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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.

1.1. Description of the Reactor System and Its Operation

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 Conversion

The work-up procedure used in coal liquefaction experiments was 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 2 days. The liquid portion is bottled and nitrogen blanketed for subsequent analysis.

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:

$$\text{Conversion} = \left(1 - \frac{X_0}{X}\right) \times 100 \quad (\text{wt}\%) \quad (1)$$

where X_0 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%.

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. This correction depends upon the type of catalyst used.

1.3. 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 report.

2. EXPERIMENTAL PROGRESS

2.1. Kinetic Experiments

2.1.1. Uncatalyzed liquefactions

In the previous quarterly, it was reported that the kinetics of thermal liquefaction (no added catalyst) of Illinois #6 coal 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 an induction period which was in turn followed by a slower solubilization of the coal structure (Figure 1). 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 2), regardless of whether the system is in hydrogen or nitrogen. However, the Fixed Carbon increases at a very rapid rate above 408°C (Figure 3). This is indicative of the retrograde process which results in low liquid yields and the formation of tar and coke.

2.1.2. Catalyzed Liquefactions

Figure 4 summarizes the conversion vs time for liquefaction of Illinois #6 in Hydrogen at 390°C in the presence of about 1% sulfided molybdenum naphthenate in tetralin. The rapid initial extraction is again observed in the first minute, followed by the induction period. The subsequent conversion is faster than for the uncatalyzed liquefaction. More importantly, the retrograde process is very significantly reduced as is shown by the build up of Fixed Carbon in the residue as a function of time. The precursors to the retrograde reactions are apparently being hydrogenated in the presence of hydrogen and the catalyst. While these retrograde processes are greatly reduced, they still represent a significant yield loss even at the mild temperatures used. A catalyst which will be more active at lower temperature is needed. Other liquefaction catalysts are being investigated to determine their effect on the retrograde processes.

As reported in the previous quarterly report, there is evidence that pyrite (or its conversion product pyrrhotite) is a weak catalyst for coal liquefaction in the presence of hydrogen. This is shown by liquefaction of coals in the presence of hydrogen and nitrogen in the absence of added catalyst. There is a substantial difference in the conversion of Illinois #6, which contains 2.81 % pyritic sulfur, in hydrogen and in nitrogen (Figure 5)

whereas with Wyodak Black Thunder coal, which contains only 0.17% pyritic sulfur, there is very little difference in the conversion curves in hydrogen and in nitrogen (Figure 6).

2.1.3. Liquefaction in the Presence of Solvents Other than Tetralin

The presence of a hydrogen donor solvent in the direct coal liquefaction process is an important factor in determining the liquefaction yield. Several runs have been made in the presence of Methyl naphthalene, a solvent having very similar solubility parameter and boiling point as tetralin, but with little or no hydrogen donor capability. The analytical results for these samples will be presented in the next report. More active hydrogen donors will also be tested.

2.1.4. Kinetics of Gas Formation During Coal liquefaction

During the direct liquefaction of coal, various gases (CO_2 , CO , CH_4 , and others) are also formed, which not only represent a loss in liquid yield but are an important indication of the chemistry going on in the process. Due to the lack of analytical equipment, we have not been able to follow amount and the chemical composition of these gases. Now we have obtained a gas chromatograph which will be installed in the off gas of the reactor which should give us a continuous monitoring of the gases produced during the course of our kinetic experiments.

2.2. Analytical Methods

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

During the direct liquefaction process, the coal is not only converted into a liquid but the liquid is hydrocracked during the process continuously into successively lower boiling products. It was therefore desirable to have an analytical method for measuring the boiling range of the coal liquefaction products we produce using a very small sample. Existing simulated distillation methods did not appear to be suitable for these materials. For that reason, an analytical procedure has been developed which is capable of measuring the boiling range of the coal liquids. This is complicated by the fact that there are high boiling materials produced in the liquefaction process, and the liquids tend to be thermally unstable with respect to the formation of retrograde products. The method chosen was based on thermogravimetry. This required design of a special TGA pan which was a cylindrical pan with a small aperture at the top. The objective of the change is to make the rate of weight loss from the sample pan primarily determined by the vapor pressure of the sample. Three pans of different sizes of circular aperture were fabricated. The diameters of the apertures were 0.615, 0.974 and 1.538mm. In each TGA test, about 80mg of liquid sample was injected into the sample pan by a syringe.

Analytical variables, such as carrier gas flow rate and type, pressure and temperature or heating rate were held constant during the analysis. Two methods, i.e. a ramp method and an isotrack method, have been used in the SimDis TGA technique. In the ramp method, a constant heating rate was used and the rate of the weight loss determined versus temperature. In the isotrack method, the temperature of the sample is very rapidly heated

to a predetermined temperature within 2 minutes, and precisely controlled at this preset temperature within 0.01 to 0.05 °C after 5 minutes. The weight change and the DTG (the differential of the weight loss curve) decay are determined as a function of time.

In the ramp method, a constant heating rate is used (ca. 10°C per minute) and the weight loss and differential of the weight loss (DTG) determined versus temperature. If a sample contains material boiling above 400°C, a second TGA run is made under vacuum which allows us to differentiate volatile material from material that pyrolyzes during the distillation.

Both methods must be calibrated with samples of known boiling range under the exact conditions of the test (hole size, sweep gas flow rate etc.). In this work, a known mixture of aliphatic hydrocarbons from C₁₀ to C₃₂ was used (see Table 1). Similarly, a not completely chemically analyzed mixture of known boiling range can be used.

A SimDis TG analysis using the ramp method at two pressures on a light paraffinic vacuum distillate from Amoco is shown in Figure 7. Since in this case both DTG peaks appear to move with little change in shape when vacuum is applied, there appears to be no high boiling materials that pyrolyze during the analysis. A boiling point curve for that same material determined by the Isotrack method is shown in Figure 8.

A SimDis TG curve by the isotrack method on a liquid sample of hydroprocessed Wilsonville coal derived vacuum resid is shown in Figure 9. This clearly shows the high boiling fraction in that material. This SimDis TGA method will be used to characterize selected coal liquefaction liquids produced in this project.

2.2.2. Determination of Phenolic Hydroxyl in coal, coal liquids and coal residues

A system has been devised for determining the hydroxyl content of coal and coal residues. It is potentially more rapid and precise than the Blom method we have been using. This method is being further evaluated before it will be adopted for use in this project.

3. PUBLICATIONS

Two papers referred to above (Introduction 1.1) describing the design and testing of the bench scale reactor (SCTBR) have been published in Energy and Fuels. In addition, two papers have been presented at scientific meetings:

- 1). "The Kinetics of Coal Liquefaction at Short Reaction Times" W.H. Calkins, He Huang, and M.T. Klein *Proceedings of the 11th Annual Pittsburgh Coal Conference* Vol I pp 474-480 (1994).
- 2). "The Use of Thermogravimetric Analysis to Follow Changes During Short Contact Time Coal Liquefaction" He Huang, Keyu Wang, William H. Calkins and Michael T. Klein *ACS Fuel Chemistry Division Preprints* 39 (3) 741-746 (1994).

In addition, three papers have been submitted for presentation at the *ACS National Meeting* in Chicago August 20-24, 1995 (Copies are attached):

- 3). "Kinetics of Coal Liquefaction at Very Short Reaction Times" He Huang, Keyu Wang, Shaojie Wang, M.T. Klein and W.H. Calkins*.
- 4). "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*.
- 5). "Determination of Coal Rank by Thermogravimetric Analysis" He Huang, Keyu Wang, M.T. Klein and W.H. Calkins*.

Also, two papers have been accepted for presentation at the *8th International Coal Conference in Oviedo*, Spain Sept 11-15, 1995 (Copies are attached):

- 6). "Kinetics of thermal and catalyzed coal liquefaction at very short reaction times using a novel batch reactor and thermogravimetric analysis" He Huang, Keyu Wang, M.T. Klein and W.H. Calkins*.
- 7). "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). Determine the kinetics of direct liquefaction of Beulah-Zap lignite, Blind Canyon HVB, Pittsburgh #8 HVB and Pocahontas LVB coals;
- 2). Continue the determination of the effect of other solvents (H-donor and non-donor) than tetralin on the liquefaction kinetics;
- 3). Investigate the chemistry of the retrograde reactions by determining the kinetics of formation and attempting to inhibit those processes with additives;
- 4). Investigate the effect of liquefaction catalyst type (Hydrogenation strength, acidity etc) on the retrograde reactions; and
- 5). Follow the changes in concentrations of the various organic oxygen species present, in an effort to determine their role in the liquefaction process.

5. SUMMARY AND CONCLUSIONS

Conversion vs time curves have been determined at short reaction times for uncatalyzed direct liquefaction in tetralin of Illinois #6 bituminous and Wyodak Black Thunder subbituminous coal in hydrogen and in nitrogen at three temperatures. The initial conversion (over 20%), which lasts 1 - 2 minutes, is due to the extraction of tetralin soluble material in the coal. This extraction stage is followed by an induction period of several minutes depending on the temperature. It is probably due to the build up of free radicals in the system at the temperature of the liquefaction. The slow breakdown of the coal structure is then observed. The conversion of the coal to a liquid is competitive with retrograde processes forming tars and coke. The higher the liquefaction temperature, the more rapid the retrograde processes.

Conversion vs time curves for direct liquefaction of these same coals in the presence of hydrogen and sulfided molybdenum naphthenate catalyst were also determined at three temperature. The same three stages i.e. extraction, induction period and liquefaction are observed. The induction period is shorter in this case, and the liquefaction stage is more rapid. The retrograde processes are much reduced in the presence of a hydrogenation catalyst.

A method for simulating the boiling range of coal (or other) derived liquids (SimDis TGA) which can be run on small samples (30 - 80 mg) and provides a measure of the fraction boiling so high that it pyrolyzes and a reliable boiling range for the volatile fraction.

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.

Table 1 Concentrations and properties of the C₁₀-C₃₂ components in the synthetic mixture

No. of Carbon	Name	MW	b.p., °C	m.p., °C	W, g	C, wt%
10	Decane	142.28	174.1	-29.7	1.2298	18.26 %
15	Pentadecane	212.41	270.6	10.0	1.2068	17.92 %
20	Eicosane	282.54	343.0	36.8	1.1238	16.69 %
25	Pentacosane	352.67	401.9	55.0	1.0716	15.91 %
30	triacontane	422.80	449.7	65.8	1.0402	15.45 %
32	Dotriacontane	450.85	467.0	69.7	1.0618	15.77 %

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

Figure 1

Figure 2 VM (volatile matter) in liquefaction residues determined by TGA (Liquefaction: T/C = 8, 1000 psig N₂; TGA: 100 cm³(STP)/min N₂, 100 °C/min)

Figure 3 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)

Figure 4 Conversion vs time for liquefaction of Illinois #6 in Hydrogen at 390°C in the presence of about 1% sulfided molybdenum naphthenate in tetralin

Liquefaction conversion of the Illinois #6 coal under 1000 psig H₂ or 1000 psig N₂
(390 °C; T:C = 8:1)

Figure 5

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

Figure 6

Figure 7 DTG curves from SimDis TGA runs using the ramp method at two pressures on a light paraffinic vacuum distillate from Amoco

Simulated distillation curve for the light paraffinic vacuum distillate

Figure 8

Simulated distillation curve for the liquid sample of Wilsonville # 258 resid conversion run C024
(catalyst: sulfided molybdenum naphthenate; 403°C; 60 minutes; 1500 psig H₂)

Figure 9