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REPORT OF INVESTIGATIONS

UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

. SOME CHEMICALS FROM SYNTHETIC LIQUID FUELS PROCESSES 1/

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INTRODUCTION

The primary purpose of the Bergius (hydrogenation of coal) and Fischer-Tropsch (hydrogenation of carbon monoxide) processes is the production of synthetic liquid fuels. This objective is of importance in insuring an adequate supply of motor fuels and lubricating oils in the United States. In the urgency of the basic research and process development work on synthetic liquid fuels, the possibilities for the production of synthetic chemicals inherent in these processes have hitherto received little attention

in this country. However, the by-products, as well as the primary products, from the Bergius and Fischer-Tropsch processes are rich source materials for organic chemicals. The overhead oil from liquid-phase hydrogenation of coal, for example, contains benzene, toluene, xylene, cyclohexane, methylcyclohexane, aromatic solvents, about 20 percent tar acids (largely phenol, cresols, and xylenols), and 3 percent nitrogen bases. Wax, alcohols, and acids are by-products of the Fischer-Tropsch synthesis. In addition, techniques have been developed which make possible the production of aliphatic hydrocarbons, alcohols, acids, aldehydes, and other oxygenated organic compounds. These chemicals are more valuable on a unit basis than gasoline. Because of continued rapid expansion of the plastic, resin, lacquer, and solvent industries, larger amounts of many of these chemicals will be needed in the near future.

It was believed of interest to review the available literature and the experimental results of the two synthetic liquid fuels processes now under investigation by the Bureau of Mines and to summarize the information regarding the relative amounts of various industrially valuable chemical products thus produced. This report is divided into two sections. It contains, first, a brief description of the Fischer-Tropsch and related processes, with emphasis on the effect of the important variables upon the composition of the product, and a review of the by-products and chemicals possible from the hydrogenation of carbon monoxide. The second section is devoted to a review of the Bureau of Mines work on the hydrogenation of typical United States coals, including a description of the liquid-phase hydrogenation assay procedure and a summary of the results of the characterization of the oils produced during the hydrogenation of Pittsburgh-seam (Bruceton) coal under various conditions in the Bureau of Mines experimental plant.

ACKNOWLEDGMENTS

USES OF CHEMICALS FROM SYNTHETIC LIQUID FUELS PROCESSES

Important by-products from the Fischer-Tropsch synthesis are water-soluble organic chemicals, such as ethyl alcohol, acetic acid, and acetone. These products will be available in sufficiently large quantities to have a tremendous economic effect upon established sources and uses. They may become the principal source of many basic organic chemicals, particularly those used in the cellulose plastics and fibers, acetate rayon, pharmaceutical, and aliphatic solvent industries. Another potential source of important organic chemicals is the production of high-boiling alcohols from the OXO and synol processes, which are related to the Fischer-Tropsch synthesis. Oil from the liquid-phase hydrogenation of coal is an important source of organic chemicals of commercial value, such as tar acids for plastics, tar bases for pharmaceuticals, and benzene, toluene, and xylene for explosives manufacture and solvents.

When the fluidized iron catalyst process is put into operation at the Hydrocarbon Research plant in Brownsville, Tex., the by-product water-soluble oxygenated fraction will comprise approximately 15 percent of the total production, or 152,450,000 pounds per year. The development of these by-product chemicals will strike with greatest force on the acetic acid industry.[3] The acetic acid production will be 24,700,000 pounds annually; this is 10 percent of the total acetic acid production in the United States in 1946. Ten such plants will yield as by-product acetic acid equal to the total current production. In addition, propionic and butyric acids will also be available for the production of cellulose thermoplastics. The most likely use of the propyl alcohol produced will be as a raw material for oxidation to the acid. Consequently, total acids from these four sources would not be 87 percent of 1946 production, as shown in table 1, but 193 percent on a weight basis, or 170 percent on a molal basis. Because the greatest uses of acetic acid are for plastics and acetic anhydride, and because the latter is also used almost exclusively for fibers and plastics, this development probably will have its greatest impact on the manufacture of cellulose esters. The production of acetic acid from carbide and the production of acetic anhydride from acetone by way of ketene would meet strong competition.

TABLE 1. - Production of important chemicals by ten Hydrocol plants compared with U. S. production [1]

		Annual production			
			Ten Hydrocol plants		Ratio
		United States		Value[2] (million dollars)	Hydrocol to U. S. production
Product	Date (U. S.)	(1,000 lb.)	(1,000 lb.)		
Acetaldehyde	1946	[3]/352,000	91,000	7.3	0.26
Acetone	1946	335,000	112,000	6.7	.33
Ethanol	1943-45	[4]/830,000	636,800	[5]/40.0	.77
n-Propyl alcohol ..	1946	[6]/141,000	144,000	[7]/ 7.2	
n-Butyl alcohol ...	1946	126,000	43,700	5.7	.35
n-Amyl alcohol	1946	[8]/ 15,000	10,600	[9]/ 1.2	.71
Acetic acid	1946	285,000	247,000	19.8	.87
Propionic acid			87,000	[10]/ 7.0	
Butyric acid			42,000	[10]/ 3.4	
		2,084,000	1,414,100	92.3	.68

[1] Sullivan, F. W., Jr., Work cited in footnote 1.
[2] At 1946 prices, according to the Preliminary Report of the U. S. Tariff Commission on Synthetic Organic Chemicals for 1946 (Sept. 1947), except where stated.
[3] All figures in this column from the Preliminary Report of the U. S. Tariff Commission, except where stated otherwise.
[4] Average annual consumption corrected for allocations to acetaldehyde and acetic acid.
[5] At 40 cents/gal.
[6] Isopropyl alcohol less the percentage used in production of acetone.
[7] At price of isopropyl alcohol, 1945, 5 cents/lb.
[8] Total amyl alcohols.
[9] At price of refined amyl alcohol.
[10] At price of acetic acid.

[3] Sullivan, F. W., Jr., Fuel Synthesis By-Products as a Source of Chemicals: Chem. Eng. Progr., vol. 43, No. 12, 1947, pp. 13-17.

Table 1 shows the production statistics for several important chemicals from 10 Hydrocol plants in comparison with total United States production. The value and the percentage which this production will constitute of the past production are also shown. The total weight of the chemicals from Hydrocol operation on this scale is more than two-thirds of the present production of these chemicals.

The impact of this new source of chemicals will also be felt on ethyl alcohol, already under strong competition from methyl alcohol and isopropyl alcohols. If the volume of ethyl alcohol (29,652,000 gallons, 190 proof) that was used as antifreeze were lost to competitive materials, production estimated from the 10 Fischer-Tropsch plants would supply more than enough alcohol for the remaining demand. There is an additional channel of use for alcohol that does not exist for the acids. Alcohol can always be burned as motor fuel and, therefore, can be disposed of at about the price of gasoline.

Straight-chain primary alcohols, such as are produced by the OXO and synol processes, are of importance as chemical intermediates. German main interest in the higher alcohols from a commercial standpoint from 1940 onward was apparently for the production of washing and wetting agents, obtainable by sulfonating alcohols. Test proved that the mixture of OXO alcohols produced better detergents than the fraction of similar alcohols that could be obtained from the synol process. In this country, the octyl and nonyl alcohols obtained from the OXO reaction are being used in plasticizers with phthalic anhydride and phosphoric acid. When OXO-octyl alcohol is made into phthalate or phosphate esters, the efficiency and extraction losses from synthetic resins are the same as those obtained with a commercial di-2-ethylhexyl phthalate (DOP) or tri-2-ethylhexylphosphate (TOF).

Very little wax is obtained as by-product of the Hydrocol process. However, important quantities of paraffin wax (m.p. 40° to 110° C.) were obtained from the German commercial fixed-bed, cobalt-catalyzed, Fischer-Tropsch plants. Between 10 and 40 percent of the hydrocarbon product of molecular weight higher than three carbon atoms was paraffin wax; two-thirds of this fraction was soft wax. The bulk of the soft wax was converted to fatty acids, which were the raw materials for the manufacture of soaps and edible fats. A part of these waxes was also used for the preparation of lubricating oils. The hard wax was used in the manufacture of polishes, candles, and explosives.

Of the by-product tar acids present in the oil from the liquid-phase hydrogenation of coal, one-half to two-thirds of the total tar acids produced are low-boiling; that is, phenol, cresols, xylenols, distributed as follows: Phenol 10 to 25 percent, cresol 30 to 50 percent, and xylenols 25 to 60 percent. Of the tar acids boiling above 235°C., about 55 percent boil in the range 235° to 270°C., 28 percent 270° to 300°C., and 17 percent 300° to 330°C. The total tar acids yield increases with decreasing rank of coal from about 8 percent for high-volatile A bituminous to about 14 percent by weight of the moisture- and ash-free coal for subbituminous coals and lignites. The highest yields of tar acids, upon the basis of

coal as mined, are obtained from high-volatile B and C bituminous coals
and possibly from some subbituminous A coals. From Bruceton (bituminous
high-volatile A) coal hydrogenated at 200 to 300 atmospheres pressure at
440°C., the estimated ultimate yield of total tar acids in 9 tons per 100
tons of moisture- and ash-free coal.

The largest single peacetime outlet for phenol is in phenol-formaldehyde
plastics; next, is in phenol-formaldehyde resins for surface coatings and
as bonding agent in laminated products. Together, these consume 60 percent
of the total phenol production[4]. The consumption of phenol indicates the
magnitude of the industries producing plastics, plywood, dyes, petroleum,
and pharmaceuticals. Indicative of the breadth of phenol usuage is the
following list, which Dow Chemical Co. states represents typical consuming
industries: Plastics and resin; chemical and dyestuffs; explosives; leather;
paint, varnish, lacquer; perfume; petroleum; pharmaceutical; photographic
and engraving; rubber; soap; textile. The phenomenal postwar growth of the
phenol industry is partly accounted for by the large new export market,
partly by the unsatisfied demand in war years for industrial plastics, and
partly by the maturation of the plywood industry in the Pacific Northwest.
The use of phenol in petroleum refining has continued to grow, and exceptional
activity at present is reported. In addition, the demand for pentachlorophenol
for wood treating, insecticides, slime and algae suppression, and tanning is
expected to require 55 million pounds of phenol within 2 years. The develop-
ment of the use of 2,4-dichlorophenoxyacetic acid is even more striking.
Probably 20 million pounds of phenol will be used for this product in 1948;
the potential market in terms of phenol is variously estimated from 40 to
100 million pounds for weed control alone and an additional 13 million for
the production of phenolic detergents.

Since the beginning of the domestic phenol industry in 1913, its pro-
duction has increased from 1,000,000 pounds to 270,000,000 pounds in 1947.
In 1913, phenol was recovered from tars; last year 90 percent of the total
phenol production was synthetic. Because the amount of phenol native to
tars is limited both in content and by coke-oven and gas-works practice,
expansion of the industry has of necessity been by way of the synthetic
product. Synthetic phenol has hitherto been obtained by any of several
processes from benzene, which has been available in adequate supply. How-
ever, lack of sufficient benzene raw material resulted in a shortage of
phenol last year, and producers were forced into voluntary allocation of
the supply. It is apparent, therefore, that an additional source of syn-
thetic phenol, such as is available in the by-product from the hydrogena-
tion of coal, is of great interest. It has been estimated[5] that if
sufficient coal were hydrogenated by the present process to produce 10 percent
of the 1945 gasoline demand, there would be produced about 1,125,000 tons

[4] Skeen, J. R., Phenol: A Statistical Review: Chem. Eng. News, vol. 26,
     1948, pp. 2256-2257.
[5] Clarke, E. A., Tar Acids: Estimated Production Possible if Coal is
     Hydrogenated to Produce 10, 20, and 50 Percent of the Country's
     Gasoline Requirements: Office of Synthetic Liquid Fuels Report,
     Pittsburgh, Pa., 1947, 7 pp.

of marketable tar acids (phenol, cresol, xylenol). This represents about 16 times the 1943 requirements for tar acids in the plastics industry, using present recovery methods. Converting 20 percent of the higher-boiling crude acids to marketable tar acids increases the production to 19 times the 1943 consumption; converting 40 percent of the high-boiling crude acids raises the production to 22 times the 1943 consumption. Hydrogenating coal to produce 20 percent of the 1945 gasoline requirements would double the above ratios; production of 50 percent of the 1945 gasoline requirements would multiply the above ratios five-fold.

One of the xylenols which is simple to isolate from the by-product tar-acid mixture and which is present to the extent of one-half the quantity of phenol is 3,5-xylenol (table 30). Even more abundant than 3,5-xylenol is one of the C_9 tar acids, 3-methyl-5-ethylphenol. These compounds sell at a higher price than phenol and may find use as resin components in the future.

Oils containing 20 to 40 percent of tar acids can be used as creosoting oil, which is an important wood preservative. If a mixture containing phenol, cresol, and xylenols were available at a very low price of about 3 cents per pound, the demand for it probably would be enormous. With a phenolic raw material in this price range and the cost of formaldehyde decreasing, phenolic resins could find use in many products where their use is now economically unsound. For example, phenolic materials are too high-priced to compete with wood, asphalt, slate, and tile as roofing materials. However, there is little doubt that excellent roofing materials could be made from phenolic resin plus filler. The same reasoning may apply to wallboard, siding, insulation, and many other items of construction.

The principal constituent of all of the fractions of liquid-phase coal hydrogenation oils is neutral oil. It was estimated that 1 ton of bituminous coal as mined, yielding 160 gallons of middle oil, could produce about 0.5 gallon benzene, 0.6 gallon toluene, 2.1 gallons xylene, and 1.5 gallons dimethylcyclohexane under the conditions of operation of the assay tests. If enough coal were hydrogenated to supply 10 percent of the 1945 gasoline demand, it is estimated that 10,000,000 gallons of benzene, 12,000,000 gallons of toluene, 42,000,000 gallons of xylene, and 30,000,000 gallons of dimethylcyclohexane could be obtained. If the hydrogenation were carried through the next step, or vapor-phase stage, 1 ton of bituminous coal as mined, yielding 160 gallons of gasoline, could produce 9 gallons of benzene and 11.5 gallons of toluene. These yields are based on the assumption of a gasoline composition similar to that shown in table 18. Extending the estimate to the hydrogenation of enough coal to supply 10 percent of the 1945 gasoline demand shows that 180,000,000 gallons of benzene and 230,000,000 gallons of toluene could be obtained. These products are important as solvents and as raw materials for synthesis of organic chemicals.

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PRODUCTS FROM THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE

In the Fischer-Tropsch process [6], coal, lignite, or natural gas is first converted to synthesis gas, a mixture of carbon monoxide and hydrogen, which, in proper proportion and after suitable purification, is passed over a solid catalyst in one or more stages, with or without recycle of the unconverted gas, at relatively low pressures (1 to 20 atmospheres) and temperatures ranging from 180° to 300°C. The heavier products are condensed from the residual gas; the lighter products are adsorbed on charcoal (in the atmospheric pressure synthesis) or adsorbed in oil (in the medium-pressure synthesis).

The primary products of the synthesis consist chiefly of straight-chain paraffinic and olefinic hydrocarbons, ranging from methane to high molecular weight solid paraffins, and minor amounts of aromatic hydrocarbons, naphthenes, and oxygenated organic compounds. The chief commercial products from the conventional fixed-bed cobalt-catalyzed process are gasoline, Diesel oil, liquefiable gases, and paraffin wax.

GERMAN COMMERCIAL OPERATION

All of the German Fischer-Tropsch plants in 1938-1944 [7] were operated according to the Ruhrchemie process using the $Co-ThO_2-MgO-Kieselguhr$ catalyst at 180° to 200°C., at either 1 or 10 atmospheres pressure, and with 2 or 3 stages with product recovery after each stage. The average yield was 150 grams (per cubic meter of $2H_2+1CO$ gas) of hydrocarbons ranging from propane-propylene to waxes of 2,000 molecular weight. The space velocity employed was 60 to 100 volumes of feed gas per volume of catalyst space per hour.

The converters in atmospheric pressure Fischer-Tropsch plants consist of rectangular steel boxes about 15 feet long, 8 feet high, and 6 feet deep. These contain vertically placed steel sheets about 2 mm. thick spaced about 7 mm. apart. The spaces between the steel plates contain the catalyst. The steel sheets are perforated by horizontally placed cooling pipes about 5 cm. O.D., through which water under pressure is circulated. The cooling tubes are manifolded and connected to a steam boiler that generates steam for power and heating purposes. The converters in medium-pressure (10 to 15 atmospheres) Fischer-Tropsch plants are essentially similar to tube boilers, except that the tubes are double, with the catalyst contained in a narrow annulus between two concentric tubes. A top and bottom weld through the outer tube connects the inner tube with the boiler space, so that it is filled with cooling water. The annular layer of catalyst has an inside

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[6] Golumbic, N., Review of Fischer-Tropsch and Related Processes for Synthetic Liquid Fuel Production: Bureau of Mines Inf. Circ. 7366, 1946, 24 pp.

[7] Storch, H. H., Review of Development of Processes for Synthesis of Liquid Fuels by Hydrogenation of Carbon Monoxide: Chem. Eng. Progr., vol. 44, 1948, pp. 469-480.

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diameter of 24 mm. and an outside diameter of 44 mm. and is 15 feet high. Each converter contains about 2,000 such tubes welded into tube sheets and is about 8 feet in diameter.

Rheinpreussen at Moers operated 96 conventional Ruhrchemie atmospheric-pressure converters, of which 60 were normally in the first stage and 30 in the second stage. The operating temperature was in the range 195°-200°C. The synthesis gas charging rate averaged about 630 cubic meters per hour per oven. The total liquid product, including "Gasol" (C_3 and C_4), averaged 150 to 155 grams per cubic meter. The product distribution is shown in table 2.

TABLE 2. - Rheinpreussen product distribution

Constituent	Weight percent
Gasol (C_3+C_4)	10.0
Gasoline	52.2
Diesel oil	26.5
Soft paraffin wax	7.6
Hard paraffin wax	3.7

Ruhrbenzin at Sterkrade-Holten operated about 48 atmospheric-pressure reactors and 72 middle-pressure reactors, all of conventional design. The normal pressure ovens are operated in two stages on charge gas containing the usual two volumes of hydrogen and one volume of carbon monoxide. In middle-pressure operation, the H_2:CO ration of the inlet gas to the three stages is adjusted to 1.4, 1.6, and 1.8, respectively, by introducing the requisite amount of converted water gas before each stage.

For stage 1 of the medium-pressure operation, the inlet gas rate is 1,000 cubic meters per hour per oven, the temperature 180°-200°C., and the gas contraction 50 percent. Similar conditions obtained for stage 2. In stage 3, where all newly charged ovens are started, higher rates, namely, 2,000 cubic meters per hour per oven, and lower temperatures, 165°-185°C., can be employed. The over-all contraction is about 75 percent and the yield is 150 grams C_3 and higher hydrocarbons per cubic meter of ideal gas (that is, $2H_2+1CO$). The advantage of starting with a gas relatively deficient in hydrogen and then increasing the proportion of hydrogen in later stages lies in combining the beneficial effects of low hydrogen partial pressure on olefin content and methane production with the efficient utilization of the carbon monoxide achieved with normal synthesis gas ($2H_2$:1CO). The products produced by this method of operation are shown in table 3.

TABLE 3. - Product at Ruhrbenzin, Sterkrade-Holten

Product	Weight, percent total product	Percent of olefins in fraction
Gasol (C$_3$+C$_4$)	10	40
C$_5$ to 170° C. [1]	25	24
170°-280° C.	30	9
280°-340° C. (soft wax)..............	20	-
Residue (hard wax, m.p. about 90° C.).	15	-

[1] Motor octane number about 45.

When normal synthesis gas (2H$_2$+1CO) is used throughout, 14 percent of the total hydrocarbons produced is methane; but with the above scheme the proportion is reduced to 10 percent. The middle-pressure synthesis yields two to three times as much wax as the synthesis at atmospheric pressure.

Each plant was given a free choice as to the use of atmospheric or medium pressure. The latter has the advantage of giving three times as much hard wax as does the normal-pressure synthesis, and hard paraffin can be used for the manufacture of higher alcohols, such as C$_{25}$, which can be made by no other process. Also, medium-pressure operation extends the catalyst life by about 2 months. Dr. Martin, managing director of Ruhrchemie A. G., stated that the medium-pressure process should be chosen for any post-war project [8].

Although Fischer's pioneer work on the hydrocarbon synthesis was carried out mainly with catalysts containing iron as the active component, and although cobalt was ultimately adopted in Germany as the catalyst for large-scale operation in view of its higher activity and lower temperature of operation, research on the iron catalysts continued. The outbreak of World War II, which restricted and later stopped the importation of cobalt, caused an intensification of research on iron catalysts, first with a view to using them in any new plants erected, and later, when the cobalt situation became more acute, to replacing cobalt in existing plants. Research was proceeding in six different organizations, each developing what they regarded as the most suitable iron catalyst. Details of this research are described in several reports. [9][10][11][12]

[8] Atwell, H. V., Powell, A. R., and Storch, H. H., Fischer-Tropsch Report No. 1: TAC Report SnMC-1, PB 2,051, 1945, p. 13.

[9] Pichler, H., Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen: Bureau of Mines Special Report, Pittsburgh, Pa., 1947, 159 pp.

[10] Storch, H. H., Work cited in footnote 7.

[11] Gordon, K., et al., Report on the Petroleum and Synthetic-Oil Industry of Germany: B.I.O.S. Over-all Report 1, His Majesty's Stationery Office, London, 1947, pp. 82-103.

[12] Reichl, E. H., The Synthesis of Hydrocarbons and Chemicals from CO and H$_2$: U. S. Naval Technical Mission in Europe Report 248-45, 1945, 130 pp.; PB 22,841.

The possible variations in process conditions and products obtainable are very great when iron catalysts are used. The products may consist largely of the low-boiling hydrocarbons or contain over 50 percent of hard wax. The olefin content can range from 30 to 80 percent and the alcohol content from 2 to 60 percent. In contrast to the reaction with cobalt catalysts, where hydrogen and carbon monoxide always react in the proportions 2.0 to 2.3:1, with iron catalysts the ratio can vary from 0.5:1 to 2.0:1, according to the extent to which carbon dioxide or water appears as the oxygenated product. This extreme flexibility of the iron-catalyzed process has the disadvantage of introducing difficulties in reproducibility of catalyst performance. Despite the amount of research work carried out, it would appear that no iron-catalyzed process developed in Germany had reached the stage where it could be put into operation on the industrial scale and be expected to work as smoothly and efficiently as the cobalt-catalyzed process.

UNITED STATES PILOT-PLANT DEVELOPMENTS

In the United States, several oil companies have developed a fluidized iron-catalyzed process for producing motor gasoline by the Fischer-Tropsch process.[13] In the pilot-plant work on this fluidized iron process, doubly promoted synthetic-ammonia catalyst, Fe_3O_4-Al_2O_3-K_2O (97:2.5:0.5 percent by weight) has been used. The fused catalyst is finely ground and completely reduced by hydrogen before use. It is then introduced while protected by an inert atmosphere, such as carbon dioxide or oxygen-free flue gas, into the converter. The pilot-plant converters are about 12 inches I.D. by 24 feet high and contain an internal heat-exchange surface. This heat exchanger consists of a bundle of about 12 1-inch closed-end tubes, each containing an inner tube, through which water or Dowtherm is circulated at the pressure corresponding to the operating temperature. In an alternative design, the converter is jacketed, and the internal heat-exchange tubes are connected to this jacket at the top and bottom of the converter.

Pilot-plant operation is conducted usually at 300° to 325° C. and 20 atmospheres pressure, with recycle of 3 to 4 volumes end gas per volume fresh feed. The latter is 1.8 to 2.0 H_2 to CO, prepared by oxidation of natural gas with oxygen-steam mixtures at 300 to 400 p.s.i. and 1,200° C. The synthesis operation is in "fixed" fluidized bed; that is, the bed of catalyst is suspended in the flowing gas, with no "carry over" of powdered catalyst outside the converter. Carry over is completely avoided by the use of Aloxite filters in the expanded section of the top of the converter. Catalyst density in the fluidized bed is 60 to 80 pounds per cubic foot at the start. This density decreases during the first 2 to 14 days of operation to 10 to 20 pounds per cubic foot because of "spalling" of the catalyst induced by carbon formation. With a hydrogen-rich total feed gas, 1,600 hours of continuous operation was achieved, and with a carbon dioxide-rich feed gas, only about 400 hours. Operation is limited to 1.5 to 2.5 linear feet per second gas velocity; at this velocity, conversions of 90 to 95 percent are obtained per pass, so that multistage operation is unnecessary.

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[13] Storch, H. H., Work cited in footnote 7.

Carbon dioxide-rich feed gas operation results in a product which is chiefly highly olefinic gasoline with minor amounts of Diesel oil and oxygenated compounds (chiefly C_2 to C_5 alcohols, plus some aldehydes and ketones). Only a fraction of 1 percent of wax is produced, but this is sufficient to occasionally cause defluidization of the bed. The gasoline, with only little refining, is a suitable motor fuel of about 75 motor octane number, which can be increased appreciably by addition of poly-gasoline from the C_2 and C_3 olefins and by tetraethyl lead.

Based upon this pilot-plant work, a plant of about 7,000 barrels per day has been designed and is to be erected at Brownsville, Tex. Synthesis gas is to be made by reacting natural gas at about 400 p.s.i. with oxygen and steam in two vessels, each about 2,000 cubic feet in volume. The synthesis converters reportedly will be six in number, and each will be of about 3,500 cubic feet volume. They are to be fed with 350,000,000 cubic per day of fresh synthesis gas and 750,000,000 cubic feet of recycle gas. Anticipated production is 6,000 barrels per day of high-octane motor fuel blending agent, 900 barrels of gas oil, 200 barrels of fuel oil, and 300,000 pounds of oxygenated chemicals [14].

During the past 2 years the Federal Bureau of Mines [15] has developed a process in which the heat of reaction is removed from a granular or pelleted catalyst bed by circulation of an oil introduced along with the synthesis gas. The converter contains no metal heat-exchange surfaces, and the operation is essentially adiabatic.

The estimates in table 4, for all except the Ruhrchemie process, are based upon very meager data and therefore are only preliminary approximations. As may be seen in table 4, the fluidized iron-catalyst process has a space-time yield about three times that of the Ruhrchemie cobalt process, while requiring only one-fourth as much steel for installing the converter. The internally cooled converter process at the present time has a space-time yield about two-thirds that of the fluidized iron catalyst process, with about 30 percent more steel necessary for installation of the converter and its auxiliary equipment.

[14] Oil and Gas Journal, Phenomenal Expansion Continuing in the Petrochemical Industry: Vol. 47, 1948, pp. 237-244.
[15] Crowell, J. H., and Benson, H. E., Direct Evaporative Cooling in the Synthesis of Liquid Hydrocarbons from Hydrogen and Carbon Monoxide: Presented at Am. Chem. Soc. meeting, Atlantic City, N. J., April 1947.