The ignition delay correlations by Noorani et al. [2] will now be used to compare with other literature data on shock tube ignition of these alcohols. In Fig. 5, ignition delays of stoichiometric methanol/air mixtures at an average pressure of 13.2 atm by Fieweger et al. [8] are compared with the methanol ignition correlation by Noorani et al. [2]. It shows that at higher temperatures, the correlation predictions are in closer agreement with the literature data, but are shorter than measured data at lower temperatures, mostly due to a difference in the overall activation energy. The global activation energy is higher in the data by Fieweger et al. [8]. The trend is different for ethanol as seen in Fig. 6, where excellent

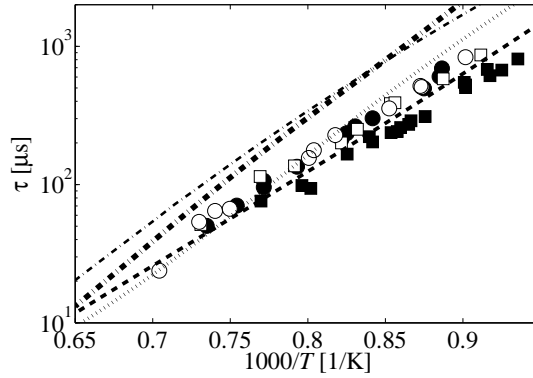


Fig. 4: Comparison of observed ignition delays with model predictions for stoichiometric fuel in oxygen/argon mixtures with argon/oxygen ratio, D , of 10 at an average pressure of 10 atm (adapted from Noorani et al. [2]). Experiments: methanol (■), ethanol (●), n -propanol (□) and n -butanol (○). Simulations: methanol [7] (dashed lines), ethanol [11] (dotted lines), n -propanol [14] (thin dash-dotted lines) and n -butanol [19] (thick dash-dotted lines).

agreement is observed between the correlation prediction and three other sets of ignition delays from the literature. One also observes that, although the study by Heufer and Olivier [13] uses air as the oxidizer, the correlation obtained from linear regression of ignition delays of alcohols in oxygen and argon mixtures, does capture the measured data.

Figure 7 shows the comparison between the n -propanol data by Johnson et al. [14] and the correlation prediction. Although the correlation predicts slightly longer ignition delay times, there is overall good agreement with the literature data. In the case of n -butanol in Fig. 8, the correlation predictions are in good agreement with the literature data by Black et al. [17] and Heufer et al. [18]. In Fig. 9, the correlations are compared to recent n -butanol data at 19 atm and 22 atm by Stranic et al. [22]. It should be noted that the correlations were developed based on ignition data obtained at temperatures above 1000 K. Thus, at temperatures above 1000 K, predictions by the correlations are in close agreement with experimental measurements. However, at temperatures below 1000 K, the onset of low-temperature ignition is observed, characterized by a possible negative-temperature coefficient behavior.

The ignition delays of ethanol/air by Heufer and Olivier [13] and n -butanol/air by Heufer et al. [18] were obtained under similar conditions using the same shock tube facility at the

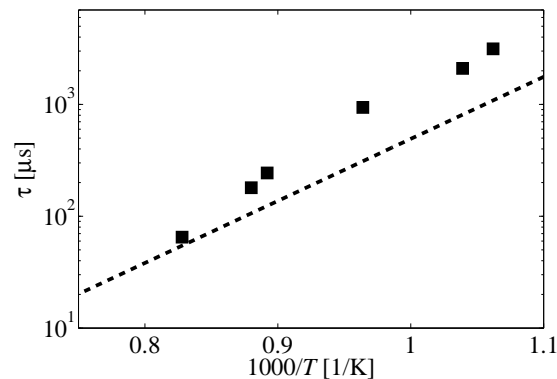


Fig. 5: Comparison of ignition delay correlation [2] (dash lines) with ignition delays of methanol by Fieweger et al. [8] (■). The conditions are $\phi = 1.0$, $D = 3.76$ and $p = 13.2$ atm.

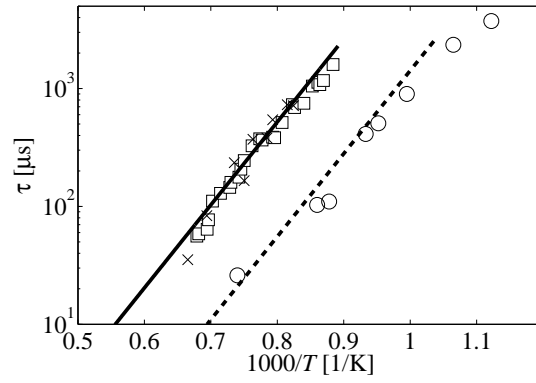


Fig. 6: Comparison of ignition delay correlation [2] with other literature data: (\square) Dunphy and Simmie [10] , (\times) Akih-Kumgeh and Bergthorson [12] (in both cases conditions are: $\phi = 0.5$, $D = 12.2$ and $p = 3.3$ atm, corresponding correlation is the solid line) and (\circ) Heufer and Olivier [13] (conditions are: $\phi = 1.0$, $D = 3.76$ and $p = 19$ atm, corresponding correlation is the dashed line).

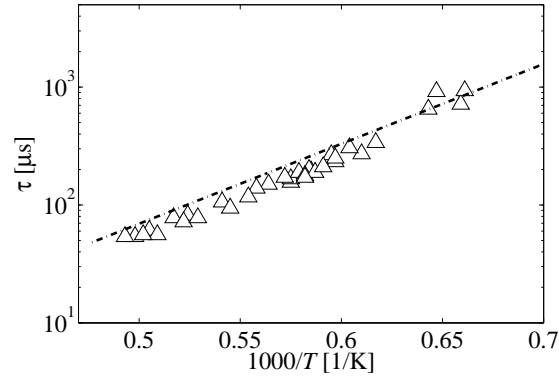


Fig. 7: Comparison of ignition delay correlation [2] (dash-dotted lines) with ignition delays of *n*-propanol by Johnson et al. [14] (\triangle). The conditions are $\phi = 2.0$, $D = 83$ and $p = 1.1$ atm

RWTH Aachen Shock Wave Laboratory, so that it is of interest to compare them directly. The relative behavior is shown in Figs. 10 and 11 at average pressures of 10-13 atm and

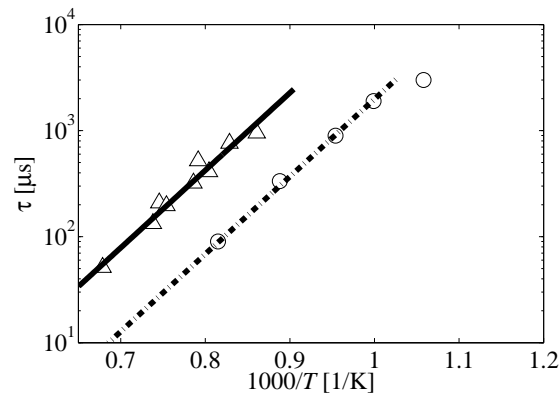


Fig. 8: Comparison of ignition delay correlation [2] with ignition delays of *n*-butanol. Black et al. [17] (\triangle), correlation (solid line), the conditions are $\phi = 1.0$, $D = 26.6$ and $p = 8$ atm; Heufer et al. [18] (\circ), correlation (dash-dotted lines), the conditions are $\phi = 1.0$, $D = 3.73$ and $p = 13$ atm.

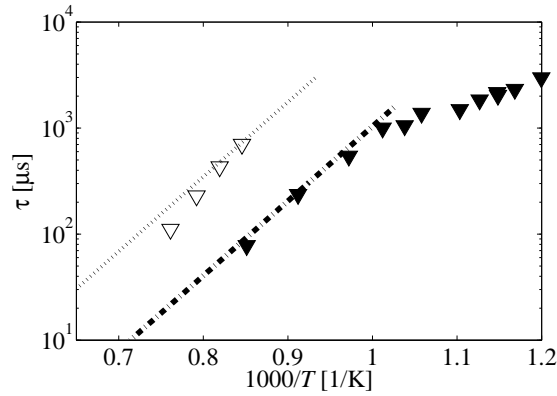


Fig. 9: Comparison of ignition delay correlation [2] with ignition delays of *n*-butanol by Stranic et al [22]. Stranic et al. [22] (▽), correlation (dotted lines), the conditions are $\phi = 0.5$, $D = 23.8$ and $p = 19$ atm; Stranic et al. [22] (▼), correlation (dash-dotted lines), the conditions are $\phi = 1.0$, $D = 3.76$ and $p = 22$ atm.

40 atm, respectively. It is found that the ignition delays of both fuels are comparable. The correlations for each fuel are also in reasonable agreement at temperatures above 1000 K as discussed above.

In the light of the previous discussions, the development and optimization of *n*-propanol chemical kinetic models could also benefit from these sets of data, as it would be expected that its ignition delays would be similar to both ethanol and *n*-butanol.

This review highlights the merit of systematic comparison of combustion properties. The emergence of trends and similarities can be exploited not only at the level of model development and refinement but also at the level of combustion system design for flexible fuels.

4. Discussion

A similar comparative study of primary alcohol reactivity was carried out by Veloo et al. [23] based on the atmospheric laminar flame propagation in fuel/air mixtures at 343 K. They found that under lean conditions methanol, ethanol and *n*-butanol had comparable laminar burning velocities. Under rich conditions, however, methanol flames were observed to be faster. From these two perspectives of comparisons, burning velocities and shock ignition, it

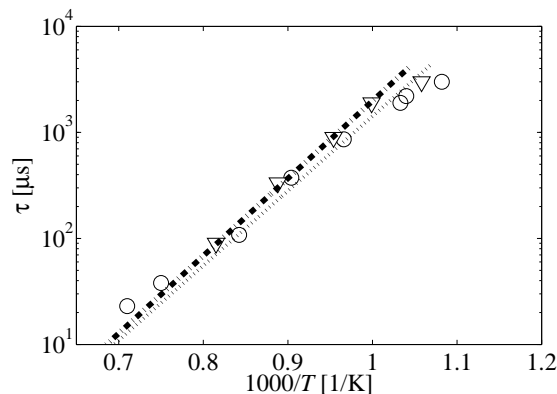


Fig. 10: Comparison of ignition delay correlation [2] with ethanol and butanol ignition data from Aachen Shock Wave Laboratory [13, 18]. Stoichiometric fuel/air mixtures at pressures of 10-13 atm (ethanol (▽) , *n*-butanol (○)). Correlations: ethanol (dotted lines), *n*-butanol (dash-dotted lines)

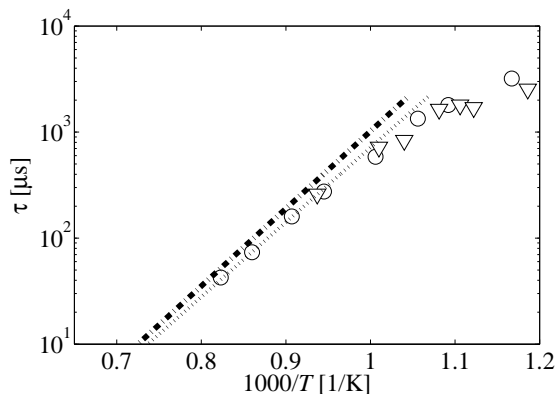


Fig. 11: Comparison of ignition delay correlation [2] with ethanol and butanol ignition data from Aachen Shock Wave Laboratory [13, 18]. Stoichiometric fuel/air mixtures at average pressures of 40 atm [ethanol (∇), *n*-butanol (\circ)]. Correlations: ethanol (dotted lines), *n*-butanol (dash-dotted lines)

can be concluded that the high-temperature ignition combustion chemistry of alcohols from ethanol to *n*-butanol is similar.

A set of rules have emerged for the development of detailed chemical kinetic models, for instance, as reported by Curran et al. [24]. Applying these rules to the development of models for the primary alcohols discussed here, will lead to mechanisms of different sizes in terms of participating chemical species and the elementary chemical reactions. Existing models for *n*-butanol are more than twice the size of ethanol models. However the observed similarities in global properties such as ignition delays and laminar burning velocities are intriguing and point to the possibility of describing the combustion of these fuels with simplified chemical kinetic schemes. The quest for such schemes can be guided by systematic studies and reviews such as attempted in this paper. Initial concentration on one fuel can yield the essential features and processes whose timescales determine the global timescales.

These similarities are not unique to the primary alcohols considered here. Similar results have been observed for longer chain *n*-alkanes with regards to ignition delays, such as those of Shen et al. [25] and laminar burning velocities, such as in Ji et al. [26]. In an earlier study by Warnatz [27], the high-temperature combustion of *n*-alkanes up to octane was investigated. The author concluded that the high-temperature combustion is controlled mostly by the C0-C2 combustion chemistry. The combustion of longer-chain hydrocarbons can be reasonably described by providing global reaction pathways which lead to the generation of radicals of the C0-C2 systems. From this perspective, the observed similarities in the the combustion properties of a class of hydrocarbons can be understood to be linked to the similarity in the composition of the radical pool and the rate parameters for their formation from the original fuel molecules. However, adequate scaling of the number of energy containing bonds is necessary. The equivalence ratio, and the diluent/oxygen ratio do provide such a scaling. This coincides with the constant air composition used in technical combustion systems. In fuel/air systems, the scaling is therefore sufficiently described by the equivalence ratio, at a given pressure and temperature. These similarities provide a guarded optimism with regards to developing size-conscious mechanisms for multi-fuel turbulent combustion simulations.

5. Conclusion

Observations on the trends of the high-temperature ignition of primary alcohols has been presented. Most studies have often concentrated on the detailed characterization of the combustion properties of individual fuels or on the comparative behavior of iso- and primary alcohols. Recent comparative approaches adopted in the literature have revealed interesting results with important implications in the study of alternative fuels of this class. Based on a detailed study by the current authors, ignition delay correlations are used to compare with data from other groups.

Under the constraints of equivalence ratio, argon/oxygen ratio and pressure, the first four primary alcohols from methanol to butanol portray similar ignition behavior. The global temperature sensitivity is found to be comparable, though a lower activation energy for methanol is observed. This trend is observed over a range of conditions including variations in pressure, equivalence ratios and dilution.

The results suggests that the key chemical processes in the oxidation of these fuels proceed with similar timescales and simplified chemical kinetic models can be sought to describe combustion properties such as ignition delays and laminar burning velocities.

Acknowledgment

Support from the Natural Sciences and Engineering Research Council of Canada and the AUTO21 Network of Centres of Excellence program is gratefully acknowledged.

References

- [1] K. Kohse-Höinghaus, P. Oßwald, T. A. Cool, T. Kasper, N. Hansen, F. Qi, C. K. Westbrook, P. R. Westmoreland, *Angew. Chem. Int. Ed.* 49 (2010) 3572–3597.
- [2] K. E. Noorani, B. Akih-Kumgeh, J. M. Bergthorson, *Energy Fuels* 24 (2010) 5834–5843.
- [3] D. F. Cooke, M. G. Dodson, A. Williams, *Combust. Flame* 16 (3) (1971) 233–236.
- [4] C. T. Bowman, *Combust. Flame* 25 (1975) 343–354.
- [5] K. Natarajan, K. A. Bhaskaran, *Combust. Flame* 43 (1981) 35–49.
- [6] T. J. Held, F. L. Dryer, *Int. J. Chem. Kinet.* 30 (1998) 805–830.
- [7] J. Li, Z. Zhao, A. Kazakov, M. Chaos, F. Dryer, J. Scire, *Int. J. Chem. Kin.* 39 (2007) 109–136.
- [8] K. Fieweger, R. Blumenthal, G. Adomeit, *Combust. Flame* 109 (1997) 599–619.
- [9] K. Natarajan, K. Bhaskaran, *Int. Shock Tube Symp.* 13 (1981) 834–842.
- [10] M. Dunphy, J. Simmie, *J. Chem. Soc.–Faraday Transactions* 87 (1991) 1691–1696.
- [11] N. Marinov, *Int. J. Chem. Kinet.* 31 (1999) 183–220.
- [12] B. Akih-Kumgeh, J. M. Bergthorson, *SAE Int. J. Fuels & Lubr.* 3 (2011) 598–609.
- [13] K. Heufer, H. Olivier, *Shock Waves* 20 (2010) 307–316.
- [14] M. V. Johnson, S. S. Goldsborough, Z. Serinyel, P. O’Toole, E. Larkin, G. Malley, H. J. Curran, *Energy Fuels* 23 (12) (2009) 5886–5898.
- [15] A. Frassoldati, A. Cuoci, T. Faravelli, U. Niemann, E. Ranzi, R. Seiser, K. Seshadri, *Combust. Flame* 157 (1) (2010) 2–16.

- [16] J. T. Moss, A. M. Berkowitz, M. A. Oehlschlaeger, J. Biet, V. Warth, P.-A. Glaude, F. Battin-Leclerc 112 (43) (2008) 10843–10855.
- [17] G. Black, H. Curran, S. Pichon, J. Simmie, V. Zhukov, *Combust. Flame* 157 (2) (2010) 363–373.
- [18] K. Heufer, R. Fernandes, H. Olivier, J. Beeckmann, O. Röhl, N. Peters, *Proc. Combust. Inst.* 33 (1) (2011) 359–366.
- [19] S. M. Sarathy, M. J. Thomson, C. Togbé, P. Dagaut, F. Halter, C. Mounaim-Rousselle, *Combust. Flame* 156 (4) (2009) 852–864.
- [20] M. R. Harper, K. M. V. Geem, S. P. Pyl, G. B. Marin, W. H. Green, *Combust. Flame* 158 (1) (2011) 16–41.
- [21] B. Akih-Kumgeh, J. M. Bergthorson, *Energy Fuels* 24 (2010) 396–403.
- [22] I. Stranic, D. P. Chase, J. T. Harmon, S. Yang, D. F. Davidson, R. K. Hanson, in: *Proceedings of the 7th US National Meeting, Combustion Institute, paper # 1B11*, 2011.
- [23] P. S. Veloo, Y. L. Wang, F. N. Egolfopoulos, C. K. Westbrook, *Combustion and Flame* 157 (10) (2010) 1989–2004.
- [24] H. Curran, P. Gaffuri, W. Pitz, C. Westbrook, *Combust. Flame* 114 (1998) 149–177.
- [25] H.-P. Shen, J. Steinberg, J. Vanderover, M. Oehlschlaeger, *Energy Fuels* 23 (2009) 2482–2489.
- [26] C. Ji, E. Dames, Y. L. Wang, H. Wang, F. N. Egolfopoulos, *Combustion and Flame* 157 (2) (2010) 277–287.
- [27] J. Warnatz, *Proc. Combust. Inst.* 20 (1) (1985) 845–856.