

## HIGH CONVERSION IN COAL LIQUEFACTION WITH LOW HC GAS PRODUCTION

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### INTRODUCTION

For the past 30 years or more the projected cost of producing a synthetic crude from coal has been from 50% to 100% (sometimes more) higher than the cost of crude petroleum at the time of comparison. The work in this research program addresses that fact, and represents an attempt to significantly reduce the cost of producing liquids from coal. Inasmuch as hydrogen is an expensive reactant, a principal objective in this research is to avoid large-scale use of hydrogen, to be achieved by minimizing the production of hydrocarbon gases in the conversion process. It is noted that one can exercise much greater control over the chemistry intended to occur in a system if the reactions can be carried out in a fluid phase, liquid or gaseous, compared with reactions in the solid phase. This is particularly true when coal is the solid-phase reactant. An objective in this work, therefore, is to proceed from solid coal to a liquid as inexpensively as possible.

A process for direct conversion of coal to liquids usually begins by slurring the coal in a liquid. Inasmuch as there does not exist a reliable technology for introducing dry solids into a region in which pressures of 1500 psig or higher must exist, slurring the coal in a liquid is used to permit pumping the coal into the pressurized region. The presence of a liquid phase surrounding the coal particles after introduction into the reactor, as well as inside of the pores and channels of the coal, inhibits heat transfer into the particle by any means one may choose to use to heat the coal particles to reaction temperature (generally above 400 °C), resulting in residence times in the hot zone of many minutes, characteristically between 15 minutes and one hour. One loses control over most of the chemistry of the process. Specifically, when the coal and its primary conversion products are exposed to temperatures above 375 °C for such long periods of time, many thermal degradation reactions occur, most of them undesirable. These reactions lead to high yields of hydrocarbon gases, hence high hydrogen consumption. They also lead to asphaltene production, making the downstream processing of the liquids more difficult.

The experiments being conducted in this work were designed to examine the chemistry which may occur when the coal particle

is heated to reaction temperature in times of one or two seconds, and the liquefaction process to form primary liquids is completed in times measured in seconds rather than minutes. It was expected, and is now observed, that conversions greater than 70% by weight of the coal, accompanied by ratios of liquids/HC gases of 10/1 or greater, can be achieved. The question of how coal may be introduced into a system to achieve these results, a question probably in the mind of the reader, is not an objective of this research program. However this question is now being addressed in a proposal now in preparation. The theoretical considerations which underlie that concept indicate a reasonable promise of success experimentally.

#### EXPERIMENTAL

Two reactor systems have been designed and constructed, namely a batch micro-reactor and a continuous-flow tubular reactor.

A sketch of the micro-reactor is shown in Figure 1. The reactor has an internal volume of 107 cc, and is constructed of stainless steel. It is designed to accommodate pressures up to 3000 psig at temperatures up to 600 °C. The coal sample is supported on a stainless steel gauze, attached to two electrodes to provide for electrical heating. A thermocouple is mounted immediately above the wire gauze, not touching the gauze but such that it will be embedded in the coal sample. A second thermocouple is placed to read temperatures in the gas space between the coal sample and the wall of the reactor. Cooling coils are located in the walls of the reactor, but they have not been required for experiments at the short times of these experiments. A special temperature controller was constructed which provides for rapid heat-up to the required temperature, while avoiding temperature over-shoot of more than a few degrees.

In a typical experiment, coal is crushed to pass through a 200 mesh Tyler Series screen (coal particles -74 microns). The soluble acid catalyst (see Table I) is impregnated into the pores of the dry coal, and the solvent evaporated. Two hundred grams of coal are placed on the wire gauze, exercising care to ensure that the coal particles completely surround the tip of the thermocouple. The reactor is closed, and pressurized with hydrogen to a calculated pressure such that the pressure at operating temperature will be about 1500 psig. At the completion of the experiment at a predetermined time, the reactor system is quenched. The gases are passed to a gas sampler, then to a wet-test meter. Gas samples are analyzed by gas chromatograph (GC). From the GC analysis and wet-test meter measurements, quantities of individual hydrocarbon gases are calculated. The liquids collected from the vessel are combined with liquids removed from the solids by extraction, and weighed. The solids are weighed.

The continuous flow reactor consists of a straight stainless steel tube, 5/16 inch inside diameter, heated by a series of electrical heating jackets, each operated from a temperature controller. The length of the reactor is increased by adding tube sections. Coal is prepared as described above, and fed to the reactor from a lock hopper utilizing a star feeder. Hot hydrogen gas is injected into the reactor with the coal. Residence times in the reactor are established by changes in gas flow rates, coupled with changes in coal feed rates by the star feeder, and by changes in reactor tube length. The products from the reactor pass through a solids separation vessel, maintained at the temperature of the reactor, then through two cooled vessels for liquids removal. The gases pass to a gas sampler, then to a wet-test meter. Determinations of product quantities and analyses are as described above.

#### RESULTS AND DISCUSSION

Representative experimental data from the microreactor are presented in Table I. The coal sample consisted of 200 mg of a Wyodak sub-bituminous coal. The experiment was conducted as described above. After 20 seconds, the system was quenched, and products removed and analyzed as described above. Fifty percent by weight of the coal was converted to liquids and gases in this experiment, with a ratio of liquids/HC gases of 10.6/1.0. The extracted char was then used as the solid feed for a second pass of 20 seconds duration. An additional 58% of the char (representing 29% of the original coal), was converted in this second pass, resulting in a total conversion of 79% by weight of the coal. In the second pass the ratio of liquids/HC gases was extremely high, namely about 23/1. When the results of the two passes are combined, the overall ratio liquids/HC gases is 15/1. Duplicate experiments revealed very good reproducibility of the data.

The data of Table I reveal important information relative to the potential for conversion of coal to high liquid yields with low yields of hydrocarbon gases. In the microreactor the coal sample sits on the heating mantle, with the thermocouple buried inside of the coal sample. The thermocouple indicated achieving reaction temperature in the coal sample in about 2-3 seconds. A second thermocouple located midway between the coal sample and the wall of the reactor indicated a maximum temperature at that location in the gas phase of 80 °C. During the experiment of 20 seconds (per pass) as the coal structure is depolymerized and molecules formed, made possible in large yields by the catalyst, much of the liquid-size molecules with sufficient vapor pressure at 500 °C distill from the residual coal mass to be almost instantly quenched in the surrounding gas phase, which is at a temperature well below that required for extensive cracking of these molecules, thus leading to very low gas yields. Under

these conditions, in the first pass those easily-released units in the coal, which upon release yield HC gases, together with any HC gases formed by thermal cracking, constitute not more than about 8% by weight of the total products evolving from the residual coal in that pass (approximately 4% of the weight of the original coal). The additional gases formed following the first pass constitute an extremely small portion of the products evolving during the second pass (about an additional 1% of the weight of the original coal). Thus the results in Table I reveal a liquid yield of about 74% by weight of the coal, while limiting hydrocarbon gases to about 5% by weight of the coal.

A sample of the data obtained from experiments conducted in the continuous-flow tubular reactor are presented in Table II. The coal utilized in this experiment was also a Wyodak sub-bituminous coal. Gas-flow rates in this experiment indicated a solids (and products) residence time in the reactor of about 17 seconds. In the first pass of the solids through the reactor, about 56% of the coal, by weight, was converted to liquids and gases, with a ratio of liquids/HC gases of 8.3/1.0. Following removal of the liquids from the solids by extraction, these solids were fed to the tubular reactor for a second pass, under reactor conditions identical to the first pass. In the second pass, 37% of those solids (representing about 16% by weight of the original coal fed in the first pass) was converted, for a total combined conversion in the two passes of 72%. The ratio of liquids/HC gases in the second pass was about 14/1, and the overall ratio liquids/HC gases for the two passes was 9.5/1.0.

The mechanics of the liquids and solids in the continuous-flow system utilized in these experiments are different from those which obtain in the microreactor, leading to lower ratios of liquids to HC gases. However one can visualize a continuous-flow system which may give yields and product ratios approaching those observed in the microreactor system. It may be difficult to operate such a system configuration at a bench scale.

The liquid products obtained from reactions of the Wyodak coal in the microreactor in the presence of  $\text{MoS}_2$  or  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  catalyst were subjected to GC and FTIR analysis.

Gas chromatography on a 12-ft x 1/8-in column packed with 8% OV-17 on 100-120 mesh Chromosorb HP indicated that essentially all of the product components are distillable between ca 100-300 °C. The chromatogram consisted of well-resolved peaks corresponding to low-molecular weight cleavage products. The chemical compound types present were clarified by FTIR analysis of product films, using a Perkin-Elmer, 1600 Series FTIR Spectrometer. Figure 2 provides an example of FTIR spectra for the liquid products.

The spectrum indicates the presence of several types of functional groups and characteristic aromatic ring substitution patterns in components of the liquid product, as follows: phenolic (and possibly alcoholic and carboxylic acid) groups, (O-H stretching bands between  $3200-3650\text{ cm}^{-1}$ ; non-associated OH groups, sharp band near  $3640\text{ cm}^{-1}$ ; associated OH groups, broad band between  $3250-3450\text{ cm}^{-1}$ );  $\text{CH}_3$ ,  $\text{CH}_2$  and CH groups in alkyl substituents (or paraffins) and  $\text{CH}_2$  and CH groups in naphthenic rings (at least three C-H stretching bands in the  $2830-2980\text{ cm}^{-1}$  region); carbonyl groups in esters and possibly carboxylic acids ( $\text{C}=\text{O}$  stretching bands near  $1731$  and  $1767\text{ cm}^{-1}$ , due to aromatic and saturated esters, correspondingly); aromatic rings (breathing band near  $1602\text{ cm}^{-1}$ );  $\text{CH}_3$ ,  $\text{CH}_2$  and CH groups (C-H bending maxima between  $1340-1470\text{ cm}^{-1}$ ); phenolic and aryl etheric groups (C-O stretching bands in the  $1150-1310\text{ cm}^{-1}$  region); penta-substituted aromatic rings, viz., a single non-substituted aromatic hydrogen (weak C-H out-of-plane bending band at  $885\text{ cm}^{-1}$ ; low concentration); tetra- and penta-substituted aromatic rings, viz., 1 or 2 adjacent non-substituted aromatic hydrogens (C-H out-of-plane bending band near  $861\text{ cm}^{-1}$ ); tri- and tetra-substituted aromatic rings, viz., 2 or 3 adjacent non-substituted aromatic rings (C-H out-of-plane bending band at  $811\text{ cm}^{-1}$ ); ortho-disubstituted aromatic rings, viz., 4 adjacent non-substituted aromatic hydrogens (C-H out-of-plane medium-intensity bending band near  $767\text{ cm}^{-1}$  and a strong bending band at  $745\text{ cm}^{-1}$ , indicating relatively high concentration of this ring-substitution type); and monosubstituted aromatic rings, viz., 5 adjacent aromatic hydrogens (very weak band at  $697\text{ cm}^{-1}$ ; very low concentration of this ring-substitution type).

The molecular weight distribution of product components and more precise structural information are presently being sought by GC/MS.

TABLE I

Experimental Data from the Microreactor

Coal feed: Wyodak sub-bituminous, -200 mesh

Reactor temperature: 500 °C

Reactor pressure: 1500 psig

Time at reactor temperature: 20 seconds per pass

Catalyst:  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , impregnated from acetone solution

| <u>Run No.</u> | <u>Pass</u> | <u>Pass % Conv.<br/>Liquids +<br/>HC gases</u> | <u>Cum. Conv.<br/>Liquids +<br/>HC gases</u> | <u>Pass ratio<br/>Liq/HC gases</u> | <u>Cumulative ratio<br/>Liq./HC gases</u> |
|----------------|-------------|--|--|------------------------------------|---|
| 23-1           | 1st         | 50.0   | 50.0   | 10.6                               | 10.6                                      |
| 23-2           | 2nd         | 58.0   | 79.0   | 22.6                               | 15.0                                      |

TABLE II

Experimental Data from the Continuous Reactor

Coal feed: Wyodak sub-bituminous, -65, +100 mesh

Reactor temperature: 450 °C

Reactor pressure: 1500 psig

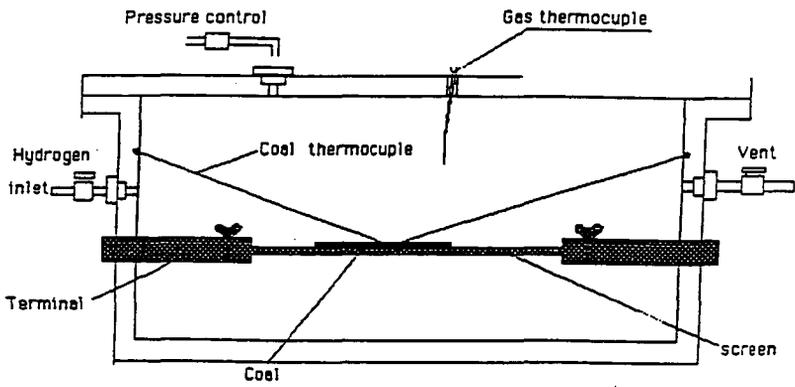
Gas flow velocity: 0.8 feet/sec

Catalyst:  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , impregnated from acetone solution

Material balance: 93%, based upon dmmf coal

| <u>Pass</u> | <u>Pass % Conversion<br/>Liq. + HC gases</u> | <u>Cumulative % Con.<br/>Liquids + gases</u> | <u>Pass ratio<br/>Liq/HC gases</u> | <u>Cumulative ratio<br/>Liq./HC gases</u> |
|-------------|--|--|------------------------------------|---|
| 1st         | 55.6 %                                       | 55.6 %                                       | 8.3                                | 8.3                                       |
| 2nd         | 37.2 %                                       | 72.7 %                                       | 13.7                               | 9.5                                       |

FIGURE 1  
The Micro-reactor



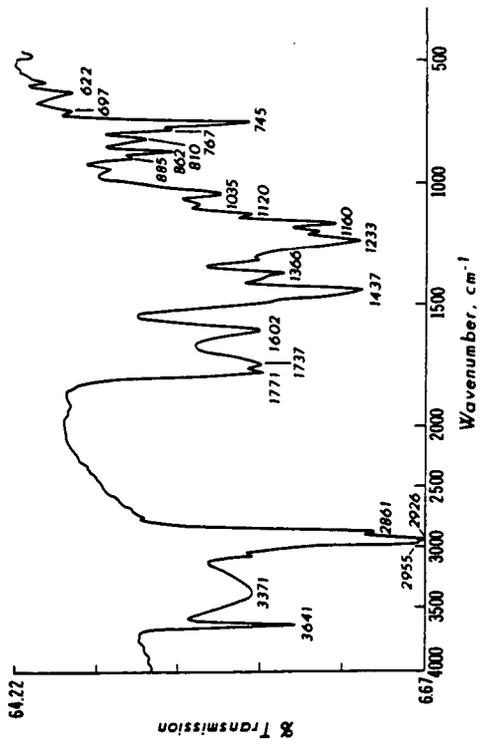


Fig. 2. FTIR Spectrum of Liquids from the Short Residence Time Procedure.