Methane and hydrogen ignition with ethanol and butanol admixtures

A V Eremin¹, N A Matveeva¹,² and E Yu Mikheyeva¹,²

¹ Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
² Bauman Moscow State Technical University, 2nd Baumanskaya Street 5, Moscow 105005, Russia
E-mail: nataliematveeva1@gmail.com

Abstract. This work is devoted to the investigation of combustion of simple and complex gaseous fuels: methane and hydrogen with admixtures of the most promising alcohols: ethanol and butanol. The process of ignition of investigated blends behind reflected shock waves in the temperature range of 1000–1600 K and pressure range of 4.5–6 bar was studied. The temperature dependences of ignition delay times for stoichiometric methane–oxygen–ethanol (or butanol) and hydrogen–oxygen–ethanol (or butanol) mixtures diluted in argon were obtained. The possible kinetic description is discussed.

1. Introduction
The great attention is paid to investigation of alternative and renewable fuel due to necessity to ensure the environmental safety of energy production. Strengthening of requirements for the concentration of emissions of the greenhouse gases and soot particles from the combustion of hydrocarbons requires the development of new fuels. The fossil fuels are considered as the main source of greenhouse gas formation. Alcohols are supposed as the perspective additives for different fuels and as the fuels themselves because they can be synthesized from the renewable vegetable sources. In particular, ethanol is widely used as automotive fuel in Brazil. Ethanol can operate at high compression ratios as opposed to other various hydrocarbons (paraffins, aromatics, olefins, naphthenes). Ethanol also provides the required combustion characteristics in a conventional and innovative engines [1], reducing the concentration of harmful emissions into the atmosphere of the fuel combustion products at the same time. Butanol has even some advantages over ethanol: larger energy density, less hygroscopic and volatile, and it can be blended with gasoline in higher concentrations. In [2] the operation of the diesel engine on a mixture of diesel fuel with ethanol and butanol in transient conditions was investigated. This study shows that the using mixtures with alcohols decreases the amount of soot and CO, at the same time the emission of unburned hydrocarbon and aldehydes (CH₂O, C₂H₅O, C₃H₆O etc) increases. Based on [1], it can be argued that it is possible to use ethanol and butanol as an additive to the fuel in internal combustion engines without substantial modification of the structure. For the approbation of kinetic oxidation of alcohols mechanisms it was conducted a large number of experiments in the various reactors: flames, shock tubes etc. (the list of works is presented in the review [1]). However, the kinetic ways of fuel oxidation for different fuels and alcohols can vary considerably depending on the composition of the co-fuel mixture.
In the present study, the ignition process of methane and hydrogen mixtures with ethanol and butanol in a shock tube reactor was investigated for the first time. In the first part of work the temperature dependence of ignition delay times of stoichiometric mixtures methane–oxygen, hydrogen–oxygen, ethanol–oxygen, butanol–oxygen and methane–ethanol–oxygen, methane–butanol–oxygen, hydrogen–ethanol–oxygen, hydrogen–butanol–oxygen mixtures were measured. In the second part of study the testing of the kinetic mechanisms from literature on new experimental data was carried out.

2. Experimental methods
The experiments were performed behind reflected shock waves in a conventional diaphragm type shock tube with an inner diameter of 50 mm. The initial parameters behind the reflected shock wave were calculated from the measured velocity of the incident shock wave with one-dimensional gas dynamic model without consideration of chemical reactions. The time profile of pressure was recorded by two calibrated PCB113B26 piezoelectric pressure sensors. The ignition delay time was detected as simultaneous peaks at pressure profile and OH chemiluminescence emission at 306–310 nm, the example of typical signals is presented in figure 1.

3. Kinetic modeling
The first kinetic mechanism for high temperature ethanol oxidation suggested in [3] is in a good agreement with previously obtained shock tube experimental data [4, 5]. Some kinetics mechanisms for ethanol were suggested in a last decade [6–9]. In the work [6] kinetic mechanism is based on reactions from [3] with some updated rate constants of reactions of ethanol with radicals H, O, OH, CH$_3$ from quantum chemical calculations [10–14] and GRIMech [15] and validated on low pressure laminar premixed flames and jet-stirred reactor data. In the work [7] the kinetic mechanism of ethanol combustion included in a general scheme describing the pyrolysis and oxidation of hydrocarbons was developed. In the work [8] the kinetic mechanism was validated against experimental data of premixed laminar flames of ethanol and methane. In the work [9] the kinetic mechanism was validated against rapid compression machine results. Thus, in the present study the mechanisms from [3, 6–9] were tested on obtained shock tube data with ethanol admixture. For modeling of ignition delay times with butanol the kinetic mechanisms from [16–18] were used. Besides that for the modeling of combustion of methane and hydrogen the well known mechanisms—GRIMech [15] and [19] were used.

The experimental conditions were simulated in Chemkin program in the constant-pressure reactor using kinetic mechanisms from literature discussed above. Since in all experiments the observed pressure rise in the moment of ignition coincided with a rapid rise of the concentration of OH radical, the theoretical ignition delays were calculated in all investigated combustible mixtures as the time from the beginning of the calculation until a sharp increase in the concentration of OH radicals.

4. Results
The temperature dependences of ignition delay times are presented in figures 2–7, 9–10.

One can see that most mechanisms are in a good agreement with experimental data for methane–oxygen and hydrogen–oxygen mixtures (figures 2 and 3). However [3] shows underestimation and [8] slight overestimation of ignition delay time for methane.

For ethanol–oxygen mixture (figure 4) the kinetics from [3] and [6] gives good coincidence with experiment and the other mechanisms show slight underestimation. Additionally experimental data from [4, 5] added to figure 4. One can see a good agreement of new experimental data with literature data. For mixture of methane–ethanol–oxygen (figure 5) the kinetics from [7] and [9] fits well, the other mechanisms show slight overestimation.
Figure 1. Experimental time profiles of pressure (black curve) and OH* emission at 306–310 nm (green curve) obtained in the mixture 6.7%H₂ + 3.3%O₂ + Ar, T₅ = 1032 K, p₅ = 5.9 bar.

Figure 2. Ignition delay times measured and calculated for the mixture 3.3%CH₄ + 6.7%O₂ + Ar, p = 5.3 bar: 1—experiment, this work; 2—Marinov [3]; 3—Ranzi [7]; 4—Tran [8]; 5—Curran [9]; 6—Leplat [6]; 7—GRIMech [15]. Points—experimental data; curves—results of kinetic modeling.

For mixture hydrogen–ethanol–oxygen the only mechanism from [3] shows good agreement, the other ones underestimate the ignition delay time (see figure 6). One of possible explanation of such disagreement between experimental data and most mechanisms is the increase of influence of reactions of ethanol with active radicals O, OH, HO₂. Hydrogen ignites earlier than ethanol at our experimental conditions (see figures 3 and 4) that leads to acceleration of reactions of
Figure 3. Ignition delay times measured and calculated for the mixture $6.7\% \text{H}_2 + 3.3\% \text{O}_2 + \text{Ar}$, $p = 5.8$ bar: 1—experiment, this work; 2—Marinov [3]; 3—Ranzi [7]; 4—Tran [8]; 5—Curran [9]; 6—Sarathy [16]; 7—Hanson [19]. Points—experimental data; curves—results of kinetic modeling.

Figure 4. Ignition delay times measured and calculated for the mixture $2.5\% \text{C}_2\text{H}_5\text{OH} + 7.5\% \text{O}_2 + \text{Ar}$, $p = 5.2$ bar: 1—experiment, this work; 2—Marinov [3]; 3—Ranzi [7]; 4—Tran [8]; 5—Curran [9]; 6—Leplat [6]; 7—experiment $2.5\% \text{C}_2\text{H}_5\text{OH} + 7.5\% \text{O}_2 + \text{Ar}$, $p = 2.0$ atm, Natarajan [4]; 8—experiment $1.25\% \text{C}_2\text{H}_5\text{OH} + 3.75\% \text{O}_2 + \text{Ar}$, $p = 4.5$ bar, Dunphy [5]. Points—experimental data; curves—results of kinetic modeling.

ethanol oxidations. A analysis of difference of the rate constants of reactions

$\text{C}_2\text{H}_5\text{OH} + \text{O} \rightarrow \text{products}$,
Figure 5. Ignition delay times measured and calculated for the mixture 1.5%CH$_4$ + 1.5%C$_2$H$_5$OH + 7.5%O$_2$ + Ar, $p = 5.2$ bar: 1—experiment, this work; 2—Marinov [3]; 3—Ranzi [7]; 4—Tran [8]; 5—Curran [9]; 6—Leplat [6]. Points—experimental data; curves—results of kinetic modeling.

Figure 6. Ignition delay times measured and calculated for the mixture 1%C$_2$H$_5$OH + 4%H$_2$ + 5%O$_2$ + Ar, $p = 5.5$ bar: 1—experiment, this work; 2—Marinov [3]; 3—Ranzi [7]; 4—Tran [8]; 5—Curran [9]. Points—experimental data; curves—results of kinetic modeling.

\[
\begin{align*}
C_2H_5OH + H &\rightarrow \text{products}, \\
C_2H_5OH + OH &\rightarrow \text{products}, \\
C_2H_5OH + HO_2 &\rightarrow \text{products}
\end{align*}
\]
Figure 7. Ignition delay times measured and calculated for the mixtures $1.5\%\text{C}_4\text{H}_9\text{OH} + 9\%\text{O}_2 + \text{Ar}$, $p = 5.6$ bar: 1—experiment, this work; 3—Sarathy [16]; 5—Curran [17]; 7—Ranzi [18]; 0.5$\%\text{C}_4\text{H}_9\text{OH} + 3\%\text{O}_2 + \text{Ar}$, $p = 5.3$ bar: 2—experiment, this work; 4—Sarathy [16]; 6—Curran [17]; 8—Ranzi [18]; 9—experiment $0.67\%\text{C}_4\text{H}_9\text{OH} + 4\%\text{O}_2 + \text{Ar}$, $p = 3$ atm, Hanson [20]; 10—experiment $0.6\%\text{C}_4\text{H}_9\text{OH} + 3.6\%\text{O}_2 + \text{Ar}$, $p = 8$ atm, Curran [17]. Points—experimental data; curves—results of kinetic modeling.

Figure 8. Experimental time profiles of pressure (black curve) and OH* emission at 306–310 nm (green curve) obtained in the mixture $1\%\text{C}_4\text{H}_9\text{OH} + 2\%\text{H}_2 + 7\%\text{O}_2 + \text{Ar}$, $T_5 = 1141$ K, $p_5 = 5.7$ bar.

used in current kinetic mechanisms was done. It turned out that the most sensitive for ignition delay time are the following reactions:
Figure 9. Ignition delay times measured and calculated for the mixture 0.5\%C\textsubscript{4}H\textsubscript{9}OH + 2\%CH\textsubscript{4} + 7\%O\textsubscript{2} + Ar, $p = 5.0$ bar: 1—experiment, this work; 2—Sarathy [16]; 3—Curran [17]; 4—Ranzi [18]. Points—experimental data; curves—results of kinetic modeling.

$$
\text{C}_2\text{H}_5\text{OH} + \text{HO}_2 \rightarrow \text{C}_2\text{H}_4\text{OH} + \text{H}_2\text{O}_2,
$$

$$
\text{C}_2\text{H}_5\text{OH} + \text{HO}_2 \rightarrow \text{CH}_3\text{CHOH} + \text{H}_2\text{O}_2.
$$

The hydrogen peroxide subsequently decomposes, resulting in the formation of two reactive hydroxyl radicals in a chain branching reaction. However, an attempt to use the greatest rate constants known in the literature for the reactions mentioned above resulted in a slight improvement of agreement, but did not lead to a satisfactory description of the experimental results.

The kinetic mechanisms for butanol [16,17] shows slight underestimation of the ignition delay times of butanol–oxygen, while the kinetics of [18] is not in an agreement with experimental data at all (figure 7). Additionally experimental data from [17, 20] were added to figure 7. One can see a good agreement of new experimental data with the literature data. The slopes of all experimental temperature dependences of ignition delay times are the same. The data from [20] obtained for stoichiometry mixture containing 0.67\%C\textsubscript{4}H\textsubscript{9}OH at pressure $p = 3$ atm are extremely close to results of this study for stoichiometric mixture with 0.5\%C\textsubscript{4}H\textsubscript{9}OH and pressure $p = 5.3$ bar.

Experiments in shock tube [20, 21] and rapid compression machine [22] have shown the pre-ignition pressure rise in butanol combustible mixtures. It was mentioned in the work [20] that this effect decreased at temperatures $T > 1000$ K and vanished with high dilution. In our experiments with high diluted mixtures at high temperature ($T > 1000$ K) the weak pre-ignition pressure rise was observed only in the mixture of butanol with hydrogen (figure 8).

The kinetics of [16, 17] shows excellent agreement with experimental data for butanol–methane–oxygen mixture and slightly underestimates the ignition delay times for butanol–hydrogen–oxygen mixture (figures 9 and 10). Kinetics of [18] shows different from obtained experimental data slope of temperature dependence of ignition delay time for butanol–methane–oxygen (similar to butanol–oxygen) mixtures (figures 7 and 9) and overestimates the ignition delay time for butanol–hydrogen–oxygen mixture (figure 10).
5. Conclusions

New experimental data were obtained on the ignition delay times for stoichiometric methane–oxygen–ethanol (or butanol) and hydrogen–oxygen–ethanol (or butanol) mixtures diluted in argon. Existing literature kinetic mechanisms have been tested on the data. Generally a good agreement was found for experimental data and modeling results. However, a significant difference between various kinetic mechanisms and between modeling and experimental data was found for the mixture hydrogen–ethanol–oxygen. This effect could be regarded to the unaccounted increase of influence of reactions of ethanol with active radicals. The results obtained in this work can be useful for further development of the kinetic mechanisms of combustion of different fuels with alcohols.

Acknowledgments

This work was supported by the Russian Science Foundation, project No. 14-19-00025.

References

[1] Sarathy M S, Offwald P, Hansen N and Kohse-Höinghaus K 2014 Prog. Energy Combust. Sci. 44 40–102
[2] Giakoumis E G, Rakopoulos C D, Dimaratos A M and Rakopoulos D C 2013 Renewable Sustainable Energy Rev. 17 170–90
[3] Marinov N M 1999 Int. J. Chem. Kinet. 31 183–220
[4] Natarajan K and Bhaskaran K A 1981 Proc. 13th Int. Symp. Shock Tubes and Waves ed Treanor C E and Hall J G (State of University of New York) p 834
[5] Dunphy M P and Simmie J M 1991 J. Chem. Soc., Faraday Trans. 87 1691–5
[6] Leplat N, Daugaut P, Tog C and Vandooren J 2011 Combust. Flame 158 705–25
[7] Frassoldati A, Cuoci A, Faravelli T and Ranzi E 2010 Combust. Sci. Technol. 182 653–67
[8] Tran L S, Glande P A, Fournet R and Battin-Leclerc F 2013 Energy Fuels 27 2226–45
[9] Mittal G, Burke S M, Davies V A, Parajuli B, Metcalfe W K and Curran H J 2014 Combust. Flame 161 1164–71
[10] Park J, Zhu R S and Lin M C 2002 J. Chem. Phys. 117 3224–31
[11] Park J, Xu Z F and Lin M C 2003 J. Chem. Phys. 118 9990–6
[12] Park J, Xu Z F and Lin M C 2004 *J. Chem. Phys.* **120** 6593–9  
[13] Xu S and Lin M C 2007 *Proc. Combust. Inst.* **31** 159–66  
[14] Wu C W, Lee Y P, Xu S and Lin M C 2007 *J. Chem. Phys.* **111** 6693–703  
[15] Smith G P et al GRI-Mech 3.0 URL http://www.me.berkeley.edu/gri_mech/  
[16] Vasu S S and Sarathy S M 2013 *Energy Fuels* **27**(11) 7072–80  
[17] Black G, Curran H J, Pichon S, Simmie J M and Zhukov V 2010 *Combust. Flame* **157** 363–73  
[18] Frassoldati A, Grana R, Faravelli T, Ranzi E, Obwald P and Kohse-Hoinghaus K 2012 *Combust. Flame* **159** 2295–311  
[19] Hong Z, Davidson D F and Hanson R K 2011 *Combust. Flame* **158** 633–44  
[20] Stranic I, Chase D P, Harmon J T, Yang S, Davidson D F and Hanson R K 2012 *Combust. Flame* **159** 516–27  
[21] Heufer K A, Fernandes R X, Oliver H, Beeckmann J, Roehls O and Peters N 2010 *Proc. Combust. Inst.* **33** 359–66  
[22] Weber B W, Kumar K, Zhang Y and Sung C 2011 *Combust. Flame* **158** 809–19