4. HYDROGENATION OF LIGNITE

Introduction

The use of hydrogenation as a means of converting lignite to more valuable products, such as liquid fuels or chemicals, deserves consideration as a method of utilizing this important natural resource. The information available on direct hydrogenation of lignite may be roughly classified into (a) data from commercial plant operation and laboratory experiments in Germany, (b) results from bench-scale and laboratory investigation at the Bruceton Station of the Bureau of Mines, and (c) operating results from Bureau of Mines demonstration plant programs at Louisiana, Mo. In addition, literature data are available on hydrogenation of tars obtained by the carbonization of lignite. An excellent bibliography on hydrogenation has been prepared and contains abstracts of literature and patents to 1950 (8).[1] It should be pointed out that the data available on industrial hydrogenation plant operation on German brown coal are not directly applicable to North Dakota or other American lignites, and therefore this information is only briefly summarized in this report, primarily to provide some background on plant design, process problems, and types of products. Considerably more information is presented on recent research developments that might provide some basis for rather speculative estimates of hydrogenation as a process tool in the future utilization of lignite.

Commercial Plant Operation

The process of hydrogenating coal to produce liquid fuels as practiced in Germany consists in pumping a mixture of about equal parts of dried powdered coal and recycle heavy oil, along with hydrogen, at about 200 to 700 atmospheres pressure into reactors maintained at 450° to 485° C. (liquid-phase hydrogenation). A small amount (0.1 to 1 percent by weight of the coal) of powdered catalyst is included in the coal-oil paste. During the reaction period of 1/2 to 3 hours, the coal-oil mixture is converted to a product oil (usually termed "middle oil") boiling below 325° C. and heavy oil, which is recycled to be mixed with coal and then fed to the plant. The middle oil is hydrogenated in one or more stages over fixed beds of catalyst particles and converted to gasoline. The process is described in greater detail by Gordon and a group of investigators (6). The ultimate analysis on a moisture- and ash-free basis of the coal utilized at the I.G. Farben.Leuna Plant is given in table 43, together with ultimate analyses of various American lignites and coals.

TABLE 43. - Ultimate analysis of coals on moisture- and ash-free basis

	County	State or country	Ultimate analysis, weight-percent				
			Hydrogen	Carbon	Nitrogen	Sulfur	Oxygen
Brown coal	-	Germany	5.4	71.2	0.8	4.3	18.3
Velva	Ward	North Dakota	4.5	70.2	1.0	.2	24.1
Beulah	Mercer	do.	4.4	69.5	1.0	.9	24.2
Arkansas	Manning	Arkansas	7.1	71.8	1.1	.9	19.1
Washington	Lewis	Washington	5.5	68.0	1.4	1.1	24.0
Rock Springs	Sheridan	Wyoming	5.3	78.0	1.6	1.0	14.1
Bruceton	Allegheny	Pennsylvania	5.4	82.8	1.6	1.0	9.2

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[1] Underlined numbers in parentheses refer to citations in the bibliography at the end of this section.

The yields, based on moisture- and ash-free coal, obtained from this coal by liquid-phase hydrogenation, were as follows:

	Pounds per 100 pounds of m.a.f. coal
Gasoline plus middle oil <325° C.	50.0
Hydrocarbon gas...	15.2
Oxides of carbon.......................................	10.6
Unconverted coal.......................................	1.5
Losses in solids removal...............................	8.5
Water, ammonia, H2S etc.	20.9
Hydrogen chemically absorbed...........................	6.7

The middle oil was converted to gasoline by further hydrogenation, and the overall yields, based on m.a.f. coal, were as follows:

	Pounds per 100 pounds of m.a.f. coal
Motor gasoline...........................	46.2
Hydrocarbon gases........................	19.3
Hydrogen chemically absorbed.............	9.1

The figures given for hydrogen consumption include only the hydrogen chemically combined, and additional hydrogen is required to make up for losses in gas streams and dissolved hydrogen in liquid products.

A comparison of brown coal and bituminous coal as hydrogenation plant feed is given in the Ministry of Fuel and Power report (2, p. 69). The brown coal produces about 25 percent less gasoline, causes higher oil losses in solids-removal processes owing to its higher ash content, requires more drying capacity owing to its higher as-mined moisture content, but requires about 15 percent less hydrogen. The effects of higher ash and moisture content in North Dakota lignites on hydrogenation yields have also been pointed out by Hirst and others (4), who estimate that 22,000 tons per day of run-of-mine lignite will be required for a plant producing 30,000 bbl. per day of liquid products, whereas only 11,800 tons per day of Rock Springs coal are needed. These values include coal required for hydrogen and power production. The costs of gasoline produced from these two coals are estimated to be almost the same if the lignite can be obtained for half of the cost of Rock Springs coal.

Laboratory Investigation

Considerable experimentation on hydrogenation of lignites in batch autoclaves and bench-scale hydrogenation units has been done at the Bruceton laboratories of the Bureau of Mines. This research has been directed toward the production of synthetic liquid fuels at lower cost through the development of improved catalysts, the study of process variables, the use of novel processing methods, and the utilization of byproducts.

The experimental procedures and methods of evaluation for batch autoclave hydrogenation have been given in detail (3, 7). Special precautions were exercised in the case of lignites, owing to the tendency of these coals to pick up or lose moisture. They were dried from a moisture content of 30 percent to an equilibrium moisture content of about 10 percent. Hydrogenation tests indicated no change in amenability to hydrogenation due to the drying process.

The product distribution obtained by the hydrogenation of several lignites and two bituminous coals in the absence of catalyst is given in table 44. The reaction time in all cases was 1 hour at 450° C. under an initial hydrogen pressure of 1,000

p.s.i.g. These conditions are less severe than those used in commercial plants; and, although conversions are therefore lower, the differences between coals are more evident. The lignites tend to produce considerably more carbon dioxide and water, and the North Dakota lignites show rather low total oil yields. The total oil has been separated into an oil fraction, soluble in n-hexane, and an asphaltene fraction, insoluble in n-hexane. Each of these fractions has rather similar ultimate analyses even from various coals. The average analyses for these two fractions are given in table 45, with an average analysis for gasoline prepared from coal.

Tables 46 to 49 present data on the effects of various catalysts on the hydrogenation of lignites at 450° C. and 1,000 p.s.i.g. initial hydrogen pressure. Beulah and Velva lignites still show lower oil yields than those obtained with Washington and Arkansas lignite. The effect of molybdenum catalyst in decreasing carbon dioxide production appears to be due to the conversion of some carbon dioxide to methane and water. The effect of temperature of hydrogenation on the product distribution is shown in table 50 for Beulah lignite. It can be seen that above 450° C., at the initial hydrogen pressure of 1,000 p.s.i.g., the gas yield is increased at the expense of oil production. The effect of initial hydrogen pressure on distribution of products obtained by hydrogenation of Beulah lignite is given in table 51. The data indicate that increasing hydrogen pressure causes a decrease in the formation of carbon dioxide, benzene insolubles, and asphaltenes. The amount of hexane-soluble oil increases, with some indication, due to increased hydrocarbon-gas production, that a maximum will be observed at higher pressures. The effects of temperature and pressure, shown for one lignite, are quite similar for most coals.

The tests discussed above were all at conditions not normally used for industrial coal hydrogenation. As previously mentioned, these conditions were selected primarily to show the effects of various catalysts and type of coal. In table 52 product distributions obtained by the hydrogenation of Rock Springs coal and Velva lignite at 4,000 p.s.i.g. initial hydrogen pressure are presented. The reaction time was 1 hour and the temperature 450° C. for both coals. We can see that, in the absence of catalyst, both coals produce approximately equal amounts of total benzene-soluble oil. However, the Rock Springs coal is particularly amenable to catalysis, producing over 70 percent oil with both iron and molybdenum catalyst. Velva lignite does not respond too well to iron catalyst, and only a moderate increase in oil yield is obtained with molybdenum catalyst. The lower carbon content and higher oxygen content of Velva lignite reduce the maximum potential oil yield, compared with that possible from Rock Springs coal. However, the larger amount of benzene-insoluble matter obtained with Velva lignite might be reduced by developing special and more active catalysts. The ultimate analyses of the total benzene-soluble oils obtained with both coals are given in table 53. Although the oils obtained in the absence of catalyst are quite similar, the oils obtained from Rock Springs coal in the presence of iron and molybdenum contain more hydrogen and thus indicate a greater extent of hydrogenation.

The autoclave studies indicate that, in general, the North Dakota lignites, owing to a larger production of carbon dioxide, water, and gaseous hydrocarbons, produce less oil by hydrogenation than that observed for other coals. In addition, catalysts that show good results with most coals do not perform as well when used with these lignites, as evidenced by the higher production of benzene-insolubles observed. These results might be due to the higher ash content of these lignites and the alkalinity of the ash, which has been shown by others to be deleterious to some hydrogenation catalysts. Possibly some pretreatment of these lignites might improve their amenability to hydrogenation. For example, mild thermal treatment of lignites will tend to remove some of the oxygen content as carbon dioxide and water, the residue having the ultimate analysis of a bituminous coal. This residue might be more amenable to hydrogenation. In addition, development of specific catalysts for these lignites is a definite possibility.

TABLE 44.—Product distribution, uncatalyzed hydrogenation for 1 hour reaction at 450°C, and 1,000 p.s.i.g. initial H₂ pressure

Coals	Benzene Insolubles	Yield, % M.A.F.						H₂ consumed, MAF %
		Benzene solubles		n-Hexane solubles	Gaseous hydrocarbons	CO_2	H_2O	
		Total oil	Asphaltene					
Velva lignite	44.81	22.10	7.7	14.40	13.20	11.3	11.20	2.58
Beulah lignite	51.12	19.24	8.06	11.18	11.15	10.35	10.32	2.36
Washington lignite	18.95	46.13	31.48	14.88	12.72	12.05	11.53	2.1
Arkansas lignite	13.80	50.40	23.60	26.80	14.60	12.00	13.72	4.46
Rock Springs coal	66.64	12.51	2.78	9.73	9.43	4.11	8.80	1.88
Bruceton coal	53.10	27.83	16.47	11.36	13.35	0.61	6.50	2.2

TABLE 45.—Ultimate compositions of asphaltene, n-hexane soluble oil and coal hydrogenation gasoline

	Hydrogen	Carbon	Percent		Oxygen
			Nitrogen	Sulfur	
Asphaltene	6.5	88.0	1.6	0.3	3.6
n-Hexane soluble oil	9.0	86.8	1.0	.2	3.0
Coal hydrogenation gasoline	11.8	88.0	.1	-	.1

TABLE 46.—Product distribution of uncatalyzed and catalyzed Arkansas lignite hydrogenation for 1 hour at 450°C, and initial hydrogen pressure of 1,000 p.s.i.g.

Arkansas lignite	Benzene Insolubles	Yield, % M.A.F.						H₂ consumed, MAF %
		Benzene solubles		n-Hexane solubles	Gaseous hydrocarbons	CO_2	H_2O	
		Total oil	Asphaltene					
Uncatalyzed	13.80	50.40	23.60	26.80	14.60	12.00	13.72	4.46
Neutralized 1/ and impregnated with 1% Mo	6.5	59.71	1.20	58.51	19.60	3.89	18.00	6.70
1% nickel, as NiCl₂	4.4	58.45	8.45	50.00	16.32	10.06	14.80	4.40
1% Sn + 0.5% NH₄Cl	7.2	55.25	17.75	37.50	18.75	8.30	14.50	4.75
1% Fe, as FeSO₄	10.00	53.75	27.50	28.25	16.25	10.80	10.0	3.90

1/ Neutralization (90%) was affected by adding 6.0 N. solution of H_2SO_4 to 1,000 gm. of coal.

TABLE 47.—Product distribution of uncatalyzed and catalyzed Washington lignite hydrogenation for 1 hour at 450°C. and initial hydrogen pressure of 1000 p.s.i.g.

Washington lignite	Yield, % M.A.F.							H_2 con-
	Benzene insolu-bles	Benzene solubles			Gaseous hydro-carbons	CO_2	H_2O	sumed, MAF %
		Total oil	Asphaltene	n-Hexane solubles				
Uncatalyzed	18.95	46.36	31.48	14.88	12.72	12.05	11.53	3.6
1% Mo (impregnated and neutralized)	7.30	53.06	1.00	52.06	15.07	5.61	16.58	6.9
1% Sn + 0.5% NH$_4$Cl	12.10	54.0	26.05	28.0	12.80	10.80	13.67	4.2

TABLE 48.—Product distribution of uncatalyzed and catalyzed Beulah lignite hydrogenation for 1 hour at 450°C. and initial hydrogen pressure of 1000 p.s.i.g.

Beulah lignite	Yield, % M. A. F.							H_2 con-
	Benzene insolu-bles	Benzene solubles			Gaseous hydro-carbons	CO_2	H_2O	sumed, MAF %
		Total oil	Asphaltene	n-Hexane solubles				
Uncatalyzed	51.12	19.24	8.06	11.18	11.15	10.35	10.32	2.58
Neutralized + 1% Ni (NiSO$_4$)	32.92	28.10	15.87	12.23	16.31	10.20	17.98	4.84
Neutralized + 1% Mo	18.34	46.54	12.80	33.74	14.40	6.70	19.52	5.80
Neutralized only	39.47	23.98	10.20	13.78	12.30	11.20	16.30	3.70
Un-neutralized: 1% Mo	27.13	37.50	14.7	22.80	17.63	7.50	16.25	5.30
1% Fe (impregnated)	29.02	27.03	19.00	8.03	21.20	13.92	13.22	4.1
1% Sn (SnCl$_2$)	25.00	44.84	22.68	22.16	11.21	12.83	13.43	4.73

TABLE 49.—Product distribution of uncatalyzed and catalyzed Velva lignite hydrogenation for 1 hour at 450°C. and initial hydrogen pressure of 1000 p.s.i.g.

Velva lignite	Yield, % M. A. F.							H_2 con-
	Benzene insolu-bles	Benzene solubles			Gaseous hydro-carbons	CO_2	H_2O	sumed, MAF %
		Total Oil	Asphaltene	n-Hexane solubles				
Uncatalyzed	44.8	22.10	7.7	14.40	13.20	11.3	11.20	22.10
1% Sn + 0.5% NH$_4$Cl	19.10	49.20	25.90	23.0	14.73	10.00	10.70	5.10

TABLE 50.—Effect of temperature on product distribution of catalyzed Beulah lignite hydrogenation for 1 hour, using Mo catalyst and initial hydrogen pressure of 1000 p.s.i.g.

Beulah lignite Temperature °C.	Benzene insolubles	Yield, % M. A. F.						H2 consumed, MAF %
		Total oil	Benzene solubles		Gaseous hydrocarbons	CO2	H2O	
			Asphaltene	n-Hexane solubles				
400	33.10	35.46	22.32	13.14	10.75	8.85	16.41	4.27
425	27.52	39.40	15.30	24.10	12.10	7.78	17.40	4.62
450	18.34	46.54	12.80	33.74	14.46	6.70	19.52	5.80
475	16.70	42.85	8.63	34.22	20.00	6.53	20.49	6.75

TABLE 51.—Effect of hydrogen pressure on product distribution of catalyzed Beulah lignite hydrogenation for 1 hour, using Mo catalyst at 450°C.

Beulah lignite Initial hydrogen pressure, p.s.i.g.	Benzene insolubles	Yield, % M. A. F.						H2 consumed, MAF %
		Total oil	Benzene solubles		Gaseous hydrocarbons	CO2	H2O	
			Asphaltene	n-Hexane solubles				
500	34.71	31.91	11.91	20.00	13.20	8.90	16.70	4.50
1000	18.34	46.54	12.80	33.74	14.46	6.70	19.52	5.8
1750	14.80	48.75	5.35	43.40	17.31	4.67	20.73	6.85
2500	14.94	47.8	2.00	45.8	19.1	3.39	22.68	7.60

TABLE 52.—Product distribution of hydrogenated coals at 4000 p.s.i.g. initial hydrogen pressure 1 hour reaction at 450°C. using various catalysts

Coal	Catalyst	Benzene insolubles	Yield, % M. A. F.						H2 consumed, MAF %
			Total oil	Benzene solubles		Gaseous hydrocarbons	CO2	H2O	
				Asphaltene	n-Hexane solubles				
Velva lignite	None	22.45	37.72	16.70	21.02	20.91	8.09	14.01	5.25
"	1% Fe as FeSO4	21.67	40.71	14.76	25.95	17.24	9.84	14.74	4.73
"	0.1% Mo	16.15	47.06	7.88	39.18	20.57	5.67	14.98	6.91
Rock Springs	None	40.42	39.70	20.77	18.93	7.32	4.78	10.82	3.04
"	1% Fe as FeSO4	4.23	73.15	45.48	27.67	14.79	2.60	9.29	5.30
"	0.1% Mo	2.70	74.61	5.88	68.73	13.57	.95	12.15	6.23

TABLE 53. - Ultimate compositions of total oils obtained from hydrogenation of Velva lignite and Rock Springs coal

Coal	Catalyst	Percent				
		Hydrogen	Carbon	Nitrogen	Sulfur	Oxygen
Velva lignite	Uncatalyzed	8.40	87.50	0.95	0.2	2.95
Do.	1% Fe as FeSO₄	8.20	87.57	.76	.1	3.37
Do.	0.1% Mo as ammonium molybdate	8.82	87.47	.73	.44	2.55
Rock Springs	Uncatalyzed	8.54	87.38	1.13	.17	2.77
Do.	1% Fe as FeSO₄	8.73	86.77	1.19	.10	3.21
Do.	0.1% Mo as ammonium molybdate	9.15	87.23	.92	.1	2.60

Thus far the standard coal-hydrogenation processes for converting lignites to oil have been considered. In addition, some experimental work has been completed on the low-pressure hydrogenation of lignite in a bench-scale fluidized reactor. The techniques used in this work have been previously described (1). The objective of this process was to convert about half of the lignite into hydrocarbon gas and oil, with the residue char used as fuel or for hydrogen or synthesis-gas production. The data are summarized in table 54 for the preliminary work completed at this time on North Dakota, Arkansas and Texas lignites. Although the yields of oil and gas are quite satisfactory, the quality of the oils, particularly those obtained from the North Dakota lignites, are poor. In addition, considerable engineering development must be undertaken to eliminate problems of coal agglomeration, hydrocarbon-gas recovery, coal feeding, and product-oil handling. This type of processing, although still only a laboratory development, does offer an additional prospect for the future of lignite processing by hydrogenation.

Demonstration-Plant Operations

At the Bureau of Mines Coal-Hydrogenation Plant in Louisiana, Mo., the high-pressure hydrogenation of Velva, N. Dak., lignite was investigated on a semiplant-scale unit. In an extended run from October to December 1953, 1,665 tons of raw lignite was processed in the liquid phase, yielding 120,000 gallons of vapor-phase charge stock and 30,000 gallons of heavy oils. Subsequently 90,000 gallons of the charge stock was converted in the single-step vapor-phase unit into 89,000 gallons of 83 (Research) octane motor gasoline.

Liquid-Phase Hydrogenation

Description of Coal

Velva lignite is found in the Coteau bed in the extreme southeastern corner of Ward County, N. Dak. The bed is 10 to 18 feet thick and comprises an area, indicated to be some 250 square miles, underlying parts of 8 or 9 townships (5). The coal processed was mined about 10 miles southwest of Velva, N. Dak., and was obtained through the cooperation of Truax Traer Coal Co., Chicago, Ill.

Analyses of the coal are given in table 55. Several objectionable characteristics already discussed under Laboratory Investigation were recognized as inherent in the Velva lignite. However, despite these characteristics, the abundance and availability at low cost justified investigation of semiplant-scale processing of the lignite.

TABLE 54. - Amounts and characterization of products obtained from hydrogenated lignites in fluidized bed

Run No.	Name	Press., p.s.i.g.	Temp., °C.	Yield, percent M.A.F. Organic solids	Oil	H_2O	CO_2	Gas	H_2 consumed M.A.F. percent	Asphalt, percent	Product oil properties Atomic H/C	H	C	N	S	O	Residue properties Atomic H/C	H	C	N	S	O	Ash
224	Velva	1,000	600	23.2	29.5	17.0	11.2	23.6	4.38	53.6	0.98	7.07	86.68	1.02	0.08	5.15	0.40	2.47	73.32	0.61	0.24	1.82	21.54
236	do.	500	600	29.7	25.6	19.3	11.9	22.1	4.76	58.8	.97	7.01	86.70	1.04	.05	5.20	.42	2.58	73.02	.65	.18	6.39	17.18
226	do.	250	600	38.8	18.7	11.0	11.0	18.8	3.90	36.9	1.00	7.24	87.00	0.78	.06	4.92	.43	2.86	79.31	.75	.15	2.78	14.15
260	do.	1/0	600	61.1	5.7	11.0	15.2	7.5									.36	2.41	81.19	1.22	.20	5.45	9.53
228	do.	1,000	500	40.6	22.4	19.0	10.8	14.5	4.00	63.4	1.05	7.44	84.95	1.02	.06	6.53	.61	3.93	76.86	1.10	.19	4.48	13.44
229	do.	500	500	47.8	14.1	18.5	11.8	15.2	3.72	52.9	1.08	7.69	85.81	0.94	.09	5.47	.58	3.73	77.24	1.07	.19	6.01	11.76
227	do.	250	500	55.2	8.5	16.5	12.1	12.8	2.85	37.3	1.21	8.49	84.13	.49	.10	6.79	.56	3.67	79.28	1.18	.26	5.23	10.38
246	Beulah	1,000	600	20.8	31.0	18.1	11.5	23.8	5.33	64.5	1.00	7.18	85.91	.92	.24	5.75	.45	2.40	64.56	.58	.93	.00	31.53
252	do.	500	600	31.3	23.0	18.5	13.0	20.0	4.40	58.1	1.01	7.16	85.46	.92	.32	6.14	.45	2.72	72.20	.63	.76	.33	23.36
250	do.	250	600	39.	14.8	18.4	14.0	18.8	3.84	41.8	1.13	8.03	85.19	.92	.25	5.61	.41	2.55	75.30	.70	.78	.89	19.78
259	do.	1/0	600	59.4	5.8	10.4	14.4	9.9									.36	2.35	77.94	1.10	.84	3.70	14.07
251	do.	1,000	500	34.6	24.8	17.2	13.5	13.5	4.06	69.8	1.04	7.29	84.47	.90	.30	7.04	.59	3.50	71.13	.89	.44	2.66	21.38
248	do.	500	500	44.7	17.3	17.3	13.0	13.1	3.39	48.8	1.11	7.70	83.38	.93	.29	7.70	.57	3.58	74.88	1.05	.37	3.15	16.97
249	do.	250	500	50.4	13.7	16.5	13.4	10.4	2.70	48.8	1.13	7.79	82.43	.82	.36	8.60	.56	3.54	76.17	1.02	.46	3.13	15.68
245	Texas	1,000	600	14.6	41.4	15.2	9.2	25.6	4.09	34.4	1.14	8.14	85.52	1.17	.51	4.65	.42	1.84	52.25	.65	.00	.00	45.26
240	do.	500	600	24.2	34.0	15.7	9.9	22.2	3.33	32.7	1.19	8.48	85.27	1.07	.55	4.63	.43	2.27	63.46	.88	.50	.00	32.89
242	do.	250	600	37.7	23.3	15.5	10.2	18.3		11.5							.43	2.53	70.26	.98	1.10	.68	24.45
258	do.	1/0	600	59.1	12.1	13.3	12.5	4.1									.39	2.45	74.56	1.47	.92	3.44	17.16
238	do.	1,000	500	36.7	31.7	15.9	9.0	13.3	2.08	45.1	1.21	8.54	84.49	1.14	.52	5.31	.58	3.25	67.51	1.31	.57	3.77	23.59
239	do.	500	500	40.6	27.2	14.5	9.7	13.1	1.72	22.2	1.26	8.81	84.23	1.01	.54	5.41	.56	3.25	69.30	1.49	.51	2.93	22.52
241	do.	250	500	48.7	15.5	15.5	10.4	15.7	1.78	11.7	1.36	9.48	83.78	.80	.80	5.14	.56	3.36	72.52	1.56	.66	2.33	19.57
230	Arkansas	1,000	600	15.6	47.4	16.0	6.9	18.3	3.43	19.1	1.33	9.46	85.35	.77	.28	4.14	.51	1.16	27.06	.34	.08	1.14	70.22
231	do.	500	600	23.2	36.2	16.9	6.9	20.9	3.37	12.9	1.38	9.84	85.71	.64	.28	3.53	.45	1.35	35.79	.53	.13	1.15	61.05
234	do.	250	600	29.6	28.4	16.4	6.8	17.4	3.17	9.9	1.44	10.24	85.61	.56	.26	3.23	.47	1.61	41.15	.59	.18	1.12	55.35
244	do.	125	600	33.5	29.2	15.7	6.4	17.4	2.08	7.9	1.51	10.75	85.32	.38	.33	3.22	.43	1.56	43.95	.65	.20	1.87	51.77
254	do.	25	600	40.0	24.0	14.9	7.0	15.4	1.53	9.1	1.46	10.41	85.60	.24	.30	3.45	.44	1.77	47.83	.68	.40	1.75	47.57
257	do.	1/0	600	44.7	21.7	14.5	7.7	12.0									.41	1.69	48.95	.99	.40	3.12	44.85
237	do.	1,000	500	26.2	42.6	13.2	6.2	10.5	2.38	17.6	1.39	9.84	85.14	.70	.16	4.16	.61	1.87	36.77	.67	.12	2.78	57.79
232	do.	500	500	33.9	32.9	15.5	6.6	14.7	2.44	12.9	1.46	10.32	84.65	.57	.31	4.15	.59	2.08	42.63	.82	.25	2.72	51.50
233	do.	250	500	39.1	25.5	15.5	6.5	11.1	2.40	6.9	1.48	10.47	85.04	.52	.29	3.68	.58	2.16	44.99	.91	.31	3.49	48.14
243	do.	125	500	44.4	26.6	13.5	6.1	11.7	1.37	5.5	1.51	10.75	85.32	.38	.33	3.22	.60	2.34	47.07	.97	.43	4.09	45.10
253	do.	25	500	47.2	22.3	13.1	6.6	12.9	1.28	7.1	1.53	10.84	84.85	.26	.39	3.66	.57	2.29	48.02	.96	.42	4.51	43.80

1/ In zero-pressure runs, helium was used as the fluidizing gas.

TABLE 55. - Coal analyses - Velva (N. Dak.) lignite

	As rec'd	M.a.f.		M.f.	M.a.f.
Proximate:			Ultimate:		
Moisture................	35.9	-	Carbon.................	63.0	70.6
Vol. matter.............	28.3	49.5	Hydrogen...............	4.2	4.7
Fixed carbon............	28.9	50.5	Nitrogen...............	1.1	1.2
Ash.....................	6.9	-	Sulfur.................	.7	.7
			Oxygen.................	20.2	22.8
Petrographic:[1]			Ash....................	10.8	-
Anthraxylon.............		61	C/H....................	15.0	15.0
Trans. attritus.........		27			
Opaque attritus.........		9	Alkalinity:		
Fusain..................		3	Grams H_2SO_4/Kg coal....	70.5	70.5

1/ Storch, H. H., Hirst, L. L., Fisher, C. H., and Sprunk, G. C., Hydrogenation and Liquefaction of Coals, Part I: Bureau of Mines Tech. Paper 662, 1941.

Processing

The liquid-phase process was essentially that for high pressure hydrogenation as practiced in Germany and briefly described under Commercial Plant Operation but incorporated American-designed equipment and instrumentation throughout. Operating conditions and yields typical of the liquid-phase operations on Velva lignite are presented in table 56 and analyses of pertinent process and product streams in table 57.

The high moisture content of this coal taxed the capacity of the grinding and drying equipment, designed for processing 8 to 10 tons per hour of low-moisture bituminous coals and from the beginning determined the rate of coal input to the hydrogenation unit. It was not possible to supply enough prepared coal for acceptable converter operations and to dry the coal to less than 8 to 10 percent moisture. A maximum drying rate of some 2.5 to 3.5 tons of "dry" coal per hour was attained by maintaining the temperature of the inert gas to the ball mill at 650° F., some 200° hotter than was required for normal operation on bituminous coals. The high moisture in the prepared coal did not present serious difficulties. Some foaming occurred in paste making, which was eliminated by reducing the paste oil temperature to 190° F.

The catalysts used were copperas, $FeSO_4 \cdot 7H_2O$, and copperas plus ammonium molybdate, $(NH_4)_2MoO_4$. The copperas was added dry to the wet coal before grinding and drying, and the ammonium molybdate was added as a powder to the dried coal at the paste-mixing tank in the quantities shown in table 56.

The yields as shown were good with both catalysts. Conversion to light oils, although low in percentage of the total organic coal substance, was of the order of 58 to 60 percent based on the coal carbon. Liquefaction was consistent with the amount, as indicated by petrographic analyses of relatively inert substances of the coal. Gasification was not excessive, considering that over one-third of of the gas produced was CO_2, which eliminates coal oxygen without consumption of hydrogen.

TABLE 56. - Operational and yield data - liquid-phase
processing of Velva lignite

	Period I	Period II
Operational:		
Pressure, p.s.i.:		
Inlet...	8,400	8,400
Outlet..	7,600	7,800
Conversion temperature........................°F. (average)	85.8	84.6
Coal, moisture-free.............................tons/day	58.9	50.8
Coal, moisture and ash free...................... do.	51.8	44.8
Coal, moisture and ash free.................lb./cu.ft./hr.	24.0	20.7
Paste..................................... do.	76.6	75.0
Paste.................................percent m.a.f. coal	31.7	27.6
Paste oil.......................... percent < 620° F.	13.7	12.2
Total gas to converters............cu.ft./lb. m.a.f. coal	85.2	106.7
H_2........................... percent by volume	83.4	81.9
Makeup H_2.......................cu.ft./lb. m.a.f. coal	18.8	21.8
Yields, weight-percent on m.a.f. coal:		
Total gases..	18.9	18.1
Hydrocarbon gases......................................	11.9	11.1
Light oils.......................... C_5 + to 620° F.	47.4	49.9
Benzene soluble heavy oils....................... >620° F.	15.0	13.5
Asphalts..	3.0	4.2
Coal liquefaction......................................	94.8	94.8
Oil yields, bbl./ton m.a.f. coal:		
LP gases...	0.6	0.5
Light oils...	2.9	3.1
Heavy oils (benzene-soluble)...........................	.8	.7
Total oils......................................	4.3	4.3
Space time yields, lb./c.f.h.:		
Light oils...	11.4	10.3
Heavy oils...	3.6	2.9
Hydrogen consumption, lb./lb. m.a.f. coal:		
Total H_2..	0.094	0.109
Reaction H_2...	.058	.059

TABLE 57. - Typical analyses of process streams and products -
liquid-phase hydrogenation of Velva lignite

	Catalyzed m.f. coal	Paste oil	H.O.L.D.	L.O.B.	Middle oil	Naphtha	Gasoline
Ultimate - wt.-percent:							
Ash......................	12.2	6.4	16.9	Nil	-	-	-
Carbon...................	61.8	82.7	73.4	88.2	86.7	82.8	84.2
Hydrogen.................	4.3	7.5	6.1	8.4	9.4	9.8	13.1
Nitrogen.................	0.9	0.9	0.8	0.8	0.9	0.8	0.3
Sulfur...................	0.8	0.5	1.3	0.03	0.05	0.04	0.1
Oxygen...................	20.0	2.0	1.5	2.6	2.9	6.5	2.3
C/H......................	14.3	11.0	12.0	10.5	9.2	8.5	6.4
Insoluble materials - wt.%:							
Benzene-insol.		8.5	22.6	Nil	-	-	-
Pet. ether-insol.		12.3	29.2	do.	-	-	-
Density:							
Sp. gr........ 60/60° F		1.126	1.274	1.056			
API.....................		-	-	-	10.8	16.4	48.5
Distillation - °F.:							
I.b.p.				570	313	209	122
10%.....................				658	532	350	178
30%.....................				685	565	412	217
50%.....................				708	582	443	245
70%.....................				742	596	473	273
90%.....................				-	614	513	313
E.p.				-	643	565	355
Recovery, percent:							
Total....................				81.2	98.2	98.3	97.6
At 500° F.					5	84	-
At 620° F.		12.9	13.0	4	93	-	-
Chemical analyses, percent:							
Tar acids...............					21.7	39.2	3.5
Tar bases...............					5.0	4.6	1.5
Olefins.................					19.8	12.7	20.8
Aromatics...............					46.9	30.0	16.3

Distribution in the hydrogenation products of the organic components of the lignite was as follows:

	Period I weight-percent	Period II weight-percent
Carbon:		
Gasification..................	16.0	15.1
Light oils[1]/.................	57.1	61.2
Total oils[1]/.................	77.4	78.3
Liquefied....................	93.4	93.4
Nitrogen: To NH_3	47.0	50.0
Sulfur: Organic S to H_2S......	53.3	36.1
Oxygen:		
To CO and CO_2...............	22.0	22.1
To water....................	63.8	64.8
Total elimination...........	85.6	86.9

1/ Includes tar acids and bases in the liquor.

The percentage of conversion of coal carbon to light plus heavy oil equaled that attained previously in bituminous-coal operations.

Performance of Equipment

In general, processing equipment performed well on lignite. Improved operation was obtained from nearly all the injection pumps. Stellite inserts were used successfully, for the first time, as valve seats. Packing replacements were low - only six during the entire run. The largest maintenance item on the injection pumps was replacement of ball-type valves. More than normal failure for these valves seemed to occur during the run.

No difficulties were encountered in operating the paste preheater. For the first time, no scaling or deposition of solids occurred in any tubes of this radiant-type heater. Better heat transfer was evinced by lower tube temperatures for the same heat load as for previous runs. Whether this good performance was due to characteristics of the coal and paste oil, better firing, or the low solids content of the paste (38 to 42 percent) was not ascertained.

Inability of the coal-preparation unit to furnish enough coal steadily for proper operation of the converters caused considerable difficulty. Hot-spot reactions developed several times, necessitating quenching of excessive temperatures with cooling gas and pasting oil. The sudden coolings caused small leaks in flange joints, which required lowering of the system pressure for sealing. As the run progressed, it became evident that solids had deposited in the converters, and the run was stopped to make corrective changes. As the coal-preparation plant was unable to handle the requisite quantities of lignite for proper operation of the converters, plans were made to reduce their internal diameter to suit the capacity of the coal-preparation plant.

Removal of solids from the heavy-oil letdown (H.O.L.D.) was more difficult than in previous operations. Apparently, either because of the character of the heavy oil and solids or because of a high rate of feed to the centrifuge, the efficiency of solids removal by centrifugation decreased appreciably. Low solids removal by centrifugation forced removal of the major portion of the solids made

by flash distillation - an operation accompanied by exorbitant oil losses, result-
ing in depletion of heavy oils by 30,000 gallons more than was made in hydrogenation.
The total oil loss incurred in removing solids was equivalent to 1.4 barrels per
ton of m.a.f. coal processed.

The pitch made in flash distillation was very viscous and sticky, and three
times during the operations the bottom head had to be removed to permit the lower
section of the flash drum to be cleaned. Improved flash nozzles performed well
with little or no trouble from the coking experienced in previous runs.

Vapor-Phase Hydrogenation

Conversion of the Velva lignite liquid-phase light oils into a good-grade motor
gasoline did not offer particular problems. These light oils responded to vapor-
phase hydrogenation similarly to light oils from hydrogenation of bituminous coals,
both in yields and quality of gasolines made.

Approximately 90,000 gallons of lignite light oils were processed during 10
days' operation in April 1953. Typical onstream operating conditions are presented
in table 58 and yields and analyses of pertinent streams in tables 59 and 60,
respectively.

The catalyst used was a pelleted fixed-bed-type German catalyst (2) designed
for one-step conversion and refining of coal-hydrogenation oils.

TABLE 58. - Typical operating conditions - vapor-phase
hydrogenation

Pressure, p.s.i.:	
Stall inlet.............................	10,000
Stall outlet............................	9,350
Converter temp., °F.:	
Average............................	892
Maximum............................	930
Feed injection:	
Gallons per hour......................	945
Lb./cu.ft./hr., total oil.............	72.1
Lb./cu.ft./hr. >375 °F.	64.9
Recycle, vol.-percent.................	51.8
Gas flows, cu.ft./lb. feed consumed:	
Feed injection gas....................	94.9
Cooling gas..........................	13.6
Total to stall.......................	108.5
H$_2$, percent........................	-
Makeup H$_2$ gas......................	10.6
Catalyst:	
Type................................	K-536
Volume, cu.ft.	100

TABLE 59. - <u>Typical yields - vapor-phase hydrogenation</u>

Yields based on total oil feed, wt.-percent:	
Gasification:	
Carbon monoxide, carbon dioxide..............	-0.8
Net hydrocarbon gases........................	5.3
Gasoline.....................................	38.4
Recycle bottoms..............................	55.1
Total oils...........................	93.5
Conversion of >375° oils, wt.-percent:	
Gasoline.....................................	33.5
Hydrocarbon gases............................	6.6
Total................................	40.1
Yields based on converted material, wt.-percent:	
Gasoline.....................................	83.5
Hydrocarbon gases............................	16.5
Yields based on feed consumed:	
Gasoline....................... wt.-percent	85.5
vol.-percent	102.6
Hydrocarbon gases....................wt.-percent	11.8
Space time yields, lb./cu.ft./hr.:	
Total gasoline...............................	28.6
Gasoline from > 375° F. feed.................	21.5
Reaction hydrogen based on feed consumed,	
wt.-percent........	4.0

TABLE 60. - <u>Typical analyses of feed and product streams - vapor-phase hydrogenation</u>

	Virgin feed	Feed blend	Recycle bottoms	Finished gasoline
Gravity-°A.P.I.	22.8	23.3	23.3	54.2
Distillation, °F.:				
I.b.p......................................	124	156	408	92
10..	202	382	432	136
30..	406	440	448	186
50..	496	472	472	227
70..	552	512	506	270
90..	628	580	574	324
E.P.......................................	666	630	642	392
Percent recovered.........................	-	97.5	98.0	98.0
Percent at 375° F.	25.0	9.0	0	-
Chemical analyses, vol.-percent:				
Tar acids.................................	24.8	12.6	2.4	0.8
Tar bases.................................	2.8	1.4	2.4	.8
Olefins...................................	20.8	11.5	4.5	3.3
Aromatics.................................	29.9	49.1	61.8	27.2
Ultimate analyses:				
Carbon....................................	85.4	86.9	88.4	86.3
Hydrogen..................................	10.6	10.9	10.8	13.4
Nitrogen..................................	.4	.3	.1	.02
Sulfur....................................	.4	.3	.3	.03
Oxygen (by diff.).........................	3.2	1.6	.4	.3
Octane number (clear):				
Motor method..............................				
Research..................................				83.0

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