Dust was removed from the gas by passing it consecutively through a cyclone, a cascade-type washer, and two electrostatic precipitators, leaving less than 0.2 grain of dust per 100 std.c.f. of gas. Most of the carbon dioxide and sulfur compounds were then removed by absorption in aqueous diethanolamine. Further removal of sulfur was effected in wood chips impregnated with iron oxide, and finally in activated carbon. The purified gas contained less than 2 percent of carbon dioxide and 0.05 grain of sulfur per 100 std.c.f. Recycle gas was purified with monoethanolamine.

Mill scale and smaller amounts of magnesia and potash were the raw materials for the catalyst. These components were mixed, fused, crushed, screened, reduced with hydrogen, and stored under oil before use. About 7 tons of catalyst was needed to fill the reactor, which had a capacity of 50 to 80 barrels of liquid product per day.

Based on experience in pilot-plant tests, the synthesis reactor (6 feet diameter by 30 feet overall; see fig. 73) was modified before the first test to operate with an oil-immersed, expanded bed of 4- to 10-mesh catalyst particles and about $0.8H_2$:1CO fresh gas. At the start of each test the catalyst was conditioned by raising the temperature from about 221° C. (430° F.) by 11°-14° C. (20°-25° F.) each day over a 5-day period, while conversion of synthesis gas increased from 10 to more than 70 percent. Representative conditions of operation are shown in table 13. Over 40,000 gallons of liquids was obtained in these four tests. Production from the last test included more than 5,000 gallons of polymer gasoline, 17,000 gallons of debutanized gasoline, 3,600 gallons of lean oil, and 2,000 gallons of coolant oil.

The second test had shown that a diesel oil could be produced that surpassed military specifications for class 1 diesel oil. The refined gasoline (fig. 74) from the test had a research octane number of 70.2 clear, 80.0 with 1 ml. and 86.4 with 3 ml. of added tetraethyl lead.

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	1/	1/	1/	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.

Nevertheless, the tests had not been entirely satisfactory because of spalling of catalyst and its attendant difficulties. Up to 25 weight-percent

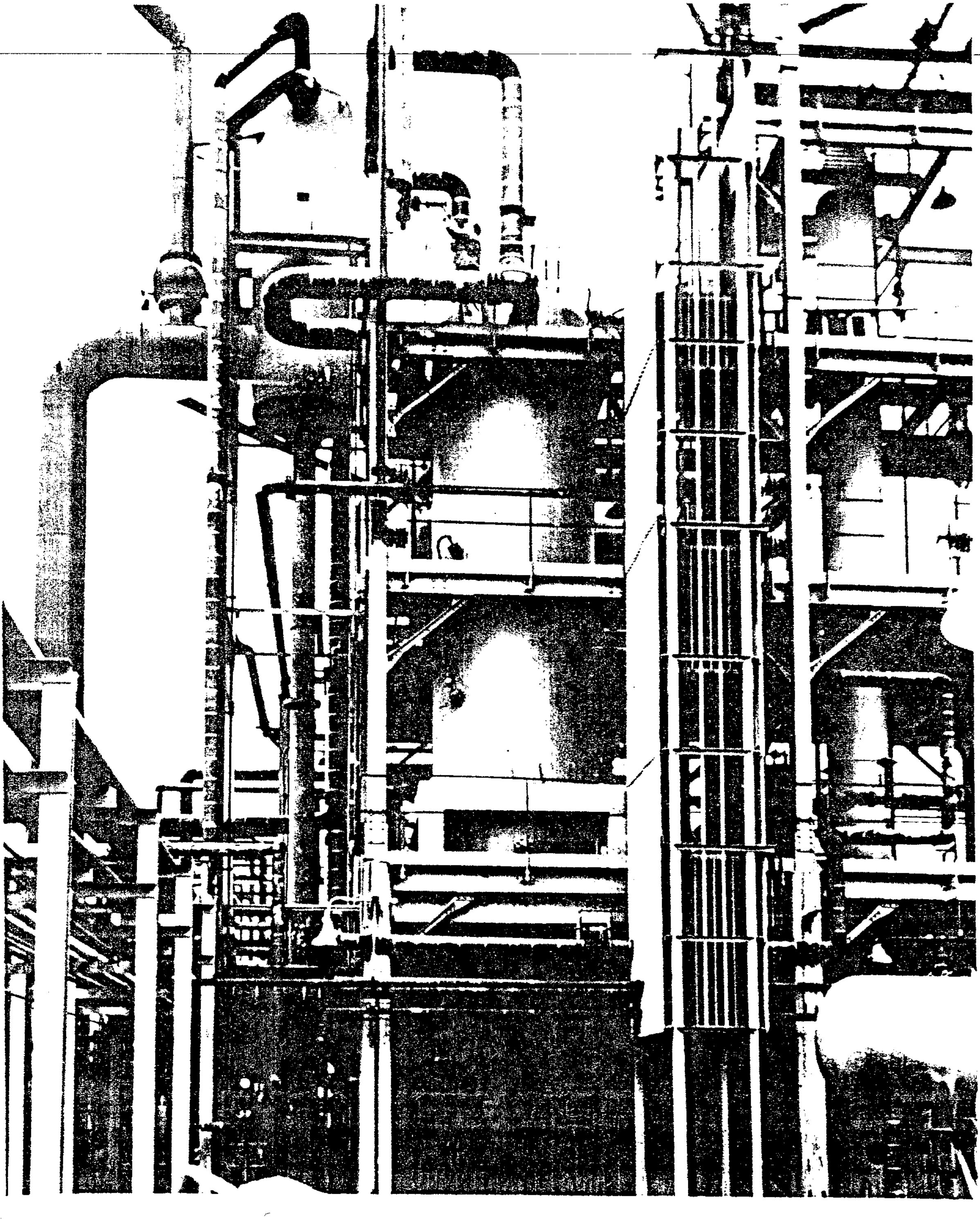

FIGURE 73. - Fischer-Tropsch Reactor at Bureau of Mines Demonstration Plant.

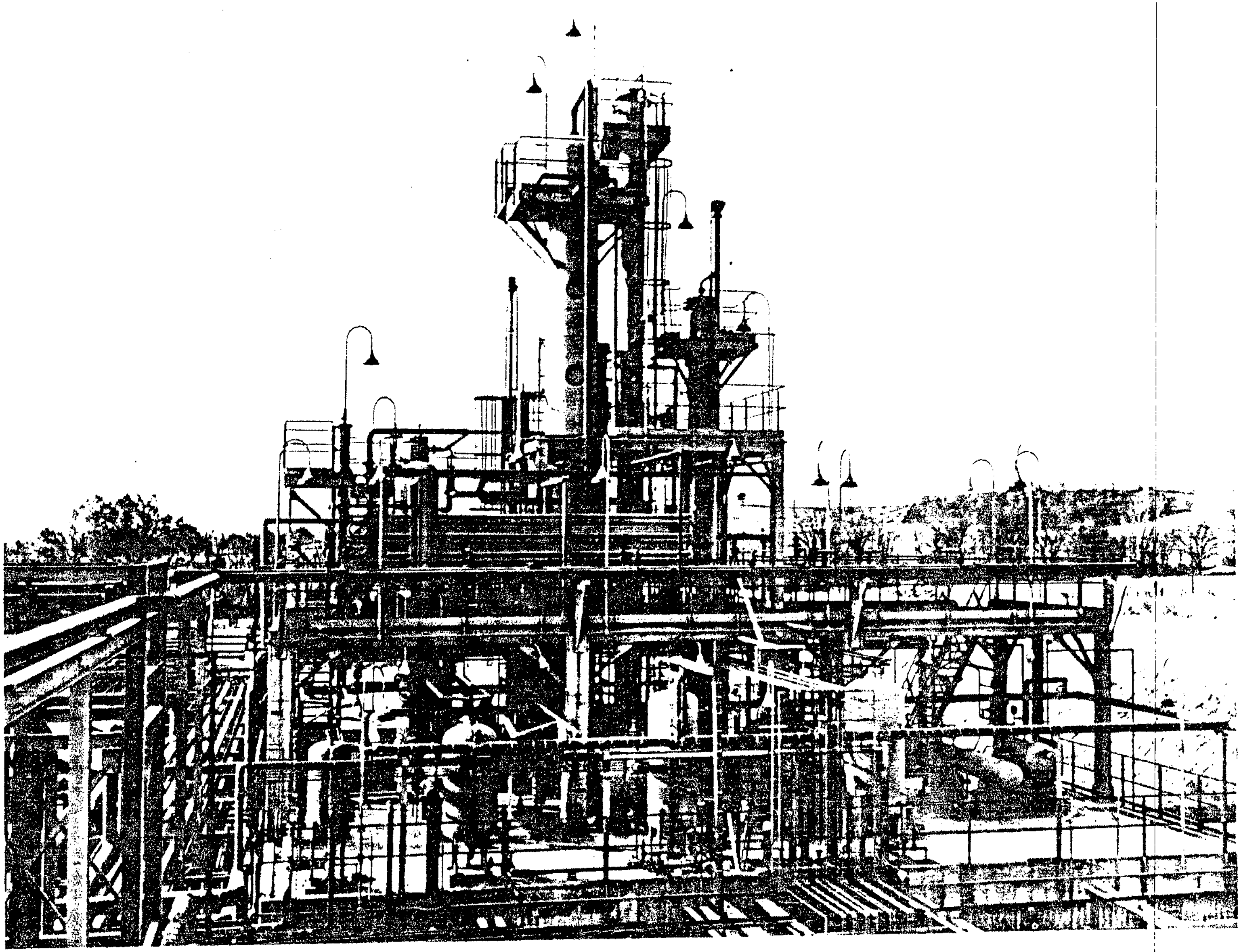

FIGURE 74. - Distillation Columns for Refining Crude Fischer-Tropsch Products Obtained at Bureau of Mines Demonstration Plant.

f fines was found in the coolant oil, making the process a combination
lurry-expanded bed operation. Although up to about 10 weight-percent fines
nhanced the activity of the catalyst, the higher concentrations damaged the
il pumps and made frequent repairs necessary. The rate of spalling increased
ore than sixfold when the temperature was raised from 268° C. (515° F.) to
79° C. (535° F.); even at the lower temperature, 40 percent of the catalyst
as suspended in the oil after 39 days of operation. As noted above, spalling
f catalyst might perhaps have been reduced by changing the inlet system so as
avoid excessive turbulence in the reactor.

This demonstration plant had represented a radical departure from estab-
ished practice, in both catalyst and mode of operation. Had the more recent
provements in Fischer-Tropsch catalysts been available at that time, the
ifficulties experienced might have been circumvented.

Miscellaneous Projects, Including Methanation, Thermal Cracking, and Alumina Treatment

thanation

The production of a high-B.t.u. gas from coal is closely allied to the
nthesis of liquid products and may have more immediate economic interest be-
use of the rapidly increasing demand for gaseous fuels. Utilization of coal
a source of pipeline gas may become necessary sooner than as a source of
quid fuel.

The steps involved in the synthesis of high-B.t.u. gas by the hydrogena-
on of carbon monoxide are similar to those required for the Fischer-Tropsch
ocess - gasification of coal, purification of gas, synthesis over suitable
talysts, and purification of product. However, there are appreciable dif-
rences with regard to operating conditions and techniques. The methanation
synthesis step was studied from 1952 to 1954 (28).

Catalysts for methanation were assayed in fixed-bed reactors. Those that
re satisfactory were tested in a fluidized bed. The test reactor consisted
1-inch, schedule 80, seamless steel pipe, enclosed in a Dowtherm jacket and
ntaining a 3/8-inch-diameter baffle tube (fig. 75). Synthesis gas was fed
rough three gas inlets: One at the bottom and the others at 18 and at 36
ches above the bottom. This feed system was designed to distribute the heat
reaction throughout the bed, minimizing localized heating. The settled
ight of catalyst was about 3 feet, and catalyst size was finer than 80-mesh.
essures were 100 to 300 p.s.i.g., and hourly space velocities of fresh feed
re 800 to 14,000, depending upon the catalyst.

Iron catalysts tested were synthetic ammonia type, Alan Wood magnetite,
eel shot fines, and a sintered mixture of 85 percent magnetite and 15 per-
nt ball clay. Large quantities of carbon and liquid hydrocarbons were pro-
ced; it was difficult to obtain a product gas with a heating value greater
an 700 B.t.u. per cubic foot.

Nickel catalysts have been used in fixed-bed operations for the synthesis of methane for many years (13). Many variations of nickel were effective in the fluidized bed. Most of them consisted of NiO, Al_2O_3, and MnO on varying amounts of kaolin, activated alumina, silica, or kieselguhr as carrier. Fluidized beds were operated at high gas throughputs (hourly space velocities up to 10,000) with virtually complete conversion of synthesis gas. The catalyst life was limited by loss of activity with time, probably because of chemical changes, spalling, and apparent lack of circulation of particles among various zones of the bed. However, use of a fluidized rather than a fixed bed appeared to be advantageous from a comparison of the results obtained with a nickel-thoria catalyst of the type formulated by the British Gas Research Board. About 30 percent more methane was produced per pound of nickel during the life of the catalyst in a fluidized bed than was reported by the Gas Research Board for a fixed bed. This higher yield was obtained during operation at a high conversion to make gas with a heating value of over 900 B.t.u. per cubic foot, whereas gas of 400 to 600 B.t.u. was produced in the British tests.

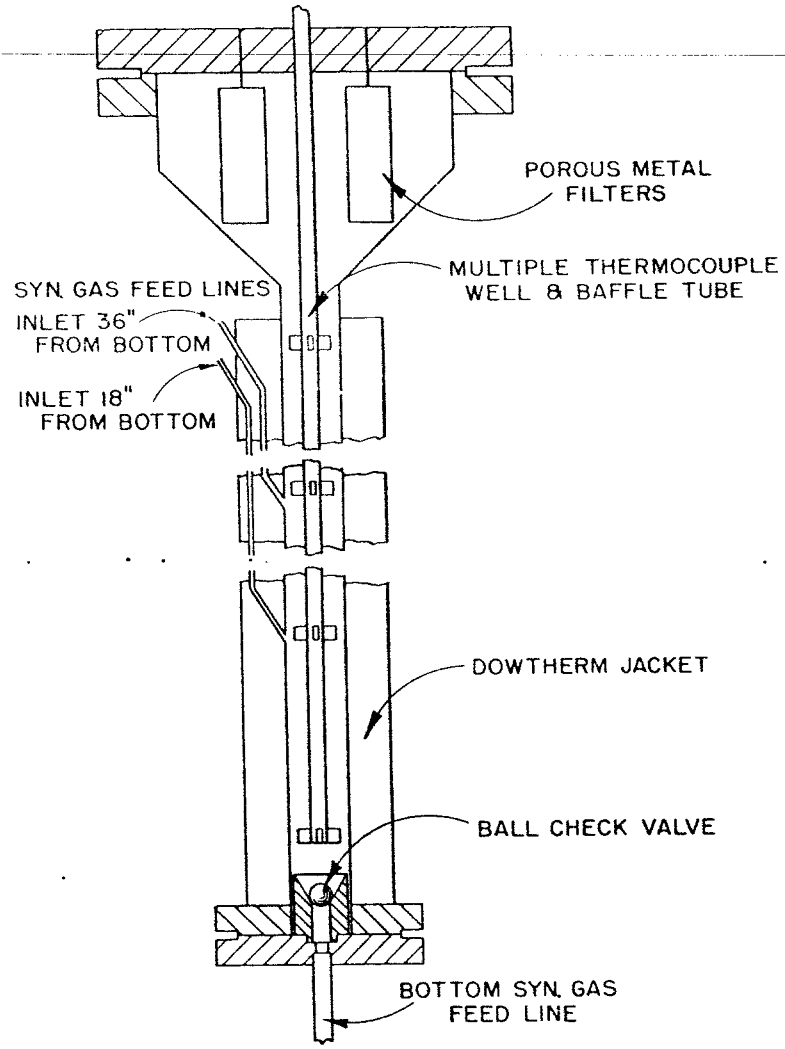

FIGURE 75. - Multiple-Feed, Fluid-Bed Reactor for Converting Synthesis Gas to Methane.

Raney nickel (containing 42 percent nickel and 58 percent aluminum) was an effective catalyst. Before synthesis the aluminum was partly extracted with alkali, and then the catalyst was washed with water until the wash water was neutral. The wet catalyst was charged to the reactor, and water was removed by passing hot hydrogen through the bed. High activity was obtained in a fixed bed with 6- to 8-mesh granules and in a fluidized bed with 80- to 230-mesh (U.S.S.) particles. High gas conversions were attained at hourly space velocities as high as 1,500 in the fixed bed without producing runaway temperatures. The catalyst withstood temperatures of 400° to 450° C. (752° to 842° F.). With temperatures of 370° to 395° C. in the fluidized bed, 95 to 98 percent of the synthesis gas was converted at hourly space velocities of 7,700 o 10,000. The heating value of the product gas was about 950 B.t.u. per ubic foot for the first 500 hours of methanation. Thereafter, activity de- lined slightly, and the heating value of the gas dropped to 850 B.t.u. The atalyst was reactivated by another partial extraction with alkali and used or 500 hours more before the heating value of the gas fell to 850 B.t.u. per ubic foot. The catalyst was reactivated again by alkali extraction, and the xperiment was terminated voluntarily after an additional 165 hours of meth- ation. Repeated reactivation is believed to be possible until extraction ields particles too small for the fluidized bed.

Temperature control was excellent in the 1-inch fluidized-bed reactor ith its multiple gas entry. Whether equally satisfactory removal of the heat reaction and adequate temperature control would be possible in large re- tors cannot be determined from such small-scale operations.

ermal Cracking

Under certain operating conditions in the Fischer-Tropsch synthesis, an preciable portion of the product consists of hydrocarbons boiling above the soline range. Because gasoline is usually the desired end product, thermal acking of high-boiling synthesis oil was studied. The total oil boiling ove gasoline, and three distilled fractions, were used as feed stock: Diesel l, boiling from 204° to 316° C.; heavy distillate, boiling from 316° to 0° C.; and wax, boiling above 450° C. The object was to determine optimum acking conditions and yields.

The thermal cracking unit consisted of a charging reservoir, a metering mp, a reactor constructed from a 32-inch length of 1/8-inch Schedule 80 amless pipe, a condenser, product receiver, pressure controller, and gas- tering system. The feed stock was pumped at rates of 100 to 1,000 cc. per ur to the reactor, which was contained in a lead bath.

At atmospheric pressure, temperatures of 600° to 650° C. (1,112° to 202° F.) were required to attain a reasonable amount of cracking, and the s yield was too high. Excellent yields were obtained at 475° to 500° C. 87° to 932° F.), 300 p.s.i.g., and a liquid hourly space velocity of about , the ratio of yields of gasoline-to-(C_1+C_2) hydrocarbons being 10.

To determine the ultimate gasoline yield obtainable from high-boiling scher-Tropsch oil, the total oil was subjected to a multipass operation. ter passing through the cracking reactor, the oil was distilled to remove soline, and the residue was passed through the cracking unit again. Four sses were made. The conversion to gasoline was 32, 21, 19, and 18 weight- rcent, respectively, of the material fed. The overall gasoline yield was weight-percent of the original charge, equivalent to about 65 percent of e original volume. Of the rest of the feed, 20 percent was converted to C_1 C_4 gases, 15.3 percent remained as oil boiling above 200° C., and 8 percent s charged to coke formation and losses.

A comparative cracking study was made of Fischer-Tropsch diesel oil and a troleum fraction of comparable boiling range (Mid-Continent gas oil). Three types of tests were made - single pass, multipass, and recycle. In the recycle experiments 2 volumes of oil boiling above 204° C. from a once-through run were mixed with 1 volume of fresh feed. In all tests the Fischer-Tropsch product gave higher gasoline yields, higher ratios of gasoline to (C_1+C_2), and lower formation of coke than the Mid-Continent stock.

Alumina Treatment

Another bench-scale project was vapor-phase treatment of synthetic gasoline over alumina (65) for improving the octane rating. The unit consisted of a metering pump, oil preheater and vaporizer, a reactor pipe (1-inch Schedule 40) with traps, and a pressure-control system. Two commercial catalysts were used - activated alumina, F-1, 4- to 8-mesh; and Phillips Cyclocel bauxite, 4- to 12-mesh. After several tests at 260° to 450° C., 0 and 25 p.s.i.g., and hourly liquid space velocities of 0.5 to 3.0, the following conditions were established as most satisfactory:

Temperature....................	350° C. (662° F.)
Pressure.......................	25 p.s.i.g.
Liquid space velocity..........	1.5 per hour

At and above 350° C. oxygenated groups were removed virtually completely by both catalysts. The octane rating was improved by shifting olefin double bonds from end to internal positions. For example, the octane number was raised from 50 to 67 for the gasoline from oil-circulation experiment 21. Cyclocel bauxite was more active than the alumina for isomerizing olefins.

Problems of Fischer-Tropsch Synthesis

Although the Fischer-Tropsch synthesis has been investigated for more than 30 years, a number of practical and theoretical problems remain unsolved. They concern primarily the composition and properties of catalysts, mechanism and kinetics of the reactions that constitute the Fischer-Tropsch synthesis, and mode of operation to insure rapid removal of heat and provide maximum flexibility of operation and product distribution.

Catalysts

Current studies have indicated that the rate of synthesis is roughly proportional to the external or geometric area of the catalyst. Therefore, methods for increasing the external area as well as the number of large pores, which can function as external surface, should be investigated. Such structures might be realized by the techniques of fiber and powder metallurgy. Skeletal type catalysts like Raney iron may also offer possibilities.

No method is known as yet for preparing high-surface-area alloys of metals such as iron, cobalt, or nickel, with readily oxidized metals such as chromium and manganese. Alloys of this kind and nonferrous alloys may have desirable catalytic properties, although their optimum operating conditions may differ sharply from those of the usual Fischer-Tropsch catalysts. Methods also need to be developed for preparing hexagonal close-packed iron carbide and iron borides in a form suitable for catalyst testing.

The function of alkali as a promoter for iron Fischer-Tropsch catalysts
s never been adequately explained. A study of the variation of physical
operties of the catalyst as a function of alkali content and of the influ-
ce of alkali on a number of reactions related to the Fischer-Tropsch synthe-
s may aid in solving this problem.

Poisoning of Fischer-Tropsch and similar catalysts by sulfur, selenium,
llurium, and the halogens has not been studied systematically. Tolerances,
per limits of concentration, and methods of regenerating poisoned catalysts
main to be determined for the most part. Fragmentary evidence indicates
at sulfur-poisoned iron catalysts operate satisfactorily at considerably
gher temperatures than those normal for the Fischer-Tropsch synthesis, but
operating characteristics of these catalysts are not definitely estab-
shed, and nothing is known about possible differences in the behavior of
rides, carbides, and carbonitrides of iron under conditions of sulfur
isoning. Controlled poisoning may be beneficial for directing product dis-
ibution. Development of sulfur-resistant catalysts would also decrease the
t of gas for the process.

The useful life of Fischer-Tropsch catalysts may be terminated by cata-
t disintegration and related processes caused by oxidation and/or carbon
osition, or by loss in activity due to poisoning by sulfur and other com-
nds, as well as by sintering and reorientation of the active phases. Fac-
s that determine the rates of oxidation and carbon deposition are known in
y a general way and should be investigated in greater detail.

Kinetics and Mechanism

Current studies indicate that the pores of active Fischer-Tropsch cata-
ts are filled with liquid hydrocarbons through which the gases must pass
solution and diffusion. Reaction on pore walls produces concentration
dients that cause diffusion. Thus, surface reaction and mass transfer are
imately related, and their effects cannot be easily separated. The charac-
istics of reactions and diffusional processes in liquid-filled pores have
been systematically investigated.

Few reactions have been studied of simple molecules that may be regarded
intermediates or products of the synthesis. A moderately satisfactory
ies of reaction steps has led to a mathematical expression for carbon num-
and isomer distributions observed in the synthesis. However, few data are
ilable to demonstrate the variation of the constants of these expressions
changes in operating variables.

Che [illegible] d structural studies of the carbonyls of cobalt and iron have
ided information that relates to the mechanism of the Fischer-Tropsch syn-
sis. Further work on this topic and on the adsorption of gases on metal
aces should lead to closer correlations among catalytic reaction systems
lead to a better understanding of the fundamentals of catalysis.