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THE OXO PROCESS FOR ALCOHOL MANUFACTURE FROM OLEFINS

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A. INTRODUCTION

Early in 1945 a group of petroleum and fuel technologists from both England and the United States investigated the status of oil technology and research in Germany. This mission was carried out under the sponsorship of C.I.O.S. (Combined Intelligence Objectives Subcommittee) and with the cooperation of the British and American armies in the European theater of operations. Among the processes discussed with German personnel at appropriate plants and locations was the so-called OXO process for making higher alcohols from olefins. Though the present tense will be used frequently in this report, it should be understood, of course, that the process is not operating now and has not been since the termination of the war.

B. SOURCE AND CHARACTER OF THE DATA ON THE OXO PROCESS

The information in this report was assembled from the following sources:

1. Interviews with personnel, for the most part at Ruhrchemie A.G. at Sterkrade in the Ruhr, and at I. G. Farben A.G. at Leuna in Saxony. These interviews, as made by mission members, have been summarized for the most part by preliminary reports by E. B. Peck and V. Haensel.

2. Review of Microfilm No. 14 of documents seized at the Leuna works of the I. G.

3. Notes and personal observations of the writer.

Microfilms of all the seized documents were not available for the writing of this report. If and when finally received, the additional data contained therein can be summarized in an appendix hereto.

The present report covers the essential features of the process. Consistent citation of the source of many of the statements contained herein could not be made, so that names

are seldom given. Where deemed useful, reference is made to Microfilm No. 14 by page number; e.g., (14-650) for page stamped 00000650 on Microfilm No. 14. Except where expressly stated otherwise, the opinions and facts as given are those of the German workers obtained either in interview or by abstracting the documents.

C. GENERAL FEATURES

The OXO process is a two-stage process for producing alcohols from olefins, first, treating the mixture of olefins with carbon monoxide and hydrogen to form aldehydes, and second, reducing them by the use of commercial hydrogen. Operation may be batch-wise or continuous.

A wide range of pressures may be used in both stages, but the order of 150 to 200 atmospheres is most common. Temperatures likewise may vary considerably, but the aldehyde-producing stage is typically operated at about 140°C. and the second stage at about 180°C.

A standard Fischer-Tropsch catalyst, containing cobalt, thorium oxide, magnesium oxide, and kieselguhr, is used in the first stage and may be carried through the second stage, though cheaper catalysts have been suggested and used in the second stage.

A wide enough range of olefins has been treated, using pure substances or mixtures with or without inert diluents, to justify the statement that the process is applicable to all olefins from the chemical standpoint only. Practical application of the process in Germany was directed mainly to processing olefin mixtures in the range of C_{11} to C_{17} carbon atoms. Such fractions were cut directly from the primary standard Fischer synthesis liquids or were cut from the product of low-temperature cracking of Fischer waxes. Selection of the raw material was guided by the desire to produce mixtures of alcohols in the range of C_{12} to C_{18} which, after sulphonation, gave effective detergent mixtures. Plasticers were also made by applying the OXO process to C_7-C_{10} olefin mixtures and subsequently forming the phthalic acid ester of the alcohols produced.

D. DEVELOPMENT OF THE OXO PROCESS

The OXO process was developed as the result of joint efforts and sponsorship of Ruhrchemie A. G. and I. G. Farbenindustrie. The process was discovered by Ruhrchemie's Dr. Ruelen, or was at least actively studied by him at an early date.

A company called the OXO Gesellschaft g.m.b.H was formed with offices at Oberhausen-Holten. The date of organization of the company and the distribution of the stock is not known, but the latter was presumably held jointly by the above two companies, with some participation by Henkel and Cie. g.m.b.H, Dusseldorf. In any case, the latter company was destined to make the sulphonated products from the alcohols manufactured by the OXO Gesellschaft.

In a document dated October 12, 1942 (14-667), the patent situation was summarized as follows:

Relating to	Patent or Application in DRP Amt.	Assigned to or Owned by
OXO reaction itself	R 103362[1]	Ruhrchemie
Carrying through reaction as at Leuna	R 105066 IV D/120	Ruhrchemie
	I 72948/120	I.G. Farben
Carrying through reaction as at Leuna	I 72924/120 (Also protected through OZ 13634 and OZ 13631 Patent Div. Ludwigshaven)	I.G. Farben
Sulphonation of alcohols in general	R 106644 IV D/120	Ruhrchemie
Sulphonation of alcohol and paraffin	I 67906 IV D/120	Possibly but not certainly I.G. Farben

[1] U.S. Patent 2,327,066, August 17, 1943, Otto Ruelen inventor, unassigned, but seized by U.S. Alien Property Custodian presumably corresponds to R 103,362. Application date April 15, 1939, refers to filing in D. Reich September 19, 1938.

The German documents are not available for review.

In developing the process to a commercial conclusion, both Ruhrchemie and I. G. Farben took an active part, starting about 1940. C.I.O.S. mission members gathered from the interviews, and the review of seized documents confirms, the fact that representatives of both companies were in substantial agreement as to the efficacy and utility of the reactions for the production of higher alcohols.

Laboratory work was done not only at Ruhrchemie and Leuna but also at the Ludwigshafen laboratories of I.G. Naturally, these operations were done batch-wise. The Ruhrchemie operated the process batch-wise on a semi-plant scale, but workers at Leuna translated the process into a continuous semi-plant operation or a small plant operation. The OXO Gesellschaft equipment at Ruhrchemie was also to be operated batch-wise. It appears, however, that continuous operation was finally looked upon by both Ruhrchemie and Leuna as most effective, and that the reason for batch-wise large-scale operation was that original designs could not be changed in wartime. Interview elicited the information that the annual capacity of the OXO plant at Ruhrchemie was nominally 8,000 to 10,000 metric tons of product. However, the plant was very slow in building, due to the war, low priority, etc., and the information through interview was to the effect that the plant had not been operated as a whole at the end of the war, though a few test runs had been made on part of the equipment.

In the semi-plant equipment at Leuna, about 1-1/4 metric tons per day of OXO alcohol were produced during the first four months of 1944. In May, only 7 tons were produced, and thereafter no production was made. From the tenor of both documents and interviews, it seems certain that lack of raw materials, difficulties due to bombing, poor priority for construction, and other matters reflecting war conditions, rather than on the confidence in the process as a chemical tool, caused the cessation of semi-plant operations and retarded progress of construction by the OXO Gesellschaft.

E. CHARACTER OF THE PROCESS FROM THE CHEMICAL STANDPOINT

Raw Materials

a. Olefins

The reactions of the OXO process can be applied to olefins having from 3 to at least 20 carbon atoms. Aromatic olefins may also be processed. Pure olefins may be used or a mixture, both either with, or without, dilution by inerts such as paraffins. The yield is not substantially affected by dilution or admixture and is of the order of 90% alcohol at least when aliphatic olefins constitute the feed stock. When diolefins are present, reaction occurs at only one of the double bonds and the yields are poor.

Apparently, almost any source of olefins may be drawn upon for charge materials.

The alcohols which result will have one more carbon atom than the olefin charged, and the choice of charge stocks for commercial purposes is thus conditioned by the nature of the product desired.

The sources which were mainly considered by the Germans were the primary aliphatic olefins produced by the Fischer Tropsch process, and the olefins with double bond at the end of the straight chain, which could be obtained from mild cracking conditions applied to the F. T. paraffin-gatsch. However, some work was done upon the olefin mixtures which might be obtained from low-temperature carbonization of brown coal. The two former sources, particularly the first, were finally looked upon most favorably as the source of raw material for alcohols for manufacture of detergents.

At the time in 1940 when the production of 40,000 tons per year of alcohols in the C_{10} to C_{20} range was being discussed, the production of olefins by the Fischer process was visualized by Dr. Martin of Ruhrchemie, according to the scheme diagrammed on the next page.

It will be noted that the Fischer process, using an iron catalyst at 20 atmospheres, was to furnish the basic raw materials. Fractionation of the heavy oil direct from the process (155°-330°C. boiling range) was to furnish slightly more than half of the raw materials, and cracking of the wax at low temperature and pressure was to supply the rest of the

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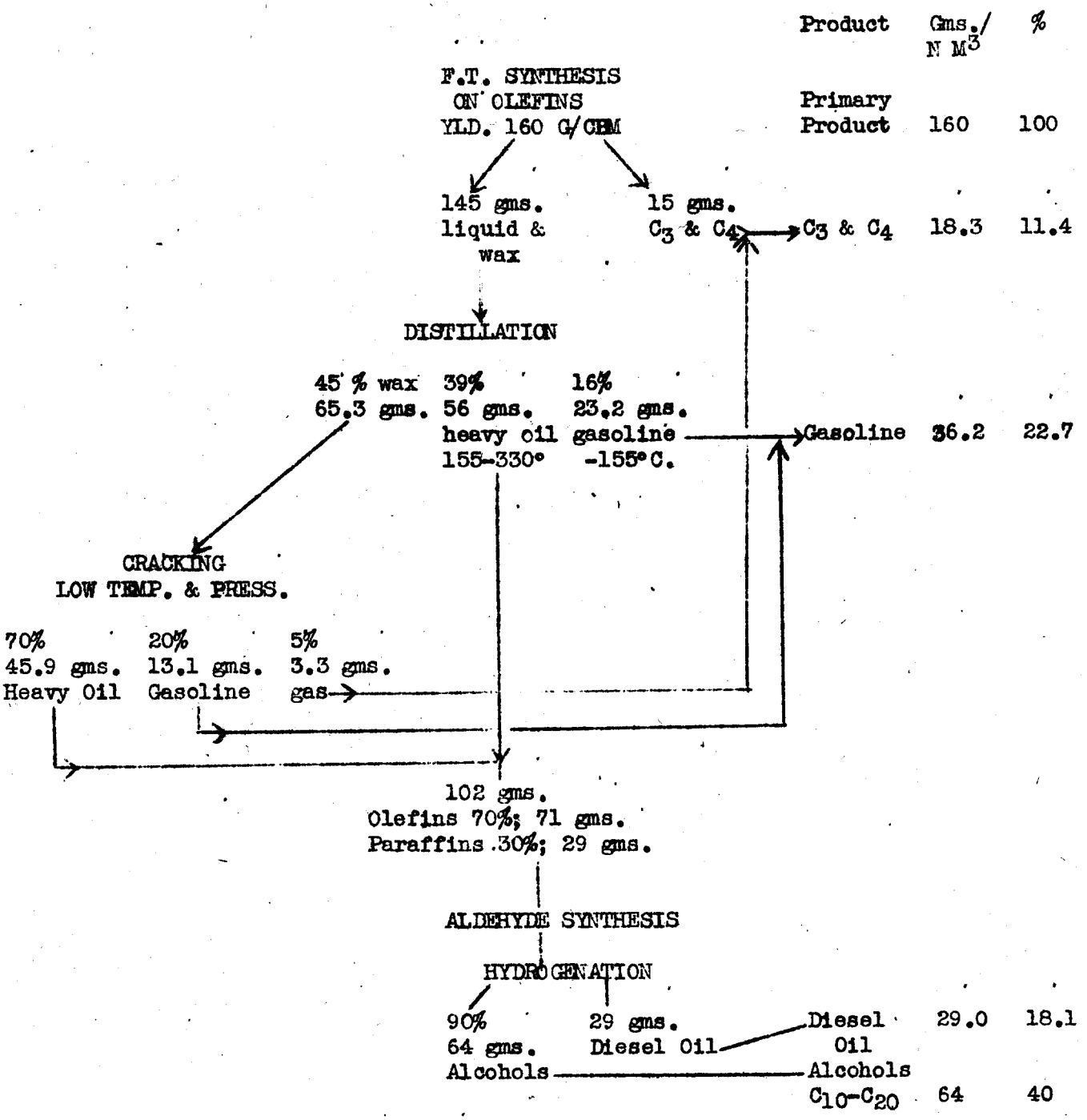
SCHEME FOR FISCHER PROCESS WITH OXO

Using Iron Catalyst at 20 atm. 280°-300°C. Yields based on $1M^3$ Ideal Synthesis Gas.



Product	Gms./ N M^3	%
Primary Product	160	100
C_3 & C_4	18.3	11.4
Gasoline	36.2	22.7
Diesel Oil	29.0	18.1
Alcohols C_{10}-C_{20}	64	40

Prepared b y Ruhrchemie 7 Feb. 1940.

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raw material. The mixture was presumed, on the basis of some actual experiments, to consist of about 70% olefins and 30% paraffins.

In the document (14-480) it appears that Dr. Martin of Ruhrchemie presented the above scheme with the statement that an 85% yield of olefins could be made from cracking F. T. paraffin with only 5% loss. He proposed to crack, thermally, at about 250°C. Long chain olefins with the double bonds at the end were stated to be mainly present in the product, but as cracking temperature was raised, the double bonds tended to wander from the end of the chain toward the middle. At a cracking temperature as high as 350°C., the double bonds are almost entirely in the middle of the chain.

While this early procedure envisioned the application of iron catalyst in the synthesis operations, we now know that the application of iron catalysts on a large scale was never attained during the war period. The trend of the development, as read from the documents, was definitely toward the use of primary olefins from the normal Fischer process using cobalt catalysts.

In a document from Leuna dated March 11, 1943 (14-772), the following statements in regard to suitable charge stocks are made: (Translation is approximate and is condensed.)

> "Olefins, made according to various synthesis procedures, and a thermally cracked product from Fischer Gatsch were analytically investigated. The degree of the transformation of the olefin content by help of the OXO reaction was determined. In the experiments, products boiling in the range of the detergent alcohol were given greatest weight. The most important results are gathered together below.
>
> "(1) The Oxierung of the olefins, i.e., treatment by the OXO process, succeeded with all materials examined, giving more than 95% yield.
>
> "(2) The 'cobalt products' (made by Fischer Tropsch with cobalt catalyst) are substantially more uniform than the 'iron products' (made by iron catalysts and Fischer Tropsch) and the former are composed substantially only of olefins, paraffins, and alcohols.

"(3) The 'iron products' contain, in amounts worth mentioning, not only olefins but also acids, esters, and aldehydes. When the OXO process is applied to such materials, they are considerably reduced in complexity of composition."

The above is cited at this point to indicate that as late as the first part of 1943, experiments were still going on to find the proper source of olefins for the process. Consideration was always directed toward obtaining raw olefins of the proper chain length, and it is indicated from the literature that little difficulty was ever experienced in carrying out the OXO process itself. Indeed, laboratory work was said to have been done successfully on such varied materials as:

Ethylene	Acetylene	Allyl Alcohol
Propylene	A-Butene	Linseed oil
N-A-Octylene	Disobutylene	Rubber
Decylene	Cetene	Acrylicacid ethylester
Mixed polymers	Octadicylene	Terpenes
Cyclohexene	Octaline	Vinyl ether
Styrol	Butadiene	Tetrahydrofuran
Olefinic Lub. oil	Oleic alcohol	(cyclobutylene oxide)

In interview, the writer noted that the reaction was said to go when elements other than oxygen are in the compound with a double bond. For example, compounds containing nitrogen, sulphur (?), chlorine, etc., may be processed.

b. Gaseous Reagents

Water gas is entirely satisfactory for the first stage of the process, after proper purification to reduce the sulphur content to the order of 2 milligrams per CBM or less. While a ratio of one volume carbon monoxide to one volume of hydrogen is theoretically required for the reaction, this ratio need not be closely maintained, since a large excess of gas is always employed to direct the reaction to completion. The attention to sulphur reduction in the gases is to prevent the well-known poisoning of the catalyst by sulphur. It is absolutely essential to satisfactory carrying out of the process.

Commercial hydrogen also processed to insure low sulphur content is satisfactory agent for the second stage of the process.

c. Catalyst

"Standard" Fischer-Tropsch catalyst generally prepared by Ruhrchemie at Sterkrade was used in most of the experimental work on the OXO process. "Standard" cobalt catalyst was stated in interviews concerning Fischer-Tropsch operation to be 100 parts cobalt, 5 parts thoria, 8 parts magnesia, and from 180 to 200 kieselguhr. While it was normal to keep the iron content of the kieselguhr less than 1%, the documents indicate that I. G. had operated the OXO process successfully with some cobalt catalyst made by them and stated to contain up to 5% iron. The documents reviewed for this report contain no precise information on the method of manufacturing any catalyst, and reference should be had to the report on the Fischer-Tropsch process itself for information in this regard. The standard cobalt catalyst was preferably ground for better contact with the reactants, but this was not always done according to the documents.

The cobalt of the catalyst is partly converted to carbonyl, $(Co(CO)_4)$ in the first stage and this dissolves in the liquid product. Subsequent hydrogenation breaks up the carbonyl leaving the cobalt in a catalytically active form.