SHORT CONTACT TIME DIRECT COAL LIQUEFACTION
USING A NOVEL BATCH REACTOR

FINAL REPORT

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EXECUTIVE SUMMARY

A small bench scale (30 ml) batch reactor (SCTBR) has been designed and constructed for running kinetic studies of high temperature-high pressure reactions at very short reaction times. By very rapid heat up and cool down, reaction times as short as 5 seconds can be accurately measured. The principle is to preheat a tubular preheater and reactor to the desired operating temperature, and to blow the reaction mixture from a blow case using high pressure gas through the preheater into the preheated reactor. Approximately the desired reaction temperature can be reached in the 0.3 seconds required to transfer the reaction mixture from a blow case into the reactor.

Fluid flow and heat transfer within the preheater have been analyzed and energy and momentum balances across the system have been made. The unit has been shown to be useful for kinetic measurements of coal liquefaction, resid hydroprocessing and on solutions of some model compounds.

The conversion vs time during liquefaction of five coals in rank from lignite to low volatile bituminous have been studied in the SCTBR reactor particularly at short contact times. The liquefactions were shown to occur in two stages: an extraction of the component of the coal which is soluble in the liquefaction solvent at liquefaction temperatures, and a stage during which the coal structure is broken down into smaller molecules. These two stages are clearly observable in the SCTBR.

The equilibrium solubility of the components of the coal soluble in the liquefaction solvent at reaction temperature is easily measured in the SCTBR at various temperatures. The log of that solubility plotted against $1/T$ gave a heat of extraction for Illinois #6 coal in tetralin to be 44.5 kJ/ mole (10.6 kcal/mol).

The rate of extraction at 390°C for Illinois #6 is two orders of magnitude faster than the coal breakdown stage and had an activation energy of 59 kJ/mol (14 kcal/mol). The breakdown of the coal structure is more complex, consisting of several consecutive processes. The most rapid process was much slower than the extraction stage, and had an activation energy of 92 kJ/mol (22 kcal/mol). A following process was still slower and had a higher activation energy, but was not accurately determined because of retrograde processes occurring simultaneously. While the activation energy of the initial coal breakdown process is somewhat lower than activation energies of coal liquefaction measured by other workers, it is in a similar range (22 vs 28 kcal/mol) and is probably due to the early processes representing lower energy processes.

A preliminary study was made of the solvent and catalyst effects on coal liquefaction. This work suggests that the high conversion rapid dissolution of coal in tetrahydroquinoline and decahydroquinoline solvents may be due mainly to simple dissolution of the coal by base cleavage of hydrogen bonds of the coal and not a free radical breakdown of the coal structure into small molecules.

INTRODUCTION

The overall goal of this research is to develop an understanding of the Direct Coal Liquefaction process at the molecular level. Many approaches have been used to study this process including kinetic studies (1,2,3.), study of the liquefaction products (4,5), study of the effect of reaction variables, such as temperature, solvent type and composition (6,7,8), the changing nature and composition of the coal during liquefaction, (9) and the distribution in the liquefaction products of the hydrogen consumed (10,11). While all these studies have contributed to our growing knowledge of the liquefaction process, an adequate understanding of direct liquefaction still eludes us. This is due to many reasons including: the complexity and variable nature of coal itself and the many different chemical reactions which are occurring simultaneously during direct coal liquefaction. We believe that a study of the liquefaction process at the very early stages will avoid the complexities of secondary reactions associated with free radical high temperature processes that are clearly involved in direct coal liquefaction. This prompted us to devise a reactor system which avoids long heat up and cool-down times associated with previous kinetic studies, and allows kinetic measurements even at as short as the first few seconds of the liquefaction reaction.

The primary objective of this research therefore was to optimize the design and operation of a bench scale batch reactor (SCTBR) for

studying direct coal liquefaction at short contact times (.01 to 10 minutes or longer). An additional objective was to study the kinetics of uncatalyzed direct coal liquefaction particularly at short reaction times using the SCTBR equipment. Both of these objectives have been achieved, however this work has also shown the great importance of the liquefaction solvent characteristics and the solvent-catalyst interaction on the liquefaction process. This has prompted us to do a preliminary investigation of the solvents and the solvent-catalyst interaction.

SCIENTIFIC DISCUSSION

Objective # 1

The Reactor System

Apparatus The key components of the reactor system are illustrated in Figure 1. The batch reactor was constructed of 3/4 in. o.d. 316 stainless steel tubing of approximately 12 in. in length with wall thickness of 0.433 in. The preheater consisted of about 21 ft of a coiled 1/4 in. o.d. stainless steel tubing with wall thickness of 0.035 in. Further details of the entire reactor system are shown in Figure 2. The heating bath is a Techne IFB-52 industrial fluidized sand bath, which maintains a reaction temperature of $\pm 2^{\circ}\text{C}$. The approximately 30 cm³ reactor is capable of containing 17 MPa (2500 psig) pressure up to 550 °C. The tubing used for the precooler was identical to that used for the preheater.

In operation, both the empty preheater and reactor are immersed in a sand bath and brought up to the desired reaction temperature prior to the start of the reaction. Using high pressure gas, the reaction mixture at ambient temperature is driven into the reactor from a small blow case through the preheater. The injected mixture in the reactor is agitated by gas bubbles introduced from the bottom of the reactor. The degree of agitation is controlled by the exit gas flow rate from the top of the reactor and the configuration of the gas orifices. Since a gas (hydrogen or nitrogen) is bubbled through the reaction mixture under pressure and out through a let down valve, a small water cooled condenser is located above the reactor to avoid loss of solvent or other low boiling components. For operability, a disengaging space above the condenser is also situated before the let-down valve. In the case where the agitating gas is also a reactant (e.g. hydrogen in hydroprocessing or coal liquefaction), the gas bubbles provide very high contact or interfacial surface between the gas and the liquid or slurry reaction mixture. At a selected time, the reactor contents are driven out of the reactor through a precooler and into a cold receiver with high pressure gas. Both receiver and precooler are immersed in a water bath or other cooling medium. Cooling of the product mixture to about 25°C is achieved during the transport.

Reaction Temperature Profile

Using high pressure hydrogen or nitrogen to provide the driving force to deliver the reaction mixture from the blow case

through the preheater into the sand bath, the transfer occurs in approximately 0.3 seconds and the reaction mixture is brought up to within 5 to 8 °C of the desired reaction temperature within that time. In the hot reactor, the reaction mixture quickly comes up to reaction temperature. A representative time-temperature profile for a typical coal liquefaction run (Illinois #6 coal in 8:1 tetralin to coal ratio at 390°C 1000 psig Nitrogen) is shown in Figure 3.

Sample Recovery

In the usual operation of this equipment, the reaction products are recovered by blowing the products out of the reactor through the precooling coil and into the product receiver. However, small pockets in the system and surface wetting cause a hold-up of some material when the reactants are driven through the reactor system. The overall recovery of material from a reactor run depends primarily on the configuration of the exit of the blow case, on the surface areas of these equipment pieces and the viscosity or fluidity of the sample plug. The preheater and precooling represent the bulk of the surface involved. This therefore requires a trade-off. The longer the preheater, the smaller the temperature drop on injection. On the other hand, the longer the preheater, the lower the overall sample recovery. This necessitates a compromise between the reactor temperature drop on injection and the degree of overall material recovery from the reactor. For the coal liquefaction process streams studied in this project, recoveries have varied from 65 to 90 wt% depending on the

viscosity of the process stream. Clearly, some surface wetting will occur and 100% recovery is not practical by this method of operation. This means that, for mechanistic studies, analytical methods must be available to follow the course of the reaction with aliquots as is done with many other kinetic experiments. In most cases, the ash content of the coal was used as the tracer. It is critical, therefore, that the aliquots used to determine conversion by tracer analysis be representative of the reactor contents. This was shown to be the case in coal liquefaction and resid conversion experiments by comparing the products discharged into the receiver with those charged to the reactor when run at ambient temperatures.

When a higher material recovery is required, the first sample can be supplemented with solvent washes of the system. The additional quantities of the reaction mixture can be recovered by solvent removal in a rotovapor. Of course, the material recovered in that way has not experienced exactly the same thermal history as the first sample and is therefore not useful for some precision kinetic measurements, particularly if the samples were taken at very short reaction times.

In subsequent work at the end of this project, a new reactor was constructed in an effort to obtain a higher recovery of reaction product when the reaction is completed. This reactor had a somewhat modified and streamlined blow case, and sharp bends and places where product could be held up were minimized. Recoveries of coal liquefaction products from this new reactor have varied from 86 to 98 %, a considerable improvement over the first reactor.

The Cleaning System

In the usual operation of the system, the reactor is cleaned in place by a series of suitable solvent washes. The number of washes and type of solvent used are selected based on the materials and processes being studied. The wash effectiveness can be monitored by analysis of the wash streams. For heterogeneous mixtures, such as involved in coal liquefaction and coal-derived vacuum resid hydroprocessing, the wash effectiveness was followed through analysis of both the soluble reactant concentration and the particulate concentration in the wash streams.

Fluid Flow and Heat Transfer within the Preheater

The concept of the SCTBR system is to bring up both preheater and reactor to the desired reaction temperature prior to the start of the reaction. This eliminates the long time involved in heating the reactor itself and provides heat to the preheater tubing for transfer to the process stream. The transport of the process stream from the blow case into the reactor through the preheater occurs very rapidly (in about 0.3 seconds) in turbulent plug flow. The rapid heat up is due to both the large amount of heat contained in the preheater tubes and the gradient developed in the axial direction that provides the efficient transfer of this heat under turbulent flow conditions.

To demonstrate that plug flow occurred through the preheater tubing, an empty bomb which was identical in dimensions to the reactor was substituted for the reactor and a valve was inserted at the entrance of the bomb. A series of experiments was carried out

in which different amounts of tetralin were blown into the bomb with 1000 psig of nitrogen through the preheater tubing from the blow case with the system at ambient temperature. The valves were closed within approximately 2 seconds from the time of injection. The bomb and the blow case were then depressurized and the amounts of tetralin in each were determined. Approximately 90 to 93 wt % of the tetralin was recovered in the bomb. Only a few drops (less than 0.5g) were found in the preheater tubing, The larger amounts and the constant quantity of the tetralin which were retained in the blow case regardless of the amount of the tetralin charged, suggests that most of the holdup occurred in the blow case itself. If there had been a significant breakthrough of the gas through the tetralin (no plug flow) during the transport through the preheater, the high and constant percentage recovery of material would not have been observed.

The time of transport of the process stream through the preheater tubing was determined by temperature measurements in the reactor using a thermocouple attached to a high speed Linseis (series 2000) strip chart recorder. The response time (t_r) of the thermocouple in the reactor, which is the time between the start of the injection and the beginning of the temperature change, was recorded at a chart speed of 100 cm/min. It includes the time delay of the thermocouple (t_d 0.38s) and the transport time of the plug (t_u) through the preheater tubing into the reactor. Multiple tests including coal-tetralin, resid-tetralin, and tetralin alone indicate that the response time of the thermocouple in the reactor

is 0.65 ± 0.03 s. Allowing for this response time, the measured transport time of the plug through the preheater tubing from the blow case into the reactor is about 0.3 s.

Energy and Momentum Balances

An example of the operation of the SCTBR system is demonstrated using 30 g of tetralin. The relevant experimental conditions involved were 1000 psig of nitrogen pressure, reaction temperature 400°C and ambient temperature 20°C . The temperature of the tetralin stream reached 392°C when the entire stream was in the reactor. The large axial gradient in wall temperature developed along the preheater tubing during this injection is the key to the efficient heat-up. For example, if the sensible heat of the preheater was transferred to the process stream uniformly along the length of the preheater, i.e. without the axial gradient in wall temperature, the process stream could only reach 353°C , according to an overall energy balance. This would leave the sample 39°C below the experimentally observed temperature. The low heat transfer coefficient between the fluidized sand and the preheater ($0.34\text{--}0.68 \text{ kW m}^{-2}\text{C}^{-1}$ or $60\text{--}120 \text{ Btuhr}^{-1}\text{ft}^{-2}\text{F}^{-1}$) and the very short residence time (0.3s) make inconsequential the heat transfer from the fluidized sand to the preheater tubing and process stream as a source of the additional heat-up. Quantitatively, the amount of this heat transfer in the short time interval is less than $0.63 \text{ kJ} - 1.26 \text{ kJ}$ accounting for only 3-7% of the total heat required to bring 30 g of tetralin from 20 to 392°C . Rather, the axial gradient allows for the early portions of the preheater tube to

fall well below the uniform transfer temperature of 353 °C, and other later portions to remain at essentially the bath temperature. This allows for essentially complete heat up as follows:

As the first increment of tetralin proceeds through the preheater tubing, the temperature of the plug rises from ambient at the entrance and closely approaches the reaction temperature (ca. 400°C) at the exit. Thus the temperature gradient for heat transfer, δT , at the entrance is much higher than that at the exit. Each incremental amount of the tetralin experiences different temperature gradients along the preheater. The temperature gradients for heat transfer along the preheater tubing are functions of both the position along the preheater and the sequence of tetralin increments going through the preheater. The result is that more heat is extracted from the preheater at the entrance, where the temperature gradient is larger and less is extracted at the exit. The net effect is that more heat is extracted overall from the preheater than that calculated from a simple heat balance. This heat is replaced in the preheater tubing by the sand bath at a slower rate after the sample has entered the reactor itself. A more complete description of the SCTBR and a more detailed energy and momentum balance across the preheater is given in references (12 and 13).

Testing the SCTBR Reactor

A series of five coals varying from lignite to low volatile bituminous have been run under coal liquefaction conditions in the SCTBR unit. Conversion of the coal to liquid products was

determined by filtering out the solid unconverted product and determining its ash content by TGA. A typical conversion vs time curve for Illinois #6 in tetralin under 1000 psig nitrogen and without catalyst at 390°C, 408 and 422°C is shown in figure 4a and 4b. This will be discussed in more detail in a later section of this report. Coal derived vacuum resid (boiling points > 850°F) were also hydroprocessed in tetralin under hydrogen pressure at 390 to 435°C with and without sulfided molybdenum naphthenate catalyst. Conversion of these materials to products boiling < 850°F were demonstrated. This is the subject of another DOE report (14). The SCTBR system was also used to determine the kinetics of breakdown of model compounds. The kinetics of dibenzylether conversion in tetralin at 375 °C in the SCTBR is shown in Figure 5. This equipment proved to be particularly useful for running kinetics on soluble chemicals such as model compounds.

Development of Analytical Methods

An important objective in coal liquefaction is to obtain liquid fuels in boiling ranges suitable for conversion to gasoline, diesel oil, heating oil and fuel oil. To this end, a SimDis TGA method for measuring boiling range up to 600 °C or higher has been developed for this purpose. This requires only a few mgs of sample and is an actual measure of boiling range, not one simulated by a calibrated gas chromatograph.

A thermogravimetric analyzer (TGA) has also been coupled to a Mass Spectrometer, capable of analyzing products up to higher m/z ratios (approximately 1000 amu). After this unit has been tested,

this may provide some molecular identification of those high boiling products which are not available previously. This may offer a way to understand the interactions between catalyst and solvent at a molecular level.

Objective 2 The kinetics of Coal Liquefaction at Very Short Reaction Times

The direct coal liquefaction consists of at least two major stages: 1) solvent extraction of the portion of the coal soluble in organic solvents and 2) breakdown of the coal structure itself into liquid products (see Figures 4a and 4b). The coal extraction stage is intuitively obvious in view of the extensive solvent extraction work with many organic solvents that has been done on coals over the years (15). However, it is clearly observable when the liquefaction process is run in equipment capable of following reactions at times as short as 5 seconds. The solvent extraction stage at 390°C is actually orders of magnitude faster than the structure breakdown stage and the activation energies are correspondingly lower. The coal structure breakdown stage also consists of consecutive reactions of different reaction rates, apparently representing the breaking of the various types of chemical bonds connecting the aromatic clusters that make up the coal structure itself. These are also distinguishable for those bonds broken early in the process in the appropriate equipment and using suitable analytical methods. It is in part to provide kinetic data on these uncatalyzed reaction stages that this project was carried out.

It has been known for a long time that the characteristics of the liquefaction solvent have a profound effect on direct coal liquefaction. The coal liquefaction conversion, the amount of hydrogen consumed during the liquefaction process, the degree and quantity of retrograde reactions, and the quality of the liquid products are all influenced by the process solvent. Several analytical approaches have been developed to determine the important characteristics of the solvent for coal liquefaction (4). The hydrogen donor ability has clearly been very important (6). However, such other characteristics of a liquefaction solvent as solubility parameter (16), content and type of higher aromatic hydrocarbons present (7), and phenolic content have also been found to be significant (4). Finseth et al. (10,11) have shown that the bulk of the hydrogen consumed from an uncatalyzed donor solvent liquefaction above 400 °C is consumed in gas generation, heteroatom removal and hydrogenolysis of the coal matrix. Wilson et al. (5) have also shown that the major amount of hydrogen consumed in uncatalyzed liquefaction is used in alkyl fission and hydrogenolysis reactions and not with hydrogenating aromatic rings. McMillan et al. (8) have postulated that a radical hydrogen transfer process along with donor solvent capping of thermally produced radicals from the coal is a possible additional process involving the solvents in coal liquefaction.

Experimental Section

Coals Studied. The kinetics of direct liquefaction of five coals from Lignite to low volatile bituminous (MT Pust lignite, Wyodak-Anderson subbituminous coal, Illinois #6, Pittsburgh #8 high volatile bituminous, and Pocahontas #3 low volatile bituminous coals) obtained from the Argonne and Penn State Coal Banks were investigated in this study. Proximate and elemental analyses on the coals studied are provided in Table 1.

Solvents Used. Three solvents: tetralin (99%), 1-methylnaphthalene (98%), and decalin (decahydronaphthalene, 99+%) from Aldrich with different hydrogen donor abilities and similar solubility parameters have been used.

Apparatus. The Short Contact Time Batch Reactor (SCTBR) was used to carry out the liquefaction experiments. The design and operation of the reactor system, including a schematic diagram, have been described earlier in this report.

Coal Liquefaction. All liquefactions were run as mixtures of processing solvent (S) and coal (C) (at a ratio of S/C = 8 to 1 by weight unless otherwise mentioned) to minimize the effect of changing processing solvent concentration during the reaction and to reduce retrograde reactions. About 4 grams of coal were used for each reactor run, together with the added processing solvent to make up the reactant slurry.

Catalyst Used. Although the majority of kinetic studies done under this project were not catalyzed, sulfided molybdenum naphthenate (6.8 wt% molybdenum from Shepherd Chemical Co.) was the

liquefaction catalyst used in some instances in this study. The catalyst was prepared by dissolving about 0.5 g molybdenum naphthenate (equivalent to about 0.9 wt% Mo based on the amount of the coal charged) in the processing solvent. The catalyst was then sulfided by reacting the solution with about 1 g of methyl disulfide during the transport into the reactor.

Workup Procedures of the Liquefaction Products. The product mixtures were filtered and the solid residues washed with cold fresh tetralin thoroughly and dried in a vacuum oven with a nitrogen purge at 105°C for 48 hours. The filter cake was then rinsed with methylene chloride and dried in a vacuum oven with a nitrogen purge at 105°C for 12 hours. The solid residue and the liquid filtrate were analyzed separately. The workup scheme is shown in Figure 6.

Thermogravimetric Analysis. The thermogravimetric analyzer was a model 51 TGA (TA Instruments, New Castle, Delaware). The TGA was run on liquefaction residues to provide a measure of the amount of volatile matter (VM), fixed carbon (FC) and ash in the residue. The mineral matter of the coal was shown to accumulate in the coal residue and not in the coal liquids. Ash in the residue was therefore used to calculate the conversion (X) to tetralin (or other selected solvent) soluble material using the formula:

$$X \text{ (daf wt\%)} = \frac{1}{1 - A_0} \times \left(1 - \frac{A_0}{A_s} \right) \times 100\% \quad (1)$$

where A_0 and A_s are the weight fractions of ash (derived from the

mineral matter) in a control sample and the liquefaction residue, respectively. A typical thermogravimetric (TGA) analysis of liquefaction residue is shown in Figure 7.

The volatile matter (VM) in the residue turned out to be only a function of the reaction time and temperature i.e. the VM in the residue produced at the same time and temperature was the same regardless of whether the liquefaction was run thermally or catalytically. The fixed carbon (FC) in the residue, however, is an approximate measure of the retrograde processes occurring during the liquefaction and is strongly affected by the presence of hydrogen and hydrogenation catalyst. The kinetics of the FC formation could be followed by TGA.

Experimental Results

Coal Liquefaction Conversion vs Time. The conversions of Illinois #6 coal liquefaction in tetralin without added catalyst under 1000 psig nitrogen at four temperatures (358 °C, 390 °C, 408 °C and 422 °C) for short reaction times (10 s to 10 min) and up to one hour are shown in Figures 8a and 8b, respectively. Two distinct stages in the process were observed: a very rapid conversion followed by a transition period and then a slower liquefaction (breakdown) of the coal structure. The initial rapid conversion in the first 30 to 60 s is due to the extraction of a soluble fraction of the coal into the hot tetralin. The slow conversion after 1 or 2 min is presumably caused by the chemical breakdown of the coal structure to liquid products.

The amount of tetralin soluble material extracted from the coal increases as the liquefaction temperature increases. The equilibrium extraction (in 8:1 wt % tetralin to coal) of the Illinois #6 coal at 358 °C, 375 °C, 390 °C, 408 °C and 422 °C at a tetralin to coal weight ratio of 8 to 1 were about 18.4, 20.0, 22.0, 31.9, and 39.8 wt% (daf), respectively. The heat of extraction is determined by plotting the log of that equilibrium extraction against $1/T$ over the temperature in Figure 9. The extraction heat into tetralin is approximately 44.5 kJ/mol (10.6 kcal/mol), suggesting that the extraction is mainly a physical process, and does not involve breaking of chemical bonds, but requires somewhat more energy than a simple dissolution process.

The rate constant of the extraction stage and the equilibrium extraction fraction are dependent on the solvent characteristics and coal type as well as liquefaction conditions. Three solvents (i.e., tetralin, 1-methylnaphthalene and decalin) having similar solubility characteristics but rather different hydrogen donor reactivities were studied. Conversion vs. time curves of the thermal (without added catalyst) liquefaction of Illinois #6 in the three solvents run under 1000 psig nitrogen at 408 °C are shown in Figures 10a and 10b for two different time intervals. The liquefaction conversions using 1-methylnaphthalene and decalin as processing solvents also show the same distinct stages of liquefaction kinetics: a very rapid extraction and followed by an extremely slow liquefaction of the coal structure. The equilibrium extractions (at the solvent to coal ratios used) of the Illinois #6

coal using 1-methylnaphthalene and decalin were 30.7 and 28.2 wt%, respectively. These values are close to that using tetralin (31.9 wt %) as a processing solvent. The Hildebrand Solubility Parameters of decalin, 1-methylnaphthalene, and tetralin are 18.0, 20.3, and 19.4 MPa^{1/2}cm³mol⁻¹, respectively (14). This suggests that the extraction stage in the coal liquefaction is dominated by the solubility characteristics of the processing solvent used. However, the rates of coal structure breakdown in tetralin is approximately 27 and 24 times faster than those in 1-methylnaphthalene and in decalin, respectively. The breakdown of the coal structure itself therefore is much slower than the extraction process and consists of consecutive steps having different rate constants and activation energies.

Similar conversion profiles were observed in the other coals and shown in Figure 11. The equilibrium extraction at 390°C of those coals is shown in Table (2). While they vary considerably in the weight fraction extracted at 390°C, they all exhibit the very rapid approach to equilibrium extraction and the characteristic transition interval when the extraction is going to completion and the breakdown of the coal structure is becoming dominant.

It is important to point out that the coal liquefaction kinetic studies reported in the literature are largely based on liquefaction to high conversions (1,2,3). Therefore, the kinetic measurements are actually combinations of the rapid extraction (15 to 40% of the coal) with the much slower breakdown of the coal structure itself.

Kinetic Analysis of Coal Liquefaction. From observations of coal liquefaction conversion vs. time, the following hypothesis is introduced to establish a model for evaluation of the kinetic parameters for each stage. In brief, the initial rapid conversion (in the first 30 to 60 s) is due to the extraction of a soluble fraction of the coal to approximate equilibrium under liquefaction conditions. This is followed by a transition period and then the slow conversion resulting from the breakdown of the coal macromolecular structure to liquid products. The transition period is due to the simultaneous occurrence of two processes: a very rapid extraction which is levelling off and a relatively slower liquefaction of the coal matrix which is becoming dominant. Based on this hypothesis, the coal itself under the liquefaction conditions consists of a soluble material and a reactive component. Therefore, the total weight of the organic portion of the coal liquefied (W_c) is the sum of these two components, i.e.

$$W_c(t) = W_s(t) + W_r(t) \quad (2)$$

where $W_s(t)$ is the weight of the extracted material and $W_r(t)$ is the weight of the reacted component. The observed liquefaction rate is the first derivative of Eq. 2, i.e.

$$r \equiv \frac{1}{W_{c0}} \frac{dW_c(t)}{dt} \quad (3)$$

where r is the overall liquefaction rate determined in the experiments and W_{c0} is the weight of the original coal on a dry-ash-free (daf) basis.

The boundary conditions for Eqs. 2 and 3 are that

$$W_{c_0} = W_{s_0} + W_{r_0} \quad (4)$$

where W_{s_0} is the weight of the extractable material in the coal, which is measured by the equilibrium extraction under liquefaction conditions, and W_{r_0} is the weight of the reactable component at $t = 0$ under the conditions of liquefaction.

Dividing both sides of Eq. 2 by W_{c_0} gives an expression of the total conversion (X) which is a measurable quantity:

$$\begin{aligned} X(t) &\equiv \frac{W_c(t)}{W_{c_0}} \\ &= \frac{W_s(t)}{W_{c_0}} + \frac{W_r(t)}{W_{c_0}} \\ &= \frac{W_{s_0}}{W_{c_0}} \frac{W_s(t)}{W_{s_0}} + \frac{W_{r_0}}{W_{c_0}} \frac{W_r(t)}{W_{r_0}} \\ &= f_s X_s(t) + f_r X_r(t) \end{aligned} \quad (5)$$

where

$$\begin{aligned} f_s &= \frac{W_{s_0}}{W_{c_0}} \\ f_r &= \frac{W_{r_0}}{W_{c_0}} \\ X_s(t) &= \frac{W_s(t)}{W_{s_0}} \\ X_r(t) &= \frac{W_r(t)}{W_{r_0}} \end{aligned} \quad (6)$$

In Eqs. 5 and 6, f_s is the fraction of soluble material in the coal under the liquefaction conditions; f_r is the fraction of reactable

component in the coal under the liquefaction conditions; $X_s(t)$ is the extraction conversion of the extractable materials in the coal at time t ; and $X_r(t)$ is the coal-structure-breakdown conversion at time t .

Based on Eq. 4, we have

$$f_r = 1 - f_s \quad (7)$$

Substituting Eq. 7 into Eq. 5 gives

$$X(t) = f_s X_s(t) + (1 - f_s) X_r(t) \quad (8)$$

From Eq. 2, the rate of the coal liquefaction can be expressed by

$$\begin{aligned} r &\equiv \frac{dX(t)}{dt} \\ &= k (1 - X(t))^\alpha C_t^\beta P_{gas}^\gamma \end{aligned} \quad (9)$$

where k is the liquefaction rate constant; $(1 - X(t))$ is the weight fraction of the residual solid coal to be liquefied; C_t is the tetralin concentration or the concentration of another process solvent; and P_{gas} is the nitrogen or hydrogen pressure. When a large amount of tetralin (or other process solvent) is used in the liquefaction (for example, 8 to 1 of tetralin to coal weight ratio was used in this study), C_t is approximately equal to a constant. P_{gas} is held constant during the liquefaction run in this study. Therefore, Eq. 9 is simplified to

$$\frac{dX(t)}{dt} = k' (1 - X(t))^\alpha \quad (10)$$

where

$$k' = k C_t^\beta P_{gas}^\gamma \quad (11)$$

Since the liquefaction rate determined in these experiments is the sum of the extraction and coal structure breakdown processes, from Eq. 9 we have

$$\begin{aligned} r &\equiv \frac{dX(t)}{dt} \\ &= f_s \frac{dX_s(t)}{dt} + (1 - f_s) \frac{dX_r(t)}{dt} \end{aligned} \quad (12)$$

where

$$r_s \equiv \frac{dX_s(t)}{dt} = k_s (1 - X_s(t))^{\alpha_s} \quad (13)$$

and

$$r_r \equiv \frac{dX_r(t)}{dt} = k_r (1 - X_r(t))^{\alpha_r} \quad (14)$$

where r_s is the rate of the extraction of the soluble materials in the coal; r_r is the rate of the chemical breakdown of the coal structure; k_s is the extraction rate constant; and k_r is the breakdown rate constant.

Assuming $\alpha_s = 1$ in Eq. 13 gives the conversion rate of the extraction process as a function of

$$\frac{dX_s(t)}{dt} = k_s (1 - X_s(t)) \quad (15)$$

Similarly, assuming $\alpha_r = 1$ in Eq. 14 and performing the similar derivations to the reaction rate of the coal matrix breakdown

process give:

$$\frac{dX_r(t)}{dt} = k_r (1 - X_r(t)) \quad (16)$$

Integrating Eqs. 15 and 16 with boundary conditions of $X_s = 0$ and $X_r = 0$ at $t = 0$, we obtain equations of

$$\ln(1 - X_s(t)) = -k_s t \quad (17)$$

and

$$\ln(1 - X_r(t)) = -k_r t \quad (18)$$

Kinetics of Coal Liquefaction. The plot of $\ln(1-X_s/X_{s0})$ against t for the Illinois #6 coal liquefaction in tetralin under 1000 psig N_2 at 390 °C is shown in Figure 12. The slope gives a measured rate constant for extraction of $k_s = 2.81$ with an r^2 of 0.97. The plot of $\ln(1-X_r/X_{r0})$ against t for the structure breakdown stage of Illinois #6 coal is illustrated in Figure 13. It shows two distinct reaction stages: a rapid one with a rate constant of 0.027 for the first 5 minutes, and a slower one of 0.0054 for times greater than 5 minutes. The liquefaction kinetic parameters of the MT Pust lignite, Wyodak-Anderson subbituminous, Illinois #6 high volatile bituminous, Pittsburgh #8 high volatile bituminous, and Pocohontas #3 low volatile bituminous coals evaluated by the proposed model are summarized in Table 3. As an example, Figure 14 shows experimental data and modelling curve at the reaction times up to 10 min for Wyodak-Anderson coal liquefaction in tetralin at 390 °C under 1000 psig N_2 . It shows that the model fits the

experimental data very well.

Rate constants of k_s and k_r at four temperatures (358, 375, 390, and 408 °C) were used to estimate activation energies of extraction and liquefaction reaction processes for liquefaction of Illinois #6 coal. The plot of $\ln k_s$ against $1/T$ and $\ln k_r$ vs $1/T$ shown in Figures 15 and 16 give activation energies of 59 and 92 kJ/mol (14 and 22 kcal/mol) for the solubilization and bond breaking processes, respectively. The activation energy observed for the structure breakdown stage of Illinois #6 (92 kJ/mol) is significantly lower than has been observed in previous studies. This is probably due to the fact that we are measuring the kinetics at very low conversions and apparently the breakdown of the most active species in the coal. The activation energy of the slower structure breakdown after 5 minutes determined from Figure 9 is clearly higher than 92 kJ/mol, but could not be accurately determined because of onset of the retrograde processes, in the absence of hydrogen and a catalyst.

It is of interest to compare these results with those obtained by others at higher conversion. Wiser (2) obtained an activation energy value of 120 kJ/mol (28.8 kcal/mol) for Utah bituminous coal liquefaction at 63 to 94% conversion. Curran et al. (1) obtained two values for a rapid and a slow rate with mean values of 125 and 159 kJ/mol on Pittsburgh Seam bituminous coal at 2.5 minutes and 2 hours, respectively. They used a process-derived solvent from 325 to 435°C. While the activation energy of 92 kJ/mol value seems rather low, it represents low conversion and coal has obviously

both weak and strong bonds which will be broken in order of their bond strength. The process derived solvent also may strongly affect the relative amounts of the extraction and liquefaction stages in the Curran work.

More recently, Xu and Kandiyoti (17) measured the kinetics of coal liquefaction in tetralin using a flow reactor in which pure tetralin was passed through a bed of coal at various temperatures, with a heat up period and hold time in the bed of coal before the tetralin was introduced. These experiments were made with a constant tetralin concentration and a constantly changing coal composition, not directly simulating an actual liquefaction process. Kinetics were followed by weight changes in the bed of coal. The kinetic calculations were based on a similar two stage model, but calculated in two different ways, i.e., 1) assuming the second stage was a single liquefaction process, and 2) assuming the second stage consisted of multiple reactions having a gaussian distribution of reactions. Their activation energies were similar to those reported in this paper for the first (extraction stage), but showed quite different values depending on whether the second stage was assumed to be a single process or a multireaction process. Since this work only attempted to follow the kinetics in the very early stages of coal liquefaction, it is not possible to meaningfully compare these results. However, since the data reported in this paper represented direct measurements of the processes involved in the early stages, we believe they accurately represent the kinetics at that stage of the process.

The Retrograde Reactions Occurring during Liquefaction. As reported above, in the absence of hydrogen and a hydrogenation catalyst, increasing temperature up to 408 °C gives high conversions to tetralin soluble products. However, above 408 °C (e.g. 422 °C), further increasing temperature results in higher conversion to fixed carbon (FC), i.e. retrograde products, and lower yield to tetralin soluble products. Understanding this onset of retrograde reactions is of great importance for improvement of the direct coal liquefaction process. Elemental analysis of these residues show decreasing hydrogen to carbon ratios as the coal residues are exposed to higher temperatures and longer reaction times (Table 4). It is not surprising therefore that introduction of hydrogen and a hydrogenation catalyst in the liquefaction process has a profound effect limiting the rate of formation of fixed carbon FC and therefore increasing the liquefaction yields.

Summary and Conclusions

The direct liquefaction of coal shows distinct stages: an extraction stage and at least two slower stages representing the breakdown of various components of the coal structure. These only become apparent with a reactor system capable of accurately distinguishing conversions at reaction times as low as 10 seconds.

The liquefaction conversion observed in these experiments is the sum of two simultaneous liquefaction processes of extraction and breakdown of the coal structure. Based on this model, the liquefaction kinetics in each stage of the entire process can be adequately described for early stages in liquefaction.

At 390 °C the extraction stages studied to date are about two orders of magnitude faster than the structure breakdown stages and have correspondingly lower activation energies. The liquefaction of the coal structure itself also consists of multiple steps of different rate constants and activation energies.

The retrograde reactions can be followed by thermogravimetric analysis of the coal liquefaction residues. They are suppressed by catalytic hydrogenation during the liquefaction process.

Objective 3 Study of Coal Liquefaction Catalyst and Solvent Interactions

In the direct liquefaction process, both the catalyst and the solvent play very significant roles. While coal liquefaction can be carried out in the absence of catalyst or even in the absence of solvent, the most effective system involves both. Based on the work of many researchers a hydrogen donor solvent plays at least two roles: a solvent for the liquefaction products, which is determined by such characteristics as solubility parameter, and as a reactant to break down the coal structure. If the solvent is a good solvent for coal liquids and a strong hydrogen donor solvent for the coal structure itself, the coal can be liquefied without a catalyst. In this case, the solvent reacts directly with the solid coal. On the other hand, if the solvent is a good solvent for the coal liquids but a poor reactant (hydrogen donor) to break down the coal structure, extraction of soluble material occurs, but liquefaction of the coal structure itself is very slow unless there is a catalyst in the presence of hydrogen gas.

For the very strong solvent 1,2,3,4-tetrahydroquinoline, (18) the extraction stage becomes indistinguishable from the liquefaction of the coal structure. This is because the rate of coal solubilization in the very strong solvent is the rate of extraction. There is a great difference between a good solvent for coal and a strong hydrogen donor solvent. Tetrahydroquinoline (THQ), for example, appears to be a very good solvent for coal and dissolves some coals rapidly and fairly completely. The extraction and solubilization stages of the Illinois #6 coal liquefaction in 1,2,3,4-tetrahydroquinoline were indistinguishable. In reaction with benzophenone, however THQ appears to have hydrogen donor properties but is not an exceptionally powerful hydrogen donor solvent (19,20,21). Thermogravimetric analysis (TGA) of the liquid products in THQ show the presence of a substantial amount of very high boiling material, (Figure 18) suggesting that the coal was solubilized but not broken down very much. Decahydroquinoline (DHQ) which would probably not be expected to be a strong hydrogen donor solvent, appears to be an equally good coal solvent as THQ, dissolving 85% of Illinois #6 coal very rapidly at 400°C. TG Analysis of the resulting liquid in DHQ also shows good solubility for coal but also little break down of the coal structure. It appears likely that the THQ and DHQ, which are strong bases, solubilize the coal by cleaving hydrogen bonds, but not breaking the covalently bonded coal structure down significantly to the desired low boiling products. Tetralin however which is not basic and a hydrogen donor solvent at 396°C (18) shile slower acting,

gives a liquid product in tetralin which shows little if any material boiling above the boiling point of tetralin by TGA. If strong liquefaction solvents such as THQ or DHQ are used, addition of catalyst and a hydrogen atmosphere has little or no effect on the rate of conversion to soluble product. If the solvent is a weak or poor hydrogen donor and not a good solvent for the coal, an active catalyst and gaseous hydrogen are necessary to supply the hydrogen, to achieve reasonable dissolution rates, and to minimize retrograde processes.

At the present time, the process envisioned for commercialization of direct liquefaction uses a portion of the liquefaction product including some high molecular weight material as recycle solvent for the liquefaction reaction. This liquefaction solvent stream is variable and can be of relatively poor hydrogen donor strength. Recognizing this, Exxon developed a rehydrogenation step on the recycle solvent in the Exxon Donor Process. This resulted in improved process performance, but added an additional step to the process. The rehydrogenation of the entire recycle solvent, while an improvement, was probably not sufficient to convert it to a very strong hydrogen donor solvent. Partially hydrogenated higher aromatic hydrocarbons, such as dihydrophenanthrene and dihydropyrene, however, are somewhat stronger hydrogen donors than tetralin. There is evidence that addition of a high boiling fraction of the liquefaction product or higher aromatic hydrocarbons to the recycle solvent stream results in an increase in conversion and yield in the liquefaction process

(7). This has been attributed to hydrogen "shuttling" from one part of the coal molecules to another, thus improving the utilization of the hydrogen in the hydrogen deficient coal. The exact mechanism of this process is not known, but the value of recycling high boiling fractions to the liquefaction process is well demonstrated. Hydrogen "shuttling" may actually be by hydrogenation of the higher aromatics to form stronger hydrogen donors which in turn transfer their hydrogens to the coal structure.

In principle, very major improvements in production rates and conversion in coal liquefaction are possible by suitable selection of catalyst and solvent which provides for rapid hydrogenolysis of the chemical bonds in the coal.

Catalysis by Molybdenum Naphthenate. Conversion of the Illinois #6 coal with molybdenum naphthenate (equivalent to 0.9 wt% Mo based on the coal) was studied in an effort to understand the role of a hydrogenation catalyst relative to the liquefaction solvent in coal liquefaction. Figure 21 summarizes the results of a series of experiments aimed at determining the active species when the molybdenum naphthenate is the added catalyst. The sulfiding agent used was methyl disulfide. Comparison of the conversions in different liquefaction conditions shown in Figure 21 indicates that: 1). sulfided molybdenum naphthenate in the absence of hydrogen is not active; 2). the sulfiding agent itself plays no direct role in coal liquefaction; and 3). only sulfided molybdenum naphthenate (presumable as Mo_2S_3 or MoS_2) in the presence of hydrogen

is the active catalyst for coal liquefaction.

Effects of Solvent, Catalyst, and Gas Atmosphere on the Coal Liquefaction. Conversion vs. time curves of the thermal (without added catalyst) liquefaction of Illinois #6 coal in tetralin, and 1-methylnaphthalene, run under 1000 psig nitrogen at 408 °C are shown in Figures 22a and 22b for two different time intervals. The liquefaction conversions using 1-methylnaphthalene as a processing solvent shows the distinct stages of liquefaction kinetics: a very rapid extraction and followed by an extremely slow liquefaction of the coal structure. The equilibrium extraction of the Illinois #6 coal using 1-methylnaphthalene was 30.7 wt%. This value is very close to that using tetralin as a processing solvent. The solubility parameters of 1-methylnaphthalene and tetralin are 20.3 and 19.4, respectively. This suggests that the extraction stage in the coal liquefaction is dominated by the solubility characteristics of the processing solvent used. However, the rates of coal structure breakdown in tetralin and in 1-methylnaphthalene were 0.0458 wt%/min and 0.00168 wt%/min, about 27 times difference.

Effects of solvent on the thermal liquefaction of the Illinois #6 coal in nitrogen and in hydrogen are illustrated in Figure 22. The liquefaction in the poor hydrogen donor solvents, such as decahydronaphthalene and 1-methylnaphthalene, show much lower conversion than in tetralin under nitrogen pressure. However, for these very poor hydrogen donor solvents, the liquefaction conversions of the Illinois #6 coal in hydrogen is much higher than that in nitrogen, showing strong sensitivity to gas atmosphere.

These results suggest that, in a hydrogen donor solvent, particularly if the solvent is a weak hydrogen donor, the hydrogen needed in the liquefaction process must be mostly derived from molecular hydrogen from a hydrogenation catalyst, such as sulfided molybdenum naphthenate. Liquefaction conversions are always higher in tetralin than in 1-methylnaphthalene for both of the thermal and catalyzed liquefactions. However, with the added catalyst, the conversions in tetralin increased only by a factor of 53%, 31%, and 29% for 30 min liquefaction at 390 °C, 403 °C, and 420 °C, respectively, compared to those in 1-methylnaphthalene by a factor of 123% and 97% for 10 min at 397 °C and 30 min at 410 °C, respectively. These results indicate that the catalysis by an added hydrogenation catalyst in coal liquefaction is more responsive when a poor hydrogen donor solvent is used. It also suggests that a hydrogenation catalyst could be used to compensate for the lack of hydrogen donor ability of a processing solvent.

To quantitatively evaluate the effects of solvent, catalyst, and gas atmosphere for the coal liquefaction, specific liquefaction conversion ratios of α , β , and γ are defined using the coal liquefaction conversion in nitrogen as a reference, i.e.,

$$\begin{aligned}
 \alpha &= \frac{X_{H_2}}{X_{N_2}} \\
 \beta &= \frac{X_{catalyst}}{X_{N_2}} \\
 \gamma &= \frac{X_{catalyst}}{X_{H_2}}
 \end{aligned}
 \tag{19}$$

where X_{N_2} is the liquefaction conversion in nitrogen; X_{H_2} is the liquefaction conversion in hydrogen; and $X_{catalyst}$ is the catalyzed liquefaction conversion in hydrogen. The α is selected to evaluate the hydrogen gas effect. The larger the α , the stronger the hydrogen gas effect. When $\alpha = 1$, it means there is no hydrogen gas effect in the coal liquefaction. The β is calculated to evaluate the catalyst reactivity and the γ is used to evaluate the net reactivity of the added catalyst. The data to show the combination of the effects of solvent, catalyst, and gas atmosphere on the Illinois #6 and Wyodak-Anderson coal liquefactions, together with the calculated specific ratios of α , β , and γ , are summarized in Table 1. Based on the α values, the order of the hydrogen gas effect on the Illinois #6 coal liquefaction for different solvents was decahydronaphthalene ~ 1-methylnaphthalene > tetralin > 1,2,3,4-tetrahydroquinoline. The stronger the hydrogen donor solvent, the less will be the hydrogen gas effect. In fact, there is no hydrogen gas effect on the Illinois #6 coal liquefaction for the very strong solvent 1,2,3,4-tetrahydroquinoline for which $\alpha = 1$. The Wyodak-Anderson coal shows no hydrogen gas effect ($\alpha = 1$) during the liquefaction in tetralin. Based on the β values, the

order of the catalyst influence on coal liquefaction in different hydrogen donor solvents was 1-methylnaphthalene > tetralin. Furthermore, the higher the liquefaction temperature, the lower the catalyst influence on liquefaction conversion. This may be because, as temperature increases, the selectivity to liquid products during the liquefaction decreases. This is also supported by the γ values for the liquefaction of the Illinois #6 in 1-methylnaphthalene.

The Role of the Catalyst

A tremendous amount of work is reported in the literature on selection of solid catalysts for coal liquefaction (22). Despite all this work, the exact role of the catalyst in coal liquefaction is still not completely understood. The interaction of catalyst with solvent has never been intensively studied.

Coal is a solid material which can nevertheless be catalyzed in coal liquefaction by solid catalysts such as a Ni/Mo on alumina or various solid metal sulfides. Ebulating bed reactors with solid supported metal catalysts have been extensively used in recent years in pilot plant studies. This, of course, raises the question of how a solid catalyst can make molecular contact with the solid coal surfaces, particularly in a slurry of coal, catalyst and solvent. Even in the absence of donor solvent, a solid catalyst, usually formed in situ in the presence of hydrogen, can catalyze liquefaction. Investigators have shown the importance of catalyst dispersion in the liquefaction process although good dispersion is hardly "molecular" contact. There must be some transport processes

between the coal and the catalyst for catalysis to occur. Almost all of the catalysts active for liquefaction (with the exception of a number of Lewis acids) are insoluble solids, usually metal sulfides. It has been shown that the pore size of the catalyst is important (particularly large pores) in catalyst activity and in reducing the rates of deactivation. Also it has been shown that a bimodal distribution of pore sizes result in better liquefaction catalysts. This certainly implies that communication of the coal with the catalyst or reaction in the liquid medium in proximity to the catalyst takes place.

One role of the catalyst is clearly the rehydrogenation of the hydrogen donor solvent as its hydrogen donor capability is dissipated. The strength of the hydrogen donor solvent has a profound effect on the liquefaction rates. This catalytic rehydrogenation of processing solvent can be carried out either in the liquefaction reactor (*in-situ*) or in a separate unit as was done by Exxon. In the later case, a more efficient process than Exxon's could be developed.

Even in poorer hydrogen donor solvents, the solvent and/or the coal liquids produced may provide some mass transport communication between catalyst sites and the solid coal. It has been shown that swelling the coal with tetralin results in higher liquefaction yields and reaction rates.

Since sulfides appear to be important components of most liquefaction catalysts, H_2S or other sulfur species may provide some transfer between coal and solid catalyst. This represents an

important question which could influence the choice of the most effective catalyst. H_2S is a known catalyst for coal liquefaction.

Assuming that very fine catalyst particles would provide greater dispersion and greater surface area for better contact between coal, the liquid medium, and catalyst, a great many research programs have been carried out to produce nanometer size catalyst particles. While some of these programs have had some degree of success in increasing liquefaction yields and reaction rates, the rate improvements have not been spectacular and the costs of producing such very fine particulate catalysts is likely to be high. Coal has also been liquefied in a solvent system using finely dispersed emulsified molybdenum catalysts (23). Solid coals have been liquefied without a solvent, generally using coals impregnated with or ion exchanged with dissolved iron salts (22), ammonium tetrathiomolybdate or sulfided molybdenum naphthenate. In most of these cases, it is believed that the active catalyst is a solid metal sulfide (e.g. Pyrrhotite or MoS_2) generally formed in situ. Again, these are solid-solid catalyzed reactions. Iron catalysts are effective generally as the sulfides ($Fe_{1-x}S$) in coal liquefaction, but tin, tungsten and molybdenum catalysts also as the sulfides have been consistently shown to be more effective although more expensive. The presence of sulfide has usually been found to be necessary for effective catalysis.

Clearly, the role of the solid catalyst in direct coal liquefaction will require further experimental work to develop a better understanding.

PROPOSED FUTURE PROGRAM

Since the liquefaction rates and conversions are to a large degree dependant upon both the quality of liquefaction catalyst and the recycle solvent, the proposed next research program will be primarily based on optimizing these two components of the process.

It is assumed that for a practical process, the solvent must come from a portion of the coal liquefaction product itself which will be recycled to the reactor. As such it must have the two characteristics of a suitable liquefaction solvent i.e. a) suitable solubility characteristics to dissolve coal liquefaction products and b) a strong hydrogen donor strength or be capable of becoming a strong donor in the presence of hydrogen and a suitable catalyst.

To address the question of the role of the catalyst and whether actual physical contact between the solid catalyst and the solid coal is necessary, it is proposed to coat a known liquefaction catalyst (e.g. sulfided Ni/Mo on alumina) with a thin porous silica layer. The coating would be selected to prevent direct physical contact between solid coal and solid catalyst, but if properly applied would allow transmission of mobile species between the two surfaces. Such a porous silica coated catalyst has been developed by DuPont for an attrition resistant catalyst for oxidation reactions, which does not reduce the activity of the catalyst. If an active catalyst is coated and found to have no activity for coal liquefaction, regardless of the thickness of the coating, it would suggest that direct contact between coal and solid catalyst may be required and nano sized uncoated catalysts

may be the right approach. If a coated catalyst is active, it would suggest that there is mass transfer between catalyst and coal and that nano sized catalyst particles may not be required. It may also provide an attrition resistant catalyst for practical usage in an ebulated bed reactor. the deactivation rates of such active coated catalysts would be explored as well as other coated active solid catalyst systems, including those with various pore sizes and pore size distributions,

Exploration of such coated catalyst systems may require the assembling of a coating process and a suitable way of workup and analysis of liquefaction reaction products using the coated catalysts. A suitable way of measuring the coating thickness will also be required.

In support of this catalysis research, we would also need to establish the role of the solvent component rigorously, including its role in catalysis, extraction, solvation and hydrogen transfer in the liquefaction process.

To follow the relationship between catalyst and recycle solvent characteristics, recycle solvent from a liquefaction unit would be fractionated into boiling ranges. The relative kinetics of liquefaction of various coals in these boiling fractions would be determined in the presence of a selected concentration of sulfided molybdenum naphthenate and possible some coated and uncoated solid catalysts. These fractions would be characterized by hydrogen donor strength, ^1H NMR. Solubility Parameter, Gas Chromatography and TG/MS.

PUBLICATIONS

The following publications or oral presentations were made as a result of this project:

1. Huang, H., Calkins, W.H., Klein, M.T. " A Novel Laboratory Laboratory Scale Reactor System for Studying Fuel Processes 1, Apparatus and Preliminary Experiments" Energy and Fuels 8, 1304-1309 (1994)
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Table 1 Proximate and elemental analyses of the coals studied

Coal	Rank	Proximate Analysis (dry), wt%			Elemental Analysis (daf), wt%				
		VM	FC	Ash	C	H	N	S	O (diff.)
MT Pust	ligA	41.98	46.17	11.85	74.60	5.22	1.07	0.82	18.29
Wyodak-Anderson	subC	44.73	46.50	8.77	75.01	5.35	1.12	0.47	18.05
Illinois #6	hvCb	40.05	44.47	15.48	77.67	5.00	1.37	2.38	13.58
Pittsburgh #8	hvAb	36.02	53.73	10.25	83.32	5.69	1.37	1.25	8.37
Pocahontas #3	lvb	18.31	77.09	4.60	89.87	4.90	1.14	0.78	3.31

Table 2 The equilibrium extraction of the coal liquefaction at 390 C
in tetralin under 1000 psig nitrogen (8 : 1 =Tetralin : Coal wt% Ratio)

Coal	Rank	Equilibrium Extraction wt% (daf)
MT Pust	ligA	23.9
Wyodak-Anderson	subC	14.6
Illinois #6	hvCb	22.0
Pittsburgh #8	hvAb	14.1
Pocahontas #3	lvb	15.2

Table 3 The rate constants of liquefaction for the five coals studied
(390 C; 1000 psig nitrogen)

Coal	Rank	Time min	Liquefaction Stage	Rate constant wt%/(lit.)/min.
MT Pust	ligA	0 - 1.5	Extraction	7.08
		0 - 60	Reaction	0.000343
Wyodak-Anderson	subC	0 - 0.5	Extraction	11.8
		0 - 15	Reaction (R1, fast)	0.0195
		> 15	Reaction (R2, slow)	0.0161
Illinois #6	hvCb	0 - 1.5	Extraction	2.81
		0 - 5	Reaction (R1, fast)	0.0276
		> 5	Reaction (R2, slow)	0.00541
Pittsburgh #8	hvAb	0 - 1.5	Extraction	8.90
		0 - 60	Reaction	0.00201
Pocahontas #3	lvb	0 - 2	Extraction	4.98
		0 - 60	Reaction	0.00132

Table 4. Elemental Analysis of the Illinois #6 Coal Liquefaction Residues
(Liquefaction solvent: Tetralin; Gas pressure: 1000 psig)

Sample#	Liquefaction Run					Elemental Analysis				H/C (atomic)
	T(C)	t(min)	Gas	Catalyst	SA	C	H	N	S	
DOE088	408	2	N2			63.76	4.14	1.43	3.77	0.779
DOE089	406	1	N2			64.35	4.22	1.45	3.68	0.787
DOE090	407	0.5	N2			65.04	4.33	1.38	3.85	0.799
DOE091	408	5	N2			63.72	3.97	1.40	3.51	0.748
DOE092	406	30	N2			63.13	3.71	1.44	3.36	0.705
DOE093	409	10	N2			63.16	3.76	1.41	3.26	0.714
DOE094	409	60	N2			63.73	3.46	1.48	2.80	0.651
DOE095	411	0.75	N2			65.16	4.33	1.31	3.91	0.797
DOE096	410	3	N2			63.75	4.08	1.40	3.61	0.768
DOE097	426	1	N2			64.77	4.09	1.39	3.55	0.758
DOE098	424	5	N2			64.88	3.97	1.46	3.05	0.734
DOE099	424	3	N2			65.76	4.06	1.46	2.87	0.741
DOE100	423	2	N2			65.24	4.18	1.45	3.19	0.769
DOE101	422	10	N2			64.14	3.83	1.48	3.81	0.717
DOE102	422	30	N2			64.63	3.18	1.51	2.63	0.590
DOE103	421	60	N2			65.21	2.97	1.48	2.60	0.547
DOE104	423	0.5	N2			65.84	5.06	1.40	3.29	0.922
DOE105	423	0.75	N2			65.71	4.66	1.44	3.36	0.851
DOE106	389	5	N2	Y		65.81	4.38	1.34	3.00	0.799
DOE107	388	5	H2	Y		64.89	4.47	1.35	3.23	0.827
DOE108	389	5	N2	Y	Y	64.68	4.23	1.39	3.61	0.785
DOE109	388	5	H2	Y	Y	63.33	4.60	1.37	3.73	0.872

Notes:

- 1). Catalyst: molybdenum naphthenate, 0.9 wt% of Mo on the basis of coal charged;
- 2). SA (Sulfiding Agent): methyl disulfide, about 1 g.

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE001	15	30			Illinois #6 from Argonne	Tetralin	N2	1000	35.22	26.6	75.5
DOE002	100	30			Illinois #6 from Argonne	Tetralin	N2	1000	34.61	27.36	79.1
DOE003	200	30			Illinois #6 from Argonne	Tetralin	N2	1000	41.85	34.58	82.6
DOE004	246	30			Illinois #6 from Argonne	Tetralin	N2	1000	35.36	29.83	84.4
DOE005	297	30			Illinois #6 from Argonne	Tetralin	N2	1000	42.28	22.38	52.9
DOE006	318	30			Illinois #6 from Argonne	Tetralin	N2	1000	42.32	36.14	85.4
DOE007	345	30			Illinois #6 from Argonne	Tetralin	N2	1000	35.05	28.5	81.3
DOE008	378	30			Illinois #6 from Argonne	Tetralin	N2	1000	35.55	29.7	83.5
DOE009	390	30			Illinois #6 from Argonne	Tetralin	N2	1000	42.53	36.29	85.3
DOE010	381	60			Illinois #6 from Argonne	Tetralin	N2	1000	42.7	34.68	81.2
DOE011	389	15			Illinois #6 from Argonne	Tetralin	N2	1000	36.73	27.55	75.0
DOE012	403	0.167			Illinois #6 from Argonne	Tetralin	N2	1000	37.07	31.96	86.2
DOE013	390	10			Illinois #6 from Argonne	Tetralin	N2	1000	41.96	34.23	81.6
DOE014	385	0.333			Illinois #6 from Argonne	Tetralin	N2	1000	39.07	33.59	86.0
DOE015	384	0.5			Illinois #6 from Argonne	Tetralin	N2	1000	38.47	35.35	91.9
DOE016	382	0.75			Illinois #6 from Argonne	Tetralin	N2	1000	40.75	36.25	89.0
DOE017	386	1			Illinois #6 from Argonne	Tetralin	N2	1000	39.28	34.74	88.4
DOE018	385	2			Illinois #6 from Argonne	Tetralin	N2	1000	40.37	32.5	80.5
DOE019	386	7.5			Illinois #6 from Argonne	Tetralin	N2	1000	38	33.35	87.8
DOE020	387	3			Illinois #6 from Argonne	Tetralin	N2	1000	38.65	32.85	85.0
DOE021	387	5			Illinois #6 from Argonne	Tetralin	N2	1000	41.07	31.51	76.7
DOE022	388	1			Illinois #6 from Argonne	Tetralin	H2	1000	39.94	34.6	86.6
DOE023	386	0.5			Illinois #6 from Argonne	Tetralin	H2	1000	40.49	35.14	86.8
DOE024	389	30			Illinois #6 from Argonne	Tetralin	H2	1000	41.07	33.04	80.4
DOE025	388	0.167			Illinois #6 from Argonne	Tetralin	H2	1000	36.84	29.65	80.5
DOE026	388	0.333			Illinois #6 from Argonne	Tetralin	H2	1000	40.13	35.33	88.0
DOE027	385	0.75			Illinois #6 from Argonne	Tetralin	H2	1000	37.84	31.96	84.5
DOE028	377	5			Illinois #6 from Argonne	Tetralin	H2	1000	39.75	30.24	76.1
DOE029	376	15			Illinois #6 from Argonne	Tetralin	H2	1000	39.43	31.03	78.7
DOE030	375	3			Illinois #6 from Argonne	Tetralin	H2	1000	41.21	34.63	84.0

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE031	372	735			Illinois #6 from Argonne	Tetralin	H2	1000	39.13	24.08	61.5
DOE032	380	10			Illinois #6 from Argonne	Tetralin	H2	1000	37.07	32.07	86.5
DOE033	381	55.5			Illinois #6 from Argonne	Tetralin	H2	1000	41.22	35.8	86.9
DOE035	356	1			Illinois #6 from Argonne	Tetralin	H2	1000	38.31	40.64	106.1
DOE036	390	1			Illinois #6 from Argonne	Tetralin	H2	1000	41.67	42.67	102.4
DOE037	395	0.167			Wyodak coal	Tetralin	H2	1000	35.03	38.12	108.8
DOE038	395	0.333			Wyodak coal	Tetralin	H2	1000	35.36	34.48	97.5
DOE039	396	0.5			Wyodak coal	Tetralin	H2	1000	35	30.97	88.5
DOE040	394	1			Wyodak coal	Tetralin	H2	1000	34.9	30.66	87.9
DOE041	392	3			Wyodak coal	Tetralin	H2	1000	34.67	30.51	88.0
DOE042	392	10			Wyodak coal	Tetralin	H2	1000	34.44	29.8	86.5
DOE043	390	0.167			Wyodak coal	Tetralin	N2	1000	34.07	30.91	90.7
DOE044	392	0.334			Wyodak coal	Tetralin	N2	1000	35.28	32.77	92.9
DOE045	393	0.5			Wyodak coal	Tetralin	N2	1000	34.36	31.53	91.8
DOE046	390	1			Wyodak coal	Tetralin	N2	1000	34.62	32.12	92.8
DOE047	392	0.5			Wyodak coal	Tetralin	N2	1000	31.82	26.07	81.9
DOE048	392	10			Wyodak coal	Tetralin	N2	1000	32.47	28.27	87.1
DOE049	384	30			Wyodak coal	Tetralin	H2	1000	35.03	15.29	43.6
DOE050	386	5			Wyodak coal	Tetralin	H2	1000	40.91	34.87	85.2
DOE051	394	60			Wyodak coal	Tetralin	H2	1000	33.51	29.31	87.5
DOE052	390	60			Wyodak coal	Tetralin	N2	1000	38.01	32.67	86.0
DOE053	388	5			Wyodak coal	Tetralin	N2	1000	34.79	31.81	91.4
DOE054	385	3			Wyodak coal	Tetralin	N2	1000	36.06	30.93	85.8
DOE055	388	0.167			Wyodak coal	1-MN	N2	1000	35.02	30.81	88.0
DOE056	390	0.5			Wyodak coal	1-MN	N2	1000	35.2	31.69	90.0
DOE057	395	10			Wyodak coal	1-MN	N2	1000	34.91	31.07	89.0
DOE058	22	30			Illinois #6 from Argonne	1-MN	N2	1000	36.32	28.37	78.1
DOE059	101	30			Illinois #6 from Argonne	1-MN	N2	1000	36.99	30.81	83.3
DOE060	18	15			Illinois #6 from Argonne	Tetralin	N2	1000	35.77	27.53	77.0
DOE061	18	15			Illinois #6 from Argonne	Tetralin	N2	1000	37.99	26.41	69.5

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE063	295	2			Illinois #6 from Argonne	Tetralin	H2	1000	38.11	29.87	78.4
DOE064	335	2			Illinois #6 from Argonne	Tetralin	H2	1000	37.73	35.53	94.2
DOE065	362	2			Illinois #6 from Argonne	Tetralin	H2	1000	40.09	21.32	53.2
DOE066	374	2			Illinois #6 from Argonne	Tetralin	H2	1000	36.34	10.55	29.0
DOE067	386	2			Illinois #6 from Argonne	Tetralin	H2	1000	37.77	21.02	55.7
DOE068	391	0.5			Illinois #6 from Argonne	Tetralin	H2	1000	38.4	34.36	89.5
DOE069	388	1			Illinois #6 from Argonne	Tetralin	H2	1000	36.69	22.29	60.8
DOE070	388	0.75			Illinois #6 from Argonne	Tetralin	H2	1000	37.42	25.14	67.2
DOE071	385	0.167			Illinois #6 from Argonne	Tetralin	H2	1000	36.67	30.82	84.0
DOE072	390	0.167			Illinois #6 from Argonne	Tetralin	H2	1000	37.98	33.08	87.1
DOE073	391	0.5			Illinois #6 from Argonne	Tetralin	H2	1000	36.78	32.28	87.8
DOE074	383	5			Illinois #6 from Argonne	Tetralin	H2	1000	37.89	33.98	89.7
DOE075	388	60			Illinois #6 from Argonne	Tetralin	H2	1000	37.7	32.04	85.0
DOE076	390	30			Illinois #6 from Argonne	Tetralin	H2	1000	36.29	30.5	84.0
DOE077	25	15			Wyodak coal	Tetralin	N2	1000	37.71	27.78	73.7
DOE078	24	15			Wyodak coal	Tetralin	N2	1000	37.93	29.13	76.8
DOE079	391	30			Illinois #6 from Argonne	Tetralin	H2	1000	34.95	25.41	72.7
DOE080	390	30			Wyodak coal	Tetralin	H2	1000	35.07	26.81	76.4
DOE081	392	30			Wyodak coal	Tetralin	N2	1000	35.08	21.58	61.5
DOE082	388	10			Wyodak coal	Tetralin	N2	1000	38.43	34.31	89.3
DOE083	385	10			Wyodak coal	Tetralin	N2	1000	36.67	34.36	93.7
DOE084	380	10			Wyodak coal	Tetralin	H2	1000	37.28	31.51	84.5
DOE085	388	10			Wyodak coal	Tetralin	H2	1000	38.39	29.28	76.3
DOE086	394	10			Wyodak coal	Tetralin	H2	1000	37.15	32.87	88.5
DOE087	394	10			Wyodak coal	Tetralin	H2	1000	37.85	28.85	76.2
DOE088	408	2			Illinois #6 from Argonne	Tetralin	N2	1000	37.02	33.78	91.2
DOE089	406	1			Illinois #6 from Argonne	Tetralin	N2	1000	37.44	34.47	92.1
DOE090	407	0.5			Illinois #6 from Argonne	Tetralin	N2	1000	37.35	33.2	88.9
DOE091	408	5			Illinois #6 from Argonne	Tetralin	N2	1000	39.06	33.72	86.3
DOE092	406	30			Illinois #6 from Argonne	Tetralin	N2	1000	37.19	33.23	89.4

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE093	409	10			Illinois #6 from Argonne	Tetralin	N2	1000	37.34	31.92	85.5
DOE094	409	60			Illinois #6 from Argonne	Tetralin	N2	1000	37.21	32.21	86.6
DOE095	411	0.75			Illinois #6 from Argonne	Tetralin	N2	1000	37.19	31.92	85.8
DOE096	410	3			Illinois #6 from Argonne	Tetralin	N2	1000	37.24	33.45	89.8
DOE097	426	1			Illinois #6 from Argonne	Tetralin	N2	1000	37.31	25.3	67.8
DOE098	424	5			Illinois #6 from Argonne	Tetralin	N2	1000	37.4	27.12	72.5
DOE099	424	3			Illinois #6 from Argonne	Tetralin	N2	1000	37.54	29.75	79.2
DOE100	423	2			Illinois #6 from Argonne	Tetralin	N2	1000	37.45	29.48	78.7
DOE101	422	10			Illinois #6 from Argonne	Tetralin	N2	1000	36.95	25.98	70.3
DOE102	422	30			Illinois #6 from Argonne	Tetralin	N2	1000	37.24	30.78	82.7
DOE103	421	60			Illinois #6 from Argonne	Tetralin	N2	1000	37.38	30.76	82.3
DOE104	423	0.5			Illinois #6 from Argonne	Tetralin	N2	1000	37.3	33.22	89.1
DOE105	423	0.75			Illinois #6 from Argonne	Tetralin	N2	1000	37.52	32.56	86.8
DOE106	389	5	MN(1%)		Illinois #6 from Argonne	Tetralin	N2	1000	35.8	29.92	83.6
DOE107	388	5	MN(1%)		Illinois #6 from Argonne	Tetralin	H2	1000	35.85	26.28	73.3
DOE108	389	5	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	N2	1000	38.15	34.1	89.4
DOE109	388	5	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	36.3	30.13	83.0
DOE110	389	5		Y	Illinois #6 from Argonne	Tetralin	N2	1000	37.72	31.93	84.7
DOE111	391	5		Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.58	29.83	79.4
DOE112	390	0.167	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.68	28.96	76.9
DOE113	386	0.5	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.62	29.44	78.3
DOE114	391	60	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	38.2	30.75	80.5
DOE115	390	0.005	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	38.81	17.84	46.0
DOE116	392	5	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.07	29.08	78.4
DOE117	388	10	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.76	30.68	81.3
DOE118	385	3	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.75	30.68	81.3
DOE119	390	1	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.91	30.48	80.4
DOE120	388	2	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	36.52	28.86	79.0
DOE121	20	15			Wyodak coal	Tetralin	N2	1000	35.78	26.84	75.0
DOE122	19	16			Wyodak coal	Tetralin	N2	1000	36.61	25.47	69.6

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE123	19	15			Wyodak coal	Tetralin	N2	1000	35.49	24.36	68.6
DOE124	20	15			Wyodak coal	S353	N2	1000	33.96	25.5	75.1
DOE125	20	15			Wyodak coal	S353	N2	1000	35.67	22.74	63.8
DOE126	395	10			Wyodak coal	S353	N2	1000	33.2	16.98	51.1
DOE127	395	10			Wyodak coal	S353	H2	1000	32.02	36.58	114.2
DOE129	393	5			Wyodak coal	Tetralin	H2	1000	38.52	36.17	93.9
DOE130	391	5		Y	Wyodak coal	Tetralin	H2	1000	36.97	34.52	93.4
DOE131	393	5	MN(1%)		Wyodak coal	Tetralin	H2	1000	36.69	35.5	96.8
DOE132	395	5	MN(1%)	Y	Wyodak coal	Tetralin	H2	1000	38.59	36.91	95.6
DOE133	392	5			Wyodak coal	Tetralin	N2	1000	36.22	35.9	99.1
DOE134	390	5		Y	Wyodak coal	Tetralin	N2	1000	36.17	34.09	94.2
DOE135	389	5	MN(1%)		Wyodak coal	Tetralin	N2	1000	38.14	37.03	97.1
DOE136	387	5	MN(1%)	Y	Wyodak coal	Tetralin	N2	1000	37.49	35.88	95.7
DOE137	390	50			Illinois #6 from Argonne	Tetralin	H2	1000	35.98	20.8	57.8
DOE139	393	40			Illinois #6 from Argonne	Tetralin	H2	1000	35.96	34.92	97.1
DOE140	394	20	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.9	32.6	86.0
DOE141	394	30	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.75	33.25	88.1
DOE142	395	20	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.46	31.95	85.3
DOE143	393	40	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.74	32.1	85.1
DOE144	390	50			Illinois #6 from Argonne	1-MN	N2	1000	35.86	3.74	10.4
DOE145	414	1			Illinois #6 from Argonne	1-MN	N2	1000	36.13	9.89	27.4
DOE146	406	2			Illinois #6 from Argonne	1-MN	N2	1000	35.99	7.38	20.5
DOE147	407	5			Illinois #6 from Argonne	1-MN	N2	1000	53.97	13.19	24.4
DOE148	402	10			Illinois #6 from Argonne	1-MN	N2	1000	54.28	32.54	59.9
DOE149	408	30			Illinois #6 from Argonne	1-MN	N2	1000	54.23	28.72	53.0
DOE150	406	45			Illinois #6 from Argonne	1-MN	N2	1000	54.61	40.08	73.4
DOE151	403	60			Illinois #6 from Argonne	1-MN	N2	1000	54.17	26.96	49.8
DOE152	396	10			Illinois #6 from Argonne	1-MN	H2	1000	54.15	40.09	74.0
DOE153	395	10	MN(1%)	Y	Illinois #6 from Argonne	1-MN	H2	1000	55.97	37.84	67.6
DOE154	410	0.167	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.99	32.36	85.2

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE155	407	0.5	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.67	31.96	84.8
DOE156	408	1	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.58	32.18	85.6
DOE157	406	2	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.65	28.4	75.4
DOE158	405	3	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.77	29.99	79.4
DOE159	400	5	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.8	28.07	74.3
DOE160	400	10	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	38.48	26.34	68.5
DOE161	400	20	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.84	27.05	71.5
DOE162	402	30	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.85	28.29	74.7
DOE163	398	60	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.94	21.68	57.1
DOE164	424	0.167	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.75	29.73	78.8
DOE165	429	0.5	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.87	33.68	88.9
DOE166	430	1	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.63	33.36	88.7
DOE167	430	2	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.87	31.65	83.6
DOE168	416	3	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.9	31.48	83.1
DOE169	416	5	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	38.04	32.38	85.1
DOE170	415	10	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.91	30.69	81.0
DOE171	415	20	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.85	28.29	74.7
DOE172	415	30	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.94	19.75	52.1
DOE173	430	60	MN(1%)	Y	Illinois #6 from Argonne	Tetralin	H2	1000	37.2	9.22	24.8
DOE174	408	1			Illinois #6 from Argonne	1-MN	N2	1000	35.78	30.83	86.2
DOE175	407	2			Illinois #6 from Argonne	1-MN	N2	1000	36.1	28.44	78.8
DOE176	410	5			Illinois #6 from Argonne	1-MN	N2	1000	35.99	25.47	70.8
DOE177	407	0.5			Illinois #6 from Argonne	1-MN	N2	1000	36.04	29.76	82.6
DOE178	406	45			Illinois #6 from Argonne	1-MN	N2	1000	36.06	14.61	40.5
DOE179	409	10			Illinois #6 from Argonne	1-MN	N2	1000	35.92	27.11	75.5
DOE180	409	30			Illinois #6 from Argonne	1-MN	N2	1000	36.05	18.77	52.1
DOE181	410	60			Illinois #6 from Argonne	1-MN	N2	1000	35.87	18.93	52.8
DOE182	412	30			Illinois #6 from Argonne	1-MN	H2	1000	36.18	25.24	69.8
DOE183	412	30	MN(1%)	Y	Illinois #6 from Argonne	1-MN	H2	1000	36.29	23.99	66.1
DOE184	412	30			Illinois #6 from Argonne	THQ	N2	1000	35.74	26.79	75.0

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE185	415	30			Illinois #6 from Argonne	THQ	H2	1000	36.36	31.24	85.9
DOE191	400	0.167			Illinois #6 from Argonne	THQ	N2	1000	36.11	27.95	77.4
DOE192	404	0.5			Illinois #6 from Argonne	THQ	N2	1000	36.14	27.87	77.1
DOE193	400	1			Illinois #6 from Argonne	THQ	N2	1000	35.57	31.08	87.4
DOE194	407	2			Illinois #6 from Argonne	THQ	N2	1000	36.19	30.24	83.6
DOE195	407	3			Illinois #6 from Argonne	THQ	N2	1000	35.8	31.9	89.1
DOE196	413	20			Illinois #6 from Argonne	THQ	N2	1000	36.36	28.59	78.6
DOE197	411	60			Illinois #6 from Argonne	THQ	N2	1000	36.34	27.54	75.8
DOE198	407	5			Illinois #6 from Argonne	THQ	N2	1000	35.74	30.91	86.5
DOE199	412	10			Illinois #6 from Argonne	THQ	N2	1000	36.54	29.58	81.0
DOE200	391	0.167			Illinois #6 from Amoco	Tetralin	N2	1000	37.01	36.23	97.9
DOE201	393	0.333			Illinois #6 from Amoco	Tetralin	N2	1000	36.42	35.59	97.7
DOE202	395	0.5			Illinois #6 from Amoco	Tetralin	N2	1000	36.14	34.49	95.4
DOE203	396	0.75			Illinois #6 from Amoco	Tetralin	N2	1000	36.1	34.52	95.6
DOE204	395	1			Illinois #6 from Amoco	Tetralin	N2	1000	36	32.46	90.2
DOE205	394	2			Illinois #6 from Amoco	Tetralin	N2	1000	36.09	22.02	61.0
DOE206	395	5			Illinois #6 from Amoco	Tetralin	N2	1000	36.03	14.07	39.1
DOE207	396	10			Illinois #6 from Amoco	Tetralin	N2	1000	36.24	36	99.3
DOE208	388	0.167			Beulah-Zap coal	Tetralin	N2	1000	36.14	33.7	93.2
DOE209	396	0.5			Beulah-Zap coal	Tetralin	N2	1000	36.17	34.7	95.9
DOE210	399	1			Beulah-Zap coal	Tetralin	N2	1000	36.14	29.42	81.4
DOE211	395	5			Beulah-Zap coal	Tetralin	N2	1000	36.02	27.52	76.4
DOE212	392	3			Beulah-Zap coal	Tetralin	N2	1000	36.22	18.99	52.4
DOE213	393	0.167			Beulah-Zap coal	Tetralin	N2	1000	36.11	35.16	97.4
DOE214	392	30			Beulah-Zap coal	Tetralin	N2	1000	36.34	34.05	93.7
DOE215	391	60			Beulah-Zap coal	Tetralin	N2	1000	35.42	32.12	90.7
DOE216	383	0.167	MN(1%)	Y	Beulah-Zap coal	Tetralin	N2	1000	37.92	30.55	80.6
DOE217	389	0.167	MN(1%)	Y	Beulah-Zap coal	Tetralin	H2	1000	37.66	34.12	90.6
DOE218	395	0.5	MN(1%)	Y	Beulah-Zap coal	Tetralin	H2	1000	38.52	33.9	88.0
DOE219	403	1	MN(1%)	Y	Beulah-Zap coal	Tetralin	H2	1000	38.39	33.86	88.2

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE220	397	3	MN(1%)	Y	Beulah-Zap coal	Tetralin	H2	1000	37.93	32.84	86.6
DOE221	385	5	MN(1%)	Y	Beulah-Zap coal	Tetralin	H2	1000	37.97	34.63	91.2
DOE222	389	10	MN(1%)	Y	Beulah-Zap coal	Tetralin	H2	1000	38.28	35.42	92.5
DOE223	414	30	MN(1%)	Y	Beulah-Zap coal	Tetralin	H2	1000	38.07	27.18	71.4
DOE224	397	30	MN(1%)	Y	Beulah-Zap coal	Tetralin	H2	1000	37.9	37.5	98.9
DOE225	393	60	MN(1%)	Y	Beulah-Zap coal	Tetralin	H2	1000	37.89	32.22	85.0
DOE226	23	10			Illinois #6 from Amoco	Tetralin	N2	1000	24.28	17.67	72.8
DOE227	400	30			Illinois #6 from Amoco	1-MN	N2	1000	36.23	31.62	87.3
DOE228	407	30			Illinois #6 from Amoco	1-MN	H2	1000	36.24	30.22	83.4
DOE229	400	30	MN(2%)	Y	Illinois #6 from Amoco	1-MN	N2	1000	38.43	32.78	85.3
DOE230	405	30	MN(2%)	Y	Illinois #6 from Amoco	1-MN	H2	1000	37.93	33.17	87.5
DOE231	23	10			Illinois #6 from Amoco	1-MN	N2	1000	36.22	31.35	86.6
DOE232	24	10			Illinois #6 from Amoco	DHN	N2	1000	35.84	32.19	89.8
DOE233	400	30			Illinois #6 from Amoco	DHN	N2	1000	35.88	24.69	68.8
DOE234	400	30			Illinois #6 from Amoco	DHN	H2	1000	35.94	33.09	92.1
DOE235	395	30	MN(1%)	Y	Illinois #6 from Amoco	DHN	N2	1000	38.26	32.34	84.5
DOE236	398	30	MN(1%)	Y	Illinois #6 from Amoco	DHN	H2	1000	38.47	32.62	84.8
DOE237	400	30			Illinois #6 from Amoco	Tetralin	N2	1000	36.17	34.26	94.7
DOE238	404	30			Illinois #6 from Amoco	Tetralin	H2	1500	29.98	23.2	77.4
DOE239	400	30			Illinois #6 from Amoco	Tetralin	H2	1500	30.05	23.67	78.8
DOE240	399	30			Illinois #6 from Amoco	Tetralin	N2	1500	30.57	22.12	72.4
DOE241	402	30			Illinois #6 from Amoco	Tetralin	N2	1500	30.54	24.81	81.2
DOE242	401	30	shell(3%)		Illinois #6 from Amoco	Tetralin	N2	1500	31.19	24.71	79.2
DOE243	402	30	shell(3%)		Illinois #6 from Amoco	Tetralin	N2	1500	31.23	20.19	64.6
DOE244	402	30	shell(3%)		Illinois #6 from Amoco	Tetralin	H2	1500	31.1	25.03	80.5
DOE245	402	30	shell(3%)		Illinois #6 from Amoco	Tetralin	H2	1500	31.14	28.13	90.3
DOE246	390	2			Illinois #6 from Argonne	Tetralin	N2	1200	36.22	22.53	62.2
DOE247	390	2			Illinois #6 from Argonne	Tetralin	N2	1000	36.39	31.52	86.6
DOE248	390	2			Illinois #6 from Argonne	Tetralin	N2	800	36.19	31.8	87.9
DOE249	400	2			Illinois #6 from Argonne	Tetralin	N2	1800	35.93	26.8	74.6

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE250	400	2			Illinois #6 from Argonne	Tetralin	N2	1600	35.55	30.96	87.1
DOE251	389	2			Illinois #6 from Argonne	Tetralin	N2	1400	36.55	30.45	83.3
DOE252	350	0.167			Illinois #6 from Argonne	Tetralin	N2	1000	36.08	30.02	83.2
DOE253	353	0.5			Illinois #6 from Argonne	Tetralin	N2	1000	36.38	29.9	82.2
DOE254	357	1			Illinois #6 from Argonne	Tetralin	N2	1000	36.81	30.33	82.4
DOE255	364	2			Illinois #6 from Argonne	Tetralin	N2	1000	35.76	32	89.5
DOE256	362	5			Illinois #6 from Argonne	Tetralin	N2	1000	35.64	31.26	87.7
DOE257	358	10			Illinois #6 from Argonne	Tetralin	N2	1000	36.29	31.52	86.9
DOE258	362	60			Illinois #6 from Argonne	Tetralin	N2	1000	36.74	29.92	81.4
DOE259	29	10			Illinois #6 from Argonne	THQ	N2	1000	36.05	20.28	56.3
DOE260	27	10			Beulah-Zap coal	Tetralin	N2	1000	36.16	29.81	82.4
DOE261	399	0.167			Illinois #6 from Argonne	DHN	N2	1000	36.18	30.43	84.1
DOE262	405	0.5			Illinois #6 from Argonne	DHN	N2	1000	36.67	30.32	82.7
DOE263	409	1			Illinois #6 from Argonne	DHN	N2	1000	36.13	29.76	82.4
DOE264	411	2			Illinois #6 from Argonne	DHN	N2	1000	36.06	28.58	79.3
DOE265	413	5			Illinois #6 from Argonne	DHN	N2	1000	36.39	12.45	34.2
DOE266	409	30			Illinois #6 from Argonne	DHN	N2	1000	36.13	21.76	60.2
DOE267	406	60			Illinois #6 from Argonne	DHN	N2	1000	36.69	22.16	60.4
DOE268	416	10			Illinois #6 from Argonne	DHN	N2	1000	36.83	8.86	24.1
DOE269	390	30			Wyodak coal	DHN	N2	1000	35.74	30.59	85.6
DOE270	391	30			Wyodak coal	DHN	H2	1000	35.66	32.45	91.0
DOE271	390	30	MN(2%)	Y	Wyodak coal	DHN	H2	1000	39.14	19.88	50.8
DOE272	391	30	MN(2%)	Y	Wyodak coal	Tetralin	H2	1000	38.4	29.65	77.2
DOE273	393	30			Wyodak coal	1-MN	N2	1000	37.72	28.93	76.7
DOE274	391	30			Wyodak coal	1-MN	H2	1000	36.3	30.99	85.4
DOE275	391	30	MN(2%)	Y	Wyodak coal	1-MN	H2	1000	39.82	26.55	66.7
DOE276	23	10			Illinois #6 from Argonne	DHN	N2	1000	36.66	29.46	80.4
DOE277	413	5			Illinois #6 from Argonne	1-MN+DHN	N2	1000	36.68	18.33	50.0
DOE278	412	5			Illinois #6 from Argonne	1-MN+DHN	N2	1000	35.93	28.55	79.5
DOE279	412	5			Illinois #6 from Argonne	1-MN+DHN	N2	1000	36.91	33.44	90.6

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE280	412	5			Illinois #6 from Argonne	1-MN+DHN	N2	1000	36.41	29.82	81.9
DOE281	413	5			Illinois #6 from Argonne	1-MN+DHN	N2	1000	36.58	32.41	88.6
DOE282	413	5			Illinois #6 from Argonne	1-MN+DHN	N2	1000	36.01	30.82	85.6
DOE283	412	5			Illinois #6 from Argonne	1-MN+DHN	N2	1000	36.73	30.51	83.1
DOE284	412	5			Illinois #6 from Argonne	1-MN+DHN	N2	1000	36.42	30.04	82.5
DOE285	412	5			Illinois #6 from Argonne	1-MN+Phe	N2	1000	36.1	29.37	81.4
DOE286	412	5			Illinois #6 from Argonne	1-MN+Phe	N2	1000	36.53	31.09	85.1
DOE287	412	5			Illinois #6 from Argonne	1-MN+Phe	N2	1000	36.14	26.55	73.5
DOE288	412	5			Illinois #6 from Argonne	1-MN+Phe	N2	1000	36.09	27.13	75.2
DOE289	413	5			Illinois #6 from Argonne	1-MN+Phe	N2	1000	36.05	28.31	78.5
DOE290	411	5			Illinois #6 from Argonne	1-MN+Phe	N2	1000	36.1	29.82	82.6
DOE291	412	5			Illinois #6 from Argonne	1-MN+Phe	N2	1000	36.59	28.14	76.9
DOE292	413	5			Illinois #6 from Argonne	1-MN+THQ	N2	1000	36.06	24.64	68.3
DOE293	412	5			Illinois #6 from Argonne	1-MN+Tet	N2	1000	36.18	26.79	74.0
DOE294	412	5			Illinois #6 from Argonne	1-MN+Tet	N2	1000	36.32	26.11	71.9
DOE295	411	5			Illinois #6 from Argonne	1-MN+Tet	N2	1000	36.04	27.91	77.4
DOE296	412	5			Illinois #6 from Argonne	1-MN+Tet	N2	1000	36.47	26.07	71.5
DOE297	411	5			Illinois #6 from Argonne	1-MN+Tet	N2	1000	36.07	26.94	74.7
DOE298	383	0.167			Pittsburgh #8 (DECS-12)	Tetralin	N2	1000	35.88	26.24	73.1
DOE299	383	0.5			Pittsburgh #8 (DECS-12)	Tetralin	N2	1000	36.35	26.87	73.9
DOE300	390	0.75			Pittsburgh #8 (DECS-12)	Tetralin	N2	1000	36.41	28.67	78.7
DOE301	392	1			Pittsburgh #8 (DECS-12)	Tetralin	N2	1000	36.23	26.57	73.3
DOE302	393	2			Pittsburgh #8 (DECS-12)	Tetralin	N2	1000	36.12	28.92	80.1
DOE303	390	5			Pittsburgh #8 (DECS-12)	Tetralin	N2	1000	36.6	29.01	79.3
DOE304	390	10			Pittsburgh #8 (DECS-12)	Tetralin	N2	1000	36.22	27.61	76.2
DOE305	389	20			Pittsburgh #8 (DECS-12)	Tetralin	N2	1000	36.64	31.55	86.1
DOE306	392	30			Pittsburgh #8 (DECS-12)	Tetralin	N2	1000	36.56	29.6	81.0
DOE307	390	60			Pittsburgh #8 (DECS-12)	Tetralin	N2	1000	36.52	29.71	81.4
DOE308	33	10			Pittsburgh #8 (DECS-12)	Tetralin	N2	1000	36.71	30.03	81.8
DOE309	412	5			Illinois #6 from Argonne	1-MN+Phe	N2	1000	36.07	25.98	72.0

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE310	413	5			Illinois #6 from Argonne	1-MN+Phe	N2	1000	36.6	27.75	75.8
DOE311	384	0.75			Beulah-Zap (HCl-treated)	Tetralin	N2	1000	36.27	30.16	83.2
DOE312	393	2			Beulah-Zap (HCl-treated)	Tetralin	N2	1000	36.05	29.42	81.6
DOE313	33	10			Beulah-Zap (HCl-treated)	Tetralin	N2	1000	36.24	22.79	62.9
DOE314	408	0.167			Illinois #6 from Argonne	Quinoline	N2	1000	36.02	24.96	69.3
DOE315	415	0.5			Illinois #6 from Argonne	Quinoline	N2	1000	36.1	25.37	70.3
DOE316	407	1			Illinois #6 from Argonne	Quinoline	N2	1000	36.11	25.43	70.4
DOE317	415	2			Illinois #6 from Argonne	Quinoline	N2	1000	35.99	24.46	68.0
DOE318	409	5			Illinois #6 from Argonne	Quinoline	N2	1000	36.03	12.69	35.2
DOE319	410	10			Illinois #6 from Argonne	Quinoline	N2	1000	36.26	27.2	75.0
DOE320	412	20			Illinois #6 from Argonne	Quinoline	N2	1000	36.18	22.47	62.1
DOE321	413	30			Illinois #6 from Argonne	Quinoline	N2	1000	36.03	26.5	73.5
DOE322	408	60			Illinois #6 from Argonne	Quinoline	N2	1000	36.22	24.16	66.7
DOE323	24	10			Illinois #6 from Argonne	Quinoline	N2	1000	36.09	24.31	67.4
DOE324	380	0.167			UT Blind canyon (DECS-17)	Tetralin	N2	1000	36.17	30.45	84.2
DOE325	388	0.5			UT Blind canyon (DECS-17)	Tetralin	N2	1000	36.12	29.65	82.1
DOE326	393	1			UT Blind canyon (DECS-17)	Tetralin	N2	1000	36.24	30.07	83.0
DOE327	394	2			UT Blind canyon (DECS-17)	Tetralin	N2	1000	36.25	29.35	81.0
DOE328	389	5			UT Blind canyon (DECS-17)	Tetralin	N2	1000	36.4	29.09	79.9
DOE329	35	10			UT Blind canyon (DECS-17)	Tetralin	N2	1000	36.22	27.8	76.8
DOE330	34	10			TX Bottom subC (DECS-1)	Tetralin	N2	1000	36.19	31.17	86.1
DOE331	391	60			TX Bottom subC (DECS-1)	Tetralin	N2	1000	36.02	11.38	31.6
DOE332	389	10			UT Blind canyon (DECS-17)	Tetralin	N2	1000	36.26	31.98	88.2
DOE333	390	20			UT Blind canyon (DECS-17)	Tetralin	N2	1000	36.06	29.56	82.0
DOE334	390	30			UT Blind canyon (DECS-17)	Tetralin	N2	1000	36.32	29.01	79.9
DOE335	392	60			UT Blind canyon (DECS-17)	Tetralin	N2	1000	36.13	28.46	78.8
DOE336	408	5			UT Blind canyon (DECS-17)	Tetralin	N2	1000	36.07	29.54	81.9
DOE337	406	5			UT Blind canyon (DECS-17)	Tetralin	N2	1000	36.21	32.51	89.8
DOE338	405	5	MN(2%)		UT Blind canyon (DECS-17)	Tetralin	N2	1000	36.23	30.91	85.3
DOE339	408	5	MN(2%)		UT Blind canyon (DECS-17)	Tetralin	N2	1000	38.86	36.4	93.7

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE340	383	0.167			TX Bottom subC (DECS-1)	Tetralin	N2	1000	35.78	26.2	73.2
DOE341	386	0.5			TX Bottom subC (DECS-1)	Tetralin	N2	1000	36.26	25.43	70.1
DOE342	374	0.167			Illinois #6 from Argonne	Tetralin	N2	1000	36.18	29.71	82.1
DOE343	375	0.5			Illinois #6 from Argonne	Tetralin	N2	1000	36.28	28.51	78.6
DOE344	372	1			Illinois #6 from Argonne	Tetralin	N2	1000	36.1	30.61	84.8
DOE345	371	2			Illinois #6 from Argonne	Tetralin	N2	1000	36.09	30.9	85.6
DOE346	372	3			Illinois #6 from Argonne	Tetralin	N2	1000	36.3	31.11	85.7
DOE347	370	5			Illinois #6 from Argonne	Tetralin	N2	1000	36.5	26.79	73.4
DOE348	370	10			Illinois #6 from Argonne	Tetralin	N2	1000	36.14	29.29	81.0
DOE349	20	5			MT Pust lig A (DECS-25)	Tetralin	N2	1000	35.9	25.66	71.5
DOE350	388	0.167			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.8	26.65	72.4
DOE351	391	0.5			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.64	29.03	79.2
DOE352	390	1			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.3	35.62	98.1
DOE353	391	2			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.54	35.77	97.9
DOE354	389	5			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.04	28.66	79.5
DOE355	390	10			MT Pust lig A (DECS-25)	Tetralin	N2	1000	35.93	28.72	79.9
DOE356	393	30			MT Pust lig A (DECS-25)	Tetralin	N2	1000	35.82	24.76	69.1
DOE357	392	60			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.17	27.23	75.3
DOE358	395	0.167			Pocahontas #3 (DECS-19)	Tetralin	N2	1000	36.08	28.12	77.9
DOE359	396	0.5			Pocahontas #3 (DECS-19)	Tetralin	N2	1000	36.18	28.32	78.3
DOE360	393	1			Pocahontas #3 (DECS-19)	Tetralin	N2	1000	36.46	27.56	75.6
DOE361	393	2			Pocahontas #3 (DECS-19)	Tetralin	N2	1000	36.12	27.73	76.8
DOE362	389	5			Pocahontas #3 (DECS-19)	Tetralin	N2	1000	35.99	27.81	77.3
DOE363	389	10			Pocahontas #3 (DECS-19)	Tetralin	N2	1000	36.82	28.42	77.2
DOE364	391	30			Pocahontas #3 (DECS-19)	Tetralin	N2	1000	36.42	26.64	73.1

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE365	391	60			Pocahontas #3 (DECS-19)	Tetralin	N2	1000	36.37	25.85	71.1
DOE366	22	10			Pocahontas #3 (DECS-19)	Tetralin	N2	1000	35.98	25.27	70.2
DOE367	391	60			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.7	21.59	58.8
DOE368	390	60			Wyodak coal	Tetralin	N2	1000	36.48	26.16	71.7
DOE369	410	10			Illinois #6 from Argonne	DHQ	N2	1000	36.46	29.5	80.9
DOE370	410	2			Illinois #6 from Amoco	DHN	N2	1000	36.03	28.37	78.7
DOE371	409	2			Illinois #6 from Amoco	HN+THQ10	N2	1000	36.39	26.8	73.6
DOE372	412	2			Illinois #6 from Amoco	HN+THQ20	N2	1000	36.39	24.09	66.2
DOE373	412	2			Illinois #6 from Amoco	HN+THQ30	N2	1000	36.2	21.3	58.8
DOE374	25				Illinois #6 from Argonne	DHQ					
DOE375	408	2			Illinois #6 from Amoco	HN+THQ40	N2	1000	36.63	23.7	64.7
DOE376	407	2			Illinois #6 from Amoco	HN+THQ50	N2	1000	36.37	23.78	65.4
DOE377	410	2			Illinois #6 from Amoco	HN+THQ60	N2	1000	36.18	21.6	59.7
DOE378	412	2			Illinois #6 from Amoco	HN+THQ80	N2	1000	36.07	23.84	66.1
DOE379	20				Resid A	THF					
DOE380	406	1			Illinois #6 from Amoco	THQ	N2	1000	36.17	21.19	58.6
DOE381	389	1			Illinois #6 from Amoco	THQ	N2	1000	36.31	19.57	53.9
DOE382	389	60			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.29	30.15	83.1
DOE383	365	1			Illinois #6 from Amoco	THQ	N2	1000	36.04	10.35	28.7
DOE384	370	1			Illinois #6 from Amoco	THQ	N2	1000	35.99	7.31	20.3
DOE385	357	1			Illinois #6 from Amoco	THQ	N2	1000	52.84	24.92	47.2
DOE386	346	1			Illinois #6 from Amoco	THQ	N2	1000	35.88	3.84	10.7
DOE387	300	1			Illinois #6 from Amoco	THQ	N2	1000	36.18	23.65	65.4
DOE388	30	1			Illinois #6 from Amoco	THQ	N2	1000	36.24	21.36	58.9

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE389	215	1			Illinois #6 from Amoco	THQ	N2	1000	36.52	19.39	53.1
DOE390	380	30	MN(1%)	Y	MT Pust lig A (DECS-25)	Tetralin	H2	1000	37.95	29.78	78.5
DOE391	376	0.167			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.02	27.52	76.4
DOE392	383	0.5			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.32	25.01	68.9
DOE393	384	1			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.19	34.12	94.3
DOE394	393	2			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.42	23.76	65.2
DOE395	387	5			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.2	29.01	80.1
DOE396	390	10			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.74	25.89	70.5
DOE397	389	30			MT Pust lig A (DECS-25)	Tetralin	N2	1000	36.78	32.39	88.1
DOE398	421	60			Processed Resid A liquid	DHN	N2	1500	23.82	1.32	5.5
DOE399	410	60			Processed Resid A liquid	Tetralin	N2	1500	30.86	21.63	70.1
DOE400	411	60			Processed Resid A liquid	DHN	N2	1500	27.86	22.12	79.4
DOE401	415	60			Processed Resid A liquid	THQ	N2	1500	25.73	19.94	77.5
DOE402	416	60			Processed Resid A liquid	DHQ	N2	1500	27.74	21.6	77.9
DOE404	414	10			Illinois #6 from Amoco	THQ	N2	1000	36.04	27.52	76.4
DOE405	410	10			Illinois #6 from Amoco	Tetralin	N2	1000	36.14	26.84	74.3
DOE406	411	10			Illinois #6 from Amoco	THIQ	N2	1000	28.18	22.72	80.6
DOE407	415	10			Illinois #6 from Amoco	TBTLN	N2	1000	35.9	11.77	32.8
DOE408	413	60	MN(3%)	Y	Processed Resid A liquid	Tetralin	H2	1000	47.21	17.16	36.3
DOE409	412	60	Shell		Processed Resid A liquid	Tetralin	H2	1000	45.78	37.09	81.0
DOE410	388	30			Illinois #6 from Amoco	Tetralin	H2	1000	36.49	34.87	95.6
DOE411	392	30			Pittsburgh #8 (DECS-12)	Tetralin	H2	1000	36.04	27.29	75.7
DOE412	392	30			UT Blind canyon (DECS-17)	Tetralin	H2	1000	36.58	33.58	91.8
DOE413	390	30			TX Bottom subC (DECS-1)	Tetralin	H2	1000	35.06	31.22	89.0
DOE414	391	30			MT Pust lig A (DECS-25)	Tetralin	H2	1000	35.82	28.86	80.6
DOE415	390	30			Pocahontas #3 (DECS-19)	Tetralin	H2	1000	36.15	27.82	77.0
DOE416	391	30	MN(1%)	Y	Illinois #6 from Amoco	Tetralin	H2	1000	37.78	29.47	78.0
DOE417	391	30	MN(1%)	Y	Pittsburgh #8 (DECS-12)	Tetralin	H2	1000	37.74	28.06	74.4
DOE418	388	30	MN(1%)	Y	UT Blind canyon (DECS-17)	Tetralin	H2	1000	38.35	31.29	81.6

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

Sample#	T(c)	t(min)	Cataly	Sulf.	Coal	Solvent	Gas	P (psig)	WT(Total)	WT(Rec.)	%Recovery
DOE419	387	30	MN(1%)	Y	TX Bottom subC (DECS-1)	Tetralin	H2	1000	37.82	29.42	77.8
DOE420	388	30	MN(1%)	Y	MT Pust lig A (DECS-25)	Tetralin	H2	1000	38.04	31.73	83.4
DOE421	390	30	MN(1%)	Y	Pocahontas #3 (DECS-19)	Tetralin	H2	1000	37.62	31	82.4
DOE422	388	30	MN(3%)	Y	Illinois #6 from Amoco	Tetralin	H2	1000	40.55	31.41	77.5
DOE423	390	30	MN(3%)	Y	Pittsburgh #8 (DECS-12)	Tetralin	H2	1000	40.07	28.15	70.3
DOE424	390	30	MN(3%)	Y	UT Blind canyon (DECS-17)	Tetralin	H2	1000	39.97	30.3	75.8
DOE425	388	30	MN(3%)	Y	TX Bottom subC (DECS-1)	Tetralin	H2	1000	40.47	30.74	76.0
DOE426	395	30	MN(3%)	Y	MT Pust lig A (DECS-25)	Tetralin	H2	1000	40.27	29.13	72.3
DOE427	389	30	MN(3%)	Y	Pocahontas #3 (DECS-19)	Tetralin	H2	1000	40.85	31.07	76.1
DOE429	413	30			Illinois #6 from Amoco	HQ+DHN50	N2	1000	35.72	16.21	45.4
Note:											
Coal:	MT: Montana lignite coal										
	TX: Texas lignite coal										
	UT: Utah bituminous coal										
Solvent:	DHN: Decahydronaphthalene										
	THQ: Tetrahydroquinolene										
	DHQ: Decahydroquinolene										
	THIQ: Tetrahydroisoquinolene										
	TBTLM: Tributylamine										
	THF: Tetrahydrofuran										
	DHN+THQ: Decahydronaphthalene+Tetrahydroquinolene										
	DHN+THQx%: DHN+THQ, x%=(THQ:DHN+THQ)%(Weight)										
	1-MN: 1-Methylnaphthalene										
	1-MN+DHN:(1-Methylnaphthalene)+Decahydronaphthalene										
	1-MN+Phe: (1-Methylnaphthalene)+Phenanthrene										
	1-MN+THQ: (1-Methylnaphthalene)+Tetrohydroquinolene										

Table 5. Conditions and Recoveries of Coal Liquefaction Runs

[illegible]

Figure 1. Short contact time batch reactor (SCTBR) for studying fuel processes at high pressures and high temperatures.

Figure 2 SCTBR system for studying fuel processes from the initial stages.

Figure 3. Representative temperature-time profile for a typical short coal liquefaction run (Illinois No. 6 coal; Tetralin : Coal = 8 : 1; 390°C; 1000 psig of N₂).

Figure 4. Liquefaction conversion of the Illinois No. 6 coal under 1000 psig of N₂ (Tetralin:coal=8:1): (a) up to 10 min.; (b) up to 60 min..

Figure 5. Kinetics of Dibenzylether (DBE) conversion in Tetralin at 375 °C in SCTBR.

Figure 6. Schematic diagram of the experimental workup procedure.

Sample: DOE102 (S1)
 Size: 42.6870 mg
 Method: DOE Coal Liquefaction
 Comment: 10 °C/min. to 950 °C. N2, 100 ml/min

TGA

File: A: DOE102S1.002
 Operator: Keyu Wang
 Run Date: 19-Sep-94 07: 47

Figure 7. Thermogravimetric Analysis (TGA) of Illinois #6 Coal liquefaction residue with Tetralin at 422 °C in 30 min.

Figure 9. Log of equilibrium extraction of Illinois #6 coal in Tetralin vs $1/T$.

Figure 8a. Conversion vs time for Illinois #6 coal liquefaction without added catalyst in Tetralin (Tetralin:Coal=8:1 mass ratio) under 1000 psig N₂ up to 10 min..

Figure 8b. Conversion vs time for Illinois #6 coal liquefaction without added catalyst in Tetralin (Tetralin:Coal=8:1 mass ratio) under 1000 psig N₂ up to 60 min..

Figure 10a. Conversion vs time curves of the direct uncatalyzed liquefaction of Illinois #6 coal in Tetralin, Decalin and 1-methylnaphthalene under 1000 psig Nitrogen at 408 °C (Solvent:coal = 8:1 weight ratio) up to 10 min..

Figure 10b. Conversion vs time curves of the direct uncatalyzed liquefaction of Illinois #6 coal in Tetralin, Decalin and 1-methylnaphthalene under 1000 psig nitrogen at 408 °C (Solvent:coal = 8:1 weight ratio) up to one hour.

Figure 11. Liquefaction conversion vs time curves for coals (390 °C, 1000 psig nitrogen).

Figure 12. $\ln(1-X_s/X_{s0})$ vs time for the Illinois # 6 coal liquefaction in Tetralin under 1000 psig N_2 at 390 °C.

Figure 13. $\ln(1-X_t/X_{t0})$ vs time for the Illinois # 6 coal liquefaction in Tetralin under 1000 psig N_2 at 390 °C.

Figure 14. Plot of the experimental data and modeling curve at the reaction up to 10 min. for Wyodak-Anderson coal liquefaction in Tetralin at 390 °C under 1000 psig N_2 .

Figure 15. $\ln(k_s)$ vs $1/T$ for the thermal liquefaction of Illinois #6 coal (Extraction stage).

Figure 16. $\ln(k_r)$ vs $1/T$ for the thermal liquefaction of Illinois #6 coal (Coal structure breakdown stage).

Figure 17. Conversion vs. time curves of the thermal liquefaction of Illinois #6 coal in 1,2,3,4-Tetrahydroquinoline (THQ), Tetralin, and 1-Methylnaphthalene under 1000 psig Nitrogen at 408 °C (Solvent:Coal = 8:1) a). up to 10 min.; b). up to 60 min..

Sample: DOE404LIQUID.001
 Size: 110.4860 mg
 Method: DOE Coal Liquefaction
 Comment: 20 DEGREES C TO 950 DEGREES C

TGA

File: C:DOE404L.001
 Operator: CALKINS
 Run Date: 13-Nov-97 07:44

Figure 18. Thermogravimetric Analysis (TGA) of Illinois #6 Coal liquefaction product in Tetrahydroquinolene at 414 °C in 10 min.

Figure 19. Thermogravimetric Analysis (TGA) of Illinois #6 Coal liquefaction product in Decahydroquinolene at 410°C in 10 min.

Figure 20. Thermogravimetric Analysis (TGA) of Illinois #6 Coal liquefaction product in Tetralin at 396°C in 10 min.

Figure 21. Catalysis of coal liquefaction by molybdenum naphthenate.

Figure 22. Effect of solvent on the thermal and catalytic liquefaction of the Illinois #6 coal.