

TABLE 11. - Yields and product distributions from oil circulation, pilot plant experiments with reduced fused iron catalysts, in Fischer-Tropsch synthesis

Experiment No.	12-A	17-B	19-A,B,C	22-B	26-A	26-A	31-C ^{1/}
Type of bed	Fixed		Expanded				
Feed gas ratio.....H ₂ :CO	1.0	1.3	1.3	1.0	0.7	0.7	1.0
Hourly space velocity, (settled bed).....hr. ⁻¹	290	302	601	600	895	602	600
Maximum temperature....°C.	283	260	246	244	275	251	255
Average pressure..p.s.i.g.	300	300	300	300	400	300	400
Space-time yield.....kg./m ³ -day	890	785	1,685	1,465	2,750	1,518	1,607
Specific yield, g./m. ³							
H ₂ +CO converted:							
C ₁ +C ₂	26.9	37.5	31.2	34.6	35.2	29.5	29.6
C ₃ +.....	173.0	154.2	166.9	148.5	170.6	157.4	160.9
Product distribution, weight-percent of C ₃ +							
Gasoline (C ₃ -204° C.)...	<u>2/</u>	65.1	62.4	58.8	63.8	52.9	64.6
Diesel (204°-316° C.)...	<u>2/</u>	12.9	11.5	13.6	11.7	12.3	14.0
Heavy distillate (316°-450° C.).....	<u>2/</u>	12.5	13.4	15.9	11.4	21.5	11.1
Wax (>450° C.).....	<u>2/</u>	9.5	12.7	11.7	13.1	13.3	10.3

^{1/} 1-barrel-per-day pilot plant.

^{2/} Insufficient analytical data.

Of the primary C₃+ hydrocarbons, 50 to 65 percent were in the gasoline boiling range (<240° C.) and about 11 to 14 percent in diesel oil. To lower the pour point of the diesel fuel, its boiling range was altered to exclude some of the higher boiling compounds; this lowered the cetane rating from 80 to 70. A gasoline blend, consisting of primary gasoline after reforming over bauxite, polymer gasoline from the C₃ and C₄ unsaturates, and butane to adjust the Reid vapor pressure to 9.9 p.s.i., had a motor octane number of 77.1 (84.8 research). The addition of 1 ml. of tetraethyl lead raised the research rating to 91.2, and a research number of 94.8 was obtained when 3 ml. of tetraethyl lead was added to the clear blend.

With nitrided, fused iron catalyst the shift in the nature of the synthesis products was similar to that obtained in dry bed tests. The C₁ and C₂ yield was high, and about 80 to 85 percent of the C₃+ product was in the gasoline range. Virtually no wax and very little high-boiling oil were produced, even though the temperature was lower than that used with the reduced catalyst. Under favorable conditions, approximately 45 percent of the C₃+ products were oxygenated compounds, principally straight-chain alcohols. Excluding water produced in the reaction, the condensed liquids contained 66 percent alcohols. A gasoline blend of reformed hydrocarbons, polymer gasoline, and C₁-C₃ alcohols produced (about 25 percent of the total blend) had a research octane rating of 92.9 clear and 98.5 with 1 ml. of tetraethyl lead added per gallon. The nitrided catalyst was particularly stable and had lost little activity after use for 5 months.

To improve the flexibility of the oil-circulation process and permit operation at high temperatures where fused iron oxide catalysts disintegrate rapidly, more durable catalysts - iron or steel lathe turnings and 1/8-inch-diameter steel shot - were tried in the oil-circulation process. After oxidation with steam at about 600° C. (1,112° F.) (until the outer 20 percent was oxidized), impregnation with a 2-percent solution of potassium carbonate, and reduction with hydrogen at 400° C. (752° F.), these so-called massive catalysts were operated successfully at 270° to 290° C. (518° to 554° F.). Micrographs showing cross sections of a raw lathe turning after partial oxidation and after reduction are shown in figure 68.

Catalytic activity depended upon the porous, active surface. The beds of steel shot had to be expanded 5 to 10 percent to avoid cementation, but lathe turnings with 80 to 90 percent voids did not require expansion. Turnings were therefore preferred rather than steel shot.

Lathe turnings resisted disintegration and oxidation and maintained their activity for long periods. One catalyst, for example, operated continuously over 2,700 hours, including 1,200 hours at 290° C. (554° F.) or higher, without difficulty. At 283° C. (541° F.) 85 weight-percent of the C₃+ material boiled in the gasoline range, and only 2 percent was wax. No oxidation of the active coating of the catalyst was detected for the first 500 hours. Oxidation was gradual up to 2,000 hours and more rapid later because of operation at higher temperatures. On the other hand, fused iron was oxidized at a nearly linear rate from the beginning of synthesis; after 1,000 hours of synthesis at temperatures not exceeding 275° C. (527° F.) this catalyst contained about as much magnetite as the lathe turnings after 2,500 hours.

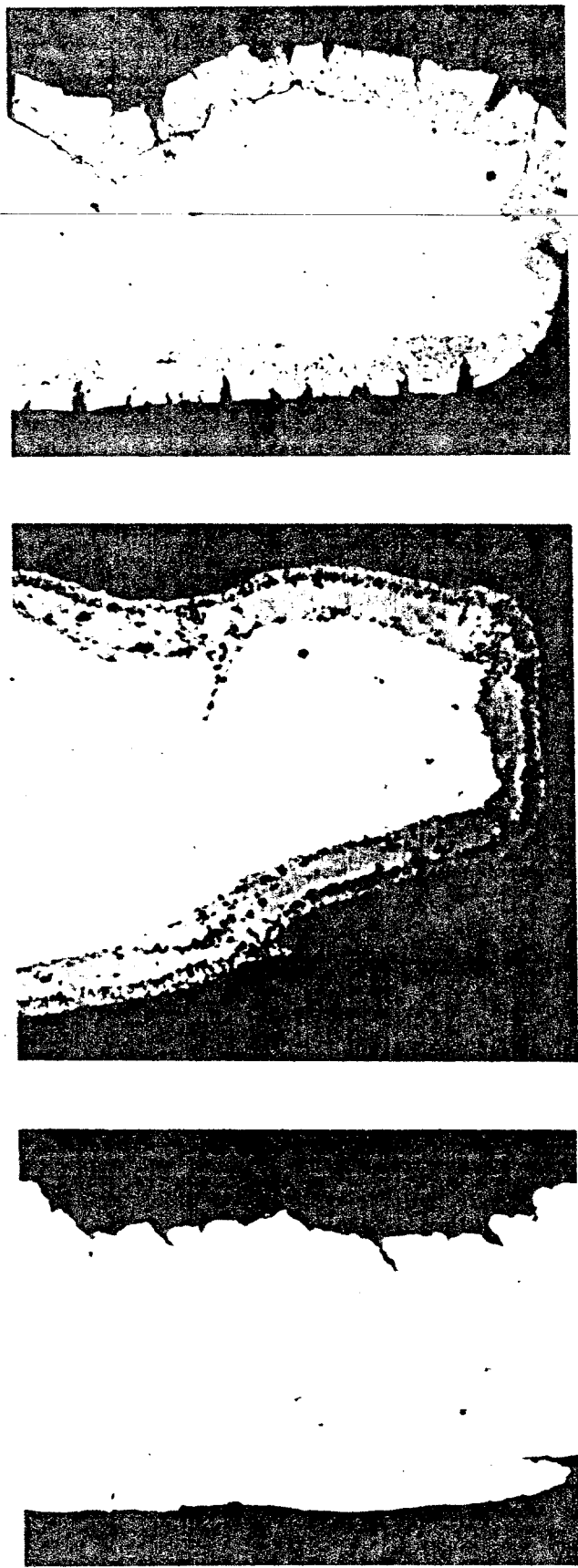
Development of the oil-circulation process on a small scale (3- and 8-gallon reactors) has been virtually completed. Although periodic experiments may be necessary as new catalysts or methods of pretreatment are developed, internal cooling by oil circulation has been shown to be practical. The process is versatile, as hydrogen-rich or carbon monoxide-rich gas may be used, and the distribution of products can be varied over a relatively wide range.

Slurry Process

The slurry process employs a suspension of finely ground catalyst in boiling oil. The catalyst particles are held in suspension by gas agitation or by circulation of the slurry. Large units are cooled by a system of internal bayonet tubes or by circulation of the slurry through an external heat exchanger to recover the heat of reaction as high-pressure steam.

After some exploratory studies, laboratory units and a small pilot plant were constructed, covering a range from 0.25 to 5 gallons of product a day. Figure 69 is the flowsheet of the pilot plant. The 3-inch-diameter reactor is a 10-foot height of slurry, of about 15 liters (4 gallons) volume.

Initial experiments utilized precipitated Fe₂O₃-CuO-K₂CO₃. This active catalyst was particularly suitable for the slurry system, as mechanical weakness presented no problem. The most reproducible pretreatment utilized



After reduction

20% oxidized

Raw lathe turnings

FIGURE 68. - Photomicrographs Showing Development of Porous Surface on Iron Lathe Turning.
(Magnification 125X.)

ynthesis gas at atmospheric pressure and 270° C. (518° F.). No appreciable ynthesis took place, but carbon dioxide was formed by reduction of oxides and arburization. During synthesis at 100 to 300 p.s.i. and hourly space veloci- ies of 100 and 300 volumes of gas per volume of slurry in reactors, 65 to 80 ercent of gas was converted at about 270° C.

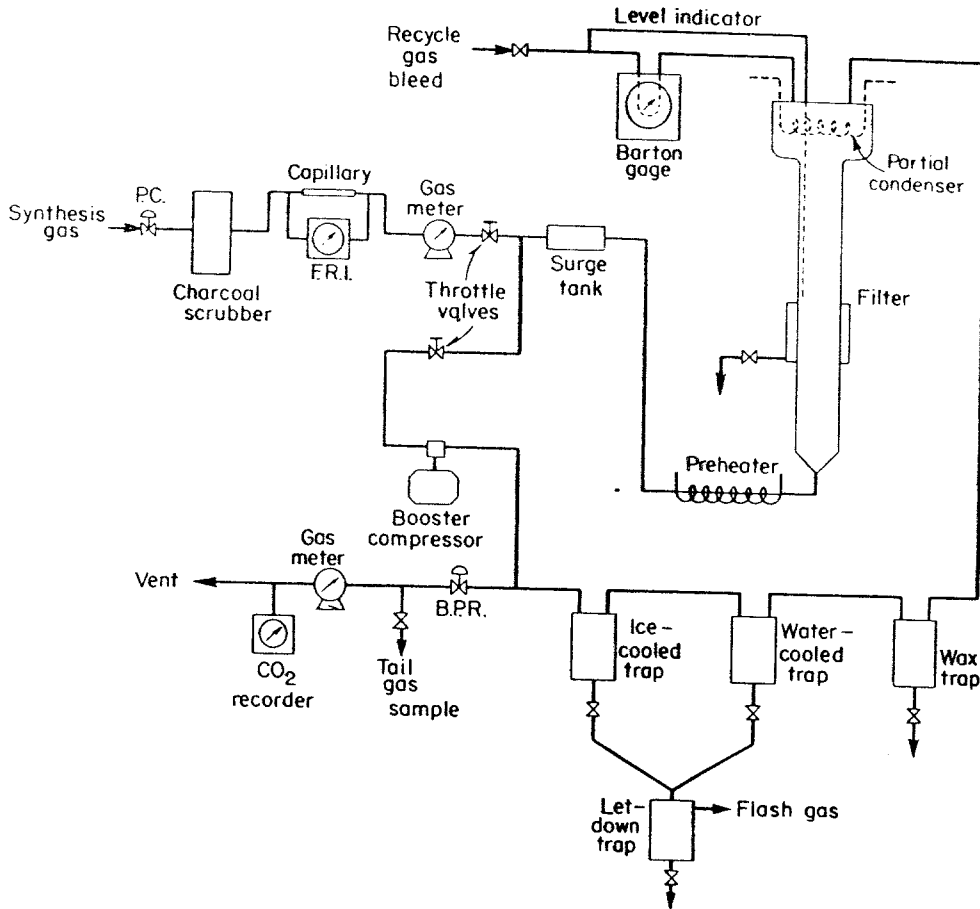


FIGURE 69. - Flow Diagram of Fischer-Tropsch Slurry Unit.

Other catalysts tested were mill scale, iron ores, ignited iron nitrate, and promoted fused iron. The most promising materials were Alan Wood magnet-ore and fused iron oxide.

In 124 experiments lasting up to 4 months each, studies were included on the effects of catalyst concentration, gas composition, pressure, space velocity, and composition of suspension oil. The results indicated that:

1. Catalyst concentrations of 50 to 500 grams of iron per liter of slurry are operable.

2. Ratios of synthesis gas produced most easily by gasification of coal (1.7:1 to 1.3:1 $H_2:CO$) can be used.

3. Pressures of 300 to 400 p.s.i. are preferred.

4. A wide range of space velocities can be used. The lower limit is the gas rate required to keep the particles suspended; the upper limit is the velocity at which frothing or other major disturbance of the oil phase occurs.

5. Certain additives appear to aid in keeping catalyst particles suspended, although their role is still obscure. With nitrided iron, relatively large concentrations of alcohol were present in the oil, and agglomeration was not observed.

Concurrent with process development, reactor design was studied. The straight tube was modified by inserting a smaller concentric tube through which synthesis gas was passed. The center tube caused circulation of slurry within the reactor. For larger scale operation, reactors with offset circulation legs were constructed. Circulation was induced by gas lift in some instances and pumps in others. With a pump, slurry could be made to flow countercurrently or cocurrently to the gas flow. No significant variation was found in the conversion or product distribution with change of direction of flow.

Product distribution from slurry reactors is shown in table 12. Experiment 35, with the temperature only 221° C. (430° F.), indicated the high activity of precipitated catalyst. Gasoline yield was low but increased with increasing temperature and approached that obtained with fused iron. In experiment 73B alkali added to the slurry decreased the gasoline yield from 89 to 43 percent of the C₃+ product and decreased the yield of gaseous hydrocarbons.

TABLE 12. - Yields and product distributions from Fischer-Tropsch slurry experiments with iron catalysts

Experiment No.	LP-35	LP-60	LP-73	
Type of catalyst.....	Precipitated	Fused	Alan Wood magnetite	
Feed-gas ratio.....H ₂ :CO	0.7:1	1.0:1	1.0:1	
Temperature.....°C.	221	257	285	
Hourly space velocity...vol./vol. slurry-hr.	250	300	300	
Pressure.....p.s.i.g.	200	300	300	
Specific yields, gm./m. ³ H ₂ +CO converted:			A	B ^{a/}
C ₁ +C ₂	14	37	48	21
C ₃ and heavier.....	163	125	149	190
Product distribution, weight-percent of C ₃ +: Gasoline (C ₃ -204° C.).....	41	83	89	43
Diesel oil (204°-316° C.).....	14	10	9	18
Heavy distillate (316°-450° C.).....	18	6	2	20
Wax (>450° C.).....	27	1	0	19

a/ With added sodium hydroxide.

Nitrided iron catalyst could be prepared by reducing with hydrogen and nitriding with ammonia, either under oil in the reactor or in a separate dry-bed unit. Several experiments proved the catalyst to be stable and active

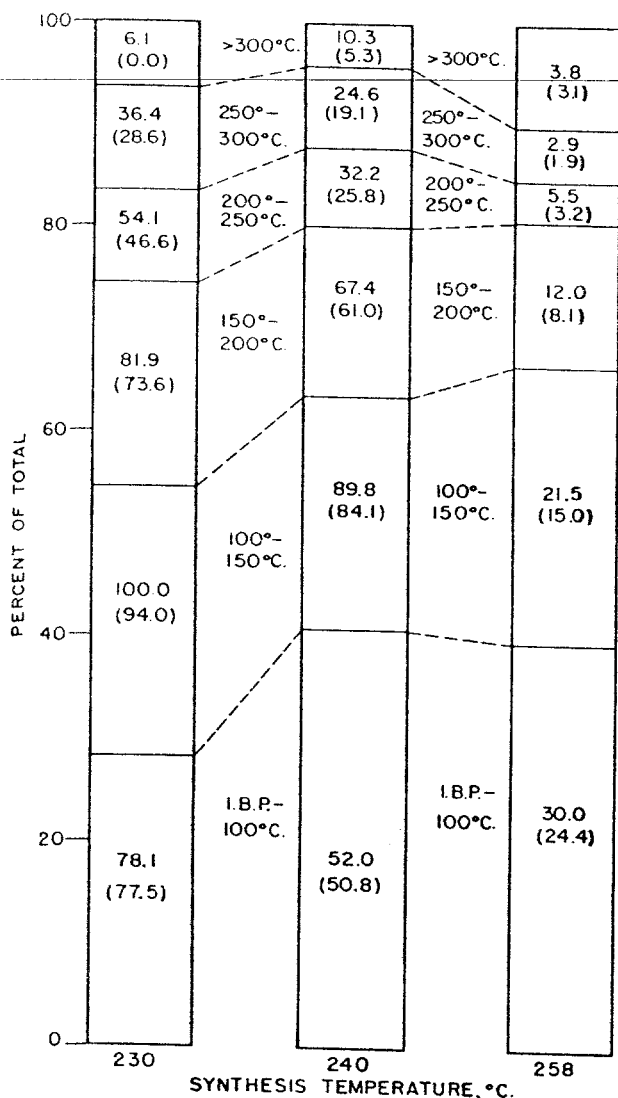


FIGURE 70. - Effect of Synthesis Temperature on Occurrence of Oxygenates in Product From Fischer-Tropsch Slurry Synthesis With Nitrided, Fused Iron Catalyst.

(For each fraction boiling within temperature range shown between columns, upper figure indicates total oxygenates and lower figure in parentheses the alcohols, both expressed as percentages of that fraction.)

gas, catalyst preparation and reduction units, and facilities for refining liquid products (39). A simplified perspective sketch of the plant is shown in figure 71 and a view of part of the plant in figure 72.

(66). Product distributions are shown in figure 70, in which the yields of oxygenated compounds in various fractions are given. Of the condensed product, 60 to 70 percent was oxygenated chemicals. Nitrided catalysts are thus a means of converting coal to aliphatic oxygenated chemicals, predominantly alcohols.

Although many successful experiments were made in the slurry units, unpredictable erratic behavior (usually resulting in low catalytic activity and short life) was obtained in about half of the tests. The factors that adversely affect catalyst activity have not been clearly defined; however, in many instances loss in activity can be attributed to the catalyst settling out of the slurry. Although some progress has been made, this problem remains the major obstacle to successful operation of a slurry reactor. Additional research will be required on catalyst form and composition and on reactor design.

Demonstration Plant

The Fischer-Tropsch demonstration plant at Louisiana, Mo., was completed in 1950 and operated in four tests from 1951 to 1953 (10). In addition to the reactor proper it contained coal-handling and coal-preparation equipment, Koppers- and Bureau of Mines-type units for gasifying coal with steam and oxygen at atmospheric pressure, a Kerpely producer as an alternate means for obtaining synthesis gas from coke or char, a Linde-Fränkyl oxygen producer for use with any of these gasifiers, equipment for removing solid and gaseous impurities from the raw synthesis

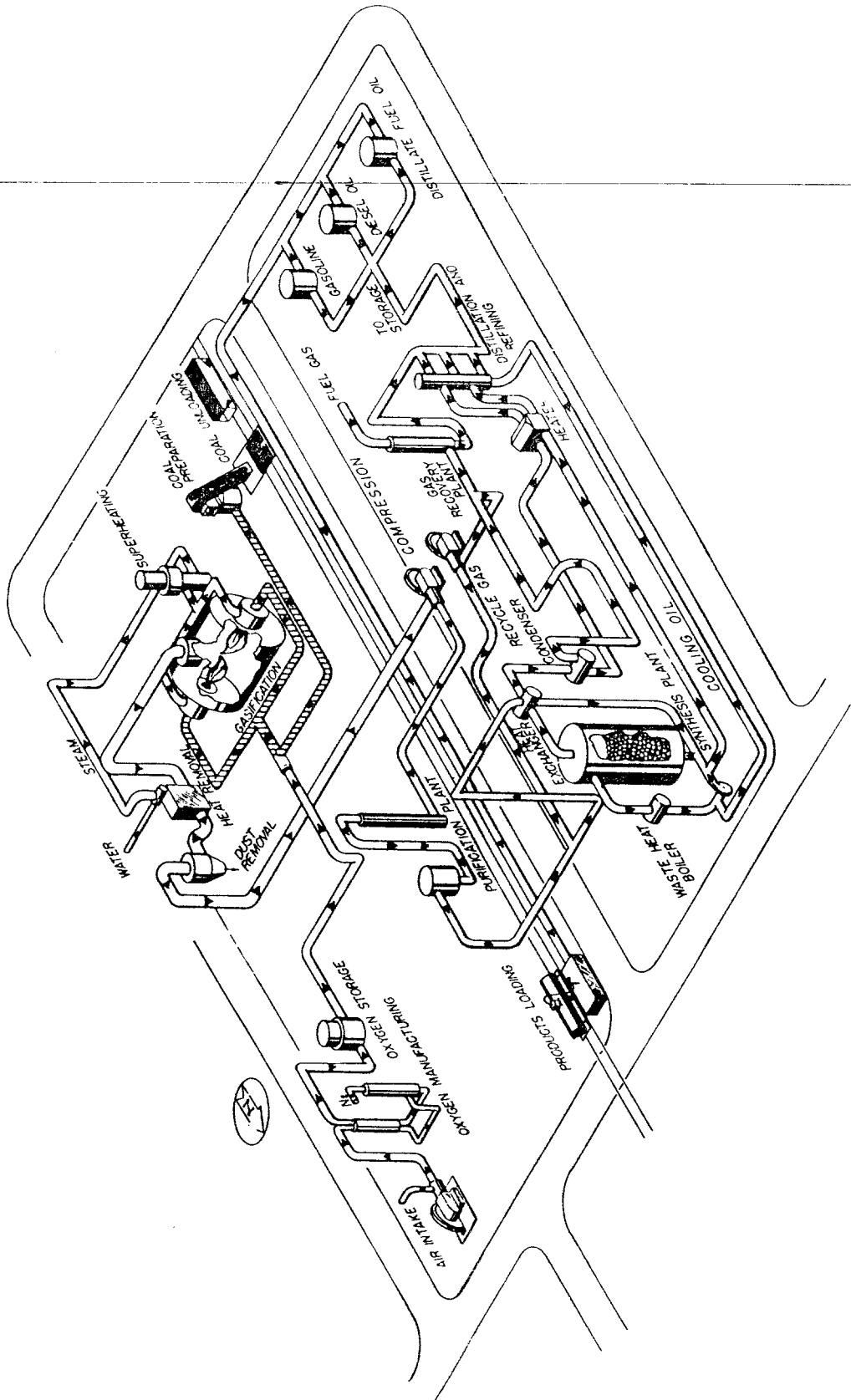


FIGURE 71. - Simplified Sketch of Fischer-Tropsch Demonstration Plant at Louisiana, Mo.

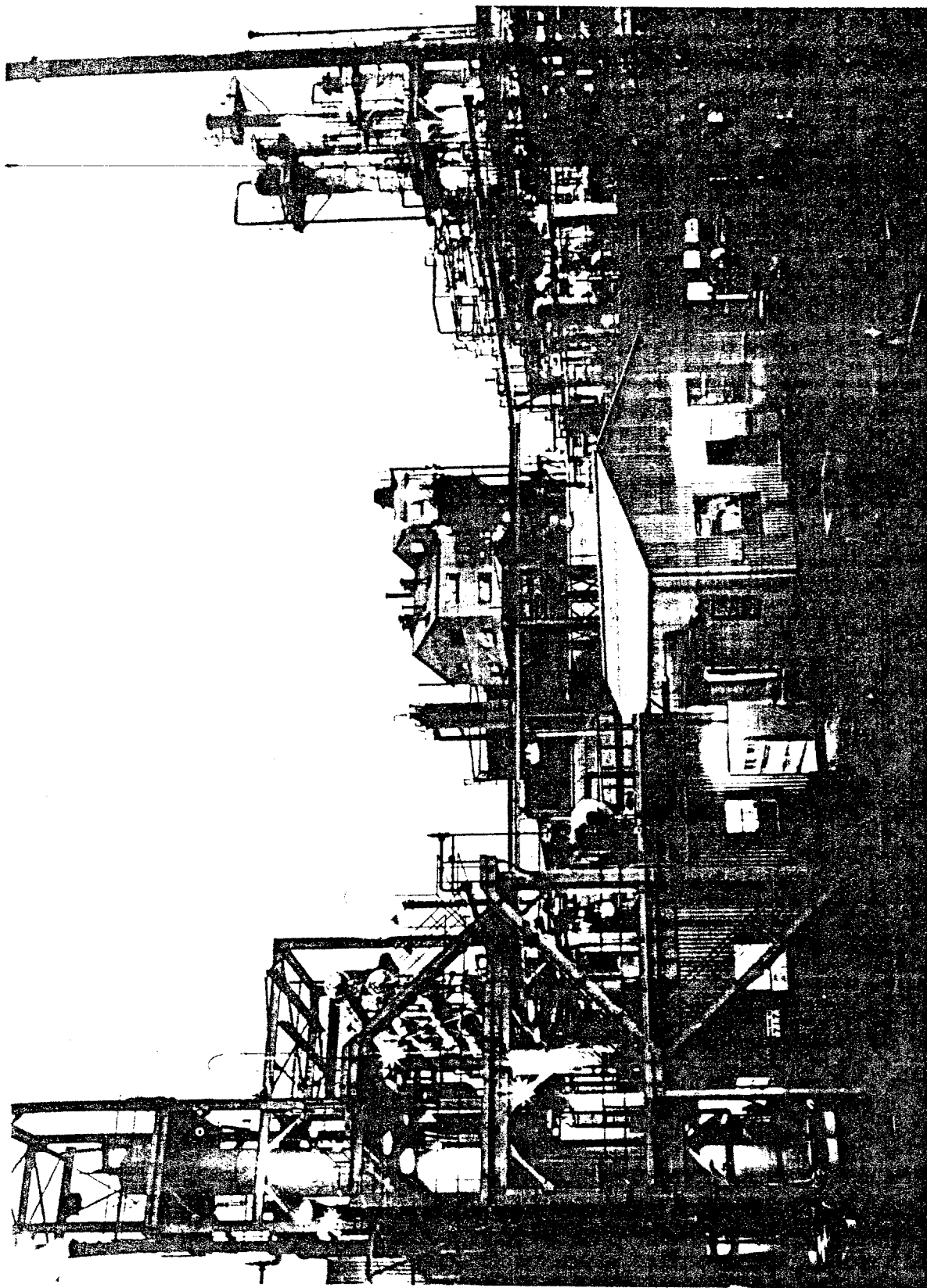


FIGURE 72. - View of Fischer-Tropsch Demonstration Plant at Louisiana, Mo.