

### III. COAL LIQUEFACTION

#### Introduction

Sandia National Laboratories is actively engaged in R&D programs involving the direct conversion of coal to liquid products. The primary thrust of the program is aimed at advanced concepts for multi-stage processing and catalyst studies in coal liquefaction. In addition, we have completed a program in coal liquefaction preheater coking and are involved with refractory (e.g., titanium diboride) coatings for coal liquefaction letdown valves.

The technical program in advanced concepts for multi-stage processing is organized into the following tasks: 1) the study of coal dissolution chemistry as a function of process severity and solvent quality; 2) the study of hydrogen transfer kinetics utilizing polynuclear aromatic hydrocarbons; and 3) an investigation of novel direct liquefaction front-end configurations such as continuous solvent extraction, zero-hydrogen-feed dissolution and pretreatment of coal slurries.

The technical program in catalyst studies is organized into the following tasks: 1) upgrading behavior; 2) a study of catalyst deactivation utilizing model compounds; and 3) a continuing study of catalyst characterization. In addition, we have completed work on mineral matter effects, including the role of iron sulfides, and have been actively involved in the development of novel classes of ion exchange materials as slurry-phase catalysts.

## A. Catalysis

CHARACTERIZATION OF AGED CATALYST SAMPLES, SAND82-2410, Frances V. Stohl, Sandia National Laboratories, Proceedings of the ITSL Contractors' Conference, October 6-7, 1982, Albuquerque, New Mexico.

Catalyst samples from runs 2LCF23 and 3LCF7 were characterized to determine the changes which occur in the catalyst during ITSL runs and to determine how these changes affect catalytic activity. Kinetic data on conversion of 850°F+ during runs 23 and 7 indicated that the catalyst in run 23 was extremely deactivated whereas the catalyst in run 7 showed only minor deactivation. The run conditions, feeds and catalyst ages for these two runs were very different. Results of the catalyst analyses showed that the catalyst from run 23 had a much higher metals content (5.8 wt % Fe and Ti) than the catalyst from run 7 (4.3 wt %). SEM photographs of the catalyst showed the presence of an iron, sulfur-rich crust on the outside of the catalyst from the first reactor in run 23. This crust was not found on any other samples. This crustal deposit was probably due to the very high chlorine content (400-1400 ppm) in the feed for run 23. This chlorine caused a tremendous amount of corrosion in the reactor during this run.

THE EFFECTS OF SURFACE AREA OF IRON SULFIDE CATALYSIS, SAND81-1846, Frances V. Stohl, Sandia National Laboratories, Fuel.

The purpose of this work was to determine the effects of surface area on iron sulfide catalysis in coal liquefaction. Several iron sulfides have been synthesized including pyrite ( $\text{FeS}_2$ ) with 46.6 wt % Fe, pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) with approximately 60 wt % Fe and mackinawite ( $\text{Fe}_9\text{S}_8$ ) with 66.2 wt % Fe. Surface areas of the synthetic pyrites varied from 2 to greater than 10  $\text{m}^2/\text{g}$ , pyrrhotite surface areas were 6 and 10  $\text{m}^2/\text{g}$ , and mackinawite surface areas were 40 and 80  $\text{m}^2/\text{g}$ . These iron sulfides were tested for catalytic activity in tubing reactor runs with West Virginia Blacksville #2 coal and SRC-II heavy distillate. All these materials showed catalytic effects as compared to uncatalyzed thermal runs, although the effects were not as large as those obtained with Co/Mo on alumina catalyst. Large variations in surface area did not cause any significant differences in conversion. The results from an additional series of tubing reactor runs, which was carried out to determine how iron sulfide surface areas change during liquefaction, showed that the surface areas were drastically changed during the two-minute heat-up of the reactor. Robena pyrite with a surface area of 2.2  $\text{m}^2/\text{g}$  and mackinawite with a surface area of 80  $\text{m}^2/\text{g}$  yielded iron sulfides with surface areas of 5.2 and 10.8  $\text{m}^2/\text{g}$  after a two-minute heat-up to 425°C and subsequent quench.

CATALYST DEACTIVATION DURING COAL LIQUEFACTION, SAND82-2318,  
M. G. Thomas, Sandia National Laboratories; Deepak S. Thakur,  
Texas A&M University, Catalysis Reviews.

A review of the research and development efforts in catalytic direct liquefaction has shown that, just as in petroleum residuals refining, catalyst lifetime is more important than initial activity. Deactivation studies indicate that contamination by 20-30 weight percent carbonaceous material and 2-8 weight percent inorganics result in deactivation best described by the shell progressive deactivation mechanism. Metals contamination is confined to the outer several hundred microns of the catalyst and pore volume distributions show a marked change towards higher average pore size in support of this mechanism. Close examination of the mechanistic behavior of catalysts in direct liquefaction indicate that their primary function is hydrogenation of solvents.

EXPENDABLE CATALYSTS FOR DIRECT COAL LIQUEFACTION, SAND81-0452,  
H. P. Stephens, F. V. Stohl, Sandia National Laboratories,  
Synfuels: A National Need for 1990 and Beyond - ASME  
Symposium, March 19-20, 1981, Albuquerque, New Mexico.

Use of expendable slurry-phase catalysts shows promise for making direct conversion of coal to distillate liquid products an economically attractive process by reducing the need for catalyst recovery and regeneration. Batch micro-reactor techniques have been used to investigate two aspects of expendable catalyst development, the role of the iron sulfide system in direct liquefaction and the feasibility of using aged commercial catalysts as slurry-phase catalysts.

MINERAL MATTER EFFECTS IN COAL LIQUEFACTION, SAND82-1409,  
Howard P. Stephens, Sandia National Laboratories, DOE Con-  
tractor's Conference, U. S. DOE, Pittsburgh, Pennsylvania,  
September 1982.

Objectives: To prepare and evaluate the performance of slurry phase catalysts with respect to hydrogen consumption and conversion of coal to distillate range products; to determine the synergistic effects of slurry phase catalysts and inherent coal mineral matter.

Work Done and Conclusions: A factorially designed and statistically analyzed matrix of experiments has been completed to test the direct liquefaction slurry catalytic effects of five metals (Mo, Co, Ni, Sn, and Mn) and two organic ligands (naphthenic and octoic acid) at three metal concentration levels (0.01, 0.1 and 1.0 wt % on a coal basis). The liquefaction reactions were performed in 40 cm<sup>3</sup> micro-reactors with

Illinois No. 6 coal (Burning Star), SRC-II heavy distillate from the Ft. Lewis pilot plant (2:1 solvent: coal) and high purity hydrogen. Analysis of the pyrite content of the coal showed that  $H_2S$  would be produced in excess of the amount needed to convert the organometallics to the metal sulfide. Following reaction of the coal at 400°C for 30 minutes, the product slurry and gases were analyzed for THF insols, high molecular weight material, intermediate molecular weight products, and low molecular weight products by THF solubility, high performance liquid chromatography (gel permeation column), and gas chromatography.

SLURRY PHASE CATALYSIS OF DIRECT COAL LIQUEFACTION BY IRON SULFIDES, H. P. Stephens, F. V. Stohl, T. D. Padrick, Sandia National Laboratories, SAND81-0138, International Conference on Coal Science, September 7-9, 1981, Dusseldorf, Germany.

Although it has been demonstrated that direct liquefaction of coal can be catalyzed by pyrite, there has been little insight regarding the catalytic role of pyrite. Part of the difficulty in interpreting the effects of pyrite and other iron sulfide additions on coal liquefaction is due to their transformation to pyrrhotite under the conditions usually employed for coal liquefaction. Because of the importance of pyrite as a natural catalytic species and because of the possible use of other iron sulfides as liquefaction catalysts, we have performed studies to define: 1) the kinetics of decomposition of pyrite; 2) the rate and magnitude of the change in surface area of the initially added sulfide during coal liquefaction; and 3) the effect of pyrite, pyrrhotite, and  $H_2S$  additions on liquefaction product distributions.

OIL-SOLUBLE COAL LIQUEFACTION CATALYST SCREENING, Richard J. Kottenstette, Sandia National Laboratories, SAND82-2495.

Experiments were performed to determine the effect of oil-soluble catalysts in direct coal liquefaction. Variables included the metal type (Mo, Co, Ni, Mn and Sn), metal loading (0.01 to 1.0 wt %) and organic ligand (octoic and naphthenic acids). All runs were carried out with Illinois No. 6 coal (Burning Star mine) and SRC-II heavy distillate solvent at 400°C for 30 min under 800 psig (cold)  $H_2$ . Statistical analysis showed that for Mo and Ni, hydrogen consumption and conversion to oil increased with increasing metal concentration. For example, conversion to oil increased from 15.7% without catalyst to 28.5% with addition of 0.1% Mo naphthenate and 26.0% with addition of 0.1% Ni naphthenate. The effect of ligand type on catalyst activity was insignificant, indicating that neither of the organic acids were influential for coal liquefaction. Oil-soluble catalysts containing Co, Mn,

and Sn had no significant effect upon coal liquefaction, within the concentration range studied.

THE DECOMPOSITION OF PYRITE UNDER COAL LIQUEFACTION CONDITIONS: A KINETIC STUDY, SAND80-2474, Fuel, M. G. Thomas, T. D. Padrick, F. V. Stohl, H. P. Stephens, Sandia National Laboratories.

The decomposition of  $\text{FeS}_2$ , both as a single phase and as it exists in coal, has been studied between  $250^\circ\text{C}$  and  $350^\circ\text{C}$ , in hydrogen and nitrogen atmospheres, and in the presence of a coal-derived solvent. The first-order rate constant for decomposition of  $\text{FeS}_2$  at  $350^\circ\text{C}$  with  $\text{H}_2$  alone is  $6.7 \times 10^{-1}/\text{min}$ ; with  $\text{H}_2$  and coal-derived solvent, it is  $5.5 \times 10^{-2}/\text{min}$ ; for  $\text{FeS}_2$  contained within coal, solvent and  $\text{H}_2$ , it is  $8.6 \times 10^{-3}/\text{min}$ . Although the rate constant for decomposition is dependent upon temperature and the system, the activation energy in each case has been calculated to be  $88 \text{ kJ/mol}$ . A mechanism consistent with these data is the thermal decomposition of  $\text{FeS}_2$  to produce  $\text{Fe}_{1-x}\text{S}$  and S, followed by reaction of the sulfur with available hydrogen (from  $\text{H}_2$ , solvent or coal) to form  $\text{H}_2\text{S}$ .

THE RELATIONSHIP BETWEEN THE PROPERTIES OF IRON SULFIDES AND THEIR CATALYTIC ACTIVITY, SAND80-2361, AIChE 90th National Meeting and 11th Petrochemical & Refining Exposition, April 5-9, 1981, Houston, Texas, F. V. Stohl and B. Granoff, Sandia National Laboratories.

Iron sulfides, such as pyrite, are known as catalysts in coal liquefaction and produce significant increases in both conversion and distillate ( $850^\circ\text{F}$ ) yield. The main objective of our work is to increase the catalytic activity of iron sulfides by systematically changing the following properties: composition, source, particle size, surface area, morphology and defect level. We have synthesized several iron sulfides including pyrite ( $\text{FeS}_2$ ) with 46.6 wt % Fe, pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) with approximately 60 wt % Fe and mackinawite ( $\text{Fe}_9\text{S}_8$ ) with 66.2 wt % Fe. The source variations have included commercial material, minerals, and synthetic material. The pyrite particle sizes ranged from  $-350$  to  $-5$  micrometers, the pyrite surface areas varied from 2 to greater than  $10 \text{ m}^2/\text{g}$ , the mackinawite surface areas ranged from 40 to  $80 \text{ m}^2/\text{g}$ , and pyrite morphologies included massive material and a concentrate of framboids from Iowa coal. Mossbauer studies of the pyrrhotites in coal liquefaction residues have shown that there is a direct correlation between conversion and the number of vacancies in the pyrrhotite. Pyrites with enhanced defect levels were prepared by explosively shock loading Robena pyrite at 15 GPa. All these materials are being tested in either tubing reactor

or autoclave runs with West Virginia Blacksville #2 coal and SRC-II heavy distillate (550°F<sup>+</sup>). The runs are carried out at 425°C, 500 psi H<sub>2</sub> (cold charge) for 30 minutes with a 7.5 wt % catalyst loading. All these materials have shown catalytic effects as compared to uncatalyzed thermal runs.

THE EFFECTS OF CATALYSTS ON SCT LIQUEFACTION, SAND80-2527, ACS Meeting, Division of Fuel, American Chemical Society, March, 1981, Atlanta, Georgia, M. G. Thomas, T. C. Bickel, B. Granoff, Sandia National Laboratories.

The effects of mineral matter, supported and dispersed catalysts on SCT liquefaction are described in terms of catalytic mechanisms and changes in conversions and product distributions. The addition of pyrite is shown to increase conversion by 15-20 weight % Daf coal, and to decrease gas consumption by 1/3 at constant conversion. The mechanism of FeS<sub>2</sub> decomposition and subsequent free radical generation is related to the enhanced conversion and changes in product quality. A reactivity surface is defined by thermal and catalytic reactions that provide a quantitative guide for the testing and use of catalysts. Deactivation of supported catalyst subjected to SCT liquefaction conditions are shown to be rapid, approximately 50% deactivation in one day for hydrodesulfurization, 70% for hydrogenation, and 90% for hydrocracking.

MINERAL MATTER EFFECTS IN COAL LIQUEFACTION, R. K. Traeger, B. Granoff, Coal Processing Technology, Vol. V, p. 14 (1980).

In all liquefaction processes, coal-solvent-hydrogen slurries are heated to reactor process temperatures of 400-450°C. Subsequent cracking, hydrogenation, hydrodesulfurization, etc., may then occur, aided by catalysts (H-Coal, SYNTHOIL), by residue recycle (SRC-II) or by reaction with a catalytically hydrogenated solvent (Exxon Donor Solvent). The subsequent reactions will depend on the physical and chemical characteristics of the slurry entering the reactor (or leaving the preheater). For example, changes in preheater lengths have been shown to have significant effects on catalyst life time in the SYNTHOIL process. In addition, recent studies have shown that coal-derived liquid fuels can be produced by extended "preheating times" without catalytic treatment. Therefore, an understanding of the preheater reactions is important for process design and for the control and interpretation of results from liquefaction processes.

## B. Chemistry

THE EFFECTS OF PROCESS SEVERITY ON PHYSICOCHEMICAL PROPERTIES OF PREASPHALTENES, SAND82-0486, A. W. Lynch, M. G. Thomas, Sandia National Laboratories, Proceedings, ACS Meeting, Division of Fuel Chem., September 1982, Kansas City, Missouri.

Coal is converted from a high molecular weight solid to a low molecular weight oil, when heated in the presence of a suitable solvent. Between these two extremes exists a continuum of intermediate molecular weight materials. The intermediates are divided into three major groups by solubility in THF, toluene and pentane. Preasphaltenes are soluble in THF but insoluble in toluene; asphaltenes are soluble in toluene but insoluble in pentane; and oils are soluble in pentane and, to a large extent distillable. If the coal conversion process proceeds from dissolved coal to oil through the intermediate products, then examining the reaction mechanisms of the intermediates will provide information about the upgradeability (1-3) of the dissolved coal and about the entire coal conversion process.

This paper describes the physical character and reactions of preasphaltenes made from a bituminous coal. The preasphaltenes were obtained by reacting Illinois #6 Burning Star coal in contact with SRC-II heavy distillate under hydrogen pressure in an autoclave for various times (10-30 minutes) and temperatures (350-450°C). The preasphaltenes were separated by using conventional Soxhlet extraction techniques. The primary question addressed was: are preasphaltenes produced under one set of reaction severities (i.e., 350°C for 10 minutes) different than those made at other severities (i.e., 400 or 450°C)? The extracted preasphaltenes were analyzed for molecular weight, solubility and elemental composition. The chemical reactivities (upgradeability) were studied by further reaction of the extracted preasphaltenes with SRC-II heavy distillate solvent in shaking micro-reactors at 400°C under hydrogen for 0-30 minutes.

The conversion of the preasphaltenes was followed using a gel permeation liquid chromatographic analytical method. The results indicated that preasphaltenes generated at lower severity were more soluble, more reactive and had a higher molecular weight than those generated at higher severity.

EFFECT OF SOLVENT ON THE DISSOLUTION OF WYODAK COAL, SAND82-2404, Thomas D. Padrick, Arthur W. Lynch, Howard P. Stephens, Sandia National Laboratories, Proceedings of the ITSL Contractors' Conference, October 6-7, 1982, Albuquerque, New Mexico.

We have investigated the effect of various solvents on the liquefaction behavior of a Western sub-bituminous coal

(Wyodak-South Pit Mine) in micro-reactors (or micro-autoclaves). It was found that Wyodak conversion in hydrogenated creosote oil increased with both time and temperature reaching 90% THF conversion at 450°C for 10 minutes. We isolated the product oil (original creosote oil plus oil generated from the Wyodak coal) from experiments at 450°C and used this oil as the solvent for a single coal conversion experiment at 450°C and 5 min THF conversion in this non-rehydrogenated recycle oil was 68% compared to 83% for the original hydrogenated creosote oil. Addition of 25% quinoline and 25% tetrahydroquinoline (THQ) to the hydrogenated creosote oil increased the THF conversion of Wodak coal. Experiments in pure solvents at 400°C for 10 minutes yielded 30% THF conversion for quinoline, 55% for hydrogenated creosote oil and 83% for THQ. Addition of 10% Ni-Mo catalyst to the quinoline experiment resulted in a significant increase to 65% conversion. Product distributions indicate that in all cases, preasphaltene concentrations were less than 15% and oil production is strongly correlated to coal conversion. Also, gas analysis shows evidence of solvent hydrogenation for the highly hydrogenated solvents. The data from this limited series of experiments indicate a strong dependence on a hydrogen donor solvent for conversion of Wyodak coal.

THE EFFECT OF COAL DISSOLUTION ON SCT LIQUEFACTION,  
SAND82-0554, M. G. Thomas, Sandia National Laboratories, Proceedings of the DOE Two-Stage Liquefaction Meeting, October 15-16, 1981, Saddlebrook, New Jersey.

In the initial stages of coal liquefaction, coal dissolves and forms many large, highly functionalized molecules that produce high viscosity slurries. In the short-contact-time liquefaction concept, coal is completely dissolved and the initial dissolution products are reacted sufficiently to produce heavy oils and resids that can be easily handled and upgraded. Experimental data show that preasphaltenes, formed from three different coals, can repolymerize in this mass transfer limited regime. Reactions without solvent produced from 21-65 percent conversion to insols within 3 minutes at 425°C. Coal dissolution decreases from 90% in 30 minutes at 365°C at 10/1 solvent/coal to 80% at 395°C for 2/1 solvent/coal. At 2/1 solvent/coal, dissolution is increased from 70-95% by product removal. Increases in SRC lights in the solvent, at 2/1 solvent/coal, up to 100% in hydrogen limited conditions, results in a decrease of 30% in THF conversion. Catalysis in the form of FeS<sub>2</sub>, MoS<sub>2</sub>, and supported CoMo enhanced hydrogen transfer to decrease these repolymerization reactions by one-half.



THE EFFECTS OF SOLVENT COMPOSITION AND CONCENTRATION ON EARLY LIQUEFACTION REACTIONS, SAND81-2000, M. G. Thomas, Sandia National Laboratories, Proceedings of the H-Coal Technical Advisory Committee Meeting, September 15, 1981, Catlettsburg, Kentucky.

Current direct coal liquefaction processes were designed to rapidly heat a non-reacting solvent/coal slurry to 75-90% of the reactor temperature (850°C). Solvent was employed to 1) disperse the coal, and 2) in the reactor, to transfer hydrogen. Research over the past five years has greatly increased our knowledge of liquefaction and this knowledge can be used to better describe the early reaction chemistry of coal and the effects of solvent.

MINERAL MATTER EFFECTS IN COAL LIQUEFACTION, SAND78-0114, Proceedings of 85th National AIChE Meeting, June 4-8, 1978, Philadelphia, Pennsylvania, B. Granoff, R. K. Traeger, Sandia National Laboratories.

In all liquefaction processes, coal-solvent-hydrogen slurries are heated to reactor process temperatures of 400-450°C. Subsequent cracking, hydrogenation, hydrodesulfurization, etc., may then occur, aided by catalysts (H-Coal, SYNTHOIL), by residue recycle (SRC-II) or by reaction with a catalytically hydrogenated solvent (Exxon Donor Solvent). The subsequent reactions will depend on the physical and chemical characteristics of the slurry entering the reactor (or leaving the preheater). For example, changes in preheater lengths have been shown to have significant effects on catalyst life time in the SYNTHOIL process. In addition, recent studies have shown that coal-derived liquid fuels can be produced by extended "preheating times" without catalytic treatment. Therefore, an understanding of the preheater reactions is important for process design and for the control and interpretation of results from liquefaction processes.

KINETICS AND MECHANISMS OF THE HYDROLIQUEFACTION OF COAL: ILLINOIS NO. 6 BURNING START IN SRC-II HEAVY DISTILLATE, SAND80-0232, American Chemical Society Fall Meeting, Division of Fuel, September 1980, San Francisco, California, M. G. Thomas, T. C. Bickel, Sandia National Laboratories.

The hydroliquefaction of coal, Illinois No. 6 Burning Star high-volatile bituminous coal, H/C = .82, and approximately 10% mineral matter, in a coal-derived process solvent, SRC-II Heavy Distillate--a 550-850°F cut from the Ft. Lewis Pilot Plant -- has been extensively studied within the temperature range of 275-450°C. Reactions between 275-375°C were studied using 20 cc tubing reactors: reaction times of 6.5, 26, and 52 minutes at temperature and subsequent analysis provided kinetic

data. A multistage continuous flow reactor was employed for hydroliquefaction between 400-475°C, under 2000 psi hydrogen and at space times ranging from 0.2 to  $7 \times 10^{-3}$  h-ft<sup>3</sup>/lb. At temperatures below 350°C and at 2/1 ratios of solvent to coal, the initial dissolution of coal is the exclusive reaction observed; i.e., coal and solvent react to form preasphaltene. Above 350°C, the secondary reactions of preasphaltene to form asphaltene and gas become competitive. A kinetic model, based upon these mechanistic observations, within the 400-475°C temperature range, predicts initial solvent in balance at space times of 0.2-1  $\times 10^{-3}$  h-ft<sup>3</sup>/lb, major dependence of gas formation on the initial reactions, and activation energies of 16 kcal/mole for the formation of preasphaltene, 15 kcal/mole for the formation of asphaltene, and 23 kcal/mole for oil formation.

A LOW TEMPERATURE REACTION PATH FOR COAL LIQUEFACTION, M. G. Thomas, R. K. Traeger, Sandia National Laboratories, Am. Chem. Soc. Division of Fuel Preprint Vol. 24, No. 3, pp 224-230 (1979).

The interaction of coal and solvent to form a gel in the 250-350°C range has significant implications in the efficiency of short residence time or two-stage liquefaction processes and the operation of preheaters in existing coal liquefaction processes. This interaction has been noted during the heating of coal slurries in autoclaves where an apparent "endotherm" appears in the time-temperature curve -- the "endotherm" is currently believed to be due to a high viscosity gel reducing heat transfer to the thermowell in the autoclave. Evaluation of these transitions leads to the following qualitative results: 1) Coal Effects - as the reactivity (to benzene solubles) toward liquefaction of the coal increases, the temperature of the transition increases; - lignites do not exhibit a measurable transition; 2) Solvent - transitions are not noted with pure hydrogen donor solvents as tetralin; - magnitude of the transition increases as dissolving ability of the solvent increases.

This paper summarizes the results of initial experiments on coal-solvent interactions. Results of low temperature (300°C) batch studies are compared to results obtained from 400-450°C, short residence time continuous reactor studies.

ENGINEERING KINETICS OF SHORT RESIDENCE TIME COAL LIQUEFACTION PROCESSES, R. K. Traeger, SAND78-2154, AIChE National Meeting, April 1, 1979, Houston, Texas, Ind. Eng. Prod. Res. Dev. 1980, 19, 143-147.

Conversion of coal to liquid products occurs rapidly at temperatures over 350°C and consequently can be significant in preheaters or short residence time reactors. The extent of conversion can have an effect on the operation of preheaters or effectiveness of subsequent reactors. To obtain process information, Illinois #6 coal in SRC II heavy distillate was reacted at 13.8 MPa, temperatures of 400, 425, and 450°C, and at slurry space velocities of 3200-96000 kg/h-m<sup>3</sup>. Product compositions and viscosities were measured. High concentrations of preasphaltenes occur in early reactions resulting in a high viscosity product. Subsequent reactions to asphaltenes and oils are less rapid.

C. Properties (density, characterization, thermal conductivity)

ASPHALTENE ANALYSIS USING SIZE EXCLUSION CHROMATOGRAPHY, SAND81-2552, A. W. Lynch, M. G. Thomas, Sandia National Laboratories, Letter to the Editor, FUEL.

Sandia National Laboratories is studying details of the coal liquefaction process, such as chemical interactions, reaction rates, and the role of catalysts. These studies require larger numbers of product analyses. One commonly used analytical technique has been to separate the whole-liquid, solvent-refined coal into four major solubility classes by dissolution and precipitation. These classes are determined by solubility in organic solvents and can be commonly defined as follows: insolubles--organics and inorganic impurities which are insoluble in THF pyridine; Preasphaltenes--soluble in THF or pyridine but insoluble in toluene or benzene; asphaltenes--soluble in toluene or benzene but insoluble in pentane or hexane; oils--soluble in pentane or hexane.

The traditional separate method involves several time-consuming steps, including exhaustive Soxhlet extraction that may require 20 hours or more. An entire analysis takes 3 days to complete. Another problem is operator dependence. Some factors that may cause differences in results, making data comparisons difficult, are extraction time, drying and weighing techniques, and the order in which solvents are used.

CATALYST RESIDENCE TIME DISTRIBUTION IN THE H-COAL PDU, SAND79-2125, T. C. Bickel, M. G. Thomas, Sandia National Laboratories, AIChE 88th National Meeting, June 8-12, 1980, Philadelphia, Pennsylvania.

The internal age distribution of catalysts in Hydrocarbon Research, Incorporated H-Coal 28-day Process Demonstration Unit (PDU) Run No. 9 has been determined using Co<sup>60</sup>-tagged American Cyanamid HDS 1442A CoMo catalyst. A 3.5-pound charge of the tagged catalyst, approximately 400 micrometer Ci total activity, was added at day three of steady state operation. Standard incidence counting methods were employed to determine the concentration of tagged catalyst in the subsequent daily withdrawal and final reactor dump. The maximum concentration of tagged catalyst in the withdrawals occurred nine days after injection. Approximately 45 percent of the tagged catalyst remained in the reactor at the conclusion of the run. Catalyst resident time distribution and dispersion have been determined based upon the amount of tagged catalyst in the daily withdrawals.

#### D. Processes

DESIGN AND OPERATION OF A BENCH-SCALE COAL LIQUEFACTION SYSTEM, SAND78-0837, Richard M. Curlee, David C. Hawn, Sandia National Laboratories.

This report describes the design, fabrication, and evaluation of a continuous flow, bench-scale, coal liquefaction reactor system. While designed initially to determine engineering kinetics of catalytic hydrogenation, changes in program objectives resulted in a system configured to determine specifics of noncatalytic coal dissolution in liquifiers or preheaters. Design flexibility allowed this change in experimentation and provides for simulation of the preheater conditions of viable coal liquefaction processes. There are descriptions of system capabilities and equipment; and discussions of system operation, process conditions, and safety; and some equipment and materials problems encountered during development and operation. The system has the following features:

Temperature: 250-475°C -- isothermal or staged heating  
of four independently heated salt baths  
Pressures: to 4000 psi  
Slurry Feed Rates: 0.7-4.0 lb/hr  
Volume per Stage:  $0.5 \times 10^{-3}$  to  $2.2 \times 10^{-3}$  ft<sup>3</sup>  
(0.203 in. ID)  
 $1.6 \times 10^{-4}$  to  $8.1 \times 10^{-4}$  ft<sup>3</sup>  
(0.122 in. ID)  
Reactor Tube Length per Stage: 2 to 20 ft  
Total Length: 8 to 80 ft  
Space Velocity: 40 to 5000 (by varying tubing ID)  
Gas Flow Rates: 0-275 SCFH at 4000 psi

Seven experiments, gathering data specifically concerning preheater reactors, were conducted with good results. Several critical materials and equipment problems were solved, giving the system operational reliability. Experiments to simulate preheater conditions of the H-Coal and SRC processes are continuing.