

TWO-STAGE COAL LIQUEFACTION WITHOUT GAS-PHASE HYDROGEN

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INTRODUCTION

Current two-stage direct coal liquefaction processes require the use of high-pressure purified hydrogen to hydrogenate either the solvent or a coal/solvent slurry. This paper describes techniques to eliminate the direct use of hydrogen gas in the solvent production and primary coal liquefaction stages. The approach employs the water-gas shift (WGS) reaction to generate liquefaction hydrogen-donor solvents at low temperatures and pressures in a catalytic solvent production stage, followed by reaction of the solvent with coal, in the absence of hydrogen, in a thermal primary liquefaction stage.

Previous researchers (1,2) have used mixtures of carbon monoxide and steam to convert coal in single-stage processes operated at high temperatures (380 to 475°C) and pressures (to 5000 psi). Although pilot tests with high-reactivity, low-rank coals achieved moderate conversions to benzene-soluble products, yields of distillate oils were low (3).

In an initial portion of this study it was proposed (4) that a significant improvement in coal liquefaction using CO/H₂O mixtures may be realized by separating, or staging, the WGS-solvent production and coal liquefaction reactions, allowing each to be performed at an optimum temperature. Results of thermodynamic calculations and preliminary experiments proved that use of low temperatures (<300°C) favors solvent hydrogenation via the WGS reaction, thus allowing the use of low pressure (500 psi). In contrast, high temperature kinetically favors the reactions involved in coal liquefaction--coal molecule bond rupture and transfer of hydrogen from donor solvent compounds to coal moieties. This paper describes the results of flow reactor experiments to produce a liquefaction solvent at space velocities comparable to actual processes, and use of this solvent to liquefy coal. Both of these steps have been accomplished without the use of hydrogen feed gas, and high conversions of a bituminous coal have been achieved.

EXPERIMENTAL

Two series of experiments, described briefly here and in more detail in the following sections, were performed. The first consisted of production of a coal liquefaction solvent, rich in hydroaromatics, via the WGS reaction in a catalytic flow reactor at low temperature and pressure. In the second set of experiments coal was thermally liquefied in batch microreactors without gas-phase hydrogen using the solvent produced in the flow reactor.

Materials

Feeds to the WGS-solvent production reactor consisted of carbon monoxide, deionized water and a nearly saturated mesitylene solution of polynuclear aromatic hydrocarbons (weight basis PAH's: 11.6% phenanthrene, 12.0% pyrene and 16.7% fluoranthene). Mesitylene was chosen as the solvent for the PAH's because of its relatively low vapor pressure (75 psi at 240° C), its ability to dissolve large amounts of PAH's at room temperature, and its stability under high temperature coal liquefaction conditions. Extrudates (0.8 mm diameter by 4 mm length) of Shell 324M, a 2.8 wt. % Ni, 12.4 wt. % Mo on alumina catalyst, were used in the WGS-solvent production reactor. Prior to use, the catalyst was presulfided, in-situ for six hours, with 10 mole % H₂S in H₂ at 385° C and atmospheric pressure.

Liquefaction reactions were performed with a bituminous coal, Illinois #6 (Burning Star Mine--proximate analysis: 3.7% moisture, 9.4% ash, 34.5% volatile and 52.4% fixed carbon; dry basis ultimate analysis: 72.5% C, 4.7% H, 1.0% N, 0.1% Cl, 2.9% S, 9.8% ash, and 9.0% O by difference; mineral matter content: 13.7%).

Apparatus and Procedure

WGS-solvent production was performed in a concurrent flow trickle-bed reactor consisting of six 1.0 cm ID by 15 cm long catalyst-filled stainless steel tubes connected in series. Each tube was filled with 10.5 g of catalyst. The reactor was contained in a forced-air convection oven thermostatted to ±1.0° C. Reactor pressure was controlled with a precision back-pressure regulator and gas and liquid products were sampled subsequent to pressure letdown. After pressurizing to 500 psig with CO, the reactor temperature was ramped to 240° C at 10° C/min and water flow was initiated. Upon detection of conversion of CO/H₂O to CO₂/H₂, PAH solution flow was started. Carbon monoxide, water and the PAH solution were delivered to the reactor at weight hourly space velocities of 0.124, 0.079, and 0.48 g-feed/hr/g-catalyst, respectively. For the WGS reaction, the amount of water delivered was one percent in excess of that required by stoichiometry to ensure that conversion was limited only by thermodynamic equilibrium. It was estimated from the reactor void volume and fluid flow rates that the residence time of the gas was two minutes and that of the liquid phase was approximately sixty minutes.

Prior to use for the liquefaction reactions, the solvent produced by the flow reactor was concentrated by nearly a factor of two by evaporation of mesitylene under vacuum. This higher concentration, which allowed the use of lower solvent to coal ratios for the liquefaction reactions, could be achieved because of the increased solubility of the hydroaromatics formed in the flow reactor.

Coal liquefaction reactions were performed in batch microautoclaves with slurry capacities of 8 cm³ and gas volumes 35 cm³ (5). Four reactors could be operated simultaneously. After the reactors were charged with coal and solvent, they were pressurized to 450 psig with nitrogen. They were then heated to 445° C for 36 min (time at temperature) in a fluidized sand bath while being agitated with a wrist-action shaker at 200 cycles/min. Following the heating

period, the reaction vessels were quenched in water, the final temperatures and pressures were recorded, a gas sample was taken, and the product slurry was quantitatively removed for analysis. All experimental variables for both the flow and batch reactors were monitored and recorded with a computer-controlled data acquisition system.

Four coal liquefaction reactions were performed. To test the impact of amount of donatable solvent hydrogen on coal conversion, three reactions were performed with WGS-produced solvent to coal ratios of 2:1, 3:1, and 4:1. A control experiment, without donatable hydrogen, was performed with a portion of the flow reactor PAH feed solution, which contained no hydroaromatics. The control experiment had a "solvent" to coal ratio of 3:1.

Product Analyses

On-line analyses for the partial pressures of CO and CO₂ in the gas stream from the flow reactor were performed with a Hewlett-Packard 5710A gas chromatograph. Prior to analysis, residual water vapor was eliminated from the gas sample with a cold trap. The partial pressure of hydrogen was obtained by the difference between the sum of the CO and CO₂ pressures and the sample pressure. Gas samples from the liquefaction reactions were analyzed for N₂, H₂, CO, CO₂, and C₁-C₄ hydrocarbons with a Carle series 500 gas chromatograph with a hydrogen transfer system.

The amounts of PAH's and hydroaromatics in the flow reactor feed and liquid product samples were determined with a Hewlett-Packard 5890 capillary column-equipped gas liquid chromatograph. Coupled gas chromatography/mass spectrometry techniques were used to identify the order of elution of the PAH's and hydrogenated PAH's.

Conversion of coal to products was quantified by tetrahydrofuran (THF) and n-heptane (C₇) solubility. Dry, mineral matter free (dmmf) basis conversions were calculated from the difference between the weight of organic coal and the insoluble organic matter resulting from THF or C₇ extraction of the product. In addition, the C₇ soluble materials, which contained the post-reaction solvent components, were examined by capillary column chromatography to determine the extent of dehydrogenation of solvent hydroaromatics.

RESULTS AND DISCUSSION

WGS Solvent Hydrogenation

The performance of the WGS-solvent production reactor can be evaluated in terms of conversion of CO/H₂O to CO₂/H₂, and the extent of hydrogenation of the PAH's.

From the gaseous product analyses, the conversion of CO/H₂O to CO₂/H₂ was observed to be 97%. This is significantly greater than the value of 92% calculated from the initial partial pressures of CO and steam and the pressure equilibrium constant (6) for 240^o C. The observed larger conversion results from removal of hydrogen due to hydrogenation of the PAH's, which causes an additional shift to

products. Thus, coupling the WGS and solvent hydrogenation reactions promotes efficiency for the WGS reaction.

The extent of hydrogenation of the PAH's can be seen in Figure 1, which shows a comparison of the chromatogram of the feed solution to that of the product. Analysis of the product solution showed that 31% of the phenanthrene, 49% of the pyrene and 92% of the fluoranthene were converted to hydroaromatics. From the amount and distribution of the hydroaromatics and the extent of the WGS reaction, it was calculated that 30% of the hydrogen generated was used to produce hydroaromatics. The liquid product was found to contain 0.52 wt. % donatable hydroaromatic hydrogen. The solvent for the coal liquefaction reactions, concentrated by removal of mesitylene from the flow reactor product, contained 0.87 wt. % donatable hydrogen, a high value by current process standards.

It is notable that almost complete conversion of fluoranthene to hydrofluoranthenes (primarily tetrahydrofluoranthene, which accounted for half of the donatable hydrogen) was achieved, while only half of the pyrene and a third of the phenanthrene were hydrogenated. For pyrene (Py), the limitation for conversion to dihydropyrene (H_2 Py) is a thermodynamic one. The equilibrium ratio of $[H_2Py]/[Py]$ may be calculated from the reactor outlet hydrogen partial pressure (155 psia) and the pressure equilibrium constant (7) at 240 °C, 0.0042/psia. The calculated value of 0.65 is in agreement with the observed value of 0.66, indicating that the concentration of dihydropyrene was limited by thermodynamics, rather than kinetics. The production of hydrophenanthrenes may also be thermodynamically limited, though no thermodynamic data are available for comparison. Although the WGS-solvent production reactor yielded high concentrations of hydroaromatics, previously reported work (7) indicates that even better performance can be achieved with a more active catalyst at lower temperatures, where formation of hydroaromatics is favored.

Coal Liquefaction

The effectiveness of the coal liquefaction reactions performed without gas phase hydrogen can be judged by the conversion of the coal to THF and C_1 soluble products, and to C_1 - C_4 hydrocarbons; by the amount of hydrogen transferred from hydroaromatic hydrogen donors to the coal; and by the percentage of hydrogen lost from the solvent to the gas phase.

Table 1 presents a summary of the results of the liquefaction experiments. As can be seen, the conversion of coal was dependent on solvent hydrogen availability. For the control experiment (No. 1), containing no donatable hydrogen, the THF and C_1 conversions were very low: 30% and 17%, respectively. However, all the experiments with WGS-produced solvent, containing hydroaromatics, yielded much higher conversions, which increased with increasing solvent to coal ratio. The 4:1 solvent to coal experiment (No. 4), resulted in the highest THF and C_1 conversions, 98% and 48%, respectively. The C_1 - C_4 hydrocarbon/gas make for the experiments with the WGS-produced solvent (Nos. 2-4) were low, nominally 3%.

The fate of the donatable hydroaromatic hydrogen in the solvent was determined from the amounts in the solvent before reaction with coal H_a , that remaining in the solvent after reaction with coal H_b , and that transferred to the gas phase H_g . The percentage donated to the coal H_c can be calculated by difference:

$$H_c = 100 \times \frac{H_b - H_a - H_g}{H_b} .$$

From the values for H_g in Table 2 it can be seen that the utilization of hydrogen was efficient, as only 10% of the donatable hydrogen was lost to the gas phase, the balance being donated to the coal or remaining with the solvent. It is also noted from the values of H_b that nearly all of the donatable hydrogen was depleted from the solvent. In fact, experiment No. 2 with a 2:1 solvent to coal ratio was clearly hydrogen starved, resulting in the lowest THF and C_7 conversions for the experiments with WGS-produced solvent. In contrast, experiment No. 4, with a solvent to coal ratio of 4:1 had sufficient donatable hydrogen to achieve high conversions, as evidenced by the 20% donatable hydrogen remaining after completion of the reaction.

PROCESS IMPLICATIONS

The results of the experiments presented in this paper clearly demonstrate that coal can be effectively liquified without the use of high-pressure purified hydrogen feed gas. This suggests that substantial economic improvements in direct coal liquefaction can be achieved. Figure 2 shows a schematic flow diagram for a two-stage liquefaction process proposed on the basis of these results. Notable differences between this and current two-stage processes are: 1) elimination of high-pressure purified hydrogen for solvent production; 2) use of low temperature in the solvent production reactor; 3) elimination of gas-phase hydrogen and high pressures in the thermal liquefaction reactor; and 4) selective recycle of solvent components (primarily PAH's). Use of this process would eliminate the requirements for a separate WGS reactor and gas separation units for hydrogen production, and high pressure equipment for solvent production and liquefaction reactors. Because these units account for approximately half of the estimated \$1.5 billion capital investment of a 50,000 barrel/day plant, this process would result in substantial savings in capital costs. Operating costs such as those for compression of gases would also be significantly lower.

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ACKNOWLEDGEMENT

This work supported by the U.S. Department of Energy at Sandia National Laboratories under Contract DE-AC04-76DP00789.

Figure 1. Comparison of high resolution gas liquid chromatograms of the flow reactor feed and product solutions.

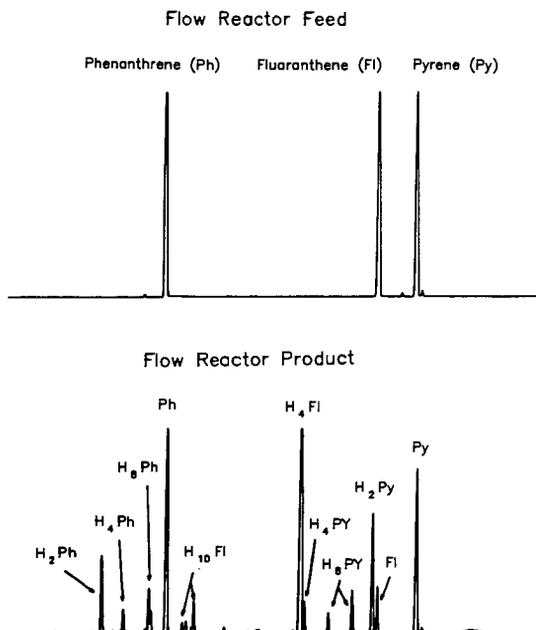


Figure 2. Schematic flow diagram for a two-stage liquefaction process via WGS-solvent production.

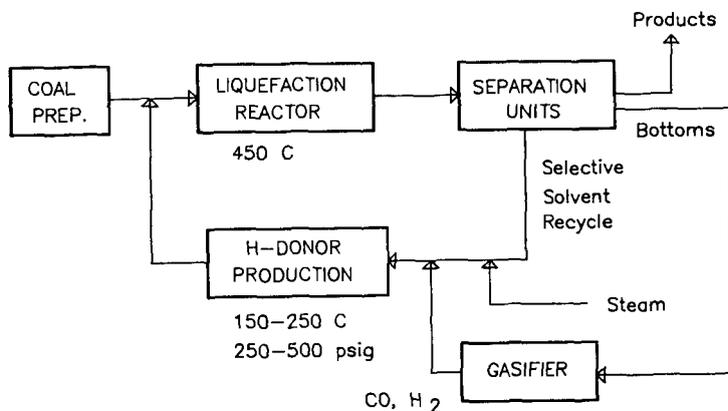


TABLE 1
Results of Coal Liquefaction Experiments^a

Exp. No.	Solvent: Coal	Conversions (% dmmf basis)			Solvent Hydrogen Balance (% donatable hydrogen)		
		THF	C ₇	C ₁ - C ₄	To Coal	To Gas	Remaining
1 ^b	3:1	30	17	1.6	--	--	--
2 ^c	2:1	91	21	2.9	90	9	1
3 ^c	3:1	97	42	3.1	84	11	5
4 ^c	4:1	98	48	3.1	69	11	20

- a) Reaction conditions for all experiments: 445 C, 36 min, 450 psig cold charge nitrogen. No gas-phase hydrogen used.
- b) Performed with flow reactor feed solution. PAH's only; no donatable solvent hydrogen.
- c) Performed with WGS-produced solvent.