



Full Length Article

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 an 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 CO₂ 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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