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. Many of those objectives have already been achieved and others are still in progress. This quarterly report covers further 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 and reported on previously. A description of the reactor system and its operation was published in the Progress Report dated January 19, 1994 (1). Two papers (2,3) have been published and reported on previously on the design and operation of the reactor. These papers describe the reactor system and its capability in terms of heat-up rates, charge times and how short a reaction times can be observed in a liquefaction process (approximately 10 sec).

1.2 Product Work-up Procedure and Determination of Liquefaction Conversion

The product work-up procedure used in coal liquefaction experiments was developed and has also been described in previous quarterly reports (4). The liquefaction products are separated into solid and liquid by vacuum filtration. The liquefaction conversion is determined by the ash content (by TGA) of the washed solid residue. Both solids and liquids are analyzed separately by various analytical methods including elemental analysis, TGA, NMR and other methods. methods.

As previously reported (4), thermogravimetric analysis of coal before liquefaction and coal residues from liquefaction show three major stages of weight loss: indicating the content of Volatile Matter, Fixed Carbon and Ash. The Fixed Carbon of liquefaction residues was shown to be a measure of the tendency to form solid retrograde products (tars and coke).

Liquefactions have been carried out both in the presence and absence of an inorganic catalyst and in either 1500 psi of nitrogen or hydrogen. The catalyst used was sulfided molybdenum naphthenate. This catalyst has been prepared by dissolving molybdenum naphthenate (6,8% 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 previous quarterly reports.

1.3 Liquefaction Conversion vs Time

Liquefaction studies have been made in an excess of tetralin of Illinois #6 coal and Wyodak-Anderson coals at three temperatures. In uncatalyzed liquefactions three distinct phases were observed i.e. a very rapid extraction of the tetralin soluble material in the coal followed and induction period and then by a slower solubilization of the coal structure itself. The induction period was shown to be an artifact in that it was the combination of two reaction rates, a very rapid extraction and a much slower coal solubilization step (5,6). At higher temperatures as the two rates become more nearly equal, the induction period was greatly reduced and in the presence of an active catalyst and hydrogen at elevated temperature, the induction period was absent.

1.4 Retrograde Reactions

We previously reported that the Fixed Carbon content (by TGA) of the liquefaction residues was a measure of the tendency of the coal to form retrograde reactions during liquefaction. This tendency was greatly enhanced by liquefaction at higher temperatures. At the same time, the tendency to form fixed carbon in the liquefaction residues was greatly reduced in the presence of an active catalyst and hydrogen. Higher temperatures (up to a point) still further reduced the retrograde processes as the precursors of the tars and coke become hydrogenated.

2. EXPERIMENTAL PROGRESS

2.1 Analysis of Coal Liquefaction Residues

Table 1 shows the elemental analyses of Illinois #6 coal liquefaction residues for liquefactions at 408 and 422°C at a range of reaction times. Figures 1 and 2 show the variation of hydrogen to carbon atomic ratio as a function of time during uncatalyzed coal liquefaction in nitrogen. The rapid decrease in the hydrogen to carbon atomic ratio as the reaction proceeds is readily apparent, showing the progress of the retrograde processes toward coke as the time and temperature increases. This is quite consistent with our previous observations of the build up of Fixed Carbon under the same conditions (see Figure 3 of Quarterly Report dated May 31, 1995).

The affect of hydrogen atmosphere and catalyst activity is also shown by the elemental analyses for runs DOE106 through DOE 108 in Table 1. These results are also shown as bar graphs in Figure 3. This shows that liquefaction in the presence of hydrogen does result in a somewhat higher hydrogen to carbon atomic ratio. However as was shown by the Fixed Carbon measurements, hydrogen in the presence of sulfided catalyst results in significantly higher hydrogen to carbon atomic ratio in the liquefaction residue. As previously reported, unsulfided catalyst had no effect on the hydrogen content of the liquefaction residues.

2.2 Analytical Methods

2.2.1 Phenolic Hydroxyl

Phenolic hydroxyl contents of the liquefaction residues is being measured but have not been completed. The method we are using is a modification of the Blom acetylation method, however it has been modified so that the distillation of the hydrolyzed acetylated coal has been modified to incorporate the concept of the Duclaux constants (7) using automatic titration and the computer to estimate the total acetic acid to be evolved without distilling to exhaustion. This method should be as accurate and much faster than the traditional Blom procedure.

2.2.2 Treatment of Thermogravimetric Analytical Data

A smoothing and filtering routine based on the use of linear regression and error analysis has been developed and successfully applied in the processing of thermogravimetric data. This method provides a filter to smooth the noise fluctuation and, at the same time, to introduce no distortions into the TGA data. This is quite important for TG analysis which produces a great volume of data points but where "fine structure in the TGA patterns represent chemical processes we wish to study.

3. PUBLICATIONS

Three papers have been prepared and submitted for presentation at the New Orleans National American Chemical Society meeting in March 1996. They cover much of our work on thermogravimetric analysis on coal and coal derived products and will be presented as part of the ACS symposium on "Thermal Analytical Techniques" in the Fuel Chemistry Division as part of that meeting. They are as follows:

- 1) "Applications of the Thermogravimetric Analysis in the Study of Fossil Fuels" by He Huang, Keyu Wang Shaojie Wang, M.T.Klein and W.H.Calkins*
- 2) "A Novel Smoothing Routine for the Data Processing in Thermogravimetric Analysis" by Keyu Wang, Shaojie Wang, He Huang, M.T.Klein and W.H. Calkins*
- 3) "Distillation of Liquid Fuels by Thermogravimetry" by He Huang, Keyu Wang, Shaojie Wang, M.T.Klein and W.H. Calkins*

4. FUTURE PROGRAM

- 1) Complete measuring the kinetics of Buelah-Zap Lignite and Blind Canyon HVB bituminous coal.
- 2) Continue the work on determination of the reaction pathways of the various oxygen species during liquefaction.
- 3) Investigate the kinetics of the retrograde reactions occurring

during coal liquefaction.

5. SUMMARY AND CONCLUSION

That the retrograde processes during coal liquefaction which lead to tar and coke is indicated by the formation of Fixed Carbon in the thermogravimetric analysis of liquefaction residues is amply confirmed by the elemental analysis of the liquefaction residues as a function of reaction time and temperature. As the liquefaction time and temperature increases, the Hydrogen to Carbon atomic ratio goes steadily down. In the presence of hydrogen and an active liquefaction catalyst, higher hydrogen to carbon atomic ratios in the liquefaction residues are observed.

6. REFERENCES

- 1) Progress Report January 1994
- 2) "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 (1994)
- 3) "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 (1994)
- 4) Progress Report September 1994
- 5) Progress Report September 1995
- 6) "Kinetics of Thermal and Catalyzed Coal Liquefaction at Very Short Reaction Times" Proceedings of the 8th International Conference on Coal Science, Oviedo, Spain, Volume II 1203-1206 (1995)
- 7) J. Am Chem Soc. 39, 731, 746 (1917)

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Table 1 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.

Figure 1 Illinois #6 Coal liquefaction residue: 408 °C; Tetralin:Coal = 8:1; 1000 psig N₂

Figure 2 Illinois #6 Coal liquefaction residue: 422 °C; Tetralin:Coal = 8:1; 1000 psig N₂

Figure 3 Illinois #6 Coal liquefaction residue: 389 °C; Tetralin:Coal = 8:1; Catalyzed runs: 0.9 Mo wt% based on the charged coal.