

I.C. 7370

OXO Processing of Cracked Middle Oil:

In addition to Kogasin and Gelbol, Leuna had investigated the treatment of cracked petroleum oil by the OXO Process. Dr. Gemassmer provided the following data from a run, the conditions of which were not considered to be optimum.

The olefinic feed material had the following properties:

Density	0.843
Pour Point	-18°C
Av. Molecular Wt.	195
Iodine No. (Hanus)	46-48
Sulphur Content	.24% by wt.
Boiling Range	230°-350°C
Volume % soluble Kattwinkel solution	51.

The charge was mixed with 3% by weight of catalyst and reacted with water gas at 240 ats. Total reaction time in the OXO stage was approximately 1 hour. The temperature at the inlet to the first reactor was 150 C and that at the exit of the second reactor 190 C. The hydrogenation of the crude product was carried out at 220 ats with hydrogen of 97% purity. The temperature was 195 - 200 C and the total reaction time approximately 1 hour. The product had the following properties:-

Density	.862
Iodine No. (Hanus)	19.6
OH No.	36-40 mgm KOH/gm.
CO No.	3.5
Saponification No.	5 mgm KOH/gm.

The OH number is determined by acetylation with acetic anhydride followed by titration with KOH solution. The CO number is a measure of the aldehyde and ketone content and is determined by forming the oximes of aldehydes and ketones followed by titration with KOH solution.

The crude product contains 16-17% alcohols which may be separated from the hydrocarbons by forming boric esters. It is not possible to separate the alcohols by simple distillation because of the wide boiling range of the charge stock.

Only about 60% of the olefines was converted and of this, approximately 80% was recovered as alcohol.

Fig. XXXI (B) is a photograph of the OXO converters.

In addition to the authors, Major A. V. J. Underwood contributed notes and these were of very great assistance in compiling the above report.

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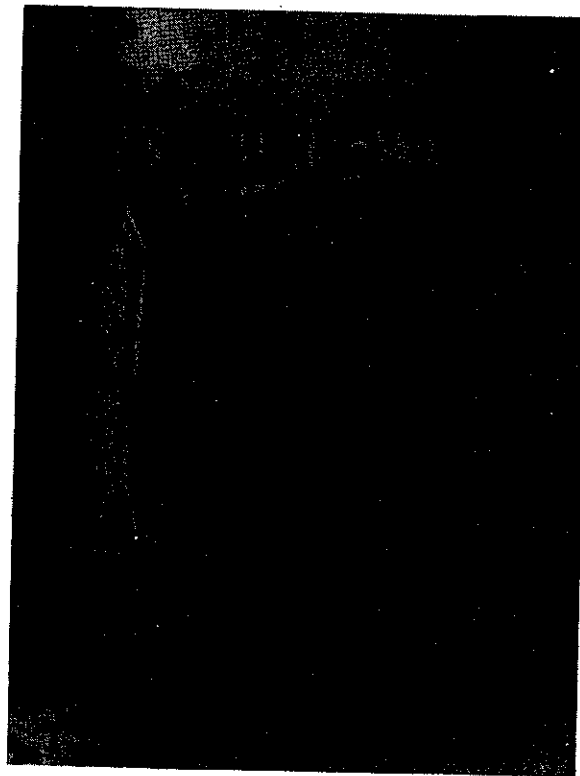
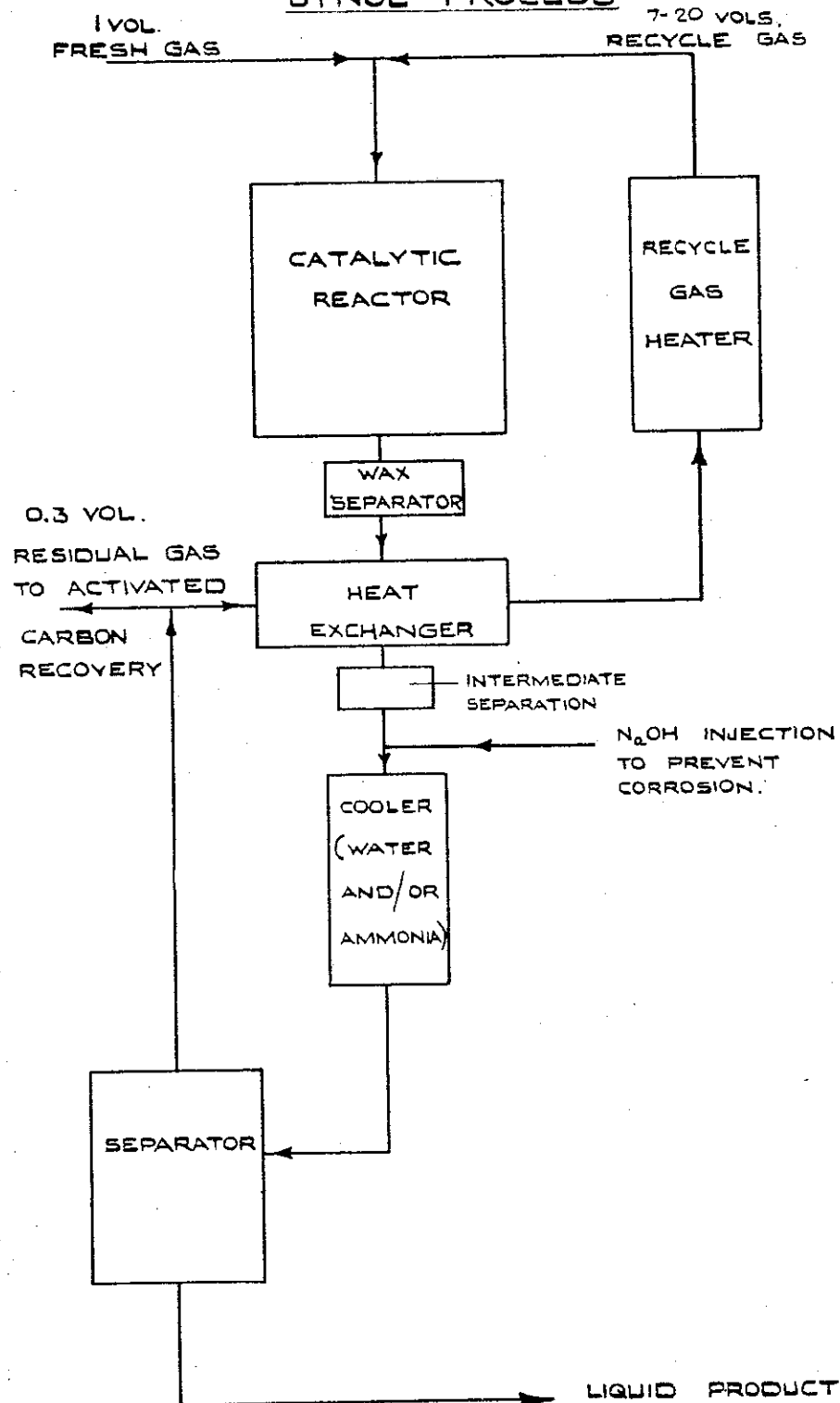


FIGURE XXXI B

FIGURE XXXII  
SYNOL PROCESS



## XV. SYNOL PROCESS

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The I.G. have always held the view that Fischer Tropsch synthesis is more likely to be of value for the production of liquid products for use as chemical intermediates than as a source of fuels. Mainly from this standpoint they have been working on the Fischer Tropsch process and modifications of it since 1925. The particular modification designated "The Synol Process" is a development made by Dr. Wenzel in which the I.G. have been interested since 1940. The process consists essentially of the reaction of a carbon monoxide hydrogen mixture (ratio of 1 CO : 0.7/0.8 hydrogen) at 18-25 ats and a temperature of 190 - 200 C over a sintered iron catalyst such as is used for ammonia synthesis. The liquid product consists principally of alcohols and hydrocarbons, the former being thought to consist entirely of straight chain primary alcohols.

### Synthesis Gas:

The synthesis gas used in the Synol Process is made at Leuna by the addition to water gas of carbon monoxide obtained from the copper liquor carbon monoxide removal plant which operates in conjunction with the main ammonia and hydrogenation systems. In the absence of this source of carbon monoxide, it was intended to produce a synthesis gas of the required composition by gasification of coke with carbon dioxide and oxygen.

### Scale of Operations:

The full commercial-scale development of the Synol Process was not complete. Some 25 small laboratories and pilot plant units, ranging in size from .2 - 36 litres catalyst capacity, had been operated to study the relative merits of multi-stage versus single-stage and gas recycle versus straight-through operating conditions. A four-stage unit consisting of 100-litre tubular reactors and with a capacity of 3-5 tons/month of liquid product had been erected and operated for 9 months in order to give pilot plant-scale data of various possible multi-stage processes. A second pilot plant consisting of a single plate-type reactor with a capacity of 10-15 tons/month of liquid product had also been erected for a further study of recycle operation. This plant had been shut down because of bomb damage before any serious work had been completed.

### Process Conditions:

Fig. XXXII is a line diagram of the process which it was proposed to operate in the large plate-type reactor. Feed gas, completely free from sulphur and containing only 1-3 mg. organic sulphur per cu. metre, together with 20 times its volume of recycle gas, is passed down-flow through the reactor at a space velocity equivalent to 110-120 vols. make up gas/vol. of catalyst per hour and at a pressure of 18 - 20 ats. When the catalyst is maintained at a reaction temperature of 185°C and the inlet and outlet temperatures of the reactor are controlled to within 1°C of this figure by means of circulating diphenyl. Diphenyl is used in place of water because of the difficulty of obtaining steel for pressure operation. As the catalyst activity falls, temperature is gradually raised so that at the end of three months it is expected to be 195 C. The estimated total life of a

catalyst is 9 months and at the end of this period the reaction temperature will probably have to be 210-225°C. The exit product from the reactor passes first to a wax separator in order to prevent plugging of the cooler parts of the plant with soft wax and thence to a heat exchanger where it gives up heat to the recycle gas. The heat exchanger exit temperature is carefully controlled so that no water is condensed or separated at this stage. Otherwise, excessive acid corrosion results. From the heat exchanger it passes to an intermediate separator where higher boiling liquid products are collected and then, via a cooler to a cold separator where C<sub>6</sub> and heavier hydrocarbons and alcohols are collected. Just before the products enter the cooler a caustic soda solution is injected into the stream in order to guard against acid corrosion. The exit gas from the separator, apart from a small purge equivalent to 30% of the fresh make up gas, is recycled via the heat exchanger and a gas heater to the reactor. The vent gas, which provides a purge for CO<sub>2</sub> from the system, is passed through an ammonia cooler and an activated carbon absorber in order to recover light hydrocarbons.

An alternative method of operation, which, according to Dr. Gemassmer, was latterly considered to be the most likely scheme to be adopted for large scale operation, is shown in Fig. XXXIII. This is a two-stage process with gas recycle and, like the single-stage process described above, does not involve CO<sub>2</sub> removal between the stages. In this method of operation, very high gas velocities are employed. Fresh gas is introduced at the rate of 100-150 vols./vol. of catalyst and the recycle rate is 50:1 in both first and second stages. Approximately 65% of the fresh gas is converted in the first stage and 25% in the second, giving an overall conversion of 90%.

When working under straight-through gas conditions and with multi-stage conversion, it appears necessary to remove CO<sub>2</sub> between the stages. This introduces the difficulty that alcohols are lost by water solution in the CO<sub>2</sub> removal step. It was stated that a two-stage process, as described above, gives approximately the same yields as a four-stage process operated without recycle but with CO<sub>2</sub> removal.

#### Yields.

The optimum yield is estimated to be 155-165 gm. of primary liquid product per M<sup>3</sup> of hydrogen + CO. Very variable data was produced on the composition of this liquid product but it would appear to be of the following order:

Alcohols	35 - 50%
Olefines	25 - 40%
Paraffins	20 - 35%

30 - 40% of the crude product boils in the range 50 - 100°C, 35 - 40% in the range 100°C - 200°C, and 25 - 30% in the range 200 - 350°C. The alcohol content appears to be greatest in the range 150 - 200°C as shown by the following yields supplied by memory by Dr. Gemassmer:-

# SYNOL PROCESS - FIG. XXXIII

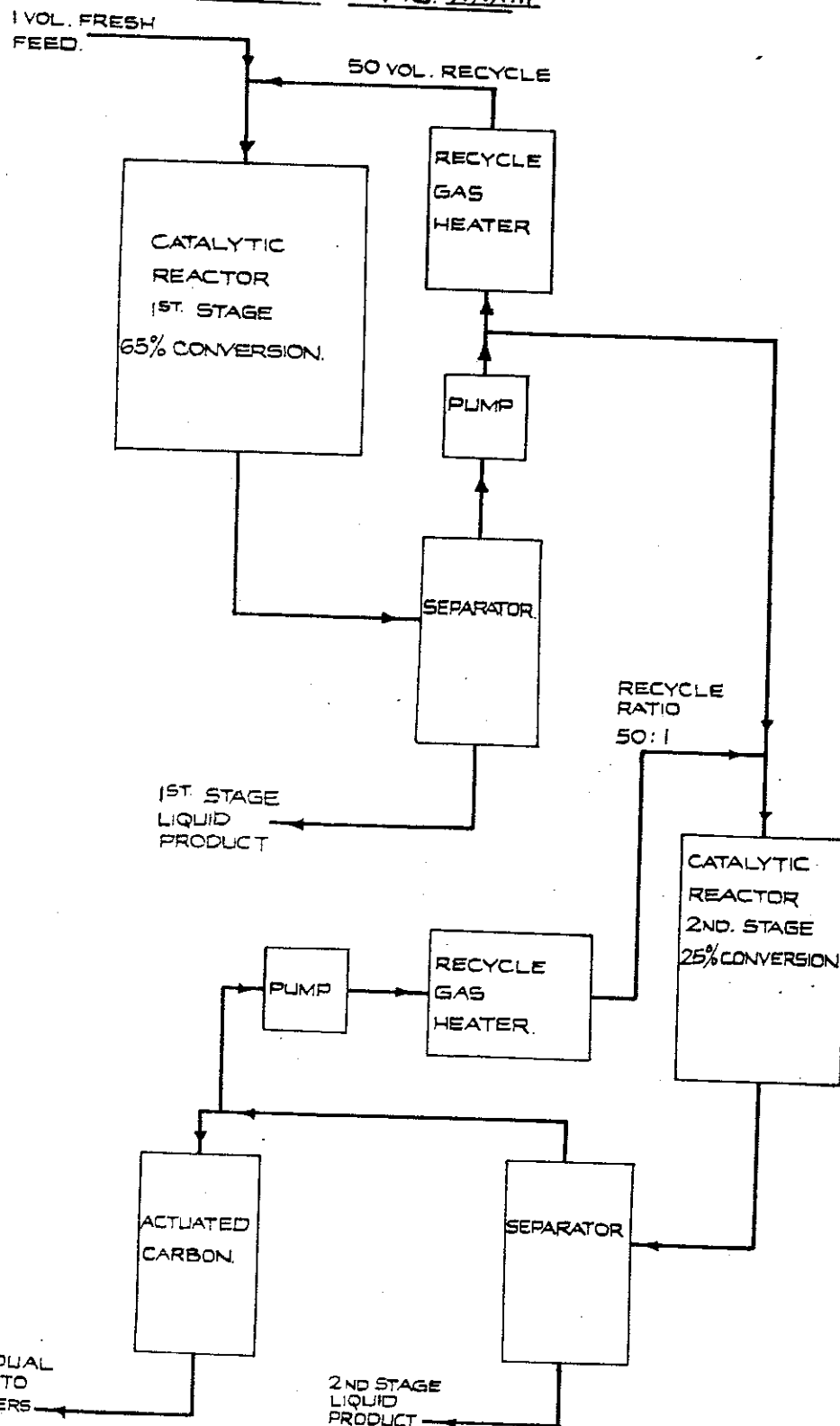
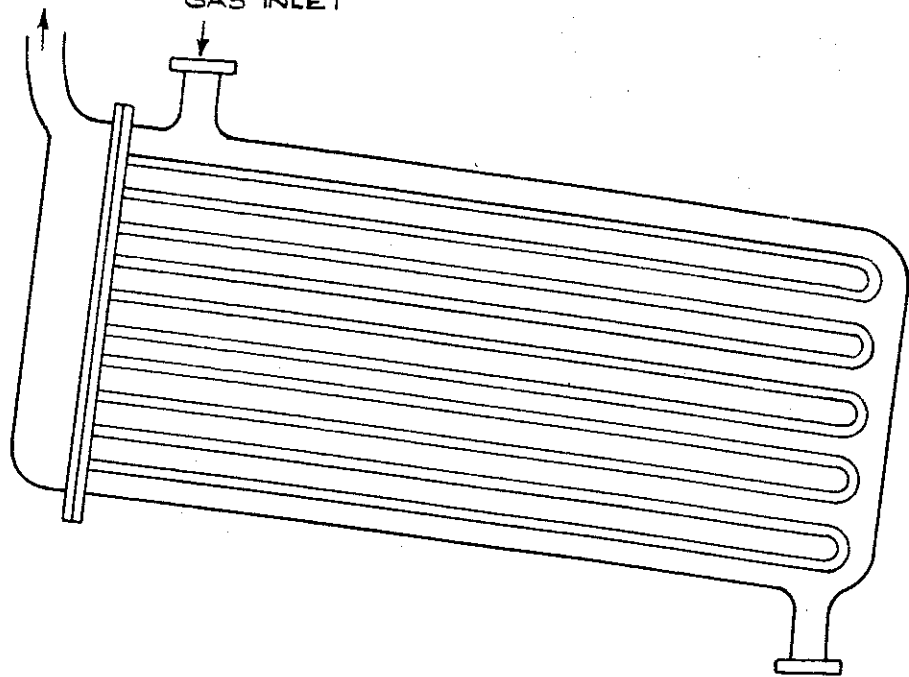


FIGURE XXXIV

PROPOSED DESIGN FOR SYNOL REACTOR

TO STEAM  
ACCUMULATOR

GAS INLET





<u>Temp. Range</u> °C.	<u>Alcohol</u>	<u>Sat. Hcs.</u>	<u>Olefine Hcs.</u>
to 150	20	40	40
150-200	70	15	15
200-300	50	20	30
over 300	30	42	28

The main essential for maintenance of a good yield appears to be high space velocity involving a low conversion per pass and a low reaction temperature. Low space velocities lead to the reaction of carbon monoxide and water formed in the reaction, and high temperatures produce iron carbonyl and also appear to lead to carbon deposition due to reaction of hydrogen and carbon monoxide.

#### Design of Reactors.

Neither tubular nor plate reactors used in the latest Leuna pilot plants were considered to be entirely satisfactory. The principal disadvantage of both was that during operation the catalyst caked badly and was very difficult to remove. In the case of the tubular reactor which was made up of 14 mm. I.D. tubes spaced 26 mm. centre to centre, it was found necessary to use an electric drill to remove the catalyst. Similarly, the plate reactor, which was essentially similar in design to the Fischer Tropsch atmospheric pressure converter, had to be dismantled and the catalyst drilled and chiselled from between the plates. It had been decided to construct a reactor of the type shown in Fig. XXXIV. The catalyst was to be packed between the cooling tubes which were to contain water under pressure. It was considered that when it was necessary to remove spent catalyst, the flange could be unbolted, the inlet and outlet connections dismantled, and the whole case removed, thereby exposing the catalyst which could be relatively easily knocked from between the cooling tubes.

#### Catalyst Preparation:

The catalyst is prepared by placing 19 kgs. of iron from a wood charcoal preparation in a shallow water-cooled iron pan 50 cm. in diameter and 15 cm. high. Pure oxygen, supplied by two nozzles, is directed toward the mass which melts in 10 minutes. 16 kgs. of aluminium nitrate, 4 kgs. of potassium nitrate and 2 litres 66° Be nitric acid is added along with 2-4 litres of water. The mixture is boiled until solid, and melting is continued from there on for 30 minutes. The melt is poured out on an iron pan and allowed to cool slowly. It is then broken up into granules (1-3 mm) while the dust is remelted electrically.

The following is the final analysis of the catalyst:

2.5%	Al <sub>2</sub> O <sub>3</sub>
0.2-0.6%	K <sub>2</sub> O
0.16%	S
0.05%	C
97%	Fe <sub>3</sub> O <sub>4</sub>

The apparent catalyst density is 2.0.



The catalyst is reduced batchwise with pure hydrogen (less than 0.502 of sulphur per  $M^3$ ) as shown in the simplified diagram, Fig. XXXV. The pressure is substantially atmospheric and the reduction temperature usually about 450°C. The reduction temperature does not appear to be critical; a range 380° - 650°C was stated to be satisfactory. The essential features of the catalyst reduction were said to be (a) a maintenance of a high hydrogen rate corresponding to a minimum linear velocity of 20 cms/second and a minimum space velocity of 2,000 l/hour per litre of catalyst, and (b) efficient drying of the recycle and make up hydrogen.

The recycle hydrogen leaving the reduction oven contains 1-2 gms water  $M^3$ . It passes through a water cooler at 20°C, an ammonia cooler at 4°C and after mixing with fresh hydrogen, goes through a silica gel dryer.

The time required for reduction of a batch of catalyst is about 50 hours. Absence of water in the exit gas is used as a criterion of completion of reduction.

After reduction and cooling to 50°C the catalyst was blanketed with  $CO_2$  and transferred to smaller steel containers. From these the catalyst, in a  $CO_2$  atmosphere, was measured into glass tubes which were used to charge the reaction tubes individually, so that exactly the same amount of catalyst was present in each tube, especially since the tubes were often only partially filled. This was to ensure equal pressure drop through each tube and therefore provide equivalent gas flow in each.

The used catalyst could be regenerated only by remelting and rereducing after which it operated at a higher reaction temperature (225 to 250°C) and the product contained a smaller percentage of alcohols.

Except for the reduction part of the catalyst preparation, the catalyst employed for the Synol process is exactly the same as that used for the ammonia synthesis at Leuna.

#### Work up of Crude Synol Product:

The method proposed for the separation of alcohols from the crude Synol product depended on the formation of boric acid esters. A flow diagram of this process is shown in Fig. XXXVI. The crude product is fractionated into 50-60° boiling range cuts which are worked up separately.

The esterification is carried out with solid boric acid present in slight excess of the theoretical requirement. The mixture is heated to 95-120°C at atmospheric pressure. The water formed, together with some of the lower boiling hydrocarbons has to be continuously removed as overhead. The secret of the esterification process was stated to be the complete removal of water as formed. The residual mixture of esters and hydrocarbons is then distilled at atmospheric pressure or under vacuum if this is necessary, in order to avoid ester decomposition. This separation of hydrocarbons and esters by distillation is a simple matter as will be seen from the following boiling range figures for charge and esters:

FIG. XXXV

SYNOL PROCESS - CATALYST REDUCTION.

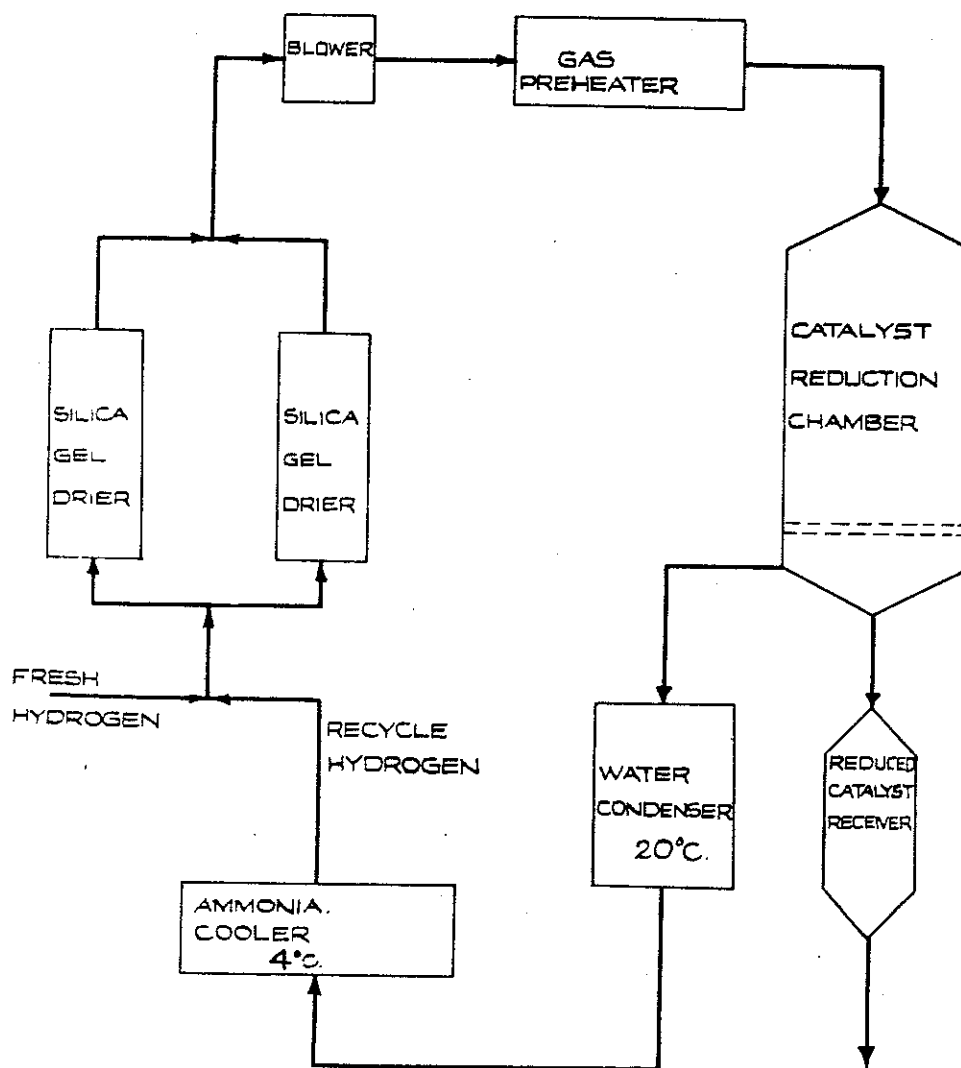
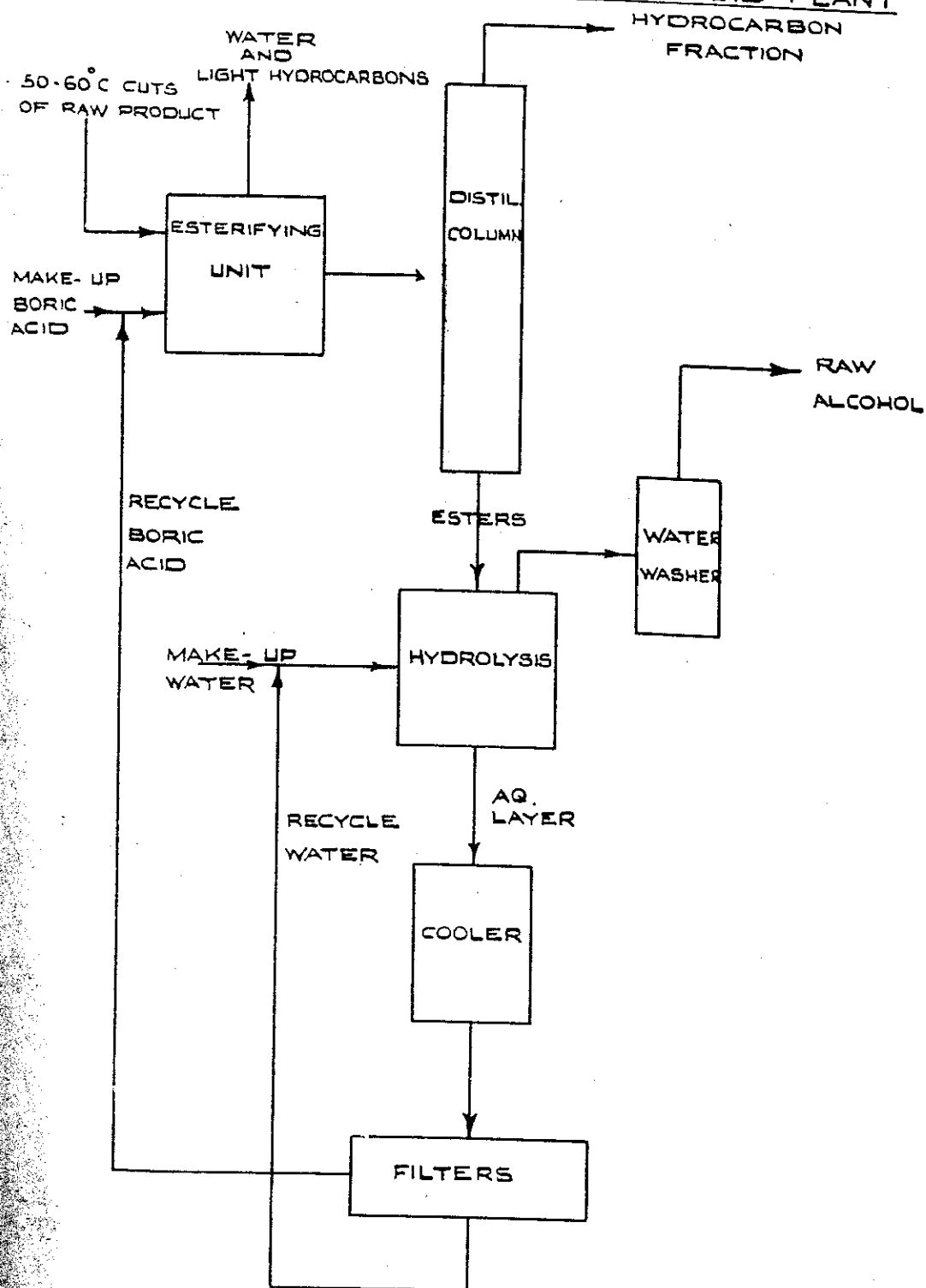


FIGURE XXXVI  
SYNOL PROCESS - BORIC ACID PLANT



Boiling Range of Charge

160 - 220°C

270 - 274°C

Boiling Range of Esters

280 - 340°C

490 - 494°C

The esters are stable up to about 300°C at atmospheric pressure.

The separated esters are mixed with recycle dilute boric acid solution and hydrolysed by heating to 95 - 120°C. The hot mixture of alcohols and boric acid (16 - 17%  $H_3BO_3$ ) separate into two layers and the upper alcohol layer is water washed and re-distilled. The boric acid solution is cooled to 5°C and the boric acid crystals filtered off for recirculation to the esterification stage. The filtrate is recycled to the hydrolysis stage.

In addition to the authors, Major A. J. V. Underwood contributed notes and these were of very great assistance in compiling the above report.