Report 4. Investigation of the OXO Process

Date of Investigation : April 7, 1945

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Administration for War

Personnel Interrogated : Dr. Landgraff, Manager of the
OXO Plant.

Reported by : Dr. E.B. Peck.

Introduction.

A joint company known as the OXO Gesellschaft had been formed by Ruhrchemie A.G., I.G. Farbenindustrie A.G. and Henkel et Cie to manufacture C_{12} to C_{18} alcohols by a process based on the reaction between aliphatic olefines and carbon monoxide and hydrogen. The object of the project was the production of detergents by sulphonation of the alcohols.

The basic reaction was discovered in the Ruhrchemie research laboratories under Dr. Roelen. In view of the great experience of I.G. in large-scale operations at high pressure they were brought in to assist with the commercial development of the process, and the Henkel concern were to carry out the preparation of the detergents. The latter were said to be very efficient but there appeared to be some doubt about their physiological properties as they were reported to have a strong de-fatting action on the skin.

The company had built a plant with a nominal annual capacity of 8-10,000 tonnes of alcohols on the Ruhrchemie site at Sterkrade-Holten, but apart from a few test runs on parts of the equipment, the plant had not been operated. The main part of the plant had almost completely escaped bomb damage. (See Figs. 9 & 10)

The information given in this report is based partly on material supplied by Dr. Landgraff and partly on the results of a preliminary examination of documents found at Sterkrade.

THE OXO REACTION

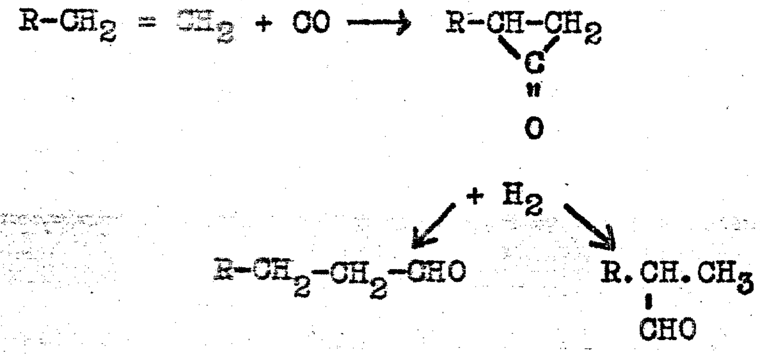
The main reaction is the addition of synthesis gas ($CO + H_2$) to olefines to form aldehydes.

$$R - CH = CH_2 + CO + H_2 \longrightarrow R - CH_2CH_2CHO$$

This reaction takes place at 100-200°C. and 100-200 ats. pressure in the liquid phase with the Fischer-Tropsch catalyst (Co-ThO_2-MgO-Kieselguhr). The aldehyde is then hydrogenated at 180°C. and 100-200 ats. with pure hydrogen and the same catalyst.

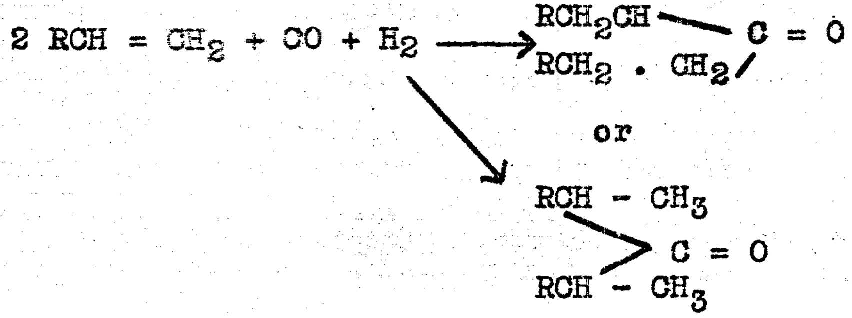
This reaction produces a variety of isomeric primary alcohols and 5-15% of heavy products consisting of ketones, condensed aldehydes, secondary alcohols and hydrocarbons.

The main reaction produces two isomeric aldehydes in about equal amounts. This is explained by the addition of CO to the olefine to form the unstable cyclopropanone linkage which is then hydrogenated to the aldehydes as follows :



Other isomers are formed due to displacement of the olefine linkage toward the middle of the molecule.

Other side reactions take place as follows (1) the condensation of aldehydes and (2) the reaction between two olefines and CO to form ketones :-



Under proper reaction conditions these side reactions can be held down to 5-15% of the olefines reacted. These conditions appear to be 130-140°C and 150 ats. for the C_{11} - C_{17} monoolefines.

The OXO reaction is quite general and a wide variety of olefines and other compounds have been tested including the following :-

Ethylene (to produce propionic acid or n-propyl alcohol)
Acetylene (to produce acrylic acid)
Propylene (see below)
α -Butene
N- α-Octylene
Diisobutylene
Decylene
Cetene
Mixed polymers
Cyclohexene
Octadiene
Styrene
Butadiene
Olefinic lubricating Oil
Oleic alcohol
Linseed Oil
Terpenes
Rubber
And certain other compounds including -
Vinyl ether
Acrylic acid ethylester
Tetrahydrofuran (cyclobutylene oxide)

OXO REACTION WITH PROPYLENE

The reaction is not clean cut as shown by the reaction products produced from propylene :

Input

I.	Propylene	2,500 gms.
	Catalyst R.B.V.[1] (Fischer Catalyst 30% Cobalt)	100 "
	Reaction conditions 1st stage 110°C. 120 ats. ($CO + H_2$)	
OXO Product yield		2,560 liters
	Theoretical yield as aldehyde	2,688 liters

II. Hydrogenation with same catalyst at 180°C. and 200 ats. H_2

Hydrogen absorbed	917 liters
Theory	1,344 liters

Hydro product	3,946 gms.
Theoretical yield	4,400 gms.

The product corresponds in weight to 89.7% absorbtion or 1 mol CO + 2 Mols H_2 per mol of C_3H_6.

PRODUCT INSPECTION

(a) Distillation

Fraction	Pressure mm	Temperature °C	Gms.
1	760.	90-103	270
2	"	103-120	1472
3	25	55-90	175
4	"	90-107	295
5	"	107-120	75
6	"	120-140	554
7	"	140-150	438
8	"	150-160	48
9	"	160-200	92
10	"	200-218	125
11	"	218-226	65
			3,609

The first fraction was a butanol-water mixture with 30% H_2O. The second fraction was a mixture of butyl alcohols (isopropylcarbinol, B.P. 108° and n-butanol, B.P. 116°C.) The fourth fraction was composed mostly of secondary alcohol, dipropylcarbinol and the fifth fraction contained alpha ethyl-hexanol ($C_8H_{18}O$). This last is explained by earlier researches of J.V. Braun by the reaction of two molecules of butyraldehyde in the presence of finely divided metals in the presence of hydrogen.

The sixth and seventh fractions contained the butyric acid monoester of ethylhexanediols which is explained by the Cannizarro reaction. The components of the higher fractions were not easily identified but are believed to be condensation products of normal and isobutyraldehydes.

The yield of butanol was 38% based on propylene with 12% of C_7 - C_8 alcohols and 23% as ethylhexandiolmonobutyrate. It is pointed out that better yields of undivided alcohols might be expected with a better choice of reaction conditions. This is in fact achieved in the reaction with C_{11} - C_{17} olefines where some 85% yield of corresponding alcohols are claimed for pilot plant operation. The alcohols in this case are branched and of various structures, though all primary alcohols.

The I.G. have developed the basic reaction with a variety of new catalysts, particularly with nickel carbonyl or the nickel halides. ($NiCl_2$ activated with iodine). This is the subject of a separate report. (Reppe Chemistry). The I.G. have also developed their hydrocarbon syntheses to make a product directly from synthesis gas ($CO + H_2$) which is about half primary alcohols and half hydrocarbons. This is separately reported in the report on the Leuna plant (30/4.02) under the title "Synol Process".

THE OXO PROCESS

The OXO Process has been directed primarily to the production of C_{12} - C_{18} primary alcohols from C_{11} - C_{17} acyclic olefines. These olefines are derived in 30 - 50% concentration either from the 180 - 320°C cut of the Fischer-Tropsch product or from cracking heavier fractions (gatsch). The olefines from cracking petroleum may also be used but it appears to be preferable to separate these olefines by solvent extraction. A pilot plant was sent to the Bombini Company in Italy for the production of alcohols or acids from ethylene but no information on this work is available.

The process is carried out with narrow fractions of olefines in order to simplify the separation of the resulting alcohols from unreacted fractions and byproducts. The Henkel Company requires alcohols of 97-98% purity for sulphonation to detergents.

For the production of detergent alcohols the 180-320°C fraction is cut in four fractions by atmospheric and vacuum distillation as follows :

Cut	Boiling Points at 760 mm of Hg.	At / mm of Hg
C_{11} - C_{12}	180-220	70-110/20
C_{13} - C_{14}	225-260	100-140/20
C_{15} - C_{16}	260-295	100-140/5
C_{17}	295-310	140-160/5

Steam at 80 ats. pressure is used for heating and the last two cuts are separated by batch vacuum distillation. Each cut is reacted separately.

The main reaction is carried out in the liquid phase with finely suspended Fischer-Tropsch catalyst (30% Co) at 130-140°C. and 150 atmospheres under which conditions the reaction is completed in 20-30 minutes. Some of the cobalt is converted to the carbonyl ($Co(CO)_4$), and this is reduced to metal in the next stage where the aldehydes are hydrogenated to primary alcohols with the same catalyst at 180°C. and 150 ats. with pure hydrogen. It appears that the carbonyl and CO brought over to the hydrogenation stage poisons the hydrogenation reaction and the CO must be removed by conversion to methane with iron catalyst in the cycle gas.

The catalyst and reduced cobalt are separated from the product by filtration under mild pressure thru ceramic thimbles.

The alcohols are then separated with 98% purity from unreacted oil and heavy oil byproducts by distillation. The distillation is carried out in vacuum stills with packed columns heated by steam at 8 ats. to prevent decomposition.

The OXO plant at Holten was built for batch operation but the I.G. at Leuna have developed a continuous process that appears to be a great improvement. (See Report on 30/4.02).

The batch plant consists of nine reactor units, each with two reactors of 1.2 cubic meters volume, one for the reaction of olefines with synthesis gas and one for hydrogenation of the aldehydes to alcohols. These reactors are 570 mm. o.d.; 400 mm i.d. and 12 meters high and contain a bundle of cooling tubes connected to a steam chest and a leg for thermosyphon circulation of cooling water. (See Fig. 11) The reaction heat is substantial, (35 Kcal. per gm. mol of olefine reacted) and there are 31 tubes 38 mm. o.d. x 8 meters with a cooling surface of about 30 square meters for removing this heat. The temperature of reaction is controlled by the pressure on the steam and the rate of circulating the synthesis gas. The reactor is charged with 700-720 liters of liquid feed containing 3-5% (15 Kgs.) of finely ground Fischer catalyst. The concentration of olefines in the feed is not critical but this plant is designed for handling a feed with 40-50% olefines. The feed is heated to 130°C. and the synthesis gas recycled thru the reactor with a compressor having a capacity of 200 N M^3/hour (1.3 cu.m. of gas at 150 ats.).

The OXO reaction is completed in 20-30 minutes when the liquid feed with suspended catalyst is pumped into the hydro-reactor where the aldehydes are hydrogenated at 180° and 150 ats. with pure hydrogen. As noted above, it is believed to be necessary to remove the carbon monoxide that comes over to the hydrogenation stage by converting it to methane over an iron catalyst in a converter in the recycle hydrogen line. This reduces the CO from 2.0 to 0.05%.

The product is filtered under moderate pressure thru a battery of ceramic thimbles (manufactured by Meisner Filterwerk, Dresden). The filters are washed with fresh oil feed which is fed with recovered catalyst and make up to the process. These filters are reported to be good for 5000 filtrations before replacement.

The filtered product is then distilled under vacuum to separate (1) alcohols in 98% purity, (2) unreacted oil and (3) thick oil bottoms which amount to 15% on alcohols and consists of a mixture of aldehydes, ketones, esters, and hydrocarbons.

The over all yield of alcohols is probably around 65-70% but firm information is not available for lack of full-scale operating data. There are undoubtedly losses of alcohol in the unreacted oil fraction aside from reaction losses. There are references to work on alcohol recovery by solvent extraction with methanol, etc., and the I.G. (Leuna) have a recovery process for the Synol Process based on esterification with anhydrous boric acid. (See Synol Process, 30/4.02).

The continuous process developed by I.G. is shown schematically in Fig. 12 and consists of two reactors in series with synthesis gas recycle, seperator and scrubbing tower for the gas that is bled off. The first reactor is identical with that used in the batch process (with inner coolers) while the second reactor of the same size does not require coolers but has 'disc and doughnut' baffles. The hydrogenation section is the same except for a converter in the gas recycle line for converting CO to methane. This is claimed to reduce the CO from 2.0 to 0.5%, and is essential for avoiding poisoning of the catalyst for hydrogenation. No release gas scrubber is required. The release gas in the first stage uses fresh feed for scrubbing which is then fed to the processes without stripping.

The continuous process was worked out at Leuna in a water-jacketed reactor of 250 liters capacity and divided into concentric sections. In this reactor the oil is fed upflow into the outer ring and down flow thru the inner section. The gas flows upward thru both sections in separate streams. The inner section is baffled. From the results in this pilot plant it is estimated that the thruput for 95% reaction would be 3 v/v./hr. which is 9-10 times as much as for the batch equipment. (See 30/4.02).

ECONOMICS

The economics of the process as calculated by Ruhrchemie is shown below and indicates a cost of alcohols of 71 pfg./kg. I.G. corrected this estimate as shown to 77 pfg./kg. These costs are based on an olefine cost of 38 pfg./kg. and a capital cost of 6 million RM. There is now 11 million RM. invested in this plant by OXO Gesellschaft. The I.G., on the other hand, estimated a cost of 60 pfg./kg. for the continuous process. Within the above limits the cost of these alcohols lies between 60 and 100 pfg./kg. which, with exchange at 5.2 RM. per dollar, would be 5 to 9 cents per pound.

Estimated Cost of Primary Fatty Alcohols by the OXO Process

	Ruhrchemie pfg./kg.	I.G. Corrections
100 Kg. Olefines (for 95% yield)	38.00	--
Gases: (CO/H_2 & H_2)	1.30	--
Catalyst	0.60	--

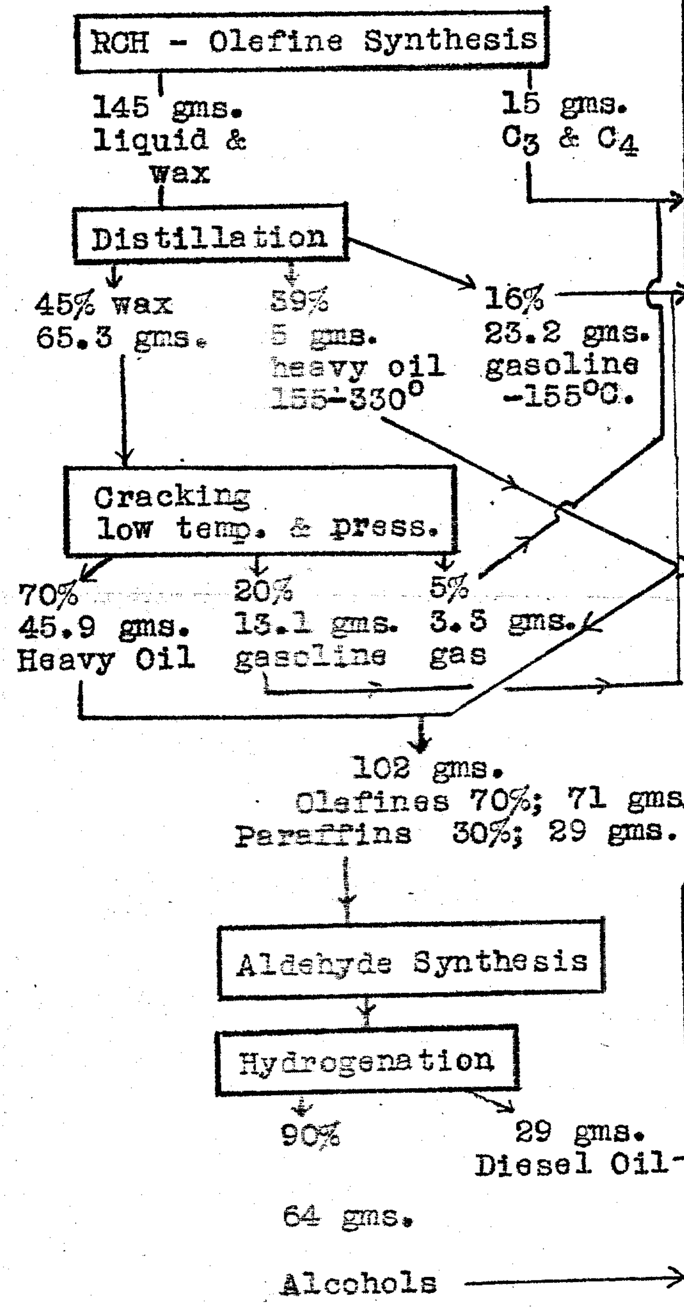
	Ruhrchemie pfg./kg.	I.G. Corrections
Distillation (Feed & Product)	6.00	10.00
Water	1.50	3.00
Power for compression, etc.	2.30	--
Charges	1.60	--
Wages & Salaries	4.80	--
Amortization & Interest 15% on RMG million	15.00	
	71.10	76.60

The overall picture of OXO alcohol production from synthesis gas is presented by Ruhrchemie in the following schematic diagram. This shows the Fischer conversion with the iron catalyst developed by Michael of I.G. and shows an overall production per N M^3 of synthesis gas ($CO/H_2 = 1/1.2$) of hydrocarbon products, 84 gms. and $C_{10} - C_{20}$ alcohols, 64 gms. The 155-330° fraction of oil with 70% olefines is processed as is also the olefines from cracking the heavier oils (gatsch). A special low temperature and pressure cracking procedure has been worked out with U.O.P. for the production of maximum olefines in the $C_{10} - C_{20}$ range.

SCHEME FOR FISCHER PROCESS WITH OXO

Using Iron Catalyst at 20 ats.
280-300°C. in M^3 Synthesis gas.

(Prepared by Ruhrchemie 7 Feb. 1940)



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

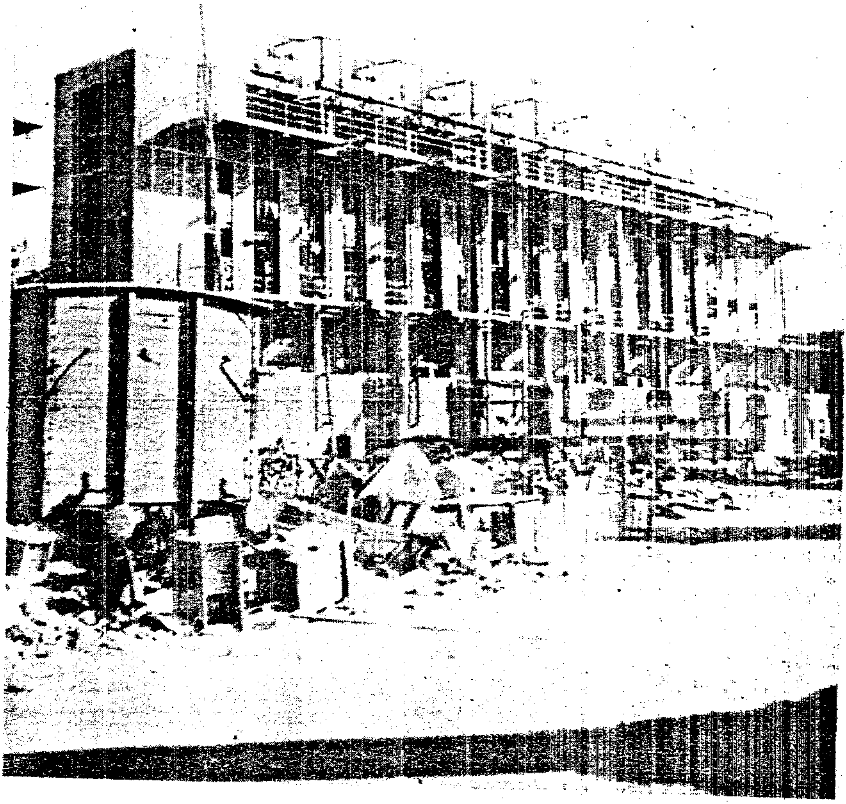


Fig.9. The OXO plant reactor building.
(30/5.01, Ruhrchemie A.G., Sterkrade-Holten)

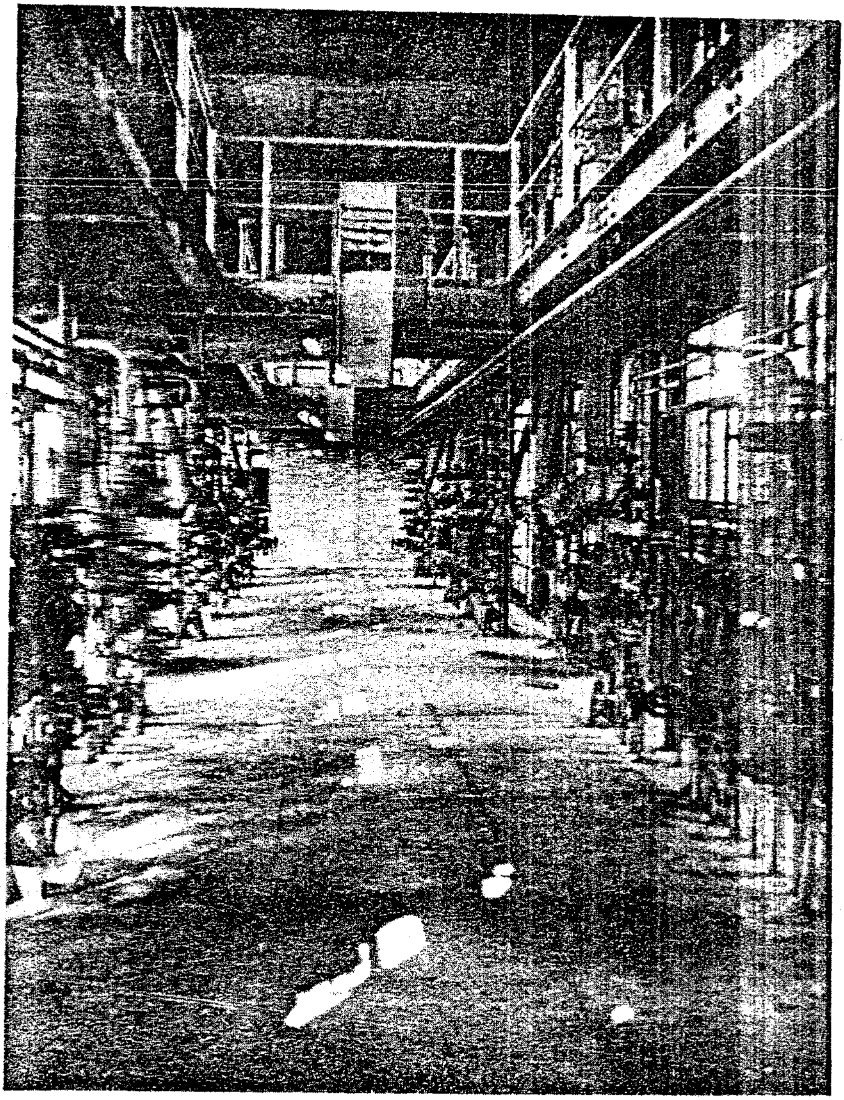


Fig.10. The control platform in the OXO reactor building.

(30/5.01, Ruhrchemie A.G., Sterkrade-Holten)

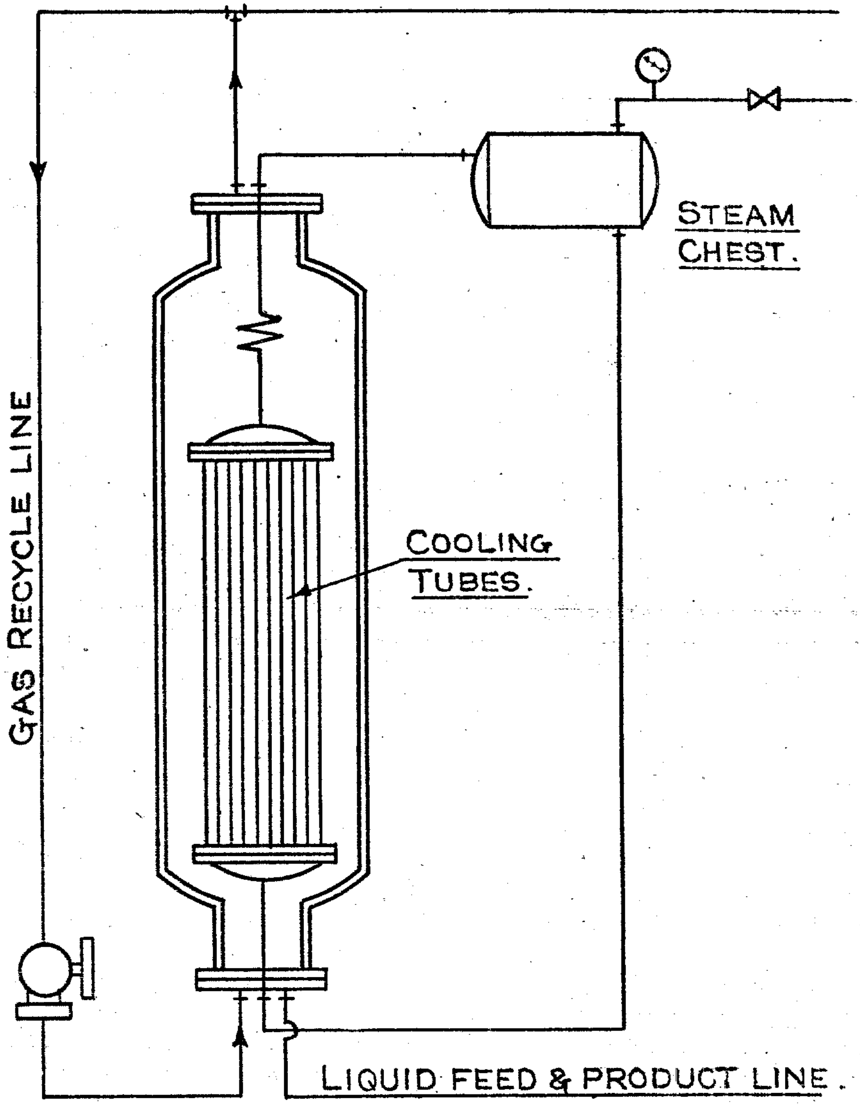


FIG. 11. OXO REACTOR UNIT.

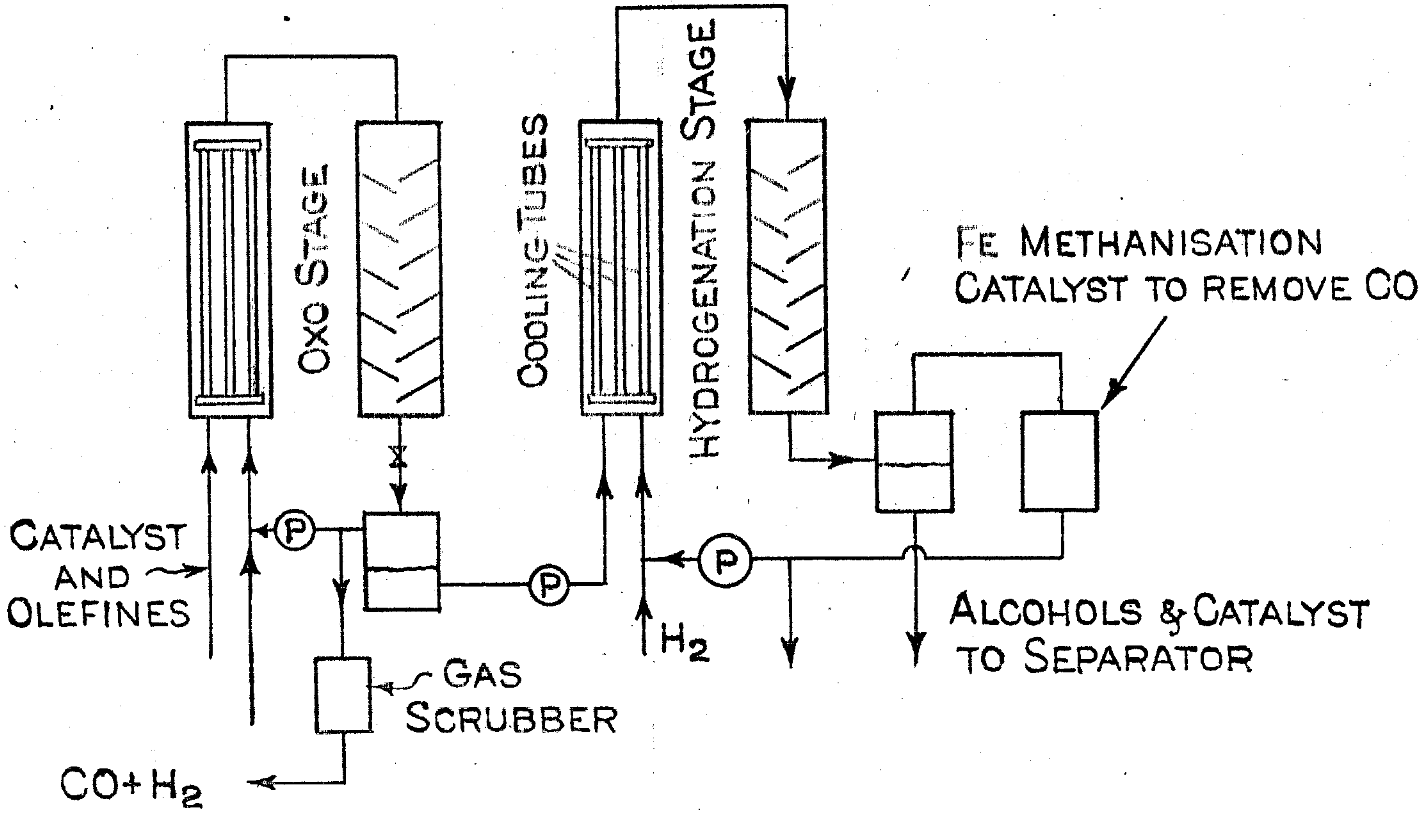


FIG. 12 FLOW SCHEME FOR I.G. CONTINUOUS OXO PROCESS