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OF COAL LIQUEFACTION.
Quarterly Report

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QUARTERLY REPORT

April 1, 1986 - July 1, 1986

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION

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Table of Contents

I	Technical Program for FY 1986	1
II	Highlights	1
III	Progress of Studies	2
IV	Accepted Papers	4

I Technical Program for FY 1986

Hydrodenitrogenation - Novel Methods for Nitrogen Removal from Polynuclear, Heteroaromatic Nitrogen Model Coal Compounds

We recently discovered that polynuclear heteroaromatic nitrogen compounds can be selectively reduced only in the nitrogen containing ring and have now turned our attention towards the cleavage of the carbon nitrogen bonds in this reduced ring.

We are currently focusing on the use of highly loaded, supported nickel catalysts for the hydrodenitrogenation of the selectively reduced aromatic, 1,2,3,4-tetrahydroquinoline, as well as for the HDN of quinoline. The conditions we are investigating are mild, i.e., 1 atm hydrogen at 200 °C to 300 °C.

We need to further characterize all of the products being formed in these reactions, both liquids and gases. We also need to determine the kinetics of the various reactions involved in the HDN process.

We are currently planning to construct a new reactor system that will allow for on-line product sampling (both gas and liquid) and so facilitate the above studies.

Additionally, more information is needed about the morphology and structure/activity relations for the catalysts we are studying. We plan to obtain XPS, TEM, SEM and BET surface area data for various catalysts in used and unused states. Hopefully this data will allow us to explain more effectively the different HDN activities we have observed in various catalysts, and will enable us to make qualitative predictions about the HDN activity of yet untried materials.

II Highlights

- (1) The Xytel semiautomated reactor system was modified, such that we can now study the various parameter of the HDN reaction we discovered with a commercial 50% nickel oxide catalyst supported on silica/alumina.

- (2) The important parameters we intend to study with the Xytel unit include kinetics of product formation as a function of residence time, partial pressure of hydrogen, catalyst concentration etc.
- (3) Preliminary findings with quinoline as the substrate reveal significant product distributions as a function of residence time and will allow pertinent data to be obtained concerning the HDN reaction with the 50% nickel oxide catalyst.

III Progress of Studies

HDN Chemistry using the SemiAutomated Xytel Unit

The further investigation of the hydrodenitrogenation reaction of 1,2,3,4-tetrahydroquinoline using a 50% nickel on silica/alumina catalyst (United Catalyst C46-7-03) requires a more in depth study of the kinetics of product formation. Since the reactor used in our previous work has limited capabilities, the Xytel catalyst activity unit at Lawrence Berkeley Laboratory, modified for our purposes, is being utilized. The semiautomated Xytel unit facilitates the investigation of kinetics at different temperatures and pressures and of catalyst activity as a function of time.

Xytel Unit Capabilities

The Xytel catalyst activity unit is a semiautomated system designed to operate in the absence of an operator. A computer continuously monitors and maintains temperatures, pressures, and flow rates within the system and can automatically shut down in the event of unsafe conditions. The operator can, via a keyboard, control the operation of valves, heaters, etc. Once the operator selects conditions the system automatically maintains them.

The unit is equipped with three reactors, two plug flow and one cstr (continuous stirred tank reactor). There are no current plans to use the plug flow reactors. The Robinson cstr is a high temperature version of the Berty reactor. It is designed to operate gradientless and simulate industrial conditions. The theory of the cstr is since the reactor is at steady state and gradientless, chemical kinetics can be investigated by changing the flow rate of reactants into the reactor. Analysis of the exit stream, which is at the same composition as the reactor, is then carried out. The Xytel unit is ideally equipped for kinetic and activity investigations.

Modifications to Xytel Unit

There were many plumbing and other modifications required before the Xytel unit could be used. The unit was designed to perform Fisher-Tropsch type experiments with CO and H₂ gas. The line previously carrying CO was plumbed to carry H₂ gas instead (see figure). A saturator was installed downstream of the flow controller previously handling CO delivery. The H₂ gas is saturated here with the substrate being studied. Substrate vapor pressure, in the saturator, is selected by means of a computer controlled heating element. A lagged line was installed to carry the saturated H₂ gas to a junction where the substrate may be diluted with more H₂ before being sent to a switching valve. Here the gas is either directed to the reactor or to the gas chromatograph via lagged lines. The Robinson reactor is being used virtually unmodified. Reaction products are sent through lagged lines to the gas chromatograph for analysis.

Absolute calibration of the gas chromatograph, for a number of pertinent compounds, has been carried out. The chromatograph was modified to perform on line gas sample injections to a capillary column. The signal from a flame ionization detector is recorded and analyzed using software installed on an IBM-PC. Other tasks included calibration of flow meters, thermocouples, pressure transducers, etc. Several thermocouples needed to be relocated. Trouble shooting required a considerable amount of time and effort.

Preliminary Experiments

Several preliminary experiments designed to uncover and solve operational problems were carried out using quinoline as the substrate. These experiments also served to give an indication of the magnitude of important parameters. Blank runs, i.e. no catalyst in reactor, were done to determine the amount of background reaction; no significant background reaction was seen for this substrate. Mass balance closures of better than 2% were achieved. Runs with the catalyst installed showed that the same products are generated in this reactor system as were generated in the previous reactor system. Thus, experiments are now underway to determine the kinetics of product formation as we change the residence time, partial pressure of H₂ gas and temperature and we will report on these experiments in future reports.

IV Accepted Papers

Two papers were recently accepted for publication

- (1) Hydrodenitrogenation Chemistry, 1: Cleavage of alkylcarbon-nitrogen Bonds, Methane and Ammonia Formation in the HDN Reaction of 1,2,3,4-Tetrahydroquinoline with a Nickel Oxide Catalyst Supported on Silica/Alumina.

R.H. Fish, A.D. Thormodsen, R.S. Moore, D.L. Perry and H. Heinemann. *J.Catal*, 1986 (in press)

- (2) Synthesis of Dimetalla-azacyclobutenes via Reaction of Polynuclear Heteroaromatic Nitrogen Compounds with Triruthenium Dodecacarbonyl: Reactivity and Structural Elucidation.

R.H.Fish, T-J Kim, J.L. Stewart, J.H. Bushweller, R.K.Rosen and J.W.Dupon. *Organometallics*, 1986 (in press).

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