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INDUSTRIAL AND ECONOMIC PROSPECTS OF CARBON MONOXIDE HYDROGENATION

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Report on the development of the Fischer-Tropsch synthesis with fixed bed catalysts. Great improvements in yield and quality of products and improvements in the gas-synthesis plant design have resulted from the development of high-activity catalysts and the study of important problems in reaction kinetics and heat transfer inside the reactors. As a result, the economic prospects of the Fischer-Tropsch process appear at present in a new light. The quality of synthetic lubricants produced by the Ruhrchemie on an industrial scale is discussed in detail.

Introduction

The Ruhrchemie A.-G., Oberhausen-Holten obtained in 1934 a general license for operating the carbon monoxide hydrogenation process by an agreement with Franz Fischer and the Studium- und Verwertungsgesellschaft, Muehlheim-Ruhr. The process was discovered by Franz Fischer and Hans Tropsch in 1926 and was developed in laboratory studies and on a semicommercial scale by the Kaiser-Wilhelm-Institut fuer Kohleforschung in Muelheim-Ruhr.1/ A large amount of industrial and scientific experience was gained in the field of this synthesis since the contract was closed.

In agreement with the license, 14 plants were erected in Germany, France, Japan and Manchukuo with a total production capacity of nearly 1,000,000 tonnes per annum. A working agreement was entered into by the Ruhrchemie A. G. and the Lurgi Ges. f. Waermetechnik, G.m.b.H, Frankfort/Main in 1939 for development work in this field, and it was greatly activated since 1945. This joint development resulted in great improvements in the Fischer-Tropsch process, or, as it may be more generally called, the carbon monoxide hydrogenation.

Carbon monoxide hydrogenation was being developed also elsewhere, especially after the seizure of German patents. No great industrial progress was so far made anywhere, as far as we know. For this reason, this article is limited to work done by the Ruhrchemie-Lurgi partnership.

As is well know, carbon monoxide hydrogenation consists in the interaction of carbon monoxide and hydrogen over catalyst, with the formation of hydrocarbons. Carbon monoxide and hydrogen can be produced from many fuels. Gases containing only carbon monoxide can be readily converted to synthesis gas. The corresponding industrial methods were reported elsewhere.2/

New Experimental Units

In the 14 industrial installations mentioned, operations were in every case with a fixed bed catalyst, a downward gas-flow and removal of heat of reaction by water boiling at high pressure. These methods were based on experience gained with a number of other synthesis processes (ammonia synthesis, oxidation of sulfur dioxide, naphthaline oxidation, methanol synthesis, etc.), where they were found to be simple, dependable and trustworthy. The partnership decided at the time of resumption of the development work to retain basically the same technique, because of the great amount of experience already gained with them. We considered this experience of such exceptional worth, that a complete rejection of it did not appear reasonable to us. It was then decided to study catalyst development, the controversial reaction mechanism, and heat transfer problems. The need of important development in catalysts, reactor construction and technique of operations was clearly understood. In addition, all efforts were made to develop the synthesis-gas production from different available fuels and to the purification of the gas.

Figure 1 illustrates the principle of our process. The granulated catalyst is located in a tube cooled from the outside with boiling water. The water temperature is regulated by the boiling pressure. The gas flows from above downwards. Generally, gas is recycled.

Figures 2 to 5 are photographs of a Ruhrchemie experimental plant. This is a three-stage process to achieve a 97 - 98 percent CO + H_2 conversion. Figure 2 shows the tops of synthesis tubes with water level indicators and make-up gas intake tubes; figure 3 shows the middle section of the reactors, figure 4 the bottom sections, with the wax separators. Figure 5 is the recycle compressor.

The products of the Fischer-Tropsch synthesis are commonly subdivided as follows:

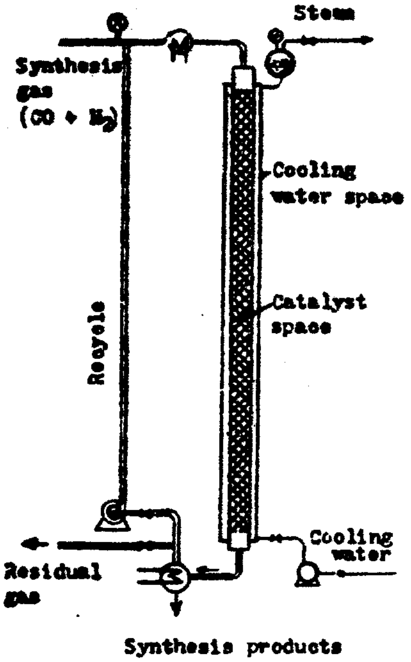


Figure 1. - Synthesis Reactor

1) Methane: This includes methane proper and any ethane and ethylene formed. Methane formation is highly undesirable by consuming the costly synthesis gas in an undesired reaction.

2) Liquefiable primary products: All hydrocarbons from propane and propylene up to the highest pour point waxes are here included. The liquefiable products are subdivided into:

"gasol"	consisting of the C_3 and C_4 hydrocarbons in the distillation range of	-58 - 32° F.
Gasoline	C_5 to C_{10} hydrocarbons, distillation range	86 - 356° F.
Diesel Oils	C_{11} to C_{18} hydrocarbons, distillation range	356 - 608° F.
Crude Wax	distillation range	608 - 680° F.
Fraction containing scale wax		680 - 752° F.
Fraction containing hard wax, boiling above		752° F.

Is the Fischer-Tropsch Process Economical ?

This question will be answered by describing the development work which led to the present status of the process of the Ruhrchemie/Lurgi Development Partnership.

Fig. 2. Head of an experimental reactor

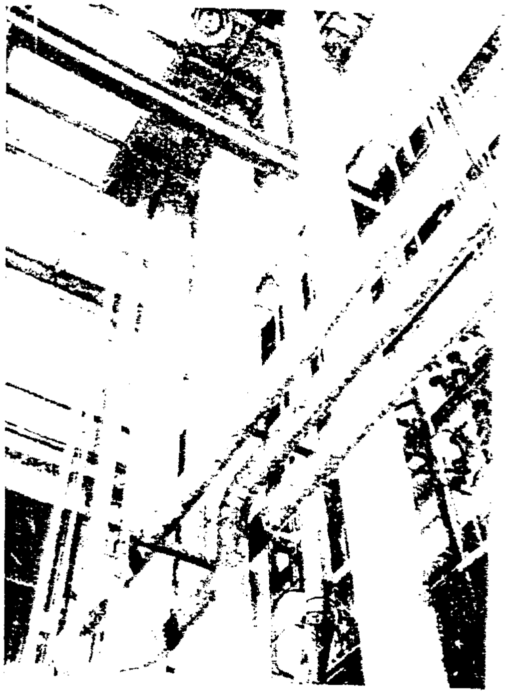


Fig. 3. Central sections of three experimental reactors.

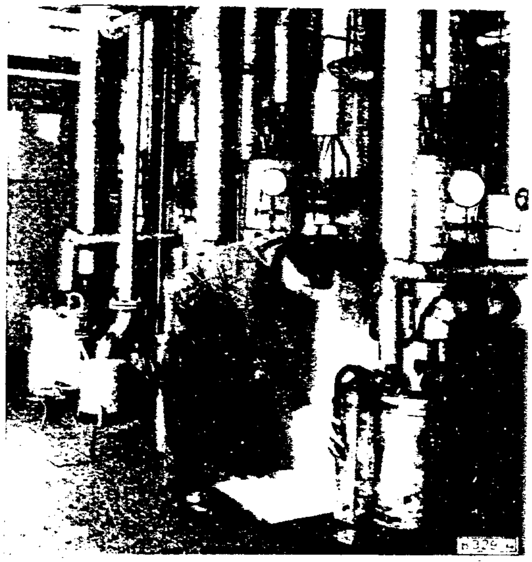


Fig. 4. Wax separators on an experimental reactor.

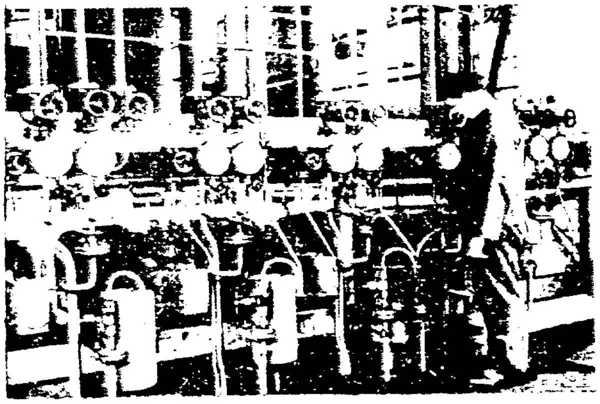


Fig. 5. Recycle compressers for experimental reactors.

In figure 6, the size of installations for up to 500,000 tonnes are plotted logarithmically on the abscissa and the production cost per ton salable end-products are plotted on the ordinate. The production cost with the coal price of 5 DM per million Kcal or 35 DM per tonne in a plant of 200,000 tonnes per annum of final products was arbitrarily set at 100.

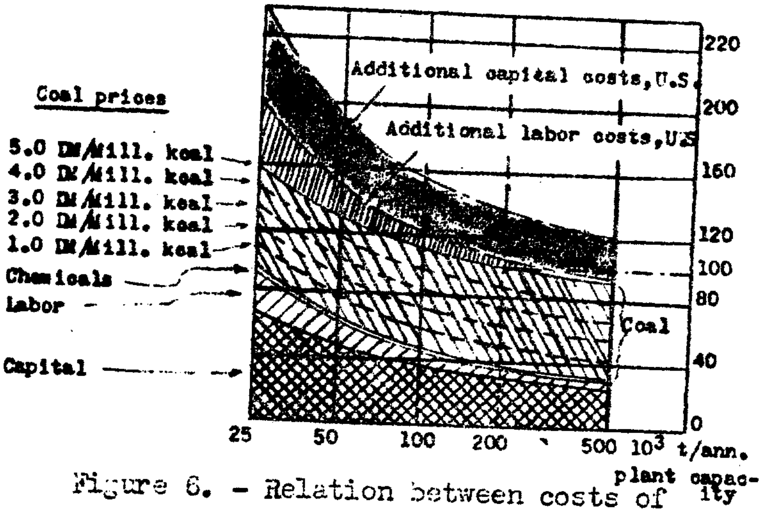


Figure 6. - Relation between costs of products and plant size.

Capital investment and labor costs greatly increase with reduction in plant size. The small strip representing the cost of chemicals naturally does not change with the size of the plant. The space above the cost of chemicals is the coal price; its divisions indicate the effect of increasing coal prices upon the final costs. The investment costs include 6 percent amortization, 6 percent interest and 3 percent maintenance cost. The data obtained by the German Coal Mining Administration Commission were used for the determination of the economics of the Fischer-Tropsch installations. Above are plotted the additional costs caused by the higher wage level in the United States. The next band above, bounded by a broken line, is the added investment cost in the United States resulting from 20 percent amortization instead of the 6 percent with, however, only 3 percent interest against the German 6 percent. The question of economics of the Fischer-Tropsch process under American conditions will be discussed later.

The labor cost and the investment capital increase progressively with the reduction in plant size, and even at a low coal price a minimum economical size of the plant will be reached.

Figure 7 shows a detail of cost estimate for different economic conditions taken from figure 6. The first column shows the construction cost of a 200,000 tonne capacity plant under the present German conditions; its cost is set arbitrarily at 100, and is taken as the standard. It consists of

Cost of coal.......	55.4%
Investment cost....	33.8%
Labor cost.........	5.3%
Chemicals..........	5.5%

of the total cost.

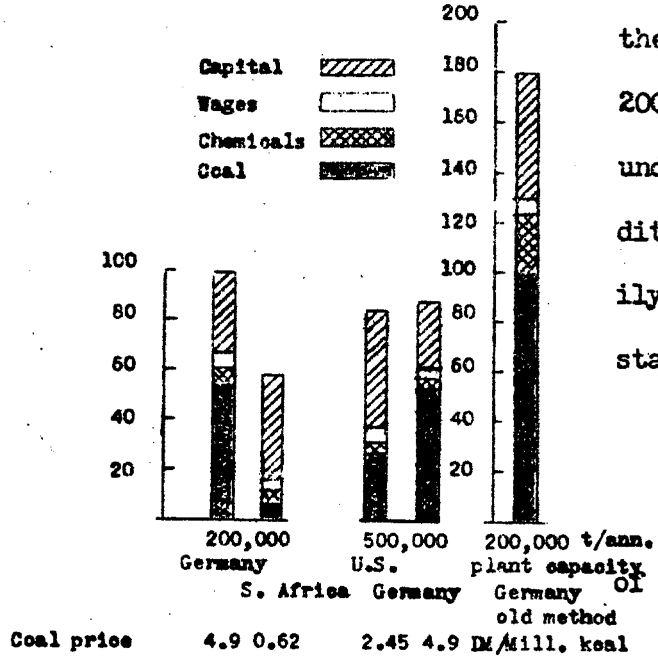


Figure 7. - Production cost of Fischer-Tropsch products.

A plant of the same size in countries where coal is extremely cheap is shown in column 2 and amounts to only 58 percent of the standard cost. In this case:

Capital investment......	69.4%
Labor cost..............	9.1%
Chemicals...............	9.4%
Coal....................	only 12.1%

While the coal cost is 1.6 times as high under standard conditions as the investment cost, in this latter case the capital investment amounts to about 6 times the cost of coal. In practice this shift in costs plays an important role upon construction. E.g., when coal prices are high capital will have to be used to reduce coal costs, while with cheap coal investment costs may be kept lower.

Two 500,000 tonne plants are compared in the next two columns in which the third column represents American conditions, while the fourth column the corresponding German conditions. The coal prices in America are about 1/2 as high as in Germany. On the other hand, Americans pay very low interest on investment but expect a 5-year amortization against the 16 years in Germany. The total production cost in the two plants are practically equal, namely, 85 and 88 percent of the standard cost, but the cost distribution in the two plants is entirely different. The investment costs amount to 56.3 percent under American conditions and to only 29.8 percent under German conditions. On the other hand, the coal cost under American conditions amount to only 31.4 percent, and rise under German conditions to 60.6 percent.

Computations so far were based on the newly developed process and for comparison column 5 shows the production cost with the earlier processes on the assumption that its design is left unchanged today, and with the present prices. The plant is intended for 200,000 tonne yearly production, and can therefore, be directly compared with the standard plant in the first column. The total production costs per ton of the primary products is 180 percent of the cost with the modern standard design. Improvements have affected nearly equally the coal consumption and the capital investment costs. The cost of chemicals, which are principally the cost of the catalyst, have been greatly reduced.

earlier catalyst reactors. This is followed by condensation and purification.

Figure 10 shows the cost break-down of the modern carbon monoxide hydrogenation. The costs are composed of 3 principal components: Gasification, synthesis and refining, and are plotted with their proportionate power and other costs. The total cost of marketable final products is set as 100 at a coal cost of 0. This point represents then the labor, capital, chemicals and the overhead. The coal price is plotted on the abscissa, and the resulting cost on the ordinate. The large bottom area shows the share of gas production, purification and compression in the total cost, and is dependent on the coal price. Above it is the area of synthesis cost. It is practically independent of coal price and represents only a relatively small part of the total cost. Refining costs are low in comparison with total costs.

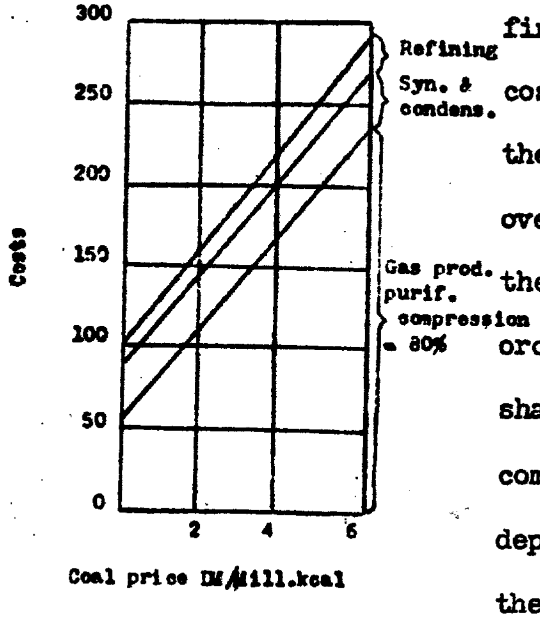


Figure 10. - Cost break-down in modern CO hydrogenation.

This cost structure shows the demands made upon gasification, the necessity of developing the lowest cost gasification process, possibly by combining gasification with iron ore reduction in blast furnaces or other similar slagging processes which produce cheap gas. To be economical, the gas must, however, contain a high percentage of CO + H_2 or CO, the active gas constituents.

The principal task of synthesis consists in converting the costly gas as completely as possible, with the production of the maximum yield of products of the highest market value. A synthesis which fails to meet these requirements increases the production cost.

Reduction in synthesis costs proper are difficult to realize, because the cost of synthesis is relatively small in the total cost. Should such economies in the cost of synthesis result in higher methane formation, reduced conversion, or low quality of the final products, they will generally mean self-deception. The cost of final products may not be reduced, and may be actually raised.

The costs of gas are shown in figure 11. They are plotted for this gasification process against coal prices. Four typical processes were selected of the more or less industrially developed gasification processes: Pressure gasification with oxygen (a), atmospheric pressure gasification with oxygen (b), atmospheric pressure coal-gasification without oxygen (c), with which, however, 90 - 92 percent active constituents are obtained, and the usual water-gas generators (d) with the formation of about 60 percent non-combustible constituents and only 40 percent $CO + H_2$ in the gas. With low coal prices, the cost of the first two processes

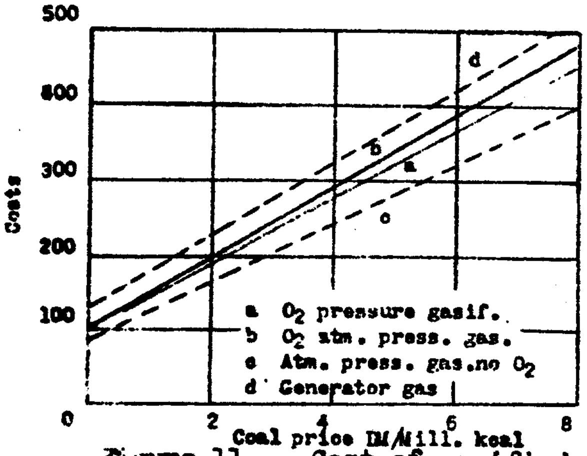


Figure 11. - Cost of purified compressed gas.

differ very little, while with high coal prices, such as in Germany, pressure gasification, a, is definitely more economical because of the lower power requirements, and also because of the credit for certain carbonization products. The atmospheric pressure processes, shown by the two broken lines c and d, are of interest. The line d is the cost for the 40 percent generator water-gas. The lower curve c gives the price of the 90 percent water-gas. All prices are computed to purified gas, compressed to the synthesis pressure before synthesis. The 40 percent generator gas is shown by accurate cost computations to be a very expensive gas because of the high compression costs of the inert constituents as well as the cost of purification of large gas volumes and of the condensation from this gas, which have an adverse effect on the total cost. For this reason, the use of blast furnace gas or similar gases is only economical under certain conditions, and these limitations do not depend on the nature of the synthesis, but are generally true at least for pressure processes. On the other hand, a high concentration gas with about 90 percent $CO + H_2$ produced without oxygen will prove economical through avoiding the oxygen production costs. The development of such gasification processes has fortunately progressed far enough to create hopes of making them shortly industrially available.

Direct gasification of coal depends on the coal quality. The tar content, the agglomerating properties and the ash content may result in limiting the choice of gasification processes and direct the selection of one based upon the quality of the coal. It is therefore, gratifying that various firms, especially in Germany, have studied this problem intensively, and gasification processes are available for different coal qualities. The Fischer-Tropsch synthesis makes high demands on the quality and amount of gas and has furnished important incentives in this field of modern industrial development.

Iron Catalyst

The modern development depends on improvement in iron catalysts. Iron catalysts are essentially highly dispersed iron with definite activators and promoters. It was shown elsewhere,2/, that the inner surface of our catalyst reaches 350 M^2 per gram of iron. A closer study of the pore structure shows that the average wall thickness is close to 5×10^{-7} cm. Such dispersed iron loses much in its magnetic power, because its average particle size is less than the size of molecular magnet (so-called Weiss range) of about 10^{-5}cm. Should two equally heavy tubes be filled with an iron catalyst, and should the catalysts in one of the tubes be sintered in the absence of air at 600 to 700° C. for a few hours, the tube filled with the unsintered catalyst will be found to be no longer attracted by a permanent magnet, while the sintered catalyst becomes attracted to it. This simple test shows the highly dispersed nature of the catalyst.

What are the demands made upon such an iron catalyst?

1) It must possess a long life.

2) It must be active at lowest temperatures to permit the simplest form of cooling of the process by boiling water.

3) It must cause a maximum conversion of the synthesis gas.

4) A minimum of methane should be formed with a maximum yield of high-grade hydrocarbons.

5) The conversion rate must be at a maximum in order to raise the space-time yield.

6) The conversion proportion of CO and H_2 must correspond to their proportion in the gas; unless CO and H_2 are consumed in the same proportion as present in the make-up gas, the two equivalent gas constituents cannot be economically used.

7) The activity and other properties of the catalyst must be adjusted to the reactor construction, and vice versa.

8) The catalyst must possess maximum strength, be uniform in quality and be readily regenerated.

9) The cost of the catalyst must not be excessively high.

The evaluation of such catalyst demands great experience and is very costly because they must be tested over extended periods.

Figure 12 shows how complicated the effects are of gases upon the carbon monoxide hydrogenation catalysts. In this figure the conversion is plotted against the nitrogen, carbon dioxide and steam content in the reacting gas. U_{N_2} shows that a 60 percent conversion is possible in the presence of up to 70 percent N_2, and the corresponding curve t_{N_2} shows that the temperature must be continuously reduced to maintain a constant carbon monoxide—hydrogen conversion with increasing N_2 concentration. Steam and carbon dioxide have the reverse effect. U_{H_2O} shows that the conversion is greatly reduced by the presence of steam. U_{CO_2} shows a similar but smaller effect of carbon dioxide, while the $t_{H_2O,\ CO_2}$ line shows that the temperature must be kept constant, which is the reverse of the temperature effect in the nitrogen tests.

The total amount of gas remained constants in all these tests, while the proportion of nitrogen, steam or carbon dioxide to the CO + H_2- mixture was changed. Should the amount of CO + H_2 - mixture be kept constant, or at least approximately constant, the amount of conversion at a given temperature will be practically the same even with 65 percent nitrogen addition.

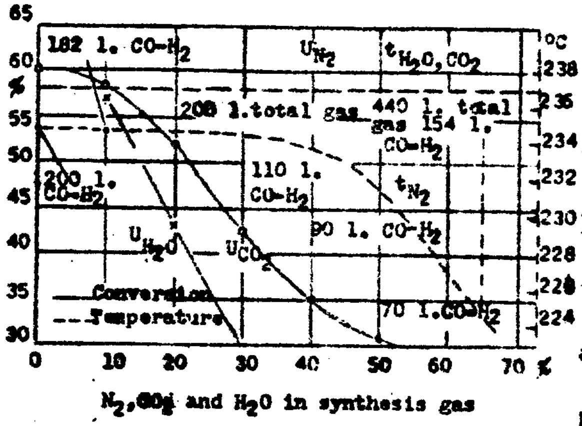


Figure 12. - Effects of CO_2, H_2, and N_2 upon the reaction rates.

Carbon dioxide and steam formed in the reaction slow down the reaction rate, while nitrogen actually accelerates it by reducing the carbon dioxide and steam partial pressures, but the space-time yield of the reactor will, however, be reduced.

Reaction Equations

We have recently succeeded in proving that the reactions with an iron catalyst proceed simultaneously by the following equations:

Reaction Equations	Reaction Rates
1) $CO + 2\ H_2 = CH_2 + H_2O$	$n_{H_2O} = k_1 \frac{P^2_{H_{2x}}}{P_{CO}} \frac{1}{1 + k_2\ (CO_2 + H_2O)^5}$
2) $2\ CO + H_2 = CH_2 + CO_2$	$n_{CO_2} = k_3 \frac{P_{H_{2x}}}{P_{CO}} \frac{1}{1 + k_4\ (CO_2 + H_2O)^7}$
3) $CO + H_2O = CO_2 + H_2$	$n_k = k_5 \cdot P_{H_2O}$

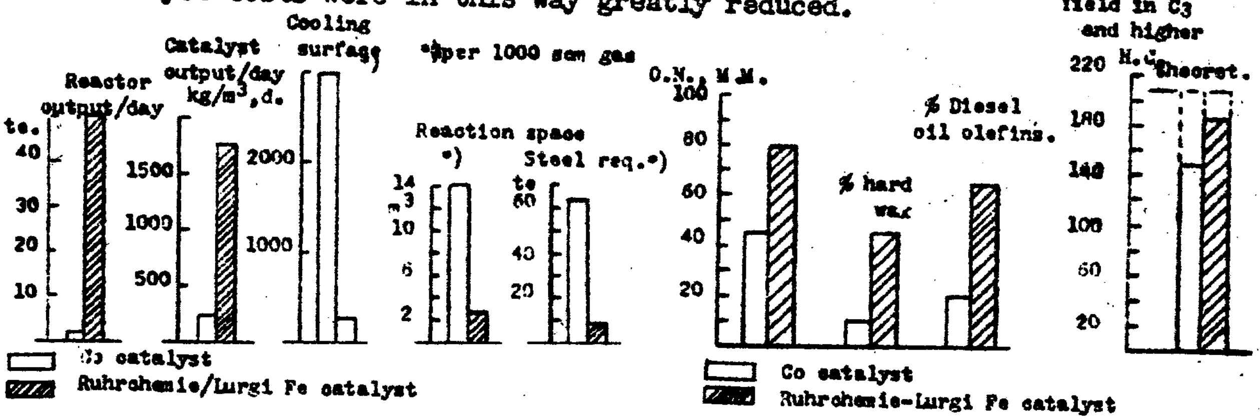
It was further found possible to express quantitatively the reaction rates with our catalyst and synthesis conditions. Details of it are shown elsewhere.2/,5/ These formulas and their classified presentation gave us for the first time a chance to predict synthesis results quantitatively.

Important Recent Progress

Problems of material and heat transfer through loosely filled space had to keep step with the development,6/ to furnish a basis for computation. This basis furnishes to today's designer of carbon monoxide hydrogenation installations the required relations between conversion, recycling, heat of activation, concentration of active components and tube lengths and diameters.

Important progress was achieved after these data were determined, and illustrated on figures 13 and 14.

The reactor productivity has been increased from about 2 to around 50 te. and over in the modern reactors. The output per unit volume of catalyst, referred to primary products, was increased from 250 to about 1,750 kg/m^3, day. The cooling surface per 1,000 m^3/hr. of converted gases was reduced from 3,000 to 240 m^2. The reaction space requirements per 1,000 m^3, hr. of converted $CO + H_2$ was reduced from 14 to 2.5 m^3, and the steel requirements for the same output from 63 to 9 te. The catalyst life, at the same price per m^3 and seven times greater output per unit time, remains at least as large. The catalyst costs were in this way greatly reduced.



Figures 13 and 14. - Comparison of Ruhrchemie-Lurgi and Cobalt catalysis systems.

The small reactor capacity, the high steel and cooling surface requirements of the early Fischer-Tropsch plants justified adverse criticism of the German synthesis technique, and were a great incentive for further development work from the classical synthesis with a gas flow upwards and a stationary catalyst. The cost structure is shown in figure 10, and is not merely indicative of our synthesis development, but is quite generally valid by showing the necessary demands on:

1) High gas utilization, and
2) High quality of the products.

It was believed in the United States that the availability of methane as a very cheap gas source permitted to some extent disregarding these demands. I am convinced of the opposite. Many economists have predicted that the price for methane will rise steeply and permanently in the United States. Several projects are being developed now to manufacture methane from coal to supply the gas required by the industry. Time will surely be reached for methane as a fuel when yield and product quality will have to be balanced against the actual synthesis costs.

Unlike the American development we have tried to increase the gas utilization and improve the quality of the products by improving the operational technique.

Theoretically, 1 nm^3 of $CO + H_2$ can yield 205 gm primary products. Earlier installation produced 150 - 160 gm as a yearly average, or 75 percent of the theoretical yield. Today 185 gm is produced, or 90 percent of the theoretical amount. (Figure 14) These figures refer, naturally, only to the liquefiable products, i.e. to the C_3 and higher hydrocarbons.

The great reduction in costs of the present synthesis production over the cobalt synthesis is largely to be attributed to these results (figure 6).

Improvements in the Product Quality

High yields and quality of the products affect profits especially greatly. The increase in yield to 90 percent of the theoretical by improving the reactor design resulted also in a great improvement in the quality of the products. The proportion of hard waxes has been raised from 10 to 45 percent. Hard wax is in greater demand today than ever. The melting point of the synthetic hard wax is above 100° C. Special extraction methods permit raising the melting point to 115-120° C. The color of the hard wax is snow white, and it must be considered a product of top quality.

The octane number of hot-refined unleaded cobalt synthesis gasoline was 45 and was raised to 78 with the iron catalyst, or to that of high-test gasoline.

The olefins in the Diesel oil distillation range are of particular interest for the production of lubricants or fatty alcohols. This has been raised from 10 - 20 percent in cobalt atmospheric or middle pressure synthesis to 65 percent in the iron catalyst Diesel oil.

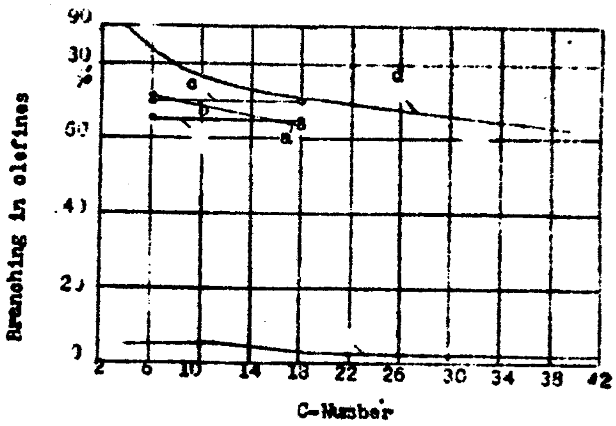


Fig. 15. - Olefin content and branching in the Fischer-Tropsch iron catalyst products.
"a" total olefins in the fraction; "b" proportion of olefins formed to those present before dehydration, "c" the same as b before dehydration, "d" straight-chain hydrocarbons, "e" branched HC/total C atoms.

Figure 15 is a general picture of iron catalyst products.

While some 90 percent of the low-boiling HC are straight-chain compounds, this proportion becomes lower with increasing chain length. When the carbon number reaches 30 - 40, some 35 percent of the molecules are branched. The curve "e" seems to explain this remarkable result. It shows, that the number of

C-atoms in the side chains is in about a constant proportion to the total number of atoms. With fewer but longer chains in the higher boiling range, a larger proportion of molecules must simply arithmetically have side chains. The side chains are apparently always CH_3 groups.

The presence of aromatics and naphthenes in the products is doubtful. The total olefins in the curve "a" drop from 72 percent in the C_5 fraction to about 62 percent in the Diesel oil fraction, or only very slightly. Seventy percent of these olefins were formed by dehydration of the small amounts of oxygenated products. Alcohols, esters, acids and ketones are distributed over the whole distillation range amongst the iron catalyst reaction products. Small amounts of recoverable water-soluble alcohols are found in the liquor, and they offer no problems in subsequen operations.

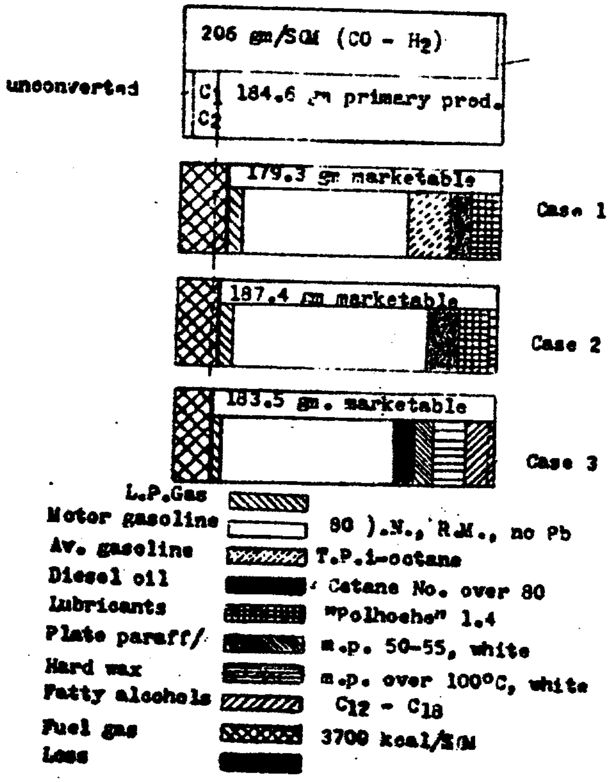


Figure 16. - Different refining schemes.

Refining

Three typical refining schemes are shown in figure 16. 185 gm per nm^3 are obtained as primary reaction products instead of the 205 gm per nm^3 which are theoretically possible. The balance are gases which can be used for heating.

The first process is designed for the production of aviation gasoline (high octane number), motor car gasoline, Diesel oil, lubricating oil and L.P. gas. The yields in this case amount to 96 percent of the primary products.

In case 2, a certain amount of hard wax is to be produced in addition to lubricating oil, Diesel oil and gasoline. Losses in this refining process are still lower, and amount to around 2.5 percent.

More chemical conversion is planned in case 3. In this case final products are obtained with practically no loss, because no loss-entailing processes are here likely except for a small amount of cracking of the unusable crude wax. On the other hand, the gain in weight in the production of fatty alcohols by addition of water (the oxo-synthesis) compensates for the small cracking loss. This illustrates the flexibility of the different methods of refining the products.

The great flexibility in refining, and the possibility of adapting the processes to market requirements result chiefly from a high olefin content, the absence of aromatics and naphthenes, the small proportion of side chains and the relatively large distillation range. These are characteristic for the process of the Ruhrchemie-Lurgi Company.

Lubricants

The importance of the high concentration of Diesel oil olefins and the absence of aromatics and naphthenes in the synthesis products is illustrated in somewhat greater detail in a synthesis of lubricants, figure 17, as practiced by the Ruhrchemie from 1939 to 1944.

The naphtha and Diesel oil olefins were then discontinuously polymerized in reactors with stirrers, with a catalyst oil as catalyst. This catalyst was obtained by interaction of anhydrous aluminum chloride and olefins. The yields amounted to 80 - 85 percent of the olefins used. The olefins were largely obtained by cracking of the crude wax or of the oil pressings in the scale oil production or in the higher Diesel oil production. The olefins produced today in the iron synthesis are a nearly ideal raw material for the lubricant manufacture.

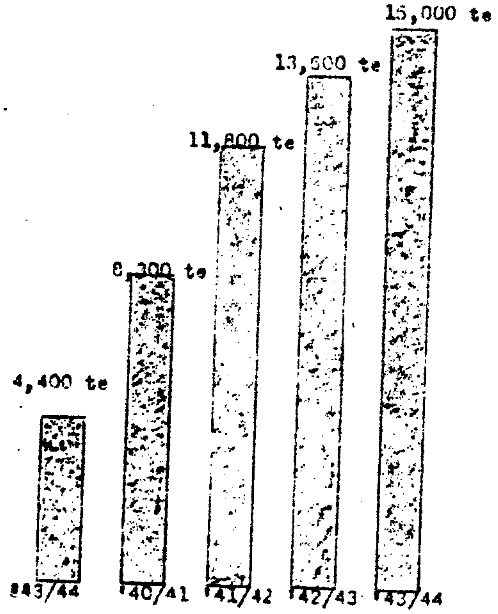


Figure 17. - Yearly lube production in the Ruhrchemie

The viscosity of a good lubricating oil must be very little affected by temperature. In Germany, polhoehe is used as a measure of the temperature relationship of a lubricant, while in the United States and generally abroad, the viscosity index is used for this purpose. These indexes are connected by a simple mathematical relationship.* Figure 18 shows the relation

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* The relation between "Polhoehe" and viscosity index, NavTecMisEu #260 (TOM Reel 196, frame 1):

Viscosity Index	"Polhoehe"
120	1.5
100	1.8 - 1.9
80	2.1 - 2.25
60	2.4 - 2.6
40	2.8 - 3.0
20	3.2 - 3.4
0	3.6 - 3.8

between the viscosity polhoehe values of lubricants and the length of the carbon chain of the polymerized olefins. Olefins of the same length of the C-chain give the lowest polhoehe values, i.e., the best lubricant qualities with the least amount of branching and the double bond in the α position. The best values found in the literature are plotted in the curve "a" against the C number of the olefins. Curve "b" shows the values obtained from olefins with the double bond in the β-position.

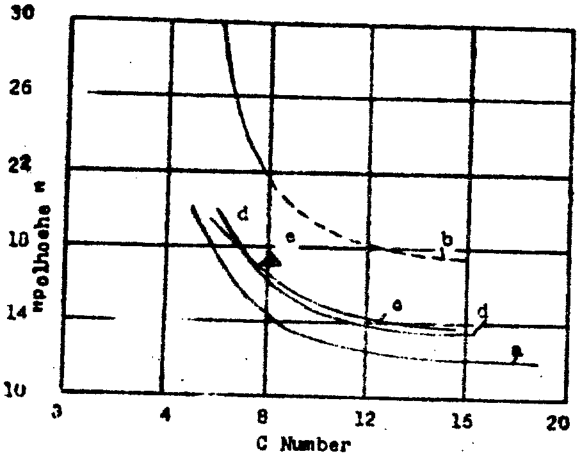

Figure 18. - Viscosity polhoehe of lubricants.
"a" from α-olefins, "b" from β-olefins, "c" from splitting olefins, "d" from the iron catalyst synthesis, "e" from the Ruhrchemie production.

Careful splitting of the soft waxes from the cobalt synthesis produced olefins which permitted the production of lubricants shown in curve "c".

Splitting and polymerization of the cobalt synthesis products of the Ruhrchemie produced values shown in the triangle "e".

The curve "d" immediately below curve "c" shows the polhoehe of oils produced by polymerization of olefins from the modern Ruhrchemie iron catalyst Diesel oils. The carbon chain length of these olefins is C_{10} to C_{16}, and the point on this curve indicated by an arrow gives a polhoehe of 1.4. There is a definite improvement over the values of oils from the cobalt synthesis.

A second advantage of the iron catalyst Diesel olefins as a source of lubricating oils is the fact, that no splitting products are formed, because the primary products are directly converted. These oils polymerize especially readily, and operations can be conducted in a continuous process recently developed by the Ruhrchemie.

It will be briefly mentioned that these oils were tested in various ways. Their dielectric loss factor and dielectric strength are outstandingly good when used as insulating oils. They were found exceptionally good as compressor oils for the compression of a great variety of gases. The exceptionally low residue formation and cleanliness of operations must also be noted. These oils were particularly thoroughly tested as motor lubricants. Cold tests of the oils showed that the minimum temperature at which these oils can still be pumped are lowest with such oils. Viscosities at low temperatures are shown in figure 19.

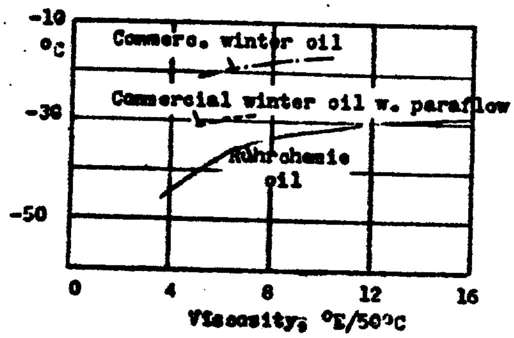

Figure 19. - Lowest pumping temperatures.

Aviation motor tests of these oils proved them to resist exceptionally well to ring sticking. No gum is formed in the aging of these oils. As a result, rings remain free even after 14 hours of extremely hard use, while with other mineral oils, formerly used by the German Air Ministry as standards, the rings froze after eight hours use.

The oils were found equally satisfactory in wear tests. Figure 20 shows that the piston-seizure, which is a measure of the limiting temperature for seizure, plotted against viscosities, are much more favorable for them than for the grease-containing and grease-free mineral oils. The curve at the right of wear tests obtained in a large number of motor tests show that for synthetic oils the wear is independent from viscosity and very small. A number of commercial motor oils showed higher wear values.

Table 1 shows the assymetry and ring values (Gross and Grodde,7/) for a number of commercial lubricants and of synthetic oils. The low solidification point of the synthetic oils, their high molecular weights for the

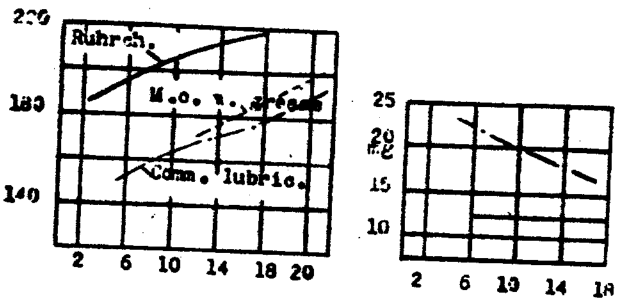

Figure 20. - Piston seizure and wear of lubricants.

TABLE 1. Review of properties of lubricants

Symbol in figs. 21 & 22	Av. mol. wt. M	Solid point E_p, °C.	Viscosity, centi-Stokes V_{100}	Assymetry A	Ring value	Fractions
○	430	-15	6.6	63	58	Mineral oil 1
	435	-21	8.4	66	85	Mineral oil 2
	455	-14	9.0	62	86	Mineral oil 3
	560	-15	14.3	72	91	Mineral oil 4
	512	-10	18.0	64	68	Mineral oil 5
	590	-17	23.0	73	60	Mineral oil 6
●	665	-50	8.6	105	13	Synthetic lubricants from Fischer-Tropsch synthesis products.
	786	-35	15.0	100	14	
	800	-35	16.5	95	13	
	999	-41	22.8	110	17	
	1390	-27	50	107	18	

$$A\ (M,E_p) = 311.\frac{M}{M+95} - 205 - 3/4\ E_p$$

$$R\ (M,d) = 10^3.d - 504 - 311\cdot\frac{M}{M+95}$$ d — density

same viscosities and their close to zero ring values and high assymetry values are outstanding. Synthetic oils contain from their very origin much fewer cyclic compounds, but acquire an isostructure by the aluminum chloride polymerization. This is particularly clearly seen in figure 21 in which indexes of refraction are plotted against molecular weights.

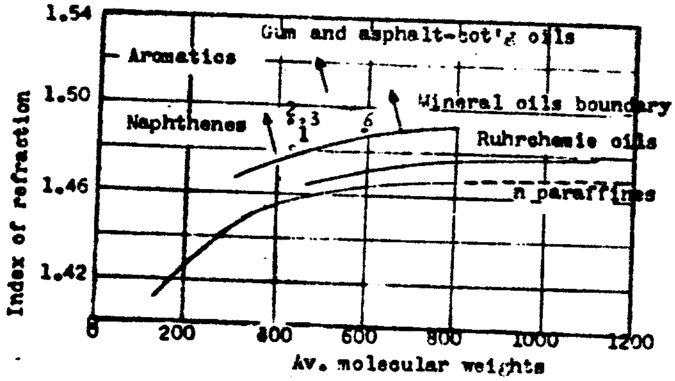

Figure 21. - Indexes of refraction.

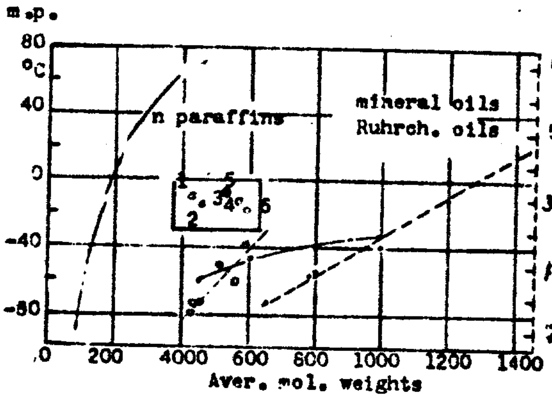

Figure 22. - Melting points and viscosities of lubes.

The index of refraction of normal paraffins is the lowest for a given molecular weight. The values for synthetic oils are very close to those of normal paraffins. The upper curve is the limiting values for highly refined mineral oils. The points plotted are results of determinations with the common lubricants on the market, and are more or less displaced in the directions of the arrows towards the gum and asphalt-containing oils according to the determinations of Zerbe 8/ and our own. The pour points and the relation between viscosity and molecular weights are particularly enlightening. The left curve in figure 22 shows the relation between the melting points of normal paraffins and their molecular weights. The same relationship for commercial lubricants is shown in the rectangular frame. The flat bottom curve which holds even for -30° C. with high molecular weights, illustrates the extremely low pour points of synthetic oils. A further characteristic of synthetic oils is shown by the broken lines of equal viscosities with mineral oils at much higher molecular weights. According to Umstaetter 9/, the lubricating properties upon bearing surfaces depend on the molecular weights, which causes a lowering of the hydrodynamic pressure maximum. It may well be that the desirable properties of these oils are due to it.

Because of the close connection between oil and fuel, the chances offered by the synthesis for the production of very high grade motor oils is a very important characteristic of our process, and this is the reason for discussing these details. Aromatics and naphthenes which are formed in the fluidized catalyst technique at above 300° C., or similar processes, are definitely objectionable in the lubricating oil syntheses.

A few words will be added about another method of chemical conversion, namely, the addition of carbon monoxide and hydrogen to aldehydes or products resulting from them, alcohols or acids, i.e. the so-called oxo-synthesis, also discovered by the Ruhrchemie. Roelen 10/, has reported in detail at the last chemical meeting in Cologne in 1951 on the flexibility of the oxo-synthesis. The high olefin content and the favorable final form of the olefins are economically extremely favorable to the oxo-synthesis, presenting an easy access to this important field of chemistry, and therefore, also to the production of plasticisers, solvents, plastics and detergents via the iron-catalyst synthesis.

The oxidation of hard waxes may also be done for the production of acids using nitroso acids and sulfuric acid. These acids are emulsifiable, and the process was also developed by the Ruhrchemie.

Economics

The production costs of the primary products could be reduced with raising the yield to a maximum with an improvement in their quality. A 200,000 te. Fischer-Tropsch plant seems to me to be entirely possible with the present coal prices and under the German conditions, with the production of the simplest products-- L.P. gas, gasoline and Diesel oil. With the use of the above mentioned further developments and the conversion of the primary products into lubricants or aldehydes, economics are further improved.

A 200,000 te. size is, however, by no means a necessity. The Wanne-Eikel plant of the Krupp Kohlechemie G.m.b.H. was recently started. It was to be partially modernized by the Ruhrchemie-Lurgi partnership, which will permit the production of hard wax in the old middle pressure equipment, and this will be economical with a much smaller yearly production.

In the United States, the Fischer-Tropsch synthesis seems the least promising. Coal is not especially cheap there, labor is very high and the investments costs are greatly increased by demanding an amortization of 20 percent of the investment. Moreover, the price of gasoline and Diesel oil are kept low by competition with petroleum production. Nevertheless, according to our computations, the high quality of our products will play a deciding role in a 500,000 te. plant. The conversion of the Diesel oil olefins to lubricants of the highest quality, and of a small part of the production into high price hard wax and other chemicals, will assure, according to our calculations, sufficient profits even in the United States. It appears, however, doubtful whether a plant limited to the production of fuels can be profitable.

If a 500,000 te. plant were erected in Germany to be operated for the same final products as in the American plant discussed above, the economic results would be appreciably more favorable because of the lower normal amortization rates and higher prices for the products, in spite of the higher costs.

Economics of the Fischer-Tropsch process under African conditions is very favorable because of the very low cost of coal there, low wages and high costs of fuel, with the high transportation charges from the coast to the interior. The South African Union has decided 1½ years ago to install a Fischer-Tropsch plant. The first general license agreement was signed by the Ruhrchemie-Lurgi Company and the South African Coal, Oil and Gas Corporation, Ltd., in Johannesburg.

The first industrial reactor unit with considerably higher load than in the earlier plants, will be put on stream in a few months by the oldest licensee of the Ruhrchemie, the Etablissements Kuhlmann at their plant in Harnes for wax production and is based on a new license agreement. Their economic conditions are similar to those in Germany.

For European conditions, a combination of the Fischer-Tropsch process with pipe-line gas projects offers fine possibilities. In this case, the combination of pressure gasification with the Fischer-Tropsch synthesis will prove most economical to bridge the already existing and steadily widening gap between gas demands and supply thus supplying to home demands the valuable energy source, gas, in greater amounts.

An attempt was made to answer the question, whether the Fischer-Tropsch process is economical. It was shown, that in all the cases considered the answer is definitely positive in the affirmative.

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