TITLE: SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

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I. ABSTRACT

OBJECTIVE: Supercritical fluids (SCFs) under supercritical conditions possess properties that have important implications for selectivity control in multi-component separation and also for kinetic rate control in the reactive processing of coals and coal liquids in SCFs. This project seeks to study the solvent effects of supercritical fluids on the kinetics of reactions involving mono- and poly-aromatic model coal compounds. The specific goal of the work is to collect and apply experimental kinetic data to the development and testing of mathematical kinetic models of coal-like reactive systems.

WORK DONE AND CONCLUSIONS:

- UV spectroscopy was applied to measure *in situ* SCF solvent/cosolvent effects on the keto-enol equilibrium of the Schiff base 4-(methoxy)-1-(N-phenylforminidoyl)-2-naphthol.
- Schiff base tautomeric equilibrium constants were measured at 35 ^{o}C in SCF ethane for several binary solvent-cosolvent pairs for fluid densities between 8 and 10 mol/L. The tautomeric equilibrium was found to depend strongly on bulk density and cosolvent concentration.
- A physical chemical mathematical model was applied the Sciff base equilibrium data, and suggested the presence of solute-cosolvent clustering in the near-critical region.
- In a second set of experiments, a solubility apparatus was constructed and used to collect solid solubility data for 4-phenyl-1,2,4-triazoline-3,5-dione.
- Fluorescence spectroscopy was applied to measure *in situ* the high pressure pseudo-first order kinetics of a dilute Diels-Alder reaction. 4-phenyl-1,2,4-triazoline-3,5-dione and anthracene were run in pure CO_2 at 40C and at various CO_2 densities.
- The reaction rate constant of this Diels-Alder reaction was “tuned” smoothly over an order of magnitude using changes in SCF CO_2 density.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The pre-treatment of coal has as one of its main objectives reduction of the sulfur and nitrogen content of coal before it is burned. Though SCFs possess "tunable" bulk properties which provide exciting advantages in both component separations and reaction kinetics, there is very little understanding of coal-like reactions in SCFs. We are collecting thermodynamic and kinetic data on coal-like compounds and using this data to develop mathematical models of SCF solvent effects on the kinetics of coal-like reactions. This will aid in the development of a supercritical coal pre-treatment approach which optimizes the economics of supercritical coal desulfurization and denitrogenation.

PLANS FOR THE COMING YEAR

- Complete modeling of the kinetics of the Diels-Alder reaction.

II. HIGHLIGHT ACCOMPLISHMENTS

- High pressure cell was developed for *in situ* UV spectroscopy.
- The tautomeric equilibrium of a Schiff base was found to depend strongly on bulk solvent density and cosolvent concentration.
- High pressure fluorescence spectroscopy was applied to measure the pseudo-first order kinetics of a Diels-Alder reaction in SCF CO_2 under dilute conditions.
- Density of SCF CO_2 was used to "tune" the reaction rate constant of the Diels-Alder reaction over an order of magnitude.

III. ARTICLES AND PRESENTATIONS

PUBLICATIONS:

B. L. Knutson, K. L. Bennett, C. L. Liotta, C. A. Eckert, "Benzophenone as a Probe of Local Cosolvent Effects in Supercritical Ethane," *Ind Eng Chem Res*, **36**, 854-868, (1997).

A. K. Dillow, K. P. Hafner, S. L. J. Yun, F. Deng, S. G. Kazarian, C. L. Liotta, C. A. Eckert, "Cosolvent Tuning of Tautomeric Equilibrium in Supercritical Fluids", *AIChE J*, **43**, 515-524 (1997).

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B. L. Knutson, A. K. Dillow, C. L. Liotta, C. A. Eckert, "Kinetics of a Diels-Alder Reaction in Supercritical Propane," in *Innovations in Supercritical Fluids*: Science and Technology, eds. K. W. Hutchenson and N. R. Foster, 1995, ACS Symposium Series **608**, ACS Books: Washington D. C.

PRESENTATIONS:

"Specific Interactions for Solvent-Based Separations, C. Judson King Award Symposium, ACS National Meeting, San Francisco, CA, April 16, 1997.

"Tuning Nearcritical and Supercritical Fluids," (1) University-wide Colloquium University of Nebraska, Lincoln, NB, April 18, 1997. (2) Hoechst-Celanese Co., Summit, NJ, June 6, 1996. (3) Specialty Minerals, Inc., Bethlehem, PA, June 24, 1996. (4) Hercules Chemical Co., Wilmington, DE, September 19, 1996. (5) "Tuning Nearcritical and Supercritical Fluids," Department of Chemical Engineering, University of Connecticut, Storrs, CN, September 30, 1996.