# Shock-tube study of the Ignition delay times of ethanol at high pressures and intermediates temperatures Experimental and numerical approaches

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Ethanol is a high performance fuel in internal combustion engines. It is a promising fuel because it burns relatively cleanly, and the carbon dioxide yield from its combustion processes is not considered for the global inventory of industrial pollutants. Several countries began, a few years ago, a "race" for the ethanol technology, Brazil, for example, is on the tip in this race in the production of ethanol and has developed and prepared vehicles to this use. Therefore, in the process of vehicles preparation the combustion process of ethanol in the engine has been one of the main focus. The present work aims at understanding the ethanol oxidation in high pressures and intermediates temperatures. This paper is composed by two parts, one experimental and other numerical approach. Ignition delay times were measured in high-pressure shock-tube facility of IVG for stoichiometric mixtures of ethanol in synthetic air, at pressure of 30 bar, covering a temperature range of 690 – 1200 K. Numerically, were imposed the same initial experimental conditions and was used the SHOCK package of CHEMKIN program. Two kinetic models for the thermal oxidation of ethanol were used and the results were compared in order to validate both kinetic models at the experimental conditions tested.

## 1. Introduction

The rapid increase of energy costs and the global warming issue have led to increased interest in alternative fuels. In this context, ethanol plays a major role as a new promising alternative fuel due to the low emission and the high availability.

Ethanol ($C_2H_5OH$) and methyl tert-butyl ether (MTBE $C_4H_9OCH_3$) are the most widely employed oxygenated fuels in the transportation sector, used both as an additive and as a neat fuel. Since 2004 on, alcohol is rapidly raising its market share because of new technologies involving multi-fuel car engines, called "Flex" by all major car manufacturers "Flex" engines work with gasoline, alcohol or any mixture of both fuels.

Additionally, ethanol and MTBE have been used as an octane number enhancer and oxygen source to reduce carbon monoxide emissions. Ethanol can be synthesized from biomass, a renewable energy source, while MTBE is obtained from isobutene, which in turn is obtained from the refining of gasoline.

The chemical kinetics of the combustion of ethanol is more complex than the kinetics of methanol [1]. While methanol has been better studied, both experimentally and theoretically,

e.g., Warnatz [2] analyzed the spark ignition of methanol using a 2D-LIF (Laser Induced Fluorescence) system; few studies have been devoted to the homogeneous combustion of ethanol ([3]; [4]; and [1]), each with a specific focus. Different mechanisms describing the ethanol combustion are available. But, there are still discrepancies in the prediction of these mechanisms. Additionally, few of them are validated against experimental data.

The main focus of this present paper is to validate two kinetic models (Marinov and Konnov mechanism) for the auto-ignition of fuel blends containing ethanol and gasoline with different proportions. At this stage of the study we report solely about the ignition delay times of pure ethanol. The ignition delay times are obtained in a heated shock-tube at temperatures ranging between 650 and 1250 K and pressures of 30 bar and at stoichiometric conditions.

## 2. Experimental

The experiments were carried out in a heated high-pressure shock tube with an internal diameter of 90 mm. It is divided by an aluminium diaphragm into a driver section of 6.1 m and a driven section of 6.4 m in length. The driven section was pumped down to pressures below $10^{-2}$ mbar. Gas mixtures were prepared by injection of liquid ethanol and subsequent complete evaporation in a stainless-steel mixing vessel. The total amount of fuel and air was controlled manometrically in order to ensure the desired equivalence ratio. The shock tube was heated to 50°C. The shock speed was measured over two intervals using three piezo-electric pressure gauges. The data were recorded with a time resolution of 0.1 μs. The temperature and pressure behind the reflected shock wave were computed from the measured incident shock speed and the speed attenuation using a one-dimensional shock-tube model (shock-tube code of the CHEMKIN package [5]). The estimated uncertainty in reflected shock temperature is less than ±25 K in the temperature and time range of our measurements. The experiments were carried out in synthetic air containing 79.5% $N_2$ and 20.5% $O_2$.

The ignition was observed by measuring pressure profiles with a piezo-electric gauge (PCB HM 112 A03) located 15 mm upstream of the end flange. Also, the *CH\** emission at 431.5 nm was selected by a narrow band pass filter and measured with a photomultiplier. All ignition delay times shown in this work were determined by extrapolating the steepest increase of the emission signal to its zero level on the time axis.

The driver gas was mixed *in-situ* by using two high-pressure mass-flow controllers (Bronkhorst Hi-Tec flow meter F-136AI-FZD-55-V and F-123MI-FZD-55-V), see Figure 1. Helium was used as the main component and Argon was added to match the acoustic impedance of the test gas. The required driver gas composition was calculated by a spreadsheet analysis prior to the experiments using equations by Oertel [6] and Palmer and Knox [7]. Concentrations of 5 to 20% *Ar* in He were required to generate tailored shock waves.
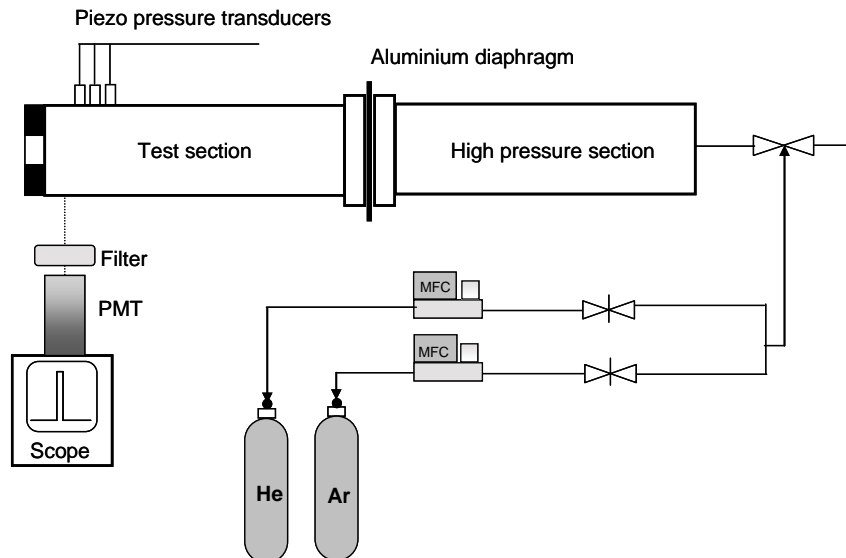
**Figure 1: Experimental setup using at IVG.**

## 3.  Results and discussions

### 3.1.  Ignition delay times

The temperature range of the present ethanol/ air ignition-delay study was 620 K $\leq T \leq$ 1180 K at pressures of about 30 bar and the fuel/air equivalence ratio, $\phi$, 1.0. All ignition delay times are summarized in an Arrhenius-representation in Figure 2. At lower temperatures (T <750 K) no ignitions occur within the measurement time observation (15 ms). The data show a linear behaviour at high temperature. At temperatures lower than 950 K the ignition delay times exhibits a slow decrease in activation energy.
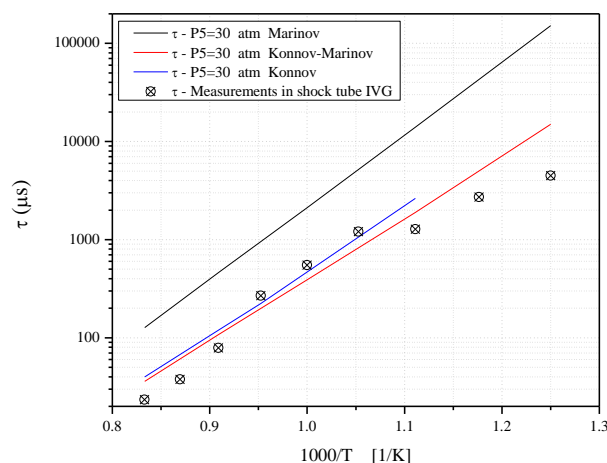


**Figure 2: Ignition delay times of ethanol in air ($\Phi$ = 1) at 30 bar. The solid lines depict simulations using Marinov, Konnov, and a blended mechanism of Marinov and Konnov mechanisms**

## 3.2.      Detailed Kinetics models

In an effort to validate available chemical mechanism against the experimental shock-tube data two mechanism are considered. The first mechanism was from Marinov [4], who developed a detailed kinetic mechanism for the high-temperature oxidation of ethanol. This mechanism was built by assembling previous mechanisms for hydrogen, methane, ethylene, ethane and propane oxidation. The main ethanol oxidation routes developed are shown in Figure 3. These oxidation routes lead ultimately to the production of methane, formaldehyde and other oxygenated hydrocarbons, whose kinetics are well treated by other detailed mechanisms (methane, etc.). The high-temperature ethanol oxidation occurs by two main routes. One route occurs by decomposition triggered by a third body collision. The decomposition reactions lead under $C$-$C$ and $C$-$O$ bond cleavage in the parent molecule $CH_3CH_2OH$ to $CH_3$-radical or to ethylene.

While the $C_2H_4$ route consumes most of the ethanol (in mass), the $CH_3$ route parameters present a higher sensitivity in calculated ignition delay times and must be determined with more care.

The other route occurs by hydrogen abstraction (*Hp, Hs, Hx* ) by a radical collision leading to $CH_2CH_2OH$, $CH_3CHOH$, and $CH_3CH_2O$. Figure 3 shows the main ethanol high-temperature oxidation routes and compare the number of reactions involved in the two detailed models analyzed in this work for the thermal oxidation.
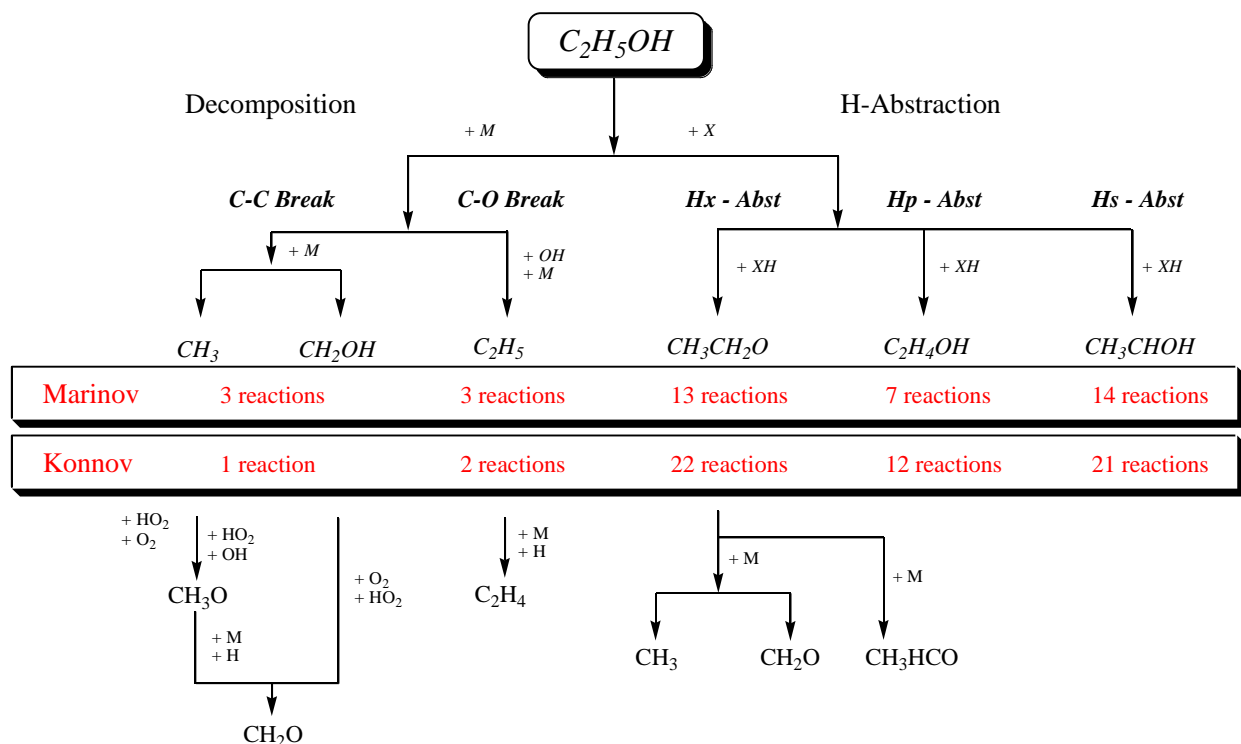


**Figure 3  Main ethanol high temperature oxidation routes (adapted from [4])**

The second mechanism used in this work was postulated by Konnov [8] and was developed for the combustion of hydrocarbons with at most three carbon atoms in the molecule. This mechanism has been compared to other mechanisms in the literature for the combustion of

methane, propane, butane and acetylene [9], [10], [11] and a good comparison was obtained. This mechanism has not been used in the literature for predicting the combustion of ethanol. Nevertheless, Konnov [12] mentioned that it might be basically able to predict the combustion of ethanol when the additional thermodynamic properties are given. We note that, the ethanol decomposition and *H*-atom abstraction leads ultimately to $C_2$ hydrocarbons and oxygenated species, whose kinetics are included into the comprehensive Konnov mechanism.

The Figure 3 shows the main ethanol high-temperature oxidation routes and compares the number of reactions involved in the two detailed models analyzed in this work for the thermal oxidation. Table 1 presents an overview of theses chemical mechanisms.

Table 1. Overview of the two chemical kinetic mechanisms used in this work.

| Mechanism | Elements | Chemical Species | Elementar Reactions | NOx Kinetics | Pressure Range (atm) |
|---|---|---|---|---|---|
| **Marinov** | 4 | 57 | 383 | No | 1.0 - 4.5 |
| **Konnov** | 5 | 127 | 1200 | Yes | 0.0921 - 7.5 |

Figure 4 shows for instance the discrepancy of both mechanisms in predicting the temperature in the shock tube at $p_5=30$ and at start temperature of $T_5 = 1100$ K.

Our experimental ignition delay times could be roughly reproduced by the Konnov and the blended Konnov-Marinov mechanism. The consensus is seen, however, only at high temperature. Future work will be focused on ignition delay times of ethanol and gasoline with variable proportions.
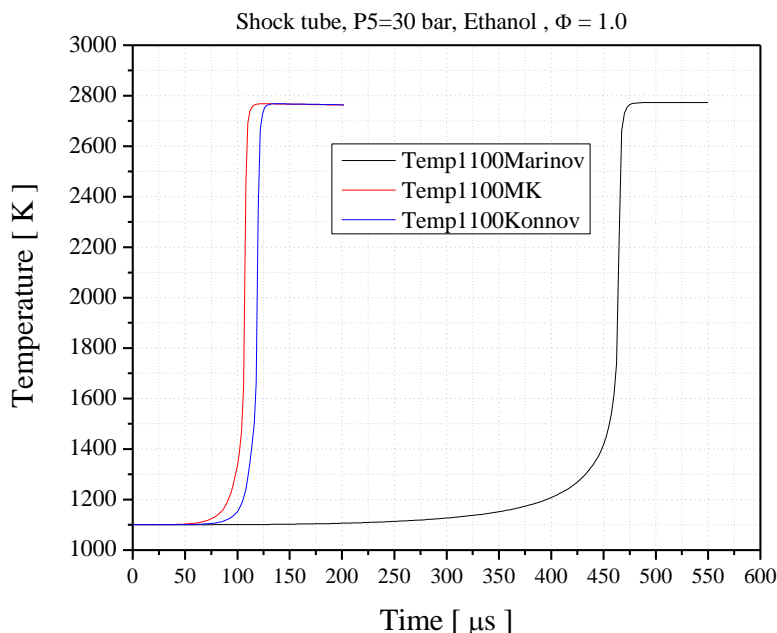


**Figure 4. Temperature-time evolution in shock tube simulations**

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