Autoignition of Biobutanol

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1 Introduction

Biofuels provide alternative fuels for the transport sector which it is hoped will both lessen our dependence on petroleum and also minimize climate change since they consume significantly lower fossil energy and produce less greenhouse gases than gasoline/petrol or diesel. Biofuels also have the potential to reduce particulate matter emissions [1]. Thus, the European Union has, for example, mandated that biofuels should comprise 5.75% of the automotive fuel market by 2010 and 10% by 2020.

It is not likely that biofuels will totally replace conventional fuels in the foreseeable future because that would require more than 20% of the current terrestrial net primary productivity of the biosphere [2] to sustain such a target. In addition there is a major environmental concern that cheap biofuel produced in palm oil plantations will impact severely on the tropical rainforest, thus essentially wiping out whatever gains are made elsewhere.

However, there is a good case to be made for the modest usage of renewable fuels sourced from crops which are not used as human foodstuffs but also waste vegetation and recycled animals fats. In a major US study Hill et al. [3] concluded that neither bioethanol nor biodiesel could do much to address future US transportation energy demands. In a recent comprehensive study Kavalov and Peteves [4] have examined the status of biomass-to-liquid fuels in the European Union and have shown that although still in its infancy it has a much bigger production potential and hence will make a larger contribution to security and diversity of supply in addition to offering environmental benefits.

Here we report on the first ever laboratory auto-ignition studies of a biofuel — bio or n-butanol — which offers significant advantages over the current market leader, bioethanol, since it has a higher energy density and is much less water soluble.

The secondary aim of this work is a presentation of a newly constructed shock tube. These results are the first experimental data obtained in this shock tube.

2 Experimental technique

The stainless shock tube has an overall length of 8.76 m, with an internal diameter of 63 mm (2.5 inch). A double-diaphragm section divides the shock tube into a 3.0-meter long driver section and a 5.73-meter test section. The operational pressure limit of the shock tube is approximately 60 bar.

Polycarbonate films were used as diaphragms in all experiments, and shock waves were fired by the self-rupture of diaphragms. Typical attenuation of the shock wave amounts to 2–4% over a distance of 1 m.

The diagnostic system involves four pressure transducers and one photomultiplier. The speed of the incident shock wave is measured at three locations and is then extrapolated to the end-plate. The shock tube has two optical windows, one in the end-plate and one in the side-wall at a distance of 7 mm from the end-plate.
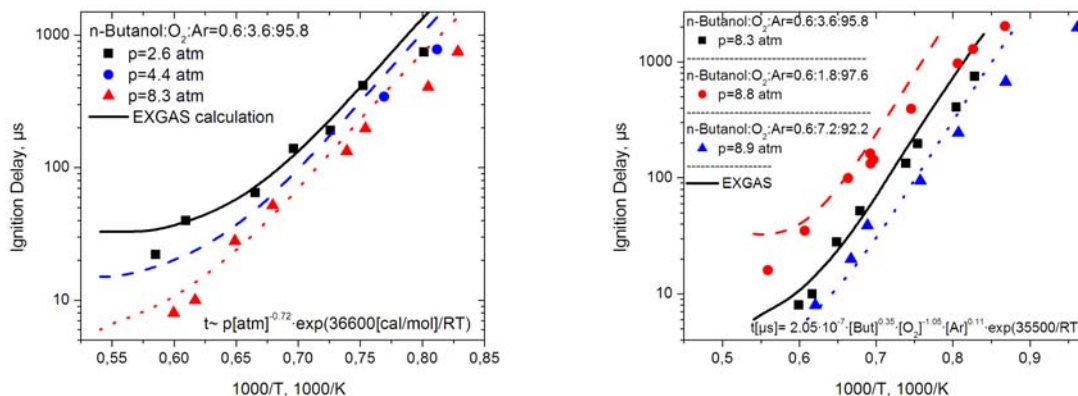
Figure 1: Ignition delay time of butanol at different pressures (left side) and equivalence ratios (right side).

Ignition delay times can be determined from time histories of pressure and/or emission at the end-plate. Ignition delay time has been defined as the time between arrival of the shock wave at the end-plate and 50%-level of the first strong peak of the light signal from the end-plate. Prior to the butanol experiments the tube was tested in experiments on n-heptane ignition; our data is in good agreement with experiments from the Hanson group [5].

Biobutanol (n-butanol) experiments have been performed at equivalence ratios of 0.5, 1 and 2 and at constant reflected shock pressures of 2.6, 4.4, and 8.5 atm over a range of temperatures from 1100 to 1800 K. The main part of the data was obtained at dilution a level of $\sim 95\%$, but one series was obtained at a dilution of 77% with argon as a diluent in all the experiments. The range of possible conditions to study the gas-phase oxidation of butanol is limited by the low vapor pressure of butanol under ambient conditions (10 mbar at 28°C). Mixtures were therefore made up with biobutanol vapour pressures well below the saturation vapour pressure.

3   Results and discussion

In order to distinguish all governing ignition factors pressure, dilution level, and equivalence ratio were varied independently in the experiments. The experimental results were compared with modelling. A kinetic model was generated using the software package EXGAS [6].

The exponent for the pressure dependence is -0.72 (Fig. 2); usually it lies between -0.5 and -1 for most hydrocarbons (~ -0.55 for all n-alkanes [7]). Meanwhile n-butanol has coefficients in the correlation expression, which are also a similar to n-alkanes:

$$\tau(\mu s) = 2.05 \times 10^{-7} [\mathrm{nC_4H_9OH}]^{0.35} [\mathrm{O_2}]^{-1.05} [\mathrm{Ar}]^{0.11} \exp\left(+35500/RT\right) \tag{1}$$

with concentrations in mol/cm^3 and the activation energy in cal mol^{-1}.

As a potential replacement of common fuels it is important that n-butanol has not only similar physical properties, but also similar kinetic characteristics to fossil fuel. It is not surprising that butanol has a similar correlation expression, because the high-temperature kinetic of saturated hydrocarbons depends on the individual properties of a fuel to a less degree. The main reactions, which define the
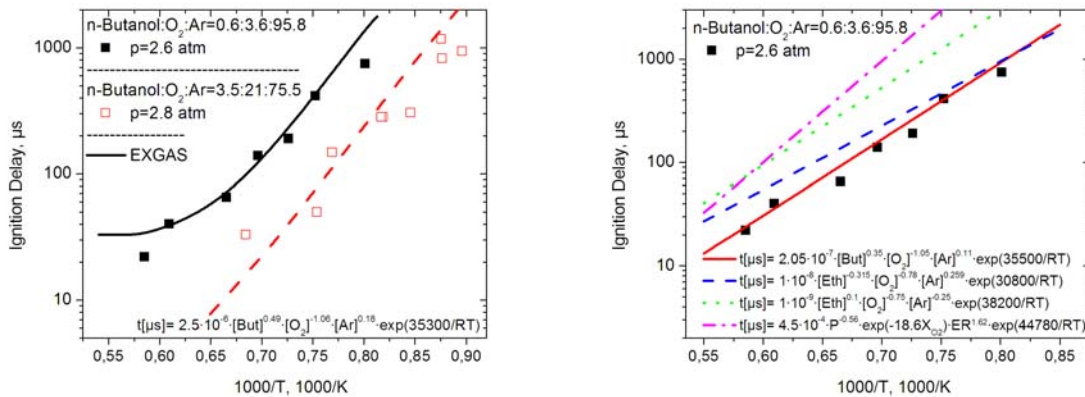
Figure 2: Ignition delay time of butanol at different level of dilution (left side) and comparison with data for ethanol and iso-octane(right side).

ignition delay time, are:

$$RH + H_2 \rightarrow \dot{R} + H_2 \tag{2}$$

$$RH + \dot{O}H \rightarrow \dot{R} + H_2O \tag{3}$$

$$RH + HO_2 \rightarrow \dot{R} + H_2O_2 \tag{4}$$

$$\dot{R} + O_2 \rightarrow Q + HO_2 \tag{5}$$

$$\dot{H} + O_2 \rightarrow \dot{O}H + O \tag{6}$$

$$\dot{C}H_3 + HO_2 \rightarrow CH_3\dot{O} + \dot{O}H \tag{7}$$

$$\dot{O}H + H_2 \rightarrow H_2O + \dot{H} \tag{8}$$

$$H_2O_2 + M \rightarrow \dot{O}H + \dot{O}H + M \tag{9}$$

$$H\dot{O}_2 + H\dot{O}_2 \rightarrow H_2O_2 + O_2 \tag{10}$$

Reactions 6-10 are the same for all hydrocarbons. The overall rate of hydrogen kinetics depend on partially only from the ratio between H and C atoms in the molecule, while the first reactions have close rates for all saturated hydrocarbons.

One particular feature of alcohols is a great influence of a reaction of uni-molecular decomposition of alcohol molecule under our conditions. It was shown by example of ethanol in work [8].

Kinetic properties of the mixture, which is close to fuel-air mixture, is more important from a practical point of view. The kinetic model has a better agreement with experimental data in case of low diluted mixture (Fig. 2). In view of the first test the automatically generated mechanism shows a good agreement with experimental data in the whole experimental range.

Butanol is a member of second generation of bio-fuels. It is important to compare it with other fuels like ethanol and iso-octane. On Fig. 2 it is plotted data derived from previous works on ethanol of Dunphy and Simmie [9], and of Natarajan and Bhaskaran [10], work on iso-octane of Oehlschlaeger *et. al* [11] (dash-dot line). For all lines it was assumed pressure of 2.6 atm, equivalence ratio of 1, and molar fraction of O_2 of 3.6%. n-Butanol has smaller ignition delay times than ethanol and iso-octane as well as octane number (RON 96). It agrees with a general tendency of a decreasing of ignition delay times and octane number with increasing of the size of the molecule. Butanol has the better physical properties than ethanol, while the kinetic properties of n-butanol are still admissible. Butanol

better tolerates water contamination and is less corrosive than ethanol and more suitable for distribution through existing pipelines for gasoline.

4   Conclusions

A new high-pressure shock tube has been built and validated in autoignition experiments on n-heptane. A preliminary set of low- and higher pressure data for bio-butanol has been obtained. The low-pressure results are in excellent agreement with on-going work in a low-pressure shock tube [12] in our laboratory.

The experimental data has been interpreted using a kinetic model and comparison with experimental data of others hydrocarbons. The kinetic mechanism, which was automatically generated by software package EXGAS [6], has the reasonable agreement with the experimental data.

n-Butanol shows faster ignition than other fuels, like ethanol and iso-octane. While n-butanol has a similar kinetic properties to other hydrocarbons in the high temperature region.

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