XV. SYNOL PROCESS.

Introduction:

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.
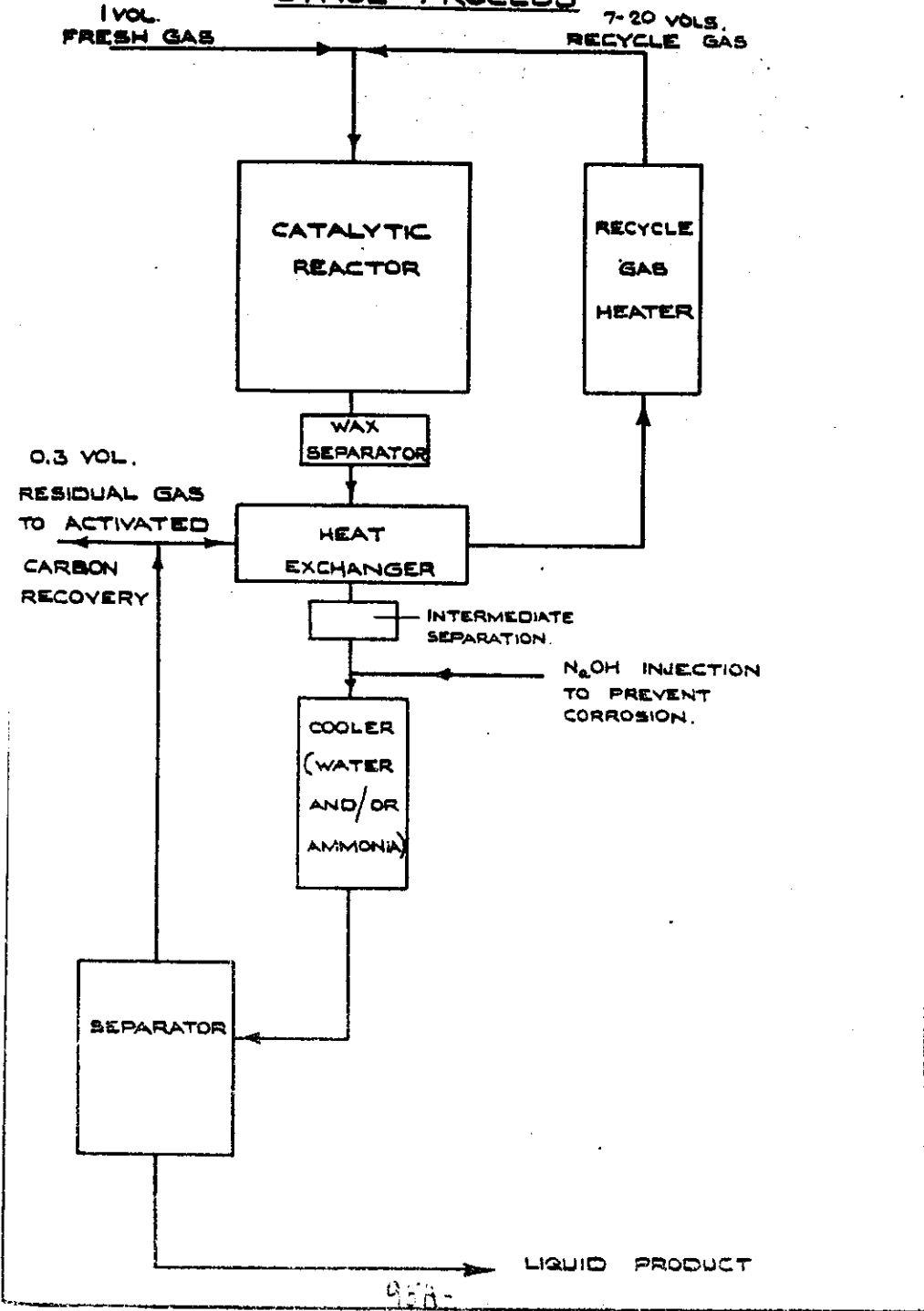
Synthesis Gas:

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.
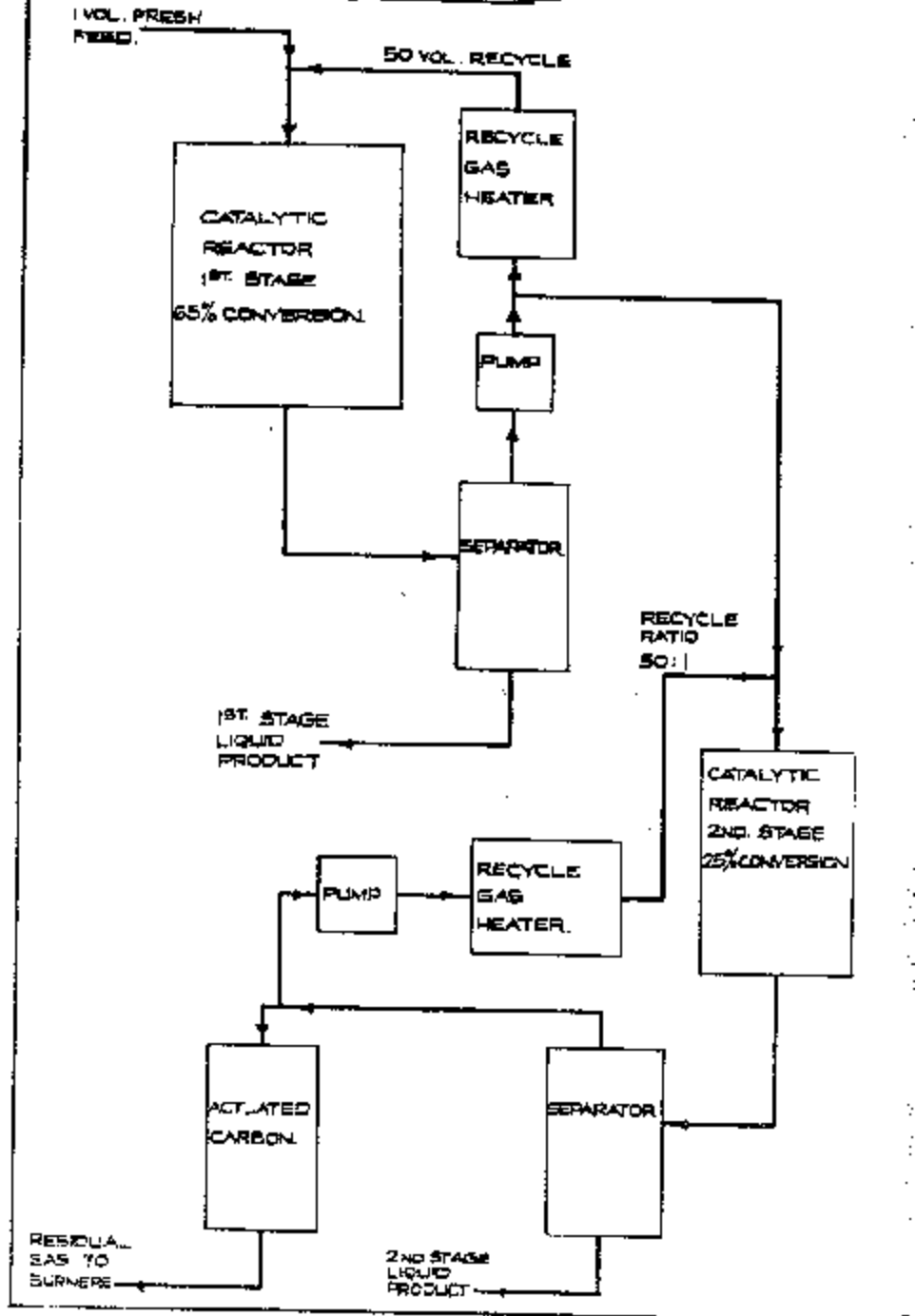
Scale of Operations:

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.

FIGURE XXXII
SYNOL PROCESS

1 VOL. FRESH GAS

7-20 VOLS. RECYCLE GAS

CATALYTIC REACTOR

RECYCLE GAS HEATER

WAX SEPARATOR

0.3 VOL. RESIDUAL GAS TO ACTIVATED CARBON RECOVERY

HEAT EXCHANGER

INTERMEDIATE SEPARATION

N_aOH INJECTION TO PREVENT CORROSION.

COOLER (WATER AND/OR AMMONIA)

SEPARATOR

LIQUID PRODUCT

SYNOL PROCESS - FIG XXXIII

I VOL. FRESH FEED.

50 VOL. RECYCLE

CATALYTIC REACTOR 1ST. STAGE 65% CONVERSION

RECYCLE GAS HEATER

PUMP

SEPARATOR

RECYCLE RATIO 50:1

1ST. STAGE LIQUID PRODUCT

CATALYTIC REACTOR 2ND. STAGE 25% CONVERSION

PUMP

RECYCLE GAS HEATER.

ACTIVATED CARBON.

SEPARATOR

RESIDUAL GAS TO BURNERS.

2ND STAGE LIQUID PRODUCT

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 H_2S and containing only 1-3 mg. organic sulphur per cu.metre, together with 7 - 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 new it 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_6 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_2 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_2 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%.

FIGURE XXXIV

PROPOSED DESIGN FOR SYNOL REACTOR

TO STEAM
ACCUMULATOR

GAS INLET

PRODUCT
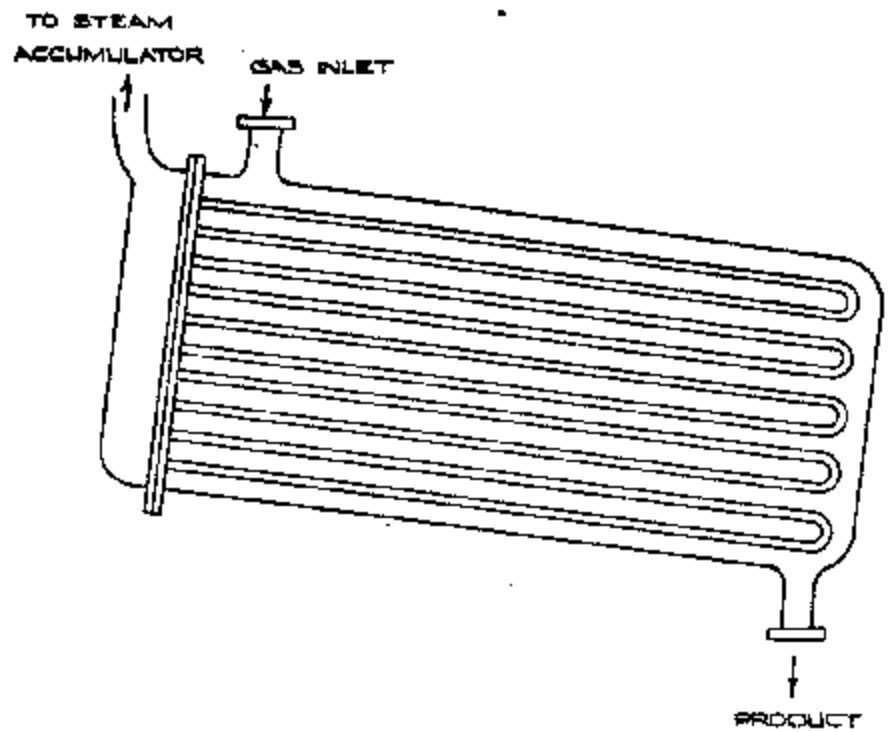
When working under straight-through gas conditions
and with multi-stage conversion, it appears necessary to remove
CO_2 between the stages. This introduces the difficulty that
alcohols are lost by water solution in the CO_2 removal step.
It was stated that a two-stage process, as described above, gives
approximately the same yields as a four-stage process operated
without recycle but with CO_2 removal.

Yields.

The optimum yield is estimated to be 155-165 gm. of
primary liquid product per M^3 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° - 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:-

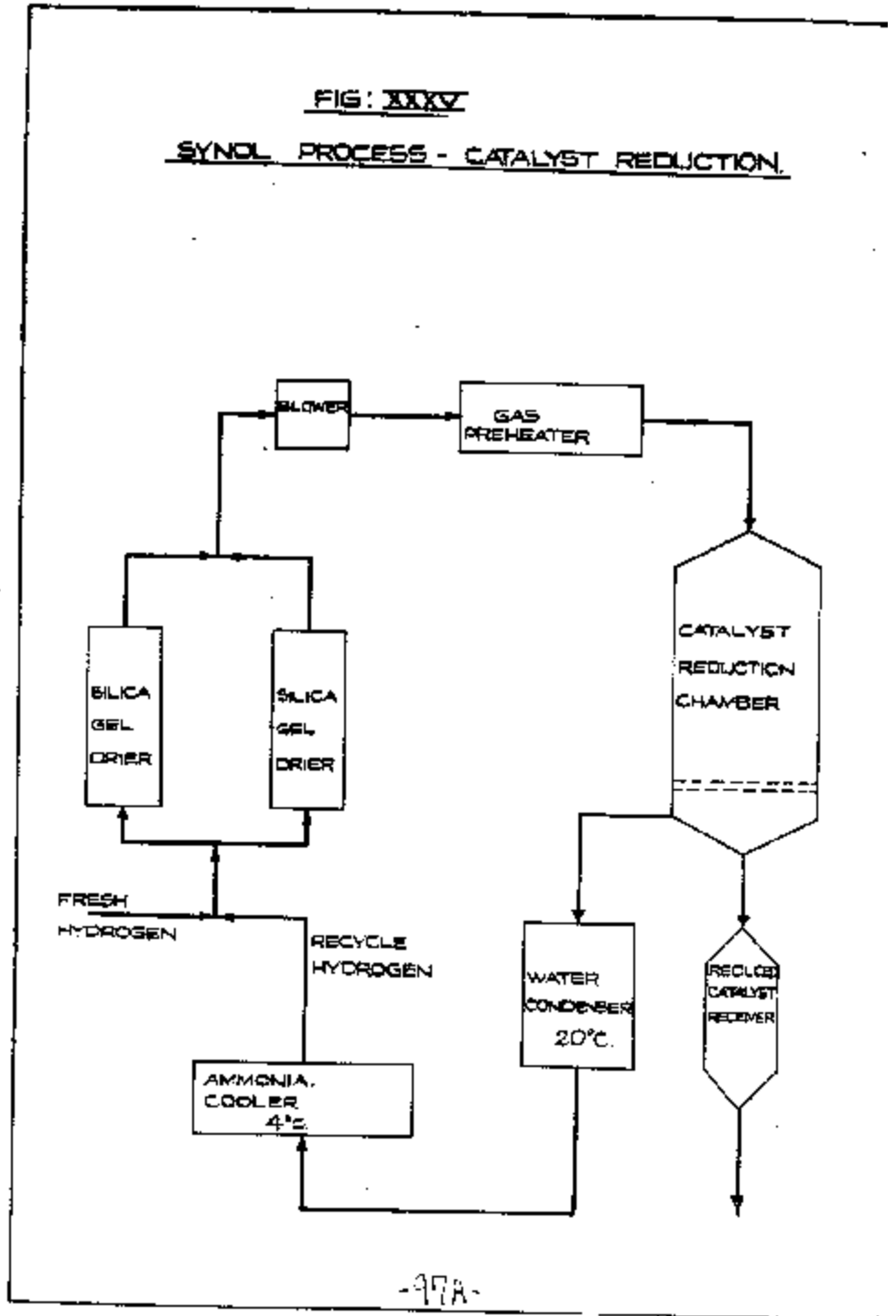| Temp. Range. °C.	Alcohol	Sat. Hcs.	Olefine Hcs.
to 150	20	40	40
150-200	70	15	15
200-300	50	20	30
over 300	30	42	28

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

FIG: XXXV

SYNOL PROCESS - CATALYST REDUCTION.

BLOWER

GAS
PREHEATER

CATALYST
REDUCTION
CHAMBER

SILICA
GEL
DRIER

SILICA
GEL
DRIER

FRESH
HYDROGEN

RECYCLE
HYDROGEN

WATER
CONDENSER
20°C.

RECLCE
CATALYST
RECEIVER

AMMONIA.
COOLER
4°c.

-97A-

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° Bé 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:

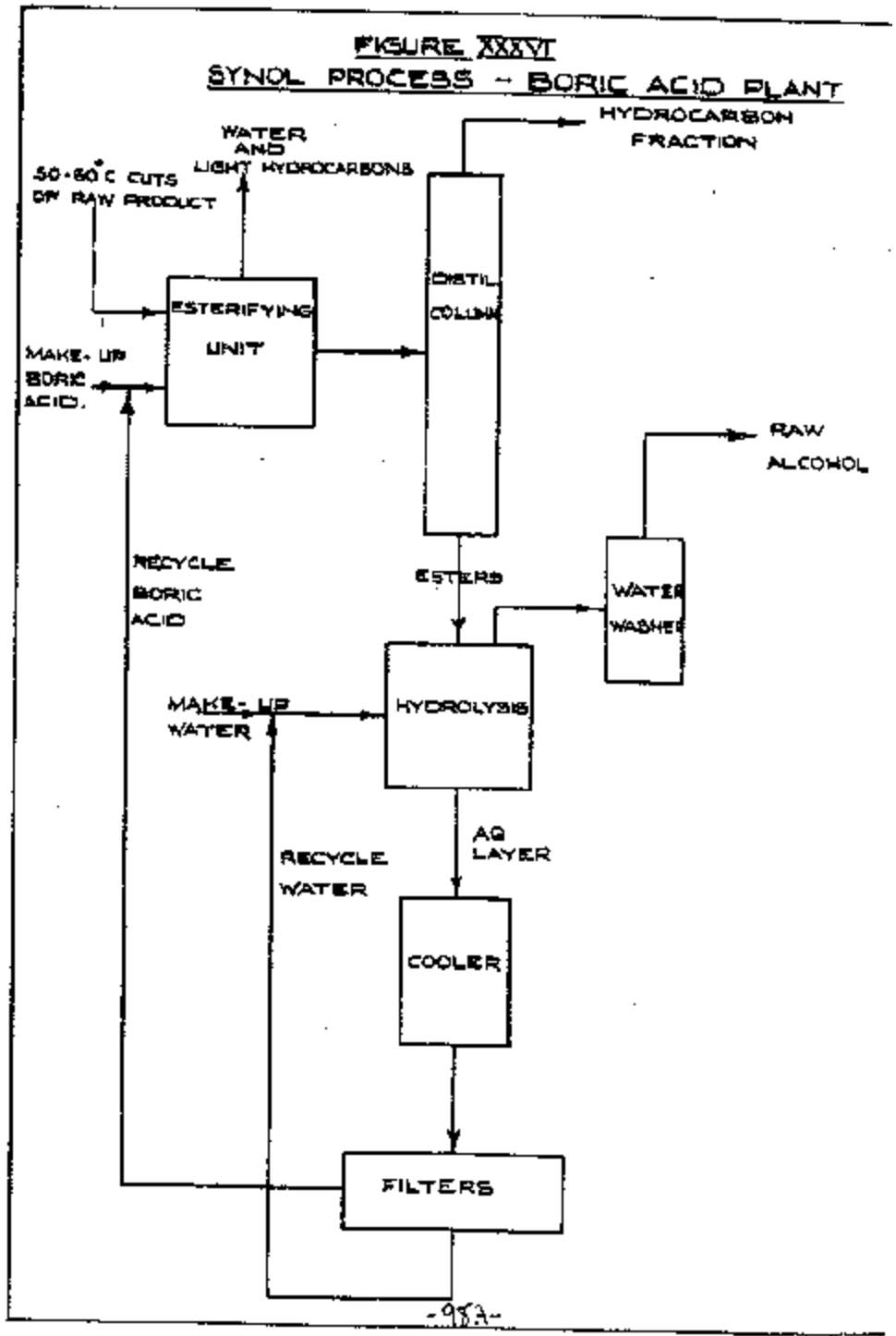|	
2.5%	Al_2O_3
0.2-0.6%	K_2O
0:16%	S
0.03%	C
97%	Fe_3O_4

The apparent catalyst density is 2.0.

The catalyst is reduced batchwise with pure hydrogen
(less than 0.02 mg. of sulphur per M^3) as shown in the
simplified diagram, Fig.XXXIV. The pressure is substantially
atmospheric and the reduction temperature usually about $450^\circ C$.
The reduction temperature does not appear to be critical; a
range $380^\circ - 650^\circ C$ 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 1/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 $20^\circ C$, an ammonia cooler at $4^\circ C$ and after mixing with fresh
hydrogen, goes through a silica gel dryer.

FIGURE XXXVI
SYNOL PROCESS – BORIC ACID PLANT

HYDROCARBON
FRACTION

WATER
AND
LIGHT HYDROCARBONS

50-60°C CUTS
OF RAW PRODUCT

MAKE-UP
BORIC
ACID.

ESTERIFYING
UNIT

DISTIL
COLUMN

RAW
ALCOHOL

RECYCLE
BORIC
ACID

ESTERS

WATER
WASHER

MAKE-UP
WATER

HYDROLYSIS

RECYCLE
WATER

AQ
LAYER

COOLER

FILTERS

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 $50^{\circ}C$ 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 $250^{\circ}C$) 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 $50-60^{\circ}$ 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 $95-120^{\circ}C$ 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:

Boiling Range of Charge	Boiling Range of Esters
$160 - 220^{\circ}C$	$280 - 340^{\circ}C$
$270 - 274^{\circ}C$	$490 - 494^{\circ}C$

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 (15 - 17% H_3BO_2) 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.