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Report on the Synol Synthesis

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Translated by Dr. W. Oppenheimer

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CONTENTS

| | <u>Page</u> |
|---|-------------|
| Hydrocarbon synthesis with cobalt catalysts | 1 |
| Cobalt catalyst experiments under pressure with water gas | 2 |
| Synthesis by iron catalysts | 2 |
| Development of the catalyst | 3 |
| Fused iron catalyst | 3 |
| Iron precipitation catalysts with promoters | 4 |
| Two component fused Fe catalysts | 5 |
| Concerning the methods of testing the activity of catalysts with special consideration of the alcohol generation | 7 |
| Experiments on the influence of various operational conditions and converter dimensions on the synthesis | 8 |
| The influence of the temperature on the course of the synthesis | 9 |
| Oxidation of paraffins by air | 16 |
| Experiment for the study of varnish formation | 17 |
| Conclusion | 18 |

REPORT ON THE STIROL SYNTHESIS

This paper deals with the development of the hydrocarbon synthesis from CO-H₂ mixtures. The experiments have been carried through at Leuna. We will describe the state of the experimental work at the end of 1940.

Concerning the purpose of this work, we may say briefly this:

The research done in Leuna on the gasoline synthesis by cobalt catalyst made it clear that a real improvement of this process was not possible. So we tried to run the synthesis by another method. First of all we turned to the Fe catalysts. It has been discovered that the Leuna ammonia catalyst can be used advantageously for the conversion. The research work done with this catalyst occupies the major portion of this report.

For quite some time this work group tried to investigate the conditions of the alcohol formation during the conversion and to turn the synthesis in that direction.

Only one short experiment with the use of a cobalt catalyst and water gas under pressure which resulted in products with high olefin content is reported.

Hydrocarbon Synthesis with Cobalt CatalystsExperiments for the Development of Catalysts

After we had failed to produce catalyst 2150c we stopped the development of catalysts altogether. The necessity for the complete absence of sulfur (also oxygen-containing S-compounds, especially sulfates) was confirmed.

Cobalt Catalyst Experiments Under Pressure with
Water Gas (Dr. Wintzer)

Normally in Leuna, cobalt catalysts have been used for the conversion of methanol fresh gas. We wanted to know how a change to C-water gas under the usual conditions would work out; that is, reaction pressure 10 atms., load 1:100, temperature 190° for 50% contraction, pipe converter with 49 pipes, 15 mm. diameter, catalyst: original Ruhrchemie catalyst. Two items are worthy of mention

1. The primary product contains noteworthy amounts of alcohol, for example:

the fractions 200-300°C. 27.2% by weight

300-350°C. 22.3% by weight

2. With C-water gas at a pressure of 10 atms. the yield can be increased by about 15%, compared with the conversion of methanol gas, without pressure and the same catalyst.

More details will be found in the file of December 7, 1940.

Synthesis by Iron Catalysts

With decreasing interest in the Fischer synthesis in relation to the production of high-grade gasoline, the importance of the Fischer process for the generation of intermediate products, mainly of olefinic nature, especially for the textile industry, is growing fast. (OXO process.) The conversion experiments in Leuna with Fe catalyst also yielded products which under the proper conditions contain considerable amounts of alcohols. For example, primary products have been generated, "the OXO fraction", (230-350°C.)

which contained mostly primary alcohols. Up to 30% the importance of this finding is evident. If we are successful and can increase the alcohol yield by the choice of the catalyst and the operating conditions, we could immediately obtain alcohols and avoid the round about OXO process.

The generation of alcohols, especially of the chain length C_2-C_{20} was our first goal. The corresponding work with Fe catalysts was carried out according to the following scheme:

1. Development of the catalyst.
2. Conversion method.
3. Analytical control.
4. Studies on the chemical nature of the reaction products.
5. Adaption of the conversion to operation on a large scale.

Development of the Catalyst

Fused Iron Catalyst

The first usable catalyst for the generation of alcohol was the normal Leuna ammonia catalyst (WK 17) which is made by fusion of the catalyst material. These catalysts worked satisfactory in respect to yield and quality and produced approximately 130 gr. primary products per Nm^3 of O-water gas and approximately 12-18% by weight alcohols of chain length C_2-C_{20} , which were distributed with 70% in the gasoline fractions up to $200^\circ C.$, with approximately 20 to 30% in the fractions $200-350^\circ$ and 0-10% in the fractions boiling over 350° . The "OXO fraction" ($230^\circ-350^\circ C.$) contained usually 20-30% by weight of alcohols. We believe that the generation of alcohol is greatly dependent on the catalyst, and with fused Fe

catalysts probably on the homogeneity of the fusion during the production. For the fusion of the iron (iron carbonyl) in an oxygen stream a different load of oxygen can be used. With extremely high loads we get catalysts (WK 17) which are very poor in oxygen. If fused catalysts are remelted in the electric arc, we get catalysts (WK 17, remelted) which are especially active with respect to alcohol formation. The GHO fraction of the primary products contains 25-35% by weight of alcohols as against 20-30% with a non-remelted catalyst. In this connection catalysts are produced at present by melting down iron carbonyl in the presence of varying amounts of Fe_2O_3 (pulverized not reduced catalyst WK 17) in an oxygen stream. We may expect that the melting temperature can be regulated more easily, and that we will get, therefore, a better insight into the relation between the melting temperature or the homogeneity and the activity. Also the porosity of the catalyst may be increased.

Iron Precipitation Catalysts with Promoters

The production in all cases was carried out by Dr. Hula under exactly the same conditions. The iron was precipitated from iron nitrate solutions of constant concentration by potash solution, also of constant concentration within a constant pH range and under the same temperature and stirring conditions. Part of the iron has been substituted in amounts of 1.5 and 10.0% by 1 or 2 different elements which were either coprecipitated with the iron or were added later by impregnation, or as solid component in a ground state (alkalized catalyst). The emptying and the drying was done also

under the very same conditions. Mechanically all these catalysts are inferior to the fusion catalysts, but some are sufficiently mechanically resistant.

On account of the great number of tested catalysts we will report summarily only about their activity. The criterion for an active catalyst, as we understand it, is first/^{its} specific total yield per Nm³ of O-water gas, and secondly the alcohol content of the most valuable portions, that means, the fractions above 200°C. Besides that, naturally, the mechanical strength and the tendency to carbon formation had to be considered.

As promoter elements the following have been tested so far:

MgO, Mn₂O₃, Ag₂O, NiO₃, ZnO, Al₂O₃, K₂O.

Two Component-Fused Fe Catalysts

The best active catalyst was the combination 96.5% Fe₂O₃ + 3.5 Al₂O₃, which with a specific total yield of 84.3 gr/Nm³, gave 42.5% alcohol by weight in the OXO fraction 230-350°C., which itself is 21% of the primary product. The second best catalyst is the combination 99% Fe₂O₃ + 1% Mn₂O₃. Average specific total yield about 90 gr/Nm³, 30% alcohol in the OXO fraction, which itself is 15.4% of the primary product. The combination 99% Fe₂O₃ + 1% ZnO is also worth mentioning.

From most of the tested two-component catalysts, those with 1-3% of the promoter element were the most active catalysts. The components with 5 or 10% promoter elements mostly proved to be less active and distinctly the less so the larger the concentration of the additional element.

An idea obtained years ago has been definitely confirmed, that is, the lower the synthesis temperature, the higher is the alcohol content in the primary product, provided the catalyst is on the whole suited for the alcohol synthesis.

The total content of alcohols in the primary product decreases during the conversion period with most of the catalysts faster than the specific total yield. The OXO fraction contains, in most cases, after 10 days, less than half the alcohol quantity than at the start of the experiment. (This is mostly caused by a considerable increase of the synthesis temperature.) There are exceptions to this rule, for example, with catalyst #2643 we get only a slow decrease in the alcohol content. Also noteworthy is the catalyst 99% Fe_2O_3 + 1% Ni_2O_3 (#2918). We observe with it an increasing alcohol content for the first 20 days.

Two component Fe precipitated catalysts have been found which can produce considerable amounts of alcohols, but which occur mostly in the gasoline fraction and in the reaction water. To this type belong the combinations #2919 (95% Fe_2O_3 + 5% Ni_2O_3) and #2660 (95% Fe_2O_3 + 5% ZnO).

The best precipitated catalysts are in the beginning very hard to operate at a constant CO_2 level of 30% in the outlet gas. Correspondingly the temperatures under these conditions are not easily controlled. These catalysts are too active and have the tendency to "run away" and to sput. We are trying to dilute these types of catalysts by carrier substances.

Concerning the Methods of Testing the Activity of
Catalysts with Special Consideration of the Alcohol Generation

All catalysts are being tested under the same conditions. The testing is done in small converters in Me 21,5 with 200 cm³ catalyst of the average granulation of 1-2 mm. The grain size of the mechanically less solid catalysts is taken somewhat larger because they disintegrate easily, from 1-3 mm. The other testing conditions are: 19 atm. pressure, load 1:300 with O-water gas (measured without pressure). The temperature is slowly increased from 160°C. on until the converter gas contains 30% CO₂.

The converter products are:

1. The primary product in the separator.
2. The reaction water.
3. Active carbon adsorbate = gasol + non-volatile portions at room temperature.
4. Exit gases not condensable in the carbon dioxide snow bath.

The primary product was combined with the portion of the active carbon adsorbate which is not volatile at room temperature. After removal of the organic acids an analysis by fractional distillation was run with the following fractions: to 200°C., to 230° to 350° and >350°. The fractions up to 200°C. under normal pressure above 200° at 8 mm. Hg. The alcohol content in the separate fractions was determined after drying by esterification with mixtures of acetic anhydride and pyridin. According to older methods, the substances soluble in the reaction water have been determined by double extraction

with ether. However, it was soon discovered that this procedure is unsuitable since catalysts exist which generate 50% by weight soluble portions in the reaction water. By a two hour extraction in a Soxhlet these portions can be determined quantitatively, as they belong to the primary product and have to be deducted from the reaction water.

Besides the alcohol content of the most important fraction, that is the OXO fraction, which varies considerably according to the catalyst and to the kind of operation, the catalysts were compared of course with regard to their specific yield of liquid portions. For the calculation of the specific oil yield the total oil, gasol^e portions and those dissolved in the reaction water, from the moment when 30% CO₂ in the exit gas was reached, have been considered inclusive of the hard paraffin which has to be extracted at the end of the test from the catalyst by hot xylene. The subsequent evaluation of the removed catalyst is sometimes injured by the latter procedure. The mass balance calculations of the conversion yields including other obtainable substances as in the final gases is not sufficiently exact in laboratory-scale experiments chiefly because gas analyses are carried out too rarely (9 converters). These catalyst activity tests are therefore preponderantly qualitative.

Experiments on the Influence of Various Operational Conditions
and Converter Dimensions on the Synthesis

Various items are of interest, that is, the influence of the catalyst aging on the course of the synthesis at constant temperature, the influences of the pipe width, the catalyst load, the kind

of circulation of the synthesis gas (rotation) different height of the catalyst layers with equal load. The influence of the gas composition on the synthesis with special consideration of carbon monoxide-rich synthesis gases, the influence of the reaction conditions of the catalyst and finally the influence of the synthesis temperature. The corresponding experiments are partly being worked at, for another part the results are already at hand. The proposed problems have been studied partly in Me 245 in the small scale converters of Dr. Reisinger, partly in Me 776 in semi-technical converters of Dr. Wintzer. The experiments in Me 776 could be evaluated much better as far as a material-balance calculation was concerned. Besides the generation of alcohol, these experiments dealt also with the yields and the losses by the formation of alcohol. Dr. Wintzer has reported separately on these experiments.

The Influence of the Temperature on the Course of the Synthesis

Experimental material for this problem is at hand in Experiment II/22 (Dr. Reisinger). Experiment II/22 was carried out in a small-scale converter II in Me 245 (15 mm. inner diameter) under the usual conditions (200 M³ catalyst WK 17, granulation 1-4 mm. height of layer approximately 1.40 m. at 420°C. with space velocity H₂, load 1:100, 21 day reduction time, synthesis gas load: O-water gas 1:300 at 19 atms.). The synthesis temperature was always kept constant within a period of 8 days, so that a constant CO₂ content in the outlet gas was assured. After the expiration of such a period the temperature was increased so that the CO₂ level was about 5% higher than before. In this manner the CO₂ levels of 10, 15, 20, 25, 30, 35, 40, and 45%

and the corresponding medium synthesis temperatures were tested according to the following diagram:

| | | | | | | | | |
|---|---------|---------|---------|---------|---------|---------|---------|------------|
| CO ₂ content in the outlet gas | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45% |
| Synthesis temperature | 200-215 | 216-220 | 224-228 | 234-236 | 238-239 | 241-242 | 249-255 | 262-282°C. |
| Medium synthesis temperature | 210 | 219 | 227 | 235 | 239 | 241 | 253 | 270 |

Results

a. Influence on the Product Distribution (Figure 1).

With rising temperatures and rising CO₂ content in the outlet gas the composition of the primary products shifts in favor of the lower boiling portions. The gasoline and gasol fraction increase according to Figure 1. The portion of the OKO fraction (230-350°C.) does not visibly change. It remains practically constant.

b. Influence on the Alcohol Content in the Primary Product

(Figure 2)

The influence of the synthesis temperature on the total content of the primary products, the alcohol content of the organic components soluble in the reaction water included, is understood only to the extent that with temperatures above 230° this content decreases. It is probable that the increase in the alcohol content (shown in the figure) with rising temperatures of 200-230°, corresponds to a CO₂ level in the final gas of 10, 15, 20, and 25% to a flat maximum is a starting anomaly because it has been frequently observed that the alcohol content during the first days after starting was somewhat lower even with the full usual synthesis

Influence of the Synthesis Temperature on Product Distribution
(Possibly Overlapped by the Influence of Catalyst Aging)

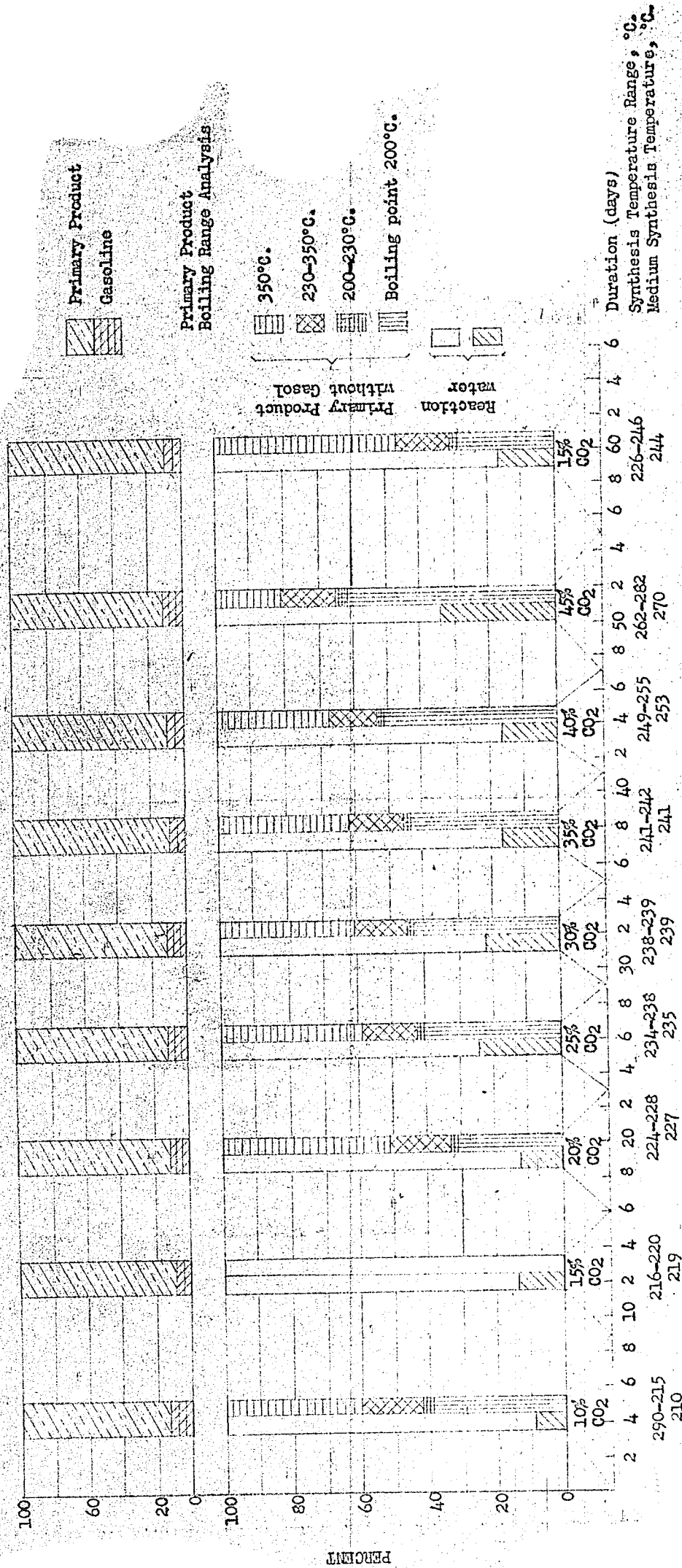


Figure 1.

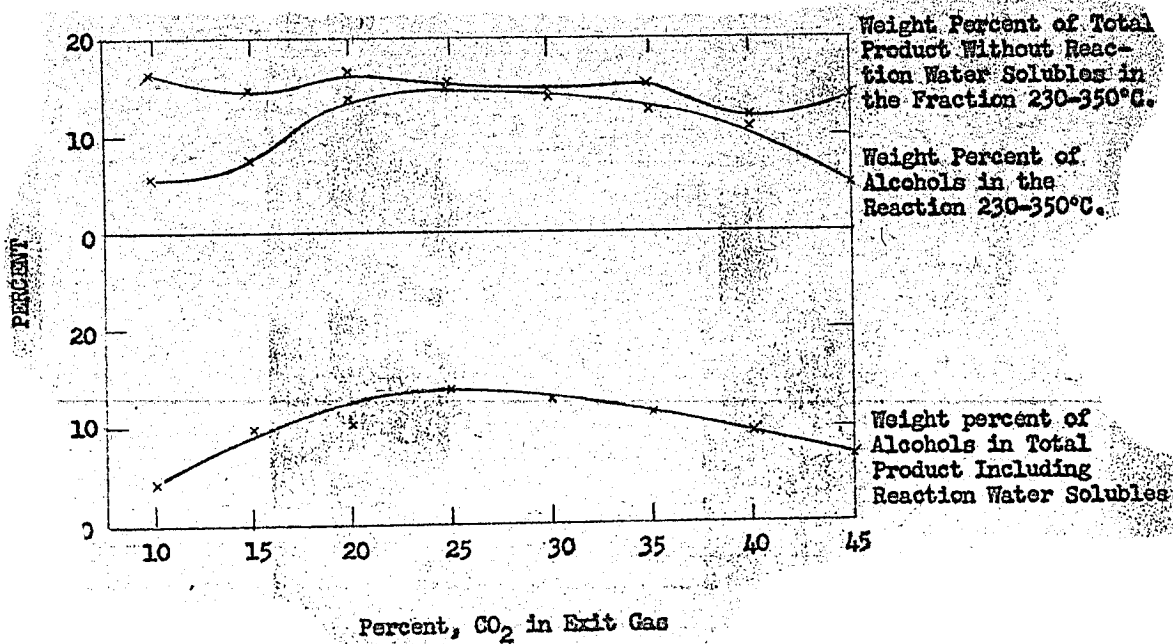


Figure 2

temperature right in the beginning corresponding to 30% CO₂.

c. Influence on the Specific Yield and the Conversion Yield

Calculated by the Obtained Product, Gasol Included

Table No. 1 illustrates the dependence of those two quantities on the temperature or the CO₂ level in the outlet gas in such a way that the specific yield with increasing temperature draws very quickly to a maximum at approximately 250°C. (40% CO₂ in the outlet gas) and decreases afterwards. The conversion yields decrease with rising temperatures. The values at lower temperatures cannot be indicated on account of the great sources of error during the separation of the small product quantities per l³ and the saturation of the catalyst with the reaction product. The conversion yields decrease with rising synthesis temperature, that means, the carbon losses by the formation of CH₄ become appreciable at temperatures of 240°.

SUMMARY

The experiment III/22 clearly showed that a maximum alcohol yield (C-number < 8) can only be obtained at low temperatures (200-240°C.) and with low gas conversions (conversions 40%). This seems to be of general validity and not connected with a specific catalyst. Relative to this experiment, lasting over a period of 65 days, we have also to consider that a certain aging effect could blot out the results somewhat as is in the case, for example, in the beginning of the curves in Figure 2. Nothing can be said yet about the extent of this effect.

Table I

| Medium Synthesis Temperature | Synthesis Temperature Range | Percent CO ₂ in Converter Exit Gas | Specific Yield g/Nm ³ | Conversion [*] Yield g/Nm ³ |
|------------------------------------|-----------------------------------|---|--|---|
| 210 (approx.) | 200-215 | 10 | 48.7 | - |
| 219 | 216-220 | 15 | 61.6 | - |
| 227 | 224-228 | 20 | 81.4 | - |
| 235 | 234-236 | 25 | 97.6 | 147.1 |
| 239 | 238-239 | 30 | 106.7 | 151.9 |
| 243 | 241-242 | 35 | 111.3 | 145.6 |
| 253 | 249-255 | 40 | 117.9 | 139.0 |
| 270 | 262-282 | 45 | 114.0 | 127.6 |
| 244 | 226-246 | 15 | 70.3 | 117.0 |

* Conversion yields are generally lower than in the larger converters No 776 on account of the greater leakiness and the possibilities of errors.

The Chemical Nature of the Fe Catalyst Primary Products.

First Analytical Determination of a "Synol" Product

The working up or the determination of the primary products was run formerly within the frame of experiments for the gasoline synthesis by a rough fractional distillation only:

- 40-200°C. (benzine fraction) distillation under atm. pressure
- 200-230°C. (intermediate fraction) distillation under atm. pressure
- 230-350°C. (so-called OXO fraction) distillation under 8 mm. Hg
- 350°C. (residue) distillation under 8 mm. Hg

The analytical determination of the single fraction was confined to a determination of the olefin number which was derived from the portion absorbable in phosphoric sulphuric acid, or by the determination of the iodine or bromine number and by their densities.

A number of new analytical methods were introduced for the thorough determination of these products and adapted to the properties of our products. They are the determinations of the acid, ester, saponification, and carbonyl number. The determinations were systematically tried on test mixtures of known composition similar to our primary product fractions, and were first applied to a primary product of converter 12 (test No. 3 by Winterer) which was operated up to the date of this report under the optional standard conditions for the alcohol production: 25 atm., O-water gas 1:400 and approximately 215°C. (pipe converter with 300 pipes, 14 mm. diameter catalyst granular: 1-2 mm., reduced 40 d. at 420°C., B = 1:1000). This primary product was fractionated in a glass rectifying column

(approximately 75 cm. height, 30 mm. dia., filled with 5 mm. Raschig rings) into 20, 20° fractions. The distillation residues above 400° have not been determined. The result is shown in Figure 3.

Such a Fe catalyst primary product is composed, in the order of their concentration, of the following classes of substances: olefins, alcohols, paraffins, ketones or aldehydes, esters and acids. But this order can shift according to the fraction range, that is, the ester concentration of the fraction above 340°C. is higher than the concentration of alcohols, acids, ketones, or aldehydes. However, the olefin content in all fractions is at the top.

1. Alcohols: The alcohol concentrations increase with rising temperature continuously and reach maximum in the fractions 100-180°C. (C_4-C_7) with a concentration of 30% alcohol. Then they decrease fast to 11% and reach again a maximum in the fraction 300-320° (approximately C_{15}). At still higher temperatures practically no alcohols are present.

2. Olefins: Very rich in olefin (that is, above 80%) are the low fractions at 60°. Their concentration decreases fast with rising temperatures to about 33% in the fraction 100-120° and increases thereafter to about the constant value of about 50% in all fractions of 200-400°.

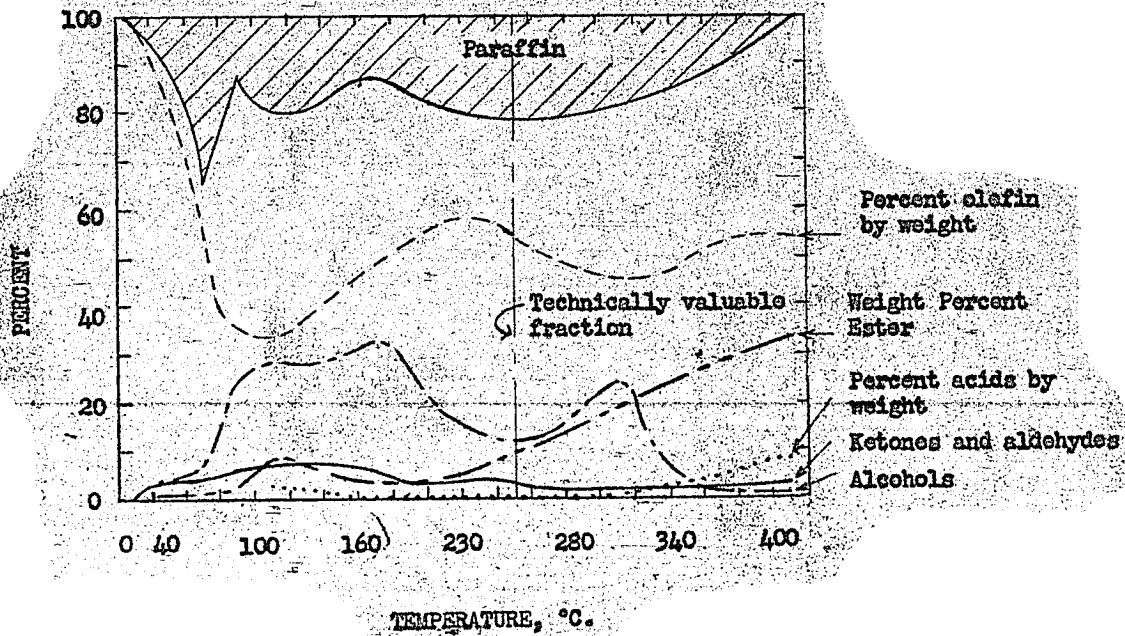


Figure 3

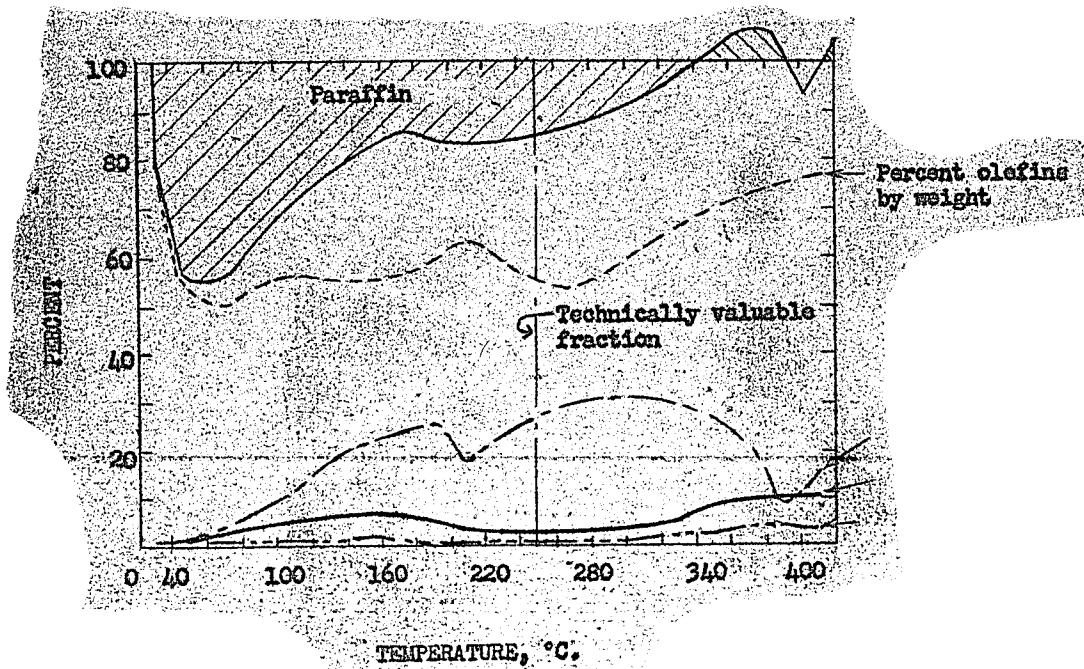


Figure 4

3. Ketones and

Aldehydes: The highest concentrations are in the fraction range 120-140° with 7-8% and fall steadily to 2-3% in the region of 400°.

4. Ester: Their concentrations are above 6% in all fractions up to 240° and rise thereafter to a maximum of 34% by weight at 400°C.

5. Acids: Their concentrations have a flat maximum of 2-3% in the fractions 100-140° (formic, acetic, and propionic acid) and increase only in ranges above 320° to a maximum of 5% at about 400°C.

6. Paraffins: Noteworthy is the fact that the sum of the olefin, ester, ketone, aldehyde, and alcohol content in all fraction ranges remains practically constant. It follows, therefore, a rather constant paraffin content of about 15% in all fractions, if we assume that the oxygen containing products are practically saturated.

The great decrease of the alcohol concentration in the boiling ranges above 320°C., and the great increase of the ester concentration (see Figure 2) suggests a secondary loss of alcohol by esterification during the distillation. The same product was therefore distilled again, but only after deacidification by methyl alcoholic potassium hydroxide (Figure 4). We will not enter into the experimental details, but we will emphasize that this pretreatment caused

certain unavoidable losses, essentially of low boiling ($<90^{\circ}\text{C}$.), mainly methanol soluble components, as olefins and light alcohols. (In Figure 4 the lower parts of the alcohol and olefin curves, and the larger paraffin surface.) The corresponding fractions in both fractions, therefore, do not agree sufficiently. However, a comparison of the alcohol, ester, and acid contents of the corresponding fractions make it evident that in fact after a deacidification no or almost no secondary loss of alcohol by esterification occurs. In this case the acid number and also the ester numbers remain low, whereas even the high fractions contain considerable amounts of alcohol, especially those ranges which contain the most valuable alcohols. (See Figures 2 and 3.)

Oxidation of Paraffins by Air

In search of a practical application of our high-melting Fischer paraffins it has been discovered, before our systematic experiments have been started, that these paraffins yield by air oxidation under the proper conditions products of a varnish-like consistency.

Dr. Wenzel and Dr. Wintzer found, for example, that they obtained varnish-like coatings when they heated sheet iron with paraffin coatings with access of air. We tried to find the optimal conditions relative to temperature, the duration of air action; quality of the paraffin for the preparation of a coating which corresponded as much as possible to a good coat of lacquer. For this purpose a large number of sheet irons of a dimension of $205 \times 31 \times 0.5$

mm. were dipped into baths of paraffins with different melting points and after a short and equal time in a drying oven at 150 to 170°C. were exposed for different periods to the influence of the air. The varnish coatings obtained in this way were roughly estimated (for want of testing equipment) regarding color, luster, elasticity, hardness (chip-test), and velability. We found that at 150° as well as at 170° absolutely usable coatings can be made. However, only paraffins with melting points above 84°, especially above 103° seem to be best. The best duration for air action is below 20 and 30 hours. The samples of varnished sheet strips were submitted to Dr. Heidinger for his expert appraisal. About 7 samples were criticized favorably by him as good enough for manufacturing purposes. But we had to keep in mind that by this kind of preparation (heating of the surfaces covered with liquid paraffin) the thickness of the film was not as uniform as it can be in the case with a normal coat of lacquer. It has to be mentioned, however, that paraffin coats on glass plates do not give varnish coats under the mentioned conditions. Only by addition of Mn or Fe either as metals, or as oxides, or of certain Mn or Fe salts, varnishes of the desired kind are formed.

Experiment for the Study of Varnish Formation

A special apparatus was built which should enable us to produce larger quantities of a paraffin in different stages of oxidation. We wanted to keep the gradient of the paraffin surface exposed to oxygen and its volume as small as possible and so provide for a continuous renewal of the surface. By this means too rapid a surface

oxidation should be prevented.

We expected the realization of this effect by the following procedure:

1. A slowly rotating iron roll was dipped within a drying oven at 150-170°C. with its lower half into a paraffin bath and pulled from it continuously a paraffin film, which was naturally destroyed after one turn by dipping again into the bath. In this manner, the partly oxidized substance was again and again mixed with unused or partly used paraffin.

2. By blowing air through the paraffin at 150-170°C. with or without a diluent.

In both cases we found that the oxidation of the paraffin can obviously not be stopped at an intermediate stage. For days the oxidation proceeds very slowly; this is indicated by the slow increase of density, acid number, and oxygen content. All of a sudden it increases very fast and the substance becomes colloidal and sticks at the roll and the walls of the bath.

At this experimental stage we had to stop in favor of some other more urgent work. Our work was transferred to Oppau and Ludwigshafen.

Conclusion

1. With cobalt catalysts and water gas at 10 atms. alcohol contents of 22-27% in the fractions 200-350° have been obtained.

2. We found that with fused Fe catalysts WK 17 (Luna ammonia catalyst) considerable alcohol contents in the primary products have been obtained (25-35% in the fraction 250-350°).

3. An iron precipitation catalyst with low nickel amounts gave a high portion of lower alcohols.

4. One precipitation catalyst was prepared on a Fe-Al basis, which was superior as far as the alcohol formation is concerned even to the fused catalyst. Precipitation catalysts with addition of Mn and Zn had unfavorable results.

5. Lower synthesis temperature favor the alcohol content of the fractions.

6. During the distillation of the primary product, the acids contained in the product esterify corresponding amounts of alcohol. By decacidification of the products before the distillation starts, the alcohol contents in the interesting fractions above 200° can be retained.

7. A comparison is given on the composition of products obtained by the two methods.

8. By heating of high-melting paraffins (64° and more in air) varnish-like coatings of good qualities have been obtained.