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STUDIES IN COAL LIQUEFACTION WITH APPLICATION TO THE
SRC AND RELATED PROCESSES

Final Report for November 1978—September 1983

By
A. R. Tarrer
James A. Guin
Christine W. Curtis

Work Performed Under Contract No. AC22-79ET13397

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STUDIES IN COAL LIQUEFACTION
WITH APPLICATION TO
THE SRC AND RELATED PROCESSES

Final Report for the
Period November, 1978 - September, 1983

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PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY

Under Contract No. DE-AC22-79ET13397

Objective and Scope

Scope:

The Auburn Coal Conversion Laboratory is engaged in a research program designed to investigate fundamental aspects of the Solvent Refined Coal (SRC) and other closely related coal liquefaction processes. The SRC process provides a method for liquefaction of coal, and removal of sulfur and ash pollutants which would result from direct combustion of the raw coal. If successful, the SRC process will permit the use of high sulfur coals as a boiler fuel, which otherwise could not be used under EPA regulations. This research program seeks to improve the economic attractiveness of the SRC process through the application of chemical engineering techniques.

Objective:

The objective of this research program is to systematically investigate, characterize, and delineate the effects of changes in process operating conditions, equipment configuration, and nature of raw materials upon the kinetics, mechanism, and extent of coal dissolution, heteroatom removal, and hydrogenation in the SRC and closely related processes, for the purpose of providing an increased fundamental understanding of SRC process chemistry as well as guidelines and recommendations leading to economic and technical improvements in SRC technology. The program objectives were carried out in cooperation with the Souther Services' SRC pilot plant operation at Wilsonville, Alabama, and with the Rust Engineering subsidiary of Wheelabrator-Frye, Inc.

Program Task Outline

Task 1. Mechanistic Studies of Coal Particle Dissolution

- A. Dissolution Behavior as a Function of Coal Characteristics
- B. Effect of Solvent Type and Gas Phase Composition on Particle Dissolution
- C. Direct Visual Observation of In-situ Particle Dissolution

Task 2. Catalysis by Coal Mineral Matter

- A. Process Variables and Kinetics
- B. Characterization of Coal Minerals
- C. Regeneration/Pretreatment of Coal Minerals and Residue
- D. Effect on Individual Species in Coal Liquefaction Products
- E. Continuous Reactor Studies

Task 3. Analytical Support

- A. Fourier Transform Infrared Spectroscopy of Coal and SRC
- B. Energy Dispersive X-Ray Fluorescence of Coal and SRC

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PROJECT TITLE: Studies in Coal Liquefaction with Application to
the SRC and Related Processes

CONTRACT NUMBER: DE-AC01-79ET13397

This is the final report under the above contract. A summary of the most important aspects of the work is presented in this report. Detailed results can be found by referring to the twenty quarterly reports and over thirty technical papers and presentations resulting from work under this contract.

SUMMARY OF WORK PERFORMED

1. Screening experiments with model sulfur, nitrogen, and oxygen compounds were undertaken to determine the relative ease of breaking C-N, C-O, and C-S bonds to remove heteroatoms in the presence of various coal mineral catalysts. Iron, pyrite, and SRC residue ash showed moderate catalytic activity. All the reactions were conducted in a small tubing-bomb reactor under coal liquefaction conditions. The importance of mass transfer in the hydrogenation reactions was observed, especially in the presence of active catalysts.

In addition, a detailed analysis of the controlling regimes in the hydrodesulfurization (HDS) of benzothiophene over pyrite catalyst in a slurry reactor was made. The primary product of benzothiophene HDS with pyrite was 2,3-dihydrobenzothiophene, but with pyrrhotite the selectivity shifted toward ethylbenzene. Also, the HDS of benzothiophene was influenced greatly by mass transfer effects as evidenced by changes in the reaction rate as function of agitation speed, pyrite particle size, and a low activation energy above 385°C.

2. Experiments and instrumental analyses were conducted to elucidate the effect of the solvent properties on coal dissolution behavior. A series of solvents was obtained by hydrogenation of creosote oil to different degrees. Reactions of these solvents with two types of coal have been performed. The dissolution yields obtained were compared to those with several reference solvents. The solvent quality parameters were measured using several

analytical techniques. Results were discussed and correlated with the coal dissolution yields. Reactions of the solvents with a hydrogen acceptor, benzophenone, were also performed. Results showed that the hydrogen donating ability of the solvents was probably not the only important factor governing the dissolution of the coal.

3. Two improved processes for the conversion of coal to a low-sulfur solid product were developed. Developmental studies were made of a single-stage processing method by which coal mineral additives can be used to improve drastically the hydrogen economy of Solvent Refined Coal (SRC) processing technology and also to meet the present new source performance standards (NSPS).

For the single-stage process, laboratory-scale batch experiments were performed to evaluate the catalytic/scrubbing activity of different coal minerals (SRC-residue, SRC-residue ash, coal ash, Kerr-McGee ash, reduced iron, magnetite, and hematite). These experiments were carried out under reaction conditions representative of those used in the SRC process. The catalytic activity and selectivity of liquefaction, hydrogenation, and desulfurization reactions were studied in the presence of the different mineral additives and compared with those obtained in the absence of additives. The effects of mass transfer and surface area were studied. An improved single-stage process was proposed, and the results of the studies made showed that it had a potential of reducing hydrogen requirements for conventional SRC processing by 30 to 50 percent.

Although a considerable reduction in hydrogen economy was realized and a significant reduction of the sulfur was achieved by this proposed single-stage process, these sulfur reductions were not sufficient to meet the newly proposed Environmental Protection Agency's (EPA) New Point Source Emission Standards

(NPSES). The proposed single-stage process was thus modified by adding a hydrotreating stage (two-stage process) to provide the additional desulfurization needed to meet the proposed NPSES. In the first-stage, residence time and hydrogen consumption were minimized by using inexpensive mineral additives, treated to improve their selectivity for desulfurization over hydrogenation. The second-stage involved hydrotreating the filtered liquid product from the first-stage using a commercial Co-Mo-Al₂O₃ catalyst.

For both processes, single-stage as well as two-stage, kinetic models for hydrodesulfurization and hydrogen consumption were developed. An experimental univariate search in combination with numerical search routines was applied to identify the optimum reaction conditions for which selectivity is a maximum. This was done for both reaction stages.

Experiments were performed to study the variation of the viscosity of light recycle oil, creosote oil, and coal-oil slurries with temperature. The variation of the viscosity of coal-oil slurry during the heat-up period was also studied. Empirical equations correlating viscosity and temperature for light SRC recycle oil and creosote oil were obtained using a least square approximation method for curve fitting.

4. It has been found that the quality of a solvent for coal dissolution depends on coal characteristics. Specifically, the hydrogen content of a solvent which results in the highest dissolution varies significantly with coal type: for example, maximum dissolution of Monterey coal occurred at a different level of hydrogen content than that for Kentucky 9/14 coal. A detailed report concerning this finding and supportive data are given in the February - April, 1979, quarterly report.

Comparative short time/high temperature and long time/low temperature reaction studies were performed using primarily Indiana V coal. The results

showed that the liquefaction as well as desulfurization rates are faster in short time/high temperature reactions than in long time/low temperature reactions. Also, less hydrogen was consumed in the short time/high temperature reactions. (Refer to the August - October, 1979 report).

The results of these studies indicate the need for a better understanding of particle dissolution at short reaction time and high reaction temperatures. Kinetic studies for short time/high temperature reaction with Kentucky 9/14 coal also have shown this reaction zone to have significant processing advantages (May - July, 1979).

It was found that solvent quality could be adversely affected by limited or excess hydrogenation. An optimum degree of hydrogenation was found to exist for a creosote oil hydrogenated to different levels of hydrogen content. (February - April, 1979).

From nuclear magnetic resonance spectroscopy studies, it was observed that a balance between aromatic and aliphatic content must be maintained for acceptable solvent quality. (February - April, 1979). Coal dissolution yield was found to correlate well with certain solvent quality parameters for a creosote oil hydrogenated to different levels of hydrogen content. The solvent quality parameters considered were total hydrogen content; atomic C/H ratio; degree of partial hydrogenation; aromatic, alpha, beta, and gamma hydrogen content and average chemical shift. The total effect of these solvent quality parameters was correlated with coal dissolution behavior using multiple regression. (February - April, 1979). Coal dissolution yield for different light recycle oils obtained from the Wilsonville SRC pilot plant could not be predicted accurately from the above solvent quality parameters using the determined correlations. This indicates these parameters above cannot be used as a general index of solvent quality, but may be limited to following

the variation in quality of a particular solvent. In other words, these parameters could possibly be used effectively to monitor the daily quality of a recycle solvent in one plant, but they could not be used to compare the quality of recycle solvents at different plants. Benzophenone acts as a hydrogen acceptor. A study was done to evaluate whether the degree of conversion of benzophenone could serve as an indicator of the hydrogen-transfer capacity of a solvent. From the results of the benzophenone study, it appears that benzophenone conversion does not correlate well with coal conversion. Agitation rates were observed to have little effect on the rate of reaction of benzophenone with tetralin. (February - April, 1979).

5. A study was made to evaluate the importance of the solution capacity of a solvent on rate of dissolution. Other researchers have observed for certain reaction conditions and coals that the addition of phenolic-type compounds results in an increase in dissolution with little accompanying increase in hydrogen consumption. The intent of this work was to determine whether this was the case for typical SRC processing conditions and Kentucky 9/14 coal. No significant effect on coal dissolution was observed to result with the addition of phenolic-type compounds. Coal dissolution rate appeared to be determined primarily by the amount of tetralin (donor solvent) present. (August - October, 1979). Recycle solvent produced at Wilsonville while processing Indiana V coal was fractionated into different distillation cuts. The different cuts were rated in accordance with their effect on conversion to cresol solubles. The 142 - 200°C cut fraction yielded the highest conversion. (August - October, 1979). The heavy recycle solvent fraction separated when using the Kerr-McGee process (commonly referred to as light SRC) was assumed to be similar in behavior to the toluene soluble fraction of SRC. A study was

done to evaluate the effect of this material on dissolution. When mixed with a portion of process solvent it proved to be an effective coal dissolution solvent. The increase in conversion due to the addition of this material could be due to either phase behavior (solubility of donor species in the solvent) or hydrogen shuttling. (August - October, 1979). In a study of the effect of hydrogen partial pressure on dissolution, the dissolution of Indiana V in 1-methylnaphthalene proved to be sensitive to initial hydrogen partial pressure. More importantly at a high hydrogen partial pressure (2000 psi) the same amount of conversion resulted with 1-methylnaphthalene as with tetralin. (August - October, 1979). Recycle solvent produced at Wilsonville while processing Kentucky 9/14 was fractionated. The use of the higher molecular weight fraction as reaction solvent did not appreciably alter the rate of coal dissolution, hydrogenation, or hydrodesulfurization. (May - 1979).

6. Hydrodesulfurization kinetics were shown to be represented well by two-parallel first-order rate expressions. That is, experimental data correlated well with the values estimated using these kinetics expressions. Also, hydrogen consumption kinetics were shown to be represented by a first-order rate expression. Using these kinetic expressions two-staged reaction was studied to estimate the variation in selectivity for desulfurization with different degrees of first-stage/second-stage reaction. Based on the approximating relationships used, the combined maximum selectivity for the reaction system studied was higher than that of the single-stage reaction. Iron oxide (Fe_2O_3) was used as a catalyst/reactant in the first-stage, and a commercial Co-Mo-Al catalyst was used in the second-stage. The selectivity for single-stage reaction with Fe_2O_3 and with Co-Mo-Al was determined experimentally as part of this comparison study. (May - July, 1979). Maximum selectivity was observed at the highest temperature and the shortest reaction time considered for

both stages of the above two-stage reaction study. In general, selectivity for desulfurization over hydrogenation was found to be very sensitive to reaction temperature, time, and hydrogen partial pressure. Almost linear relationships were observed between hydrogen consumption and reaction temperature, hydrogen consumption and initial hydrogen pressure and hydrogen consumption and amount of catalyst (Co-Mo-Al) for the second-stage reaction. (May - July, 1979). An increase in the amount of mineral matter indigenous to the coal: (i) enhances hydrogenation; (ii) enhances hydrodesulfurization, and (iii) contributes to improving or maintaining solvent quality by catalyzing the rehydrogenation of the solvent. (May - July, 1979). When the reaction was done in the presence of Fe_2O_3 , coal dissolution yield was observed to be sensitive to the initial hydrogen partial pressure, but relatively insensitive to reaction temperature and time in the ranges studied, i.e., reaction temperature = 385, 410, and 420°C, and reaction times = 15, 30, 60, and 120 minutes; whereas desulfurization and hydrogen consumption were very sensitive to reaction temperature and reaction time. Also, the formation of gas (CH_4 , CO_2 , and $\text{C}_2 - \text{C}_5$) was very sensitive to reaction temperature and time. (May - July, 1979).

7. Hydrogen consumption was observed to be higher when a Kentucky coal-SRC recycle oil slurry was reacted in the presence of SRC-residue, Kerr-McGee residue of Kentucky #6 coal, SRC-residue ash, Kerr-McGee residue ashes (Kentucky #6 and 9 coals), and Kentucky #9/14 coal ash as additives than in the absence of any additive. Also, essentially the same amount of organic sulfur was removed when either SRC-residue or Kerr-McGee residue was present during reaction as was removed when no additive was present. A higher hydrogen consumption resulted with the addition of hematite (commercial grade ore) and Fe_2O_3 (reagent grade) to the reaction mixture than that with iron and

no-additive. Almost the same selectivity resulted with the addition of coal ash, magnetite, and Fe_2O_3 in the reaction mixture; whereas iron additive gave the highest selectivity. Almost the same selectivity resulted with the addition of SRC-residue ash and Kerr-McGee ashes (Kentucky #6 and 9 coals) in the reaction mixture. Desulfurization activity was observed to increase as more SRC-residue ash was added to the reaction mixture. Kentucky #9/14 coal ash was observed to have an effect very similar to that of SRC-residue ash in the liquefaction of Kentucky #9/14 coal. The addition of CaO was observed to have a detrimental effect on coal dissolution. Increasing the concentration of iron was observed to cause a significant increase in sulfur removal, with little or no change in hydrogen consumption. In other words, selectivity for hydrodesulfurization over hydrogenation was observed to increase with an increase in the amount of iron used in the reaction mixture. If the amount of Fe_2O_3 present during reaction was less than the stoichiometric amount, less sulfur was removed during hydrodesulfurization, and if more than the stoichiometric amount was present, no additional sulfur removal or hydrogen consumption occurred. Nine to ten times the stoichiometric amount of iron had to be added to obtain the same amount of sulfur removal as results when the stoichiometric amount of Fe_2O_3 was added. (May - July, 1979).

8. Two types of processes using coal minerals were studied: those that would yield an improvement in selectivity for desulfurization over hydrogenation and those that would yield an improvement in conversion to oil. The first type of processes investigated were based on the following observations:

- (1) The use of SRC-residue ash as an additive in coal liquefaction reaction:
 - (a) enhanced coal dissolution,
 - (b) increased the rate of hydrogenation,

- (c) improved desulfurization,
 - (d) acted selectively in accelerating desulfurization over hydrogenation,
 - (e) resulted in the removal of the same amount of sulfur in 30 minutes of reaction as is removed after 120 minutes of reaction in non-additive runs,
 - (f) caused a reduction in hydrogen consumption by 40 to 50% for a specific amount of sulfur removal over that required in a non-additive run, and
 - (g) allowed the sulfur content of SRC to be reduced to as low as 0.64% while maintaining or improving the solvent quality (tetralin/naphthalene ratio) of the process solvent.
- (2) Similarly, the use of Fe_2O_3 (reagent grade) as an additive in coal liquefaction reaction:
- (a) accelerated coal-dissolution, hydrogen consumption, and desulfurization reactions,
 - (b) acted selectively to accelerate desulfurization over hydrogenation,
 - (c) reduced hydrogen consumption by 55% over that required with non-additive runs for the same level of sulfur removal, and
 - (d) scrubbed out hydrogen sulfide gas formed during the reaction, if a stoichiometric amount of Fe_2O_3 was present in the reaction mixture.
- (3) The use of reduced iron as an additive in coal liquefaction reaction:
- (a) gave a higher selectivity than that obtained with the other mineral additives studied,

- (b) did not have an appreciable effect on gas production (CH_4 , CO_2 and $\text{C}_2\text{-C}_5$),
- (c) scrubbed out all of the hydrogen sulfide gas formed during reaction, if 2 weight percent or more iron was present in the reaction mixture,
- (d) enhanced coal dissolution, and
- (e) reduced hydrogen consumption by 50-55% over that required with non-additive runs for the same level of sulfur removal.

These observations indicated that either reduction or oxidation of coal minerals might be effective ways for improving their desulfurization activity. This provided the impetus for the experiments that led to the following observations.

- (1) The surface area of an additive which acts as a sulfur scavenger (Fe_2O_3 , coal ash, residue ash, etc.) was observed to have a significant influence on desulfurization activity, and for a surface area greater than a certain limiting minimum, the influence of surface area on desulfurization was observed to be insignificant.
- (2) The oxidation temperature at which a SRC metallic waste residue is ashed was observed to have a significant effect on its surface area and its desulfurization activity. Surface area of the residue was observed to decrease with increasing oxidation temperature. Also, when heated above 600°C , the surface area of Fe_2O_3 decreased very rapidly with increasing temperature. The desulfurization activity of a residue oxidized at a lower temperature (500°C) was higher than that of a residue oxidized at a higher temperature (750°C) (May-July, 1979).

Much work has been expended in identifying processing conditions that would allow minerals (eg. liquefaction residues and disposable-type materials) to be treated, so as to improve their catalytic activity for conversion of the coal to oil. One technique has been found to improve the activity of hematite for conversion of naphthalene to tetralin (a model system) to a level comparable to or greater than that of a presulfided commercial Co-Mo-Al catalyst.

9. The importance of mass transfer in the hydrogenation reactions was studied in the presence of active catalysts. In addition, a detailed analysis was made of the controlling regimes in the hydrodesulfurization (HDS) of benzothiophene over pyrite catalyst in a slurry reactor.

Some significant conclusions of these studies are outlined below.

- (1) In preliminary catalyst screening studies, several coal minerals, such as iron, SRC residue ash, and pyrite, showed moderate catalytic activity in the heteroatom-removal (S, N, O) reactions. Of the various types of heteroatom-containing compounds considered, the heterocyclic structures were observed to be generally less reactive during the catalytic reactions.
- (2) Although very little hydrogen-transfer took place, cracking of coal-related structures took place under the reaction conditions used. The experimental data still implied that the ability of C-C bond cleavage was enhanced when the number of carbons in the straight chain increased.
- (3) The results of varying agitation speed on the reaction rate indicated that hydrogenation is essentially kinetically controlled in the absence of a active catalyst. However, gas/liquid mass transfer was

observed to be of importance when a strong catalyst was present during the reaction.

- (4) Preliminary evidence showed that pyrrhotite (FeS_{1+x}) had a moderate catalytic activity in sulfur removal, whereas that of pyrite, perhaps because of the effect of hydrogen sulfide, was less significant.
- (5) A first-order kinetic model was proposed to describe the mechanism of benzothiophene HDS with pyrite as additive catalyst. The experimental results indicated that this reaction was influenced greatly by mass transfer effects as evidenced by changes in the reaction rate as functions of agitation rate, pyrite particle size, and a low activation energy above 385°C . (November-January, 1978-1979).

10. The FTIR instrument has been utilized to characterize a series of solvents for coal liquefaction as discussed in detail in the February-April, 1979 quarterly. In addition, a high temperature IR cell was constructed for studying reactions of interest in coal research on catalytic surfaces. A high vacuum handling system for adsorbing components on catalytic plates within IR cells was also completed. A standard Energy Dispersive X-Ray Fluorescence method was developed for analysis of coal minerals. The sulfur content of the coal minerals was determined using a Leco sulfur analyzer; the carbon content, using a Perkin-Elmer C, H, N, and O analyzer. For details refer to the May - July, 1979 quarterly report.

11. A gas solubility apparatus has been designed to measure the solubilities of hydrogen and carbon dioxide in coal-derived liquids at elevated pressures and temperatures. An error analysis was performed to optimize a liquid phase analysis apparatus. The solubilities of hydrogen in tetralin (1, 2, 3, 4-

tetrahydronaphthalene) and 1-methylnaphthalene were determined at 190°, 269°, 349°, and 389°C for pressures up to 3000 psia H₂. Those data agreed well with literature values. The solubilities of carbon dioxide in tetralin, creosote oil, and SRC light recycle oil were determined at 100°, 200°, 300°, and 400°C for pressures up to 3000 psia CO₂. The results showed that the solubilities of CO₂ in the model compound tetralin were 2 to 3 times that of CO₂ in creosote oil and light recycle oil over the range of experimental conditions investigated. The solubility of methane in 1-methylnaphthalene and SRC recycle oil has also been determined. (November, 1979 - January, 1980).

12. The effect of the initial particle size of a coal on the resulting particle size of the reacted products was determined by Coulter Counter analysis of liquefaction products of Amax and Kentucky coals. Further studies of the effect in coal dissolution with different solvent/coal ratios with four different solvents (tetralin, LRO, creosote oil, naphthalene) were performed using different reaction times. Fe₂(SO₄)₃ pretreatment of Kentucky coal showed little effect on the sulfur content of the liquid product and in the liquefaction yield when followed by tetralin liquefaction. Extensive studies with SRC residue ash and coal ash as possible liquefaction catalysts were done in hydrogenation, hydrodesulfurization, and solvent quality of the coal liquefaction process. In the presence of Co-Mo-Al as catalyst and tetralin as solvent the reactivity of demineralized coal by acid extraction and magnetic separation was found to be almost the same as the untreated coal. Mineral matter present in coal strongly interacted with the LRO solvent, enhancing both the dissolution and hydrogenation reactions, but not with the tetralin solvent. Coal minerals such as Fe, SRC residue ash and pyrite had moderate hydrodesulfurization activity using phenyl sulfide, but not with dibenzothiophene. Mathematical modeling of reaction kinetics in coal liquefaction with

tetralin as the solvent was done by the Parameter Estimation Method. Coal dissolution and hydrogen transfer kinetics expressions were obtained based on a second order assumption in the following reaction scheme:

LC, GPC and FTIR were used to characterize and to obtain the molecular weight distribution of coal, SRC and coal-derived products. Flame photometric detectors (sulfur sensitive) were used to identify sulfur-containing compounds. The pattern of GPC molecular weight distribution of the THF soluble portion of coal and SRC was found to be generally broad and very similar regardless of different rank of coal. GPC chromatograms of asphaltene and oil fractions were clearly discernable, but that of preasphaltene was not observed. The arbitrary RI ratio of the GPC chromatogram showed a positive indication of the degradation of coal substances or coal-derived asphaltenes at the higher reaction temperatures, 410°C or 440°C.

13. Because of the three-phase, solid-liquid-gas nature of most coal liquefaction reactions, the opportunity presents itself for significant mass transfer limitations in the rate of the overall process. To better characterize the degree of mass transfer in coal liquefaction systems, a detailed study of mass transfer in several types of coal liquefaction reactors was performed. The methodology employed a model oxygen-sulfite reaction system to provide the needed information. Interfacial areas and mass transfer coefficients were presented as a function of agitation rate for batch autoclaves. (May, 1980 - July, 1980).

14. The liquefaction of coal was studied in several solvent mixtures. Model solvents composed of tetralin plus an added aliphatic or aromatic component of various molecular weights were employed. Liquefaction using tetralin plus a higher molecular weight cut derived from coal liquefaction was also examined. Kinetic rate constants including activation energies were obtained for conversion to cresol solubles in two of the model solvent systems. The coal liquefaction rate was found to be affected by the reactor volume, that is, the fraction of solvent vaporized at reaction conditions. Aliphatic components in the solvent tended to adversely affect liquefaction. Addition of a high molecular weight fraction from SRC processing to tetralin tended to enhance coal conversion to cresol solubles. (August -October, 1980).

15. From a study of the mixing and mass transfer characteristics of a three phase reactor system in various types of reactors it was found that: (1) the shaking tubing-bomb type reactors provide better gas-liquid mass transfer than do the stirred autoclaves. (2) the presence of solid particles, e.g. catalysts, can greatly enhance the gas-liquid mass transfer coefficient. The reaction kinetics of the quinoline-hydrogen system were studied using the coal mineral pyrite as a catalyst with quinoline/tetrahydroquinoline as a H-donor system. It has been found that certain heteroatom compounds such as quinoline can act as very good hydrogen transfer agents in coal liquefaction. Tetrahydroquinoline appears to be a much faster H-donor than the commonly used tetralin. The enhancement of coal liquefaction kinetics by pyrite catalysis was examined using a variety of kinetics models. The development of two stage coal liquefaction using a first stage disposable catalyst with second stage hydro-treatment showed that the oil yield from coal could be increased from 48% to 92% on an maf coal basis. (February - April, 1981).

16. A kinetic investigation of the Fe-S-H₂ system was conducted as an outgrowth of current research in the SRC-I (solvent refined coal) process to better understand the effects of naturally occurring iron sulfides in coal hydrogenation and hydrodesulfurization. A total of twelve closed system reactions were carried out in which 48-60 mesh pyrite, in the presence of hydrogen gas, underwent transformation to 1C hexagonal pyrrhotite. Reaction temperatures were 350°C and 400°C with four sample runs at temperature. Initial pressure of hydrogen gas was 1250 psig (8617 KPa). A comparison of the results for each reaction series was evaluated with time and temperature as variables. The transformation rate of pyrite to pyrrhotite was found to increase over the range of reaction temperatures with the 400°C samples showing the greatest amount of transformation per unit time. For the 375°C and 400°C runs pyrrhotite formation decreased after approximately 15 minutes of reaction time due to (1) reduced availability of pyrite, and (2) resistance to diffusion in the topochemical product layer. (May - July, 1981).

17. Model compound reactions were studied to evaluate the effects of mass transfer, solvent type, solvent blending, hydrogen partial pressure, temperature, reactant concentration, additive loading and its preparation, etc. Naphthalene hydrogenation and benzothiophene hydrodesulfurization were investigated under conditions comparable to commercial coal liquefaction and related processes. Both of these reaction systems were observed to be surface reaction controlled under the reaction conditions used in this work. Certain aromatic compounds were observed to cause a reduction in the reaction rates of naphthalene and benzothiophene. Single stage coal dissolution was investigated using tetralin as a hydrogen donor solvent and a commercial cobalt-molybdate catalyst. A spinning basket system was developed to allow injection of the catalyst at a desired time in the reaction cycle. This

catalyst injection technique proved to be reliable for the exploratory work done here. The degree of catalyst deactivation was rated by comparing the activities of the spent catalyst for model compound (naphthalene and cumene) reactivities relative to those of the fresh catalyst. No substantial reduction in deactivation was observed to result with delayed contacting of the catalyst with the coal-tetralin reaction mixture. The effect of reaction temperature on the initial rate of catalyst deactivation was also studied. (August - October, 1981).

18. The reduction of the iron sulfates, szomolnokite and coquimbite, to pyrrhotite during coal liquefaction was studied. This is important with regard to the functioning of pyrrhotite as a mineral catalyst. In addition, the effect of temperature, gas, and solvent type on the evolution of a known coal particle size distribution during liquefaction was examined. The particle size distribution changes in various ways depending on the process conditions, as the particles dissolve. In other work the nature of rhodium dispersed on an Al_2O_3 support was determined by IR. This system ($\text{Rh-Co-Al}_2\text{O}_3$) was used to calibrate a vacuum adsorption/IR apparatus which was utilized to study coal liquefaction sorbate molecules on coal mineral catalysts, in conjunction with their reactivity. (November, 1980 - January, 1981).

19. Work was performed using a deteriorated recycle solvent obtained from the coal liquefaction pilot-plant at Wilsonville, Alabama. The solvent had a poor quality as determined by standard solvent quality tests.

Four different routes were explored to upgrade the quality of the deteriorated solvent: catalytic dehydrogenation, thermal hydrotreatment, catalytic hydrotreatment using presulfided iron-oxide, and catalytic hydrotreatment using presulfided iron-oxide, and catalytic hydrotreatment using presulfided

Shell 324 catalyst. Each route was investigated over a wide range of temperature. A kinetic solvent quality test was conducted on the solvents, prepared using the four different routes. The results indicated that the extent of upgrading achieved met with different levels of success for the investigated routes. Good quality solvents were obtained at reduced temperatures, far removed from typical coal liquefaction operation conditions. Moreover, the temperature range over which the maximum solvent quality was obtained, differed for both catalysts.

Naphthalene hydrogenation was used as a model reaction system to provide insight about the response of solvent quality to perturbations in the reaction conditions used in catalytically hydrotreating the solvent. Observed trends in model naphthalene hydrogenation studies proved useful in interpreting the data obtained for the catalytic hydrotreatment of the solvent, in the light of selective product (hydroaromatic) formation.

Tetrahydroquinoline (THQ) is a known, powerful coal liquefaction solvent and was used as a reference for the improved solvents obtained in this work to ascertain the importance of the level of upgrading achieved.

The solvents, prepared by thermal and catalytic hydrotreatment of the recycle solvent, have been characterized using standard analytical techniques, namely, CHN and LECO analyses, NMR Spectroscopy, GC simulated distillation, and GC analysis of gaseous products. Changes in average properties that occur during upgrading, and some of the key factors that control solvent quality improvement, have been identified and discussed. Solvent quality was not found to linearly correlate with any of the measured parameters. The results of the analytical work supplement the model compound study in establishing that only mild hydrogenation conditions are desirable for upgrading, high

severity conditions are detrimental to solvent quality improvement. (August - October, 1982).

20. The amount of transferable hydrogen (H_D) in coal liquefaction solvents is regarded as one of the most important parameters in determining the effectiveness of the solvents in direct coal liquefaction processes. Methods for determining H_D utilizing ^{13}C -nmr, 1H -nmr and catalytic solvent dehydrogenation (CSD) have been applied to a series of hydrogenated creosote oils and light recycle oils. Results have been correlated with the dissolution abilities of the solvents. The removal of chemical species which interfere with the analytical techniques used to measure H_D was accomplished by high performance liquid chromatography. The resulting product fractions included saturates, aromatics, polar compounds and n-hexane insolubles.

Estimations of the amounts of H_D in the coal liquids were obtained using the ^{13}C -nmr analyses of the original whole oils and their aromatic fractions. Various ^{13}C defined windows for estimating the hydroaromatic content of the oils were examined and results were correlated with coal dissolution studies. Similar trends were observed in many of the curves. H_D estimated by 1H -nmr gave similar results to those found using ^{13}C -nmr.

CSD reactions utilizing the aromatic fractions of the coal liquids produced significant quantities of hydrocarbon gases in addition to molecular hydrogen. H_D estimated based on the hydrogen evolved showed good agreement with the ^{13}C -nmr results utilizing a 22-31 ppm hydroaromatic window.

Preliminary studies examining the effect of solvents on the product distribution in coal liquefaction reactions indicated that solvents may be an important factor in determining product selectivity.

Temperature programming of coal liquefaction reactions, as opposed to maintaining the reaction temperature constant for the duration of the reaction,

appeared to have minimal effects on the resulting product distributions. However, only one solvent (tetralin) was examined in this study. (November - January, 1983).

21. Liquid-phase adsorption was investigated as a possible method of studying the interactions between coal liquids and hydrotreating catalysts. The dual purposes of the work were to develop a method to determine specific surface areas of porous catalysts and to examine how compounds commonly found in coal liquids were adsorbed on hydrotreating catalysts.

The liquid-phase adsorption studies were performed at room temperature in tubing bomb reactors. Adsorption isotherms obtained from these experiments were assumed to follow Langmuir-type behavior.

Compounds used in these studies included PNA compounds, a basic nitrogen containing compound, and an acidic oxygen containing compound. Various commercial grade catalysts as well as presulfided CoMo/Al₂O₃ and presulfided iron oxide were used as adsorbents.

Experiments have shown that quinoline, a basic nitrogen containing compound, appears to be an excellent compound for surface area determination via liquid-phase adsorption. Adsorption of compounds such as pyrene, a PNA compound, and phenol, an acidic oxygen containing compound, may be used to determine the realative areas of different types of sites on catalyst surfaces.

The sensitivity of this liquid-phase adsorption technique was evaluated by adsorbing different solutes on various catalyst surfaces. This technique shows that the adsorptivity of different coal liquids is a distinct function of the individual properties of the adsorbate as well as the properties of adsorbent used. (May - July, 1983).

22. A series of twenty-three model donor solvents were used to rank their efficacy for the dissolution of Western Kentucky #9/14 coal. The transfer of hydrogen from the solvent to the coal fragments, as measured by coal conversion, was examined at three levels of available hydrogen. The hydrogen donors are ranked according to their ability to convert coal to THF solubles. Aromatic analogs of the model donors showed little ability to convert coal to THF solubles. Factors which influence hydrogen donation include the presence of heteroatoms or substituents both internal and external to the aromatic or hydroaromatic rings, the degree of hydrogenation, the aromaticity or nonaromaticity of the hydroaromatics, and the presence of five-membered rings. A relationship between heats of formation and hydrogen donor ability is shown for hydroaromatics within two ring or three ring homologous series. A model hydrogen acceptor, benzophenone, is also used to rank model donors and a comparison is made with the model donor ranking by coal conversion. (August - September, 1983).

Articles and Presentations

As part of the work under this contract a large number of articles and presentations were made. Since many of these are available in the open literature, a listing of these is given below.

ARTICLES AND PRESENTATIONS

1. Curtis, C. W., Hathaway, C. D., Guin, J. A., and Tarrer, A. R., Fuel, 59, 575, (1980).
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4. Garg, D., Tarrer, A. R., Curtis, C. W., Clinton, J. H., and Guin, J. A., I and EC Process Design and Development, 19, 572-580, (1980).
5. Curtis, C. W., Guin, J. A., Jeng, J. F., and Tarrer, A. R., ACS Div. Fuel Chem. Prepr., 24(3), 185, (1979).
6. Garg, D., Guin, J. A., Lee, J. M., Tarrer, A. R., and Curtis, C. W., "Use of Iron and Coal Minerals as Sulfur Scavengers in Coal Liquefaction", Symposium on Development in Experimental Kinetics and Catalysis, 75 Annual AIChE Meeting, San Francisco, CA, (1979).
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13. Rice, C. A., Worley, S. D., Curtis, C. W., Guin, J. A., Tarrer, A. R., Guin, J. A., J. Chem. Phys., 74(11), 6487, (1981).
14. Barwood, H. L., Curtis, C. W., Guin, J. A., and Tarrer, A. R., Fuel, 61, 463, (1982).
15. Henson, B. J., Tarrer, A. R., Guin, J. A., and Curtis, C. W., I and EC Process Design and Development, 21, 575, (1982).
16. Barwood, H. L., Guin, J. A., and Curtis, C. W., Fuel, 61, 470, (1982).
17. Guin, J. A., Liu, Y. A., Curtis, C. W., Tarrer, A. R., and Williams, D. C., Chemical Engineering Education, Fall, 178, (1981).
18. Gollakota, S. V. and Guin, J. A., "Assessment of Mass Transfer Effects in Coal Liquefaction Reactions", AIChE National Meeting, Orlando, FL, (February 28 -March 4, 1982).
19. Worley, S. D., Rice, C. A., Curtis, C. W., Guin, J. A., and Tarrer, A. R., "Infrared Spectroscopic Studies of CO Adsorbed on Supported Rhodium Catalysts", presented at ACS Meeting, Atlanta, GA, (March, 1981).
20. Guin, J. A. and Curtis, C. W., "Development of Two Stage Coal Liquefaction Using a First Stage Disposable Catalyst with Second Stage Hydrotreatment", presented at AIChE Meeting, New Orleans, (November, 1981).
21. Worley, S. D., Rice, C. A., Mattson, G. A., Curtis, C. W., Guin, J. A., Tarrer, A. R., J. Phys. Chem., 86, 2714, (1982).
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25. Curtis, C. W., Guin, J. A., Kwon, K. C., and Smith, N. L., Fuel, xx, xxx, (1983).
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28. Gollakota, S. V. and Guin, J. A., "A Comparative Study of Gas-Liquid Mass Transfer Coefficients in Stirred Autoclaves, Tubing Bomb Microreactors, and Bubble Columns", accepted by I & EC Process Des. and Development.
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