

## TECHNICAL REPORT

September 1, 1991 through November 30, 1991

Project Title: Coal-Derived Promoters for the Liquefaction of Illinois Coal DE-FG22-91PC91334

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## ABSTRACT

The objective of this program is to investigate the use of liquids derived from coal either by mild gasification or supercritical extraction (SCE) to promote direct liquefaction of Illinois coal. Some organic sulfur-, nitrogen-, and oxygen-containing compounds have been found to enhance liquefaction reactions. The use of Illinois coal to produce liquid fractions rich in these types of compounds could increase the rates of liquefaction reactions, thus improving the process economics. An integrated process combining direct liquefaction with mild gasification or SCE of coal is being developed by IGT.

The approach taken in this two-year program is to use recently developed molecular probe techniques to assess the reactivity of three coal-derived liquids with respect to (A) hydrogen transfer rate, (B) carbon-carbon bond cleavage rate, (C) free radical flux, and (D) hydrocracking activity. Sample liquids from Illinois Basin Coal IBC-106 are prepared by three methods: mild gasification in an isothermal free-fall reactor (IFFR), steam treatment followed by mild gasification in a fixed-bed reactor (ST/FBR), and SCE using toluene in a batch autoclave.

During the first year of the program, the IFFR and ST/FBR coal liquids were produced and characterized, and the IFFR liquid was assessed by the four molecular-probe methods. For the IFFR liquid, hydrogen transfer rate showed a mean increase of 21%, C-C bond cleavage selectivity increased by 34%, free radical flux showed a mean increase of 107%, and overall mean hydrocracking activity increased by 269%. The methods were validated by tests with benzyl phenyl sulfide (BPS), a model compound with known high reactivity for enhancement of coal liquefaction. Our data also suggested that the principal mechanism at work in molecular probe technique D is different from those in techniques A, B, and C.

During the first quarter of the second year, reactivity testing and data analysis on the ST/FBR coal liquid was completed. For the ST/FBR liquid, hydrogen transfer rate showed a mean increase of 7%, C-C bond cleavage selectivity increased by 27%, free radical flux increased 101%, and data indicated a 227% increase in hydrocracking activity.

The autoclave reactor system has been modified for production of SCE liquid during the next quarter.

MASTER

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## EXECUTIVE SUMMARY

The objective of this two-year program is to investigate the use of liquids derived from coal, either by mild gasification or by supercritical extraction, to promote coal liquefaction. Based on recent findings on the mechanisms of coal dissolution and related studies on the effects of certain classes of compounds on dissolution reactions, possible improvements in coal liquefaction and coal-resid coprocessing efficiency via the addition of chemical promoters have been suggested. Based on the experimental model-compound data available in the literature, certain classes of reactive coal-derivable compounds (e.g., aromatic thiols, benzyl thioethers, aromatic disulfides, benzyl ethers, phenols, hydroaromatics, etc.) that can increase coal dissolution rates through various chemical mechanisms have been identified. These findings suggest that the addition of a heteroatom-rich organic liquid to the recycle hydrogen-donor solvent may result in significant increases in coal liquefaction rate. Mild gasification tars and SCE liquids are expected to contain reactive components of the required type.

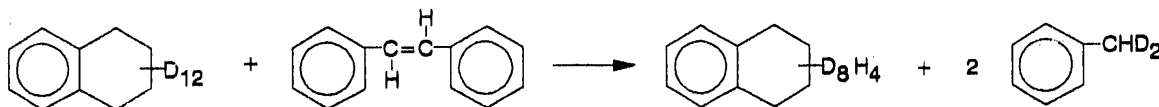
IGT is developing a coal liquefaction concept based on this idea. In this scheme, coal is slurried with a mixture of recycled distillate product liquids and liquefaction promoters, consisting of either mild gasification oils/tars or SCE extract, prior to two-stage liquefaction/hydrotreatment to produce distillate fuel. The solid residue from the mild gasification or SCE step is gasified in a conventional steam-oxygen gasifier followed by water-gas shift and gas separation to obtain the necessary hydrogen for the first- and second-stage liquefaction and hydrotreatment.

Various molecular probe techniques have been developed to understand the role of reactive functionalities on coal liquefaction reaction rates. Four of these techniques are being used in this program to assess the potential of mild gasification liquids and supercritical coal extract to act as promoters to increase coal liquefaction rates:

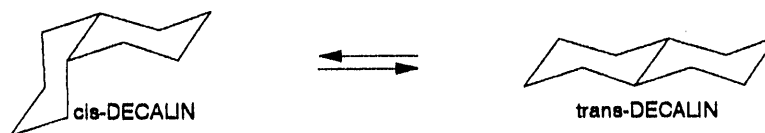
- A. Assessment of H-transfer rate via the exchange of deuterium atoms between tetralin- $d_{12}$  and diphenylmethane (DPM).



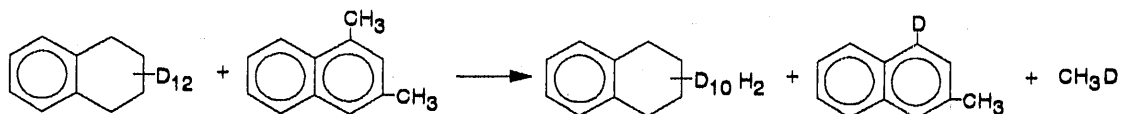
- B. Assessment of C-C bond cleavage rate via the decomposition of *trans*-stilbene in the presence of donor solvent (tetralin- $d_{12}$ ).



- C. Assessment of free radical flux via the rate of isomerization of *cis*-decalin to a mixture of *cis*- and *trans*- stereoisomers.



- D. Assessment of hydrogen atom flux via the hydrodemethylation of 1,3-dimethylnaphthalene (DMN) in the presence of a donor solvent (tetralin- $d_{12}$ ).



Three sample liquids are being prepared from Illinois Basin Coal IBC-106 by: mild gasification in an isothermal free-fall reactor (IFFR), steam treatment followed by mild gasification in a fixed-bed reactor (ST/FBR), and supercritical extraction using toluene (SCE).

During the first year, IFFR liquid was assessed by methods A-D. Method A showed that the mild gasification liquid increases the rate of hydrogen transfer by 10% to 32%, based on substitution of deuterium for benzylic hydrogen in DPM. Method B data show that the IFFR liquid increased the rate of C-C bond cleavage by 100% and, more importantly, improved the selectivity by 36%, based on the relative rates of trans-stilbene conversion to toluene (cleavage) and to diphenylethane (hydrogenation). Method C showed that the test liquid increased the free radical flux by 153%, as indicated by the approach to equilibrium of *cis*-decalin isomerization. In method D, overall hydrocracking activity, assessed by the total percent of 1,3-DMN converted to methylnaphthalenes, increased by 266% to 272% with IFFR liquid. All of these data indicate that mild gasification liquid is a viable candidate for further development as a direct coal liquefaction promoter.

A model compound, benzyl phenyl sulfide (BPS), that has been shown in other studies to be a very active liquefaction promoter has also been used to successfully validate the test methods.

Following the completion of testing with the IFFR liquid, the ST/FBR liquid was produced from IBC-106 coal and characterized. The ST/FBR liquid is slightly less aromatic than the IFFR liquid, and contains slightly more sulfur and nitrogen. Testing of the ST/FBR liquid and analysis of the reactivity data were completed during the current quarter. Method A showed a mean increase of 7% in H transfer rate, method B testing resulted in a 27% increase in C-C cleavage selectivity, method C gave a 101% increase in free radical flux, and method D indicated a 227% increase in hydrocracking activity.

The autoclave reactor system has been modified for production of SCE liquid from coal using a toluene solvent. SCE liquid will be produced and tested during the next quarter.

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## OBJECTIVES

The objective of this two-year program is to investigate the use of liquids derived from coal, either by mild gasification or by supercritical extraction, to promote coal liquefaction. Specifically, the study will evaluate the reactivity of coal liquefaction promoters produced by three separate processes: mild gasification of coal in an isothermal free-fall reactor (IFFR); mild gasification of steam-pretreated coal in a fixed bed (ST/FBR); and supercritical extraction of coal with toluene (SCE).

## INTRODUCTION AND BACKGROUND

Direct coal liquefaction is the conversion of coal to a mainly liquid product, and is generally approached via thermal dissolution in a hydrogen-donor solvent, followed by hydrogenation of the liquids with an added catalyst. The first stage, thermal dissolution, takes place at temperatures of about 700° to 870°F (371° to 466°C) and pressures of 1500 to 3500 psig (10.3 to 23.9 MPa). The product from the first-stage liquefaction, which involves hydrogen uptake from both the donor solvent and the gas phase, is a non-distillable slurry which must be further hydrogenated in the second stage to obtain distillate products. In direct coal liquefaction, the recycled hydrogen-donor solvent is typically derived from the second-stage hydrogenation step. In the related concept of coal-resid coprocessing, a major part of the recycled solvent is replaced by a petroleum-based residual oil, which results in greatly increased throughput of fresh feed for a given reactor size.

Based on recent findings on the mechanisms of coal dissolution and related studies on the effects of classes of compounds on dissolution reactions, approaches to the improvement of coal-resid coprocessing efficiency via the addition of chemical promoters have been suggested. Miller et al<sup>1</sup> have suggested that, under carefully selected conditions, the addition of the basic nitrogen-containing promoters tetrahydroquinoline (THQ) or dipropylamine (DPA) to coal liquefaction or coal-resid coprocessing can result in acceptable conversions and distillate yields at reduced severity. However, even at reduced temperature and pressure, incorporation of the promoter into the product is quite substantial.<sup>2</sup> Other workers have studied the use of H<sub>2</sub>S as a

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<sup>1</sup> Miller, R. L., R. M. Baldwin, and D. R. Kennar, "Addition of Basic Nitrogen Promoters to Enhance Low-Severity Two-Stage Coal Liquefaction and Coal/Oil Coprocessing", *ACS Div. of Fuel Chem. Preprints* 35:1 (1990), pp 9-16.

<sup>2</sup> McMillen, D. F., R. Malhotra, and S. Chang, "Adduction of Amine Solvents into Coal Structure: Identification of Coupling Modes", *Proc. 1987 Int'l Conf. on Coal Science, Maastricht, Netherlands* (1987), pp 197-200.

liquefaction promoter<sup>3,4</sup> and have found that liquefaction rates are increased in comparison to a system without H<sub>2</sub>S. Huang and Stock<sup>5</sup> reported that the activity of H<sub>2</sub>S may be largely due to its conversion to a reactive thiol in the presence of coal-derived liquids. Based on the experimental model-compound data available in the literature,<sup>6,7</sup> certain classes of reactive coal-derivable compounds (e.g., aromatic thiols, benzyl thioethers, aromatic disulfides, benzyl ethers, phenols, hydroaromatics, etc.) that can increase coal dissolution rates through various chemical mechanisms have been identified. These findings suggest that the addition of an organic liquid which is relatively rich in reactive sulfur-, nitrogen-, and oxygen-containing compounds, such as mild gasification tars<sup>8</sup> or SCE extract,<sup>9</sup> may result in significant increases in coal liquefaction rate.

A process concept developed by IGT is illustrated in Figure 1. In this scheme, coal is slurried with a mixture of recycled product liquids and liquefaction promoters consisting of either mild gasification oils/tars or SCE extract prior to two-stage liquefaction/hydrotreatment to produce distillate fuel. The solid residue from either the mild gasification or the SCE step is gasified in a conventional steam-oxygen gasifier followed by shift and gas separation to obtain the necessary hydrogen for the first- and second-stage liquefaction and hydrotreatment.

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- <sup>3</sup> Sofianos, A. G., "Pyrite-Catalyzed Coal Liquefaction With the Carbon Monoxide-Water system Using H<sub>2</sub>S as a Promoter", *Proc. 1987 Conf. on Coal Science*, Maastricht, Netherlands (1987), pp 247-250.
- <sup>4</sup> Wilson, W. G., R. Hei, D. Riskedahl, and V. I. Stenberg, "H<sub>2</sub>S Optimization for Lignite Liquefaction", *Fuel* 64:1 (1985), pp 128-130.
- <sup>5</sup> Huang, C. B., and L. M. Stock, "On the Role of Sulfur Compounds in Coal Liquefaction", *ACS Div. of Fuel Chem. Preprints* 27:3-4 (1982) pp 28-36.
- <sup>6</sup> King, H. and L. M. Stock, "Aspects of the Chemistry of Donor solvent Coal Dissolution. The Hydrogen-Deuterium Exchange Reactions of Tetralin-d<sub>12</sub> With Illinois No. 6 Coal, Coal Products, and Related Compounds", *Fuel* 61:3, (1982) pp 257-263.
- <sup>7</sup> King, H. and L. M. Stock, "Aspects of the Chemistry of Donor Solvent Coal Dissolution. The Role of Phenol in the Reaction", *Fuel* 61:11 (1982), pp 1172-1174.
- <sup>8</sup> Knight, R. A., G. J. Koncar, and S. P. Babu, "Mild Gasification Studies With Illinois Coals", Final Technical Report to CRSC (Sept 1990).
- <sup>9</sup> Bartle, K. D., T. G. Martin, and D. F. Williams, "Chemical Nature of a Supercritical Gas Extract of Coal at 350°C", *Fuel* 54:10, (1975), pp 226-235.

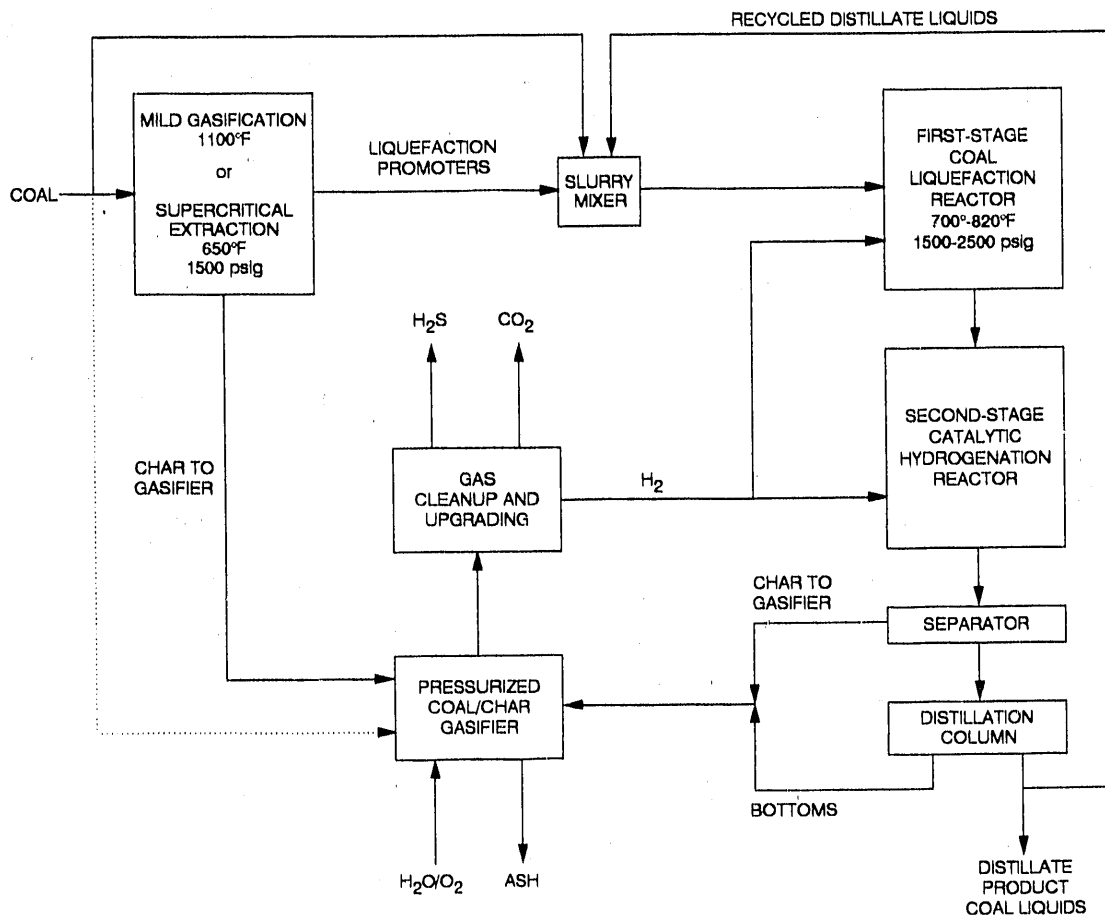


Figure 1. PROCESS FLOW SCHEME FOR IGT PROCESS USING COAL-DERIVED PROMOTERS FOR DIRECT LIQUEFACTION

Mild gasification of coal or SCE of coal with a process-derived organic solvent can supply liquids rich in polycondensed aromatic, hydroaromatics, and reactive heteroatomic components which have been shown to increase coal dissolution or liquefaction rates. This approach would be significantly less costly than the addition of purified chemical compounds which would be obtained external to the process. The integration of mild gasification or SCE with coal liquefaction or coal-resid coprocessing may result in greater overall process efficiency due to the enhancement of coal dissolution and hydrogen uptake from the vehicle. Essentially, the reactive potential of certain coal-derived liquid components would be used to greater advantage by using this potential to increase the rate of first-stage liquefaction, in comparison to simply processing that portion of the coal for liquefaction. The residual coal-derived char from mild gasification or SCE is a reactive solid which can be utilized in steam-oxygen gasification to supply hydrogen for the liquefaction process. Mild

gasification and SCE both offer the additional benefit of rendering the coal residue non-caking in the case of many bituminous coals.

A variety of molecular probe techniques have been developed to understand the role of reactive functionalities on coal liquefaction reaction rates. Four of these techniques<sup>10,11,12</sup> will be used in this program to assess the potential of mild gasification liquids and supercritical coal extracts to act as promoters to increase coal liquefaction rates.

## EXPERIMENTAL PROCEDURES

### Task 1. Preparation of Mild Gasification Liquid

A sample of mild gasification liquid is to be prepared by pyrolysis of Illinois coal in an isothermal free-fall reactor (IFFR) at 1200°F and near-ambient pressure under nitrogen. The existing reactor system is shown schematically in Figure 2. In this reactor, coal is fed from a storage hopper via a screw-feeder/star-feeder combination. Coal particles flow through a water-cooled injection probe into the hot reactor zone, and the velocity of the gas stream inside the reactor is such that a laminar flow condition is maintained to keep the sticky particles from contacting the reactor wall. The actual IFFR is an 8-foot-long 2-inch-ID electrically-heated stainless-steel core. Inside the reactor core is an adjustable char collection probe, which transmits the pyrolysis products at reduced temperatures to the char separator located below the reactor. The length of the reaction zone can be adjusted from 12 to 48 inches to vary the coal residence time. The char separator is a stainless-steel vessel maintained at about 320°F, and includes a ceramic filter element to remove entrained solids. A solvent (methylene chloride) is injected into the gas stream at the separator inlet. The solvent vapor improves the downstream recovery of oils/tars by enhancing the coalescence of tar fog and diluting the liquid products to minimize losses. The solids-free gas/vapor stream passes through a series of condensers which collect the product liquids in condensed solvent.

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<sup>10</sup> King, H., and L. M. Stock, "Influence of Illinois No. 6 Coal and Coal-Related Compounds on the Exchange Reaction Between Diphenylmethane and Perdeuterotetralin", *Fuel* 59:6 (1980) pp 447-449.

<sup>11</sup> King, H., and L. M. Stock, "Aspects of the Chemistry of Donor Solvent Coal Dissolution. Promotion of the Bond Cleavage Reactions of Diphenylalkanes and the Related Ethers and Amines", *Fuel* 63:6 (1984) pp 810-815.

<sup>12</sup> Bockrath, B. C., K. T. Schroeder, and M. R. Smith, "Investigation of Liquefaction Mechanisms with Molecular Probes", *Energy & Fuels* 3 (1989) pp 268-272.

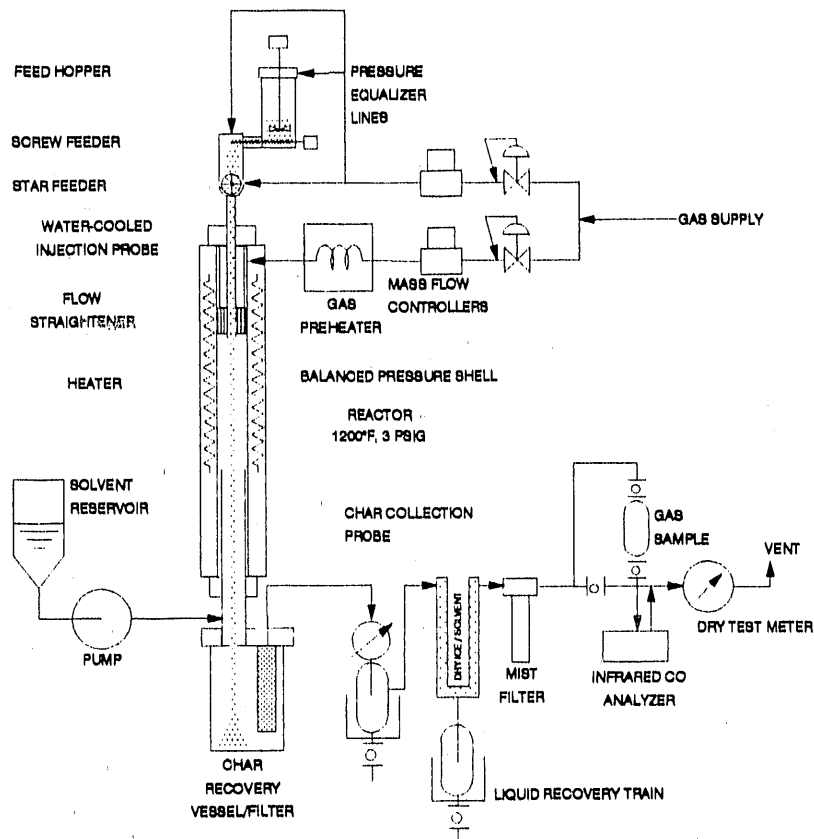


Figure 2. SCHEMATIC DIAGRAM OF ISOTHERMAL FREE-FALL REACTOR SYSTEM

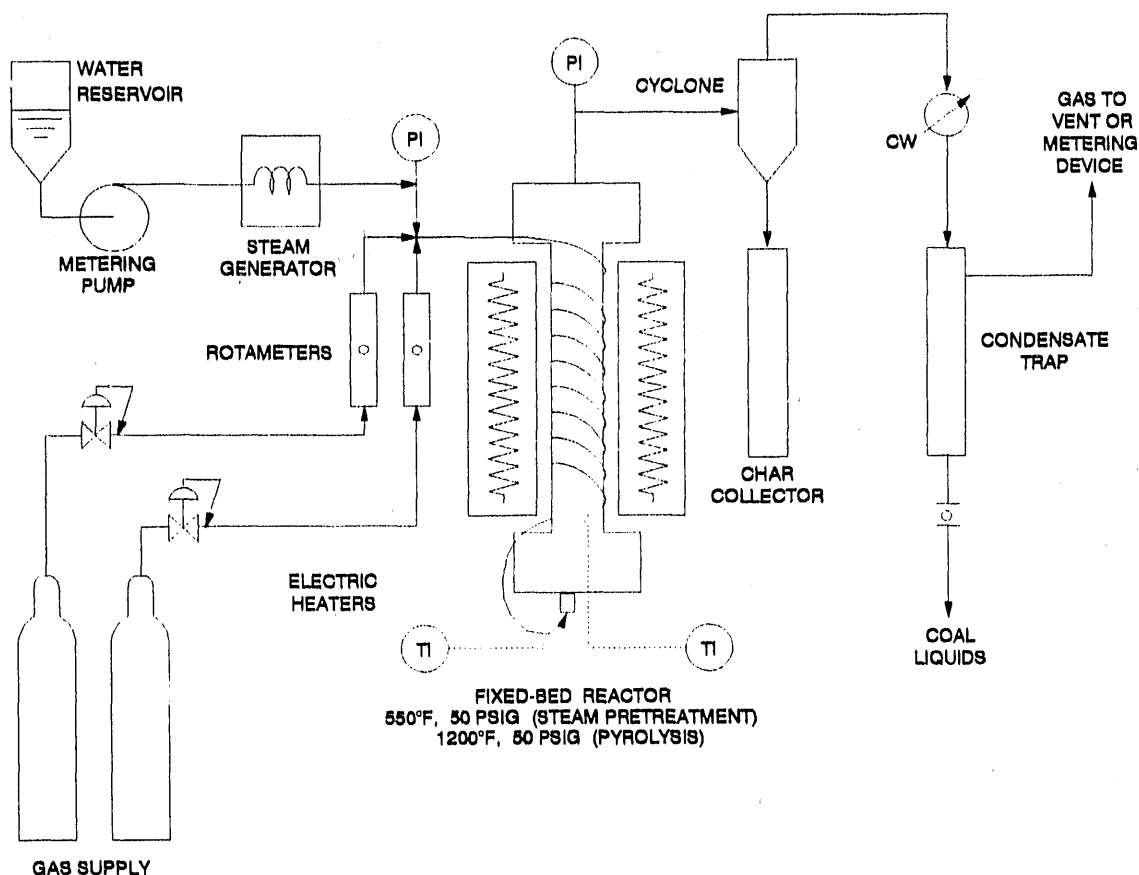
The product liquids are recovered from the solvent by rotary vacuum evaporation, which delivers primarily those components with boiling points above about 360°F (182°C). These liquids, which constitute the trial sample, are expected to be representative of those produced from the IGT mild gasification process, which has been developed under USDOE/METC sponsorship.

The IFFR liquid is to be analyzed for elemental composition by standard ASTM methods and for elemental distribution across the boiling range via gas chromatograph/atomic emission detector (GC/AED). The GC/AED analysis will be performed on a Hewlett-Packard Model 5921A using a low-resolution packed simulated-distillation column. The sample will also be analyzed by high-resolution capillary GC/MS to identify the following selected components which are expected to act as liquefaction promoters: benzenethiol, phenol, *m*-cresol, 1-naphthol, diphenyldisulfide, benzyl phenyl sulfide, benzyl phenyl ether, *N*-benzylaniline, indene, tetracene, 1,1-thiobisbenzene, 1- and 2-naphthalenethiols, 9,10-dihydroanthracene, 9,10-dihydrophenanthrene, 1,2,3,4-tetrahydronaphthalene, naphthalene, and all monomethyl derivatives of the preceding. GC/MS analyses will be performed on a Finnigan Model 4510 quadrupole GC/MS with super INCOS data acquisition/control system, using a high-resolution capillary column.



## Task 2. Preparation of Mild Gasification Liquid from Steam-Treated Coal

An alternative type of mild gasification liquid from steam-treated coal is to be produced in a fixed-bed reactor. The IBC-106 coal is to be steam-pretreated and then pyrolyzed under nitrogen in a 2-inch fixed-bed reactor (FBR), shown in Figure 3. The coal is contained in a fixed bed on a stainless-steel 100-mesh screen, and preheated gas is passed through the bed from the bottom. Entrained char dust is removed by a cyclone, and the ST/FBR coal liquids and water are condensed and collected in a series of condensers similar to that used for the IFFR.



In this sample preparation, the IBC-106 coal is to be pretreated with steam *in situ* at 550°F (288°C) and approximately 50 psig (0.44 MPa) for 30 minutes. The pretreatment is followed immediately by mild gasification in nitrogen at 1200°F and 50 psig. The collected ST/FBR liquids are separated from aqueous condensate and characterized in a manner similar to that described for the IFFR liquids, except that no solvent is used to dilute the lighter, more thermally cracked liquids

expected from the fixed-bed pyrolysis. Also, no attempt is made to avoid caking in the reactor.

It is expected that the steam pretreatment will result in increased phenolic content in the ST/FBR liquids compared to a fixed-bed pyrolysis of untreated coal, and that the nature of pyrolysis in a fixed-bed, slow-heating environment will result in liquids with significantly different properties than the Task 1 sample. These oils/tars can be viewed as being representative of conventional low-temperature carbonization liquids such as those produced by the Coalite process, with the added modification of steam pretreatment.

Analyses and characterization procedures for the liquids from the Task 2 mild gasification will be identical to those used for the Task 1 liquids.

### Task 3. Supercritical Extraction of Coal

To collect SCE extract for reactivity evaluation, the selected Illinois coal will be subjected to SCE in an autoclave at 650°F and 1500 psig (343°C and 10.3 MPa) for 30 minutes. The supercritical solvent will be toluene, which has a critical point of 609°F and 577 psig (320°C and 4.03 MPa). The autoclave reactor is shown schematically in Figure 4. Coal is contained in a stainless steel mesh basket which sits on the reactor bottom. The coal and liquid solvent are charged cold into the reactor, which is then heated slowly to the extraction temperature. A magnetically driven stirrer circulates the supercritical fluid throughout the reactor for maximized mass transfer. At the end of the extraction period, the fluid phase is withdrawn rapidly through a low-pressure, high-temperature vessel where the bulk of the extract condenses, and into a cooled vessel, where the solvent and remaining SCE extract condense. The liquids are then drained, and the test sample consists of the recovered solvent-free liquid.

Analyses and characterization procedures for the liquids from the Task 3 SCE will be identical to those used for the Task 1 and Task 2 liquids.

### Task 4. Evaluation of Reactivity of Coal Liquids

The ability of the liquid test samples from Tasks 1-3 to promote coal liquefaction will be assessed by measuring their reactivities in the four molecular probe tests outlined in Table 1. The microreactor to be used in all of these tests consists of a 316SS 1/4-inch-OD (0.64-cm) thermowell which is 3.5 inches (8.9 cm) long. The microreactor, before and after filling, is pictured in Figure 5. The open end of the microreactor is sealed with a Swagelok union and cap. For introducing reagents to the vessel, the reactor is purged by sequential evacuation and filling with inert gas via a temporary septum cap and syringe arrangement. Syringes are used to inject measured volumes of reagents into the purged microreactor. Coal liquid samples or solid reagents, if used, will be dissolved in one of the other reagents or in a suitable solvent. Before heating the microreactor in a fluidized sand bath, the

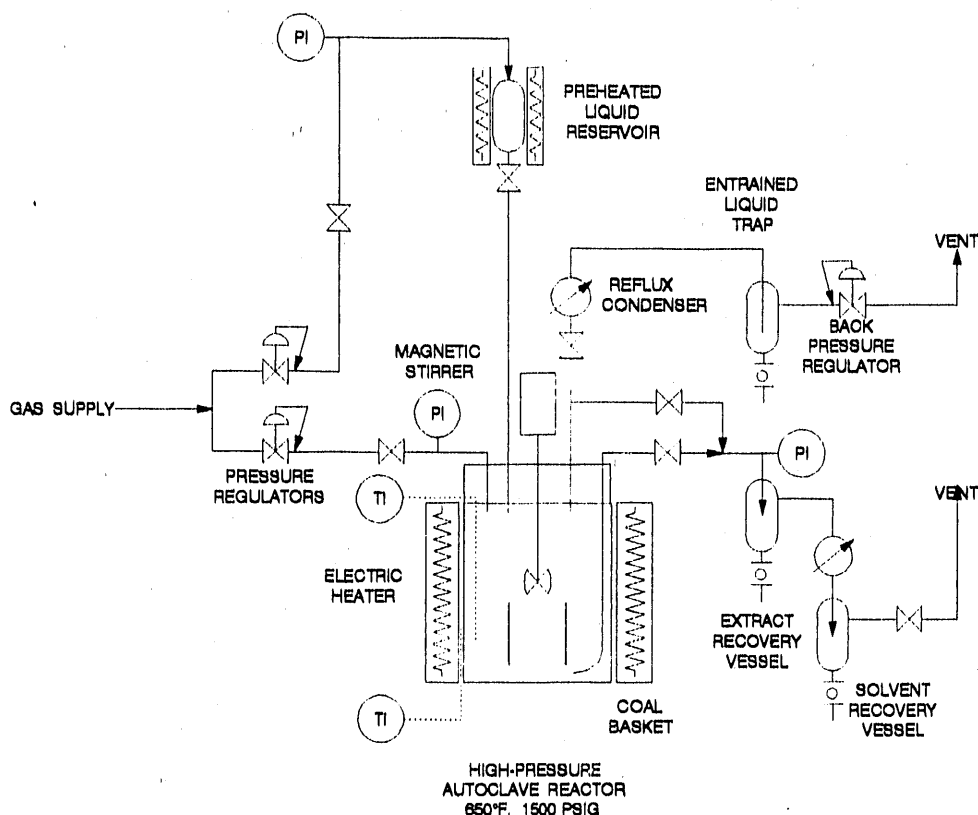


Figure 4. SCHEMATIC DIAGRAM OF AUTOCLAVE REACTOR SYSTEM

temporary septum cap is replaced with a solid Swagelok cap in a glove box under inert atmosphere. The details of the individual test procedures are outlined below.

Method A. H-Exchange: 25 mg of test sample is combined with 0.38 mmol of tetralin- $d_{12}$  and 0.38 mmol of diphenylmethane. The mixture is transferred to the microreactor under argon. The reactor is heated to 752°F (400°C) for 1 hour. After cooling, the contents are rinsed out with chloroform- $d$  (containing TMS as an NMR standard) and analyzed to determine the amount of deuterium exchange between tetralin and DPM, which should occur almost entirely at the benzylic position.

Method B. C-C bond cleavage: 25 mg of test sample and 0.38 mmol of *trans*-stilbene are dissolved in 0.38 mmol of tetralin- $d_{12}$ . The mixture is transferred to the microreactor under argon. The reactor is heated to 752°F (400°C) for 1 hour. After cooling, the contents are rinsed out with TMS-spiked chloroform- $d$  and analyzed for stilbene decomposition products (chiefly toluene- $d_2$ , styrene- $d$ ,

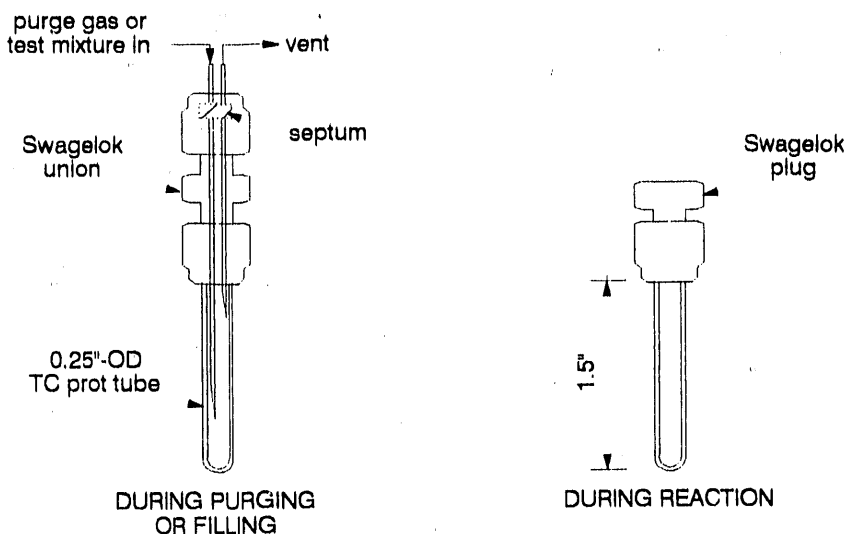


Figure 5. MICROREACTOR USED FOR MOLECULAR PROBE TESTS

benzene-*d* and ethylbenzene-*d*<sub>2</sub>). The principal product of interest is toluene, which results from cleavage of the C=C bond and, by inference based on proposed pathways for breaking of benzylic C-C bonds,<sup>11</sup> indicates the rate of C-C bond cleavage in coal liquefaction.

Method C. Free Radical Flux: 25 mg of test sample is dissolved in 0.16 mmol of *cis*-decahydronaphthalene (*cis*-Decalin) and 173  $\mu$ L of *o*-xylene solvent. The mixture is transferred to the microreactor under argon. The reactor is heated to 797°F (425°C) for 1 hour. After cooling, the contents are rinsed out with unstabilized tetrahydrofuran (THF) and analyzed for *cis*- and *trans*- stereoisomers. The approach to equilibrium (about 5:1 *trans*- to *cis*- ratio) indicates the free radical flux.

Method D. Hydrocracking Activity: 25 mg of test sample is dissolved in 0.16 mmol of 1,3-DMN and 0.82 mmol of tetralin. The mixture is transferred to the microreactor under argon. The reactor is heated to 797°F (425°C) for 3 hours. After cooling, the contents are rinsed out with chloroform-*d* and analyzed for products of hydrodemethylation (1- and 2-methylnaphthalenes). The degree of conversion indicates overall hydrocracking activity, and the relative abundance of 1- and 2-methylnaphthalene species indicates the selectivity of hydrogen atom attack, which is related to hydrogen utilization in liquefaction. Compared to free

Table 1. REACTIVITY ASSESSMENT METHODS

<u>Method</u>	<u>Reactants</u>	<u>Analyses</u>	<u>Interpretation</u>
A. Hydrogen-deuterium exchange between tetralin- $d_{12}$ and diphenylmethane	Tetralin- $d_{12}$ Diphenylmethane Chloroform- $d$	GC/MS	increased D transfer from tetralin- $d_{12}$ to diphenylmethane indicates increase in rate of hydrogen transfer
B. C-C bond cleavage of <i>trans</i> -stilbene in H-donor solvent	<i>Trans</i> -stilbene Tetralin- $d_{12}$ Chloroform- $d$	GC/MS	Increased conversion of <i>trans</i> -stilbene to toluene indicates increased rate of carbon-carbon cleavage
C. Free-radical isomerization of <i>cis</i> -decalin into equilibrium mixture of <i>cis</i> - and <i>trans</i> - isomers	<i>Cis</i> -decalin <i>o</i> -Xylene Tetrahydrofuran	GC/MS	Increased rate of isomerization indicates increased free radical flux in reaction mixture
D. Hydrodemethylation of alkyl-naphthalenes in H-donor solvent	1,3-Dimethylnaphthalene Tetralin Chloroform- $d$	GC/MS	Increased rate of hydrodemethylation indicates H-atom flux; selectivity of methyl group removal at 1- or 3-position shows selectivity for H transfer from gas or H-donor solvent

hydrogen atoms, hydrogen transferred from  $\sigma$ -complexes formed with reactive aromatic species tends to selectively attack the 1-position, thus producing more 2-methylnaphthalene.

This method has been modified slightly from that described in the original proposal. The results of the initial Method D testing during the second quarter, in which the rate and selectivity of hydrodemethylation of 1,3-DMN is investigated, showed that the reaction rate was insufficient to give high enough product levels for reliable chromatographic measurement at one hour of residence time, and so the residence time was increased to three hours. Furthermore, the use of tetralin- $d_{12}$  as a H-donor resulted in many peaks from different deuterated tetralin isomers, which may have interfered with the identification of the 1- and 2-methylnaph-

thalene peaks. Therefore, it was decided to use non-deuterated tetralin as a hydrogen donor to simplify the product chromatogram.

For all four methods, a reaction blank containing the test reagents without the promoter liquid is run simultaneously with each test sample. The analyzed data are expressed relative to the blank to account for variations in time-temperature history between tests.

Analyses of the reaction mixtures are to be performed on the Finnigan GC/MS described earlier.

## RESULTS AND DISCUSSION

### Task 1. Preparation of Mild Gasification Liquid

Task 1 was completed during the first year of the project.

### Task 2. Preparation of Mild Gasification Liquid from Steam-Treated Coal

Task 2 was completed during the first year of the project, but a summary of the work is given here because the reactivity tests on the ST/FBR coal liquid were completed during the current quarter.

The fixed-bed reactor was operated at 550°F and 50 psig for 30 min with steam, and at 1200°F and 50 psig for 98 min with nitrogen gas. The analysis of the parent coal is shown in Table 2, and analysis of the ST/FBR liquid is shown in Table 3. The ST/FBR liquid is less aromatic than the IFFR liquid, and contains higher levels of sulfur and nitrogen.

### Task 3. Supercritical Extraction of Coal

The preparation of the autoclave reactor for production of an SCE sample has been completed. A condenser, liquid recovery vessels, and connecting lines were installed. The reactor, collection vessels, and associated lines and instruments were pressure-tested, a new coal basket and suction tube were fabricated, and a new stirrer was installed. Production of the SCE liquid is scheduled for the next quarter.

### Task 4. Evaluation of Reactivity of Coal Liquids

The reactivity evaluation of the IFFR liquid was completed and reported in the first year. During the current quarter, tests on the ST/FBR liquid were completed, and the results are summarized in Table 4 and summarized below.

Table 2. PROPERTIES OF IBC-106 COAL

Proximate Analysis

Moisture, wt% as rec'd	2.46
Volatile Matter, "	35.24
Ash, "	12.28
Fixed Carbon, "	50.02

Ultimate Analysis

Carbon, wt% maf	79.20
Hydrogen, "	5.09
Nitrogen, "	1.88
Sulfur, "	5.09
Oxygen (by diff), "	8.74

Sulfur by Type

Sulfide, wt% of total sulfur	0.61
Sulfate, " " " "	0.76
Pyritic, " " " "	52.36
Organic, " " " "	46.29
H/C Atomic Ratio	0.766
Heating Value, Btu/lb (measured)	12,736

Table 3. PROPERTIES OF ST/FBR LIQUID

Elemental Analysis, wt% dry basis

Ash	0.62
Carbon	78.05
Hydrogen	8.46
Nitrogen	1.07
Sulfur	2.85
Oxygen (by diff)	8.95
H/C Atomic Ratio	1.292

Physical Properties

Specific Gravity, 60°F	1.088
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Selected Compounds, wt% of total liquid

Phenol	1.84
m,p-Cresols	4.77
Naphthalene	0.08
C <sub>1</sub> -Naphthalenes	0.34

Method A -- Hydrogen Exchange

The effect of the ST/FBR coal liquid on this reaction is assessed principally by comparison of the percent of benzylic hydrogen in the reactant DPM that has been exchanged for deuterium from the tetralin- $d_{12}$ . A blank, containing reactants with no added coal liquid, is run with each sample to normalize minor differences between test conditions. Table 4 shows the results of triplicate tests, including the sample:blank (S:B) ratios for each key reactivity measurement. The S:B ratio is the indicator of reactivity enhancement.

The results indicate that the ST/FBR liquid increased the extent of deuterium exchanged to DPM by 12%, 7%, and 2% in the three replicates, resulting in an average increase of 7%. This was less than the effect of the IFFR liquid, which gave an average increase of 21% in this test. Tetralin- $d_{12}$  also donates deuterium to the coal liquid and undergoes dehydrogenation to naphthalene and  $D_2$  gas, which accounts for the fact that deuterium loss from tetralin- $d_{12}$  is higher than the deuterium uptake by the DPM.

These results suggest that aging of the sample may have affected the reactivity. This pattern was also observed with the IFFR liquid.

**Table 4. METHOD A TEST RESULTS WITH ST/FBR COAL LIQUID**

	<u>Repl 1</u>	<u>Repl 2</u>	<u>Repl 3</u>	<u>Mean</u>
Percent of benzylic DPM hydrogen exchanged				
Blank	18.33	21.23	23.21	20.92
Sample	21.19	22.69	23.56	22.48
Ratio (S:B)	1.12	1.07	1.02	1.07

Method B. C-C bond cleavage

The effect of coal liquid on C-C bond cleavage can be assessed by its effect on the conversion of *trans*-stilbene to toluene in the presence of a hydrogen donor. The competing reaction in this case is hydrogenation of the stilbene double bond to yield diphenylethane. The selectivity of the cleavage reaction can be estimated by the relative yields of toluene and diphenylethane. Examination of the data also gives an additional measure of overall hydrogen donor activity for comparison with Method A.

Data from Method B tests with ST/FBR liquid are shown in Table 5. These data represent three replicate tests. Although the hydrogenation reaction predominates in all cases, the selectivity of the cleavage reaction is increased by 38%, 17%, and 27% with the coal liquid present, which results in a mean increase of 27%. This is similar to the results with IFFR liquid, which gave a mean selectivity increase of 32%.



Table 5. METHOD B TEST RESULTS WITH ST/FBR COAL LIQUID

	Repl 1	Repl 2	Repl 3	Mean
Percent of <i>trans</i> -stilbene converted				
To toluene (cleavage)				
Blank	1.81	1.52	1.48	1.60
Sample	5.01	4.52	4.62	4.72
Ratio (S:B)	2.78	2.98	3.12	2.96
To diphenylethane (hydrogenation)				
Blank	44.77	36.47	37.98	39.74
Sample	90.21	92.76	93.43	92.13
Ratio (S:B)	2.02	2.54	2.46	2.34
Selectivity of cleavage reaction*				
Blank	4.03	4.17	3.91	4.03
Sample	5.56	4.88	4.95	5.13
Ratio (S:B)	1.38	1.17	1.27	1.27

$$* \text{ Selectivity} = \frac{(\% \text{ stilbene converted to toluene})}{(\text{total } \% \text{ stilbene converted})}$$

#### Method C. Free Radical Flux

The third method provides a measure of overall free radical flux in the system by indicating the relative rate of *cis*-decalin stereoisomerization, which is a radical-catalyzed molecular rearrangement. The data is best expressed as a degree of approach to equilibrium, where the equilibrium mixture consists of 83% *trans*-isomer. As shown in Table 6, the ST/FBR liquid increased this parameter by 80% and 122% for the two replicates performed, indicating significantly increased free radical activity in the presence of the ST/FBR test sample.

Table 6. METHOD C TEST RESULTS WITH ST/FBR COAL LIQUID

	Repl 1	Repl 2	Average
<i>Cis</i> -decalin isomerization			
Percent approach to equilibrium			
Blank	16.00	23.76	19.88
Sample	28.75	52.84	40.80
Ratio (S:B)	1.80	2.22	2.01

Method D. Hydrocracking Activity

The results of Method D testing on ST/FBR liquid are shown in Table 7 below. Only one sample/blank set is reported, because the blank used in a duplicate test was found to be contaminated. The overall hydrocracking activity, assessed by the total percent of 1,3-DMN converted to methylnaphthalenes, increased by 227% in the test, and the selectivity to 2-methyl vs 1-methylnaphthalene was +40%.

Table 7. METHOD D TEST RESULTS WITH ST/FBR COAL LIQUID

Total DMN hydrocracked

Blank	2.32
Sample	7.58
Ratio (S:B)	3.27

Selectivity (2-MN/1-MN ratio)

Blank	2.54
Sample	3.56
Ratio (S:B)	1.40

### CONCLUSIONS AND RECOMMENDATIONS

The steam-treated/fixed-bed reactor (ST/FBR) mild gasification liquid produced from IBC-106 coal at 1200°F promotes increased rates of hydrogen transfer, C-C bond cleavage, free radical flux, and hydrocracking activity, and increases the selectivity of C-C bond scission over hydrogenation. All of these trends indicate a potential for increased coal dissolution rate in the first stage of direct coal liquefaction. Compared with IFFR liquid tested in the first year, the ST/FBR liquid gave similar results for C-C bond cleavage selectivity and free radical flux, and was slightly less reactive in the H transfer and hydrocracking assessments. These differences were not statistically significant, so it can be stated that the IFFR and ST/FBR liquids possess virtually the same potential for liquefaction enhancement.

Preparation of the autoclave reactor for production of SCE coal liquid was completed, and production and testing of SCE liquid will proceed during the next quarter. Results from testing of the IFFR, ST/FBR, and SCE coal liquids will be compared, GC/AED analyses will be used to interpret differences in behavior, and recommendations for further development of the process scheme will be made.

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**PROJECT MANAGEMENT REPORT**  
September 1 - November 30, 1991

Project Title: **Coal-Derived Promoters for the Liquefaction of Illinois Coal**

Principal Investigator: Ronald H. Carty, Institute of Gas Technology  
Co-Investigator: Richard A. Knight, Institute of Gas Technology  
Project Monitor: Frank Honea, CRSC

**COMMENTS**

No changes to management or budget have been implemented. The schedule for Task 3 has slipped by approximately eight weeks because of delays in fabrication of parts for the autoclave reactor.

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