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High-pressure pyrolysis and oxidation of ethanol

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ABSTRACT

The pyrolysis and oxidation of ethanol has been investigated at temperatures of 600–900 K, a pressure of 50 bar and residence times of 4.3–6.8 s in a laminar flow reactor. The experiments, conducted with mixtures highly diluted in nitrogen, covered fuel-air equivalence ratios (Φ) of 0.1, 1.0, 43, and ∞. Ethanol pyrolysis was observed at temperatures above 850 K. The onset temperature of ethanol oxidation occurred at 700–725 K over a wide range of stoichiometries. A considerable yield of aldehydes was detected at intermediate temperatures. A detailed chemical kinetic model was developed and evaluated against the present data as well as ignition delay times and flame speed measurements from literature. The model predicted the onset of fuel conversion and the composition of products from the flow reactor experiments fairly well. It also predicted well ignition delays above 900 K whereas it overpredicted reported flame speeds slightly. The results of sensitivity analyses revealed the importance of the reaction between ethanol and the hydroperoxyl radical for ignition at high pressure and intermediate temperatures. An accurate determination of the rate coefficients for this reaction is important to improve the reliability of modeling predictions.

1. Introduction

In recent years, ethanol has attracted both scientific and commercial attention as an additive to conventional liquid fuels or even as a alternative neat fuel. Gasoline doped with ethanol is widely used in spark-ignited (SI) engines [1]. Ethanol addition to gasoline promotes the overall octane number of the fuel while it potentially reduces the emission of particulate matter [2,3] and CO [4]. Ethanol addition to diesel fuels has also been studied [5,6] and a positive effect on fuel economy was found [5].

The relatively high energy density of ethanol makes it attractive also as a neat fuel. Using ethanol-based fuels produced from bio-sources can reduce the pressure on fossil fuels resources and reduce CO_2 release to the atmosphere. However, a widespread usage of ethanol as a fuel may increase the emission of aldehydes [1,4,7], which can cause health risks.

Compared to studies of hydrocarbon oxidation, research in the oxidation chemistry of oxygenated fuels is more recent, motivated by their importance in engines. In addition to the interest due to its role as a fuel or fuel additive, the reaction mechanism of ethanol is a crucial part in models for heavier alcohols often found in complicated biofuels [1]. Due to its relevance, e.g., for homogeneous-charge compression-ignition (HCCI) engines [8], ethanol ignition has been studied at high pressure and intermediate temperatures in flow reactors, rapid compression machines (RCM), and, to some extent, in shock tubes.

Data from high-pressure turbulent flow reactors are available for ethanol pyrolysis (950 K, 3–12 atm) [9] and ethanol oxidation (523–903 K, 12.5 atm) [10]. Ignition delay times at intermediate temperatures are mostly obtained in rapid compression machines (RCM),but the relatively short ignition delays of ethanol make it possible to conduct such experiments also in shock tubes. Ignition delay data from RCM have been reported by Lee et al. [11] (750–1000 K, 20–40 atm), Mittal et al. [12] (825–985 K, 10–50 bar), Lee et al. [13] (700–1300 K, 67–80 bar), and Barraza-Botet et al. [14] (880–1150 K, 3–10 atm), while shock tube ignition delays are available from Noorani et al. [15] (1070–1760 K, 2–12 atm), Heufer and Olivier [16] (800–1400 K, ⩽40 bar), and Cancino et al. [17] (650–1220 K, 10–50 bar). Some of these studies cover partly the pressure and temperatures of the current study, but ignition delay times provide only an overall characteristic of combustion. Additional insight into the combustion chemistry can be obtained by measuring more detailed characteristics such as species profiles.

A number of chemical kinetic models for ethanol oxidation has been published over the years [10,12,13,18–25], but only some of them have been applied at elevated pressure. Marinov [21] conducted the first comprehensive modeling study of ethanol oxidation, estimating a number of rate constants by analogy to known reactions. Whereas most of the data used for validation were obtained at low pressures and high

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temperatures, his model has been adopted also for high-pressure studies [15]. Dryer and co-workers [10,22] developed a kinetic model and validated it against flow-reactor data at 12.5 bar as well as against ignition delays up to 50 bar. This model was largely adopted by Lee et al. [13] who extended the validation range to 77 bar. Cancino et al. [17] modified earlier kinetic models to address ethanol oxidation chemistry at high pressures and intermediate temperatures. However, their model was solely validated against shock tube data. Mittal et al. [12] optimized a model for ethanol oxidation at intermediate temperatures.

By the advent of more reliable data for the key reactions in ethanol oxidation, a careful reevaluation of reactions focusing on medium temperatures and high pressure seems desirable. In this paper we present species concentration profiles from ethanol pyrolysis and oxidation in a flow reactor at high pressure and intermediate temperatures. A detailed chemical kinetic model based on earlier high-pressure studies from our laboratory [26–33] is extended with a subset for ethanol oxidation and evaluated against the data from the present work as well as from literature.

2. Experimental approach

The experiments were conducted in a laboratory-scale high-pressure laminar-flow reactor designed to approximate plug flow [26]. The setup was described in detail elsewhere [26] and only a brief description is provided here. The system was used here for the investigation of ethanol oxidation chemistry at a pressure of 50 bar, temperatures up to 900 K, and a flow rate of 4.78 Nliter/min (4.42 Nliter/min for the pyrolysis experiments, STP: 1 atm and 273.15 K).

The reactions took place in a tubular quartz reactor (inner diameter of 8 mm), enclosed in a stainless steel tube that acted as a pressure shell. The system was pressurized from the feed gas cylinders and the reactor pressure was monitored upstream of the reactor by a differential pressure transducer and controlled by a pneumatically operated pressure control valve positioned after the reactor. The pressure fluctuations of the reactor were limited to ± 0.2%. The pressure in the shell-side of the reactor was retained close to that inside the reactor in order to prevent breaking the quartz tube.

The steel tube was placed in a tube oven with three individually controlled electrical heating elements that produced an isothermal reaction zone (± 6 K) of 42–48 cm in the middle of the reactor. A moving thermocouple was used to measure the temperature profile inside the pressure shell at the external surface of the quartz tube after stabilizing the system.

The liquid feeding system is described in detail elsewhere [34]. The liquid was pressurized by an HPLC pump and its flow to the reactor was controlled by a liquid mass flow controller. The liquid was mixed with the incoming gas and heated to temperatures around 520 K in evaporator before entering the reactor. A tube of more than 4 m in the evaporator ensured sufficient time for evaporation and mixing. A long stabilization period prior to each test served to limit the fluctuations of the liquid feeding system to ± 5%.

Downstream of the reactor, the system pressure was reduced to atmospheric level prior to product analysis, which was conducted by an on-line *6890N Agilent Gas Chromatograph* (GC-TCD/FID) calibrated according to the procedure in [32]. The GC allowed detection of O_2, CO, CO_2, C_2H_4 and C_2H_6 with estimated uncertainties around 10%. The uncertainty for ethanol was higher due to its calibration procedure. Methane could not be quantified accurately due to signal overlapping with CO. Distinguishing methanol from acetaldehyde was not possible due to signal overlapping for the GC configuration used. However, it was possible to measure the signal areas corresponding to sum of these components. Using the response factor of acetaldehyde, the sum of acetaldehyde and methanol was estimated but a relatively large uncertainty must be acknowledged. Moreover, due to the small signal to noise ratio of formaldehyde, a larger uncertainty especially in measuring low quantities of formaldehyde was expected.

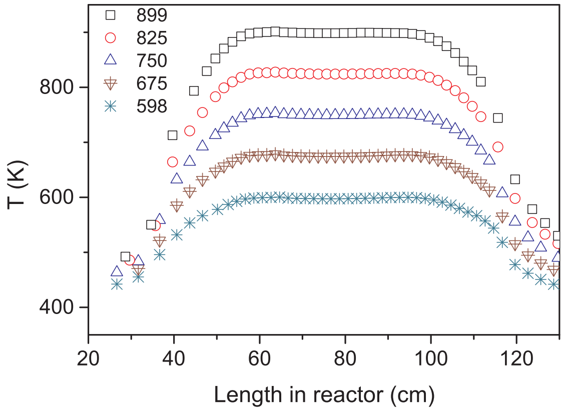

Fig. 1. Measured temperature profiles across the reaction zone. The nitrogen flow rate was 4.78 NL/min at a pressure of 50 bar. The flow rate and temperature profiles were slightly different for the ethanol pyrolysis experiments.

All gases used in the present experiments were high purity gases or mixtures with certified concentrations (± 2% uncertainty) and the ethanol purity was above 99.8%. The total flow rate was measured by a bubble flow meter downstream of the reactor.

For each set of experiments, the concentrations of reactants as well as the pressure of the system were maintained while the temperature of the isothermal zone was increased in small steps. Fig. 1 shows the measured temperature profiles for different isotherms in pure nitrogen. The residence time of the gases in the isothermal zone of the reactor can be estimated as $\tau\,[\mathrm{s}] = 3840/T\ [\mathrm{K}]$ (± 8%) for all the oxidizing experiments and $\tau\,[\mathrm{s}] = 4098/T\ [\mathrm{K}]$ (± 8%) for the pyrolysis tests.

The temperature rise due to exothermic reactions was limited by strongly diluting the reactants in nitrogen. The adiabatic temperature increase was estimated to a maximum of 107 K. However, measurements of the temperature profile under oxidizing conditions indicated only a marginal difference compared to the flow of pure nitrogen. This is attributed to a fast heat transfer between the quartz reactor and its surrounding, facilitated by the small diameter of the quartz tube.

The possible impact of surface reactions is a concern in flow reactor studies. In this work, surface reactions were minimized, partly by the use of quartz as reactor material and partly by the high pressure, inhibiting diffusion to the wall. Previous work in the reactor, covering a range of fuels [26,29–33,35,36], have shown no indications of wall reactions. In a recent study of oxidation of ammonia [36], known to be sensitive to surfaces, we found that replacing the quartz reactor by an alumina reactor did not affect the oxidation behavior. Hence, it seems safe to assume a negligible contribution from surface reactivity on the gathered data.

3. Chemical kinetic model

The reaction mechanism and the corresponding thermodynamic and transport data were based on previous work by the authors on high-pressure oxidation of hydrogen [31], methane [32], acetylene [35], ethylene [29], ethane [33], and methanol [30]. The acetaldehyde subset is reviewed in a companion paper [37]. Here, the reactions important for ethanol oxidation at high pressure and moderate temperatures are discussed. Selected reactions are listed in Table 1.

The thermal decomposition of ethanol (R1), a key reaction at high temperatures [10], is believed to proceed through three channels [38]:

$$CH_3CH_2OH(+M) = C_2H_4 + H_2O(+M) \tag{R1a}$$

$$= CH_3 + CH_2OH(+M) \tag{R1b}$$

$$= C_2H_5 + OH(+M) \tag{R1c}$$

We have adopted the rate coefficients from Sivaramakrishnan et al. [38], who combined measurements of ethanol dissociation over