COSTEAM LIQUEFACTION OF LIGNITE

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INTRODUCTION

COSTEAM is a process for liquefying lignite in the presence of added catalysts using synthesis gas as the reducing agent and the moisture in the coal as the source of hydrogen. This development has its roots in the early, largely ignored work of F. Fischer (1). This work was extended at the Bureau of Mines and brought to a point where it now appears to have commercial possibilities (2-5). L. Berg and his group at Montana State University have also reported on coal liquefaction using carbon monoxide (6,7).

The product formed in the early work was too viscous to be easily filtered or used as a vehicle oil for preparing pumpable lignite-oil slurries. The work described here had the objective of replacing the carbon monoxide with lower cost synthesis gas and finding operating conditions where the product is of sufficiently low viscosity to be used as a recycle oil and also be readily filtered.

EQUIPMENT AND PROCEDURES

The experimental work was conducted in a 300-ml stainless steel rocking autoclave. This autoclave required 0.4-0.5 hr to bring the temperature from 300°C, below which little reaction occurred, to the operating temperature. After the desired heating period agitation was stopped. No beneficial reaction was observed after agitation ceased. The reported reaction times do not include heating and cooling times. Product workup included decantation of the free water in the autoclave followed by filtration at about 95°C through a Buchner funnel. The residue was rinsed with benzene. This wash solution was collected separately and stripped free of solvent before adding to the hot filtrate. The conversion is 100% less the percent of residue on a dry, ash-free (maf) basis. The oil yield is the actual recovered yield, also on an maf basis, without correction for mechanical losses.

In experiments studying material balances, the autoclave was weighed on a bullion balance having a sensitivity of 50 mg. This enabled the weight, as well as volume of the gas charged to the autoclave and discharged from the autoclave, to be measured accurately. Material balances better than 98% were obtained.

Unless noted otherwise, North Dakota lignites were used in this work. The laboratory-grind material was prepared by ball milling under nitrogen and then storing under refrigeration until used. The laboratory lignite contained 33% water. The plant-grind material from the Beulah mine was partially dried in air, pulverized in a hammer mill under inert gas, and then put through a bull-ring mill, also under inert gas. Seventy percent of this material was minus 200 mesh. Composition: moisture, 15.4%; ash, 9.5%; Btu's/lb 8930 on an as-received basis. On an maf basis: H, 4.9%; C, 71.2%; N, 1.0%; S, 1.2%; O (by difference), 21.7%; Btu's/lb, 11,890.

The lignite used in most of this work was the laboratory preparation from the Beulah Mine, unless noted otherwise. Twelve grams of this material, on an mf (moisture-free) basis and 28 g of Reilly cut No. 4 anthracene oil were charged to the autoclave, unless noted otherwise.

RESULTS AND DISCUSSION

Effect of Gas Composition. A major change from earlier work in liquefying low rank coals with carbon monoxide and water was the replacement of the carbon monoxide with synthesis gas. This was done not only because of the lower cost of the synthesis gas but because hydrocracking occurs more in the presence of hydrogen than carbon monoxide. Although extensive cracking is not desirable, some is needed to reduce the molecular weight and viscosity of the product. The somewhat higher reactivity of carbon monoxide is counterbalanced by the lower cost of the synthesis gas and by the necessity to increase the extent of cracking sufficiently to obtain a liquid material.

A comparison of hydrogen and carbon monoxide for the hydrogenation of acetophenone (Table 1) shows that carbon monoxide is selective with respect to reduction of the carbonyl group, whereas hydrogen causes more cracking. The high activity of carbon monoxide for reducing carbonyl groups is believed to be the reason that low rank cials are liquefied more readily in the presence of carbon monoxide than hydrogen (1,2). Low rank coals not only contain more carbonyl groups than higher rank coals but also contain the alkaline materials that are converted to formates, the probable active reducing agents (8).

TABLE 1. Reduction of acetophenone

(100 g acetophenone, 25 g water, 5 g Na_2CO_3, 1000 psig initial pressure, 1 hr)

Temp, °C	Gas	Product composition, percent					
		$PhCOCH_3$	$PhCHOHCH_3$	C_6H_6	PhMe	PhEt	Styrene
300	CO	57	43	-	-	-	Trace
300	H_2	98.8	1.2	-	-	-	-
350	CO	55	40	.5	.2	1.6	1.8
350	H_2	92	1.7	3	.1	1.6	0.1
380	CO	54	27	3.2	1.8	6.0	2.0
380	H_2	61	2.3	8.6	5.2	10.5	0.4

Hydrogen becomes more effective in hydrogenating coal as the temperature is increased. The difference in behavior between carbon monoxide and hydrogen decreases as the temperature increases. Nevertheless the data in Table 2 show higher conversion with carbon monoxide at all temperatures, over the range of 375° to 425°C, despite the higher pressures used with hydrogen. The data in Table 2 were obtained in the absence of a solvent in order to keep the conversion low where the differences are large enough to be meaningful.

Table 3 shows quantitative data for the initial gas, product gas, gases consumed and gases generated during a typical run. The moles of carbon oxide gases recovered is slightly lower than the moles charged (98.5% of charged $CO + CO_2$). Experiments using pure hydrogen have shown that some CO_2 is split from the lignite during processing. Some CO_2 may have been lost as a result of reacting with alkaline ash components to form bicarbonates. Some CO may have been converted to methane by hydrogenation promoted by iron in the lignite.

TABLE 2. Effect of temperature on the relative effectiveness of carbon monoxide and hydrogen

(30 g Elkol Mine subbituminous coal, no solvent)

Gas	Water, ml	Pressure, psig Initial	Pressure, psig Maximum	Time, min	Temp, °C	Conversion, percent
CO	15	1500	4200	15	375	43
H_2	None	2500	5400	15	375	27
CO	30	1000	3970	30	400	60
H_2	None	2000	4670	30	400	40
CO	30	1000	4200	30	425	70
H_2	None	2000	4650	30	425	63

TABLE 3. Reducing gas balance

(10.65 g maf lignite, 28 g anthracene oil, 5.9 g H_2O, 0.87:1 H_2:CO, 30 ml autoclave, 0.46:1 weight ratio gas:coal-oil slurry, 4000 psig, 15 min at 450°C)

Gas in	Gas out	Difference
1900 psig	1760 psig	140 psig
1.034 std ft^3	1.010 std ft^3	0.024 std ft^3

Composition:

	Mole-pct	Gram	Mole-pct	Gram	Gram
H_2	46.73	1.23	47.36	1.22	0.01
CO	51.57	18.88	30.54	10.92	7.97
CO_2	0.10	0.06	19.10	10.73	-10.66[1]
C_1	-	-	1.90	.39	-0.39[1]
C_2	0.20	0.08	0.55	0.21	-0.31[1]
		20.25		23.49	

[1] A negative value indicates weight of gas produced.

Figure 1 shows that as the operating pressure increases it is possible to increase the concentration of hydrogen in synthesis gas and still obtain high conversions. Although 100% hydrogen gave poor results at 420°C in the pressure range investigated, an improvement in conversion was obtained at the higher pressures with relatively small percentages of carbon monoxide in the reducing gas. The high conversions were obtained by using an excess of gas and good agitation in the rocking autoclave. Under conditions where gas-liquid contact is poor, higher pressures are needed to obtain conversions near 90%. The addition of tetralin, a hydrogen donor, increased the conversion but the same improvement was also obtained by increasing the operating pressure a few hundred pounds. Because of the increase of hydrogen activity with temperature, the curves in Figure 1 would be expected to be flatter at higher temperatures and steeper at lower temperatures.

Effect of Temperature. Increasing the temperature causes an increase in gas consumption and a decrease in product viscosity (Figure 2). Based on our experience with recycle operation a viscosity of 50 centistokes (cs) at 60°C was chosen as an upper limit for a desirable product obtained using 12 g of lignite to 28 g anthracene oil. Using this viscosity criterion, Figure 2 indicates that at 3000 psig the minimum operating temperature is about 430°C.

In order to minimize the reaction time necessary for desirable viscosity, temperatures near 450°C are recommended. Table 4 shows that at constant reaction time the product viscosity continues to drop with increased operating temperature but that the oil yield drops significantly. At the shorter contact times possible at the higher temperatures, gas consumption also decreases. The consumption of carbon monoxide is relatively constant with temperature between 450° and 475°C. Most of the increase in gas use is due to greater consumption of hydrogen at the higher temperatures. A breakdown of the gas consumption in Table 4 shows that considerably more hydrogen is formed, via the water-gas shift reaction than is consumed in all but the highest temperature experiments.

TABLE 4. Effect of temperature and time (4000 psig)

Temp, °C	Time, min	Conversion, percent	Oil yield, percent	Kinematic viscosity, cs at 60°C	Gas used, ft^3 CO	Gas used, ft^3 H_2
450	15	96	62	39	.250	-.075[1]
460	15	94	43	36	.229	-.014[1]
475	15	94	42	28	.259	.019
450	3	94	56	52	.221	-.018[1]
460	3	92	53	48	.217	-.010[1]
475	3	94	50	44	.222	.031

[1] Minus figures indicate hydrogen formation.

Effect of Pressure. Table 5 suggests that the minimum operating pressure for obtaining a product of desirable viscosity is 3000 psig. Conversions of lignite are good at all of the conditions listed in Table 5 but the best oil yields and viscosities were obtained at the higher pressures. Gas consumption also increases with pressure. Surprisingly, the extent of cracking to C_1 to C_4 hydrocarbons does not appear to increase significantly with an increase in pressure from 3000 psig to 4000 psig. When the temperature is near 450° C, with about a 15 minutes reaction period, the percent of lignite converted to hydrocarbon gases is 7 to 8% (Table 6).

TABLE 5. Effect of operating pressure (1 hr reaction time)

Operating Temp, °C	Operating Pressure, psig	Conversion, percent	Oil yield, percent	Kinematic viscosity, at 60°C	Gas used, ft^3 CO + H_2
430	2000	95	52	79	.186
430	3000	96	55	53	.189
430	4000	98	62	39	.210
450	2000	85	44	76	.186
450	3000	93	54	45	.263
450	4000	96	55	36	.311
460	2000	87	39	73	.187
460	3000	94	48	42	.296
460	4000	94	52	31	.299

TABLE 6. Effect of operating variables on gas production

Temp, °C	Pressure, psig	Time hr	CH_4, gram	C_{2-4}, gram	Lignite gasified,[1] percent
400	3000	1	.15	.18	3.1
425	3000	1	.33	.28	5.7
450	3000	1	.66	.58	12.4
450	3000	.5	.43	.33	7.1
450	3000	.25	.42	.41	7.7
425	4000	1	.30	.29	5.5
450	4000	.5	.52	.37	8.4
450	4000	.25	.43	.34	7.2
450	4000	.05	.32	.25	5.3

[1] To C_1-C_4 hydrocarbons.

Recycle Operation. In order for a potential coal liquefaction process to have commercial possibilities, the product should be capable of being used as a recycle vehicle oil for preparing pumpable coal-oil slurries. In addition, the product oil must have sufficient reactivity or solvency power for coal so that conversions and product viscosities do not deteriorate with extended recycle operation. Table 7 shows that even at the borderline conditions of 3000 psig and 430°C, using fresh lignite, it was possible to use the product oil as solvent in 10 consecutive runs with no signs of inoperability. The initial run used anthracene oil as a solvent and the product from this first run had a kinematic viscosity near 50 centistokes at 60°C. The viscosity increased to 110 cs at 82°C by the completion of the eleventh run where over 90% of the vehicle oil was lignite derived. The viscosity appeared to have leveled and the product filtered readily at about 95°C.

The addition of a small amount of formic acid caused the product viscosity to remain lower. However, improvement in product viscosity can be obtained more inexpensively by modest increases in temperature and/or pressure.

Recycle operation using a sample of lignite that had been in storage about two years, under nitrogen, after being air dried and ball-milled in a drum sized mill showed poor behavior. By the eleventh run, the product was so viscous that it could barely be filtered and the yield of recovered oil was low. Despite the high viscosity of the product from this last run, a not unreasonable conversion of 78% was obtained.

An additional set of experiments was conducted to further evaluate laboratory versus large scale milling of lignite. The data in Table 8 show that if reasonable precautions are taken to prevent oxidation during milling, the pulverized lignite is acceptable as a COSTEAM feedstock. A comparison at two sets of conditions shows very little loss of activity of the plant-grind lignite. A small increase in viscosity and a small increase in gas consumption may have resulted from the air-drying step to which the lignite was subjected prior to grinding under inert gas. This lignite was tested about a month after grinding. The aged plant-grind lignite, however, gave a product of decidely greater viscosity and consumed more total gas. Because of the loss of activity during drying (2), it is recommended that the lignite be dried under inert gas, or if possible, the drying step omitted.

TABLE 7. Liquefaction of lignite using recycle oil

(1 hr 430°C, 1:1 synthesis gas, 3000 psig, H_2O:coal:oil ratio 9:30:70)

	Fresh laboratory-grind lignite[1]				Aged lignite[a]	
	11th Run	Average of 11 runs	11th Run	Average of 11 runs	11th Run	Average of 11 runs
Additive	-----1% HCOOH--------		--------None---------		Water to equal fresh lignite	
Conversion, %	87	90	87	90	78	85
Oil yield, %	55	54	54	56	29	34
Product:						
C	88.6	--	89.8	--	89.5	--
H	7.1	--	6.8	--	6.6	--
N	1.1	--	1.1	--	1.1	--
S	.13	--	.10	--	.12	--
O	3.0	--	3.2	--	2.6	--
Ash	.05	--	.03	--	.04	--
Kinematic viscosity,						
cs at 60°C	190	--	598	--	12,800	--
cs at 82°C	46.8	--	110	--	1,030	--
Btu/lb calcd.	17,056	--	16,886	--	16,906	11

[1] North Dakota lignite (Zap Mine, 29.5% H_2O, 9.0% ash). [a] North Dakota lignite (Beulah Mine, 20.3% H_2O, 7.3% ash), plant-grind.

TABLE 8. Effect of grinding method and lignite aging

(4000 psig, moisture adjusted to 5.9 g for 12 g mf lignite)

Grinding method	Time, hr	Temp, °C	Conversion, percent	Oil yield, percent	Kinematic viscosity, cs at 60°C	Gas used, ft^3 CO	Gas used, ft^3 H_2
Ball mill	.25	450	96	60	30	.223	-.015[1]
Ball mill	1.00	425	95	61	37	.246	.004
Plant-grind	.25	450	96	62	39	.250	-.075[1]
Plant-grind	1.00	425	95	63	39	.245	.003
Plant-grind[a]	1.00	425	96	60	45	.242	.108

[1] Minus figures indicate increase in gas. [a] Aged lignite, stored several years under N_2.

CONCLUSION

Autoclave work has established the feasibility of processing low rank coal, in the absence of added catalysts, to a low-sulfur, low-ash fuel oil, using synthesis gas and moisture in the coal as the source of hydrogen. Using oil yields, product viscosities, and gas consumption as criteria, operating values have been found which can be used as a starting point for larger scale continuous operation studies.

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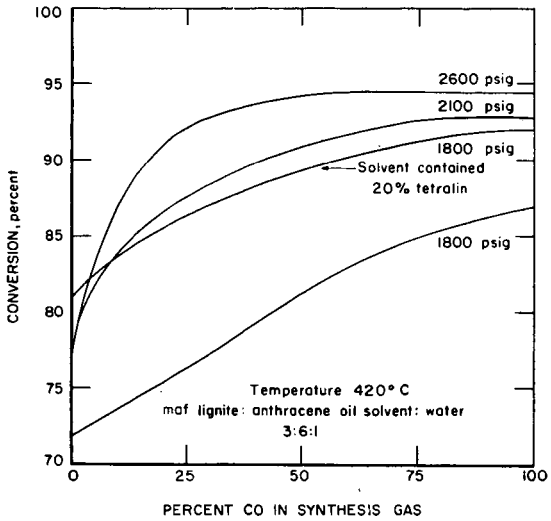

FIGURE 1- Liquefaction of lignite in autoclave at 420°C.

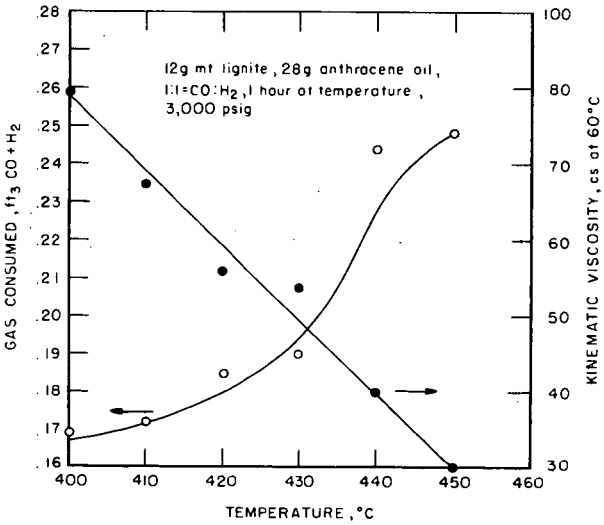

FIGURE 2- Effect of temperature on gas use and viscosity.

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