IX. DEHYDROGENATION OF BUTANE - ALKYLATION.

Introduction:

In the course of the visit to Leuna, information on catalytic butane dehydrogenation and alkylation of the resulting butylenes was obtained from Dr. Giessen, Dr. Hanisch and Dr. Strätz. Dr. Giessen is in overall charge of the manufacture of organic chemicals, alcohols and lubricating oils; Dr. Hanisch supervises the manufacture of methanol, isobutyl alcohol, amines, ester oils, synthetic lubricating oils and alkylate, as well as the manufacture of catalyst Dr. Strätz is in charge of the butane dehydrogenation and alkylation plants.

Summary of Operations:

The alkylation plant produced an average of 888 bbls. of finished alkylate per day, together with 20 bbls. of heavy alkylate and 72 bbls. of propane. The necessary amount of n-butylenes was obtained by charging 2640 bbls./day of n-butane (96%) to the dehydrogenation reactor yielding, after proper separation, 2510 bbls. of a butane/butylene mixture (533 bbls. n-butylenes, 1905 bbls. n-butane, 72 bbls. propane) as alkylation feed stock. The total amount of iso-butane (85%) charged to the alkylation step was 3797 bbls./day. The daily requirements of fresh gas to supplement the recycle gas were 558 bbls. of n-butane and 760 bbls. of isobutane. The isobutane-olefin ratio was about 6:1, the hydrocarbon-acid ratio was 1:1, and the acid consumption amounted to 1.2 lbs. of 96% H_2SO_4 per gallon of finished alkylate (45,700 lbs. of acid/day). The alkylation acid was discarded when the concentration had decreased to 50% H_2SO_4. A summary flowsheet of these operations is given in Fig. XVII.

Dehydrogenation:

The catalytic butane dehydrogenation was carried out at Leuna in 7 reactors of which 5 were operated simultaneously while one was inspected and repaired and one was held in reserve. The catalyst was regenerated in 4 regenerators. The reactor consists of a vertical firebrick-lined circular furnace containing 8 catalyst tube bundles with 16 tubes each. The tube bundles are arranged around an annular central heating space which is brick-lined in such a way as to form a Venturi tube which passes the heating gas into the upper part of the furnace from which it flows downwards around each of the reactor tube bundles. Heating gas is obtained by burning waste gas in a chamber situated below the central part of the furnace. The combustion gases are collected in a firebrick ring and thence leave the reaction chamber. Before leaving through the stack the combustion gases are used to preheat the n-butane feed. The flow of catalyst, n-butane and combustion

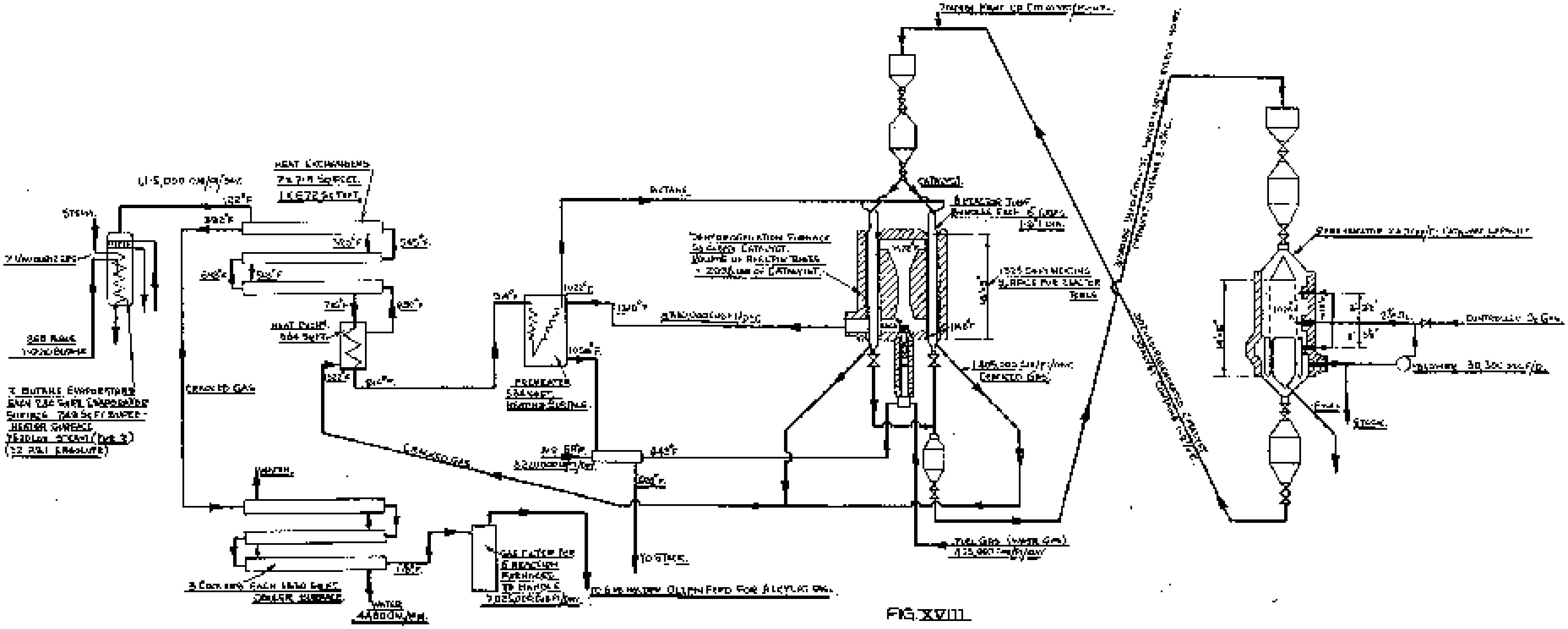


FIG. XVIII

BUTANE DEHYDROGENATION LEUNA WORKS AMMONIAKWERK MERSEBURG gases is concurrent, as illustrated in Fig. XVIII.

The tube bundles, which represent the reaction space proper, consist of 16 Sicromal-8 tubes (about 8% Cr, 1 - 2% Si) each of which has a diameter of 2.3/4" and a length of 26'3"; the tubes are arranged in a circle around a centre core which is dead space. The total catalyst capacity of each reactor is 81 cu.ft. The catalyst is introduced at the top of the reactor and distributed to the individual tube bundles by means of a cone. The catalyst moves downwardly through the tubes and the flow is controlled by means of 16 horizontal cylindrical pocket valves connected with bevel gears and driven simultaneously by an electric motor. A vertically-slotted tube (about 18" long) is placed between the reactor tubes and the pocket valves to permit separation of the reaction products from the catalyst. In the beginning catalyst flow was checked audibly by letting the catalyst drop on tuning forks and listening to the sound so produced by means of a stethoscope held to the outside of the reactor. This practice appears to have been found unnecessary and has been abandoned. The cylinders are filled with catalyst in the top position and are emptied by rotation to the bottom position. The catalyst is discharged into a catalyst receiver equipped with motor-driven slide valves at the inlet and outlet. The catalyst tubes are kept completely filled with catalyst by continuously replacing from the top hopper the catalyst discharged into the catalyst receiver. When the receiver is filled, the top slide valve connecting it with the reactor is closed and simultaneously the connection between the top catalyst hopper and the reactor is closed. The flow of catalyst through the tubes is thereby stopped but gas continues to flow through the reactor tubes which, of course, are full with catalyst. The catalyst in the receiver is stripped from hydrocarbons with nitrogen and transferred to the regenerator by means of a bucket conveyor and the top catalyst hopper is refilled in the same way with regenerated catalyst. The operation of the slide valves on the catalyst receiver and hopper are controlled by means of a photocell indicating when the catalyst receiver has been filled. The residence time of the catalyst in the reactor is 4 hours, during which time the catalyst moves for 3.5 hours and remains stationary for 0.5 hours; the time to transfer spent catalyst to the regenerator and simultaneously refill the fresh catalyst hopper consequently is 0.5 hours. Three catalyst charges of a total of 243 cu.ft. per reactor are kept in the dehydrogenation-regeneration system during operation and a catalyst make-up of 367 lbs./day/reactor is required.

In Fig.XX is shewn a photograph of the tops of two dehydrogenation reactors. The side arm, through which the catalyst enters a tube bundle, can be clearly seen in the foreground. In the background can be seen the inlet lines for the hot butane vapours.

Liquid n-butane (96% by wt. n-butane, 3% isobutane, 1% pentanes) is vaporised with indirect steam at 210°F and brought to a temperature of 932 - 1,022°F by heat exchange with the

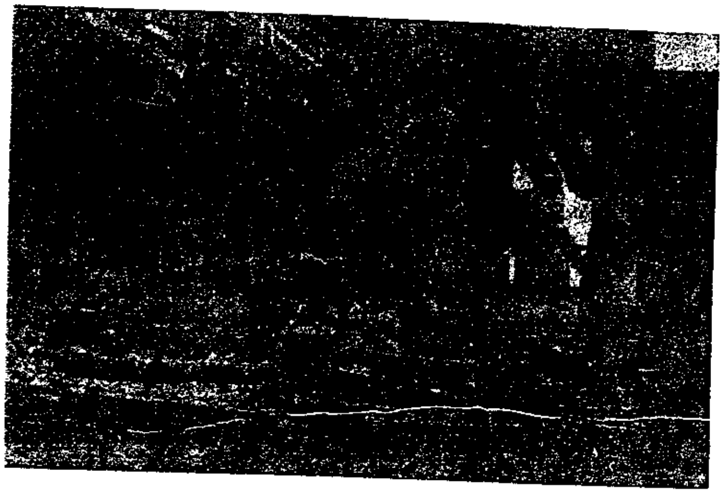


FIGURE XX

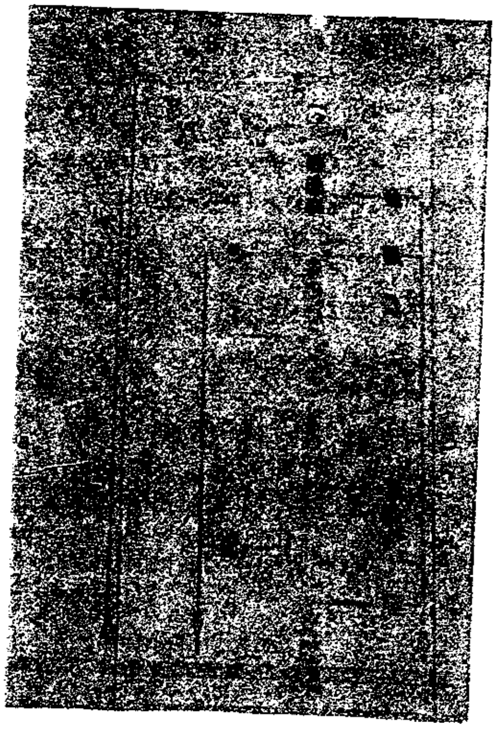


FIGURE XXI

product gas from the reactor and with combustion gases leaving the reactor. The preheated gas enters the reactor tube at the top and is heated to 1,040-1,076°F by combustion gases at about 1,472°F. The rate of gas flow is 680 cu.ft. of gas/cu.ft. of catalyst/hour. The conversion of n-butane amounts to 20-25% by wt. of which 85% is n-butylene (60% α-butylene, 40% β-butylene). The composition of the effluent gas is given as follows:-

74.2%	by wt.	n-butane
21.2%	" "	n-butylene
0.7%	" "	hydrogen
0.8%	" "	methane
0.9%	" "	C_2 hydrocarbons
2.2%	" "	C_3 "

The volume of the reacted gas has increased by 1.25 as compared to the n-butane feed. The dehydrogenated gas is cooled to 266 to 300°F by heat exchange and to about 100°F by indirect water cooling. It is then passed through a coke filter to remove high boiling hydrocarbons, mainly aromatics, as well as dust. The filter contains 231 cu.ft. coke and can be operated for 3-6 months. The gas is finally cooled indirectly to about 77°F and passed into a gas holder for immediate storage.

Catalyst Regeneration:

The spent catalyst contains about 3 - 4% carbon and is regenerated at 1,040-1,076°F to give a regenerated catalyst containing 1 - 2% carbon. The regenerator consists of a circular firebrick-lined vertical shell of about 9' diameter and 12' length. The catalyst is fed from a hopper over a conical distributor to the annular space formed by metal screens around a hollow centre duct. The catalyst space ends in 8 tubes which are provided with the same type of pocket valves for flow control as used in the reactor. The flue gas enters with a temperature of 932°F, passes through the catalyst where the heat of reaction raises the temperature to 1,040-1,076°F, flows into the centre duct which acts as dust separator and, by means of vertical slots, enters a collecting ring from where it leaves the reactor. The flue gas is circulated by means of a blower at a rate of 1,400,000 - 1,700,000 cu.ft./hr. The catalyst receiver and top hopper of the regenerator are equipped with motor-driven slide valves of the same design as the corresponding valves on the dehydrogenation furnaces. The catalyst hopper on top of the reactor is provided with vibrating screens for the removal of fines. The catalyst receiver is equipped likewise. A photograph of the control panel for one of the regenerators is shown in Fig.XXI. A detailed flowsheet of the dehydrogenation process is given in Fig.XVIII. It should be noted that this flowsheet has been prepared with the aid of design drawings for the dehydrogenation of isobutane since these were the only ones available. The dimensions of the equipment used in actual plant operation are somewhat different. The data and dimensions given in the descriptive part of the report are the actual figures for the plant as operated at Leuna.

Catalyst Manufacture:

The catalyst, which consists of activated alumina impregnated with 8% CrO_3 and 1 - 2% K_2O, is prepared as follows:-

Activated alumina is obtained by the precipitation of sodium aluminate with HNO_3. The precipitate is filtered, washed carefully and dried at about 226°F. It is then kneaded with HNO_3 in a stainless steel kneading machine, dried again and heated to 788-842°F. The material so obtained is mixed with such an amount of K_2CrO_4 that the mixture contains 8% CrO_3 and 1 - 2% KOH. Sufficient water is added to obtain a plastic mass which is pressed and subsequently formed into spheres of about ¼" diameter on a candy manufacturing machine (Frankonia machine). The spheres are dried in air, further dried in a steam chest and finally heated to 752 - 842°F. The finished catalyst is classified and only the material representing spheres is used; plugging of the catalyst tubes, which results in excessive carbon formation, is thereby prevented.

Preparation of alkylation feed stock.

The exit gas from the dehydrogenation is picked up from intermediate storage and compressed to 118 psi. It is then cooled indirectly with water to about 77°F and subsequently cooled with brine to 41°F. The material liquefied under these conditions is stored and represents the olefin feed stock for the alkylation. The composition of this butane-butylene mixture is as follows:

22% by wt. butylenes
75.5% " " n-butane.
2.5% " " propane.

The uncondensed portion of the gas is passed into an absorber and washed with oil at 118 psi and 50°F. The composition of the non-absorbed gas is as follows:

Approx. 80 - 85% by vol. H_2
" 12 - 15% " " CH_4
" 3 - 5% " " C_2^+ hydrocarbons

The absorber is jacketed and is cooled by circulating brine of 41°F through the jacket. The gas stripped from the fat absorption oil is returned to the compressor and recycled. High pressure steam (175-220 psi) is used for heating the absorption oil regenerator.

The mixture of butanes, which is the starting point for alkylate manufacture, is furnished by the high pressure hydrogenation plant. This mixture contains an excess of normal butane and a portion of

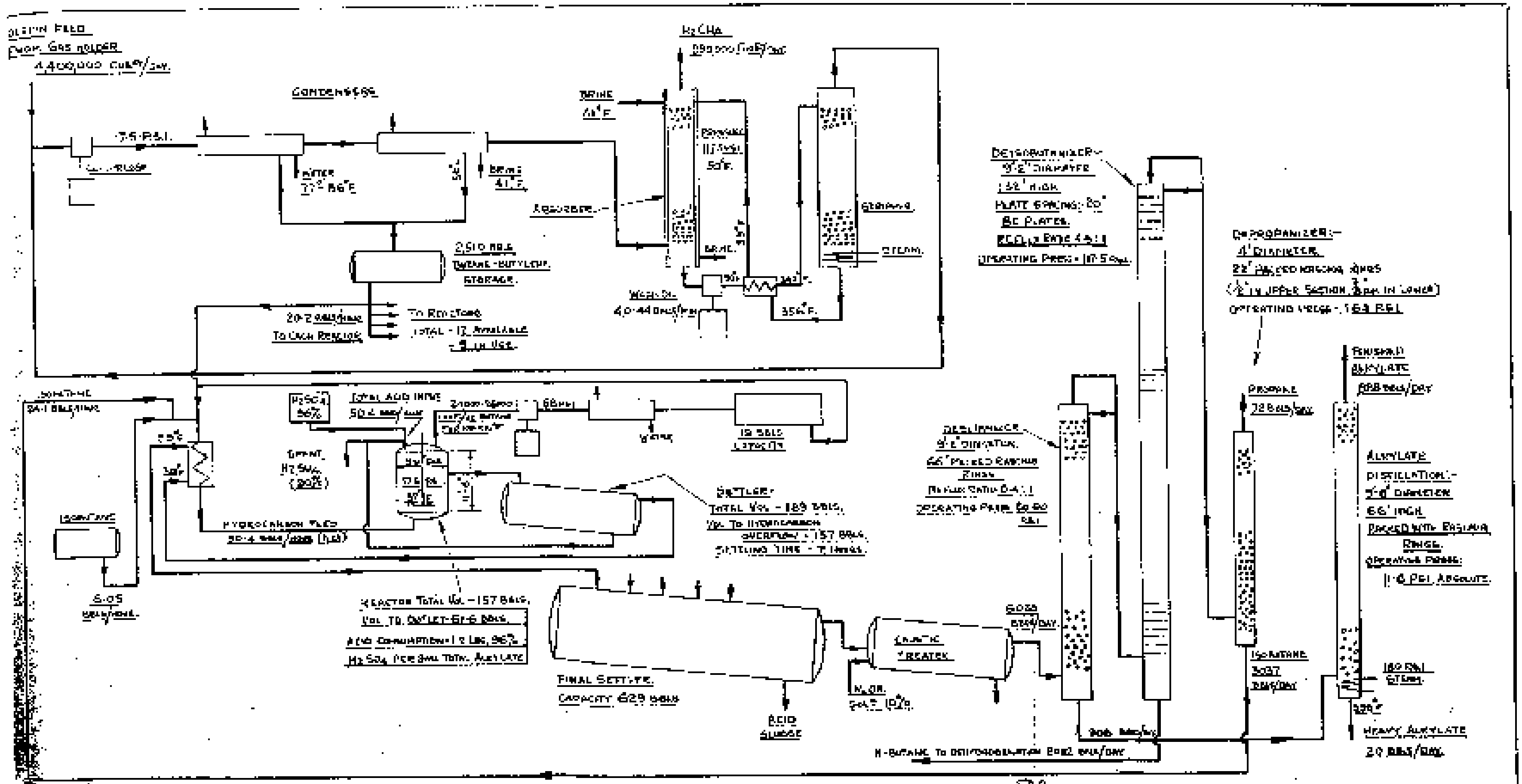


FIG. XIX SULPHURIC ACID ALKYLATION, AMMONIAKWERK MERSEBURG LEUNA WORKS.

to isobutane in the isomerisation plant discussed in another section. The material balance of Fig.XVII does not take into consideration the operation of an isomerisation unit, since it is a small proportion of the circulating normal butane.

Alkylation:

The alkylation reactors are insulated vertical cylindrical vessels, 11'6" high, with a capacity of 157 bbls. There was a total of 12 reactors, in two groups of six each, housed in adjoining buildings to protect them from bomb damage. One group has been destroyed by bombing but the other group is undamaged. The volume of a reactor up to the emulsion outlet is 61.5 bbls., and the reactor is equipped with a motor-driven stirrer with a blade 32" long rotating at 120 r.p.m. The rate of feed is 50 bbls. of hydrocarbon and 50 bbls. of acid per hour. The feed is cooled by heat exchange to 46°F and the temperature of the reaction mixture is maintained at 32°F by evaporation of butane and maintaining the pressure in the reactor at 7 psig. About 230,000-250,000 cu.ft./hr. of butane are circulated for refrigeration. Sulphuric acid containing 96% H_2SO_4 is used and the concentration of the spent acid is maintained at 90% H_2SO_4 by periodic withdrawal (every 3 hours) of spent acid. The acid consumption amounts to 1.2 lbs. 96% acid per gallon of alkylate. The isobutane-olefin ratio is maintained at about 6:1. The residence time in the reactor is 40 minutes.

The composition of the reactor effluent is as follows:

42.8%	by wt.	iso-butane
41.0%	" "	n-butane
15.0%	" "	alkylate
1.2%	" "	propane

The acid-hydrocarbon emulsion is allowed to settle for 2 hours in a settler of a total capacity of 188 bbls. and a capacity up to the overflow of about 157 bbls. The hydrocarbon effluent then passes through a heat exchanger where its temperature is raised to 59°F by exchange with the alkylation feed and enters a final settler (capacity 630 bbls). Subsequently, the hydrocarbon mixture is washed with caustic (10% NaOH solution) and fractionated in the usual manner. The debutanizer consists of a tower of about 9' diameter packed with Raschig rings to a height of about 65'. The tower is operated at a pressure of 59-99 psi and a bottom temperature of 356°F obtained with indirect steam. The reflux ratio is maintained at 0.4:1. The separation of n-butane and iso-butane takes place in an 80 plate tower of 9' diameter and 130' height; The distance between the plates is about 20". This tower is operated under a pressure of 118 psi and a reflux ratio of 4.5:1. The bottom product represents 96% n-butane. The overhead is passed into the depropanizer which is

FIGURE XXII

Low voltage KWH/barrel of Alkylate	Circulating water gals/barrel of Alkylate.	Make up water gals/barrel of Alkylate.	Fuel Gas BTU/barrel of Alkylate	Labour		
				Foremen.	Lab. Technician	Proces Workm
11.1	646	-	937,000	4		35
1.4	2,530	-	-			
8.2	3,840	-	-	3		20
2.7	3,840	27	-	4		28
2.7	3,840	27 147*			1	
25.1	14,696	201	937,000	11 +3 machinists 14	1	83

TABLE VIII

Operation	High pressure steam (176-220 psi), lbs/barrel of Alkylate.	Low pressure steam (37 psi) lbs/barrel of Alkylate.	Power high voltage KWH/barrel of Alkylate.
Dehydrogenation	-	320	-
Compression of dehydrogenated gas and absorption unit.	35	-	23.2
Alkylation, including Refrigeration.	** 1,225	-	-
Butane-isobutane separation, Depropanizer.	-	1,100	-
Debutanizing of Alkylate, distillation of alkylate.	302	382	* 18.5
TOTAL	1,562	1,802	41.7

** for butane refrigeration

* for water circulation.

a packed tower of 4' diameter and 20' of packed height. The packing consists in the upper section of Raschig rings of $\frac{1}{2}$" diameter and in the lower section of rings of 1" diameter. The operating pressure is 265 psi. The bottom product has the following composition:-

85% by vol. iso-butane
12% " " n-butane
3% " " propane.

The alkylate is distilled under vacuum in order to make it possible to use steam (175-220 psig) as heating medium. The distillation is carried out at a pressure of 11.6 psia and bottom temperature about 350°F in a tower of about 5'6" diameter and a height of about 65'; the tower is packed with Raschig rings.

A flowsheet of the alkylation process is shown in Fig.XIX. A photograph of an alkylation reactor is presented on Fig.XXII.

Alkylate Quality:

The alkylate produced has the following properties:

IBP	185°F
80-85%	248°F
E.P.	392°F

Reid vapour pressure below 7.4 lbs.
Octane No.93-94
(Research)

Alkylate production in Germany:

The Leuna alkylation plant was designed for an annual production of 50-60,000 tons (445,000 to 533,000 bbls) but the actual production averaged only 36,000 tons per year (320,000 bbls.)

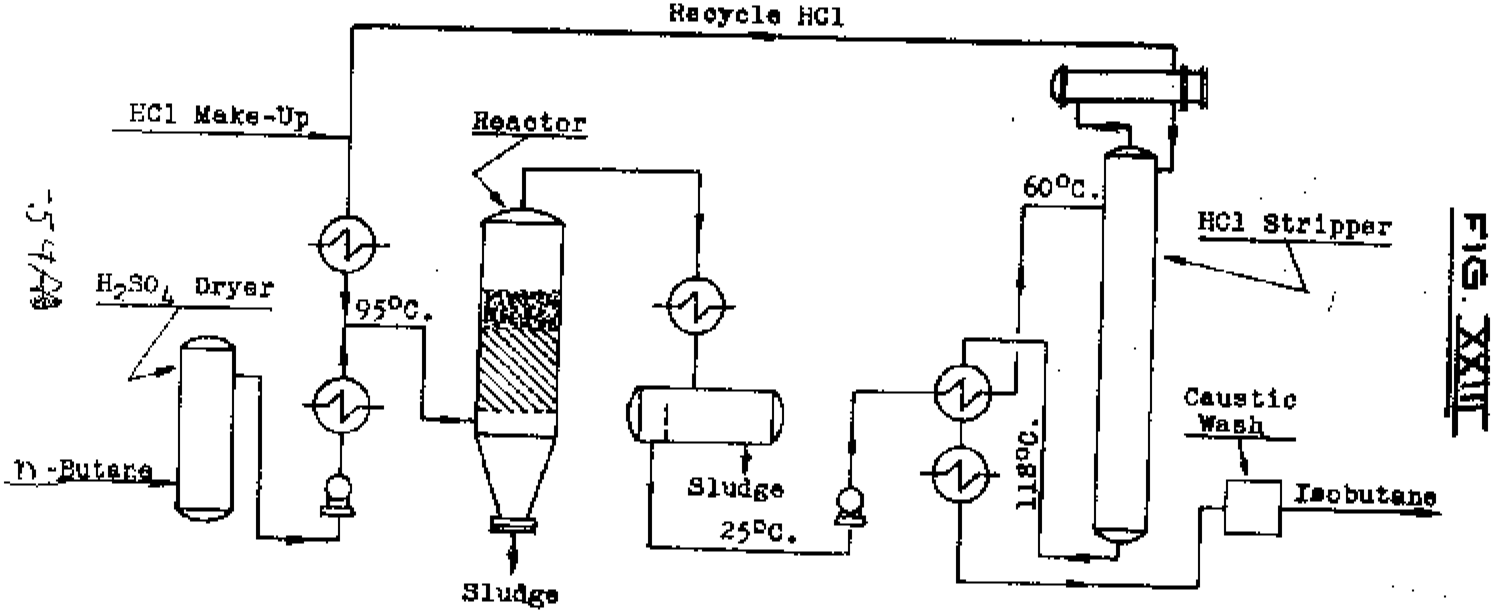
The only other German alkylation plant which was completed and in operation was at Scholven. This unit operated only for 6 months in 1944 and during this time its rate of production was the same as the actual rate of production at Leuna (2-3,000 tons/month, 17,800 - 26,800 bbls./month).

The Leuna plant started operations in Spring, 1942, and ceased operation in December 1944. The butane dehydrogenation equipment has not been extensively damaged. Half of the alkylation reactors, and auxiliary equipment, has been completely destroyed together with most of the tankage serving the entire unit. The fractionation section appears to be intact.

Economics of Leuna operation:

Data on energy and labour requirements for butane dehydrogenation and alkylation were provided by the foreman of the plant, Dr.Strätz, and are given in Table VIII. The photographs were taken by J.P.Jones.

FIG. XXIII



FLOW DIAGRAM - BUTANE ISOMERIZATION PROCESS

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