3/8" SCH. 40

1/4" SCH. 80

6"

1/4" SCH. 40

1/8" SCH. 40

1/2" SCH. 40

1/2" SCH. 40

3" SCH. 40

1/4" SCH. 40

SECTION A-A

21 1/2"

3 5/8"

6"

A

A

2"

20"

1 1/2" SCH. 40

1/4" SCH. 40

4" R.

14 MESH GAUZE SILVER-
SOLDERED TO TUBE

6 1/2"

RETENTION TUBE

3"

6"

Note: Fusion weld
according to
A.S.T.M. standards

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

figure 62. Liquid and solid hydrocarbons and water collected in a brass container within the wax trap. More volatile hydrocarbons and part of the water were collected in the second trap, cooled by a refrigeration system to about 1° C. The exit gas passed through a wet (41) and a dry carbon dioxide scrubber; the latter also removed most of the water vapor. C_3+C_4 and volatile liquid hydrocarbons were removed by a charcoal trap, and a final exit gas sample was collected for analysis.

In routine tests (2, 6), space velocity and pressure were held constant and the temperature was varied to obtain a carbon dioxide-free contraction of about 65 percent with $1H_2 + 1CO$ (for iron) and 70 percent with $2H_2 + 1CO$ (for cobalt or nickel). Testing was usually continuous, with the exception of a 2-hour period once a week when the products were removed from the reactor and analyzed to obtain information regarding molecular weight range and types of molecules present (6).
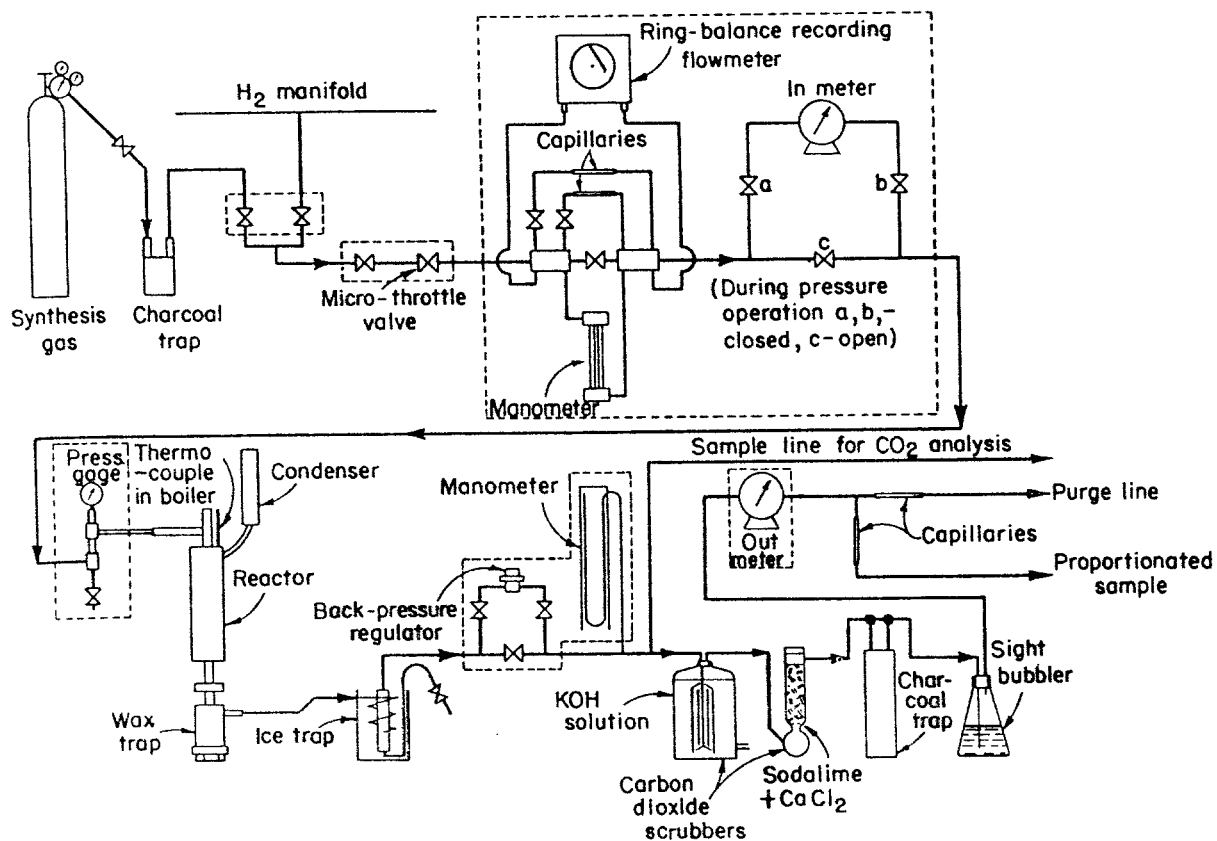

FIGURE 62. - Flow Diagram of Unit for Fischer-Tropsch Synthesis Catalysts.

Cobalt Catalysts

Suitability of Kieselguhrs as Catalyst Support. - Early in the testing program the activity of catalysts was observed to depend upon the kieselguhr used as a carrier. Catalysts containing flux-calcined kieselguhr were the least active. Preparations containing calcined kieselguhrs were more active, but not as active as most untreated kieselguhrs. Activity of catalysts on natural kieselguhrs varied only as an inverse function of the content of extractable iron. Catalysts containing acid-treated natural kieselguhrs usually had high activities. The low activities with calcined and flux-calcined kieselguhrs must have resulted from their small surface area or from their ordered cristobalite structure, compared with the completely amorphous structure of natural kieselguhrs (3).

Effect of Pelleting. - German commercial reactors employed cobalt catalysts prepared as broken filter cake, but in Bureau of Mines experiments the use of pelleted catalysts was found desirable. The activity of 1/8- by 1/16-inch cylinders was the same as that of broken filter cake of approximately the same size. However, repelleting to dense 1/8- by 1/4-inch cylinders affected adversely both activity and selectivity.

Activity of Carburized Cobalt. - Catalysts in which cobalt had been converted to cobalt carbide (by carburizing the reduced catalyst with carbon monoxide at about 200° C.) had low activity in the synthesis. Removal of the carbide carbon by hydrogenation at about 200° C. restored activity to essentially the value obtained for a reduced catalyst. Carbon deposited at 270° C. did not decrease the activity significantly but increased the production of gaseous hydrocarbons. Perrin has shown that nickel catalysts converted to carbide also have lower activity than reduced nickel catalysts (56).

From X-ray diffraction studies of catalyst after use in the synthesis, it was inferred that sizable amounts of cobalt carbide were not present at any stage of the synthesis with reduced catalysts. The reasoning was as follows: (1) After synthesis, reduced catalysts showed only the pattern of disordered cobalt; (2) cobalt carbide was found only in the patterns of precarbided catalysts; (3) when catalysts converted to cobalt carbide were subsequently reduced in hydrogen, the metallic cobalt produced was not in the disordered form but had been transformed to the hexagonal, close-packed form.

Iron Catalysts

For many tests of iron catalysts, activity was computed for arbitrary standard conditions, 240° C. (464° F.) and a conversion of 65 percent, by the empirical equation (4)

$$-\ln(1-x) = [\beta \exp.(-E/RT)]/S,$$

where x was the fraction of H_2+CO converted, β the empirical rate constant, E the activation energy taken as 19 kcal. per mole, T the temperature in degree Kelvin, R the gas constant, and S the hourly space velocity of feed gas.

Activities, as milliliters (S.T.P.)[10] of H_2+CO consumed per hour at 240° C., with the flow adjusted to maintain a conversion of 65 percent, were expressed per milliliter of catalyst, A_v, or per gram of iron, A_{Fe}. Activity and selectivity data were usually reproducible to within about 10 percent.

Chloride Poisoning. - In German laboratories (57) and at the Bureau of Mines (35), active precipitated catalysts could be prepared from ferrous chloride and mixtures of ferrous and ferric chloride, but not from ferric chloride. X-ray diffraction revealed that precipitates from ferrous and ferrous-ferric chlorides contained magnetite and precipitates of ferric chloride β-FeOOH. The magnetite precipitates contained virtually no residual chloride ion, but the samples containing β-FeOOH had substantial amounts. These data are consistent with published results, indicating that the β-FeOOH phase acts as an ion-exchange medium and the removal of chloride ion by washing is virtually impossible. The observed inactivity of catalysts prepared from solutions of ferric chloride probably resulted from poisoning by residual chloride.

Alkali as a Promoter for Iron Catalysts. - The average molecular weight and yield of oxygenated products from precipitated, sintered, cemented, and fused iron catalysts increased with alkali (K_2CO_3 or KOH) content up to about 1 part K_2O per 100 Fe and then remained constant. The activity of precipitated catalysts increased slowly with alkali content; the activities of other types of iron catalysts increased sharply to a maximum at about 0.4 K_2O and then decreased. These and other alkalis were the only chemical promoters found effective for iron catalysts.

Pretreatment and Activity of Iron Catalysts. - The method of pretreating iron catalysts frequently caused large changes in activity and selectivity. Precipitated catalysts and a few reactive iron ores could be activated with synthesis gas at about 250° C.; fused sintered, and cemented catalysts and many ores required reduction in hydrogen at higher temperatures as a first step.

Reduced iron catalysts were converted to relatively pure iron carbides, nitrides, and carbonitrides. The outstanding discovery was that nitrides and carbonitrides were very active and stable in the Fischer-Tropsch synthesis and produced exceptionally high yields of oxygenated compounds.

To demonstrate the influence of pretreatment, samples of precipitated catalyst P3003.24 ($100Fe:10Cu:0.5K_2CO_3$) were tested in synthesis with $1H_2+1CO$ at 7.8 atmospheres and an hourly space velocity of 100. The average activities were about equal, regardless of pretreatment, as shown in figure 63; however, the activity of nitrided catalysts decreased with time, while that of the sample pretreated with synthesis gas increased. The selectivity

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[10] Throughout this chapter, volumes of gas were calculated, according to the metric standard, as dry gas at 0° C. and 760 mm. Hg.
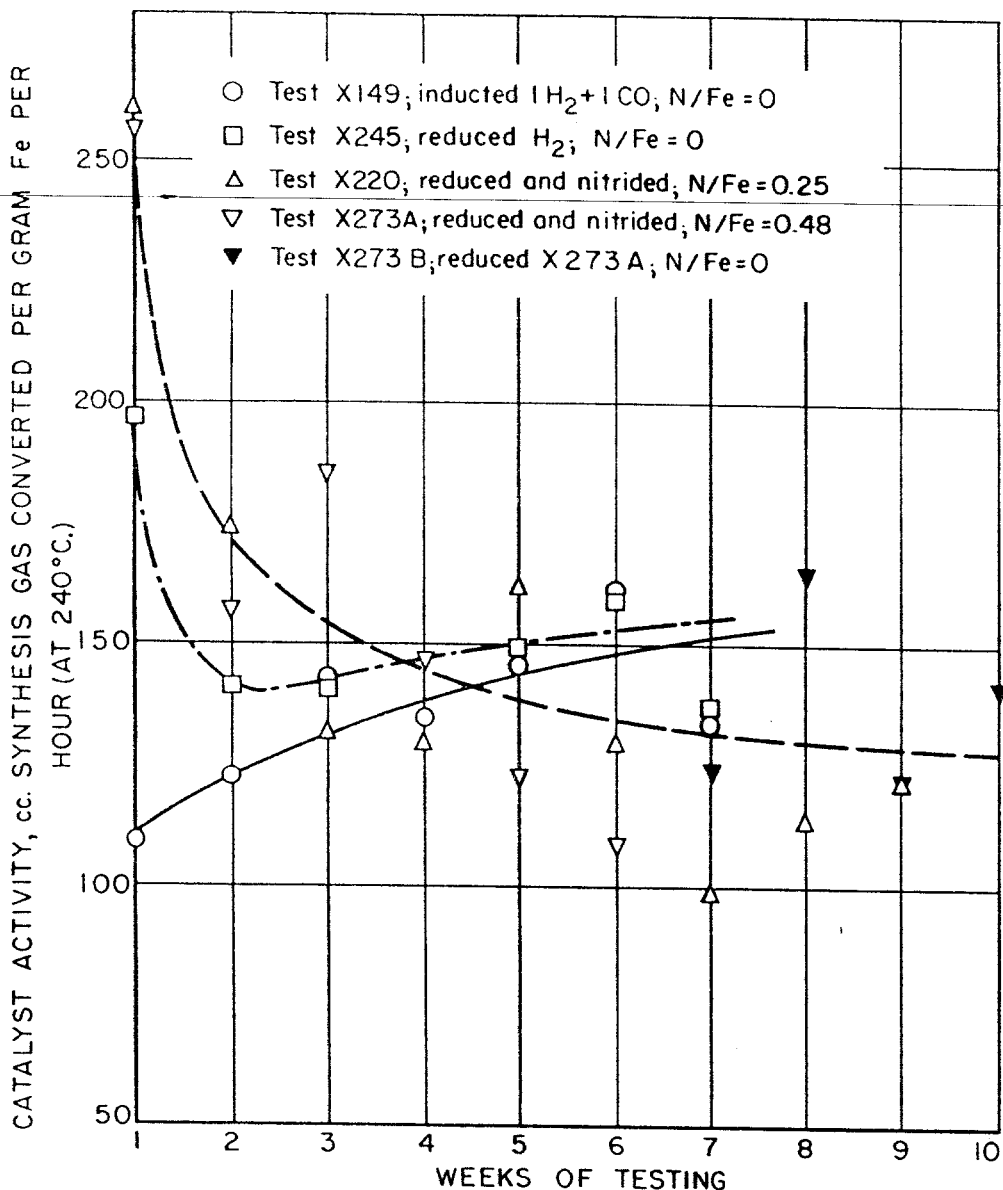
FIGURE 63. - Effect of Catalyst Pretreatment on Activity of Precipitated
Iron Fischer-Tropsch Catalyst P3003.24.

changed remarkably, as shown in figure 64.[11/] The sample inducted in synthesis gas (test X149) yielded products of high molecular weight, of which 92 percent was C_3+ and 51 percent boiled above 464° C. (867° F.). In the products from the reduced catalyst (X245), 84 percent was C_3+, and 18 percent

[11/] Within block diagrams, figures 64 and 66, use is made of the following symbols: In C_2 and $C_3 + C_4$ fractions, a number following the double-bond symbol (=) indicates the percentage of olefins in the fraction; Br indicates the bromine number calculated from the amount of olefin; OH is the weight-percent of hydroxyl group; and CO indicates the weight percent of carbonyl group present as aldehydes, ketones, and acids.

boiled above 464° C. The reduced and nitrided catalysts (tests X220 and X273A) produced a product of still lower molecular weight. Hydrogenation of the catalyst in test X273A after 6 weeks gave no significant change in activity but increased the average molecular weight of the products, making them intermediate between those from the inducted and reduced samples. The liquid products from nitrided catalysts contained larger quantities of alcohols and correspondingly smaller amounts of olefins than nonnitrided samples.

Fused catalysts (Fe_3O_4-MgO-K_2O) converted to Hägg iron carbide and cementite were more active than reduced catalysts, but their selectivity was about the same. At 7.8 atmospheres with $1H_2+1CO$ these carbides had high constant activity, whereas at 21.4 atmospheres the high initial activity decreased with time so that, after several weeks of synthesis, the carbides had the same or a lower activity than the reduced samples.

Iron nitrides have unusual properties in the Fischer-Tropsch synthesis (1, 5, 6, 70). The selectivity differs greatly from that of reduced or carburized iron, and nitrides often have greater activity. Figure 65 shows activities of two fused catalysts at 7.8 and 21.4 atmospheres with $1H_2+1CO$ at 240° C. Magnesia-promoted catalyst D3001 was more active than alumina-promoted catalyst D3008, both reduced and nitrided. The activity of the nitrides at 21.4 atmospheres was about twice that at 7.8 atmospheres. Although the fraction of liquid in total hydrocarbons plus oxygenates was about the same for reduced and nitrided preparations, nitrided catalysts yielded larger concentrations of alcohols, aldehydes, ketones, and esters, and smaller amounts of olefins (fig. 66).12/ Nevertheless, the usage ratios of gas were virtually the same for reduced and
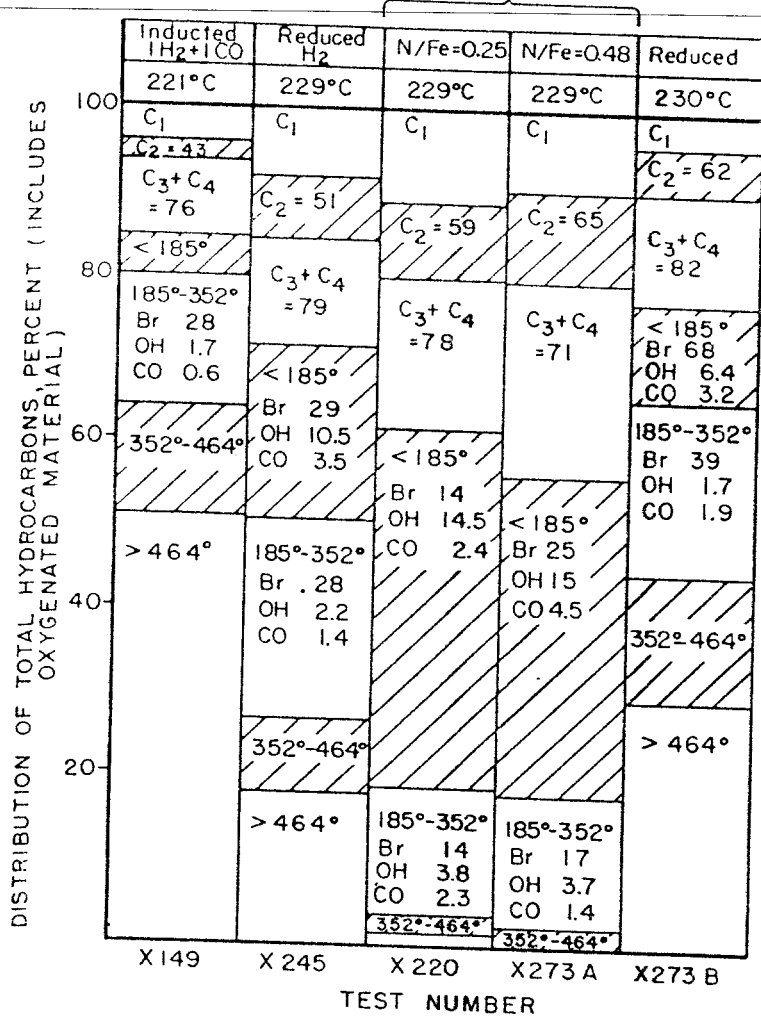

FIGURE 64. - Effect of Catalyst Pretreatment on Composition of Products Obtained From Precipitated Iron Fischer-Tropsch Catalyst P3003.24.

12/ See footnote 11 on p. 170.

nitrided catalysts. Carbonitrides have essentially the same characteristics as nitrides of iron.

Process Development

The commercial Fischer-Tropsch synthesis process in Germany, although operable, had low productivity per unit volume of catalyst space, required complex, expensive reac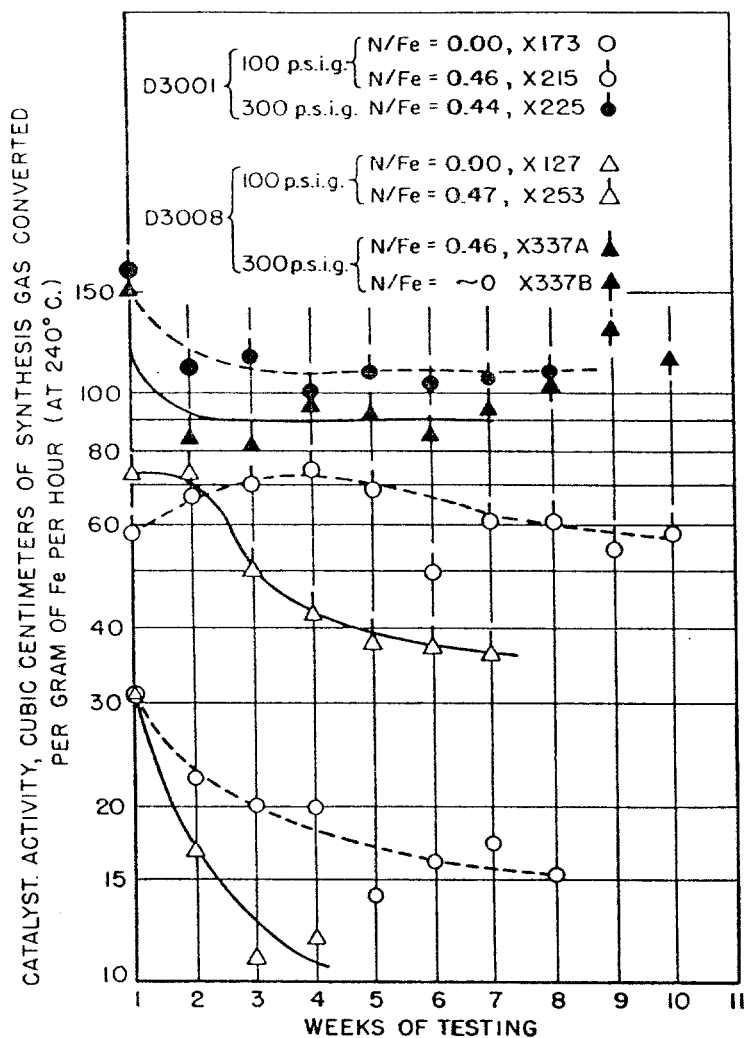tors, and was not versatile with respect to operating conditions and selectivity. Hence, German research was continued to investigate processes utilizing different methods of heat removal. Although no fully developed process resulted from these studies, the principles of operation and some of the major difficulties were outlined for the hot-gas-recycle, oil-circulation, and slurry processes.

Hall, Gall, and Smith at the British Fuels Research Station, Department of Scientific and Industrial Research, have since compared the properties of fixed, fluidized, and liquid-phase systems (32). The results of recent German work with the slurry process were revealed in a recent U. S. patent (40), and the process was described (11).

A commercial plant was completed in 1955 in South Africa (73), with a capacity of about 5,000 barrels of total products per day. Plentiful and inexpensive coal is the raw material. Two types of synthesis reactors are being used. The first is a tubular fixed-bed process, developed by Ruhrchemie, in which much higher heat-transfer coefficients and throughputs are attained than in the early units; the second is a dilute-phase fluidized-bed system developed by M. W. Kellogg Company.

FIGURE 65. - Effect of Catalyst Pretreatment and Pressure on Activity of Fused Iron Fischer-Tropsch Catalysts D3001 and D3008.

As American industry has been developing the fluidized-bed version of the Fischer-Tropsch process intensively, the Bureau of Mines has restricted its

work in reactor development to the oil-circulation, slurry, and hot-gas-recycle processes. Other pilot-plant development included work on methane synthesis and refining of Fischer-Tropsch products.

Oil-Circulation Process

A bench-scale investigation was begun in 1944 on a system in which cooling oil was trickled over the catalyst bed. The heat of reaction was removed by vaporizing the oil, and thus the synthesis temperature depended upon the boiling range of the oil, which could be varied by adjusting the pressure. Good temperature control, with negligible radial or longitudinal gradients, was obtained with countercurrent flow of gas and cooling oil, and neither the catalytic activity nor the product distribution was altered appreciably by the presence of the oil.

A pilot plant with a reactor of 3-inch inside diameter and an 8-foot bed height was constructed in 1946. Countercurrent flow was abandoned after a short time because of flooding difficulties, and concurrent downward gas-oil flow was employed. When the hourly space velocity was increased to about 300 (S.T.P. volumes of gas per volume of catalyst), hot spots often developed at the entry. This difficulty was eliminated only when the bed was completely submerged in oil, rather than merely wetted. Gas and liquid were now fed to the bottom of the reactor and flowed concurrently upward. No difference in activity was observed between wetted and submerged beds.

Because pelleted precipitated iron catalysts disintegrated and caused considerable pressure drop after only a few weeks of operation, fused, synthetic ammonia type, iron oxide catalysts were substituted.

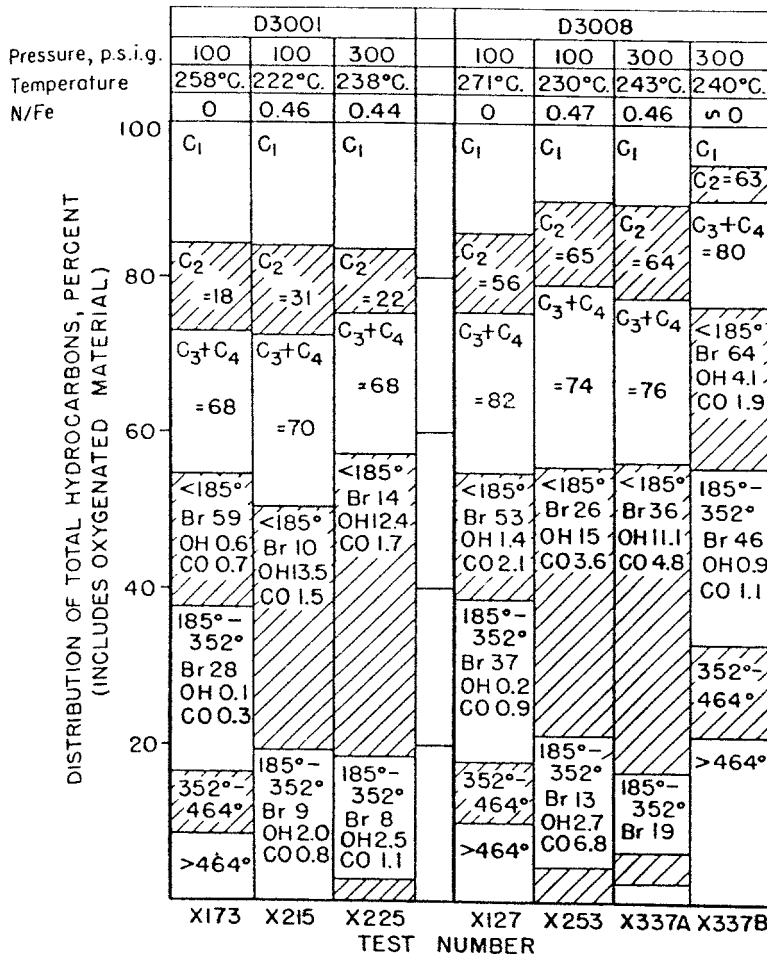|	D3001			D3008			
Pressure, p.s.i.g.	100	100	300	100	100	300	300
Temperature	258°C.	222°C.	238°C.	271°C.	230°C.	243°C.	240°C.
N/Fe	0	0.46	0.44	0	0.47	0.46	∽0
Test Number	X173	X215	X225	X127	X253	X337A	X337B

FIGURE 66. - Effect of Catalyst Pretreatment and Pressure on Composition of Products Obtained From Fused Iron Fischer-Tropsch Catalysts D3001 and D3008.

Particle sizes of 6- to 20-mesh were generally employed. Removal of the heat of reaction by sensible heating of the circulating oil (rather than vaporization) required greater flow of oil but effected smoother operation. An advantage of this method over evaporative cooling was that pressure, temperature, and composition of cooling oil were essentially independent of each other, allowing more flexible operation.

In experiments with $1H_2:1CO$ over reduced iron catalysts, pressure drop across the catalyst bed increased progressively until synthesis had to be terminated after 1 to 3 months, even though the catalyst was still active. The catalyst particles were found to be cemented together and could be removed only by chiseling and drilling. With a hydrogen-rich gas ($1.3H_2:1CO$) catalyst cementation was much less and did not cause difficulty in a 3-month period of operation; catalyst activity remained stable.

Longer runs were made also with larger catalyst particles. However, as larger particles had less external surface area per unit volume, their activity was lower.

An expanded catalyst bed was developed to eliminate cementation. Flow of oil was increased to expand the catalyst bed 10 to 20 percent above its settled height and to produce slow movement of the catalyst particles. The plant was operated in this manner with fused iron catalyst without any difficulty either from increased pressure drop or catalyst cementation during runs, usually of 2 to 3 months.

Some disintegration of catalyst occurred, especially at high synthesis temperatures or with high partial pressures of carbon monoxide. Expanded beds of fused catalyst also were used in a barrel-per-day pilot plant and in the 40-barrel-per-day demonstration plant. The reactor in the barrel-per-day unit (see fig. 67) was 8 inches in diameter, with a bed height of 8 feet, while the reactor in the demonstration plant was 3 feet in diameter and was charged to a height of about 16 feet. Disintegration of catalyst was more severe in the demonstration plant than in the pilot plants, probably because of excessive turbulence at the bottom of the reactor resulting from the very simple gas- and liquid-inlet system. Excessive disintegration probably could have been eliminated by distributing the gas uniformly across the bottom of the reactor.

Pilot-plant operating conditions were varied over a wide range: Reactor pressures from 300 to 450 p.s.i.g.; synthesis-gas ratios of 0.7, 1.0, or 1.3 volume of hydrogen to 1 of carbon monoxide; ratios of recycle gas to fresh gas from 0.5 to 2.0; and conversion of gas from 70 to 90 percent. An hourly space velocity of 600 was frequently used, with temperatures around 250° C.(482° F.). Yields and distribution of products from fixed and expanded beds are shown in table 11. Higher space velocities and space-time-yields, based on reactor or catalyst volume, were obtained with expanded beds. Specific yields of C_3+ hydrocarbons for both operations ranged from about 150 to 175 grams per cubic meter of H_2+CO converted.
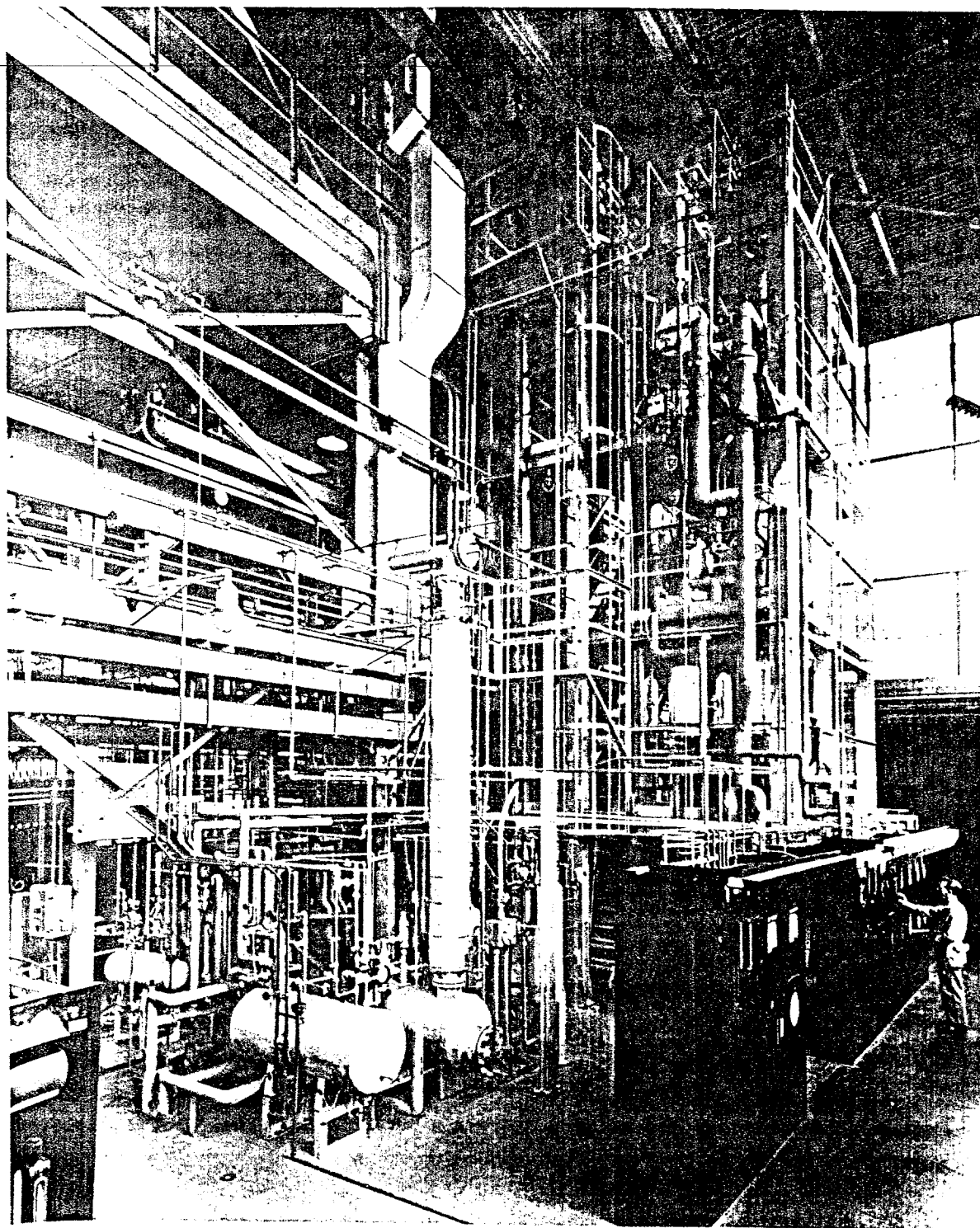
FIGURE 67. - Barrel-per-Day Pilot Plant for Fischer-Tropsch Synthesis