

High Pressure Oxidation of Alternative Fuels for Diesel Engines

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Introduction

To reduce the environmental and climate impact of combustion in engines, there is an incentive to replace conventional transport fuels (Diesel, heavy fuel oil) with alternative fuels such as natural gas, LPG, and bio-derived alcohols. To guarantee safe and efficient operation of engines, insight in the autoignition and flame properties of these fuel alternatives at high pressure is desirable. Characterization of chemistry at high pressures is challenging, however, both experimentally and theoretically.

Experimental approaches to study high-pressure chemistry include work in batch reactors, flow reactors, jet-stirred reactors, laminar flames, shock tubes, and rapid compression machines (RCM). The most common experimental techniques for elevated pressure are shock tubes and Rapid Compression Machines (RCM), both of which potentially can be operated at very high pressure. Most of the other techniques are employed mainly at lower pressure. Experiments in batch reactors, jet-stirred reactors, flow reactors and flames are largely limited to pressures of 10-20 atm or below. High-pressure work in batch reactors and jet-stirred reactors have been constrained by safety concerns and technical challenges. Laminar premixed or counter-flow diffusion flames suffer from reduced spatial resolution at enhanced pressure. Furthermore, flame speed measurements at high pressure are complicated by the occurrence of cellular structures that break down the laminar flame structure. Flow reactor setups can be designed to operate at pressures of 100 atm below 1000 K, but above this temperature, the maximum pressure decreases with increasing temperature.

The present study examines the high-pressure pre-ignition chemistry of C₁-C₄ hydrocarbons and oxygenated fuels like alcohols and DME. Special emphasis is put on the potential of DME as an additive to promote ignition. Experiments are conducted in a specially designed high-pressure flow reactor. The results are interpreted in terms of a detailed chemical kinetic model, developed with emphasis on the peroxide chemistry subset. Modeling predictions are also compared high-pressure results from literature, including ignition delay data from shock tubes and RCM. The practical applications of this knowledge is discussed.

Experimental

Experimental data were obtained in a flow reactor operating at high pressure (20–100 bar) and temperatures in the range 500–925 K. The flow reactor was designed to approximate plug flow in the laminar regime [1]. Reactant gases were premixed before entering the reactor and reaction took place in a tubular quartz reactor located inside a steel pressure shell. The residence time in the isothermal reaction zone was of the order of 10 s. The adiabatic temperature rise due to heat of reaction was limited by using very dilute mixtures. The product analysis was conducted by gas chromatography.

As shown in Fig. 1, the experimental regime covered by the present high-pressure flow reactor, here for ignition and oxidation of ethane, supplements well those reported for shock tubes and RCM since it extends the high-pressure regime to lower temperatures.

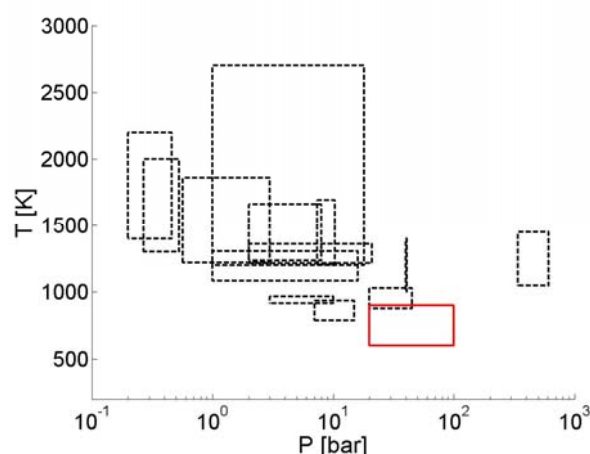


Figure 1: Temperature / pressure regimes for experimental work on ethane ignition and oxidation. The high temperature work is from shock tubes and RCM, while the medium temperature results were obtained in batch and flow reactors. The red square denotes the operating range of the present reactor.

Kinetic model

The kinetic model was established sequentially, using the hierarchical structure of high-temperature chemical processes. Combustion of practical fuels include within them sub-mechanisms for the oxidation of simpler molecules. The reaction mechanism was based on the hydrogen-oxygen kinetics [2], which was then extended to describe oxidation of methane [3-4], C₂-hydrocarbons [5-7], and propane [8]. The oxidation mechanisms of oxygenated fuels such as alcohols and ethers also include within them subsets for CH₄/CO/H₂ oxidation, and the mechanism was further extended with subsets for oxidation of methanol [9], ethanol [10], and DME [11]. In developing the kinetic model, particular emphasis was put on the peroxide chemistry, which plays an important role for ignition and oxidation at elevated pressure and low-intermediate temperatures.

Selected results

Alternative fuels under consideration for use in marine Diesel engines, for instance natural gas and ethanol, typically require pilot flames because they exhibit ignition delays that are too long. Chemical kinetic models for high-pressure oxidation of simple hydrocarbons and alcohols, e.g., [4-10], are able to describe the pre-ignition and ignition chemistry satisfactorily. Figure 2 shows the predicted ignition delay time at 900 K and 100 bar for methane, ethane, propane, various natural gas mixtures, ethanol, and DME. As a rule of thumb, ignition has to occur within 1 ms for the fuel to be suitable for a 2-stroke Diesel engine. Clearly none of the fuels or fuel mixtures satisfy this criterion, with the exception of DME.

We have investigated the oxidation of dimethyl ether (DME) and its mixture with methane highly diluted in nitrogen at pressures of 50-100 bar and intermediate temperatures (450-900 K) in the laminar high-pressure reactor. For DME oxidation at 50 bar, the onset temperature of reaction was 525 K, independent of fuel-air equivalence ratio. The DME oxidation was characterized by a negative temperature coefficient (NTC) zone, which was found sensitive to changes in the mixture stoichiometry but always occurring at temperatures of 575-625 K. The kinetic modeling predictions were in satisfactory agreement with the experimental data [11].

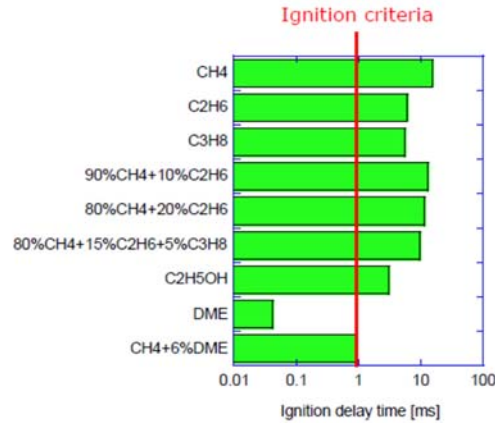


Figure 2: Predicted ignition delay for a stoichiometric mixture at 900 K and 100 bar.

It is of interest to evaluate the potential of using DME as an ignition promoter in Diesel engines. The oxidation of methane doped by DME was studied in the flow reactor at 100 bar, varying the fuel-air equivalence ratio ϕ was varied from 0.06 to 20, and the DME/CH₄ ratio changed over 1.8-3.6%. A profound promoting effect of DME addition on methane ignition was observed as the onset of reaction shifted to lower temperatures by 25-150 K.

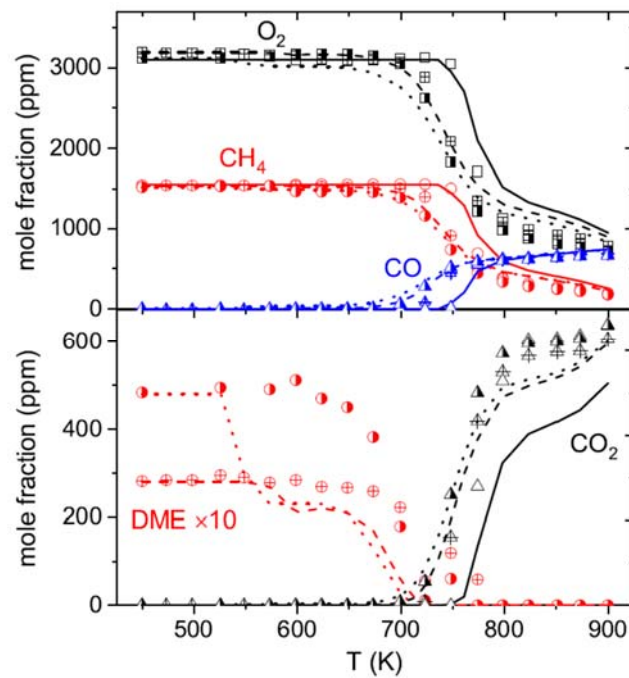


Figure 3. Comparison of experimental and predicted concentration profiles as a function of the reactor temperature for DME addition to methane under stoichiometric conditions and at 100 bar. Open symbols/solid lines: neat CH₄ [4] (1550 ppm CH₄, 3100 ppm O₂); crossed symbols/dashed lines: CH₄/DME [11] (1540 ppm CH₄, 28 ppm DME, 3200 ppm O₂); half-open symbols/ dotted lines: CH₄/DME [11] (1520 ppm CH₄, 48 ppm DME, 3320 ppm O₂; all diluted in N₂).

Figure 3 shows results obtained under stoichiometric conditions for neat CH₄ and CH₄/DME mixtures. For both doped cases, the DME conversion starts around 675 K, but there is no consumption of CH₄ and O₂ below 700-725 K. While neat methane ignites at 750 K, the addition of DME triggers methane oxidation at 25-50 K lower temperatures. The major products at high temperatures are not strongly affected by DME addition. Since the onset

temperature for neat DME was 525 K (at 50 bar), it seems that methane suppresses the ignition of DME in the mixture. The model predicts well the onset of methane conversion as well as the mole fractions of O_2 , CH_4 , and CO , but it underestimates the ignition temperature of DME in both doped mixtures by 100 K. Conceivably methane activates some chain-terminating paths in DME oxidation at low temperatures that are either omitted or underpredicted by the mechanism.

Since the prediction of the concentrations of methane and oxygen is not affected by the premature ignition of DME, the model can be used to predict the amount of DME that would allow a CH_4 /DME mixture to ignite within 1 ms at 900 K and 100 bar. As shown in Fig. 2, a methane/DME mixture with approximately 6% DME appears to fulfill the rule-of-thumb ignition criteria set up for the Diesel engine.

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