

Title: Coal-Conversion Wastewater Treatment by Catalytic Oxidation in Supercritical Water

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Abstract: The objective of this research project (DE-FG22-95PC95213) is to determine the reaction pathways and kinetics associated with the destruction of organic compounds in coal-conversion wastewaters by catalytic supercritical water oxidation (SCWO). An environmental hazard associated with coal liquefaction and gasification is the generation of aqueous waste streams containing phenolics and carcinogenic organics such as polynuclear aromatics. Most coal conversion schemes treat or propose to treat the wastewaters by a series of techniques that include gas stripping, solvent extraction, biological degradation, and adsorption. Catalytic SCWO is an attractive alternative method, and it can simplify the overall process flowsheet for waste treatment. Catalytic SCWO is an emerging technology, and little is known about the reaction pathways, kinetics, and mechanisms for the oxidative degradation of compounds representative of those in coal conversion wastewaters. This project addresses these issues.

Our first set of experiments employed a CARULITE-150 commercial VOC oxidation catalyst. The active species is MnO₂ along with some other metal oxides, supported on amorphous alumina. Experiments were performed between 380 - 430°C and 250 atm and with phenol as the reactant. We used a catalytic flow reactor and analyzed the reactor effluent chromatographically. We examined the effects of the catalyst contact time and the phenol and oxygen concentrations on the conversion. Within the phenol concentration range from 0.07 to 1.24 mmol/liter and with excess oxygen, we found that the use of the commercial catalyst improved SCWO of phenol dramatically in terms of both rate and selectivity. The rates of phenol destruction and CO₂ formation improve by more than an order of magnitude. In fact, the oxidation rates were so fast that the rate of diffusion through the catalyst pores limited the observed reaction rate. Thus, our kinetics analysis incorporated pore diffusion effects. We found that the intrinsic kinetics of phenol disappearance and of CO₂ formation were both roughly first order. The activation energies were 31 and 47 kcal/mol respectively. These results show the potential that catalytic SCWO might have for completely oxidizing phenol at relatively mild conditions, perhaps at temperatures just above T_c (374 °C) instead of over 600 °C that is commercially proposed to treat organic waste like phenol by non-catalytic SCWO.

Because pore diffusion limitations intruded upon the kinetics study with the commercial catalyst, we initiated another set of experiments with a less active catalyst. We used bulk MnO₂ as the oxidation catalyst in these experiments. With this catalyst we were able to measure intrinsic reaction rates and determine the global rate laws. We also identified and quantified many byproducts that arose from incomplete oxidation of phenol.

Published Journal articles and students receiving support

Article:

X. Zhang and P. E. Savage, "Fast Catalytic Oxidation of Phenol in Supercritical Water" *Catalysis Today* (in press).

Students:

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