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INDUSTRIAL HYDROGENATION OF CARBON MONOXIDE

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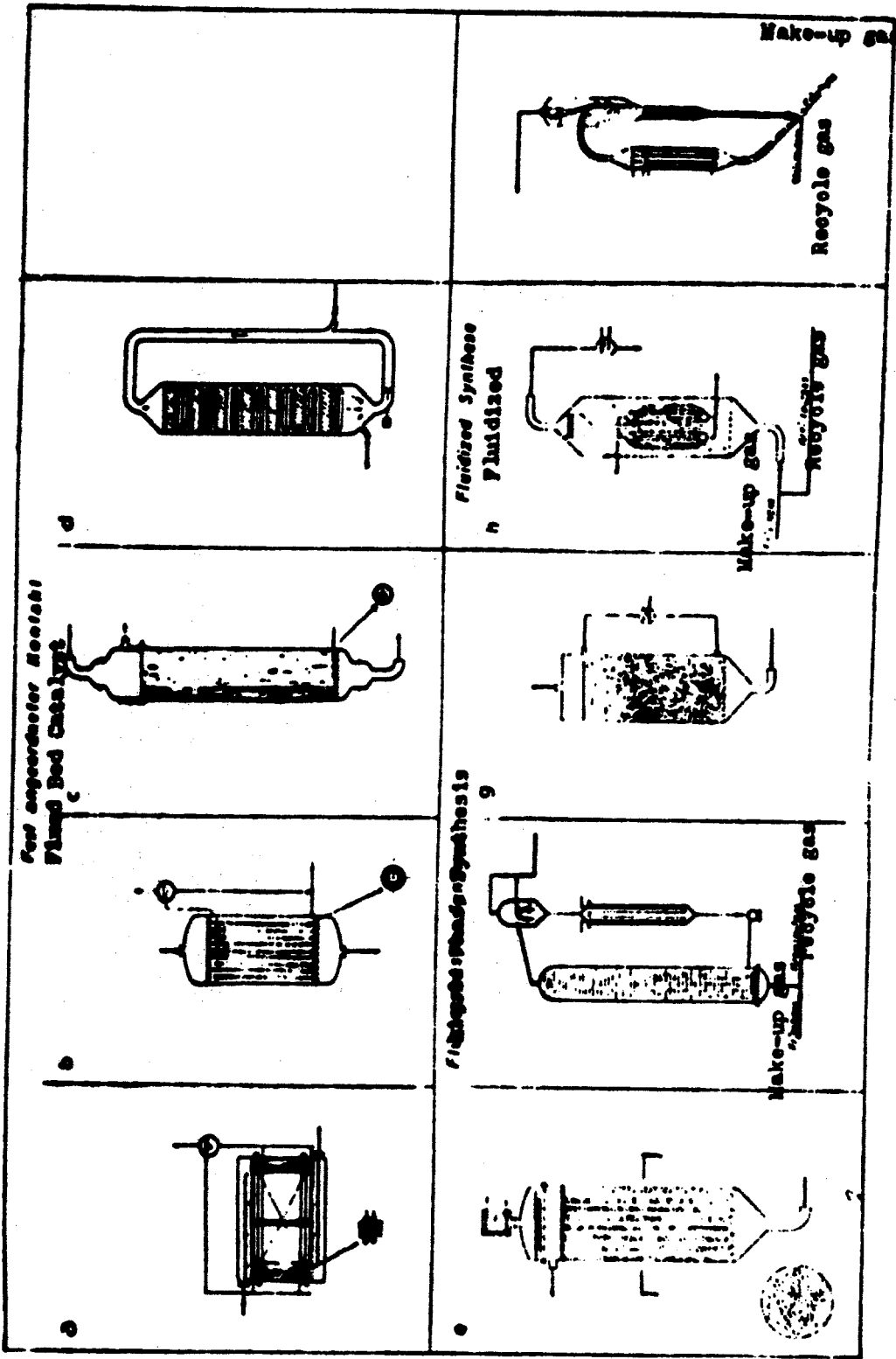
1. General Survey

Hydrogenation of carbon monoxide for the industrial production of higher aliphatic compounds in all the already erected and operated plants is based on the process developed by the Ruhr-Chemie A.G., Oberhausen-Holten, and licensed by them for operations with fixed-bed mixed cobalt catalysts at atmospheric or medium pressures up to about 10 atmospheres.

These large installations, which include a total of 14 plants, namely 9 in Germany, 1 in France, 3 in Japan, and 1 in Manchukuo are based on the discoveries of Franz Fischer and Dr. Hans Tropsch and developed at the Kaiser Wilhelm Institut fuer Kohleforschung in Muelheim-Ruhr. The combined average capacity of these plants was 200,000 tonnes per annum, and they produced up to 160 grams liquefiable hydrocarbons per normal cubic meters of CO + H<sub>2</sub>. The raw material used for gas production was bituminous coal coke, coke-oven gas and lignite.

Work on the industrial development of the process was done in America as well as in Germany ever since the publication of Fischer and Tropsch's paper. The development work was particularly rapidly accelerated by the confiscation of German patents upon the close of the war, and a number of proposals were made since then to conduct operations under different conditions (temperature, pressure and flow rates), with different catalysts and with many changes in plant design.

The mastery of removal of the reaction heat of gases is particularly important in carbon monoxide hydrogenation. 600 to 700 kcal. are liberated per cubic meter of converted gas. This heat would be sufficient to raise the gas temperature to over 1500° C. The best temperature for the reaction varies with the process used and the catalyst between 170° and 320° C. The reaction temperature must be maintained within a few degrees, which means that the heat of the reaction must be led away sufficiently rapidly to prevent spontaneous overheating,



changing the course of the reaction towards the formation of methane and carbon deposition, and making operations difficult to manage. The problem of heat removal plays accordingly a deciding role in all the proposed designs of synthesis equipment.

a. Atmospheric pressure plate reactors (Lamellenofen) 1/,2/,3/

In this type of reactors the catalyst is located between vertical cooling plates, interconnected by horizontal cooling-water pipes. The heat of the reaction is led away by boiling water inside the pipes. Existing large scale installations in Germany, Japan and France were largely operated with these atmospheric pressure reactors.

b. Middle pressure synthesis reactors 1/,2/,4/

In these reactors the catalyst is located in vertical tubes; some 2000 such tubes were connected into bundles and immersed in boiling water. This reactor type was also used in many large installations and found satisfactory.

c. Middle pressure reactors of more recent design

High performance middle pressure reactors were developed after the war by the Ruhr-Chemie/Lurgi Development Company (Arbeitsgemeinschaft Ruhr-Chemie/Lurgi). They differ principally in their greater height and the use of larger diameter catalyst tubes.

Progress made with these reactors is more fully described below. A number of different size units were used in the Ruhrchemie plants for several years in full scale operations. Large plants are now under construction or ready to go on stream. Synthesis in such reactors is preferentially conducted with gas recycling.

d. Reactors with catalyst layers bounded with cooling surfaces 5/

Only a part of the synthesis gas is converted in each single layer of these reactors, and the heat there liberated is removed by the cooling system located between the catalyst layers. Gas is again recycled in this system.

e. Liquid phase sludge systems with inside cooling 1/,2/,6/

While the catalyst is arranged in fixed beds in systems a)-d), the catalyst in system e) is suspended in oil. Gas bubbles rise through the suspension. The heat is led away through pipes also located inside the reactors, and filled with water boiling under pressure.

f. Liquid phase systems with outside cooling

This method differs from the preceding one by having the cooling means located outside, instead of inside the reactors, and in having

the catalyst sludge forced by pumps through the reactors and cooler. This method was recently described in detail.<sup>5/</sup>

g. Liquid phase system with granulated catalyst (in motion)<sup>5/7/</sup>

This is a third type of liquid phase synthesis method. The granulated catalyst is suspended in oil inside the reaction space, as in the other two methods. Gas and oil are introduced at such a rate, that the catalyst granules are kept in slight motion to prevent caking, but are not carried over by the gas stream. As a result, the catalyst in this method stays inside the reactor, while oil is recycled through a cooling system located above the reactor. In this method, plugging of the cooling system by the catalyst is supposed to be avoided.

h. Synthesis with a fluidized bed <sup>9/</sup>

This system is characterized by a lively motion of the catalyst caused by the ascending gas. The heat is led away by a cooler system filled with water or other cooling media and located in the fluidized bed. The 300,000 tonnes per annum Brownsville, Texas plant uses this method.

To judge by the American daily press,<sup>10/</sup> technical difficulties have up to now interfered with the starting, so that nothing can so far be said about the success of the installation.

i. Catalyst-dust recycle system <sup>11/</sup>

The gas velocity in this system is so high, that powdered catalyst is blown upwards from below through the synthesis tubes. Heat is led away through a cooling system arranged in the gas phase.

2. Hydrogenation of Carbon Monoxide by the New Ruhrchemie/Lurgi Method

Improvements in Ruhrchemie/Lurgi reactor design with fixed-bed catalyst will be described in somewhat greater detail in the forthcoming section (fig. 1, c).

Exhaustive study of the advantages and disadvantages of the other designs listed and the large volume of experience gained in the 14 existing large scale installations showed this method to possess such great advantages as to cause the company to decide to retain the principles of operation between cooling surfaces with a granular catalyst arranged in a fixed bed and with a downward gas stream. This principle affords a doubtless advantage of great design simplicity, and is used in a large number of other industrial processes (ammonia synthesis, oxidation of SO<sub>2</sub>, of naphthaline, the methanol synthesis, etc.).

It was possible to arrive at a new understanding of the process by a careful study of reaction conditions, development of new catalysts,

experimental and theoretical investigation of heat and material transfer through granulated systems. Improvements in the process are presented graphically in figure 2. The daily production per reaction unit may be seen to have been increased from 2 to 50 tons. The space-time yield of the modern catalysts is about six times greater than with the old catalysts, their life at least as high, so that the catalyst consumption amounts to only about one-sixth of the former. The new catalysts are based on iron. With other economic conditions remaining unchanged, the cost of the iron catalysts is about the same per cubic meter as of the cobalt catalyst.

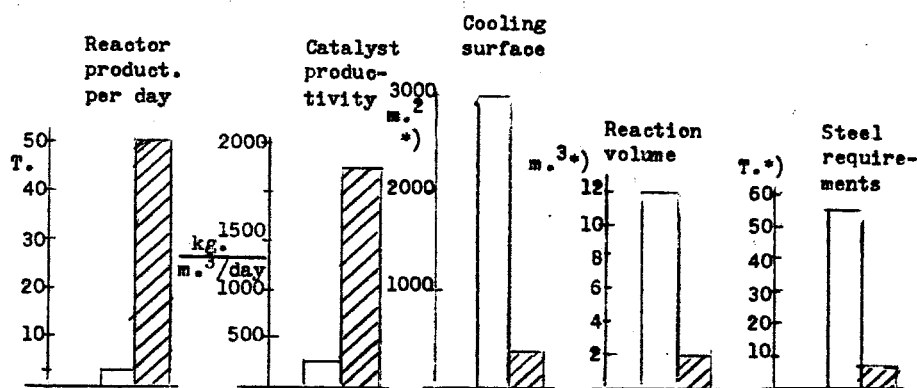


Figure 2. - Comparison data for high production synthesis.

- Earlier cobalt catalyst synthesis  
 High-production iron catalyst synthesis, Ruhrchemie/Lurgi

\*Referred to 1000 m.<sup>3</sup> converted CO + H<sub>2</sub>.

The size of the cooling system could be reduced from 3000 m.<sup>2</sup> to 235 m.<sup>2</sup> per 1000 m.<sup>3</sup>/hr. of converted gas. The reaction space required for the conversion of 1000 m.<sup>3</sup>/hr. of gas was reduced from 14 to 2.5 m.<sup>3</sup>. The great progress in design resulted in reducing the steel requirements per 1000 m.<sup>3</sup> converted gas from 65 tonnes to 9.5 tonnes.

These definite improvements have resulted in changing the order of magnitude for the yields of the fixed-bed catalyst synthesis. Several practical difficulties, such as the emptying of the reactors, could also be completely overcome. It may be desirable to emphasize that gases of a great variety of CO/H<sub>2</sub> proportion can be used in these reactors, that methane production dropped with them to a fraction of the former, in spite of the higher space-time yield, and amounted to only 6 percent with a 6-months' old catalyst, which may be considered an average for the whole catalyst life. Moreover, it also became possible largely to equalize the converted proportion in the gas constituents and their proportion in the gas supply, and 185 grams primary products (with more than 2 C atoms/molecule) are obtained from 1 m.<sup>3</sup> of CO + H<sub>2</sub> (0.262 lb./100 cu.ft.).

Technical improvements were based on exact study of heat and material transfer relations, as already mentioned. Data learned in these studies permitted the development of equations permitting the calculation of the minimum required cooling surface necessary for certain given synthesis conditions, or the reverse, the calculation of the maximum permissible catalyst tube dimensions. This maximum catalyst tube diameter depends on the heat conductivity of the catalyst layer and the temperature relationship of the reaction velocity. The equation contains the activation energy, the desired CO + H<sub>2</sub> conversion, the height of the catalyst layers, the make-up gas feed, the CO + H<sub>2</sub> concentration in the gas feed and the recycle proportion. The maximum tube diameter can be calculated from the mathematical expression of relationship between these variables. The complete reliability of the computations could be confirmed by a large number of practical synthesis tests.

### 3. Economic Considerations

A few results of economic studies will be reported below. Figure 3 shows the cost make-up in relation to the fuel cost. In this study, the production costs were set at 100 when the fuel cost was 0.

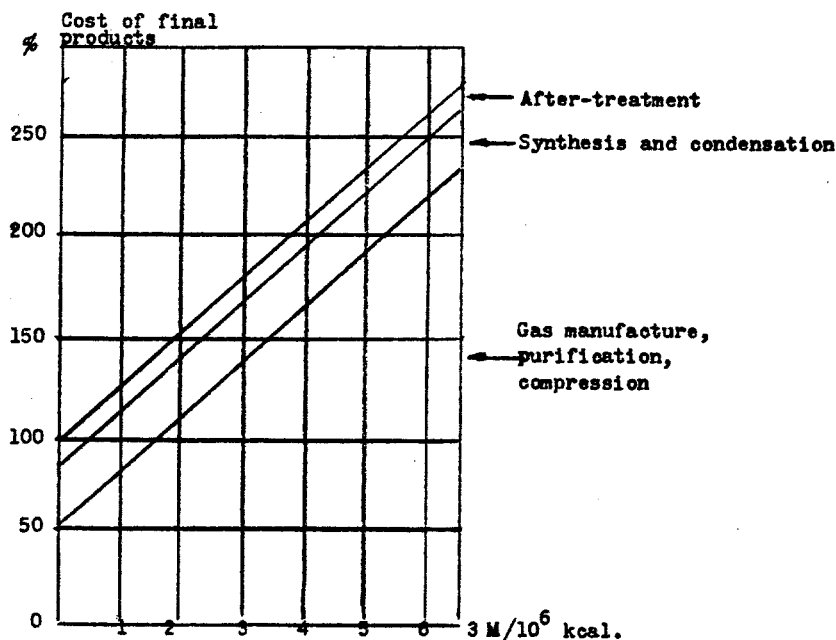


Figure 3. - Costs of modern carbon monoxide hydrogenation.

The large bottom area represents the costs of gasification, gas purification and compression. Extensive economic computations have shown that, as a first approximation in overall studies, the nature of the gasification process in use is of prime unimportance.

The figure shows that the costs of gasification, which depend on the fuel cost, are a deciding influence on the cost of the final product. The cost of synthesis and of subsequent operations are

practically independent from the fuel cost, while the gas costs rise proportionally with the fuel price. The cost components were broken down into three principal groups of operations, and with cheap coal, the gas cost forms 62% of the total, synthesis 27%, and after-treatment 11%, while with expensive coal, as for instance under German conditions, the gas costs form 80%, synthesis costs 12½% and the after-treatment 7½% of the total costs. This computation was specifically developed for conditions of the Lurgi-Ruhrchemie process, but may represent a general rule.

These results lead to the following tasks:

- a. Testing cost reduction possibilities in gasification.
- b. Establishing the possibilities of complete gas conversion with the production of salable products.

The economics of a process depend not only on production costs, but also on the price of the products, which creates the problem of:

- c. To so develop the gas synthesis process, as to make it meet market requirements, i.e. to produce principally products amongst the multitude of possible hydrocarbons from power gas to paraffin waxes melting above 100° C., which are most readily marketable and most profitable.

a. Lowering the gasification costs

Three different gasification processes are compared in figure 4 to test the possibility of lowering the gasification costs. The gasification processes compared are:

1. Blue water gas produced with air and containing 8% inerts.
2. Oxygen gasification gas (20% inerts).
3. Producer gas (60% inerts).

Computations are based on a coal price of DM 6.-/10<sup>6</sup> kcal., a synthesis pressure of 30 atmospheres, and an interest rate of 15 percent.

Such a comparison is of interest because it answers the question, whether producer gas, with its high proportion of inerts which require compression for the middle pressure synthesis, is more economical to use than the oxygen gasification gas, which requires additional oxygen production costs.

When comparing the first two gasification processes, the coal consumption with oxygen gasification must be remembered to be appreciably higher than for air gasification by containing the additional item for power in the oxygen production. The inerts in air gasification were assumed to be 60 percent, and the power consumption for the purification

and compression of the gas, with a partial recovery of power by expansion of the gas, is nevertheless so much higher than the power required for the compression and purification of oxygen, that the total coal

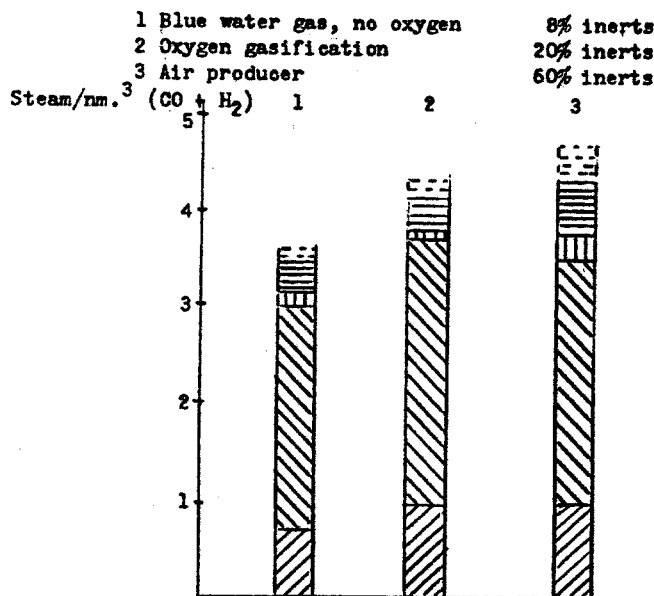







Figure 4. - Coal and capital costs for compressed purified synthesis gas.

-  Capital and repairs.
-  Gasification.
-  Purification and condensation.
-  Compression, less power recovery.
-  Power recovery in pressure release of gas.

consumption for air gasification is practically the same as in the oxygen gasification. The capital costs are 20 to 25 percent higher for air gasification in spite of the costs of the oxygen plant, because of the more unfavorable load upon the producer shafts, larger compressors and the much higher purification and condensation plants. As a result, the total costs at the synthesis reactor inlet are more favorable for oxygen gasification than with the, at first glance, apparently cheaper air gasification process. This result does not depend on the price of coal, because the coal consumption is practically the same with the two gasification processes. Similar relationships will also be found in the study of application of blast-furnace gas, so that in principle the use of gases with high inerts is not very attractive.

The problem in gasification is therefore the production of low-inert gas without the use of oxygen and from cheap fuels, i.e. from coal instead of coke, because in such case the savings in capital costs by omission of the oxygen installation is not offset by increases in compression, purification and condensation costs, and coal consumption



is reduced by saving in power for the compression of air or of inert ballast. Such a process may result in 15 to 20 percent savings over the at present realizable minimum costs.

The development of gasification processes must proceed along these lines.

#### b. Gas utilization

The most complete conversion demands that the catalyst would convert the gas in the proportion found in the gas feed. Composition of catalysts, synthesis operations and the gas composition must be so adjusted, that carbon monoxide and hydrogen are removed from the gas in the proportion found in the original feed gas. If the original proportion changes, it is an indication that one of the two components of the gas remains unutilized. Considered from the economic standpoint, carbon monoxide and hydrogen are of equal worth, disregarding for the sake of simplicity the vanishingly small conversion costs; the nonfulfilment of this requirement is always a fault of the synthesis process. One may frequently read in the literature data on high degrees of conversion, where a closer inspection may prove that only the carbon monoxide conversion was considered, or in rarer cases, the hydrogen conversion. When conversions are discussed, only the conversion of both, carbon monoxide and hydrogen, should be considered.

In order to obtain a complete conversion, i.e. 96 to 97 percent, with a low methane formation, synthesis will best be conducted as

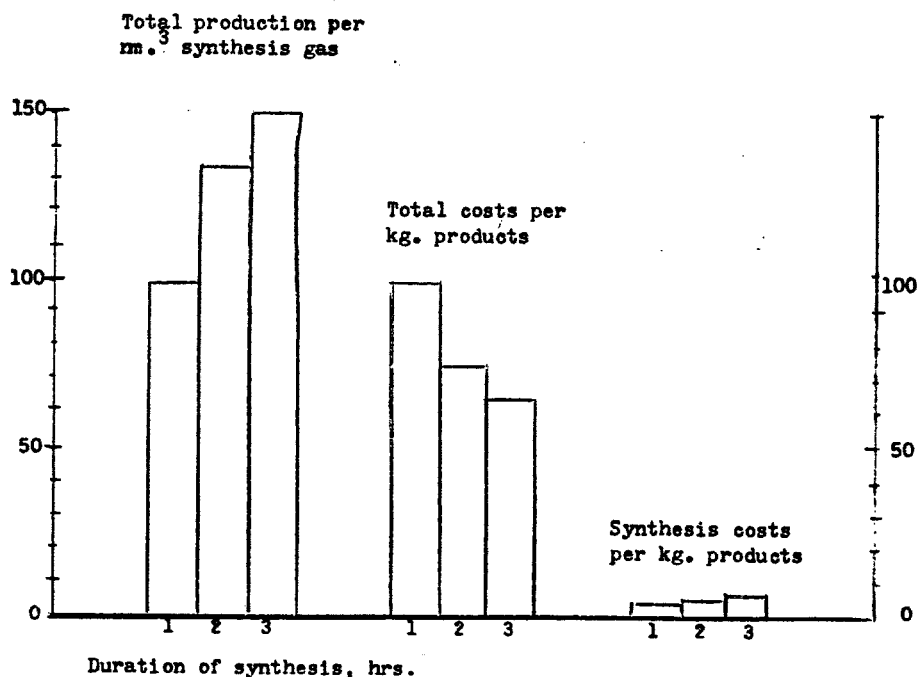


Figure 5. - Increase in production and lowering in costs in multi-stage operations.

a multi-stage iron catalyst process. This follows from figure 5, where the production of primary products per cubic meter of gas and the true synthesis costs per kilogram of products is shown for operations in a one, two and three stage process. The total production or earnings of a single stage process were set here at 100. One may readily see the rise in total production when changing over from the single stage to the two or three stage processes. The specific costs of synthesis also increase slightly, but they are rather small in comparison with the total costs of the process, which decrease strongly, because the greater production per gas unit outweighs greatly the synthesis costs.

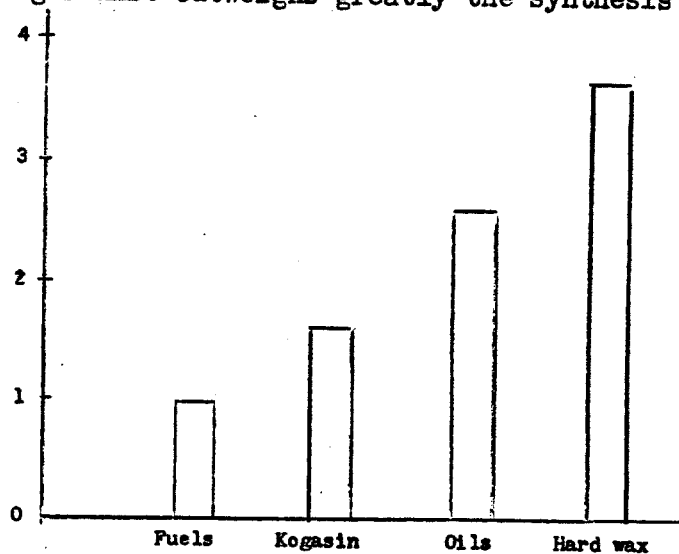


Figure 6. - Attainable plant earnings; 1951 price basis.

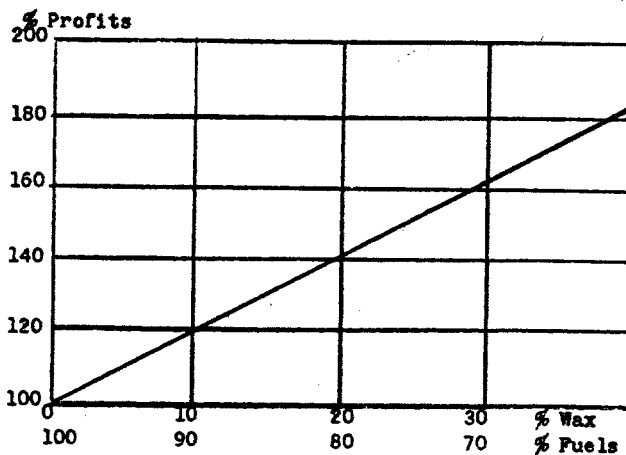


Figure 7. - Increase in earnings through production of more valuable byproducts.

c. Adaptability of synthesis

The attainable plant earnings from fuel, kogasin, oils and hard waxes are shown in figure 6. With the present German price per tonne basis with fuel taken as unity, they are 1.5 for kogasin, 2.25 for oils, and 3.5 for waxes.

Should earnings of a plant producing fuel be set at 100, the increase in earnings with increasing production of hard waxes in the primary products is shown in figure 7.

If the curves are based on production of high-grade lubricants or other chemicals instead of hard wax, similar shaped curves would be obtained. A definite composition of primary products is here important, e.g. that the primary products should not vary in proportion of naphthenes or aromatics, as may happen with other synthesis processes, and that the composition may be to some extent affected by the process.

Figure 8 shows the possible variation in the composition of the products with high-productivity processes in comparison with paraffin and oxyl synthesis. Proportions of hard wax, crude wax, kogasin, gasoline and alcohols is presented in block diagrams.

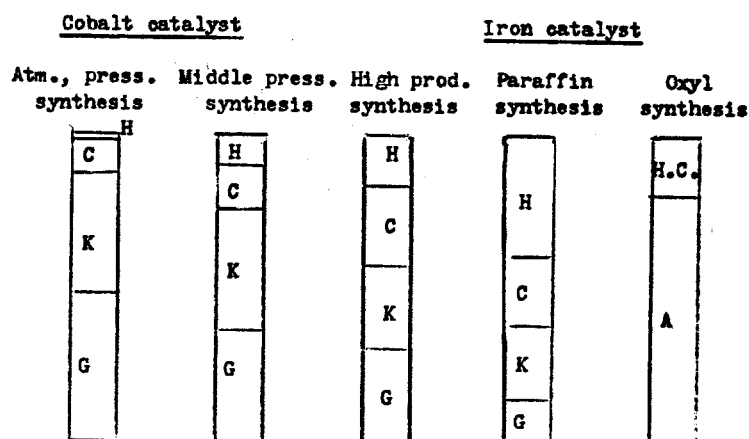


Figure 8. - Combinations of primary products.

H - hard wax; C - crude paraffin wax; K - kogasin; G - gasoline H.C.;  
A - alcohols; H.C. - hydrocarbons

4. Physico-Chemical Studies

The physical chemistry of the catalysts and the course of the synthesis reaction were investigated. The inner surface of the iron

catalysts used was measured by adsorption, and the connection of the inner surface with the composition of products found is shown in figure 9.

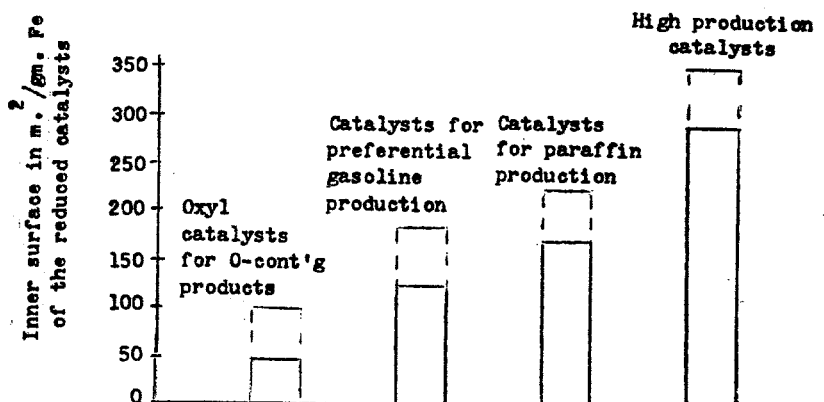
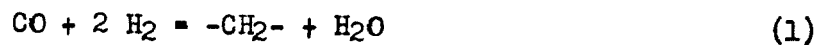


Figure 9. - Inner surfaces of different iron catalysts.

The height of the blocks in this diagram represents the inner surface, referred to 1 gram reduced iron in the catalyst. An oxyl synthesis catalyst is required to have 50-100 m.<sup>2</sup>/gm. reduced Fe, for the preferential production of gasoline 120-170 m.<sup>2</sup>/gm. Fe, and a catalyst for the preferential production of hard wax 200-250 m.<sup>2</sup>/gm. Fe, while in the high productivity catalysts it is increased to 300-350 m.<sup>2</sup>. These catalysts do not differ greatly in chemical composition and an interesting connection between physical structure and the course of the reaction could be discovered here.

Cobalt catalyst was formerly used, but during the last years iron catalyst came increasingly into the foreground. Unavoidably the question arises for the reason of the cobalt synthesis intruding between the earlier K.-W. Institut iron catalyst and the present development of iron catalyst synthesis. Cobalt synthesis has the advantage over the iron synthesis of permitting easy and smooth operations at atmospheric pressure, and chemical relationships are simpler with it, which permitted a more rapid development to an industrial stage.

It appeared necessary to understand the partial processes in the synthesis with iron catalysts and to follow them up quantitatively. No valuable information on this subject can so far be found in the literature. These processes cannot be explained by equilibrium considerations, to which one would naturally turn first, because equilibria are not reached during the course of reactions. Unavoidably, the kinetics of the reactions must be studied, and these involve large amounts of mathematical treatment. We have already previously reported on the simpler cobalt kinetic equations.<sup>12/</sup> The cobalt synthesis is known to proceed according to the equation



The rate of carbon monoxide conversion was found to be proportional to the square of the hydrogen concentration and inversely proportional to the carbon monoxide concentration

$$\dot{n}_{CO} = k \cdot \frac{P_{H_2}^2}{P_{CO}}$$

Water is almost exclusively formed in the cobalt Fischer-Tropsch synthesis in addition to the desired hydrocarbons, while varying amounts of carbon dioxide in addition to water is formed with iron catalysts. This indicates at least two parallel reactions proceeding simultaneously, that is reactions resulting in the formation of carbon dioxide must proceed parallel to the reactions of conversion with cobalt. These reactions may be based on



and a synthesis reaction producing carbon dioxide directly with the hydrocarbons, according to the equation



Franz Fischer made the assumption that the last reaction predominated in the synthesis with an iron catalyst, i.e. the synthesis proceeded by way of formation of carbon dioxide, but the opinion was also frequently discussed in literature of carbon dioxide formation entirely by the shift conversion (equation 2).

Calculations of synthesis with an iron catalyst would be simplified by making the assumption that carbon dioxide is formed entirely by shift conversion, and that the shift conversion equilibrium is always reached.

$$K = \frac{P_{CO} \cdot P_{H_2O}}{P_{CO_2} \cdot P_{H_2}} \quad (4)$$

This question of equilibrium was investigated by us in many tests, and only in case of a few tests at atmospheric pressures with special catalysts was shift equilibrium found to have been practically reached.

Table 1 reproduces the different shift conversion quotients measured at the gas outlet and compares them with the shift conversion

$$\phi = \frac{P_{CO} \cdot P_{H_2O}}{P_{CO_2} \cdot P_{H_2}}$$

equilibrium constants at the synthesis temperatures. The water gas equilibrium is not reached in any of the tests run with different catalysts and a great variety of synthesis conditions. These results led

TABLE 1. - Comparison of conversion ratios with the shift conversion equilibrium

No.	Catalyst type	Temp. °C.	Press. atm.	Conversion %	Utiliz. H <sub>2</sub> CO	Shift conversion quotients (experimental)	Shift conversion equilibrium
1	Atm. press. catalyst	217	1	74.8	0.72	0.0134	0.0072
2	Atm. press. catalyst	206	1	52.3	0.65	0.0282	0.0054
3	Oxyl M 184	211	10 ?	48.8	0.76	0.0766	0.0065
4	Oxyl M 184	211	10	51.9	0.76	0.087	0.0065
5	M 92	195	20	55.5	0.71	0.065	0.0045
6	M 92	195	10	52.2	0.74	0.085	0.0045
7	Oxyl M 184	205	10	57.4	0.66	0.0216	0.0057

to the prediction that a quantitative explanation of the mechanism of reaction of carbon monoxide hydrogenation with iron catalysts would be very difficult, and velocity expressions for at least two, and probably for the three reactions 1-3 will have to be found. The kinetic analysis of numerous measurements made with catalysts of the iron type resulted in the determination of the following three reaction velocity expressions:

The velocity of the reaction with formation of carbon dioxide depends on the composition of the gas according to the equation

$$\dot{n}_{\text{CO}_2} = k_3 \frac{P_{\text{H}_2}}{P_{\text{CO}}} \frac{1}{1 + k_4 \cdot (\text{CO}_2 + \text{H}_2\text{O})^7} \quad (5)$$

The synthesis reaction with water formation proceeds according to the equation

$$\dot{n}_{\text{H}_2\text{O}} = k_1 \frac{P_{\text{H}_2}^2}{P_{\text{CO}}} \frac{1}{1 + k_2 \cdot (\text{CO}_2 + \text{H}_2\text{O})^5} \quad (6)$$

and the shift conversion reaction

$$\dot{n}_K = k_5 \cdot P_{\text{H}_2\text{O}} \quad (7)$$

These equations reproduce qualitatively a number of known synthesis experiences. They permit to see, that the synthesis reaction is slowed down with increasing carbon monoxide concentration. Further, it is known, that the reactivity of the catalyst is reduced by carbon dioxide and water, especially after certain threshold value has been exceeded. The third factor in the rate equations has the peculiarity, that as long as the carbon dioxide and water concentrations are small in comparison with 1, the factor remains unimportant, and that only beginning with a certain range of carbon dioxide and water concentrations does this factor rapidly become greater than 1. The conversion reaction naturally proceeds the more rapidly, the greater the water partial pressure is in the gas space.

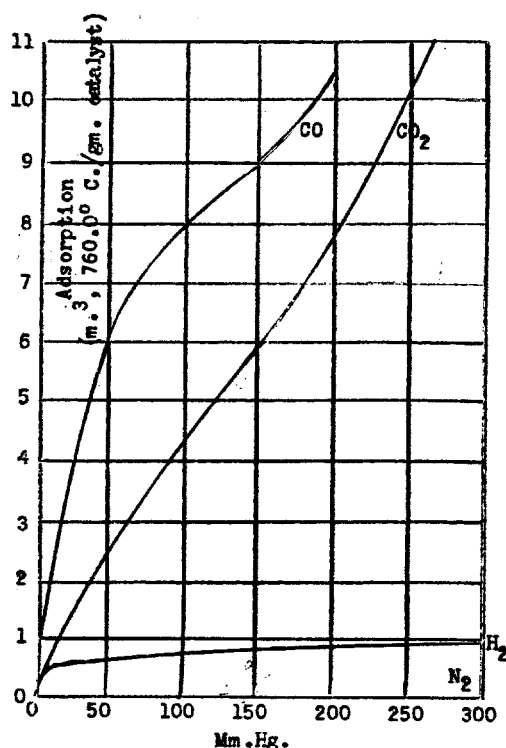


Figure 10. - Adsorption on the iron catalyst at 250 mm. pressure.

The form of the velocity equations points to the fact that the effect of the square of the hydrogen partial pressure in the first iron catalyst equation would affect a displacement of the conversion proportion at higher pressures to an increased hydrogen consumption, while the addition of an inert gas, e.g. nitrogen, will similarly affect the carbon dioxide formation in the same direction. A study of the adsorption behavior furnishes a qualitative explanation of the varying effects of the different gases participating in the conversion, and therefore also an understanding of the above velocity equations. Figure 10 shows the adsorption of N<sub>2</sub>, H<sub>2</sub>, CO, and CO<sub>2</sub> in the synthesis temperature range. Of these gases, nitrogen alone is physically adsorbed, while

the rest are chemisorbed. The activated adsorption of hydrogen is proven by the fact of its much greater adsorption than of nitrogen. Carbon monoxide is chemisorbed to a much greater extent than hydrogen, which can certainly be no simple adsorption. The great demands of carbon monoxide upon the catalyst surface forces hydrogen away from it. The inverse proportionality of the reaction velocity and carbon monoxide concentration is based upon this fact. The velocity-determining step consists in having hydrogen approach carbon monoxide, and, according to equation 1, two hydrogen molecules are required by one molecule of carbon monoxide. This explains the square of the hydrogen pressure in equation 6. In the synthesis reaction 3 with carbon dioxide formation, only one molecule of hydrogen is converted by one molecule of carbon monoxide, which explains why hydrogen pressure in the velocity equation 5 is present in the first power, unlike in equation 6. The water adsorption is as yet unmeasured. Carbon dioxide exhibits as exceptional adsorption behavior as carbon monoxide. The high exponents (5 or 7) in the velocity equations which are expressions of the effect of  $\text{CO}_2 + \text{H}_2\text{O}$  concentration show, in agreement with the special behavior of carbon dioxide in adsorption, the activity-reducing effect of carbon dioxide upon the reaction velocity to be no simple kinetic effect, but the result of a reversible oxidation of the catalyst surface by increasing amounts of higher-oxygen gases.

The relationship between the carbon monoxide conversion and the  $\text{CO}_2 + \text{H}_2\text{O}$  concentration to be found in equations 5 and 6 was found by constructing a 5-meter long synthesis column which had a number of

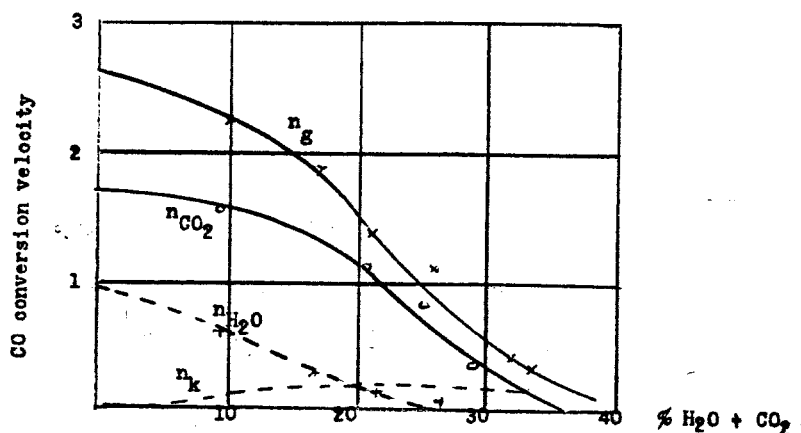


Figure 11. - Rate of carbon monoxide conversion with iron catalysts.

- $n_g$  - Total CO conversion rate  
 $n_{\text{H}_2\text{O}}$  - CO conversion in synthesis with  $\text{H}_2\text{O}$  formation  
 $n_{\text{CO}_2}$  - Do.  $\text{CO}_2$  do.  
 $n_k$  - Do. the water gas reaction



sampling connections distributed over its length. Analytical results were plotted and differentiated. The conversion velocity found in that way was plotted as the upper curve in figure 11 as a function of  $\text{CO}_2 + \text{H}_2\text{O}$  concentration. The lower velocity curve is plotted in agreement with the equation of direct formation of carbon dioxide which is reduced by splitting, and with consideration of shift conversion velocities found from other series of tests which were separated on the bases of material balance of the upper total curve into the carbon dioxide and water formation curves.

The bottom broken curve represents the conversion velocity made from tests with the addition of water. It may thus be seen that the conversion reactions in these synthesis tests are largely of a magnitude of a correction factor.

The mathematical treatment of the curves in figure 11 brings us to the previously presented forms of the kinetic equilibrium for the three reactions proceeding side by side.

The help to be obtained from the equations found may be illustrated by some examples. Figure 12 contains the results of measurements

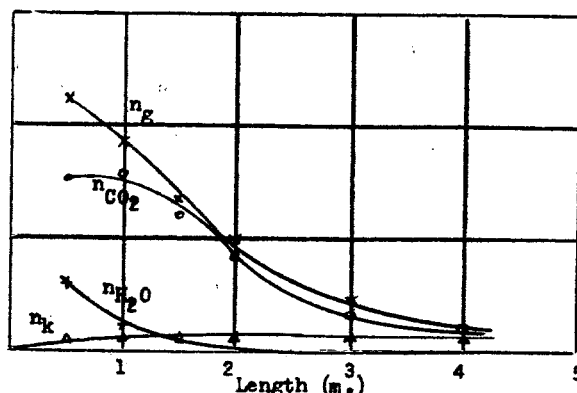


Figure 12. - Carbon monoxide conversion velocity at different parts of the sampling reactor.

- $n_g$  - Total CO conversion velocity
- $n_{\text{H}_2\text{O}}$  - CO conversion velocity and synthesis with  $\text{H}_2\text{O}$  formation
- $n_{\text{CO}_2}$  - Total CO conversion velocity in synthesis with  $\text{CO}_2$  formation
- $n_k$  - CO shift reaction velocity during conversion

obtained in a reactor with sampling devices, under conditions which were not used in computing the velocity equations. The curves were calculated from the velocity equations. The agreement between measurements and computation may be seen to be excellent.

Figure 13 shows a second example. The  $\text{CO}_2 + \text{H}_2\text{O}$  content is again plotted on the abscissa and the consumption proportion on the ordinate, and these proportions are not the total consumption proportions from reactor inlet to outlet but the differential consumption proportions at the different parts of a reactor. This method of presentation is probably of particular interest in that curve 1 was

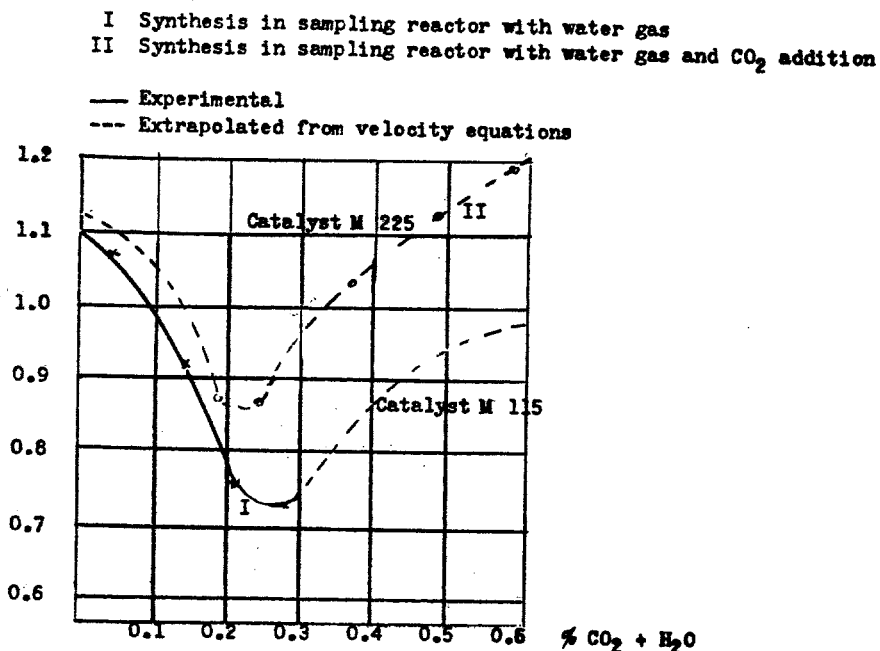


Figure 13. - Differential conversion proportion in relation to the  $\text{CO}_2 + \text{H}_2\text{O}$  contents.

drawn on the basis of measurement with a  $\text{CO}_2 + \text{H}_2\text{O}$  content of below 20 percent. Computations show that with the  $\text{CO}_2 + \text{H}_2\text{O}$  content of over 25 percent, the curve must again rise. In order to experimentally confirm this rise, we evaluated tests with another catalyst, with which carbon dioxide was added to the feed gas, and in which, therefore, operations were conducted with a higher carbon dioxide content. The upper curve was calculated from a single analysis from this group.

The experimental results may be seen to be in a satisfactory agreement with the theoretically computed curve. The curve is somewhat displaced with respect to curve 1, which must be attributed to the fact that the constants with the catalyst M 225 are somewhat different than those with the catalyst M 115.

The technician is less interested in the conversion velocities in single converter sections, than in the total balance of the synthesis. The usefulness for this purpose of the kinetic computations may be seen from tables 2 and 3.

In the first of these tables the different carbon dioxide additions to the intake gas are compared with measured end gas analyses calculated theoretically, while in the second table the corresponding values are given from two experimental series with the addition of water. These were based on the velocity constants for the catalysts and the given reaction temperature, which could be found from a single test when the nature of the equation was known. It may be seen that the calculated and experimental results are in general in as good agreement as can be expected from data obtained from gas analyses.

The problem is, therefore, solved at least for definite iron catalysts, and the course of the reaction, activity and properties of the catalyst are so definitely characterized as to permit predetermining results for a great variety of reaction conditions.

TABLE 2. - Comparison of experimental and computed gas compositions at the gas outlet obtained with varying CO<sub>2</sub> additions

	CO	40.8%
	H <sub>2</sub>	49.6%
Intake gas (average):	CO <sub>2</sub>	5.1%
	CH <sub>4</sub>	0.3%
	N <sub>2</sub>	4.2%

CO <sub>2</sub> additions vol., %	Outlet gas (referred to H <sub>2</sub> O-containing gas)				
	% CO	% H <sub>2</sub>	% CO <sub>2</sub>	% N <sub>2</sub>	
0	20	41	26	6	Experimental
	23	38	25	6	Calculated
5	19	36	31	6	Experimental
	21	33	33	6	Calculated
17	23	31	35	5	Experimental
	22	32	38	5	Calculated
28	22	29	42	3	Experimental
	23	29	43	3	Calculated

Naturally, the four equations given are applicable only to certain catalyst types and reaction conditions; they are specific expressions of the behavior of catalysts used in deriving the kinetic equations. Thus, for certain synthesis conditions, the reverse shift conversion  $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2$  may become important. Moreover, strongly aged catalysts deviate in a peculiar way, and additions of large amounts of

nitrogen or methane may occasionally exert effects which might necessitate making certain changes in the equations given. Nevertheless, the equations given are already useful for the computation of the synthesis process, and permit thus, for the first time, a quantitative insight into these, far from simple, reaction mechanisms.

TABLE 3. - Comparison of experimental and calculated gas computations at the gas outlet with varying additions of H<sub>2</sub>O

Intake gas (average):	CO	48.8%
	H <sub>2</sub>	49.6%
	CO <sub>2</sub>	5.1%
	CH <sub>4</sub>	0.3%
	N <sub>2</sub>	4.2%

a.

H <sub>2</sub> O addition vol., %	Outlet gas (referred to H <sub>2</sub> O-containing gas)					
	% CO	% H <sub>2</sub>	% N <sub>2</sub>	% CO <sub>2</sub>	% H <sub>2</sub> O	
0	17	42	6	29	8	Experimental Calculated
	19	38	6	27	11	
20	16	40	6	19	23	Experimental Calculated
	13	37	6	19	27	

b.

H <sub>2</sub> O addition vol., %	Outlet gas (referred to H <sub>2</sub> O-containing gas)					
	% CO	% H <sub>2</sub>	% N <sub>2</sub>	% CO <sub>2</sub>	% H <sub>2</sub> O	
0	33	48	4	13	8	Experimental
21	25	43	4	11	18	Do. Calculated
	25	38	4	11	24	
34	17	34	4	10	37	Experimental Calculated
	19	34	4	11	34	

## 5. Conclusions

The above exposition surveys the economic, industrial and scientific development of carbon monoxide hydrogenation by the Arbeitsgemeinschaft Ruhrchemie/Lurgi. This poses again the question of the economics of the process.

We are in a position to produce a number of substances by hydrogenation of carbon monoxide, which can be put to numerous uses. Power gas, motor gasoline, aviation gasoline, Diesel oil, lubricating oils, plate wax, hard wax, are more or less direct products of the synthesis. Alcohols, acetals, ethers, unsaturated ethers, ketones, acids, and esters are other valuable products which are used in the manufacture of softeners, solvents, detergents, wetting agents. It is impossible to give a universal answer to whether carbon monoxide hydrogenation can become profitable under all conditions. One will always have to study the production cost of synthesis, and the coal price, or more generally the fuel price, which will have a deciding effect. Furthermore, the market conditions will have to be taken into consideration, and what products can be manufactured with a prospect of satisfactory profits and continuity of consumption.

Corresponding studies at the Arbeitsgemeinschaft Ruhrchemie/Lurgi and in different countries in the world have shown that the great flexibility of synthesis results in meeting the market demands in almost all cases with more than satisfactory economy. For this reason, an increasing interest in the process is more and more observable in almost all the industrialized countries of the world, substantiating the expectation that this important German development will be able not merely to maintain its place amongst industrial processes, but will increase in importance.

I will not fail mentioning in this place thanks to my collaborators who have been particularly active in obtaining the different results. The experimental work was under the leadership of Dr. Roettig, the physical-chemical investigations were handled by Dr. Broetz and Dr. Spengler. The scientific industrial computations were under the leadership of Mr. Schnur. Dr. Roelen has supplied much important motivation. I must mention in particular the activity of Dr. Hagemann, who conducted the development work of the Ruhrchemie up to his fatal accident on April 27, 1951.

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