

Fischer-Tropsch Synthesis and Distillation

Synthesis Run 2

The second synthesis run was described in the 1951 Annual Report. The run was followed by a rerunning operation to produce specification-grade Diesel oil and a reforming operation in the Perco catalytic conversion unit to upgrade the synthesis gasoline. Following these operations, essential revisions were made in equipment, piping, and instrumentation; it was hoped that they would improve operation of the synthesis and distillation units of the Gas-Synthesis Demonstration Plant.

During the second synthesis run, a large portion of the synthesis condensate was fractionated as it was produced into gasoline, Diesel oil, cracking stock, and coolant-oil fractions. At the end of the synthesis operation, an appreciable quantity of synthesis condensate remained to be fractionated. The primary fractionating unit was operated separately during the early winter, and about 7,500 gallons of synthesis condensate was processed to yield the product fractions mentioned above. This operation was conducted specifically to produce a Diesel oil meeting current military specifications. About 800 gallons of Diesel oil was recovered, but this product did not meet the specifications, because the initial boiling point, flash point, and corrosion were below standard. The products were reprocessed by treating with caustic alkali solution and redistillation. The material obtained after this treatment met the chemical and physical requirements of a Class 1 Diesel oil of military specifications - MIL-D-896. The characteristics of the synthetic Diesel oil were as follows:

Characteristics of synthetic Diesel oil

	<u>Product</u>	<u>Specification requirement</u>
Cetane rating	60.0	50
Flash point	196	140 minimum
Pour point	-5	0 maximum
Viscosity at 100° F. centistokes	2.44	2.1-6.0
Carbon residue on 10 percent residuum	0.06	0.20 maximum
Sulfur	0.021	1.25 Do.
Color, N.P.A.	1.75	5 Do.
Corrosion (3 hours at 212° F.)	Negative	Pass
A.P.I. gravity at 60° F.	43.8	-
Distillation, °F.:		
I.B.P.	298	-
5	458	-
10	462	-
20	470	-
50	490	-
70	504	-
90	528	675° F. maximum
E.P.	578	725° F. Do.

To test the utility of this Diesel oil in commercial operations, a cooperative agreement was negotiated between the Pond Creek Pocahontas Co. and the Bureau of Mines. This company will test the synthetic Diesel oil in a Diesel-engine-powered mine locomotive, and several barrels of the synthetic fuel have been supplied for this purpose.

The debutanized gasoline was subjected to a catalytic reforming treatment over a bauxite catalyst in the Perco catalytic conversion unit. Approximately 9,000 gallons of the debutanized gasoline was processed at a catalyst temperature of 710° to 720° F. About 7,600 gallons of product, plus 400 gallons of heavy polymer, was recovered. Test data of the charge material and product are:

Perco-treated synthetic gasoline

	<u>Charge</u>	<u>Product</u>
Gravity	66.5	67.5
Reid vapor pressure	7.6	6.8
Distillation, °F.:		
I.B.P.	91	97
10	126	133
20	150	156
50	224	226
70	273	277
90	335	345
End point	407	400
Octane numbers:		
Research, clear	61.5	70.2
+1	72.0	80.0
+3	82.6	86.4
<u>1/</u> Pounds per square inch gage.		

Higher octane ratings are desirable. In this initial operation of the Perco catalytic reforming unit, the reforming operation was conducted at 710° to 720° F.; a temperature of 750° or 800° F. might have been more beneficial. This operation demonstrated the need for additional insulation on the pipeline between the feed heater and the Perco reactors, and this was installed later. In general, the operation was fairly smooth, with only minor mechanical troubles with the feed pumps.

In operating any new processing unit, it is not unusual for mechanical troubles to develop, and it was not unexpected when some of the equipment in the synthesis and distillation units of the Gas-Synthesis Demonstration Plant did not function properly. At the end of the second synthesis run, the functioning of all units of the plant was carefully analyzed, and recommendations were made for improvements in equipment, piping, and instrumentation for better operation and control.

In the Synthesis Section, the coolant oil-circulation pumps are very important to successful operation. They must maintain a continuous, uniform flow of coolant oil through the reactor, so that the heat of reaction will be removed and uniform temperatures maintained. The pumps are provided with double-ring mechanical seals. For best operation, these seals must be provided with an uninterrupted supply of a proper oil, which cools and lubricates the moving parts of the seal assembly. The oil must be supplied at a pressure above the working pressure of the pump, so that there will be no backflow of the material being pumped into the seal. To supply this oil for the mechanical seals, a separate pressure unit, complete with reservoirs, cooling coil, gear pump, and relief valve, is employed. During the second synthesis run some malfunctioning of the mechanical seals was experienced, most of which could be traced directly to wide pressure fluctuations in the seal oil-system. To correct this condition, an auxiliary electric motor-driven gear pump and relief valve were installed. It was believed that these additions to the system would reduce difficulties to a minimum.

The centrifugal separators, for separating coolant oil from the gas stream after the synthesis reactor and for separating synthesis condensate from the gas stream after the heat exchangers and condenser, have been designed for higher gas flows and did not achieve the desired separations at the gas-flow rates employed. First, the separators were modified by installation of smaller throats, so that proper velocities for separation would be obtained, and as the separations actually attained were still unsatisfactory the separators were replaced before the third synthesis run was begun. A new combination baffle and centrifugal-type separator now separates the coolant oil from the gas stream, and a baffle-type separator removes the synthesis condensate from the gas.

Cold-weather operation clearly demonstrated the need for additional insulation and steam tracing on pipelines carrying coolant oil, synthesis condensate, and aqueous condensate. The functioning of some instruments, particularly liquid-level controllers and gage glasses, was improved when steam tracing and insulation were added. The functioning of some flow controllers can be improved by installing differential-pressure transmitters (DP-cells), and recommendations have been made for using such instruments in certain specified locations.

In the distillation unit of the plant, functioning of the primary fractionating unit, the absorbers, and the debutanizer system left much to be desired. These units depended on each other, and an upset in one unit was reflected in the others. Several changes in piping and instrumentation were made to correct this situation: These changes included connecting the coolant oil and synthesis-condensate flash tanks in parallel to permit measurement of the condensate alternately in each; installation of a return pump for automatic removal of condensate from the inlet of the absorption-system compressor; increasing the size of the vapor connections and pipeline from the Diesel-oil stripper to the primary column; installation of a cracking-stock recycle line between the cracking-stock stripper and the primary column; installation of steam-driven transfer pumps for synthesis condensate and debutanized gasoline; steam-tracing of some process lines; and adding extra insulation to other process lines. None of these constituted a major change, but all were necessary for improved operation.

Synthesis Run 3

After the changes indicated were completed, preparations were made for the third synthesis run, which was carried on during May and June 1952. (See figs. 16 and 17 for diagrams of the synthesis unit and of the revised distillation unit, respectively.) The second synthesis run had shown that $H_2 + CO$ conversions better than 80 percent could be maintained over an extended period. It was an objective to improve these conversions, if possible, striving for near 90-percent conversions without serious deterioration of catalyst or use of excessively high operating temperatures.

After the synthesis converter was charged with 13,204 pounds of reduced fused synthesis catalyst and the system filled with coolant oil (which, in this case, was a mixture of Primol "D" oil and coolant oil from previous operations), a stepwise induction with synthesis gas from the Kerpely producer was begun on May 27, 1952. This operation employed a modification of the induction procedure, which consisted of heating the circulating coolant oil with steam to about 400° F. in the waste-heat boiler and then continuing the heating to initial reaction with Dowtherm vapor in the coolant-oil preheater, instead of the usual procedure of heating the oil with Dowtherm vapor alone. This method had the advantage of more rapid heating to 400° F. because of the better heat-transfer rate obtained with steam. The conversion levels and temperatures employed in the induction were 15 percent at 435° F., 25 percent at

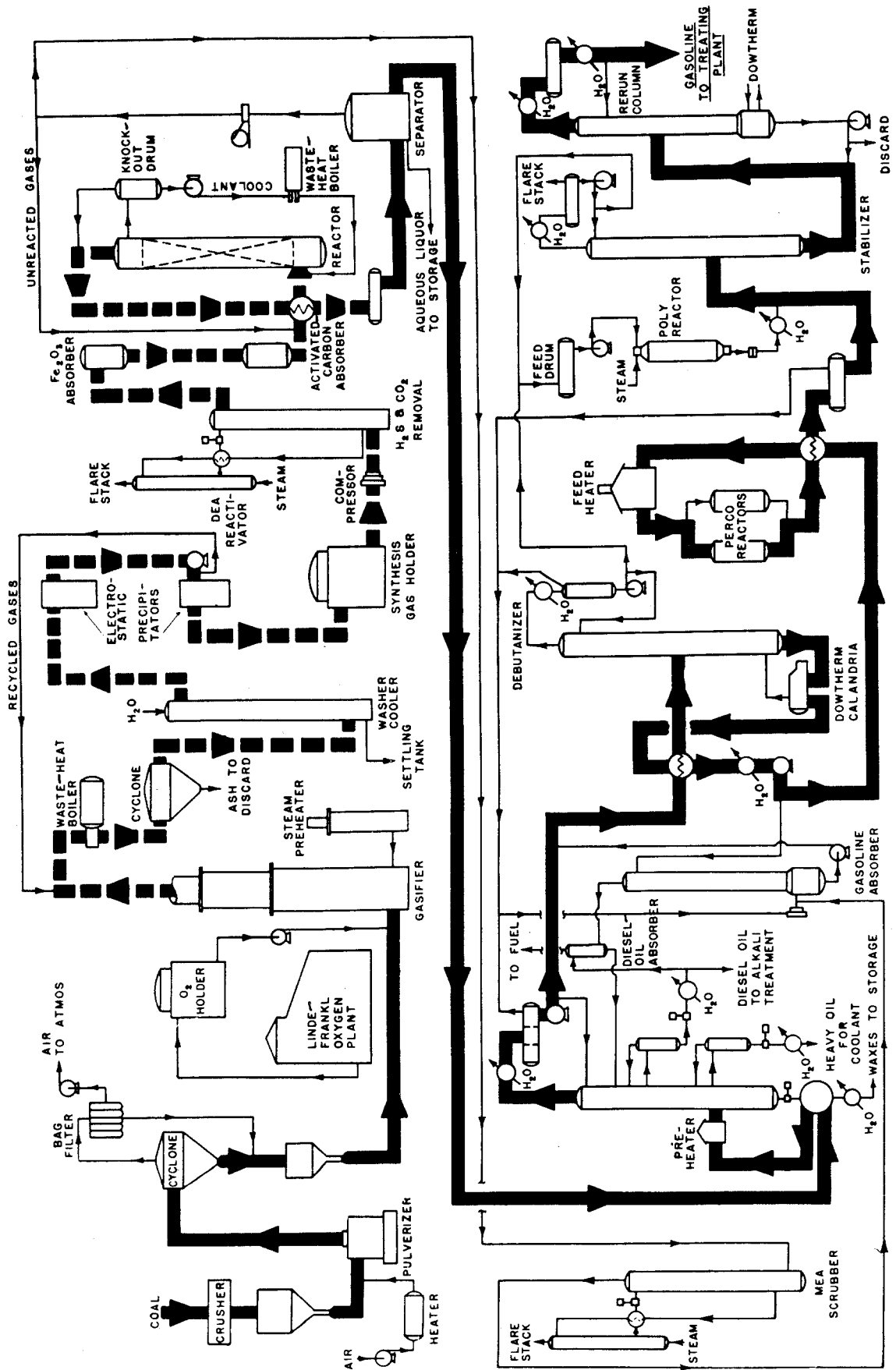


Figure 16. - Flow sheet of Gas-Synthesis Plant, with original distillation unit.

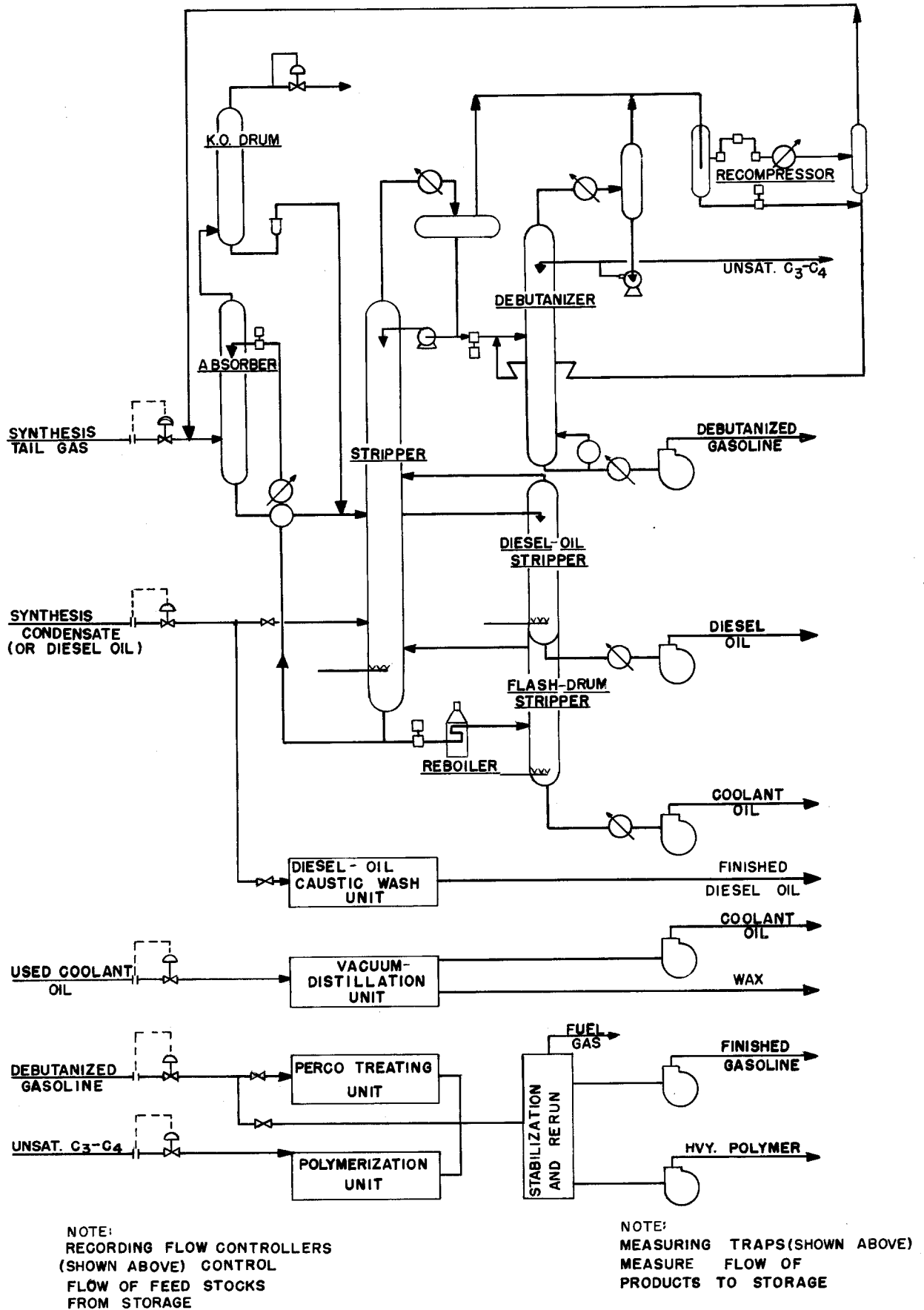


Figure 17. - Revised flow diagram of distillation unit, Gas-Synthesis Plant.

460° F., 40 percent at 510° F., and 55 percent at 529° F. The conversion was maintained at each temperature level for approximately 18 hours. The conversions then gradually stabilized at about 65 percent at a 525° F. operating temperature.

As operation continued, it was necessary to raise the temperature to 540° F. At the same time, conversions began to drop. Investigation showed that the seal oil for the mechanical seals contained appreciable quantities of sulfur compounds, and it was assumed and later proved that the catalyst was being poisoned by sulfur and gradually lost activity. This situation was corrected by substituting a sulfur-free oil for the seal oil previously employed.

During the first 2 weeks of the third synthesis run, the maintenance required to keep the mechanical seals on the coolant-oil circulating pumps in top operating condition was very high; however, as the operators gained experience in operating the pumps, they recognized trouble earlier and so reduced the need for extensive maintenance.

Some catalyst carry-over and disintegration occurred. This was evidenced by the build-up of solids in the circulating coolant-oil stream. Although most of the solids particles were very small, they were sufficient to cause erosion in some of the piping, particularly in small lines where velocities were high. The piping was replaced, and no further erosion was experienced.

As operations proceeded, conversions dropped from around 65 to 58 percent at 535° F., at a space velocity of 533 volumes per volume per hour. At this point the gas flow was reduced to 350 volumes per volume per hour space velocity, and operations were continued at 535° F. until June 24, 1952, when a leak in the coolant-oil flow-control valve interrupted operations. During this period, conversions improved appreciably and reached 84.4 percent. When the synthesis unit was restarted, it was discovered that some of the coolant oil from the reactor had been carried over to other parts of the system, and it was decided to terminate the run June 26, 1952.

Typical operating conditions during the stable periods of operation are given in table 8.

TABLE 8. - Typical operating conditions - synthesis run 3

Date	June 9, 1952	June 24, 1952
Fresh feed-gas flow std. cu. ft./hr.	65,400	38,560
H ₂ :CO in fresh feed gas	0.935	0.994
Recycle ratio	1.48	1.86
Maximum temperature °F.	545	534
ΔT across synthesis converter do.	13	7
Maximum pressure p.s.i.g.	317	321
ΔP across synthesis converter do.	17	11
Space velocity vol./vol./hr.	584	345
Conversion percent	66.8	83.9
Usage ratio	0.752	0.858
CO ₂ in fresh feed gas percent	2.9	3.2
CO ₂ in recycle gas do.	0	0.3
CO ₂ in gas from synthesis converter do.	9.5	9.2
C ₁ +C ₂ yield, gm./m ³ (CO+H ₂) in fresh feed	37.4	46.6
C ₃ + yield, gm./m ³ (CO+H ₂) in fresh feed (theo.)	101.5	127.9

Approximately 14,000 gallons of synthesis condensate was recovered during operation of the synthesis unit. This was separated into gasoline, Diesel-oil, cracking-stock, and coolant-oil fractions in the distillation unit.

A large portion of the gasoline produced was subjected to a reforming treatment in the Perco catalytic reforming unit. The mechanical operation of this unit was very satisfactory, and the reforming operation and subsequent regeneration of the catalyst proceeded smoothly. This operation was conducted at temperature levels of 700°, 750°, 775°, and 825° F. to determine the optimum temperature of operation. Although the improvement in the octane rating of the gasoline was not as high as desired, much valuable information on the process and experience in operation were gained.

The vacuum column was operated for the first time on a coolant-oil fraction to separate wax. This run was of short duration, and a limited amount of coolant oil was processed. Additional runs will be made later to supplement the information obtained in this run.

Following termination of synthesis run 3, some important changes have been made in the synthesis system. A new gas distributor has been designed and installed in the synthesis converter. With this new distributor, the gas will enter separately and not concurrently with the coolant oil, as in past synthesis runs. A continuous coolant-oil make-up system will replace the pumps originally installed and will insure relatively uniform temperature levels during operation. In the past coolant-oil additions always were attended with wide temperature fluctuations, which caused a drop in conversion and slow return to the normal operating temperature. The seal-oil supply to the coolant-oil circulating pumps was also improved.

The distillation system has been entirely redesigned, and a new philosophy of operation has been developed. In this new system a heavier absorption oil, obtained by stripping the synthesis condensate, will be utilized to recover the hydrocarbons in the tail-gas stream. The enriched absorption oil will be stripped, along with the synthesis condensate, in the primary column. The stripped overhead product, gasoline, will be debutanized and later processed in the Perco catalytic reforming unit. The recovered light hydrocarbons from the debutanizer will be processed to polymer gasoline in the U.O.P. catalytic polymerization unit. A portion of the stripped bottoms from the stripping column, consisting largely of Diesel oil, will be used to recover the hydrocarbons in the tail gases, and the balance of the stripped bottoms will be sent to storage for later processing. Final separations into commercial fractions will be made after synthesis operations are terminated.

These changes in the synthesis and distillation systems have necessitated revisions in operating directives, log sheets, analytical schedules, and other material, and these have been accomplished.

Future Plans

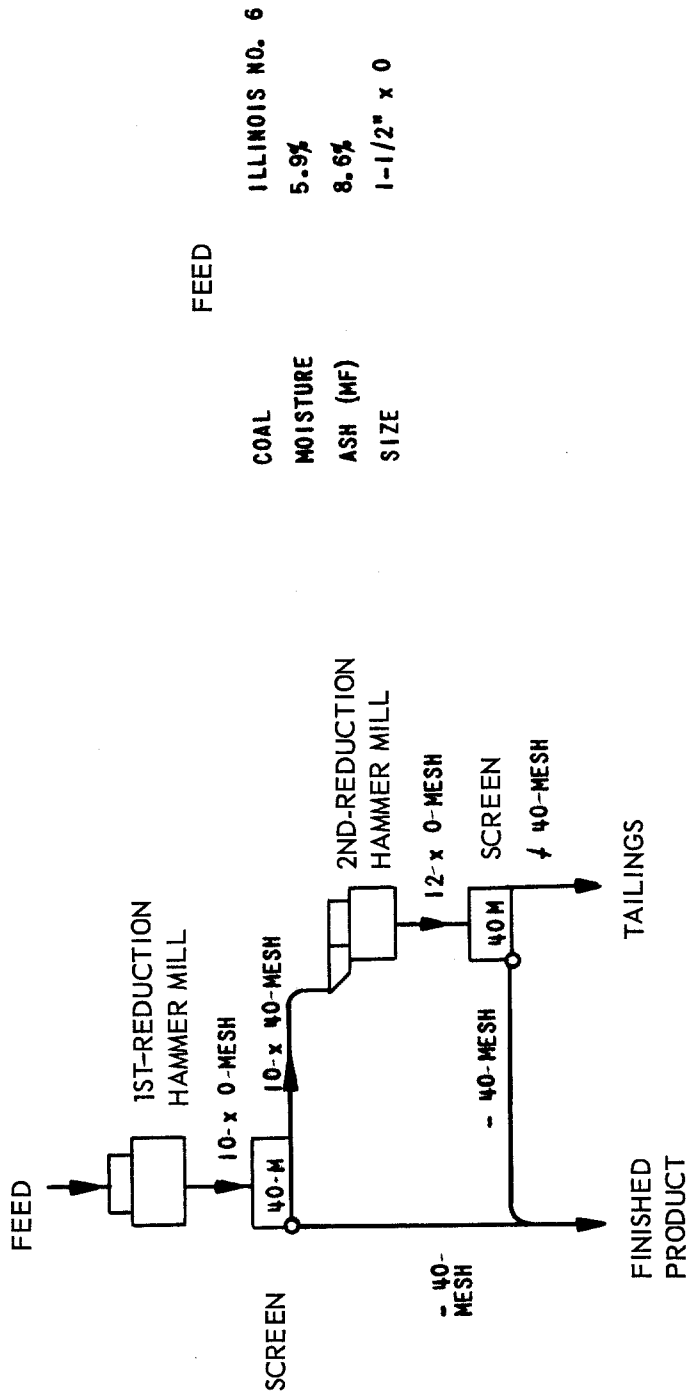
For synthesis run 4, scheduled to begin late in the year, it was proposed to use purified synthesis gas from the vertical gasifier if it was available; otherwise, purified synthesis gas from the Kerpely producer was to be used, as in past runs. No change was planned in the synthesis catalyst. To learn more about the effect of operating temperature on catalyst disintegration, it is purposed to limit the maximum temperature to 520° F. Synthesis run 4 will also permit a full trial run of the revised distillation unit.

Other synthesis runs are contemplated in the current year to obtain complete information on yields, characteristics of products, and the effect of operating variables when iron catalysts promoted with potassium and magnesium oxides are used.

Engineering and Economic Studies for Commercial-Size Operations

Coal Preparation

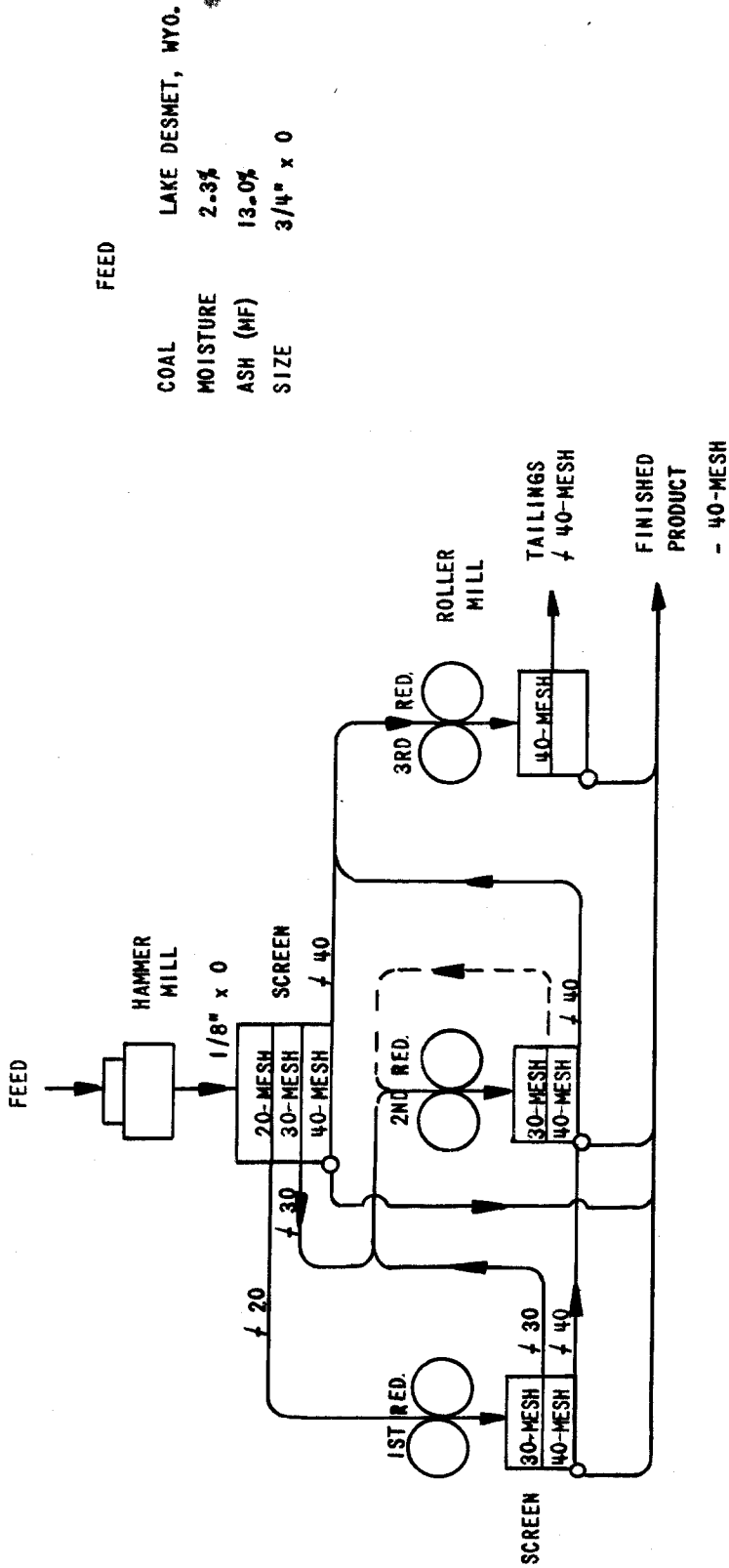
A basically new approach to the problem of pulverizing coal for the coal-hydrogenation process was investigated. This departure from the conventional use of air-swept ball mills was based on the idea of reducing the coal size in stages and removing sized coal after each reduction by screening. This method lowers the percentage of fines and, in addition, by using different pulverizing equipment,



MATERIAL BALANCE OF COMBINED PULVERIZING AND SIZING

SCREEN U.S.S.	1ST REDUCTION WGT., %	2ND REDUCTION WGT., %	TOTAL YIELD WGT., %
ON	17.0	1.3	1.3
THRU	<u>83.0</u>	<u>15.7</u>	<u>98.7</u>
	100.0	17.0	100.0

Figure 18. - Two-stage hammer-mill reduction.



MATERIAL BALANCE OF COMBINED PULVERIZING AND SIZING

SCREEN U. S. S.	SIZING OPERATION WGT., %	FIRST REDUCTION WGT., %	SECOND REDUCTION WGT., %	THIRD REDUCTION WGT., %	TOTAL YIELD WGT., %
ON 20	20.6				
THRU 20 ON 30	13.9	2.4	1.1		
THRU 30 ON 40	13.8	4.4	4.1	0.3	
THRU 40	<u>51.7</u>	<u>13.8</u>	<u>11.1</u>	<u>23.1</u>	<u>99.7</u>
	100.0	20.6	16.3	23.4	100.0

Figure 19. - Hammer mill and three-stage roller mill.



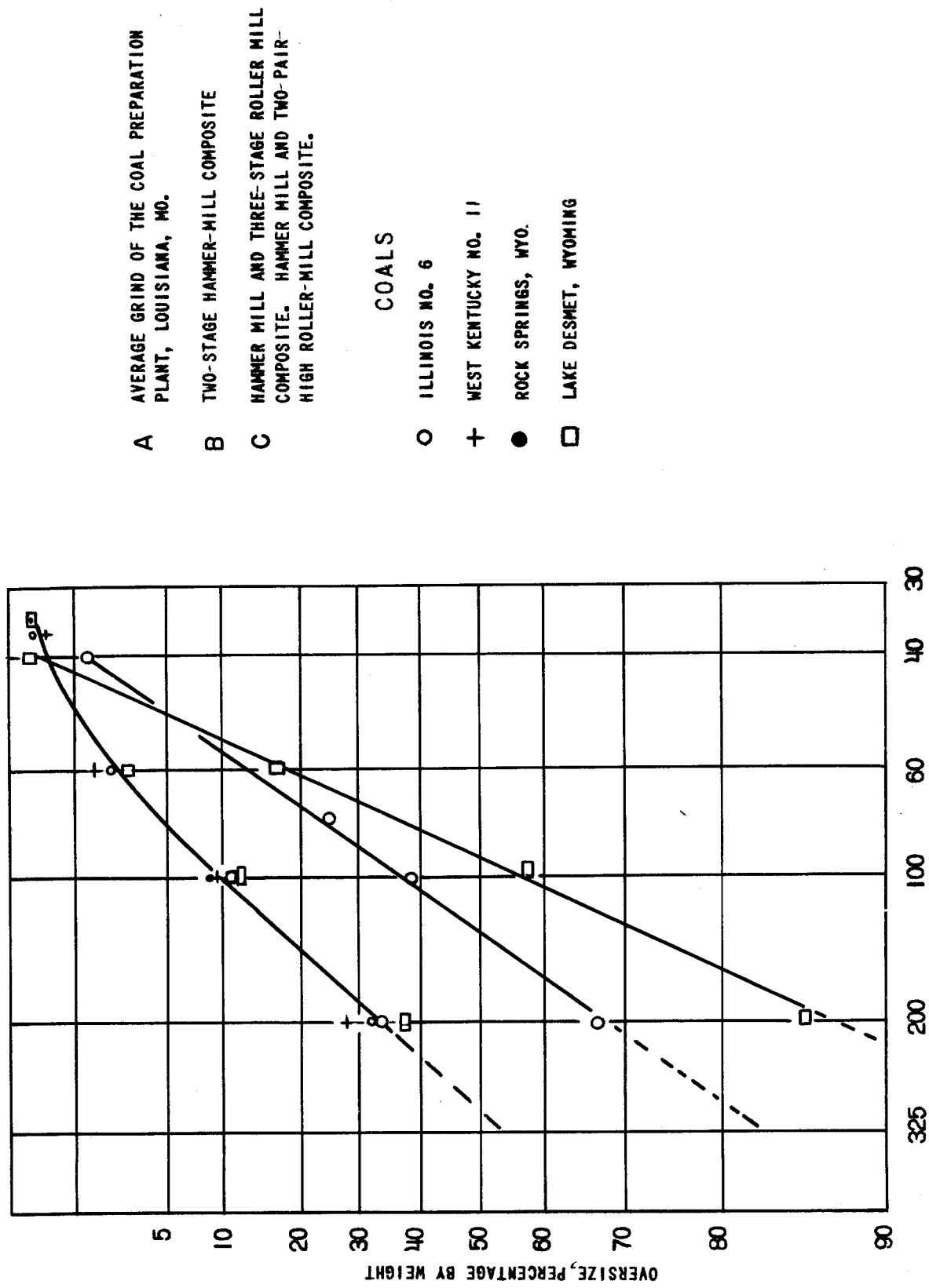
FEED

COAL LAKE DESMET, WYO.
 MOISTURE 2.3%
 ASH (MF) 13.0%
 SIZE 3/4" x 0

MATERIAL BALANCE OF COMBINED PULVERIZING AND SIZING

SCREEN U.S.S.	HAMMER MILL WGT., %	FIRST REDUCTION WGT., %	SECOND REDUCTION WGT., %	TOTAL YIELD WGT., %
ON 40	48.3	10.6	1.2	1.2
THRU 40	<u>51.7</u>	<u>37.7</u>	<u>9.4</u>	<u>98.8</u>
	100.0	48.3	10.6	100.0

Figure 20. - Hammer mill and two-pair-high roller mill.



A AVERAGE GRIND OF THE COAL PREPARATION PLANT, LOUISIANA, MO.

B TWO-STAGE HAMMER-MILL COMPOSITE

C HAMMER MILL AND THREE-STAGE ROLLER MILL COMPOSITE. HAMMER MILL AND TWO-PAIR-HIGH ROLLER-MILL COMPOSITE.

COALS

○ ILLINOIS NO. 6

+ WEST KENTUCKY NO. 11

● ROCK SPRINGS, WYO.

□ LAKE DESMET, WYOMING

Figure 21. - Coal-size distribution.

power requirements, investment, and operating costs are also reduced. The over-all reduction in costs is, to a large extent, determined by the coal-drying requirements. Additional investigation is required before a conclusion can be reached as to the magnitude of the over-all reduction in costs.

Three methods were investigated, namely, two-stage hammer mill, hammer mill and three-stage roller mill, and hammer mill and two-pair-high roller mill. The two-stage hammer-mill reduction, as shown in figure 18, had the highest capacity and product yield per stage. The three-stage roller mill (see fig. 19) has the next-highest capacity and the two-pair-high roller mill (see fig. 20) the lowest capacity of the units tested. A composite size distribution of the end products of the three methods tested and an average grind of the present coal-preparation plant at Louisiana, Mo., are shown in figure 21.

Results of the tests indicate the two-stage hammer-mill method to be the most economical of the three methods tested. The power requirements of the three methods tested, including drying equipment, are compared with conventional ball mills, as follows:

Gas swept ball mills	hp./ton	22
Two-stage hammer mills	do.	7
Hammer mill plus three-stage roller mill	do.	13
Hammer mill plus two-pair-high roller mills	do.	20

Ammonia from Coal vs. Natural Gas

A study was undertaken to determine the economics of using coal instead of natural gas as the raw material for ammonia production. The investment requirements and operating costs were estimated for three plant sizes, namely, 200, 400, and 600 tons per stream-day of ammonia.

Tables 9 and 10 show the estimated investment and utility requirements for the plants using natural gas and coal, respectively.

The estimated daily operating costs for both types of plants are shown in tables 11 and 12. The operating costs, before profit and taxes, per ton of ammonia produced are indicated at various costs of raw materials.

To make the comparative study, it was necessary to obtain cost data for a typical ammonia plant utilizing natural gas as the raw material. 5,000 p.s.i.g. was chosen as the operating pressure. Information on investment and operating costs was obtained from several operating companies, contractors, and published reports. These data were correlated and adjusted to first-quarter 1952 prices. Tables 9 and 11 were prepared to show investment and operating costs for plants using natural gas. For the coal-gasification cases it was assumed that, from the 400- to 5,000-p.s.i.g. compression step on through storage and recovery, the same capital costs, utilities, and operating costs would apply as in the natural-gas cases. For the oxygen plant, oxygen compression, coal gasification under pressure, primary purification, and CO conversion, flow sheets and equipment summaries were prepared and utilized in determining the required investment and operating costs. Table 10 indicates an excess steam production of 500 pounds of steam from waste-heat boilers, and in the study this was utilized without power production to make up part of the 50-pound steam requirement.

Special attention should be called to the figures on coal costs listed in the tables. The estimates are based on the use of Wyoming subbituminous coal from the Lake DeSmet area where strippable deposits 100 to 200 feet thick result in unusually favorable mining costs. This coal has a calorific value of 8,000 B.t.u. per pound, and therefore with high-rank coals similar ammonia production costs could be obtained with fewer tons at much higher prices per ton.

Taking freight rates into account also, it was concluded that there are areas in the United States where coal can be economically utilized for producing anhydrous ammonia.

TABLE 9. - Estimated plant-investment and utility requirements for ammonia plant (synthesis gas from natural gas)

Unit	Tons per stream-day		
	200	400	600
Reforming, including shift	\$ 2,326,000	\$ 4,047,000	\$ 5,605,000
Compression to 400 p.s.i.g.	720,000	1,253,000	1,735,000
Compression from 400 to 5,000 p.s.i.g.	930,000	1,618,000	2,242,000
Purification	1,210,000	2,105,000	2,915,000
Synthesis	1,750,000	3,045,000	4,220,000
Storage and recovery	370,000	643,800	892,000
General utilities	1,100,000	1,910,000	2,655,000
Steam and power plant	3,840,000	6,720,000	9,600,000
General plant	900,000	1,570,200	2,164,000
Total plant cost (tax and ins. base) ...	13,146,000	22,912,000	32,028,000
Interest during construction	552,000	962,000	1,345,000
Subtotal (for depreciation)	13,698,000	23,874,000	33,373,000
Working capital	1,390,000	2,705,000	4,000,000
Total investment	\$15,088,000	\$26,579,000	\$37,373,000
Process utility requirements:			
Power	10,668	21,336	32,004
Water	31,399	62,798	94,197
450 lb. steam	12,061	24,122	36,183
50 lb. steam	39,084	78,168	117,252
Fuel requirements:			
Natural gas	6.06	12.12	18.18
(for process and fuel to cracking furnace)	.	.	.
Natural gas	5.7	11.4	17.1
(for power plant)	.	.	.

TABLE 10. - Estimated plant-investment and utility requirements for ammonia plant (synthesis gas from coal gasification)

Unit	Tons per stream-day		
	200	400	600
Oxygen plant	\$ 2,090,000	\$ 3,415,000	\$ 4,552,500
Oxygen compression	149,000	284,000	428,000
Coal gasification	1,885,000	3,282,000	5,068,000
Primary purification	524,000	642,000	933,000
Shift	441,000	882,000	1,323,000
Compression from 400 to 5,000 p.s.i.g.	930,000	1,618,000	2,242,000
Final purification	1,210,000	2,105,000	2,915,000
Synthesis	1,750,000	3,045,000	4,220,000
Storage and recovery	370,000	643,800	892,000
General utilities	1,100,000	1,910,000	2,655,000
Steam and power plant	4,210,000	7,800,000	10,500,000
General plant	945,000	1,640,200	2,280,000
Total plant cost (tax and ins. base) ...	15,604,000	27,267,000	38,008,500
Interest during construction	655,000	1,143,000	1,591,500
Subtotal (for depreciation)	16,259,000	28,410,000	39,600,000
Working capital	1,390,000	2,400,000	3,470,000
Total investment	\$17,649,000	\$30,810,000	\$43,070,000
Process utility requirements:			
Power	12,296	24,592	36,888
Water	26,790	53,580	80,370
500-lb. steam (required)	28,226	56,452	84,678
500-lb. steam (produced)	37,792	75,584	113,376
50-lb. steam (required)	27,123	54,246	81,369
Fuel requirement:			
Coal ^{1/} to process	409.6	819.2	1,228.8
Coal ^{1/} to power plant	434	868	1,302

^{1/} Lake DeSmet, Wyo., strip coal with calorific value of 8,000 B.t.u. per pound.

TABLE 11. - Estimated daily operating-cost summary for ammonia plants
(synthesis gas from natural gas)

	Tons per stream-day		
	200	400	600
1. Raw materials (including natural gas at \$0.10/1,000 cu. ft.)	\$1,302	\$ 2,604	\$ 3,906
2. Direct Labor:			
Operators	942	1,671	2,405
Supervision	141	248	361
3. Plant maintenance:			
Labor	307	537	756
Supervision	61	107	151
Material	153	268	378
4. Payroll overhead	233	411	588
5. Operating supplies	104	182	257
6. Indirect costs	1,370	1,808	2,154
7. Fixed costs:			
Local, county, and State taxes, and insurance	360	628	877
Depreciation	1,877	3,270	4,572
Total	\$6,850	\$11,734	\$16,405
Operating cost per ton with natural gas at \$0.10/1,000 cu. ft.	37.85	32.45	30.25
Operating cost per ton with natural gas at \$0.20/1,000 cu. ft.	44.35	38.95	36.75
Operating cost per ton with natural gas at \$0.30/1,000 cu. ft.	50.85	45.45	43.25

TABLE 12. - Estimated daily operating-cost summary for ammonia plants
(synthesis gas from coal gasification)

	Tons per stream-day		
	200	400	600
1. Raw materials (including coal ^{1/} at \$0.75/ton..	\$ 790	\$ 1,575	\$ 2,365
2. Direct labor:			
Operators	1,463	1,992	2,510
Supervision	219	299	376
3. Plant maintenance:			
Labor	460	625	789
Supervision	92	125	158
Material	230	312	395
4. Payroll overhead	358	486	614
5. Operating supplies	156	212	268
6. Indirect costs	2,097	2,139	2,248
7. Fixed costs:			
Local, county, and State taxes, and insurance	428	747	1,041
Depreciation	2,227	3,890	5,424
Total	\$8,520	\$12,402	\$16,188
Operating cost per ton with coal ^{1/} at \$0.75/ton..	47.00	34.25	29.80
Operating cost per ton with coal ^{1/} at \$1.25/ton..	49.34	36.59	32.14
Operating cost per ton with coal ^{1/} at \$2.00/ton..	52.84	40.09	35.65

^{1/} Lake DeSmet, Wyo., strip coal with calorific value of 8,000 B.t.u. per pound.