Sandia Combustion Research

Technical Review

Hydrothermal Oxidation Kinetics of Methanol

An optically accessible flow reactor is used in conjunction with Raman spectroscopy to measure the kinetics of methanol oxidation over a range of conditions. Recently developed elementary reaction models show good agreement with the experimental results.

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Supercritical water oxidation (SCWO) is a technology under development by government laboratories, universities, and private industry for the treatment of aqueous wastes. However, the current understanding of the rates and mechanisms of reactions in supercritical water is restricted to a handful of empirical mechanisms for very simple chemicals. These mechanisms are of limited use in the formulation of predictive models of SCWO that will be needed in the future for the design and operation of large-scale waste processing equipment. To be generally applicable as design tools, models must be based on elementary reaction steps or at least on a detailed quantitative mechanistic description incorporating all the key fundamental reactions.

We are developing an experimental data base, using an optically accessible flow reactor, for evaluating the details of methanol oxidation. Our experimental results are compared to the predictions from an elementary reaction step model that has been developed for these high-density hydrothermal conditions. The mechanistic details of the oxidation of methanol in supercritical water serve as important building blocks in developing useful models for the destruction of hazardous waste by supercritical water oxidation.

Sandia's optically accessible supercritical water reactor consists of two feed lines that preheat oxidizer and fuel to reaction conditions. These two lines are joined at a tee to generate a single line that incorporates a high-pressure, high-temperature optical cell to allow a direct view of the reacting flow. The reacting flow is maintained at near isothermal conditions by a series of individually controlled cable heaters helically wrapped around the tubing to overcome losses due to imperfect insulation. The lines can be cooled to remove heat generated from the oxidation reaction. The cell has three sapphire windows positioned at 90° relative to each other to provide for a laser beam probe and the collection of Raman scattered light. The Raman spectrum of individual species present in the reaction, when calibrated, is used as a diagnostic to identify the absolute concentration of that particular compound. In addition to monitoring the initial feed material, Raman signals due to stable intermediates including formaldehyde and carbon monoxide have been identified. By varying the position of the cell relative to the mixing point along with varying the reactant flow rates, reaction times ranging from 0.15 s to 10 s can be probed in the same apparatus.

We have examined the oxidation of methanol by oxygen in supercritical water over the temperature range from 440 °C to 500 °C and residence times from 0.17 s to 3.0 s. A subset of the results from these measurements at an equivalence ratio of Φ= 0.5 is shown in Figure 1. The initial methanol concentration was 0.5 moles/liter at ambient conditions, which corresponds to approximately 0.05 moles/liter at reaction conditions, depending on experimental temperature. Oxygen was added at a varying equivalence ratios to complete the experimental set.

The Raman spectroscopic diagnostic has allowed us to collect a large set of data to compare with predictive models. In collaboration with researchers at MIT, LLNL, and The University of Iowa [1,2], we have developed an elementary reaction model that is in good agreement with the observed rate of methanol consumption over this temperature

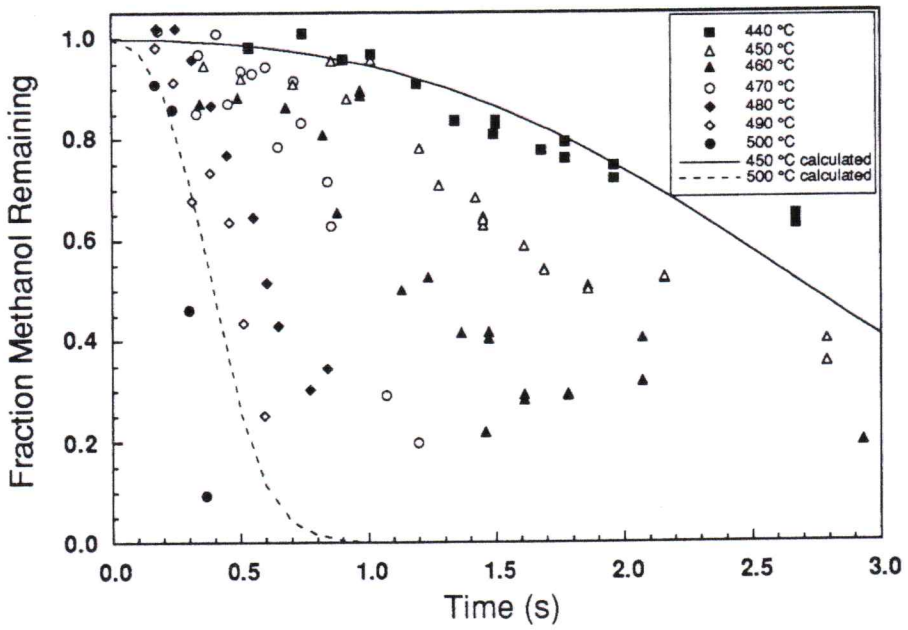

Figure 1. Plot of all the data collected on the oxidation of methanol between 440°C and 500°C. Included on the plot are the curves predicted by the model for 450°C and 500°C at the same conditions as the experiment.

range. The model appears to be slightly underpredicting the conversion at a given temperature.

In addition to testing the model's ability to represent the loss of initial fuel, we have examined how well it represents the production of formaldehyde, a key intermediate. The concentration of formaldehyde in the reaction mixture is predicted by the elementary model to be as high as 15% of the initial feed concentration at 500°C and 0.3 s into the reaction. The result observed using the *in situ* Raman spectroscopic diagnostic is in good agreement with this value.

These results show that the present model for the oxidation of methanol can represent the important aspects of the oxidation process. We intend to extend this modeling and experimental effort to several more complicated alcohols, including 2-propanol and eventually phenol.

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References

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