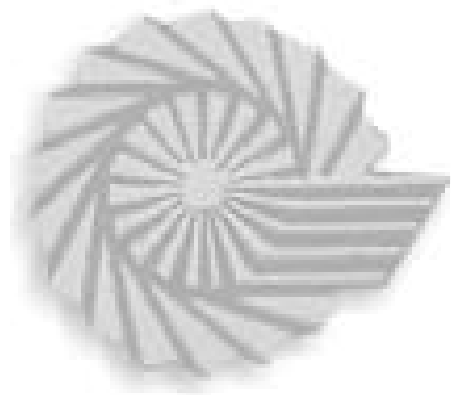


Center for Applied Energy Research



Research and Testing Center
at the UK Center for Applied Energy Research



Center for Applied Energy Research

at University of Kentucky

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Catalysis Research and Testing Center

2540 Research Park Dr.

Lexington, KY 45011



Research and Testing Center
at the UK Center for Applied Energy Research

An Overview of Fischer-Tropsch Synthesis at the U.S. Bureau of Mines

Burtron H. Davis

Center for Applied Energy Research, University of
Kentucky

2540 Research Park Drive

Lexington, KY 40511

FIRST FUEL RESEARCH IN AMERICA ?

April 7, 1826

A paper was read by Marcus Bull at American Philosophical Society of Philadelphia and published as brochure by the society the next month.

The paper described Bull's work on determining the relative value of different fuels.

EXPERIMENTAL

The apparatus was fuel calorimeter in the form of a small-sized room. The outside walls were insulated and provisions within the room were made for burning various fuels under conditions where the temperature in the room could be kept constant. The amount of fuel was kept constant and the time to burn the fuel was determined.

Fuel	Value
Shell-bark hickory wood	100
Soft maple	56
Elm	58
Anthracite coal	200

The Beginning

S. W. Parr, Ind Eng Chem, **19** (1927) 7

The next epoch-making event in the study of American fuels was the work inaugurated by the U.S. Government at the St.. Louis Exposition of 1904 and which resulted finally in the development of the research laboratory of the Bureau of Mines at Pittsburgh.

J. K. Clement, Ind Eng Chem, Feb. 1911, 96

The organization of the chemical laboratories of the Bureau of Mines is perhaps unique, in that there is no chief chemist. The work is divided among a number of separate laboratories, each carrying on its own lines of work, under the direction of its own chief – the whole forming a group of more or less independent units.

J. K. Clement, Ind Eng Chem, Feb. 1911, 96

- Fuel-Testing Lab (Pittsburgh and DC)
- Fusibility and Clinkering of Coal Ash
- Chemistry of Petroleum Technology Combustion Investigations
- The Composition of Coal
- The Volatile Matter of Coal
- Weathering and Deterioration of Coal
- The Burning of Coal in Mines under Diminished Supply of Oxygen
- The Chemistry of Explosives
- Coal Dust Explosions

Synthetic Liquids - UOP

- 1920-30s: Concern for oil supply
- I. G. Farben and Standard (NJ) studying heavy oil hydrogenation
- Bergius and F-T process for oil from coal
- UOP set out to engage experts in catalysis to develop their synthesis of oil
- Egloff recruited Ipatieff; arrived in 1930; recruited Tropsch but worked on cracking

R. B. Anderson Version

- 1920's research on catalysis
- 1931, AC Fieldner persuaded Dr. Henry H. Storch to transfer from N.J. to Pittsburgh
- 1943 FT synthesis research started again

Norma Golumbic catalyst preparation
with larger scale by C O Hawk and H
Brown

L.J.E. Hofer began studying carbides of
iron



R. B. Anderson Version

- 1944 R. B. Anderson and S. Weller join and Anderson to FT Catalyst Testing Section in 1945
- FTS in small pilot plants at Bruceton initially under J.H. Crowell, followed by H. E. Benson in 1947 and J. H. Field in 1958.
- Benson and Field major contributors to the development of oil recirculation and hot-gas-recycle processes.
- M.D. Schlesinger studies FTS in slurry and fluidized-bed reactors.

R. B. Anderson Version

Organic Chemistry Section determined structure of coal, analyze direct coal liquefaction products, metal carbonyls and homogeneous catalysis. Mechanism of hydroformylation reactions was elucidated. Directed by Milton Orchin until 1953 and then Irving Wender. Heinz Sternberg made valuable contributions to this.



Midcareer at the Bureau of Mines. Circa 1948 (at age 34). Taken after Dr. Orchin's return from a year as a Guggenheim Fellow at the Sieff Institute in Israel.

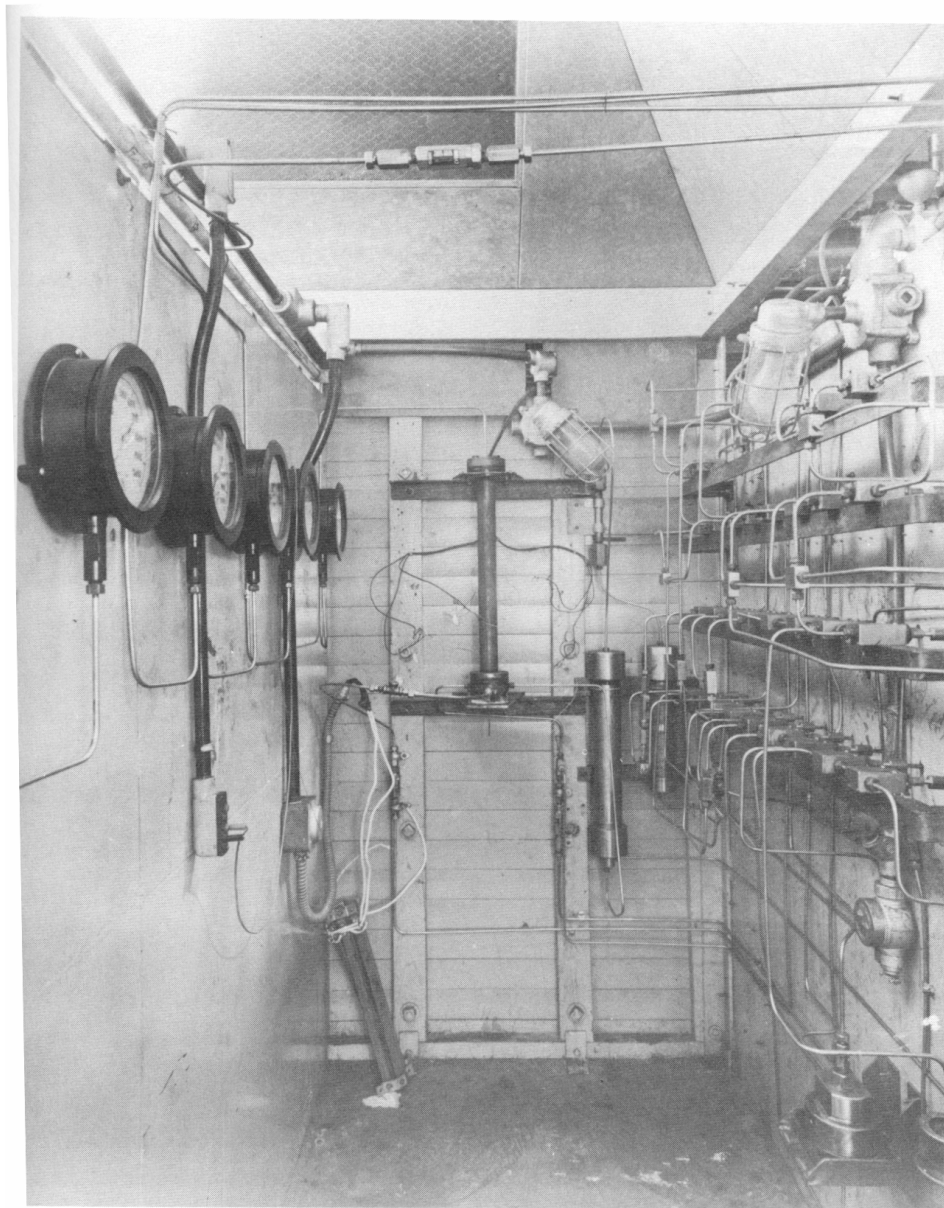


Figure 37. - Continuous OXO unit.

R. B. Anderson Version

The election of November 1952 and the advent of a Republican Administration portended changes in the research at Bruceton. At other locations programs were drastically altered, and work at the demonstration plant at Louisiana, Missouri, was stopped. Other maladies that eventually led to the demise of the Bureau of Mines might have been discerned by the careful observer. Research was becoming increasingly mixed with politics.

M. D. Schlesinger's View

- 1904-07 Demonstration of fuels evaluation at Louisiana Purchase Exposition.
- 1924-26 Coal Conversion Technologies introduced in US
- 1930-35 Depression – reduced budgets – petroleum supplies ample for the foreseeable future
- 1936-43 Increased funding – large synfuels in Germany WW II puts strain on existing resources
- 1944-55 Synthetic Liquid Fuels Act provided significant funds for research – process evaluation and petroleum availability indicated no need for commercial synthetic fuels development

M. D. Schlesinger's View

- Office of Coal Research developing new and more efficient methods of mining, preparation and utilization of coal
- 1975 – Energy Research and Development Administration (ERDA) consolidates energy research activities
- 1977 Department of Energy further consolidates the energy activities of the Nation
- 1978 Energy policy bills passed

Annual Report of the Director of the Bureau of Mines (Scott Turner) to the Secretary of Commerce (Herbert Hoover) for 1928

“Synthetic Motor fuels from water gas ... Equipment has been assembled for use at high pressures and temperatures in the catalytic conversion of coal (through water gas) to methanol and other organic compounds and mixtures suitable for motor fuels and other needs. The preliminary tests of the synthesis themselves can now proceed.”

Bureau - 1920-1930s

- Synthesis of higher hydrocarbons from water gas, D F Smith...I&EC, 20 (1928)462
- Synthesis of higher hydrocarbons from water gas-II, D F Smith...I&EC, 20 (1928) 1341
- The Mechanism of the formation of higher hydrocarbons from water gas, DF Smith, ..., JACS, (1930, 3221
- Conversion of methane to carbon monoxide and hydrogen, CO Haw, ... I&EC, 24 (1932) 23.



The Mechanism of the formation of higher hydrocarbons from water gas, DF Smith, CO Hawk and PL Golden, JACS, (1930, 3221

- Fischer thought reaction proceed through metal carbide although cannot get higher hydrocarbons passing hydrogen through metal carbide.
- Ethylene in concentrations greater than 10% of syngas over Co-Cu-Mn oxide catalyst forms higher hydrocarbons and large quantities of oxygen containing compounds.
- Oxygenates dehydrate to form hydrocarbons, and may be accompanied by polymerization
- Mechanism of hydrocarbon formation on iron-copper catalyst is different from cobalt-copper-manganese oxide catalyst.



A. N. Stranges, *Annals of Science*, 54 (1997) 29-68.

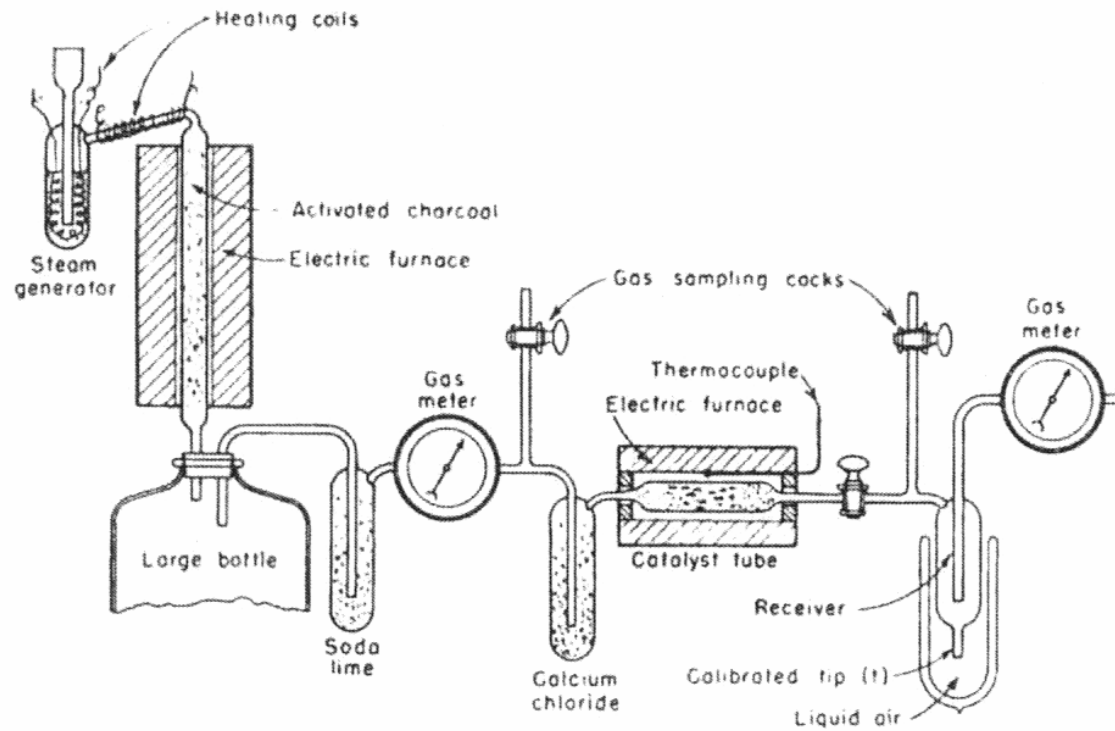


Figure 4. Early Bureau of Mines F-T apparatus, 1928.

Basic Ideas of FT Reactors in 1944

Processes classified by heat removal

A. EXTERNAL COOLING

1. Fixed Bed

a. Plate type

b. Double tube

2. Fluidized fixed bed

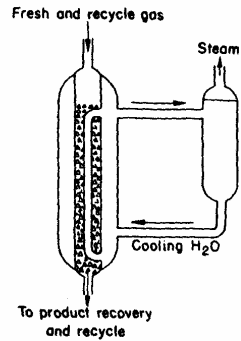
A. INTERNAL COOLING

1. Oil as heat-transfer medium

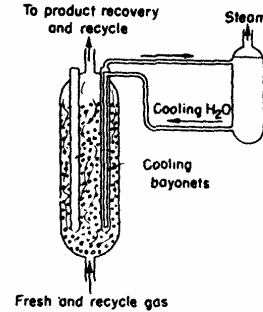
a. Fixed-bed, oil-circulation process

b. Fluidized-bed, oil-slurry process

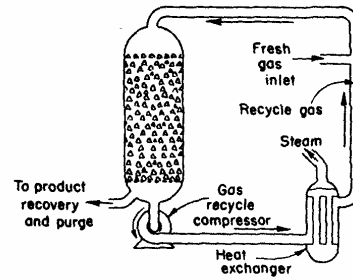
2. Gas as heat-transfer medium, hot-gas-recycle process



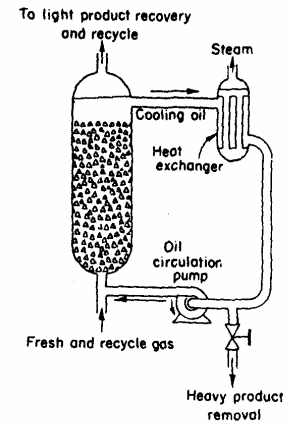
Double tube fixed-bed reactor



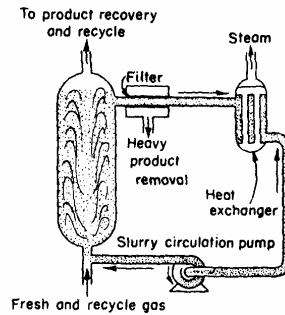
Fluidized fixed-bed reactor



Hot gas recycle process



Oil circulation process



Slurry process

	Fixed-bed catalyst
	Catalyst suspended in gas
	Catalyst suspended in oil

FIGURE 56. - Schematic Flow Diagrams of Five Modifications of Fischer-Tropsch Process.



Henry H. Storch (1894-1961).

Basic Research Objectives – Catalyst Characterization Bureau of Mines

Studies started in 1940s was designed to:

1. Were metal carbides intermediates in FT?
2. Correlate and expand knowledge about carbides
3. What phases are good FT catalyst
4. Prepare these phases with large surface area
5. Investigate those phases previously untried as catalysts

Bureau Program 1040s

Studies started in 1940s was designed to:

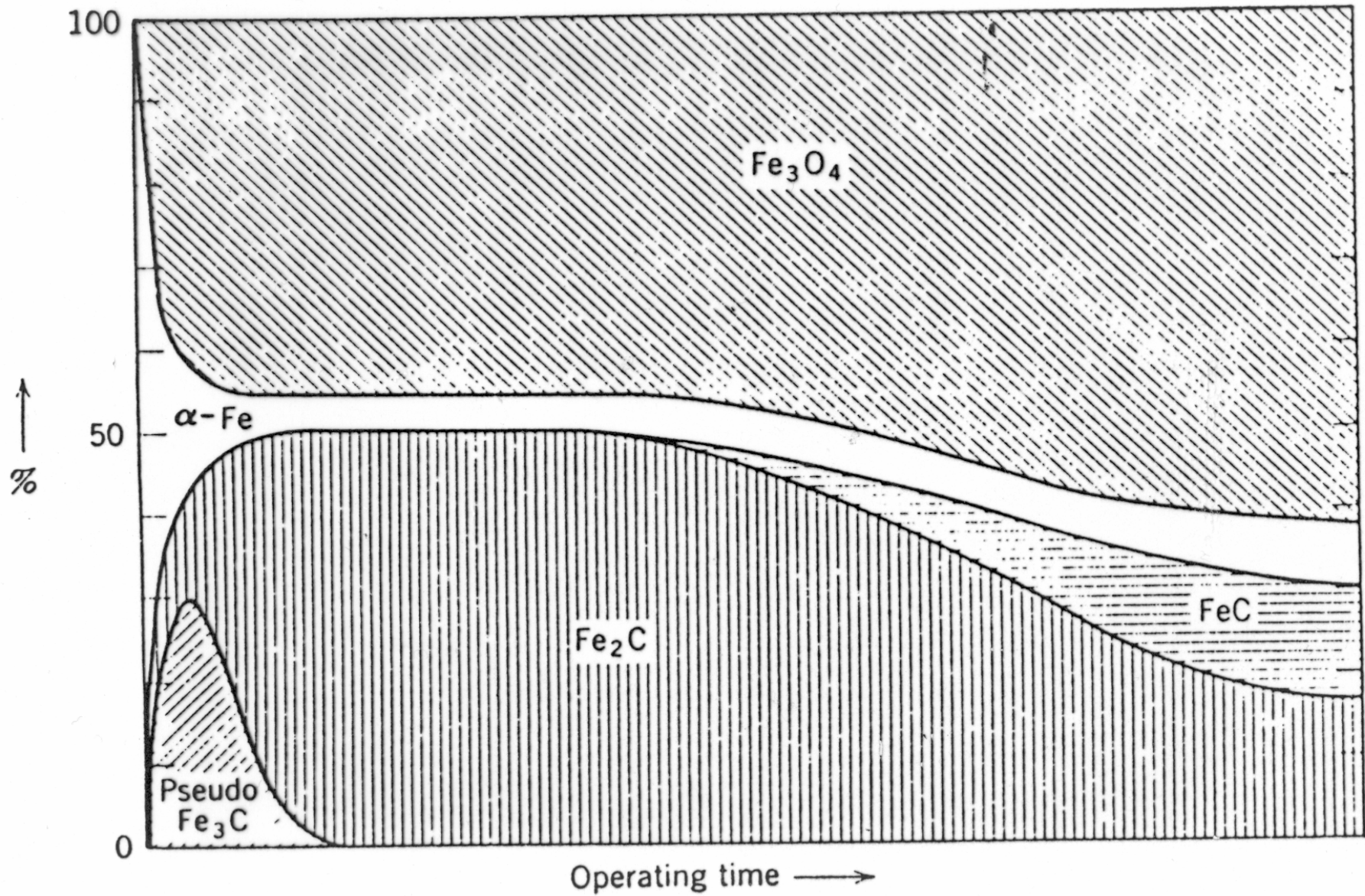
1. Were metal carbides intermediates in FT?
2. Correlate and expand knowledge about carbides
3. What phases are good FT catalyst
4. Prepare these phases with large surface area
5. Investigate those phases previously untried as catalysts

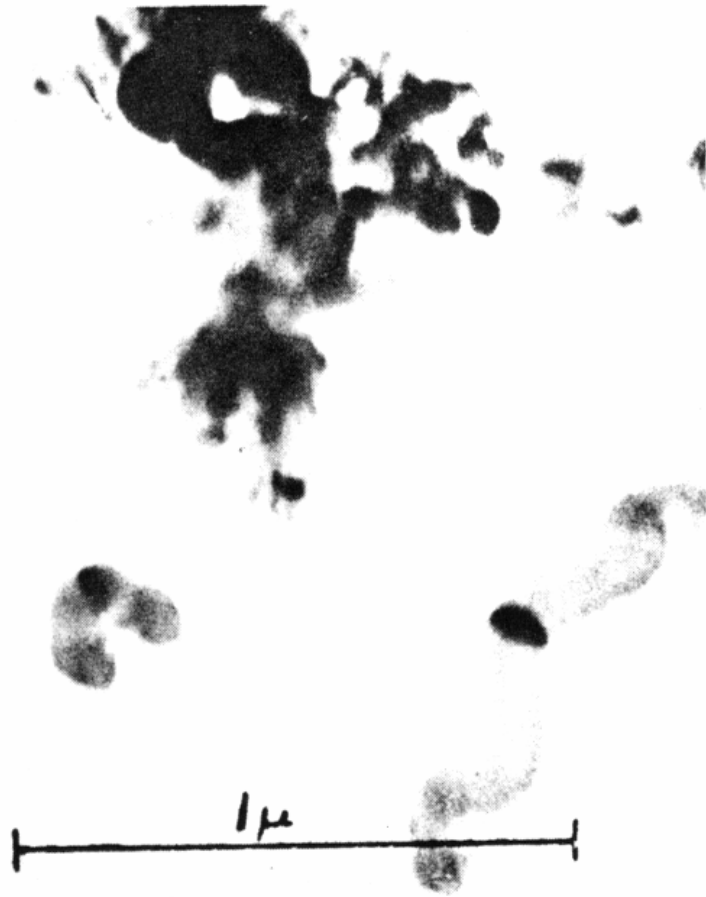
Bureau Reactor Development -1940-1960s

- Fluidized-bed version was not investigated since American industry was **intensively** developing this version.
- Bureau worked on developing:
 - Oil-circulation
 - Slurry
 - Hot-gas-recycle

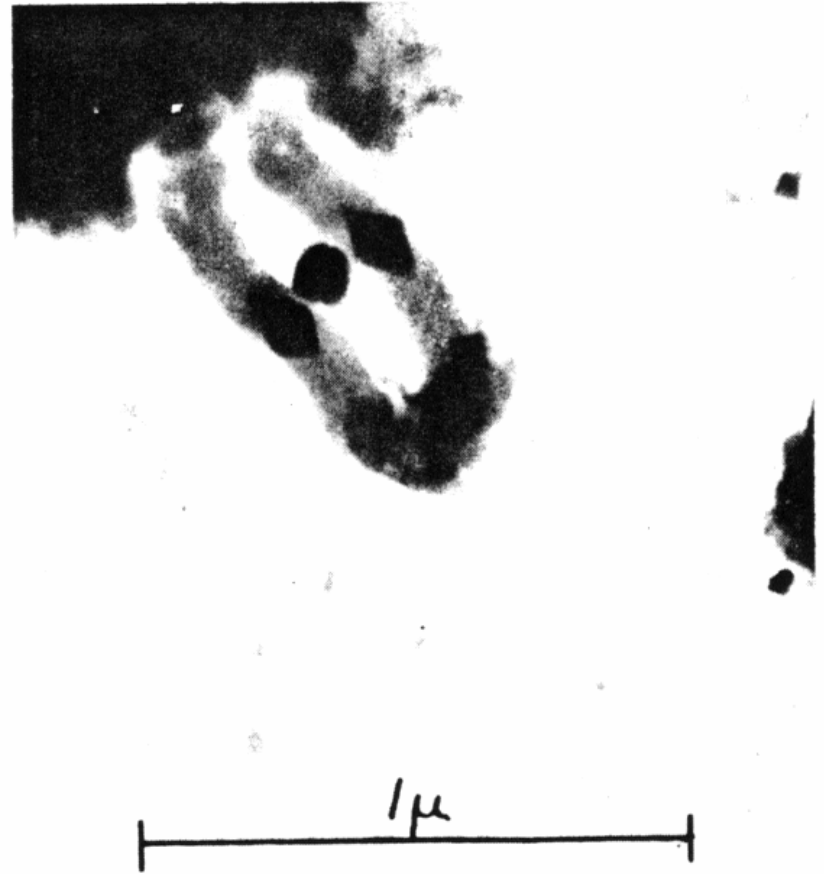
Active Catalyst Phases

- Co and Ni carbide only slightly active; thus, bulk metal carbides are not intermediates. Emmett and co-workers ^{14}C tracer studies validate this.
- Thermomagnetic, crystallographic, and chemical properties of three iron carbides explored and correlated further. All these carbides (cementite, ϵ -carbide and ϵ' -carbides) were active catalysts.
- Iron nitrides and carbonitrides were good catalysts with long life and produced products with large amounts of alcohols.





a



b

Carbon deposited from carbon monoxide on (a) iron and (b) cobalt.

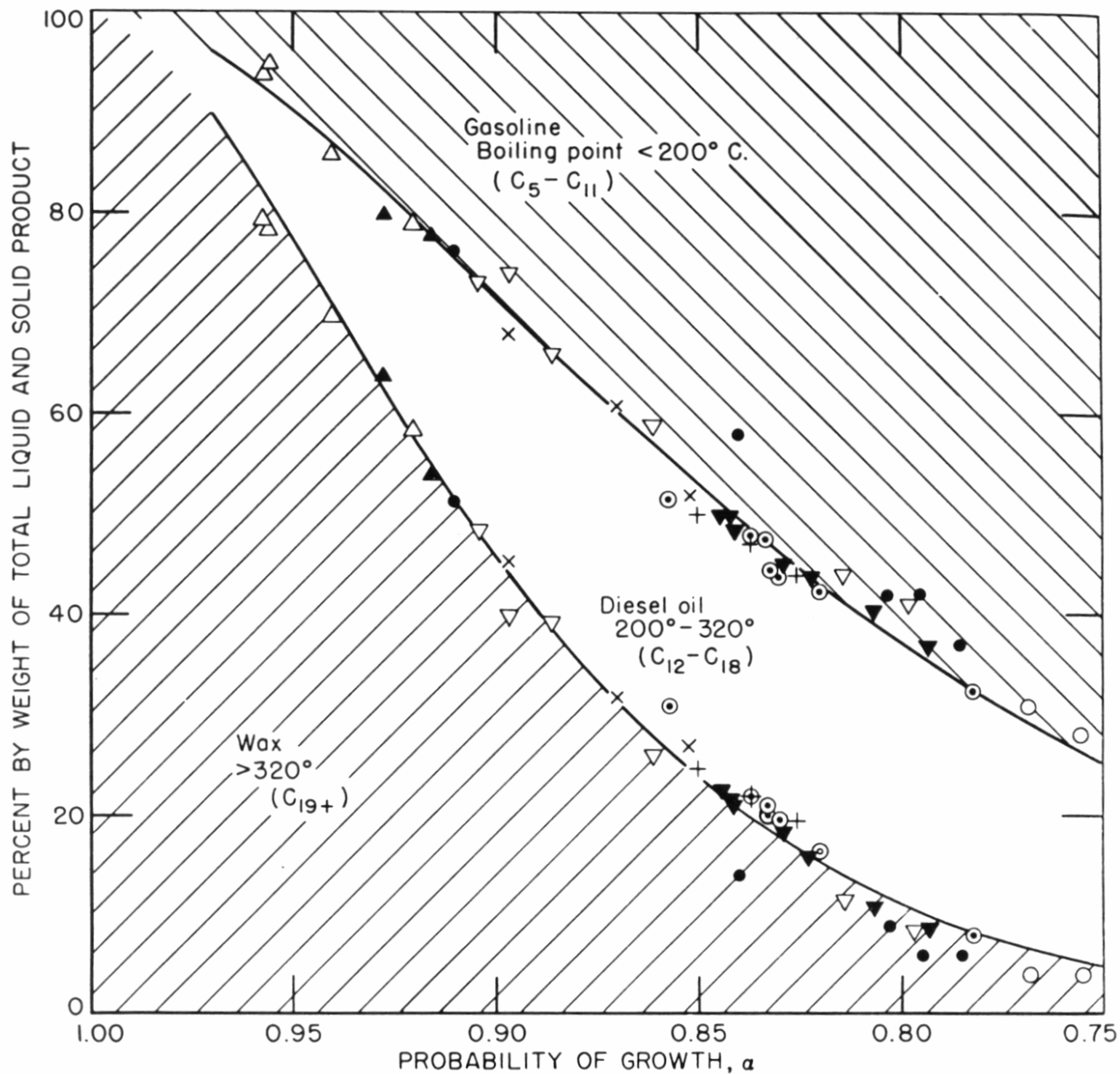


FIGURE 60. - Correlation of Theoretical (curves) and Actual (points) Product Distributions Obtained With Cobalt Fischer-Tropsch Catalysts.

R. B. Anderson, 2nd ICC, 1960 (discussion following paper)

“We do not believe that the effective parts of the catalysts are oxidized in the synthesis. Only the outer portions of the particles seem to be effective in the synthesis, and the remainder is not used due to diffusional problems. The ineffective interior of the particle is exposed to high concentrations of H₂O and CO₂ and the catalyst oxidizes from the inside. Thus the catalyst activity remains constant while the degree of oxidation increases from zero to 85 per cent during the course of an experiment.”

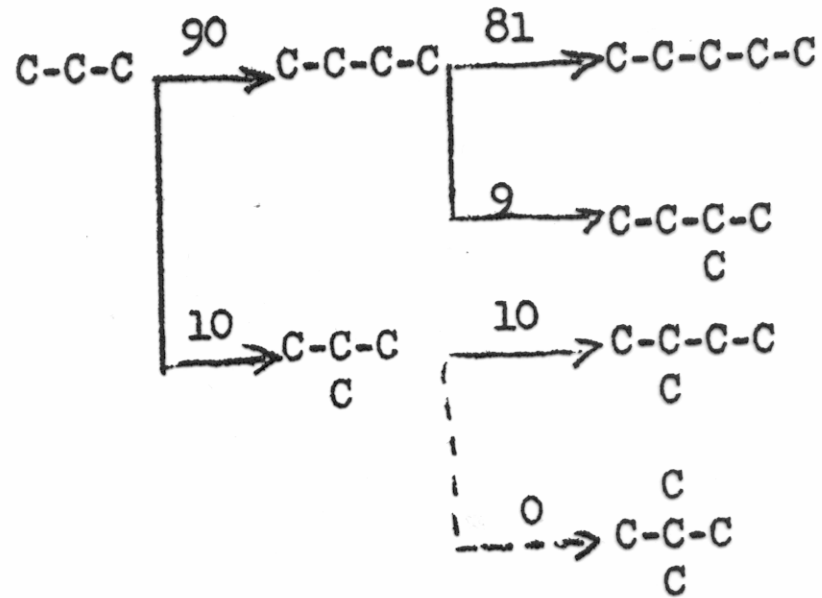
W. K. Hall, R. J. Kokes and P. H. Emmett, *J. Am. Chem. Soc.*, **82**, 1027, (1960)

In spite of the apparent complexity of the Fischer-Tropsch reaction, it is possible to explain many experimental facts on the basis of the relatively simple mechanism postulated by **Storch, Golumbic and Anderson** as modified by **Kummer and Emmett**. According to this picture, the carbon monoxide and hydrogen react on the surface to form a species similar to adsorbed methanol. These C_1 surface complexes then react by splitting out water to form a C_2 complex similar to ethanol. The production of higher molecular weight products is presumed to occur by the reaction of C_n with C_1 complexes to form water and C_{n+1} complexes.

H. H. Storch, N. Golumbic and R. B. Anderson, "The Fischer-Tropsch and Related Syntheses," John Wiley and Sons, Inc., New York, 1951.

J. T. Kummer and P. H. Emmett, *J. Am. Chem. Soc.*, **75**, 5177, (1953).

Chain Growth



g. Equilibrium distribution of hydrocarbons is not obtained.

Active Catalyst

Almost all active FT catalysts are ferromagnetic, indicating that activity is related to the presence of an unfinished “d” shell, a necessary but not adequate condition for ferromagnetism.

Bureau “Standard Reactor”

- Set about 1945 and used through 1950-60s
- Laboratory maintained 16 of these reactors
- Reactor constructed of 0.625 i. d. with catalyst supported on wire gauze soldered to tube. Temperature was controlled by pressure on the boiling liquid in outer steel jacket. Can operate to 21 atm
- Routine tests SV and pressure held constant and temperature varied to get 60% contraction ($H_2/CO = 1$) and 70% ($H_2/CO = 2$). Testing continuous for about 6 weeks.

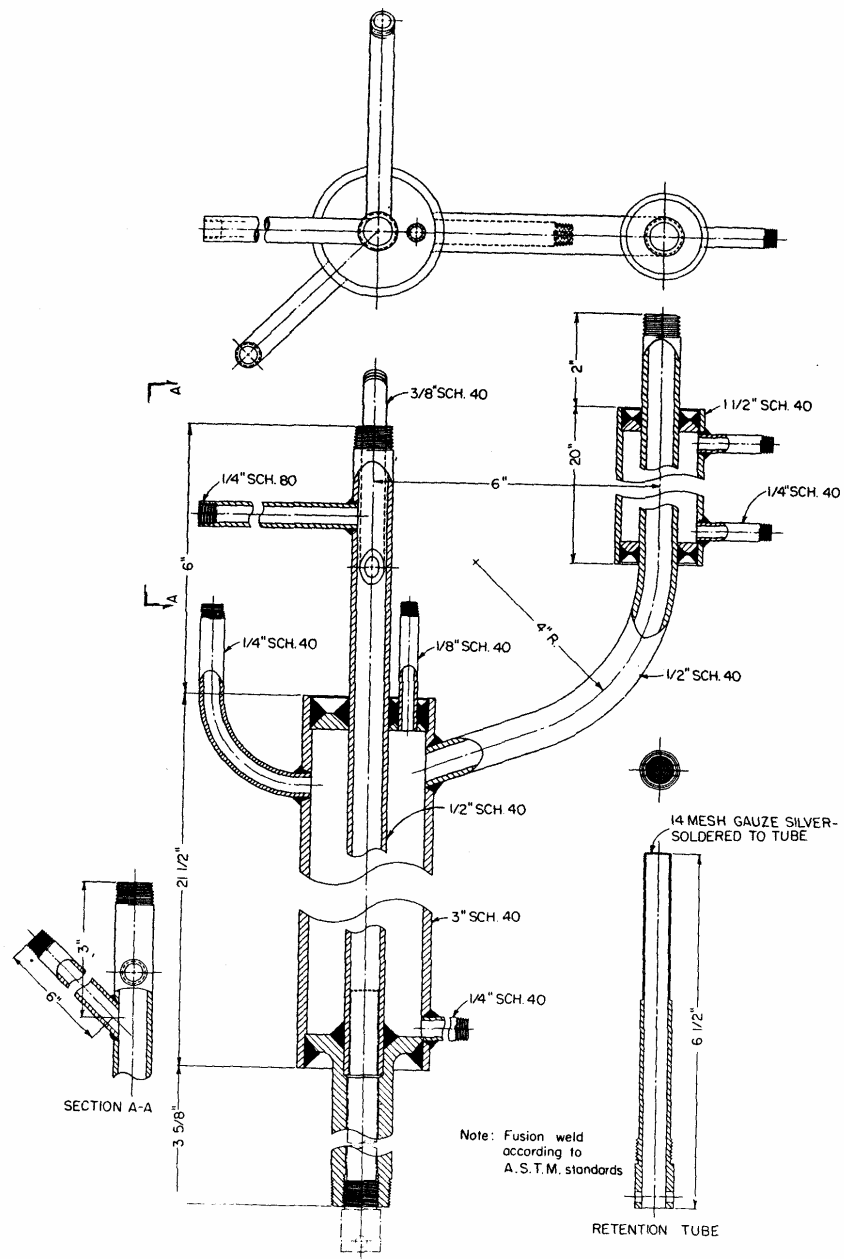


FIGURE 61. Construction of Standard Reactor for Testing Fischer-Tropsch Synthesis Catalysts.

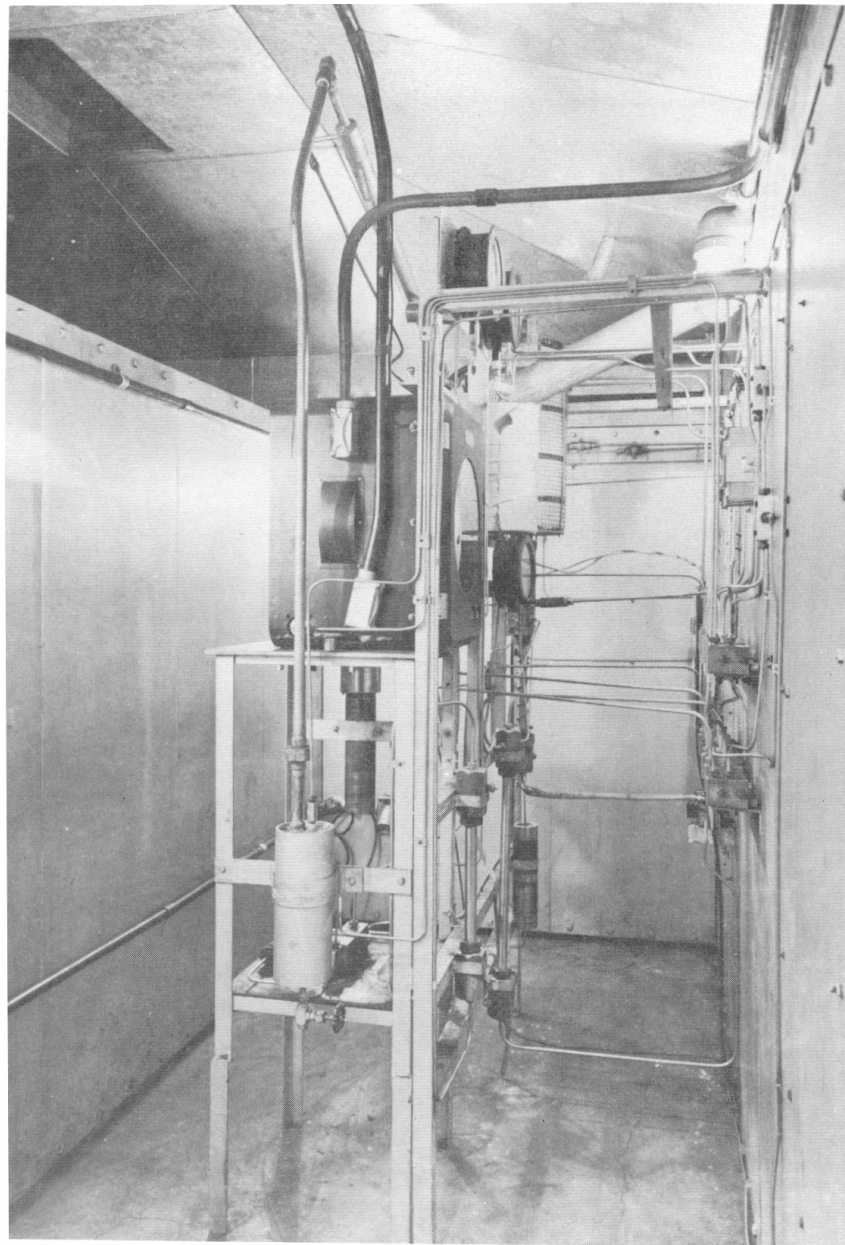


Figure 33. - High-pressure Fischer-Tropsch unit.

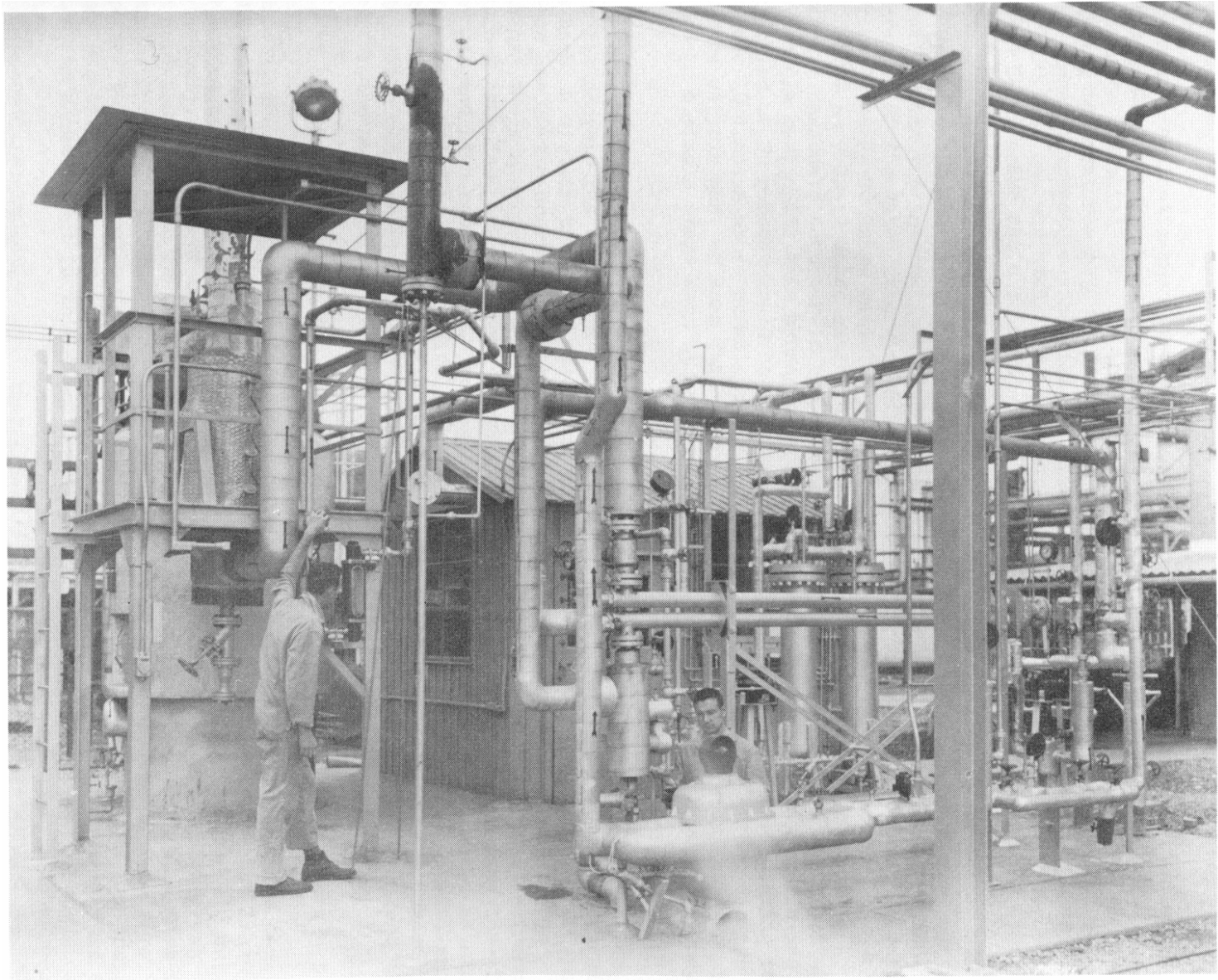


Figure 27. - Catalyst reduction unit.



Figure 34.- Catalyst testing units. Front view.



Figure 35.- Catalyst testing units. Rear view.

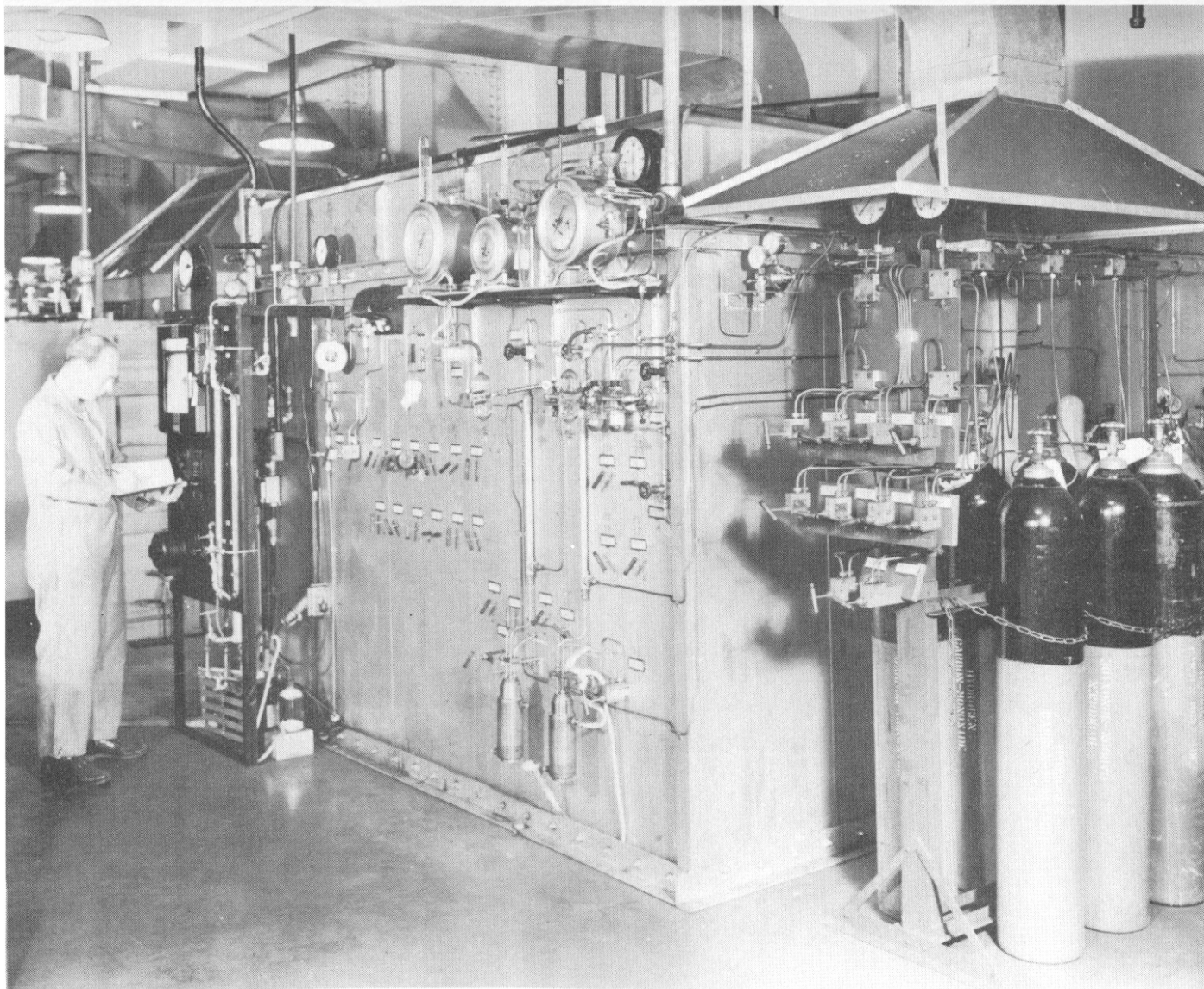


Figure 34. - Control panel for high-pressure Fischer-Tropsch unit.

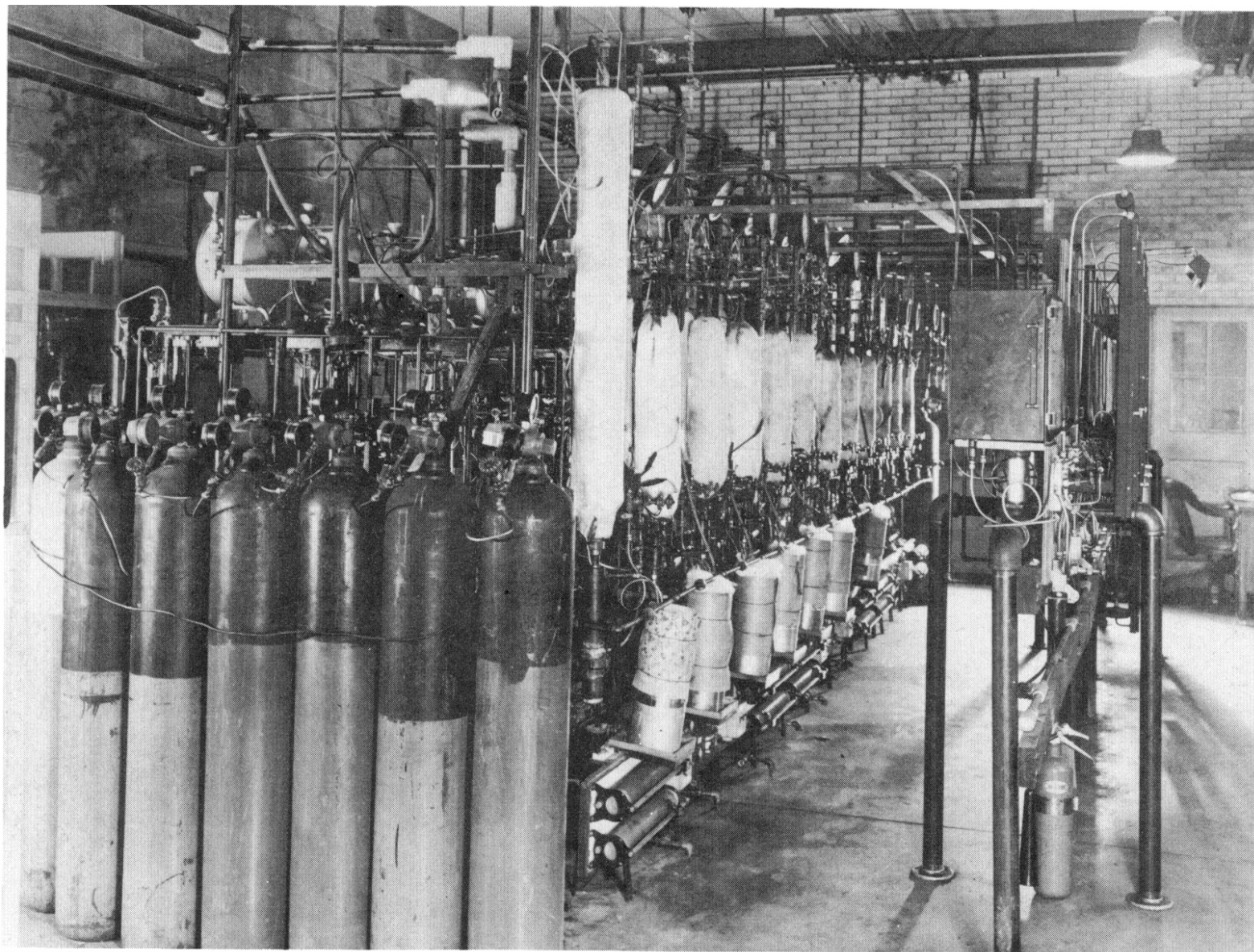


Figure 26. - Fischer-Tropsch catalyst testing units.

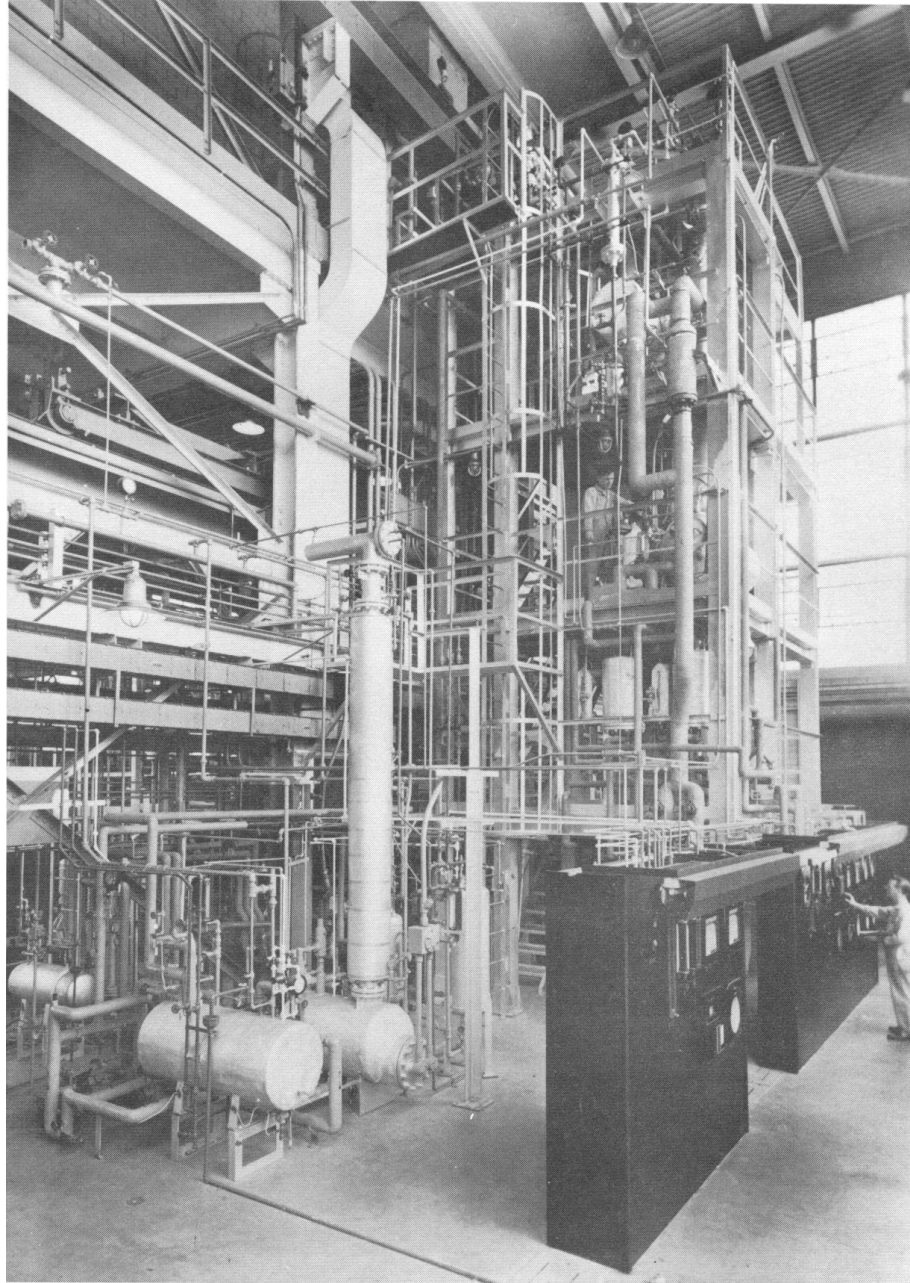


Figure 28. - Barrel-a-day Fischer-Tropsch pilot plant.

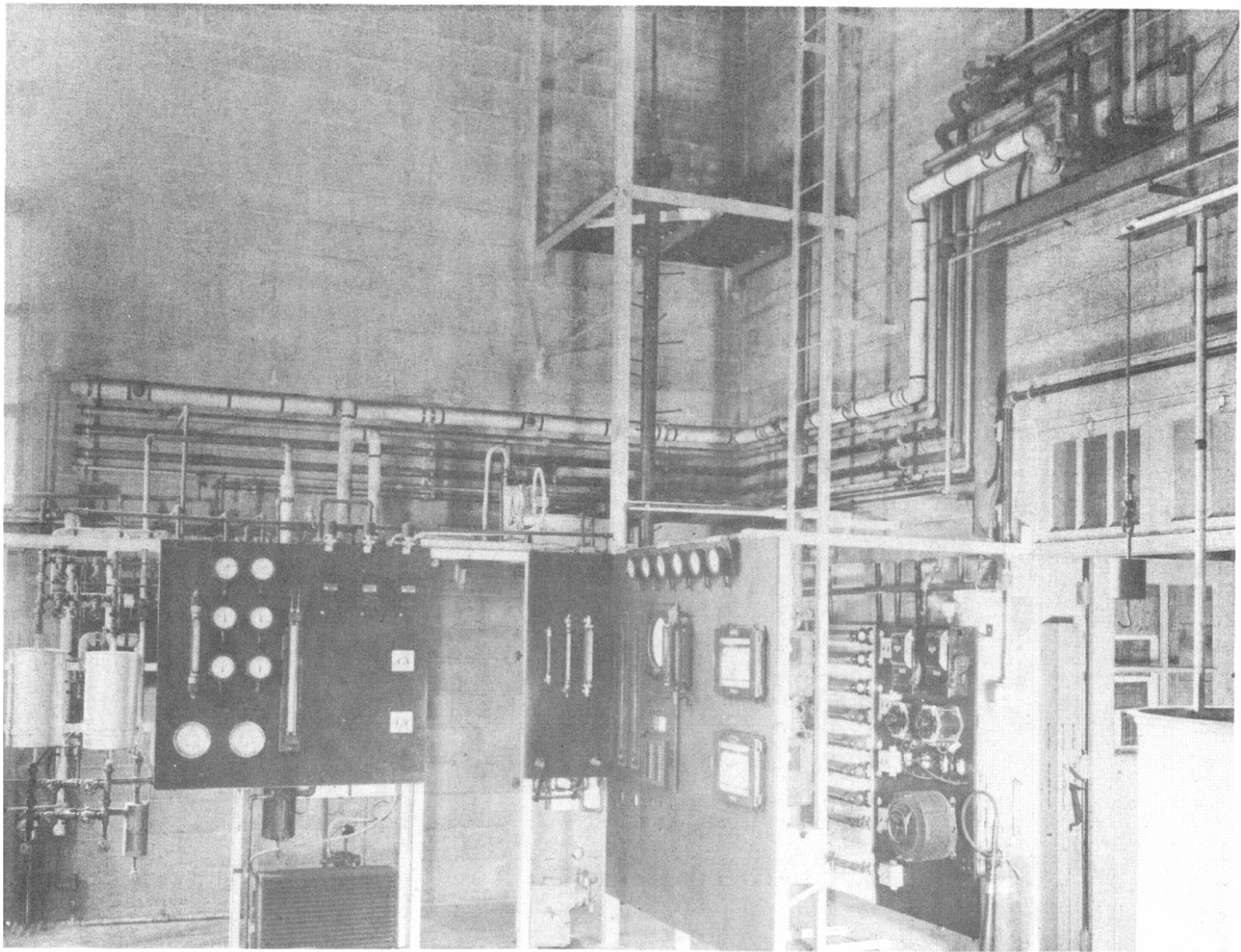


Figure 29. - Fischer-Tropsch experimental plant with internally cooled converter.

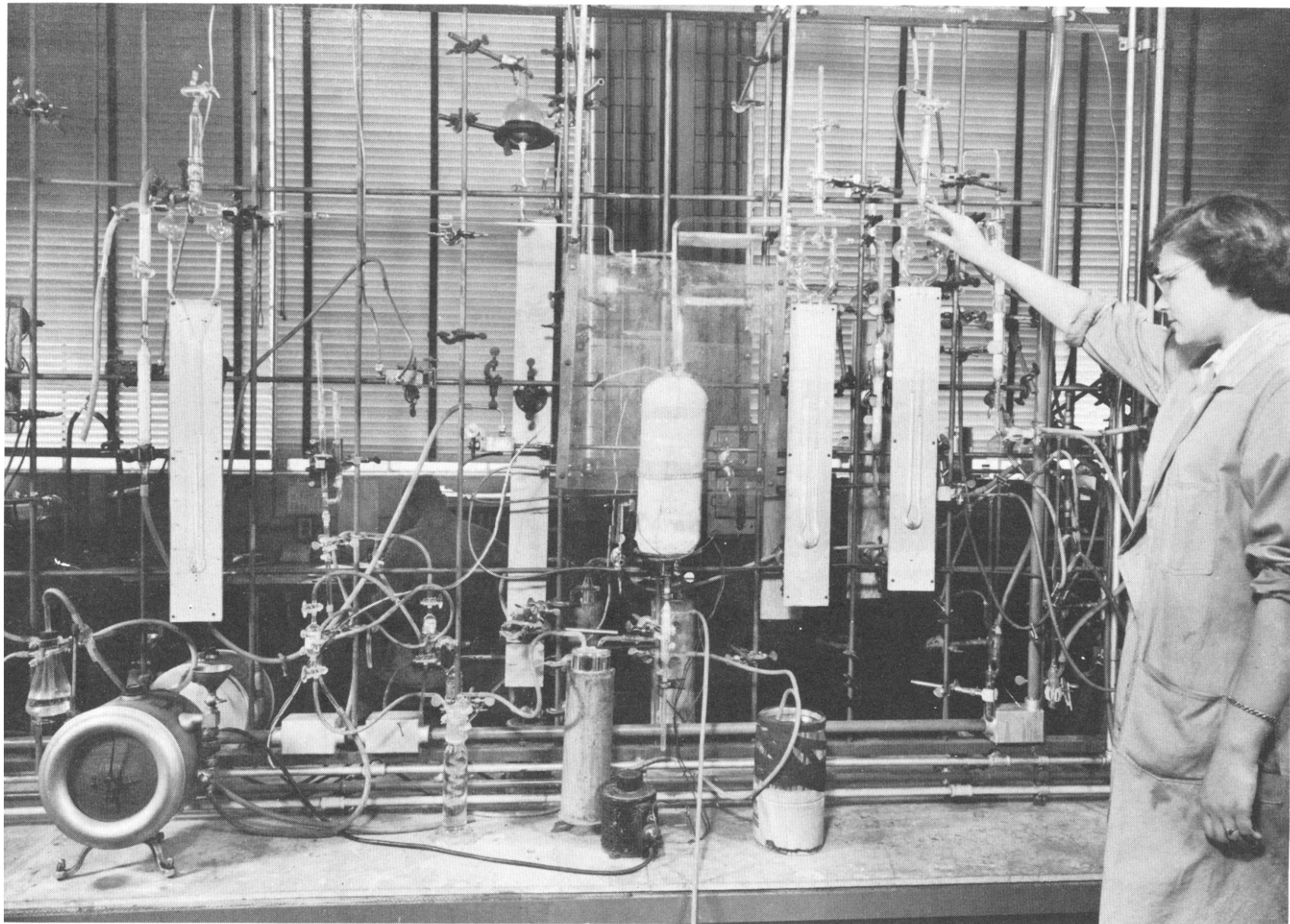


Figure 29. - Bench-scale catalyst-testing apparatus.

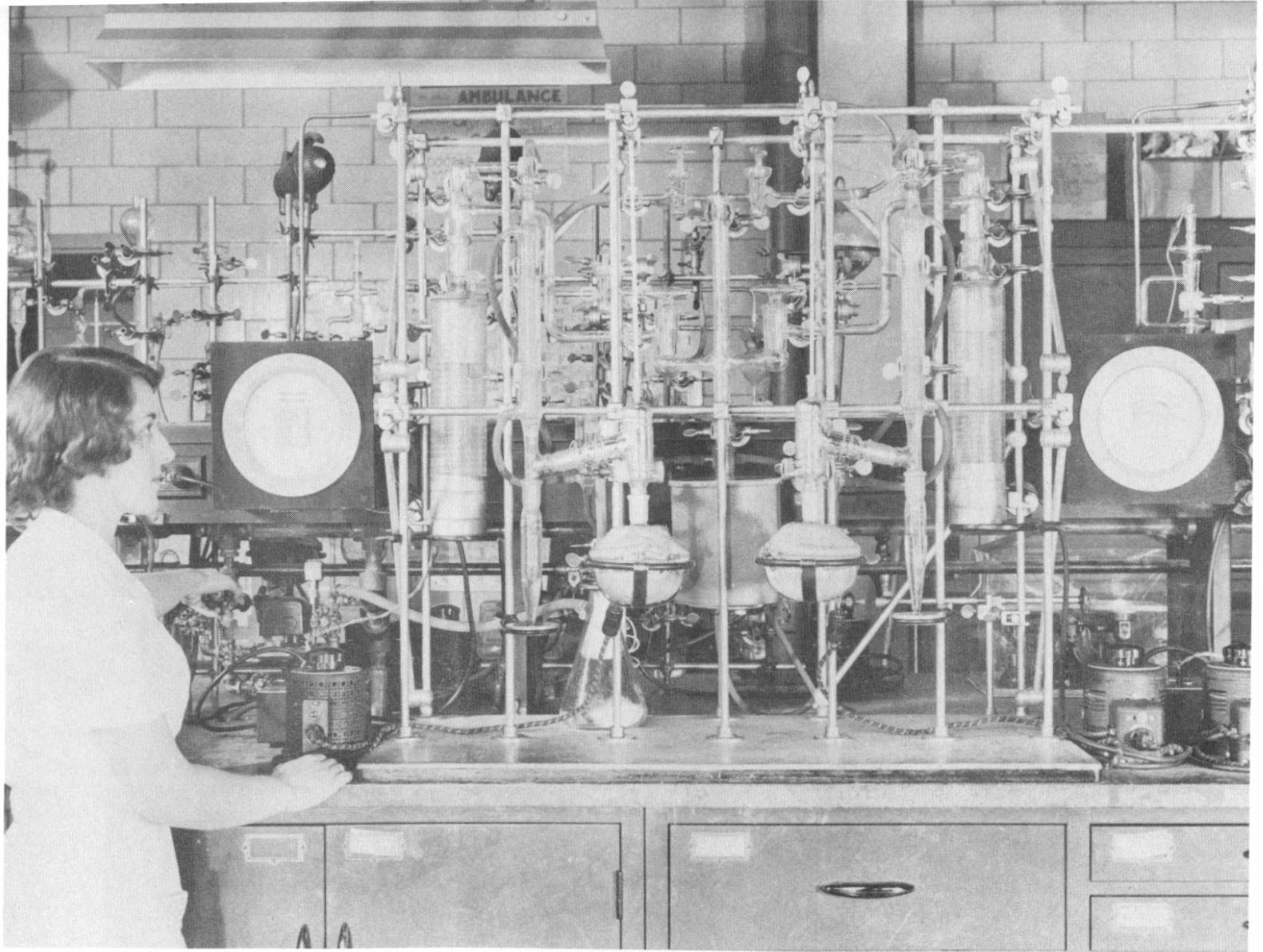


Figure 39. - Vacuum-distillation equipment for characterizing Fischer-Tropsch products.

Oil-Circulation Process

- 1944: bench-scale with oil trickling over catalyst bed. Countercurrent flow of gas and oil. Oil did not affect activity or product distribution.
- 1946: pilot plant: 3-inch diameter and 8-foot bed height. Countercurrent flow abandoned because of flooding - concurrent downflow of oil and gas. Hot spots developed at entry above GHSV 300 - eliminated when bed completely submerged in oil. Gas and liquid fed at bottom of reactor and flowed concurrently upward. No difference between wetted and submerged bed.

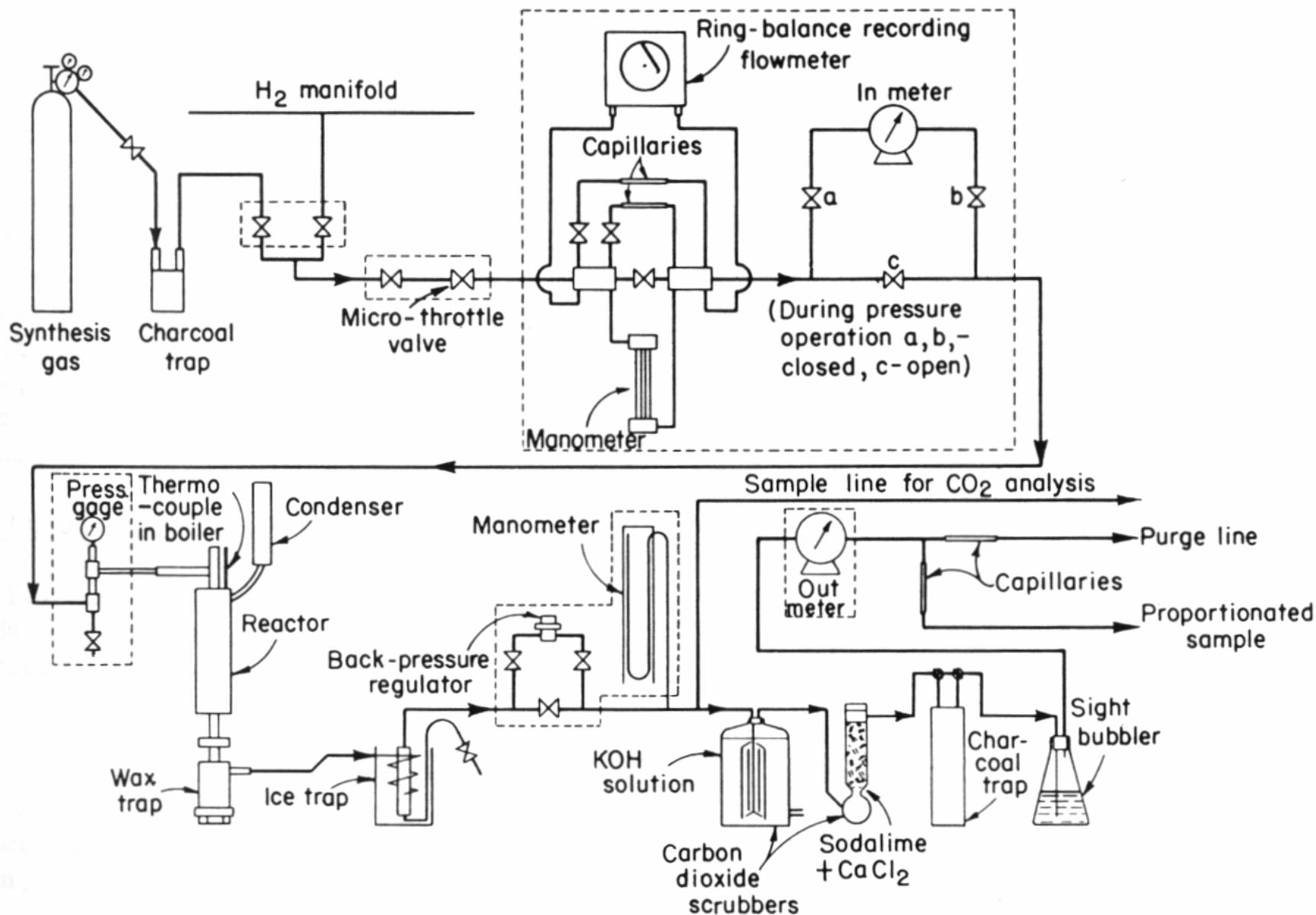


FIGURE 62. - Flow Diagram of Unit for Fischer-Tropsch Synthesis Catalysts.

Oil-Circulation Process

- Pelleted precipitated iron catalysts disintegrated and caused pressure drop after few weeks of operation.
- Fused, synthetic ammonia type iron catalyst was then used (6-20 mesh) and oil, not vaporization, removed heat of reaction.
- Catalyst particles cemented together after 1-3 months even though catalyst was still active.
- Switch to expanded catalyst bed (10-20%) by increasing oil flow. In this mode, plant operated for 2-3 months without disintegration or cementation of catalyst.

Oil-Circulation Process

- More Durable Catalysts Needed: 1/8 inch diameter shot and iron or steel lathe turnings were tried for higher temperature operation.
- Lathe turnings best - one batch operated 2,700 hrs (1,200 hrs. at 283°C) - at 283°C C₃+ was 85% gasoline and only 2% wax.
- Development in 3- and 8-inch reactors complete by 1955. Process is versatile, H₂-rich or CO-rich gas may be used, and products can be varied over a wide range.

Bureau of Mines - Slurry Process

- Following exploratory studies, laboratory units and a pilot plant were constructed - 0.25 to 5 gallons of product per day.
- 3-inch pilot plant held 10-foot high of slurry with about 15 L (4 gallon) volume.
- For iron catalyst preferred activation was with synthesis gas at atmospheric pressure and 270°C.
- Synthesis at 100 to 300 psi and hourly space velocity of 100 to 300 volumes of gas per volume of slurry led to 65-80% of gas conversion at 270°C

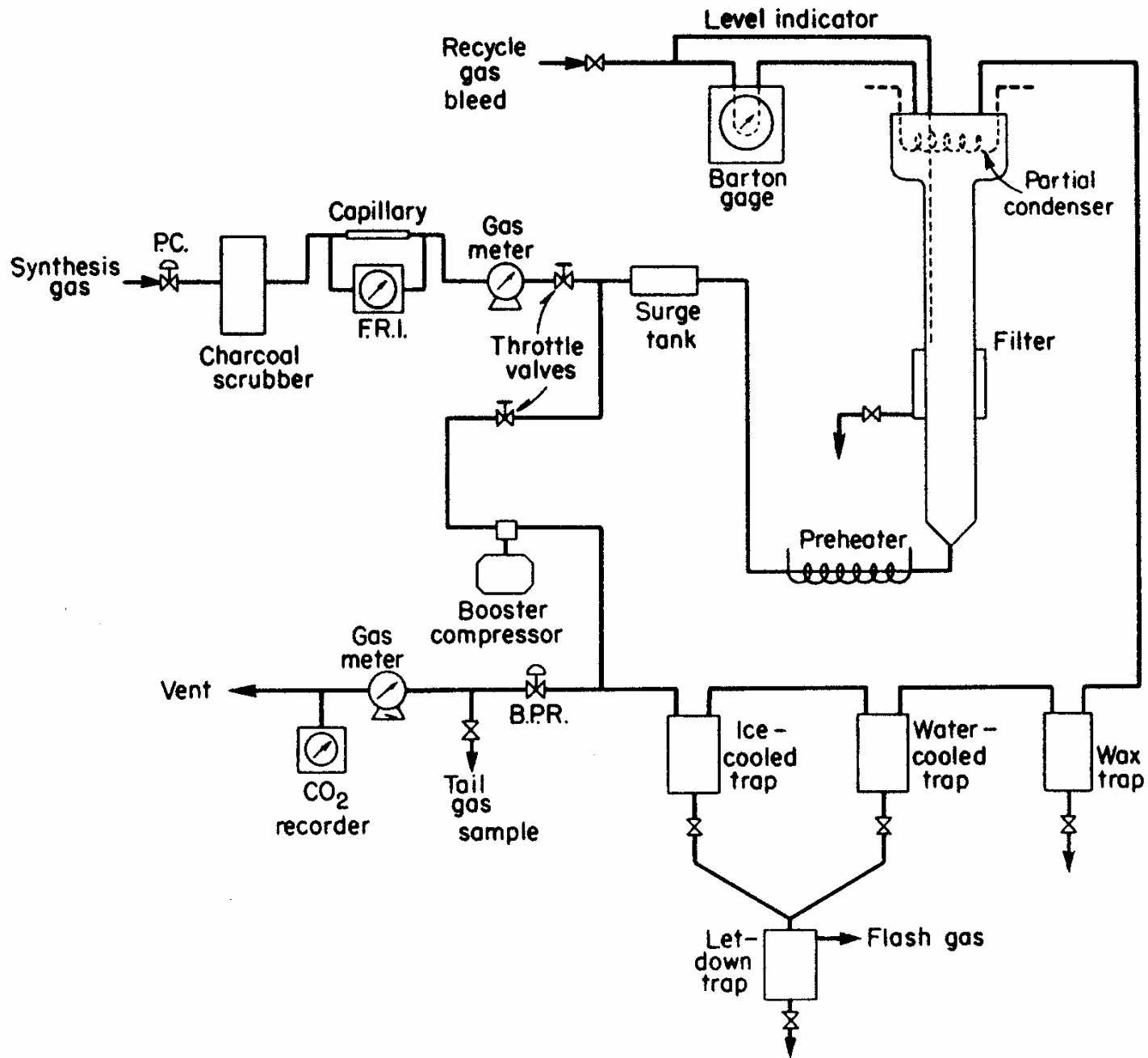


FIGURE 69. - Flow Diagram of Fischer-Tropsch Slurry Unit.

Bureau of Mines - Slurry Process

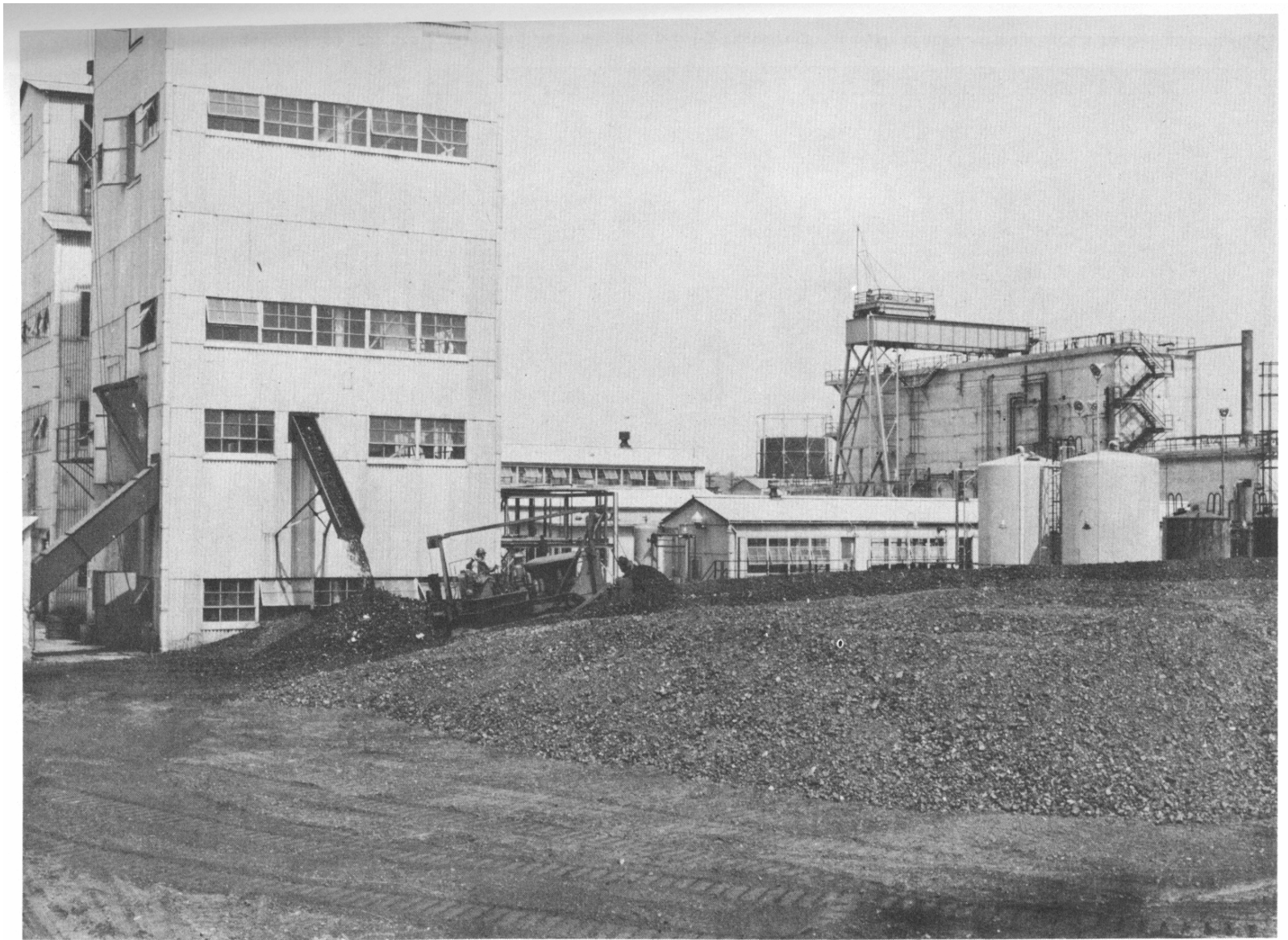
- 124 experiments lasting up to 4 months each, effects of catalyst concentration, gas composition, pressure space velocity, and composition of suspension oil were defined.
- Results indicate:
 1. Catalyst concs. 50 to 500 g Fe/L slurry are operable.
 2. H_2/CO from 0.7 to 1.3 can be used.
 3. Pressures from 300 to 400 psi are preferred
 4. Wide range of LHSV can be used: lower limit is gas rate needed to suspend particles and upper limit is velocity at which frothing or other major disturbance of oil phase occurs.
 5. Additives may aid in suspending catalyst particles

Bureau of Mines - Slurry Process

- Reactor design was studied.
- Smaller concentric tube inserted in reactor and syngas added through smaller tube. The center tube caused circulation of slurry in the reactor.
- In larger reactors, offset circulation legs were added - circulation effected by gas lift or by pumps.
- Pumps allowed slurry flow to be concurrent or countercurrently to gas flow - no variation with flow direction was observed.



Figure 39. - Air view of coal-to-oil demonstration plants at Louisiana, Mo. Missouri Ordnance Works, upper left; hydrogenation plant, upper right; gas-synthesis plant, lower right; administration buildings and employee housing development, lower left.



212686 O - 52 - 3

Figure 2. - 2,500-ton pile of Illinois coal ready for processing.

Demonstration Plant - Louisiana, Missouri

M. L. Kastens, L. L. Hurst and R. G. Dressler, Ind. Eng. Chem., **44** (1952) 450

- Gasification

- Linde-Frankl Oxygen Plant: 95%, rest N₂ and Ar
- Gasifier: vertical cylinder lined with rammed aluminum oxide. Oxygen-coal mixture enter reaction chamber about 2 ft. from bottom tangent to circle slightly smaller than i. d. and steam enters about 1/4th of way around the circle. Coal spirals upward and is gasified; solid hits wall and flows as liquid to bottom
- 70,000 ft³/hr syngas: 14.8% CO₂; 37.2 H₂; 43.5% CO; 4% N₂; 0.3% Ar, 0.1% O₂; 0.1% H₂S.
- Gas leaving gasifier mixed with 20% cool, cleaned syngas to react with oxygen if an upset in gasifier occurs - safety measure to prevent explosion in gas cleanup if upset occurs.
- Syngas stream at 1800°F passes through heat exchanger to produce 2000 pounds 275 lb/in² steam/hr (1 lb steam/lb coal)



Demonstration Plant - Louisiana, Missouri

M. L. Kastens, L. L. Hurst and R. G. Dressler, Ind. Eng. Chem., **44** (1952) 450

-

- Gas Cleanup

- Cyclone and direct-contact, cascade-type washer-cooler scrubs gas with 250 gal/min to remove more solids and cool to 100-150°F
- Two electrostatic precipitators to remove tars and solids.
- Compress to 350 psig.
- 50% Diethanolamine-water to remove CO₂ and H₂S, then iron oxide on wood chips, and then activated carbon.



Demonstration Plant - Louisiana, Missouri

M. L. Kastens, L. L. Hurst and R. G. Dressler, Ind. Eng. Chem., **44** (1952) 450

- FT Reactor
 - 3 Foot diameter and 30 ft 10 in. tall
 - Contains 1 ft graded steel balls
 - 15 foot iron catalyst (14,000 lb; 106 ft³)
 - Constructed of carbon steel; lined with hardened lime/sand mix.
 - 180,000 standard ft³/hr; 900 gal/min coolant
 - About 50/50 fresh syngas and recycle
 - 50% of gas dissolves in oil
 - Maximum temperature rise is 25°F (14°C)
 - Catalyst bed expansion of 20-30%
 - 50-80 BPD of product (90% hydrocarbons; 70% gasoline, 10% diesel, 10% distillate, 10% wax)
 - About 5% of total product is ethanol, acetic acid and acetone are 2%, higher alcohols and ketones with very small amount of acids, 2%.



Demonstration Plant - Louisiana, Missouri

M. L. Kastens, L. L. Hurst and R. G. Dressler, Ind. Eng. Chem., **44** (1952) 450

“It was originally planned to bleed off a portion of the circulating coolant and vacuum distill to remove waxes. ... However, experimental investigations revealed that the build-up of the wax constituents in the coolant will proceed only to an equilibrium concentration of about 80%. At this concentration the composition of the coolant will become essentially stable, and **no additional waxes will be formed, presumably because of mass action effect.**”

Demonstration Plant

RI 5043, Synthetic Liquid Fuels: Oil from Coal, April 1954

- Started 4th operating period Nov. 29, 1952 and shut down Jan. 24, 1953. Operated 39 days.
- GHSV of 480 obtained 84% conversion and at 370 obtained 92%.
- As catalyst disintegrated, the conversion increased. Fine catalyst suspended in coolant oil and activity reached maximum at about 12% “ash” in the coolant oil. At 12% ash, erosion of the recycle pump was severe.
- During a high conversion period, 1 million ft³ purified gas was fed and it produced 940 gallons gasoline, 530 gal. Of LP-gas and 110 gal haevy oil.

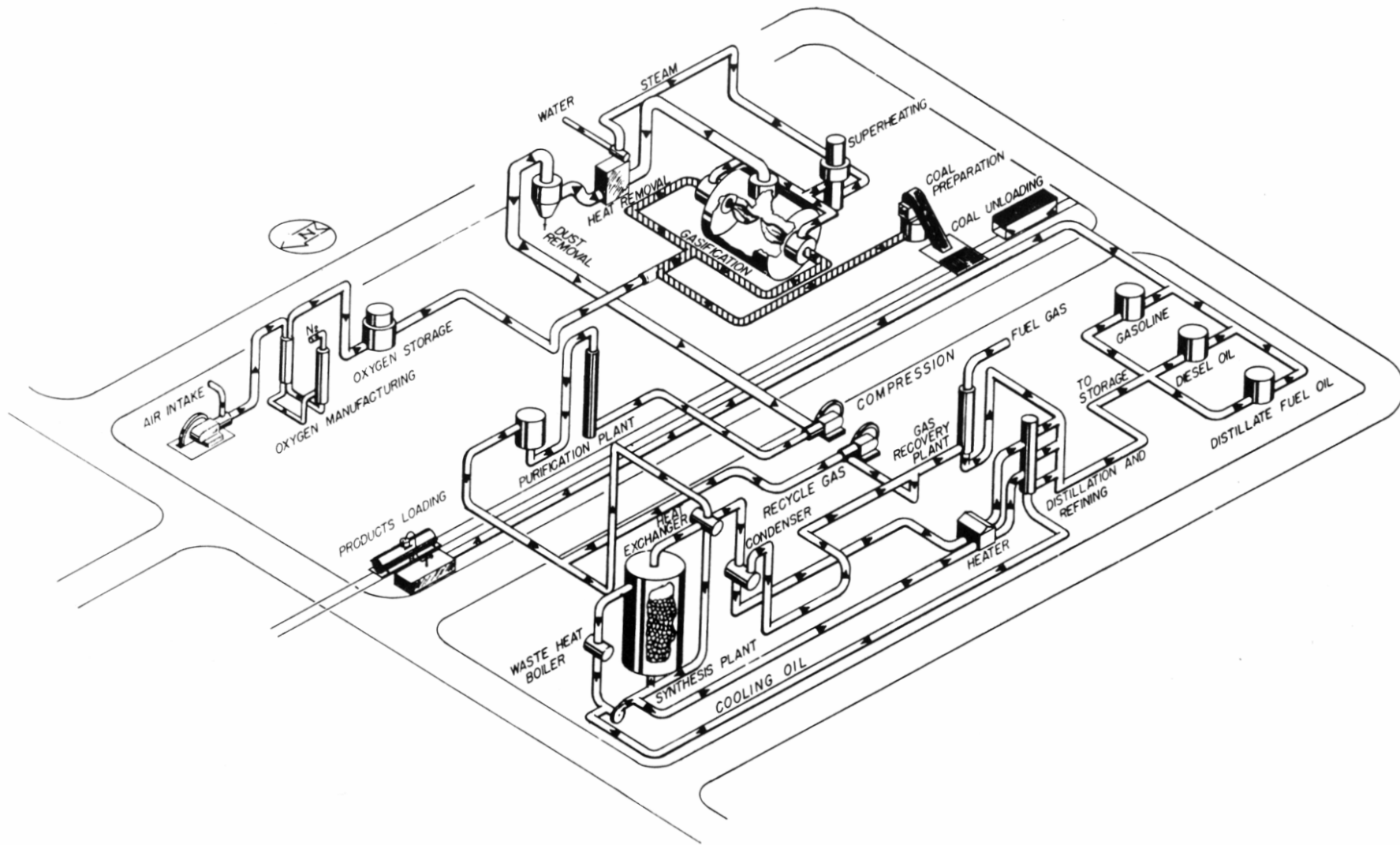


FIGURE 71. - Simplified Sketch of Fischer-Tropsch Demonstration Plant at Louisiana, Mo.

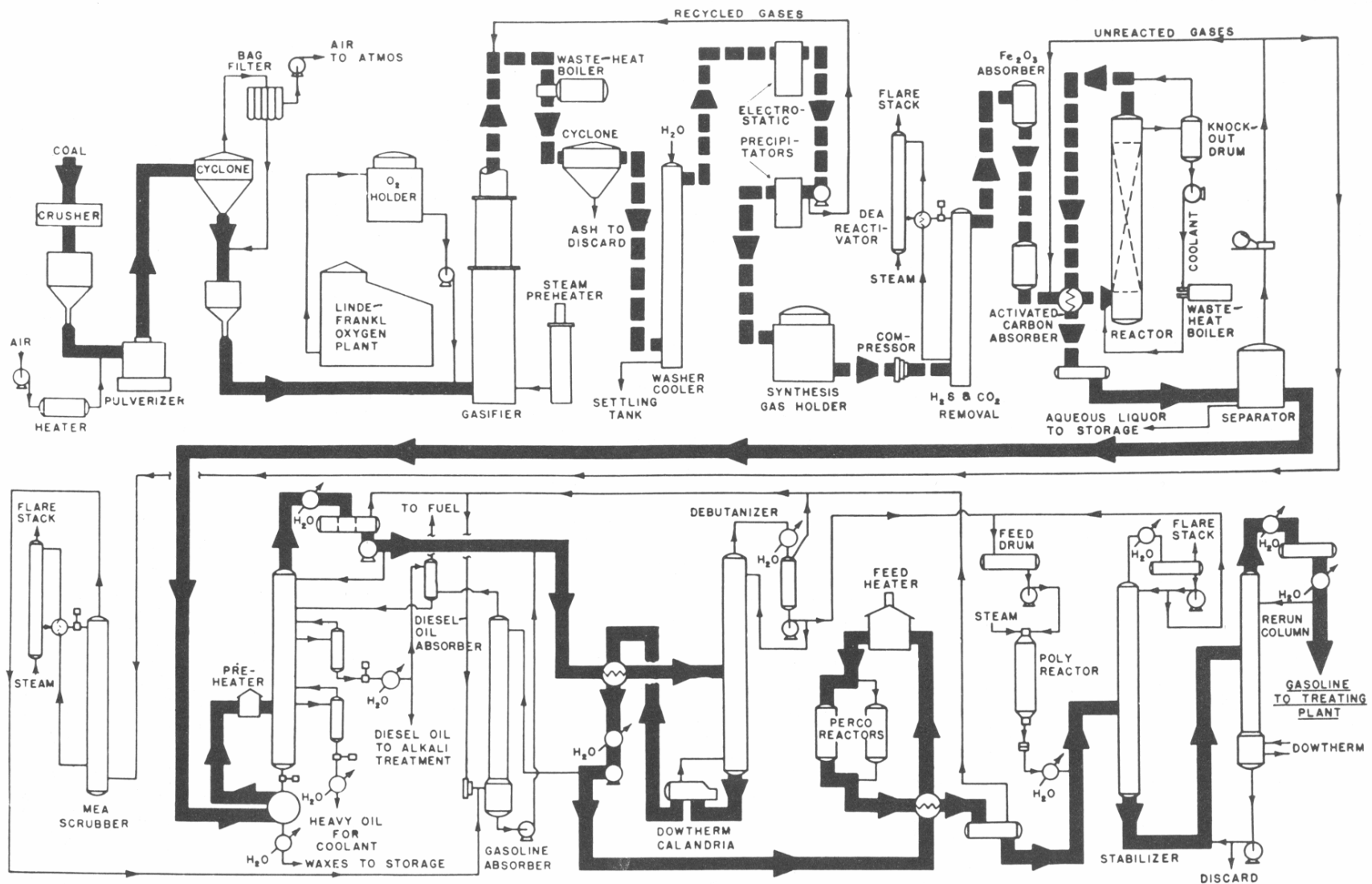


Figure 16. - Flow sheet of Gas-Synthesis Plant, with original distillation unit.

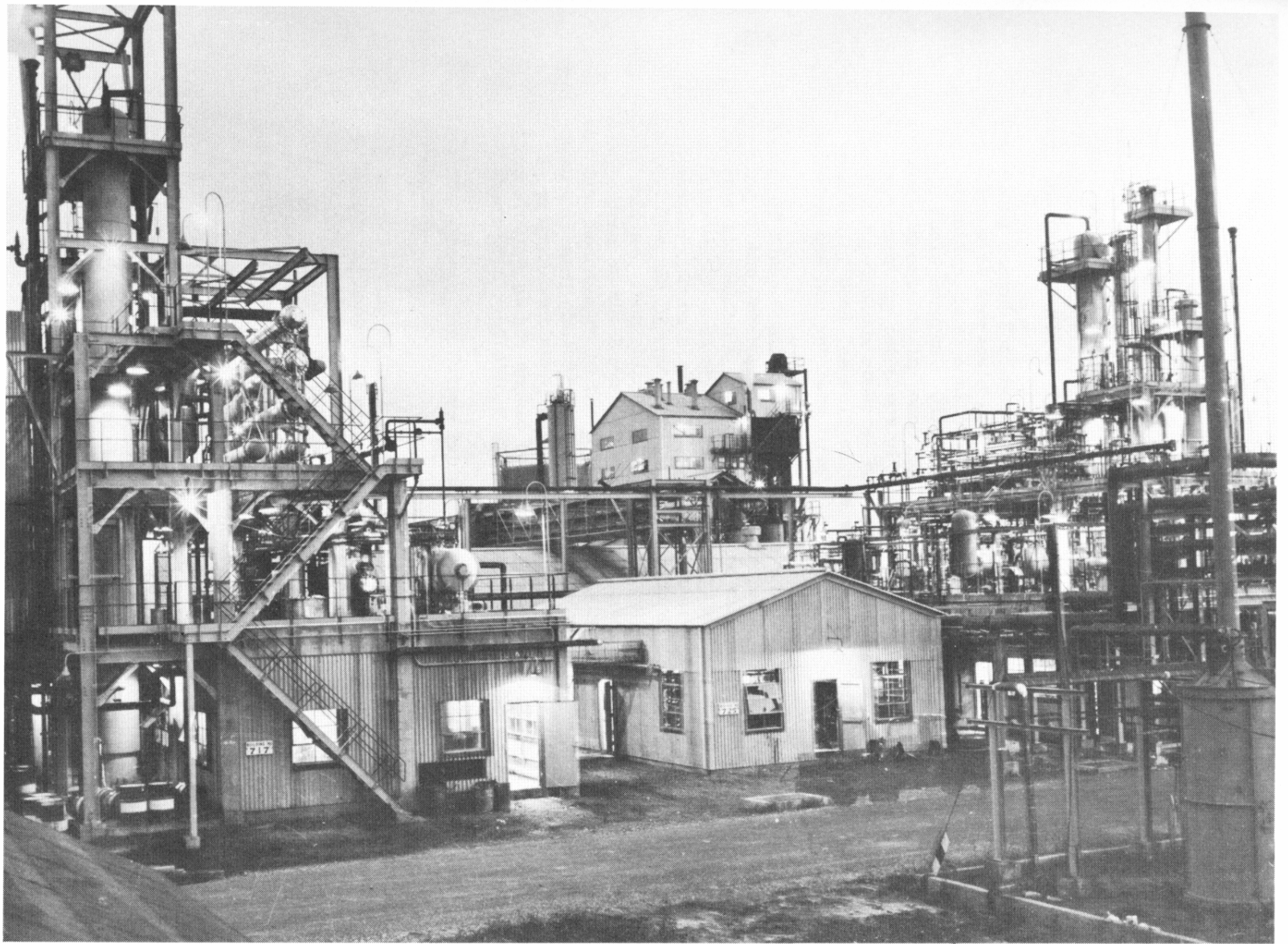


Figure 1. - Gas-Synthesis Demonstration Plant, Louisiana, Mo. (view looking east).

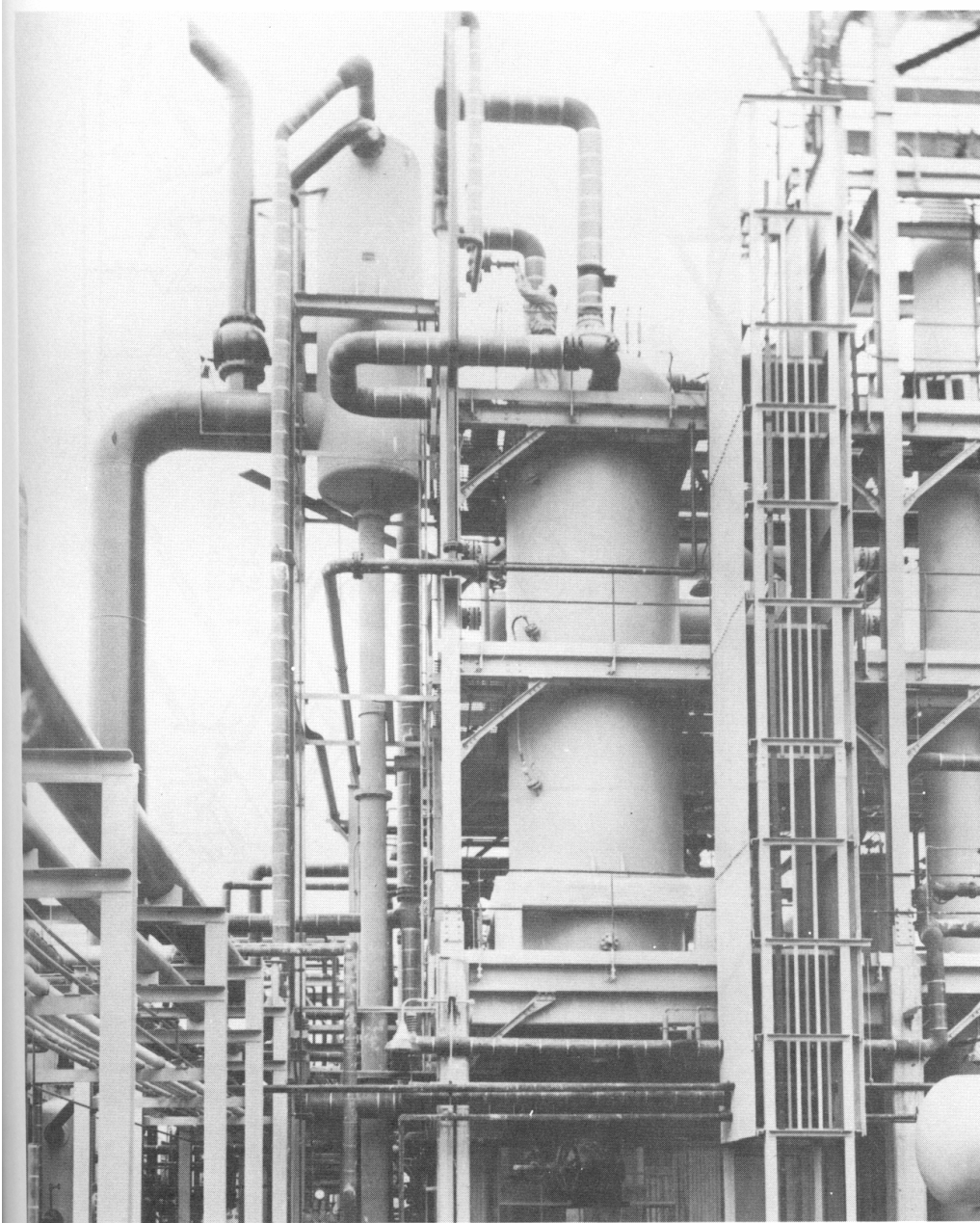


Figure 23. - Gas-synthesis reactor, Gas-Synthesis Demonstration Plant.

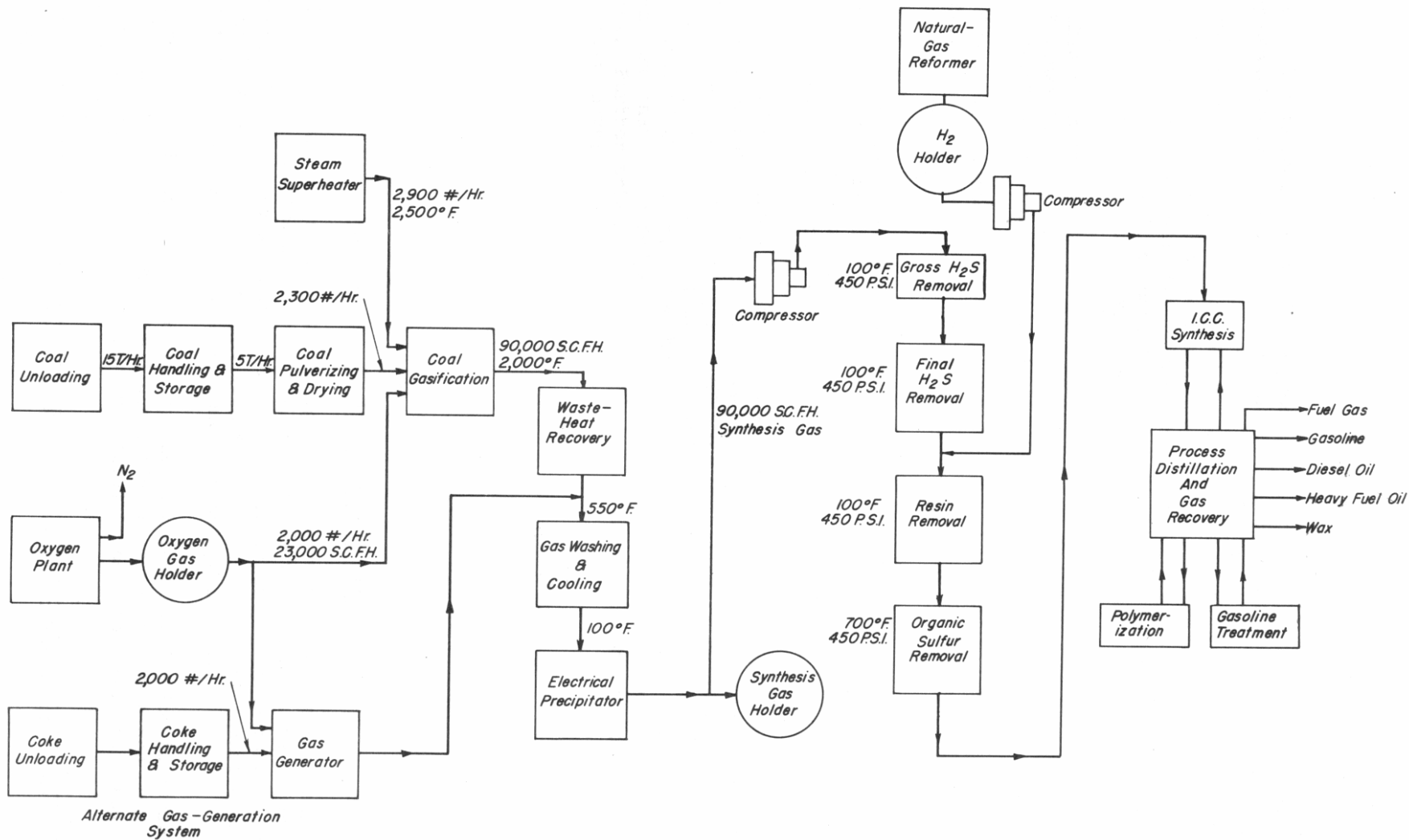


Figure 45. - Block diagram of flow, Gas Synthesis Demonstration Plant.

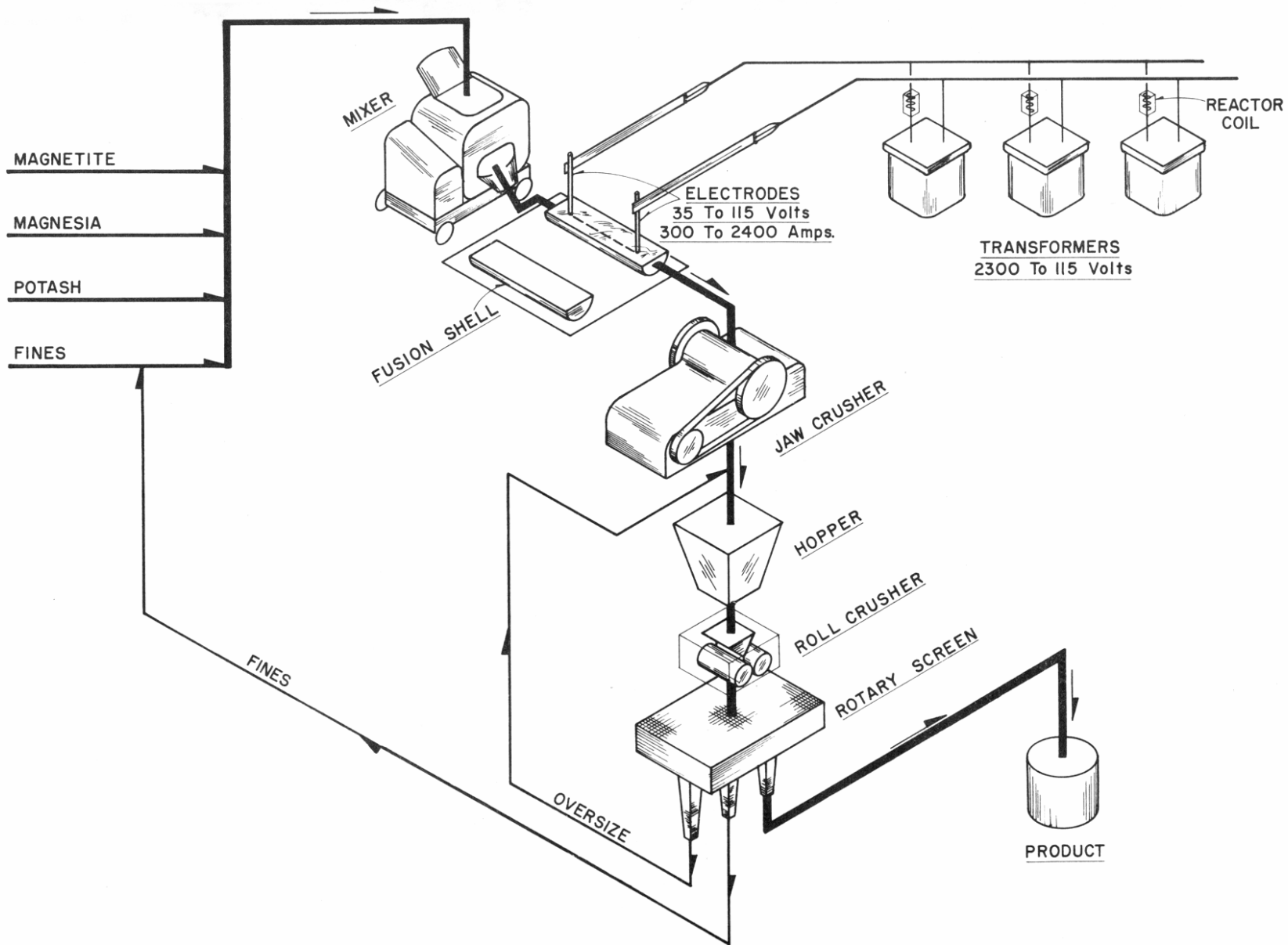


Figure 24. - Flow diagram of catalyst fusion unit.

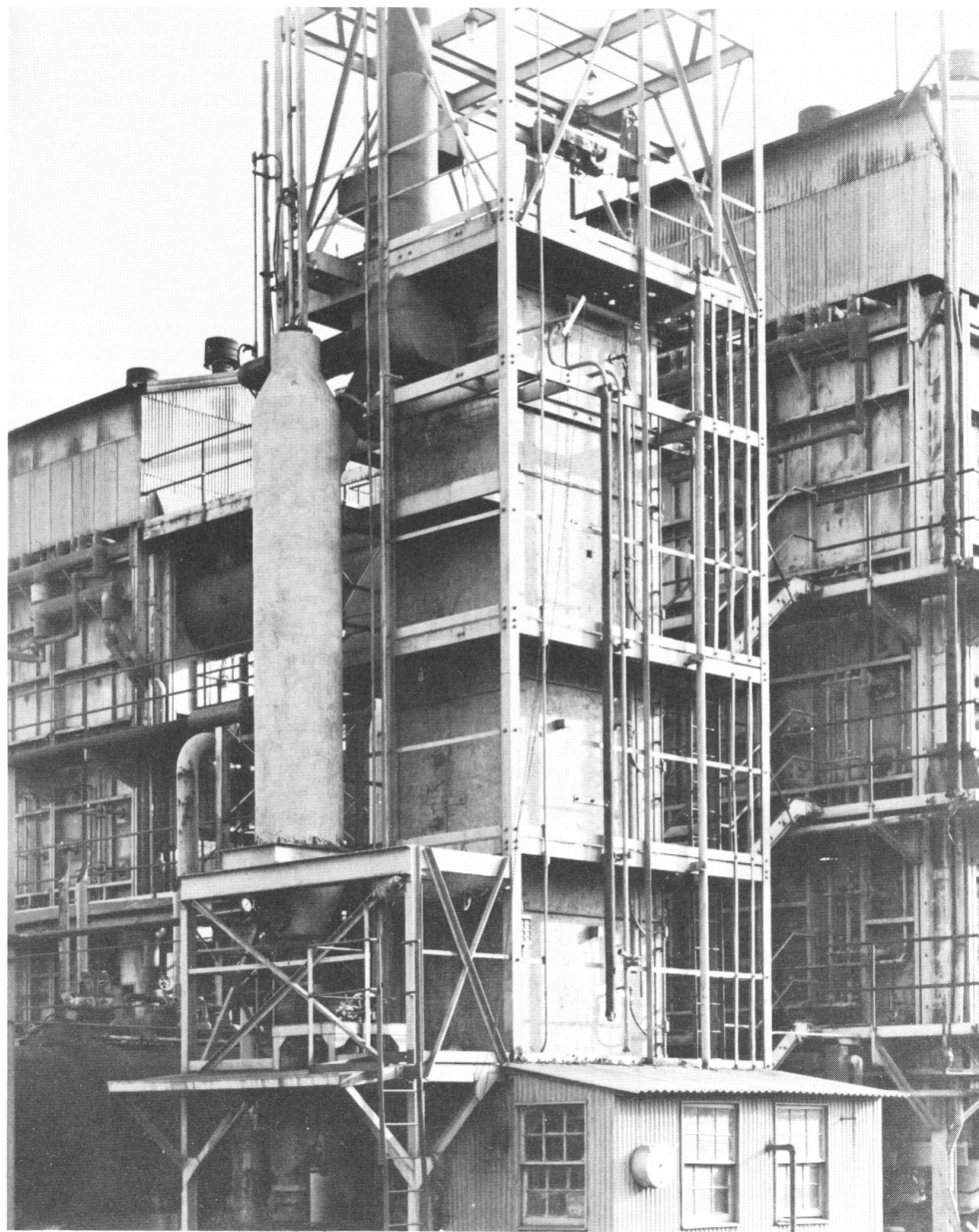


Figure 15. - Catalyst-reduction unit, hydrogen-heating furnace (center), and reduction vessel (left of center).

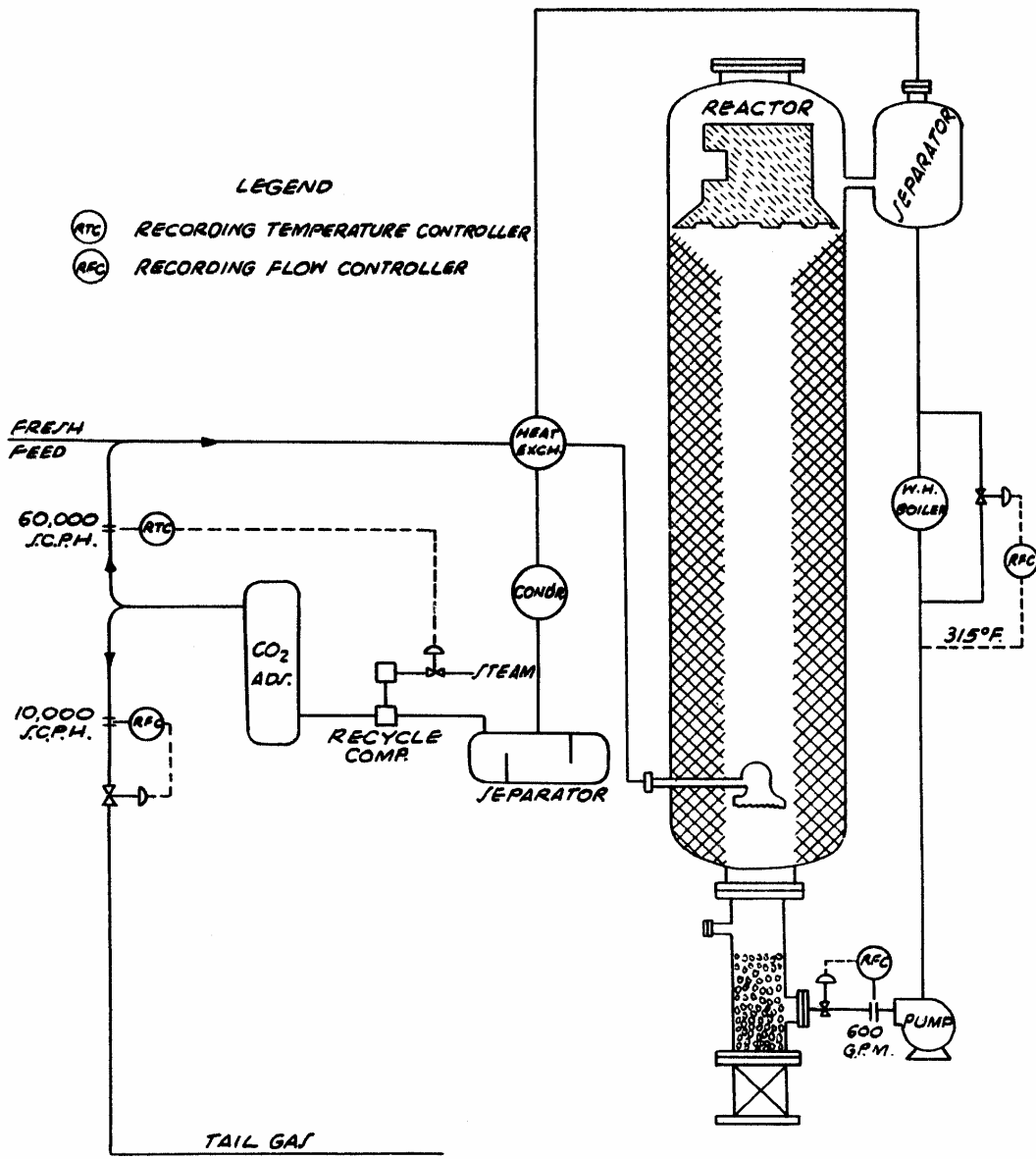


Figure 37. - Simplified flowsheet of synthesis reactor.



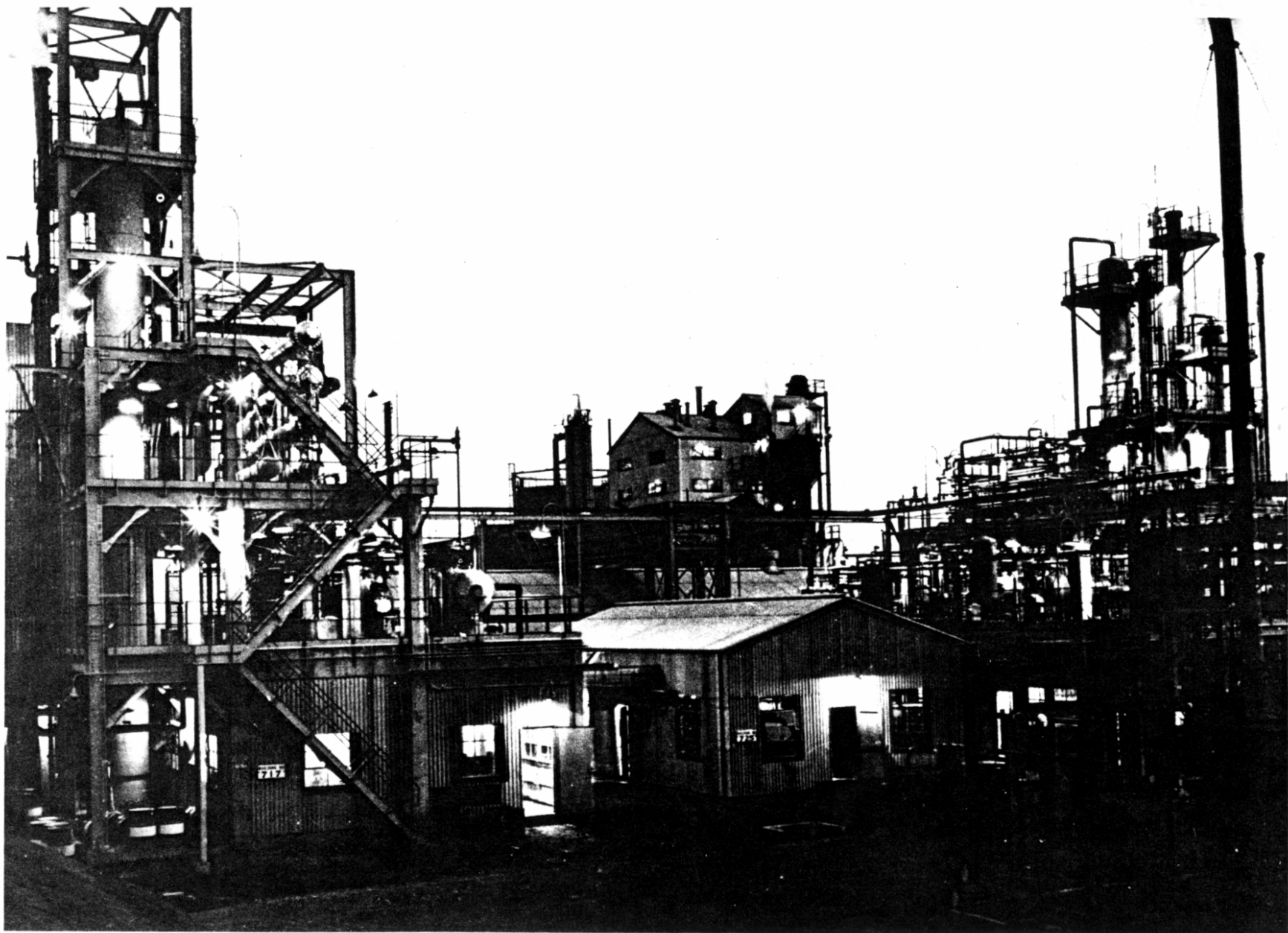


FIGURE 72. - View of Fischer-Tropsch Demonstration Plant at Louisiana, Mo.

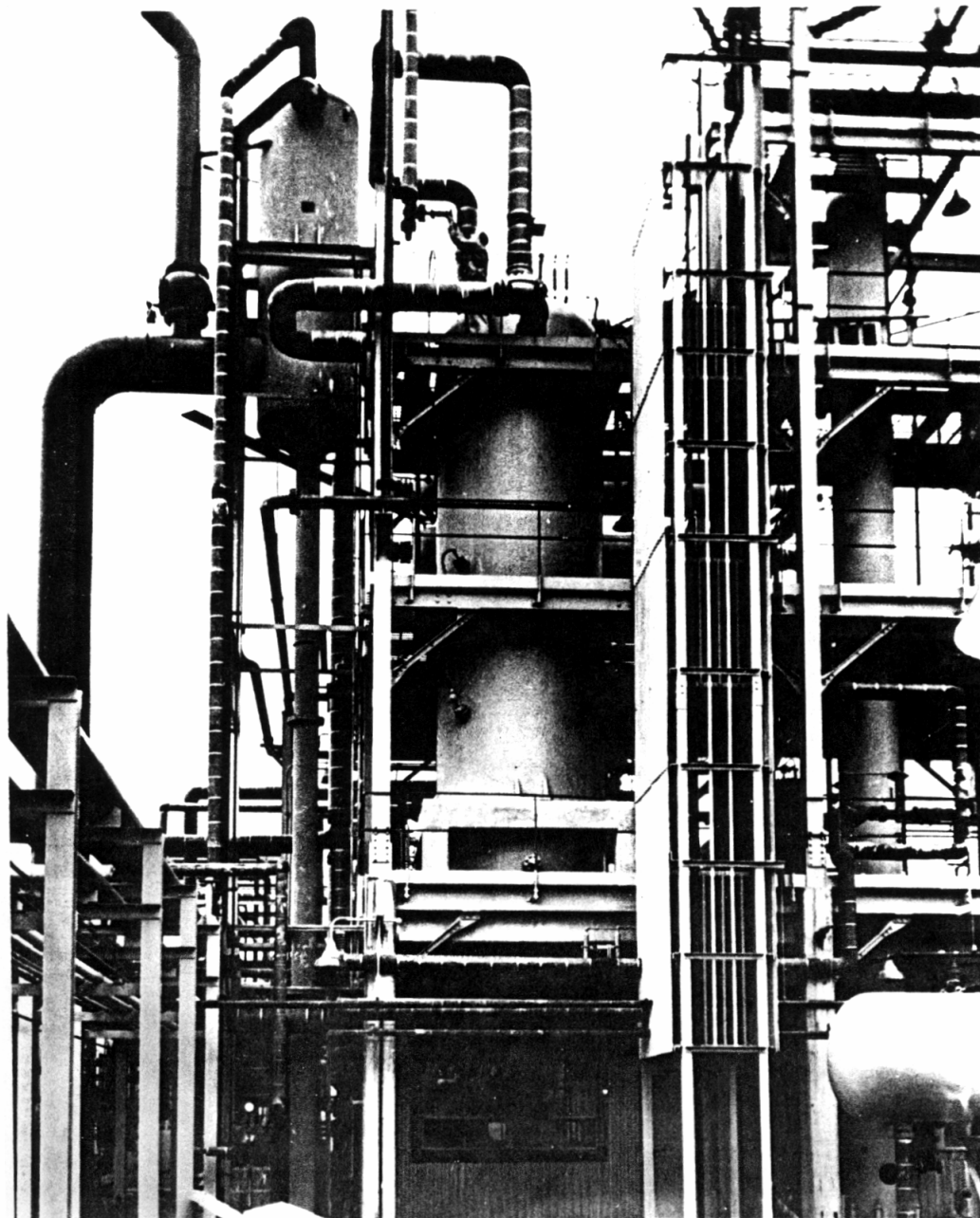


FIGURE 73. - Fischer-Tropsch Reactor at Bureau of Mines Demonstration Plant.

TABLE 13. - Typical operating conditions and conversions
obtained in the four tests at Fischer-
Tropsch demonstration plant

Test No.	1	2	3	4	
				Start	Finish
Flow of fresh gas..... c.f.h.	56,300	61,900	65,400	62,000	62,000
Maximum temperature..... °F.	549	524	545	515	515
Pressure..... p.s.i.g.	330	329	317	337	338
Space velocity..... hr. ⁻¹	600	531	584	480	373
Recycle ratio.....	-	1.63	1.48	1.35	1.43
Catalyst in coolant oil..... percent	<u>1/</u>	<u>1/</u>	<u>1/</u>	7.0	24.0
Usage ratio..... H ₂ :CO	0.68	0.71	0.75	0.91	0.88
H ₂ + CO conversion..... percent	31.0	85.9	67.0	84.3	91.9
Duration of run..... days	8	25	28	39	

1/ Not determined.



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.

Fischer-Tropsch Processes
Investigated at the Pittsburgh
Energy Technology Center since
1944.

M. J. Baird, R. R. Schehl, W. P.
Haynes and J. T. Cobb, Jr., Ind.
Eng. Chem., Prod. Res. Dev., **19**
(1980) 175.



Fischer-Tropsch Processes Investigated at the Pittsburgh Energy Technology Center since 1944.

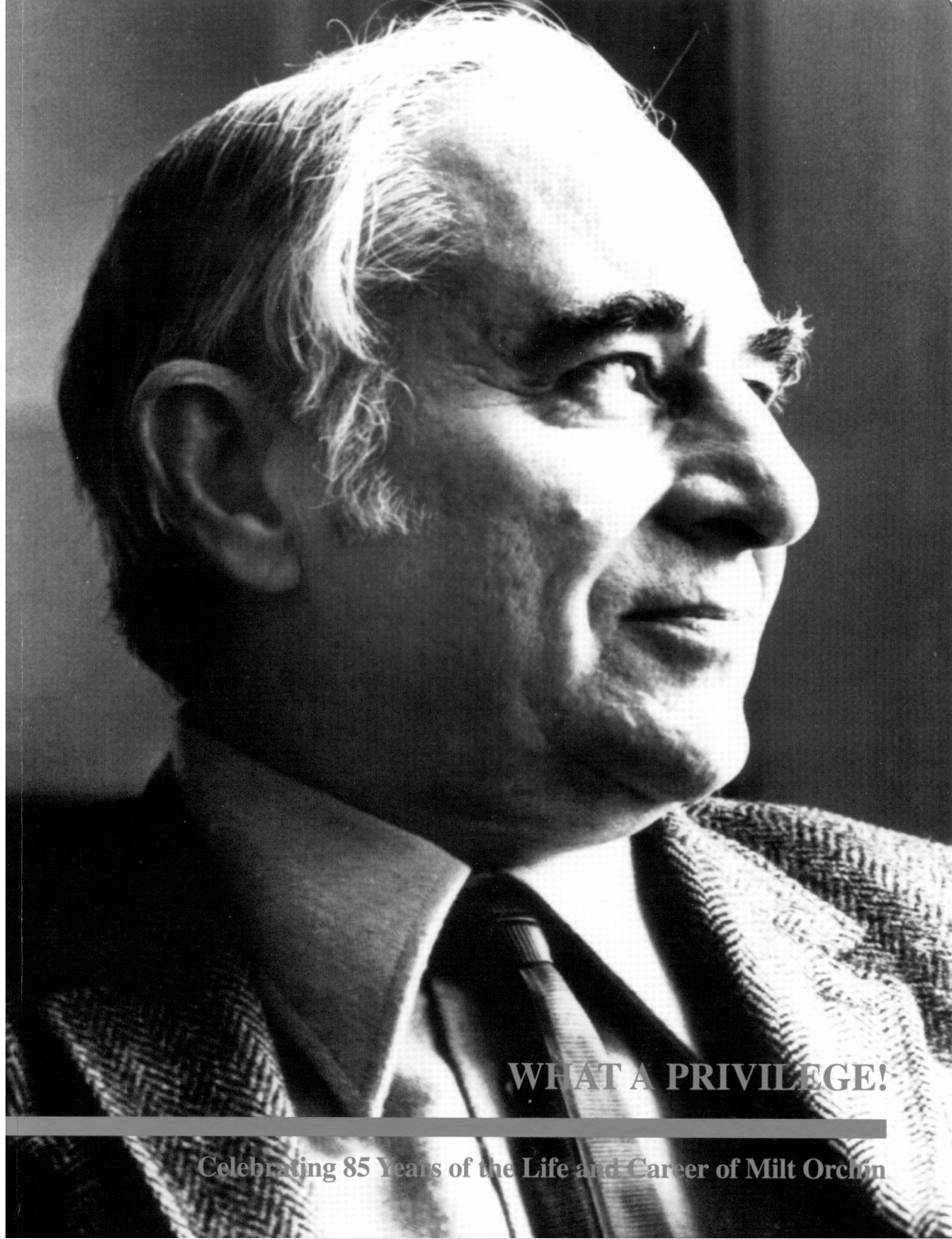
- Renewed interest by US DOE
- Ralph M. Parsons Co contracted to study FT economics and conceptual plant design
- Results indicated that it would be possible to increase overall plant efficiency and the use of a tube wall reactor would be a major factor in achieving this result.

Thompson, G. J., M. L. Riekena and A. G. Vickers;
Comparison of Fischer-Tropsch Reactor Systems,
Phase I -- Final Report, DOE/ET/10159-T2,
September 1981.

- Considered advantages of four type of reactors
- Conclusion was that bubble column reactor was the preferred reactor from the four that were considered



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