PART I - OIL FROM COAL

PROCESSING, SYNTHETIC FUELS DEMONSTRATION PLANT, LOUISIANA, MO.

Coal-Hydrogenation Demonstration Plant

Since 1949 the plant has made nine extended liquid-phase and four vapor-phase runs and processed 15,000 tons of the five representative coals investigated. One vapor-phase and two liquid-phase runs were completed in 1952, and a third liquid-phase run was begun in November. Significant progress has been made in solving many mechanical and process problems and in obtaining, presenting, and analyzing engineering data representative of the hydrogenation of these coals and the resultant oils therefrom. The experience and data procured while processing Lake DeSmet, Wyo., and Pittsburgh-seam coals are presented, and outstanding features of the Illinois No. 6 and Western Kentucky coal process results are compared.

It should be reiterated that, throughout the report, the data presented refer to coal actually processed. Coal also was required to produce steam, power, and filtered water but is not included; the hydrogen was made from natural gas.

The bulk of the gasoline output continues to serve in military fleet tests, and a smaller portion provides fuel for the demonstration-plant vehicles.

Operations

The first operation was a liquid-phase run on northern Wyoming coal, followed by a combined vapor-phase operation in which the liquid-phase products of last year's Illinois No. 6 coal run and of the northern Wyoming coal were processed into specification gasoline. The next operation was liquid-phase hydrogenation of a high-volatile bituminous coal from western Pennsylvania. The last run in progress is liquefaction of a North Dakota lignite and will not be discussed in this report. For better understanding of the detailed run descriptions, reference to the general flow diagram (see fig. 2) should prove helpful.

Liquid-Phase Run 8 (Lake DeSmet Coal)

Interest has been shown in possible utilization of this high-moisture, high-ash subbituminous coal because of the extensiveness of the deposit and its availability at low cost. The coal was obtained from a new mine 30 miles south of Sheridan, Wyo.; analyses are given in table 1. This coal run was scheduled in the winter to further ascertain operability of the hydrogenation plant under severe weather conditions.

TABLE 1. - Analyses of Lake DeSmet, Wyo., and Pittsburgh, Pa., coals

Lake DeSmet, Wyo.

Proximate, percent

	M.f.[1]	M.a.f.[2]
Moisture	-	-
Volatile matter	42.8	47.9
Fixed carbon	46.5	52.1
Ash	10.7	-

Ultimate, percent

	As received	M.a.f.[2]
Moisture	29.3	-
Carbon	44.9	71.1
Hydrogen	3.3	5.2
Nitrogen	.8	1.3
Sulfur	.6	.9
Oxygen	13.5	21.5
Ash	7.6	-

Sieve analyses, mesh

Dry, pulverized coal	
Moisture	4.0
On 35	.3
Through 35 On 60	1.5
Through 60 On 100	5.8
Through 100 On 200	24.7
Through 200 On 230	12.1
Through 230	55.6

Pittsburgh, Pa.

	M.f.[1]	M.a.f.[2]
Moisture	-	-
Volatile matter	40.4	43.1
Fixed carbon	53.4	56.9
Ash	6.2	-

	As received	M.a.f.[2]
Moisture	2.6	-
Carbon	74.8	81.8
Hydrogen	5.1	5.6
Nitrogen	1.4	1.5
Sulfur	2.7	3.0
Oxygen	7.4	8.1
Ash	6.0	-

Moisture	1.2
On 35	1.0
Through 35 On 60	2.5
Through 60 On 100	6.5
Through 100 On 200	19.0
Through 200 On 230	16.0
Through 230	55.0

1/ Moisture-free.
2/ Moisture- and ash-free.

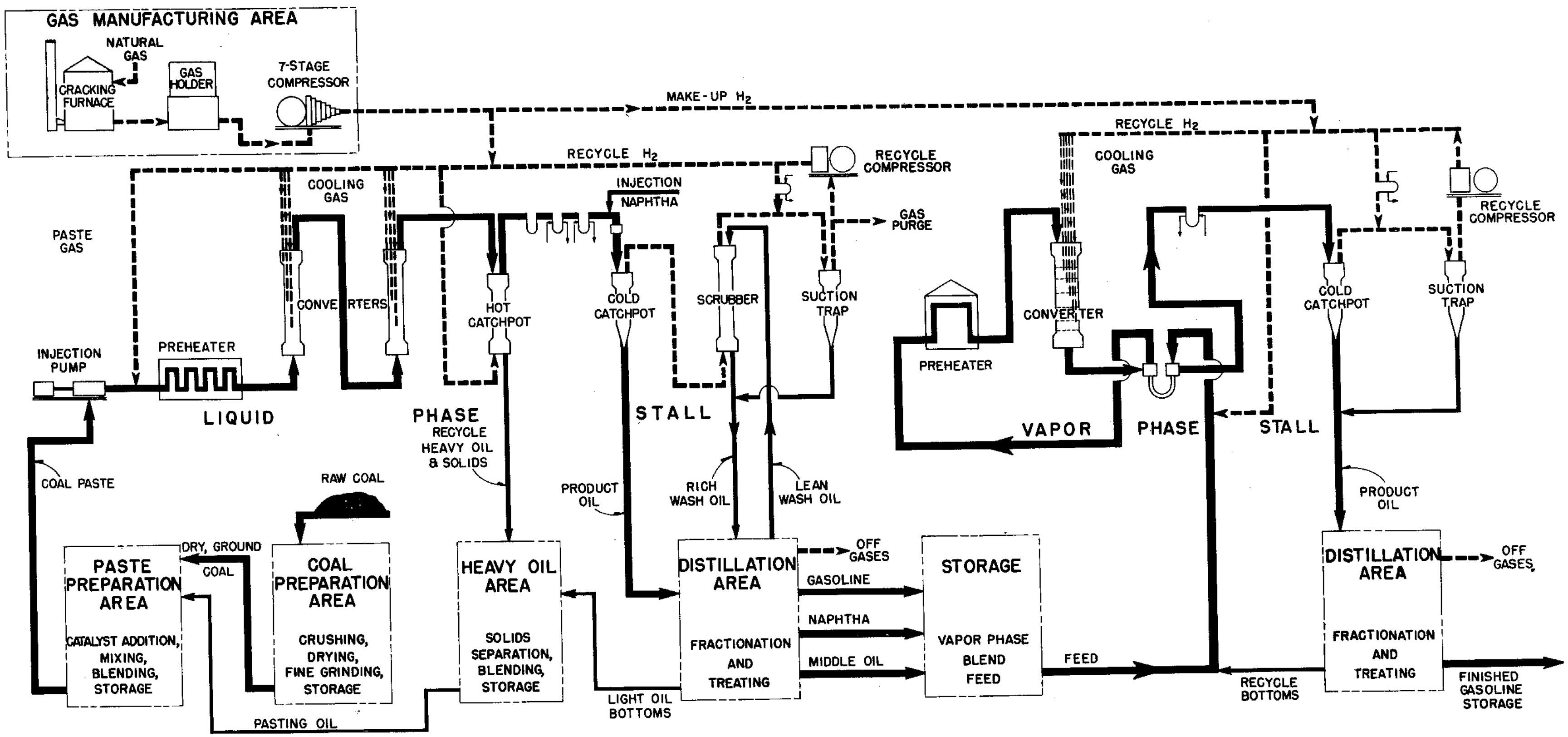

Figure 2. - Simplified flow diagram, liquid and vapor phase of hydrogenation.

Operation extended over 2 months and was divided into two parts. The first, lasting about 2 weeks, was exploratory because the coal differed radically from any previously processed. Following this, the plant was shut down to provide additional steam tracing for pipelines to enclose the control valves and to rearrange the coal-preparation dust tumbler so that it could be bypassed and the mill fan could discharge the off gas and steam directly to the atmosphere. The main portion of the run lasted 6 weeks, during which some 4,000 tons of raw coal was converted into 273,000 gallons of vapor-phase charging stock and 65,000 gallons of solids-free heavy oil. The coal was very reactive and hydrogenated readily. The coal-drying facilities were designed to process coals containing up to 10 percent moisture. This was a controlling factor, as maximum removal of moisture from raw coal containing 30 percent moisture limited plant throughput to 60 tons of moisture-free coal a day, even though the coal-drying plant was operated on a 24-hour schedule.

The performance of the high-pressure injection pumps, equipped with modified blocks and external valves, was exceptionally good throughout the entire run. The spring-loaded,outside-lubricated, chevron packing gave very good service.

Instruments and controls performed satisfactorily, except during extremely cold weather, when some of the instruments - particularly level controls - became inoperable and others required special attention to keep them operating. Atmospheric temperatures during over half of the run were low, going below 0° F. several days in succession.

The performance of exchangers and heaters was adequate throughout the run. A 1/4-inch-thick deposit of iron sulfide and coke was found in the last three banks in the paste preheater and was easily removed by burning with air, followed by mechanical cleaning.

No serious trouble was experienced with the high-pressure vessels, piping, or fittings. Some deposits of coke and solids were found in the converters; those in the first were hard and readily broken, while those in the second were soft and contained some oil.

The heavy-oil flash-distillation unit was operated except during the most extreme weather. The unheated bottom nozzle of the flash chamber was redesigned into a heated, truncated cone, so that the pitch flowed directly to the outlet nozzle. This arrangement was the best to date but required excessive attention to keep it in continuous operation.

The Bird horizontal centrifuge was unable to reduce the solids content of the filtrate below 15 percent. The German modified DeLaval centrifuge could operate only a short time before coarse particles plugged the concentrate nozzles. By operating both in series (the Bird removing the coarser particles), it was possible to reduce the solids in the filtrate to less than 10 percent when feeding straight heavy-oil let-down. The temporary pumping arrangement for the intermediate streams was inadequate for continuous operation, therefore this method of heavy-oil let-down clean-up was suspended.

Enough of the catalyst, copperas ($FeSO_4.7H_2O$), was added to give a catalyst concentration of 0.8 percent iron (as Fe). The catalyst was added dry at the inlet to the primary crusher - a procedure giving good results with this high-moisture coal. As in previous runs, the make-up hydrogen was produced by catalytically cracking natural gas with steam, followed by usual CO conversion to produce a make-up hydrogen stream with an average hydrogen content of 92 percent.

The converter temperatures (845°-855° F.) were the lowest for comparable liquefaction of any coal processed to date. Typical process conditions and yield data are given in tables 2 and 3 and analytical data on the streams in table 4. The data indicate that this coal hydrogenates readily to a high degree of liquefaction and a satisfactory yield of light oils with the moderate requirement of reaction hydrogen of 0.06 pound per pound of moisture- and ash-free coal. The carbon balance shows a recovery of 97.3 percent.

The hydrocarbon gasification (22.3 percent on light oils plus gasification and 14.4 percent on moisture- and ash-free coal) indicates that good yields of gasoline may be expected from this coal.

TABLE 2. - Typical liquid-phase processing and yield data, Lake DeSmet, Wyo., and Pittsburgh, Pa., coals

	Lake DeSmet, Wyo.	Pittsburgh, Pa.
Operational:		
Pressure, inlet .... p.s.i.[1/]	8,000	8,400
Pressure, outlet .... do.	7,500	7,800
Conversion temperature .... °F.	852	871
Coal, moisture-free .... ton/day	62.5	59.8
Coal, moisture- and ash-free .... do.	54.4	55.6
Do. .... lb./cu. ft./hr.	25.1	25.7
Paste .... do.	76.3	67.7
Do. .... percent m.a.f. coal	33.0	37.9
Paste oil .... percent $<$ 620° F.	13.0	13.0
Make-up H_2 .... cu. ft./lb. m.a.f. coal	20.7	21.4
Total gas to converter .... do.	82.3	88.0
H_2 .... percent in gas	79.5	81.9
Yields, percent on m.a.f. coal:		
Total gases	21.3	19.9
Hydrocarbon gas, C_4 and lighter	14.4	17.4
Light oils, C_5 plus	51.0	47.6
Heavy oil (benzene-soluble)	13.7	25.0
Liquefaction	98.0	95.1
Asphalt	6.6	4.8
Space-time yields, lb./cu. ft./hr.:		
Light oils (tar acids and tar bases)	12.82	12.25
Heavy oil (benzene-soluble)	3.43	6.43
Hydrocarbon gases, percent on light oil plus gases	22.3	27.1
Hydrogen consumption .... lb./lb. m.a.f. coal	0.11	0.105
Reaction H_2 .... do.	0.0605	0.0605
Carbon-balance closure	97.3	99.6

1/ Pounds per square inch.

TABLE 3. - Typical liquid-phase-yield data for Lake DeSmet, Wyo., and Pittsburgh, Pa., coals

	Lake DeSmet, Wyo.	Pittsburgh, Pa.
Oil yields, bbl./ton m.a.f. coal:		
LP-gases	0.59	0.82
Light oils, including tar acids and tar bases in liquor	3.06	2.91
Heavy oils (benzene-soluble)	.72	1.32
Total oils	4.37	5.05
Chemicals, lb./ton m.a.f. coal:		
Hydrogen sulfide	1.56	
Ammonia	9.65	
Tar acids:		
Phenol	18.4	
Cresol	37.8	
Xylenol	37.6	
Total	93.8	

Liquid-Phase Run 9 (Pittsburgh-Seam Coal)

This coal is representative of an abundant and widespread deposit of high-volatile bituminous coal in the Appalachian region. It has been used extensively in past years by the Research and Development Branch at Pittsburgh. The coal was obtained from a mine in the southern part of Washington County, Pa., as the coal from this area was particularly low in ash. The coal analyses are given in table 1.

After pressure testing of the unit, the new high-pressure paste-injection pumps were given a 2-week break-in test, using clean oil at full operating pressure. Following this, coal-paste injection was begun, and the coal concentration in the paste was increased from 15 to 30 percent, with converter temperatures of 850° to 860° F. After approximately 24 hours "on stream," it was necessary to shut down the coal-preparation plant owing to conveyor trouble. During shutting down an explosion occurred in the duct and cyclone system, which damaged the cyclones, duct work, and upper part of the building considerably. When the pulverized coal in storage was used up, the temperature in the high-pressure unit was reduced to about 400° F. and hydrogen circulation continued without oil or paste injection during the period required for repairing the damage.

When pulverized coal was again available, hydrogenation was resumed at normal rates and temperatures of 850° to 860° F. in the converters. Converter temperatures were raised during the progress of the run to a maximum of 890° F. to increase the liquefaction from 88 to 92 percent and lower the asphaltene content from 12 to 7 percent of the heavy-oil let-down. Because the moisture content of the coal was very low (3 percent), it was unnecessary to supply heat for drying while grinding the coal. This procedure was used for several days until rainy weather required addition of heat to dry the coal to less than 2 percent-moisture content to stop the foaming in the paste mixer.

The three new injection pumps operated quite satisfactorily in paste service, although some difficulty was experienced with leakage through gaskets used in the tongue-and-groove joints and suction-and-discharge valve assemblies.

Temperature measurements were satisfactory for good converter control; only 2 of 12 thermocouples became erratic during the entire run. Other instruments operated well, except for the usual difficulties with hydrogen gravity and purity instruments. The performance of all heaters and heat exchangers was good and the heat exchange of all units adequate.

TABLE 4. - Average analytical data, liquid-phase hydrogenation of Lake DeSmet, Wyo., and Pittsburgh, Pa., coals

	Coal paste	Paste oil	Heavy-oil let-down	Cold catchpot product	Gasoline	Naphtha	Middle oil	Flushing oil	Light-oil bottoms	Liquid-phase gasoline
				Lake DeSmet, Wyo.						
Distillation, °F.:										
I.B.P.		520	481	188	85	217	345	529	613	
10 .... percent at		613	620	266	112	351	469	585	652	
30 .... do.		652	685	435	143	375	510	605	676	
50 .... do.		677		594	169	386	528	614	698	
70 .... do.				637	199	400	552	625	730	
90 .... do.				-	285	440	587	650	-	
End point		690	688	752	337	485	617	680	756	
Recovery .... percent		51.8	33.9	88.6	94.1	98.9	98.7	98.5	79.7	
Gravity ....°A.P.I.	1.230	1.132	1.218	11.3	65.1	17.0	11.0	7.3	1.059	
Benzene insolubles ... wt. percent	42.46	6.82	19.73							
Pet. ether insolubles .... do.	44.97	10.72	28.74							
Tar acids .... do.					1.5	55.4	41.0			
Tar bases .... do.					1.7	.2	.04			
				Pittsburgh, Pa.						
Distillation, °F.:										
I.B.P.		538	525	173	100	220	415	415	623	107
10 .... percent at		629	642	264	130	387	503	503	654	171
30 .... do.		670		459	170	400	539	539	686	213
50 .... do.				599	200	418	559	559	712	238
70 .... do.				679	242	441	574	574	752	263
90 .... do.					336	474	596	596		299
End point		679	679	760	404	512	629	629	760	349
Recovery .... percent		32.8	22.4	87.0	96.5	98.9	99.0	99.0	74.8	98.1
Gravity .... °A.P.I.	1.224	1.127	1.237	12.1	58.8	18.5	11.7	11.7	1.056	51.5
Benzene insolubles ... wt. percent	45.41	6.85	17.73							
Pet. ether insolubles .... do.	47.83	12.24	27.78							
Tar acids .... do.				24.7	2.0	33.7	21.2	21.2		2.5
Tar bases .... do.				2.0	1.0	5.3	6.6	6.6		1.2

Inspection after the run disclosed only a thin deposit of scale on the tube walls of the coal-paste preheater. At the inlet end of the hot-catchpot overhead cooler, the first seven tubes contained an appreciable scale deposit, up to 1/8-inch in thickness, which appeared to be largely iron sulfate. The over-all performance of high-pressure vessels, piping, and fittings was good throughout the run.

After the shut-down, the converters were found to be relatively free of deposit; there was, however, some loose, granular material in the bottom of each converter, which was readily removed. During this run the new desanding system was used to purge solids from each converter periodically into the heavy-oil let-down line from the hot catchpot. Desanding with this pressure-differential system was continuous. Both the Bird-centrifuge and flash distillation were used almost continuously to remove solids from heavy oils. The quantity of solids to be removed was not as great as on some previous operations, owing to the lower ash content of the coal. However, high production of heavy-oil let-down (500 to 600 gallons per hour to maintain satisfactory converter velocity and let-down conditions) necessitated running both units. The Bird centrifuge was able to remove 25 to 30 percent of the solids; the balance of the requirement was removed by flash distillation. A water-cooled, metal belt conveyor to collect and remove the pitch facilitated handling a pitch containing 60 to 65 percent solids and substantially reduced the manpower requirements.

After about 5 weeks operation, the supply of coal on hand was exhausted. Approximately 2,250 tons of coal was converted into 240,000 gallons of vapor-phase charging stock, 116,000 gallons of solids-free heavy oils, and 7,000 gallons of slop oils. Typical operating and yield data are given in tables 2 and 3 and analytical data in table 4. This coal liquefies readily, with a high yield of total oil. The yield of hydrocarbon gases is somewhat high - 17.4 percent on the moisture- and ash-free coal and 27 percent on the light oil plus gasification - and the proportion of low-boiling materials to total oil was low under the processing conditions outlined. If other catalysts are used under the same pressure conditions in place of iron the ratio of light to heavy oils may be substantially altered in favor of the lighter oils, with little change in gasification.

Vapor-Phase Run 4 (Lake DeSmet and Illinois Oils)

Vapor-phase run 4 was made to process the light oils from liquid-phase hydrogenation of Lake DeSmet, Wyo., and Illinois No. 6-bed coals. Approximately 435,000 gallons of 76 to 77 octane, motor-method gasoline was produced during the run. In addition, 27,000 gallons of vapor-phase bottoms was set aside for wash oil. The yields ranged between 1.00 and 1.04 gallons of gasoline per gallon of feed consumed.

Approximately 75,000 gallons of gasoline and naphtha produced from Illinois No. 6 coal was withdrawn from the total Illinois stock for tar-acid extraction under a cooperative agreement. The neutral oil from the extraction was not returned to the plant in time for this run. As some of the light oils had been stored for a considerable period - 3 to 8 months - they were redistilled to remove high-boiling-point polymerized material and solids, which seriously interefere with catalyst life and heat-transfer conditions. Typical analyses of the charging stocks obtained from the Lake DeSmet and Illinois coals follow:

	Lake DeSmet	Illinois
Gravity .... °A.P.I.	16.6	18.4
A.S.T.M. distillation, °F.:		
I.B.P.1/	159	127
10 .... percent	309	246
20 .... do.	384	384
50 .... do.	472	506
90 .... do.	595	601
E.P.2/	633	628
Tar bases .... percent	3.4	2.4
Tar acids .... do.	37.6	22.6
Olefins .... do.	15.22	17.35
Aromatic hydrocarbons .... do.	30.29	41.37

1/ Initial boiling point.
2/ End point.

It will be noted that the tar-acid content of the Lake DeSmet charging stock is high (37.6 percent), although the total aromatic content of the oils from the two coals is approximately the same.

Early in the run, as a result of a short circuit in the feed-product exchanger, the flow of material through the preheater and converter virtually ceased, and the temperatures in catalyst beds 2 through 6 rose rapidly to over 1,200° F. before they were stopped by the addition of cooling gas. During the shut-down the converter was emptied for inspection of the catalyst and internal equipment. A small deposit of fine-grained, fluffy carbon was found on the catalyst in the first bed. The catalyst was screened to remove the fines produced from handling, before recharging. Approximately 1,200 pounds of new catalyst was added - 800 pounds in the sixth, and 400 pounds in the fifth bed - to make up a total weight of 4,450 pounds. The catalyst was activated according to standard operating procedure by passing hydrogen through the beds at 910° to 945° F. for 24 hours before injection of Lake DeSmet charging stock was resumed. When this stock was consumed, the Illinois oil was introduced without interruption of operations. It soon became apparent that higher temperatures were required to effect the desired conversion to gasoline. Accordingly, temperatures in the catalyst beds were slowly raised and leveled at 910° to 920° F. - about 20° F. higher than required for processing the Lake DeSmet oil.

On the eleventh day, after Illinois oil was charged, a small leak developed in a flange on the feed-product exchanger, which became very slight when the pressure was lowered from 10,000 to 9,000 pounds per square inch (p.s.i.). Therefore, the run was completed at this pressure, with little change in throughput or apparent change in quality of product.

During the last week on Illinois stock, withdrawal of approximately 27,000 gallons of distillation bottoms (recycle oil) for use as wash oil in liquid-phase operations changed the proportion of fresh-oil feed from 40 to 60 percent of the total. This radical change in feed stock did not have a noteworthy effect on the operations. Typical operating conditions and yields are given for the oils from the two coals in table 5, analytical data for the major streams in table 6, and analyses of finished gasoline in table 7. Carbon balances closed at 98.7 and 98.8, respectively, for the Lake DeSmet and Illinois operations. The reduction in tar acids was approximately 90 percent, comparable with operations of earlier runs reported in 1950 and 1951 Annual Reports.

TABLE 5. - Typical operating conditions and yields; vapor-phase processing of light oils from Lake DeSmet and Illinois No. 6 coals

	Lake DeSmet	Illinois
Pressure ... p.s.i.g.	9,700	9,800
Converter temperatures, °F.:		
Average middle of catalyst beds ...	889	910
Average bottom of catalyst beds ...	898	920
Catalyst ...	Zn-Cr-Mo	Zn-Cr-Mo
Feed, gal./day:		
Injection ...	24,560	26,150
Virgin ...	10,830	11,320
Recycle ...	13,730	14,830
Recycle to total feed ... volume percent	55.9	56.7
Gas flows, M cu. ft./day:		
Make-up hydrogen gas ...	950	1,237
Total gas to stall ...	9,130	9,135
Purge gas ...	0	0
Products from hydrogenation, gal./day:		
Catchpot liquid ... net	24,920	26,150
Gasoline ...	11,080	11,270
Wash oil ...	0	0
Bottoms ...	13,840	14,880
Stabilized gasoline ... bbl./bbl. virgin feed consumed	1.03	1.00
Gasification (C_4 and lighter):		
M cu. ft./day ...	105	151
Weight percent on feed consumed ...	10.2	15.1
Space-time rate:		
Virgin feed ... lb./cu. ft. catalyst/hr.	35.3	37.0
Gasoline produced ... do.	29.5	29.8
Reaction hydrogen ... weight percent on virgin feed	4.2	5.2
Carbon-balance closure ... percent	98.7	98.8

TABLE 6. - Typical analytical data of major stream-vapor-phase hydrogenation of light oils from Lake DeSmet and Illinois No. 6 coals

	Feed		Products					
	Total		Cold catchpot		Raw gasoline		Bottoms	
	Lake DeSmet	Illinois	Lake DeSmet	Illinois	Lake DeSmet	Illinois	Lake DeSmet	Illinois
Distillation, °F.:								
I.B.P	205	156	144	131	90	87	371	376
5 .... percent	313	282	191	178	121	111	390	395
10 .... do.	361	369	229	213	147	134	402	407
20 .... do.	393	410	284	272	183	167	411	419
50 .... do.	444	471	392	402	241	230	440	455
90 .... do.	567	583	526	544	321	324	548	561
E.P....................	623	628	594	606	357	362	619	628
Recovery ...... percent	98.0	98.0	98.0	98.0	97.0	95.0	99.0	98
Gravity .... °A.P.I.	21.5	20.1	31.2	29.4	50.7	53.9	23.6	21.3
Tar acids	17.9	11.2	5.7	3.3	4.4	3.3	6.0	3.4
Tar bases	2.1	1.9	.7	.9	1.1	1.6	.7	.7
Aromatic hydrocarbons..	45.3	53.1	-	-	-	-	56.3	67.5

TABLE 7. - Analysis of finished gasoline

	Illinois No. 6	Lake DeSmet
Octane rating .... motor method	76.5	76.2
Vapor pressure .... p.s.i.	9.0	10.5
Gravity .... A.P.I.	54.2	52.2
Sulfur content .... percent	0.036	0.026
Doctor test	Negative	Negative
Corrosion, copper strip	do.	Do.
Existent gum .... mg./100 ml.	1.2	3.0
Oxygen stability .... minutes	-	-
Aromatics .... percent	27.9	28.6
Olefins .... do.	4.0	3.0
Distillation, °F.:		
10 .... percent at	129	138
50 .... do.	218	235
90 .... do.	327	317
Residue .... percent	0.5	0.5

In general, the mechanical equipment performed satisfactorily. The performance of the high-pressure injection pumps was good, and their maintenance was almost routine. The new compound-cylinder-design high-pressure pump was used for water injection. The original ball-type valves were a constant source of trouble and were replaced with mushroom-type valves. The aluminum-clad asbestos gaskets on the valve covers and connections would not hold and were replaced with solid aluminum, which remained tight, and the pump was used without interruption during the last 3 weeks of the run. The spring-loaded, lubricated packing assemblies on the fluid ends of the high-pressure injection pumps virtually eliminated wear on the plungers and packings.

The flow through the revised feed-product exchanger was found to be uneven, resulting in poor heat transfer and erratic outlet temperature. After 9 days on stream, an inner tube in one of the outside banks pulled out of the packing gland and short-circuited the flow. As previously noted, most of the feed bypassed the converter, forcing a shut-down. After this critical situation had been studied, the flow through the feed side was rerouted so that all of the liquid and not over 15 percent of the injection gas passed through one bank and the remainder of the gas through the other banks. The hot gas and vapors from the converter were left free to seek their own path. This rearrangement was satisfactory, heating the combined gas-oil feed about 250° F. higher than the original design and substantially reducing the load on the preheater, bringing it well within the design conditions. Inspection after the run showed the tubes to be clean, and there was no evidence of coke, as in previous operations.

Instrument performance was satisfactory. The newly installed high-speed recorder for measuring catalyst-bed temperatures works well. The full instrument control of catalyst-bed temperatures in earlier runs had not been entirely satisfactory because temperature changes in one bed affected those in the succeeding beds, resulting in overcontrol. Holding the feed-flow rate and temperature constant and adjusting the flow of cooling gas manually to obtain the desired temperature almost completely eliminated the fluctuations prevalent in former operations. The control points of the instruments were set about 10° F. above the operating temperatures to guard against excessive rises.