



# A detailed chemical kinetic modeling, ignition delay time and jet-stirred reactor study of methanol oxidation



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## ABSTRACT

A shock tube (ST) and a rapid compression machine (RCM) have been used to measure new ignition delay times for methanol oxidation over a wide range of pressures (2–50 atm) and equivalence ratios (0.5, 1.0, and 2.0). These measurements include dilute and fuel/‘air’ conditions (1.5–21.9% methanol), over a temperature range of 820–1650 K. The new data has been compared to previously published studies and provides insight into internal combustion engine relevant conditions which are previously un-studied at pressures of 10, 30, 40 and 50 atm. In addition to these ignition delay times, species concentrations have also been measured using a jet-stirred reactor (JSR). In these experiments methanol concentrations of 2000 and 4000 ppm were used at equivalence ratios of 0.2–2.0, at pressures of 1–20 atm, and in the temperature range of 800–1200 K with residence times varying from 0.05–2.00 s. The newly measured experimental data was used to develop a new detailed chemical kinetic model (Mech15.34). This model was also validated using available literature data. The new model is capable of predicting all of the validation data with reasonable accuracy, with some discrepancy in predicting formaldehyde in the JSR data. All of this, results in a robustly validated and accurate, new detailed chemical kinetic model.

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## 1. Introduction

The demand for a change in the way we consume and produce our energy is motivated by increasing climate change caused by the release of CO<sub>2</sub> into the atmosphere due to burning fossil fuels leading to planet warming. Our energy demands will continue to increase into the future, and it is important that we now put systems in place that will allow us to begin to move away from our dependence on traditional fossil fuels. The European directive 2009/28/EC sets out a target for all EU member states to produce at least 10% of their energy for transport from renewable energy sources by 2020. The directive outlines the importance of using biofuels produced from biomass in reaching this target. Methanol produced from sources such as ligno-cellulosic biomass, carbon capture technologies [1] and algae make methanol potentially viable as a renewable energy resource. Currently, methanol is mainly produced from syngas.

The main disadvantage of methanol compared to conventional gasoline is its low energy density, water solubility, and toxicity. For this reason much emphasis is now being placed on looking at the production of longer chain alcohols. Chemical kinetic mechanisms can provide insight into which of these alcohols best lends itself to replacing gasoline in internal combustion engines.

These mechanisms are built in a hierarchical manner. It is therefore important to understand the simplest alcohol, methanol, if accurate mechanisms for longer chain alcohols are to be developed. Data such as ST and RCM ignition delay times and JSR species measurements presented in this paper are extremely useful in the validation of these mechanisms, and though there is a large quantity of previously published data on methanol there is a lack of high-pressure data, especially at low temperatures. If alcoholic compounds are to be considered as alternatives to gasoline in internal combustion engines, then data to represent these fuels at the conditions within an engine, such as high pressures (10–150 atm) are needed to allow for confidence in the predictive power of chemical kinetic mechanisms under these conditions.

In addition to this, methanol forms part of the sub-mechanism for larger hydrocarbon fuels in general. For example; the reaction between methyl and hydroxyl radical forming methanol is a very

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important reaction, particularly in accurately predicting hydrocarbon flames speeds.

Several existing studies have investigated the ignition characteristics of methanol. Cooke et al. [2] investigated ignition delay times for stoichiometric mixtures of methanol (and ethanol) in the temperature range 1570–1870 K and measured ignition delay times using both  $\text{CH}^*$  and  $\text{OH}^*$  emission.

Bowman [3] studied the oxidation of methanol behind reflected shock waves in the temperature range of 1545–2180 K and at reflected shock pressures of 1.5–4.2 atm while ignition delay times were defined as the attainment of the maximum concentration of CO and O-atom concentrations.

Tsuboi and Hashimoto [4] measured  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , CO and  $\text{CH}_2\text{O}$  profiles behind reflected shock waves for a variety of mixtures in Ar. All these early studies were conducted under highly dilute conditions.

Fieweger et al. [5] studied the self-ignition characteristics of several fuels including stoichiometric methanol/‘air’ mixtures at pressures of 13 and 40 bar and temperatures of approximately 800–1200 K. The authors used CH-band emissions and the maximum rate of change of pressure to define the ignition delay time. In addition they reported the appearance of mild-ignition characteristics when studying methanol autoignition.

Noorani et al. [6] studied the high temperature ignition of  $\text{C}_1$ – $\text{C}_4$  straight chain alcohols at 2, 10 and 12 atm. The authors used  $\text{CH}^*$  emissions to measure the ignition delay time.

The only RCM study of methanol oxidation to date was performed by Kumar and Sung [7]. This study included compressed pressures of 7–30 bar over a temperature range of 850–1100 K, for equivalence ratios of 0.25–1.00 diluted in ‘air’ using Ar as the bath gas. The ignition delay definition used was the maximum rate of pressure increase.

Dayma et al. [8] studied the oxidation of methanol in the absence and in the presence of NO or  $\text{NO}_2$  in a JSR at 10 atm. The authors reported species concentrations for  $\text{CH}_3\text{OH}$ , NO,  $\text{NO}_2$ , CO,  $\text{CO}_2$  and  $\text{CH}_2\text{O}$ .

Cathonnet et al. [9] performed pyrolysis experiments using a static reactor. The study was conducted at pressures of 0.3–0.5 atm over a temperature range of 875–975 K.

Methanol oxidation has been studied several times in flow reactors [10–12]. Aronowitz et al. [10] performed experiments on methanol oxidation at atmospheric pressure, in the initial temperature and equivalence ratio ranges of 950–1030 K and 0.03–3.16, respectively. Norton and Dryer [11] performed detailed methanol oxidation experiments using a turbulent flow reactor at equivalence ratios ranging from 0.6–1.6 and at initial temperatures from 1025–1090 K at atmospheric pressure. Held and Dryer [12] reported species profiles for the fuel products and intermediates at 1 and 10 atm at initial temperatures of 810–1043 K.

Other flow reactor studies include investigations by Alzueta et al. [13], Ing et al. [14], Rasmussen et al. [15] and Aranda et al. [16]. Alzueta et al. [13] studied the oxidation of methanol with and without NO in a flow reactor, performing the experiments at atmospheric pressure in the temperature range 700–1500 K. Ing et al. [14] reported experimental data for methanol in a flow reactor under pyrolysis and oxidation conditions. Methanol pyrolysis was studied at 1073 K over a pressure range of 1–10 atm while oxidation experiments were conducted over a temperature range of 873–1073 K and a pressure range of 1–5 atm. Rasmussen et al. [15] also studied the oxidation of methanol in a flow reactor with and without the presence of NO in a temperature range of 650–1350 K. Recently Aranda et al. [16] studied methanol oxidation at high pressures (20–100 atm) and low temperatures (600–900 K).

A stirred reactor study of methanol oxidation was conducted by Aniolek and Wilk [17] in 1994. This covered a temperature range of 650–700 K and a pressure of 0.92 atm.

A low pressure flame speciation study was reported by Akrich et al. [18]. The species of  $\text{CH}_3\text{OH}$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , CO and  $\text{H}_2$  were measured as a function of distance from the burner.

Egolfopoulos et al. [19] measured laminar flame speeds for methanol at 1 atm at 298–368 K using the counter-flow twin flame technique. Liao et al. [20] reported laminar burning velocities using the spherical combustion bomb technique for methanol/‘air’ mixtures at 358 K. Veloo et al. [21] experimentally determined the laminar flame speed of methanol using the counter-flow configuration technique at atmospheric pressure and at an unburned mixture temperature of 343 K. Vancoillie et al. [22] reported laminar flame speed measurements at atmospheric pressure for methanol/‘air’ mixtures at unburned gas temperatures of 298–358 K using the heat flux method.

A selection of these studies provides the validation for the detailed chemical kinetic model presented here, Mech15.34.

What is absent for the most part in the previous studies is validation data for engine relevant conditions at pressures in the range 10–150 atm in the temperature range 800–1600 K. This study provides a comprehensive set of data in this regime and covers low- to high-temperature chemistry by coupling ST, RCM and JSR measurements. This provides robust validation when combined with the literature data available for model validation.

Finally if we consider the use of longer chain alcohols as future fuels for transportation, and the fact that ethanol and methanol are currently being used as bio-fuels in petroleum engines, this shows the importance of understanding methanol at engine relevant conditions, due to the hierarchical nature of building detailed chemical kinetic models.

Mech15.34 is the first detailed chemical kinetic model available to be validated at these conditions. In addition, the incorporation of available quantum calculations of rate constants and direct measurements of rate constants is an important advancement in the knowledge of the combustion chemistry of methanol.

## 2. Experimental description

Methanol was obtained from Sigma Aldrich  $\geq 99.8\%$  purity and Tokyo Chemicals Industry  $\geq 99.5\%$  purity. All other gases were supplied by BOC Ireland; nitrogen (CP Grade)  $\geq 99.95\%$ , argon (Research Grade)  $\geq 99.9995\%$ , oxygen (Medical Grade)  $\geq 99.5\%$  and all of these were used without further purification (Table 1).

The test mixtures were prepared in stainless steel mixing vessels using partial pressures to determine the volumetric percentage of each constituent to within 1% of their reported value. Test mixtures were allowed to mix overnight before use to ensure homogeneity. Table 2 presents the range of mixtures used to measure the ignition delay times.

### 2.1. Rapid compression machine (RCM)

The RCM used here has been described in detail by Darcy et al. [23]. It has a twin opposed-piston configuration. Pressure profiles were recorded using a heat-shock resistant pressure transducer (Kistler 6045A) with the signal passing through a charge amplifier and recorded using a digital oscilloscope. Experimental compression times are short at approximately 16 ms. The ignition delay time,  $\tau_{\text{ign}}$ , is defined as the time between the end of compression, the point which the pistons are at rest at the end of their stroke, top dead centre (TDC), to the maximum rate of pressure rise due to ignition, as shown in Fig. 1. Ignition delay times are reproducible to within 15% of one another at each compressed temperature ( $T_c$ ). The estimated uncertainty of the experiments is 20% and is derived from the maximum variation of experiments from standard measurements of n-butane in this facility.

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