SHORT CONTACT TIME DIRECT COAL LIQUEFACTION
USING A NOVEL BATCH REACTOR

Quarterly Report
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1. INTRODUCTION

The objective of this research is to optimize the design and operation of the bench scale batch reactor (SCTBR) for coal liquefaction at short contact times (0.01 to 10 minutes or longer). Additional objectives are to study the kinetics of direct coal liquefaction particularly at short reaction times, and to investigate the role of the organic oxygen components of coal and their reaction pathways during liquefaction. This quarterly report covers the status of progress toward those objectives.

1.1. Description of the Reactor System and Its Operation

Optimization of the design and operation of the SCTBR has been completed. A description of the reactor system and its operation was published in the Progress Report dated January 19, 1994. Two papers have now been published on the design and operation of the reactor (1,2). These papers describe the reactor system and its capability in terms of heat-up rates, charge times and how short a reaction time can be observed in a liquefaction process.

1.2. Product Work-up procedure and Determination of Liquefaction

The work-up procedure used in coal liquefaction experiments was developed and is also described in the previous quarterly reports. The liquefaction products are separated into solid and liquid by vacuum filtration. The solid is washed with pure tetralin to remove soluble coal liquefaction products and then with methylene chloride to remove residual tetralin. The solid residue is then dried in a vacuum oven at 105°C for two days. The liquid portion is bottled and nitrogen blanketed for subsequent analysis. The dried filter cake is also bottled and nitrogen blanketed and used for further analyses including determination of liquefaction conversion by ash content using Thermogravimetric analysis.

As stated previously, we have shown that, during the liquefaction process, the mineral matter (which is insoluble in tetralin) remains with the partially reacted coal and does not go into the liquid. When the liquefaction is carried out without catalyst, this provides a means of measuring the conversion of the coal to liquid product by the ash content of the solid residue determined by TGA. The conversion is calculated using Equation 1:

$$\text{Conversion} = \left(1 - \frac{X_o}{X}\right) \times 100 \quad (\text{wt}\%) \quad (1)$$

where X_o and X are the ash contents of the control sample and the coal liquefaction residue, respectively. The control sample is the original coal which is processed exactly as a liquefaction residue except at room temperature. Multiple experiments have shown that the ash content can be determined by TGA with a standard deviation of 0.1% and is equivalent to the ash determination of ash in coal by the ASTM method.

When the liquefaction is carried out in the presence of an inorganic catalyst, the conversion calculation must be done with an ash value corrected for the ash derived from

the catalyst.

1.3. Thermogravimetric Analysis of Solid Liquefaction Residues

A typical thermogravimetric analysis of Illinois #6 coal run before liquefaction at a ramp speed of 10°C/min to 900°C is shown in Figure 1. The solid line represents the weight of sample vs time. The dotted line is the derivative of the weight loss (solid) curve. Three main stages in the weight loss are apparent. The main loss in weight which levels out by the time when 900°C is attained. This loss in weight is called the Volatile Matter. When 900°C is attained, oxygen is introduced into the system and the residual organic matter is burned off. This loss in weight is labelled Fixed Carbon. The material left after the Fixed Carbon is burned off is designated as Ash, which is used for the determination of the conversion. The three parameters, Volatile Matter, Fixed Carbon and Ash, are important in following the changes in the coal residue during the liquefaction process.

The derivative curve indicates the various pyrolysis processes occurring in the coal and coal residue during the coal liquefaction. It is an important indication of changes in the coal structure during the liquefaction process. Figure 2 shows changes in the derivative curve for liquefaction residues at various times during the liquefaction.

1.4. Catalysts Used

Sulfided molybdenum naphthenate has been the principal liquefaction catalyst used to date. This catalyst has been prepared by dissolving molybdenum naphthenate (6.8 wt % molybdenum from Shepherd Chemical Company) in tetralin and reacting the solution with methyl disulfide. That catalyst is only active for liquefaction in the presence of hydrogen and is inactive unless sulfided. This was reported in the previous quarterly reports.

2. EXPERIMENTAL PROGRESS

2.1. Kinetic Experiments

2.1.1. Liquefaction Without Added Catalyst

In the previous quarterly, it was reported that the kinetics of thermal liquefaction (with no added catalyst) of Illinois #6 in tetralin had been run at three temperatures (390°C, 408°C and 422°C). Three distinct phases in the process were observed, i.e. a very rapid extraction of the tetralin soluble material in the coal followed by a slower solubilization of the coal structure (Figure 3). The initial conversion in the first minute is due to the physical extraction of a soluble fraction of the coal into the hot tetralin which occurs in both nitrogen and hydrogen. This is followed by an induction period and then the slow conversion of the coal structure to liquid product. As the liquefaction temperature is increased, the amount of extraction increases and the induction period becomes shorter. In the absence of a catalyst, however, increases in temperature above 408°C result in little increase in soluble product. The reason for this can be found in the TG analysis of the residue. The rate of removal of Volatile Matter increases steadily as the temperature increases (Figure 4),

regardless of whether the system is in hydrogen or nitrogen. However, the Fixed Carbon increases at a very rapid rate above 408°C (Figure 5). This is indication of the retrograde process which results in low liquid yields and the formation of tar and coke.

The induction period has now been shown to be a pseudo induction period and is due to the simultaneous occurrence of two processes, a very rapid extraction and a slower liquefaction of the coal structure. As the temperature increases the induction period steadily becomes less pronounced as the rate of break down of the coal structure increases and becomes closer in reaction rate to the extraction step itself. That the induction period is not due to the build up of free radicals, as we first thought, is shown by ESR data previously obtained which shows that the radical concentration actually decreases somewhat during the liquefaction process.

2.1.2. Catalyzed Liquefactions

Figure 6 shows the conversion vs time curves for coal liquefaction at 390°C in the presence of about 0.9% sulfided molybdenum naphthenate in tetralin in 1000 psi hydrogen and without catalyst in tetralin and nitrogen. The rapid initial extraction is again observed in the first minute in both the catalyzed and thermal runs, followed by an induction period. However, the subsequent conversion is much faster for the catalyzed than the thermal liquefaction. More importantly, the retrograde process is very significantly reduced in the presence of catalyst and hydrogen as is shown by the Fixed Carbon content in the residue as a function of time (Figure 7).

When the catalyzed liquefaction is run at higher temperature, the Fixed Carbon of the residue is further reduced, indicating that the precursors of the retrograde processes are being hydrogenated and stabilized during the catalyzed liquefaction (Figure 8). Liquid yields are thereby significantly improved.

2.1.3. Effect of Solvent on Liquefaction Kinetics

It has been known for a long time that liquefaction yields are improved if a strong hydrogen donor solvent is used. To demonstrate this in the SCTBR, liquefactions of Illinois #6 coal were run in three solvents of varying hydrogen ability at two temperatures. The results are shown in Table 1. These data suggest that a very strong donor solvent such as tetrahydroquinoline gives higher conversion at a given reaction time than tetralin. Further, less hydrogen is derived from the gas phase. A weak donor solvent such as methyl naphthalene requires almost all of its hydrogen from externally supplied hydrogen.

2.1.4. Is Coal Liquefaction Mass Transfer Controlled?

The Argonne coal samples used in most of this work are relatively fine particles (-100 mesh). However to determine whether the liquefaction rates were limited by mass transfer, another Illinois #6 obtained from Amoco which was much finer was tested. The mesh analysis of the two coals is shown in Figure 9. Figure 10 shows a conversion vs time curve at 394°C for the finer coal. Little if any difference can be seen in the conversion rates of the two coals, suggesting that if the coal is finer than 100 mesh mass transport will not be

limiting. This was also concluded by Guin et al in earlier work (3).

2.1.5. Liquefaction of Other Coals

Two other coals have been investigated for their liquefaction kinetics, Wyodak Anderson subbituminous coal and Beulah-Zap lignite. Data sheets for the runs made thus far are given in Table 2. These coals still require further processing and analysis. Figure 11 shows uncatalyzed conversion vs time curves for the subbituminous coal in hydrogen and in nitrogen. Only a small increase in rate is observed in hydrogen as compared to the nitrogen. This can be compared to similar runs of Illinois #6 bituminous coal in the two gases, in which there is a significant increase in rate in the presence of hydrogen. This may be due to the higher pyrite content of the bituminous coal (2.81% pyritic sulfur in the Illinois #6 vs 0.17% pyritic sulfur in the Wyodak coal). This suggests that there is a mild catalysis by pyrite (or more likely by pyrrhotite derived from it) in the case of the Illinois #6 coal.

2.2. Analytical Methods

2.2.1. Determination of Boiling Range of Coal Liquids by Thermogravimetric Analysis

The development of a TG method for determining boiling range of coal liquids was discussed in the previous quarterly report. This was the subject of a paper given at the last National American Chemical Society meeting in Chicago and is being prepared for a full paper in a refereed journal. This method will be important for following the conversion of the coal liquids to lower boiling materials.

2.2.2. Estimating Coal Rank by Thermogravimetric Analysis

The determination of coal rank is sometimes rather subjective and usually requires determination of vitrinite reflectance, a technique not available in all laboratories. In the course of investigating the Argonne Premium coal samples by TGA, it became apparent that there is a significant difference in the TGA patterns of these coals as they varied in coal rank. Figure 12 shows the derivative (DTG) curves for eight Argonne coals. There is a progressive increase in the temperature of the principal pyrolysis peak as the rank increases. This is perhaps best shown by the curve in Figures 13 and 14. It is apparent that, as the rank increases, the peak height increases to about 81% carbon and then decreases again. While this study has not been extended beyond the Argonne coals, this does provide an objective rank criterion which may be useful particularly where two coals appear to be close in rank. This was also presented as a paper at the last National American Chemical Society meeting in Chicago.

2.2.3. Determination of Phenolic Hydroxyl in Coal

Development of a more rapid and precise method than the Blom method is still underway.

3. PUBLICATIONS

Five papers have been presented since the last quarterly report. Copies of these papers were attached with the last quarterly report. They are presented at the National American Chemical Society meeting in Chicago, August 29 - 24, 1995 (1-3) and at the 8th International Conference on Coal Science in Oviedo, Spain September 11-15, 1995:

1. "Kinetics of Coal Liquefaction at Very Short Reaction Times" He Huang, Keyu Wang, Shaojie Wang, M.T. Klein and W.H. Calkins*

2. "A Novel Method for the Determination of the Boiling Range of Liquid Fuels by Thermogravimetric Analysis" He Huang, Keyu Wang M. T. Klein and W. H. Calkins*

3. "Determination of Coal Rank by Thermogravimetric Analysis" He Huang, Keyu Wang, M.T.Klein and W.H. Calkins*

4. "Kinetics of Thermal and Catalyzed Coal Liquefaction at Very Short Reaction Times Using a Novel Batch Reactor and Thermogravimetric Analysis" He Huang, Keyu Huang, Keyu Wang, M.T.Klein and W.H. Calkins*

5. "A Novel Reactor System for Studying the Kinetics of Coal Liquefaction and Related Processes at Very short Reaction Times" He Huang, D.M Fake, M.T.Klein and W.H. Calkins*

4. FUTURE PROGRAM

- 1). Complete measuring the kinetics of liquefaction of Wyodak subbituminous coal, Beulah-Zap Lignite, and Blind Canyon HVB bituminous coal.
- 2). Follow the changes in concentrations of the various organic oxygen species present and determine the reaction pathways of these components during coal liquefaction.
- 3). Investigate the chemistry of the retrograde reactions by determining the kinetics of formation and attempting to inhibit those processes.
- 4). Investigate the effect of liquefaction catalyst type (hydrogenation strength, acidity etc.) on liquid yield and on the retrograde reactions.

5. SUMMARY AND CONCLUSIONS

Conversion vs time curves have been determined for both uncatalyzed and catalyzed liquefaction in tetralin of Illinois #6 bituminous coal and Wyodak-Anderson subbituminous coal. These curves show an initial very rapid conversion (15-20%) at 390°C which lasts 1-2

minutes due to the extraction of tetralin soluble material in the coal. This is followed by a short pseudo induction period due to two simultaneous reactions, a rapid extraction and a slower solubilization of the coal structure itself. As the temperature increases, the induction period diminishes and eventually disappears as the rates of the extraction and the liquefaction processes approach the same value.

The retrograde processes leading to tar and coke are made apparent by the amount of Fixed Carbon in the liquefaction residue indicated by thermogravimetric analysis. In the absence of a catalyst, the retrograde processes are greatly accelerated by increased temperature. In the presence of hydrogen and a hydrogenation catalyst the retrograde processes are greatly reduced apparently through hydrogenation of the precursors to these processes, thus leading to improved liquefaction yields.

Liquefaction yields are greatly increased by use of a stronger hydrogen donor solvent in which most of the hydrogen is contributed by the solvent rather than molecular hydrogen.

A method based on thermogravimetry has been devised for estimating the rank of a coal.

6. REFERENCES

- 1). "A novel Laboratory Scale Short Contact Time Reactor system for Studying Fuel Processes. 1. Apparatus and Preliminary Experiments" He Huang, William H. Calkins, and Michael T. Klein *Energy and Fuels* 8, 1304 - 1309
- 2). "A Novel Laboratory Scale Reactor System for Studying Fuel Processes from the Initial Stages. 2. Detailed Energy and Momentum Balances" He Huang, Dean M. Fake, William H. Calkins and Michael T. Klein *Energy and Fuels* 8, 1310 - 1315
- 3). "Kinetics and Solubility of Hydrogen in Coal Liquefaction Reactions" James A. Guin, Arthur R. Tarrer, Wallace S. Pitts, and John W. Prather *ACS Fuel Chemistry Div. Preprints*, 21 (5) pp. 170-179 (1976).

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Table 1

Influence of strength of hydrogen donor solvent on direct coal liquefaction (Preliminary results on the Illinois #6 coal)

Solvent	time, min	T, C	in 1000 psig N2	in 1000 psig H2
1,2,3,4-tetrahydroquinoline	30	410	67.8%	67.9%
Tetralin	30	408	49.1%	-
Tetralin	10	390	28.6%	39.7%
1-methylnaphthalene	10	392	7.2%	20.4%

Table 2 Reactor Runs of Coal Liquefaction

Sample#	T(c)	t(min)	Coal	Solvent	Gas	Catalyst	SA
DOE001	15	30	I	Tetralin	N2		
DOE002	100	30	I	Tetralin	N2		
DOE003	200	30	I	Tetralin	N2		
DOE004	246	30	I	Tetralin	N2		
DOE005	297	30	I	Tetralin	N2		
DOE006	318	30	I	Tetralin	N2		
DOE007	345	30	I	Tetralin	N2		
DOE008	378	30	I	Tetralin	N2		
DOE009	390	30	I	Tetralin	N2		
DOE010	381	60	I	Tetralin	N2		
DOE011	389	15	I	Tetralin	N2		
DOE012	403	0.167	I	Tetralin	N2		
DOE013	390	10	I	Tetralin	N2		
DOE014	385	0.333	I	Tetralin	N2		
DOE015	384	0.5	I	Tetralin	N2		
DOE016	382	0.75	I	Tetralin	N2		
DOE017	386	1	I	Tetralin	N2		
DOE018	385	2	I	Tetralin	N2		
DOE019	386	7.5	I	Tetralin	N2		
DOE020	387	3	I	Tetralin	N2		
DOE021	387	5	I	Tetralin	N2		
DOE022	388	1	I	Tetralin	H2		
DOE023	386	0.5	I	Tetralin	H2		
DOE024	389	30	I	Tetralin	H2		
DOE025	388	0.167	I	Tetralin	H2		
DOE026	388	0.333	I	Tetralin	H2		
DOE027	385	0.75	I	Tetralin	H2		
DOE028	377	5	I	Tetralin	H2		
DOE029	376	15	I	Tetralin	H2		
DOE030	375	3	I	Tetralin	H2		
DOE031	372	735	I	Tetralin	H2		
DOE032	380	10	I	Tetralin	H2		
DOE033	381	55.5	I	Tetralin	H2		
DOE034	357	1	I	Tetralin	H2		
DOE035	356	1	I	Tetralin	H2		
DOE036	390	1	I	Tetralin	H2		
DOE037	395	0.167	W	Tetralin	H2		
DOE038	395	0.333	W	Tetralin	H2		
DOE039	396	0.5	W	Tetralin	H2		
DOE040	394	1	W	Tetralin	H2		

Continued ...

Table 2 Reactor Runs of Coal Liquefaction (Continued)

Sample#	T(c)	t(min)	Coal	Solvent	Gas	Catalyst	SA
DOE041	392	3	W	Tetralin	H2		
DOE042	392	10	W	Tetralin	H2		
DOE043	390	0.167	W	Tetralin	N2		
DOE044	392	0.334	W	Tetralin	N2		
DOE045	393	0.5	W	Tetralin	N2		
DOE046	390	1	W	Tetralin	N2		
DOE047	392	0.5	W	Tetralin	N2		
DOE048	392	10	W	Tetralin	N2		
DOE049	384	30	W	Tetralin	H2		
DOE050	386	5	W	Tetralin	H2		
DOE051	394	60	W	Tetralin	H2		
DOE052	390	60	W	Tetralin	N2		
DOE053	388	5	W	Tetralin	N2		
DOE054	385	3	W	Tetralin	N2		
DOE055	388	0.167	W	1-M naph	N2		
DOE056	390	0.5	W	1-M naph	N2		
DOE057	395	10	W	1-M naph	N2		
DOE058	22	30	I	1-M naph	N2		
DOE059	101	30	I	1-M naph	N2		
DOE060	18	15	I	Tetralin	N2		
DOE061	18	15	I	Tetralin	N2		
DOE063	295	2	I	Tetralin	H2		
DOE064	335	2	I	Tetralin	H2		
DOE065	362	2	I	Tetralin	H2		
DOE066	374	2	I	Tetralin	H2		
DOE067	386	2	I	Tetralin	H2		
DOE068	391	0.5	I	Tetralin	H2		
DOE069	388	1	I	Tetralin	H2		
DOE070	388	0.75	I	Tetralin	H2		
DOE071	385	0.167	I	Tetralin	H2		
DOE072	390	0.167	I	Tetralin	H2		
DOE073	391	0.5	I	Tetralin	H2		
DOE074	383	5	I	Tetralin	H2		
DOE075	388	60	I	Tetralin	H2		
DOE076	390	30	I	Tetralin	H2		
DOE077	25	15	W	Tetralin	N2		
DOE078	24	15	W	Tetralin	N2		
DOE079	391	30	I	Tetralin	H2		
DOE080	390	30	W	Tetralin	H2		

Continued ...

Table 2 Reactor Runs of Coal Liquefaction (Continued)

Sample#	T(c)	t(min)	Coal	Solvent	Gas	Catalyst	SA
DOE081	392	30	W	Tetralin	N2		
DOE082	388	10	W	Tetralin	N2		
DOE083	385	10	W	Tetralin	N2		
DOE084	380	10	W	Tetralin	H2		
DOE085	388	10	W	Tetralin	H2		
DOE086	394	10	W	Tetralin	H2		
DOE087	394	10	W	Tetralin	H2		
DOE088	408	2	I	Tetralin	N2		
DOE089	406	1	I	Tetralin	N2		
DOE090	407	0.5	I	Tetralin	N2		
DOE091	408	5	I	Tetralin	N2		
DOE092	406	30	I	Tetralin	N2		
DOE093	409	10	I	Tetralin	N2		
DOE094	409	60	I	Tetralin	N2		
DOE095	411	0.75	I	Tetralin	N2		
DOE096	410	3	I	Tetralin	N2		
DOE097	426	1	I	Tetralin	N2		
DOE098	424	5	I	Tetralin	N2		
DOE099	424	3	I	Tetralin	N2		
DOE100	423	2	I	Tetralin	N2		
DOE101	422	10	I	Tetralin	N2		
DOE102	422	30	I	Tetralin	N2		
DOE103	421	60	I	Tetralin	N2		
DOE104	423	0.5	I	Tetralin	N2		
DOE105	423	0.75	I	Tetralin	N2		
DOE106	389	5	I	Tetralin	N2	Y	
DOE107	388	5	I	Tetralin	H2	Y	
DOE108	389	5	I	Tetralin	N2	Y	Y
DOE109	388	5	I	Tetralin	H2	Y	Y
DOE110	389	5	I	Tetralin	N2		Y
DOE111	391	5	I	Tetralin	H2		Y
DOE112	390	0.167	I	Tetralin	H2	Y	Y
DOE113	386	0.5	I	Tetralin	H2	Y	Y
DOE114	391	60	I	Tetralin	H2	Y	Y
DOE115	390	0.005	I	Tetralin	H2	Y	Y
DOE116	392	5	I	Tetralin	H2	Y	Y
DOE117	388	10	I	Tetralin	H2	Y	Y
DOE118	385	3	I	Tetralin	H2	Y	Y
DOE119	390	1	I	Tetralin	H2	Y	Y
DOE120	388	2	I	Tetralin	H2	Y	Y

Continued ...

Table 2 Reactor Runs of Coal Liquefaction (Continued)

Sample#	T(c)	t(min)	Coal	Solvent	Gas	Catalyst	SA
DOE121	20	15	W	Tetralin	N2		
DOE122	19	16	W	Tetralin	N2		
DOE123	19	15	W	Tetralin	N2		
DOE124	20	15	W	S353	N2		
DOE125	20	15	W	S353	N2		
DOE126	395	10	W	S353	N2		
DOE127	395	10	W	S353	H2		
DOE129	393	5	W	Tetralin	H2		
DOE130	391	5	W	Tetralin	H2		Y
DOE131	393	5	W	Tetralin	H2	Y	
DOE132	395	5	W	Tetralin	H2	Y	Y
DOE133	392	5	W	Tetralin	N2		
DOE134	390	5	W	Tetralin	N2		Y
DOE135	389	5	W	Tetralin	N2	Y	
DOE136	387	5	I	Tetralin	N2	Y	Y
DOE137	390	50	I	Tetralin	H2		
DOE139	393	40	I	Tetralin	H2		
DOE140	394	20	I	Tetralin	H2		
DOE141	394	30	I	Tetralin	H2	Y	Y
DOE142	395	20	I	Tetralin	H2	Y	Y
DOE143	393	40	I	Tetralin	H2	Y	Y
DOE144	390	50	I	1-M naph	N2	Y	Y
DOE145	414	1	I	1-M naph	N2		
DOE146	406	2	I	1-M naph	N2		
DOE147	407	5	I	1-M naph	N2		
DOE148	402	10	I	1-M naph	N2		
DOE149	408	30	I	1-M naph	N2		
DOE150	406	45	I	1-M naph	N2		
DOE151	403	60	I	1-M naph	N2		
DOE152	396	10	I	1-M naph	H2		
DOE153	395	10	I	1-M naph	H2		
DOE154	410	0.167	I	Tetralin	H2		
DOE155	407	0.5	I	Tetralin	H2	Y	Y
DOE156	408	1	I	Tetralin	H2	Y	Y
DOE157	406	2	I	Tetralin	H2	Y	Y
DOE158	405	3	I	Tetralin	H2	Y	Y
DOE159	400	5	I	Tetralin	H2	Y	Y
DOE160	400	10	I	Tetralin	H2	Y	Y

Continued ...

Table 2 Reactor Runs of Coal Liquefaction (Continued)

Sample#	T(c)	t(min)	Coal	Solvent	Gas	Catalyst	SA
DOE161	400	20	I	Tetralin	H2	Y	Y
DOE162	402	30	I	Tetralin	H2	Y	Y
DOE163	398	60	I	Tetralin	H2	Y	Y
DOE164	424	0.167	I	Tetralin	H2	Y	Y
DOE165	429	0.5	I	Tetralin	H2	Y	Y
DOE166	430	1	I	Tetralin	H2	Y	Y
DOE167	430	2	I	Tetralin	H2	Y	Y
DOE168	416	3	I	Tetralin	H2	Y	Y
DOE169	416	5	I	Tetralin	H2	Y	Y
DOE170	415	10	I	Tetralin	H2	Y	Y
DOE171	415	20	I	Tetralin	H2	Y	Y
DOE172	415	30	I	Tetralin	H2	Y	Y
DOE173	430	60	I	Tetralin	H2	Y	Y
DOE174	408	1	I	1-M naph	N2		
DOE175	407	2	I	1-M naph	N2		
DOE176	410	5	I	1-M naph	N2		
DOE177	407	0.5	I	1-M naph	N2		
DOE178	406	45	I	1-M naph	N2		
DOE179	409	10	I	1-M naph	N2		
DOE180	409	30	I	1-M naph	N2		
DOE181	410	60	I	1-M naph	N2		
DOE182	412	30	I	1-M naph	H2		
DOE183	412	30	I	1-M naph	H2		
DOE184	412	30	I	THQ	N2		
DOE185	415	30	I	THQ	H2		
DOE191	400	0.167	I	THQ	N2		
DOE192	404	0.5	I	THQ	N2		
DOE193	400	1	I	THQ	N2		
DOE194	407	2	I	THQ	N2		
DOE195	407	3	I	THQ	N2		
DOE196	413	20	I	THQ	N2		
DOE197	411	60	I	THQ	N2		
DOE198	407	5	I	THQ	N2		
DOE199	412	10	I	THQ	N2		
DOE200	391	0.167	A	Tetralin	N2		

Continued ...

Table 2 Reactor Runs of Coal Liquefaction (Continued)

Sample#	T(c)	t(min)	Coal	Solvent	Gas	Catalyst	SA
DOE201	393	0.333	A	Tetralin	N2		
DOE202	395	0.5	A	Tetralin	N2		
DOE203	396	0.75	A	Tetralin	N2		
DOE204	395	1	A	Tetralin	N2		
DOE205	394	2	A	Tetralin	N2		
DOE206	395	5	A	Tetralin	N2		
DOE207	396	10	A	Tetralin	N2		
DOE208	388	0.167	B	Tetralin	N2		
DOE209	396	0.5	B	Tetralin	N2		
DOE210	399	1	B	Tetralin	N2		
DOE211	395	5	B	Tetralin	N2		
DOE212	392	3	B	Tetralin	N2		
DOE213	393	0.167	B	Tetralin	N2		
DOE214	392	30	B	Tetralin	N2		
DOE215	391	60	B	Tetralin	N2		
DOE216	383	0.167	B	Tetralin	N2	Y	Y
DOE217	389	0.167	B	Tetralin	H2	Y	Y
DOE218	395	0.5	B	Tetralin	H2	Y	Y
DOE219	403	1	B	Tetralin	H2	Y	Y
DOE220	397	3	B	Tetralin	H2	Y	Y
DOE221	385	5	B	Tetralin	H2	Y	Y
DOE222	389	10	B	Tetralin	H2	Y	Y
DOE223	414	30	B	Tetralin	H2	Y	Y
DOE224	397	30	B	Tetralin	H2	Y	Y
DOE225	393	60	B	Tetralin	H2	Y	Y
DOE226	23	10	A	Tetralin	N2		

Notes:

- 1). I = Illinois #6 coal
W = Wyodak coal
A = Illinois #6 coal from AMOCO
B = Beulah_Zap coal
- 2). Catalyst: molybdenum naphthenate
SA (Sulfiding Agent): methyl disulfide
- 3). 1-M naph: 1-methyl naphthalene
THQ: tetrahydroquinoline

Sample: Argonne Coal: Illinois #6 (dry)

Size: 32.7490 mg

Method: DOE Coal Liquefaction

Comment: 10 °C/min to 900 °C in nitrogen (60 ml/min), then adding oxygen

TGA

File: A: ARGN301.001

Operator: Dr. Huang, He

Run Date: 25-Oct-93 03:55

DTG profiles for residues of the Illinois #6 coal after liquefaction in tetralin at the selected contact times (TG scan at 10 °C/min in N₂; liquefaction run at 390 °C under 1000 psig N₂ with T:C = 8:1)

Figure 2

Kinetics of the Illinois #6 coal liquefaction in tetralin under 1000 psig N₂ for up to 1 hr.
(T:C = 8:1)

VM (volatile matter) and FC (fixed carbon) in liquefaction residues determined by TGA
 (Liquefaction: T/C = 8, 1000 psig N₂; TGA: 100 cm³(STP)/min N₂, 100 °C/min)

Conversion of the Illinois #6 coal in thermal and catalyzed liquefaction at 390 °C
(Catalyst: ca. 0.9 wt% molybdenum naphthenate; T:C = 8:1)

Figure 6

Figure 7

FC (fixed carbon) in the thermal and catalyzed liquefaction residues determined by TGA (Liquefaction run: Illinois #6 coal; 390 °C; Catalyst: ca. 0.9 wt% molybdenum naphthenate; T:C = 8:1; TG scan: 100 cm³(STP)/min N₂; 100 °C/min)

Figure 8

FC (fixed carbon) in the catalyzed liquefaction residues determined by TGA (Liquefaction run: Illinois #6 coal; 1000 psig H_2 ; Catalyst: ca. 0.9 wt% molybdenum naphthenate; T:C = 8:1; TG scan: $100 \text{ cm}^3(\text{STP})/\text{min } N_2$; $100 \text{ }^\circ\text{C}/\text{min}$)

Figure 9

Figure 10

Liquefaction kinetics of extremely fine particles of Amoco Illinois #6 coal at 394 °C
(Liquefaction: T/C = 8, 1000 psig N₂)

Kinetics of the Wyodak subbituminous coal liquefaction in tetralin (390 °C; T:C = 8:1)

Figure 11

DTG pyrolysis curves of the Argonne Premium Coal Samples

Figure 12

Figure 13

Peak temperature vs. carbon content of the Argonne Premium Coal Samples

Figure 14

Rate at peak temperature vs. carbon content of the Argonne Premium Coal Samples