

E. Instrumentation

THE DESIGN AND USE OF DENSITY GAUGES FOR FOSSIL ENERGY PROCESSES, SAND81-1347, D. G. Sample, M. G. Thomas, and J. K. Linn, Sandia National Laboratories, 1981 Symposium on Instrumentation and Control for FE Processes, June 8-10, 1981, San Francisco, California.

Many of the proposed processes for alternate energy sources are being developed with little or no real data detailing mass flow rates, flow regimes, solids settling, plugging, etc. Process upsets resulting from such deficiencies require time-losses for major turn-arounds, and limit processing flexibility (necessary for these processes to provide a range of products). Although progress is being made in some areas by in-stream measurements, many times intrusive measures contribute problems necessitating process-redesign and system changes, which can be avoided by non-intrusive measurements.

Over the past years, we have been directly involved in advanced research for the processing of coal, particularly with regard to direct liquefaction. Two years ago, we suggested and provided examples for the use of radiometric techniques for analyzing ash in coal, monitoring gas/liquid and liquid/solid interfaces, solids accumulation in pipes, and flow characteristics. Last year we described in detail an experiment, utilizing the neutron activation of catalysts, that showed the mixing characteristics of the H-Coal reactor and which subsequently led to the determination of catalyst deactivation.

THE ANALYSIS OF MINERALS IN COAL, SAND79-2016, F. V. Stohl, Sandia National Laboratories.

The objective of this work was to determine the sources and magnitudes of the errors associated with the analysis of mineral matter in coal. A radio-frequency low temperature asher was used to determine the quantity of mineral matter in the coal and to separate the mineral matter from the organic portion of the coal for subsequent analysis. Analyses of three different coals, which were carried out at The Pennsylvania State University, the West Virginia Geological Survey, and Sandia National Laboratories, have yielded wide ranges of low temperature ash contents. The range of values for the West Virginia Blacksville No. 2 coal was 14.2-15.0 wt %, for the Illinois No. 6 River King coal, the range was 15.7-19.0 wt %, and for the Kentucky 9/14 Colonial mine coal, it was 12.1-14.5 wt %. The most important variable in low temperature ashing was the radio-frequency power setting, since this determined the temperature at the coal-oxygen plasma interface. The temperature at this interface was monitored through the use of an 0.025 inch diameter chromel-alumel type K thermocouple with a 304 stainless steel sheath. A radio-frequency power setting of

15 watts/chamber gave a temperature of 135°C. The qualitative and quantitative analyses of the minerals in the low temperature ash were carried out by x-ray diffraction techniques. The minimum detection limit for a phase was considered to be about 3 wt %. Quantitative x-ray diffraction analysis of the minerals quartz, calcite, pyrite and kaolinite was carried out by the use of a series of standards made up of varying concentrations of these minerals in a clay matrix with NiO as an internal standard. Under optimum conditions, such as the analysis of samples with no preferred orientation of particles and the analysis of all samples in a single laboratory, the expected error bracket was $\pm 10\%$ relative. However, the low temperature ashes analyzed in this work contained 40-50 wt % clay minerals which have high preferred orientation effects, and the analyses were carried out in three laboratories, so that the error bracket obtained was $\pm 20\%$ relative.

F. Program Summaries/Project Reviews

COAL LIQUEFACTION PROCESS RESEARCH QUARTERLY REPORT, APRIL 1 - JUNE 30, 1982, SAND82-2437, R. N. Chapman, Editor, Sandia National Laboratories.

This quarterly report, for the period April 1-June 30, 1982, summarizes Sandia's activities in coal liquefaction process research. The overall objectives of the program are to understand the mechanisms and determine the role of catalysts in the direct conversion of coal to liquids. Primary emphasis is being given to the Integrated Two-Stage Liquefaction (ITSL) process. Specific tasks include: short-contact time coal liquefaction, mineral matter effects and catalyst studies. During this period, work was done on: the characteristics of a recycle solvent obtained from the Lummus Integrated Two-Stage Liquefaction (ITSL) facility at New Brunswick, New Jersey; the kinetics of hydrogenation and dehydrogenation of pyrene and dihydropyrenes in batch micro-reactors; the impact of coal cleaning on the effectiveness of two types of slurry phase catalysts; the deactivation of aged catalyst samples obtained from the H-Coal PDU; and a catalyst deactivation model for the H-Coal PDU.

MATERIALS COATINGS FOR VALVES - COAL LIQUEFACTION COMPONENTS AND INSTRUMENTATION, QUARTERLY REPORT - OCTOBER 1, 1981 - DECEMBER 31, 1981, R. M. Curlee, Sandia National Laboratories, SAND82-1024.

This quarterly report, for the period October-December 1981, summarizes activities in the development of erosion resistant coatings for the wear-prone parts of letdown and control valves used in coal conversion process plants. The objective of this program is to demonstrate material and coating process concepts developed previously at SNLA and to effect technology transfer to industrial applications. The tasks to be performed are: 1) determine the applicability of existing materials and material processes to industrial valve materials and configurations; 2) produce sets of valve trim for initial evaluations in pilot plant operations; and 3) develop such coating materials and processes to achieve Task 2 or that will result in improved materials. In preliminary evaluations, the ability to directly apply TiB_2 coatings on K701 (WC) cermets by CVD was demonstrated. Efforts to achieve this on other commercial substrates of interest such as K703 have not produced consistent results. Hence, the substrate material favored for the first generation pilot plant prototype is K701.

Studies are being conducted to evaluate intermediary buffer coatings of metallic nickel to reduce thermal stress and chemical incompatibilities between the TiB_2 coating and the WC substrates. This appears to be a feasible approach although Ni platings produced by standard processes have not possessed

adequate adhesion to the substrate at deposition temperatures of 900°C. Special processes are under development to improve high temperature adhesion. Contracts have been initiated with a valve trim manufacturer to produce two sets of trim for the Wilsonville pilot plant.

COAL LIQUEFACTION PROCESS RESEARCH QUARTERLY REPORT, JANUARY 1 - MARCH 31, 1982, SAND82-1924, A. W. Lynch, Editor, Sandia National Laboratories.

This quarterly report, for the period January 1-March 31, 1982, summarizes Sandia's activities in coal liquefaction process research. The overall objectives of the program are to understand the mechanisms of coal liquefaction, to determine the role of catalysts in the direct conversion of coal to liquids, to determine the mechanism of catalyst deactivation and to explore slurry phase catalyst systems. Specific projects include: short-contact time coal liquefaction, mineral matter effects and catalyst studies. During this period, we performed work on: 1) the stability, at reaction temperature, of a recycle solvent obtained from the Lummus Two-Stage Liquefaction facility, 2) reactions of preasphaltenes and asphaltenes prepared under various reaction severities, 3) the evaluation of the catalyst level detector installed at the H-coal facility, 4) the characterization of oil soluble metal compounds with respect to hydrogenation activity, and 5) characterization, deactivation and regeneration of catalysts obtained from both the H-Coal and Lummus facilities.

MATERIALS COATINGS FOR VALVES, QUARTERLY REPORT FOR JANUARY 1-MARCH 31, 1982, SAND82-2137, R. M. Curlee, Sandia National Laboratories.

This quarterly report, for the period January 1-March 31, 1982, summarizes activities in the development of erosion resistant coatings for the wear-prone components of letdown and control valves used in coal liquefaction plants. These activities have followed a course of, 1) material and process development of CVD (chemically vapor deposited) TiB_2 (titanium diboride) coatings; 2) erosion testing and screening of coated cermet substrates; and 3) prototype trim fabrication with associated development of fixturing and assembly hardware. During this reporting period, additional cemented carbide substrate materials (Kennametal K801 and K151A) were evaluated along with K701 and K703. Only the K701/ TiB_2 combination has proven to be sufficiently reliable to warrant field testing in a process plant environment, and then only if the substrate has been pre-coated with electroplated nickel to promote adhesion between coating and carbide substrate and reduce thermophysical stresses. A cleaning and plating process has been developed to

produce nickel precoats stable at the temperatures of CVD. TiB₂ coated specimens have been subjected to simulated slurry erosion testing at Battelle Columbus Labs (BCL) with some materials such as K701/TiB₂ and hot pressed (HP) TiB₂/TiB₂ exhibiting very low erosion rates. Prototypes of the letdown valve plugs for the EDS and SRC-I processes have been fabricated and coated. Preliminary metallographic evaluation of the prototype plugs and descriptions of CVD furnace hardware are presented.

MINERAL MATTER EFFECTS IN COAL LIQUEFACTION, SAND79-0306,
B. Granoff, Sandia National Laboratories.

This is the first quarterly report of a study of mineral matter effects in coal liquefaction. The objectives of the program are to: 1) prepare and characterize disposable catalysts for use in coal liquefaction; 2) test and evaluate these catalysts by means of batch autoclave experiments; and 3) determine the thermal effects of slowly heating a coal/solvent slurry in the presence of a disposable catalyst. Autoclave runs have been completed with West Virginia, Illinois No. 6, and Kentucky No. 9/14 coals, in SRC-II heavy distillate as a solvent. Experimental conditions were: temperature, 425°C; pressure, 1800 psig; and residence time, 30 min. Conversion to benzene solubles ranged from 63% (WV coal) to 76% (IL 6 coal). The corresponding Brookfield viscosities (at 60°C) ranged from 333 centipoise (WV) to 157 centipoise (IL 6). The total distillate yields (850°F-) were: WV, 19.0%; IL 6, 33.0%; and KY 9/14, 30.8%. Addition of five weight percent pyrite, from beneficiated coal, to the West Virginia coal resulted in an increase in conversion to benzene solubles from 63 to 68%, a decrease in viscosity from 333 to 248 centipoise, and an increase in total distillate yield from 19.0 to 24.0%. Preliminary evidence has shown that pyrite enhanced the conversion of the 850°F+ fraction to 850°F distillates.

MINERAL MATTER EFFECTS AND CATALYST CHARACTERIZATION IN COAL LIQUEFACTION, SAND79-0505, Barry Granoff, Paul M. Baca, Sandia National Laboratories.

This is the final report of a study of mineral matter effects in coal liquefaction. The objectives were to: 1) determine the general effects of mineral content on product composition for residence times of 2, 10, and 40 minutes and 2) determine the specific catalytic effects of several iron sulfides on coal conversion and product quality. To study the effects of mineral matter at relatively short residence times, we modified an existing one-liter, stirred, high-pressure autoclave for rapid heating and cooling of a coal/solvent slurry. The rapid heatup experiments were carried out with Illinois No. 6 coal (Burning

Star Mine; 11.8 percent ash and 3.5 percent sulfur) in tetralin (1, 2, 3, 4 - tetrahydronaphthalene) solvent, at 410°C and 1500 psig. As the residence time increased from 2 to 40 min., the conversion to benzene solubles increased from 25 to 61 percent and the yield of pentane-soluble oil increased from 13 to 16 percent. The preasphaltenes increased initially from 31 to 38 percent, and then decreased to 27 percent. Addition of pyrite (7 wt. percent based on coal), at a residence time of 10 min., resulted in an increase in the yield of pentane-soluble oil and a decrease in the yield of asphaltenes and preasphaltenes. The sulfur and oxygen contents of the asphaltenes and preasphaltenes decreased with increasing residence time. Further decreases in sulfur and oxygen were noted when pyrite had been added to the feed. To study the effects of iron sulfides on coal liquefaction, we carried out a series of slow-heatup runs (1.0 hr from room temperature to operating temperature) with Illinois No. 6 (Burning Star Mine) coal in SRC-II heavy distillate solvent, at 425°C, 1800 psig and 30 min. residence time. Naturally occurring pyrite and several different pyrrhotites were used at a concentration, based on coal, of 5.5 wt. percent iron. Conversion to benzene solubles increased from 61 percent to 78 percent for runs carried out with either pyrite or a freshly precipitated pyrrhotite. Pentane-soluble oil yield increased from 14 percent without any added catalyst to 31 percent with freshly precipitated pyrrhotite, and to 36 percent with minus 325 mesh pyrite. Preasphaltenes decreased in all runs with added iron sulfides. The pyrite particle size (-325 mesh vs. 100 x 200 mesh) had an effect on oil yield and product viscosity, with the largest increase in pentane-soluble oil and largest decrease in viscosity being observed in the experiment with the -325 mesh pyrite.

MINERAL MATTER EFFECTS AND CATALYST CHARACTERIZATION IN COAL LIQUEFACTION, SAND78-1318, B. Granoff and M. G. Thomas, Sandia National Laboratories.

Coal liquefaction experiments were carried out in an autoclave facility that has been modified for the rapid (approximately 5 sec) addition of a coal/solvent slurry into a preheated solvent. Sixteen slurry addition experiments have been completed with Illinois No. 6 coal in tetralin solvent. Six runs were carried at 408°C, 1500 psig and a solvent-to-coal ratio of 4.0, in order to evaluate the effects of residence time (2, 10 and 40 min) and mineral additions (20 wt.% THF-extracted filter cake) on coal liquefaction. Conversion to benzene solubles increased from 24 to 60% as residence time increased from 2 to 40 min. An additional 1 to 4% increase in conversion occurred when mineral matter was added to the feed slurry. The preasphaltenes increased from 35 to 38%, and then decreased to 29% as residence time increased from 2 to 40 min. Additional increases in preasphaltenes occurred in the presence of added mineral matter. Hydrogen consumption increased from 0.5 to 1.4% as residence time increased.

Three fresh and two spent catalysts were received from the bench reactor at Hydrocarbon Research, Inc. A test matrix has been developed for the quantitative analysis of Co, Ni, Mo, Fe, Ti, Mg, Ca, Zn, Na, Al, Si, and S by electron microprobe analysis, emission spectroscopy and atomic absorption spectroscopy. The electron microprobe will be used for an elemental mapping of approximately 10% of the cross sectional area of a catalyst sample. Preliminary data have shown that Ti increased from approximately 2% on the surface of a spent catalyst to approximately 7-8% at 50-100 micrometers depth, and then decreased to approximately 2% at 200 micrometers.

CHEMICAL STUDIES ON THE SYNTHOIL PROCESS: MINERAL MATTER EFFECTS, SAND78-1113, Barry Granoff, Paul M. Baca, Michael G. Thomas, George T. Noles, Sandia National Laboratories.

The objective of this work was to study mineral matter effects in coal liquefaction. This was accomplished by means of batch autoclave experiments at temperatures of 395 to 430°C, residence times (at temperature) of 15 to 60 min and operating pressures of 1500 to 3000 psig. All experiments were carried out in creosote oil (No. 4 cut) as the solvent, at a solvent-to-coal ratio of 2.30 to 2.50. High volatile bituminous coals from Kentucky, Indiana, West Virginia, Illinois and Pennsylvania were used for most of this work. The mineral contents of these coals, as determined by low temperature ashing, ranged from 24.6 to 5.2%; the corresponding sulfur contents ranged from 6.7 to 0.8%.

A series of screening experiments was carried out at 430°C, with six coals whose petrographic composition was similar (reactive maceral contents ranged from 85 to 95%), but whose mineral content varied from 5.2 to 20.9%. It was found that as the mineral content increased, the conversion of coal to benzene solubles increased from 22.4 to 73.5%, the viscosity of the liquid products decreased from 761 to 75 cp (at 60°C), hydrogen consumption increased from 1.8 to 3.4% and hydrocarbon gas formation (C₁ - C₄) remained fairly constant between 2.0 and 2.5%.

COAL LIQUEFACTION PROCESS RESEARCH QUARTERLY REPORT FOR JANUARY-MARCH 1980, SAND80-1425, T. C. Bickel, R. M. Curlee, B. Granoff, T. D. Padrick, F. V. Stohl, M. G. Thomas, Sandia National Laboratories.

Objective: The objectives of this project are to determine the role of mineral matter in coal liquefaction and to explore the feasibility of utilizing various iron sulfides as disposable catalysts.

Work Done and Conclusions: Techniques were developed for the synthesis of iron sulfides with compositions ranging from pyrite (FeS_2 , 46.6 w/o Fe) to mackinawite (Fe_9S_8 , surface area and defect content). The latter was achieved by explosive shock activation at 15 GPa. Each of the iron sulfides was catalytically active for the conversion of coal to THF and toluene-soluble liquid products. Mossbauer spectroscopy (P. A. Montano, West Virginia University) was used to determine the stoichiometry of the pyrrhotites that were formed from pyrite during liquefaction. It was shown that the pyrrhotite composition was controlled by the sulfur content of the reaction mixture.

Significance to Fossil Energy Program. This work has clearly shown that iron sulfides of different compositions are active as disposable catalyst for coal liquefaction. The role of sulfur in the decomposition of pyrite was studied and related to the liquefaction mechanism. It was shown that increasing the defect content of pyrite was not sufficient for improving the catalytic activity. Mossbauer data were used to develop a relationship between coal conversion and pyrrhotite stoichiometry, but the "active" iron sulfide catalyst has not yet been unambiguously identified.

Plans for the Coming Year. Work will continue to define the role of iron sulfides in coal liquefaction, and to synthesize disposable catalysts more active than pyrite. The program will be expanded to include other metal sulfides, and will explore novel techniques for preparing highly dispersed slurry catalysts. Catalytic mechanisms will be obtained and a predictive mathematical model will be developed. The use of disposable catalysts in advanced two-stage liquefaction will be studied.

COAL LIQUEFACTION SHORT RESIDENCE TIME PROCESS RESEARCH, Second Quarterly Report, January 1 - March 31, 1979, SAND79-1834, R. K. Traeger and T. C. Bickel, Sandia National Laboratories.

Process research on short residence time studies includes kinetic studies on a bench scale reactor, resident time studies in the three-phase liquefaction systems, and characterization of the initial chemical processes. Failures of electrical heaters and a new compressor prevented operation of the reactor in the last quarter. A detector system for measuring the residence time of solids has been built. Chemical studies show the solvent and coal react to form a preasphaltene adduct resulting in a solvent imbalance. The reaction occurs in the 200-300°C range where neither the coal nor the solvent by themselves undergo reaction. The extent of adduction depends on the nature of the coal and of the solvent.

COAL LIQUEFACTION SHORT RESIDENCE TIME PROCESS RESEARCH, 79-1, SAND79-1400, First Quarterly Report, October 1-December 31, 1978, R. K. Traeger, T. C. Bickel, Sandia National Laboratories.

Process research has been initiated in three areas of coal liquefaction: 1) the determination of short resident-time engineering kinetics of coal liquefaction reactions using a non-recycle bench scale tubular reactor, 2) the measurement of the three-phase reactor residence time of reactants (coal, process solvent, hydrogen), and 3) the characterization of the physical/chemical properties of the coal-derived liquid products.

The bench-scale tubular reactor has been modified to increase heat transfer rates, obtain more precise temperature measurements, minimize line plugging, and allow reduced hydrogen flow rates. The coal chosen for the reactor experiments was Illinois No. 6 "Burning Star" coal screened to -45 mesh. Proximate, ultimate sulfur forms and particle size distribution analysis have been performed on the coal. The process solvent chosen for the reactor experiments was SRC-II heavy distillate, which was obtained from the Ft. Lewis pilot plant. This solvent had a carbon content of 89.78%, hydrogen content of 7.67%, H/C ratio of 1.02, viscosity of 11 cp at 70°C, and a specific gravity of 1.02 at 25°C. The feasibility of using x-radiography for liquid-gas void fraction has been demonstrated and further evaluation of this technique is underway. Extrapolation of coal liquid product viscosities to reaction temperatures suggests that process stream viscosities are in the 1-100 poise range. The surface tension of SRC-II heavy distillate was measured and found to be 46 dyne/cm at 25°C and 1 atm.

PREHEATER STUDIES IN COAL LIQUEFACTION, SAND79-0150, Annual Report, October 1977-September 1978, R. K. Traeger, T. C. Bickel, and R. M. Curlee, Sandia National Laboratories.

Coal slurry preheaters for liquefaction processes are short residence time reactors in which the coal-organic matter goes into solution and undergoes reaction to form lower molecular weight products. A continuous non-recycle bench-scale reactor was used for process research on short residence time reactions of Illinois No. 6 coal in SRC II heavy distillate. Goals of the research were to measure the distribution and rates of formation of coal liquefaction products, to estimate physical changes occurring in the process stream and to evaluate kinetic models of the conversion processes.

Reactions were carried out at 2000 psi hydrogen pressure and isothermally at temperatures of 400, 425, and 450°C. Slurry space times were varied from 0.3×10^{-3} - 6×10^{-3} h/ft³/lb; estimated residence times were 20-480 seconds. Coal conversion

to benzene soluble products of 25, 55, and 65% at 400, 425, and 450°C, respectively, were achieved at the longest residence times; the majority of the conversion occurring in the first 20% of the reactor. Viscosity, measured at 70°C, exceeded 100 poise at the low conversions. The solvent balance, as determined by benzene soluble product, was negative at short reaction times. The amount of solvent loss increased as the preheater operating temperature was decreased and the loss was evident for longer times at the lower temperatures.

PREHEATER STUDIES IN COAL LIQUEFACTION, April 1 - June 30, 1978, R. K. Traeger and R. M. Curlee, Sandia National Laboratories, SAND78-1872.

Illinois No. 6 coal in SRC II heavy distillate was hydroliquefied in one pass through a continuous reactor at 425°C, 2000 psi and slurry space rates of 170 to 6000 lbs/h-ft³. Coal dissolution with the formation of preasphaltenes occurs at times estimated to be less than a minute yielding a high viscosity product. Secondary reactions forming oils and asphaltenes occur with 70% conversion to THF solubles and 50% conversion to benzene solubles at space rates of 170 to 190 lbs/h-ft³.

Although conversions at 425°C were unexpectedly close to those at 450°C, the 425°C run gave a different product distribution with less oil and yielded less gas.

PREHEATER STUDIES IN COAL LIQUEFACTION JANUARY 1 - MARCH 31, 1978 QUARTERLY REPORT, SAND78-1224, R. K. Traeger, R. M. Curlee, Sandia National Laboratories.

Noncatalytic conversion of Illinois No. 6 coal to liquid products was studied at 450°C, 2000 psi and liquid space velocities of 170 to 4700 lbs/h-ft³. Initial dissolution with formation of preasphaltenes and the resultant high viscosity product occurred rapidly. Viscosities, as measured at 70°C, decreased from 28,000 cp to 120 cp as the liquid space velocity decreased from 4700 to 170 lb/h-ft³. Asphaltene and oil concentrations increased during the reaction, each accounting for 40 percent of the coal liquid that formed at the low space velocity; the preasphaltenes accounted for the remaining 20% of coal liquid formed. Liquid product distillation and analyses of the gas stream did not provide definitive data since compositional changes were small relative to the total stream compositions.

Calculations and simulation experiments indicate the reactor operates in the slug/froth region. Further work is needed to determine actual flow regimes and estimate residence times.

PREHEATER EFFECTS IN COAL LIQUEFACTION PROCESSES, First Quarterly Report, SAND78-0312, R. K. Traeger and R. M. Curlee, Sandia National Laboratories.

Process research has been initiated to define effects of preheater conditions on coal slurry reactions in coal liquefaction processes. A four-stage, continuous flow reactor was modified to provide preheater conditions representative of those used in existing processes. Illinois No. 6 coal was received from Hydrocarbon Research and SRC II, heavy distillate coal liquid was received from the Pittsburgh and Midway Coal Mining Company. Both stocks were analyzed. An initial "blank" run at 450°C and 2000 psi was made using the SRC II liquid only. As expected, no changes in the SRC II liquid were noted in the run.