

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 intermediate 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 c.f./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 actual figures for the plant as operated at Leuna.

#### Catalyst Manufacture:

The catalyst, which consists of activated alumina impregnated with 8%  $\text{CrO}_3$  and 1 - 2%  $\text{K}_2\text{O}$ , is prepared as follows:-

Activated alumina is obtained by the precipitation of sodium aluminate with  $\text{HNO}_3$ . The precipitate is filtered, washed carefully and dried at about 220°F. It is then kneaded with  $\text{HNO}_3$  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  $\text{K}_2\text{CrO}_4$  that the mixture contains 8%  $\text{CrO}_3$  and 1 - 2% KOM. Sufficient water is added to obtain a plastic mass which is pressed and subsequently formed into spheres of about 1/4" 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.

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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% by wt. 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<sub>2</sub>  
 " 12 - 15% " " CH<sub>4</sub>  
 " 3 - 5% " " C<sub>2</sub> 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 this excess, separated from the alkylation effluent, is isomerised 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<sub>2</sub>SO<sub>4</sub> is used and the concentration of the spent acid is maintained at 90% H<sub>2</sub>SO<sub>4</sub> 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 about 157 bbls. The hydrocarbon effluent then passes through a heat exchanger where its temperature is raised to 59°F by exchange where the alkylation 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 59-99psi 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 a packed tower of 4' diameter and 20' of packed height. The packing consists in the upper section of Raschig rings of 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 in 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

OLEFIN FEED  
FROM GAS HOLDER  
4,400,000 CUB.FT/DAY.

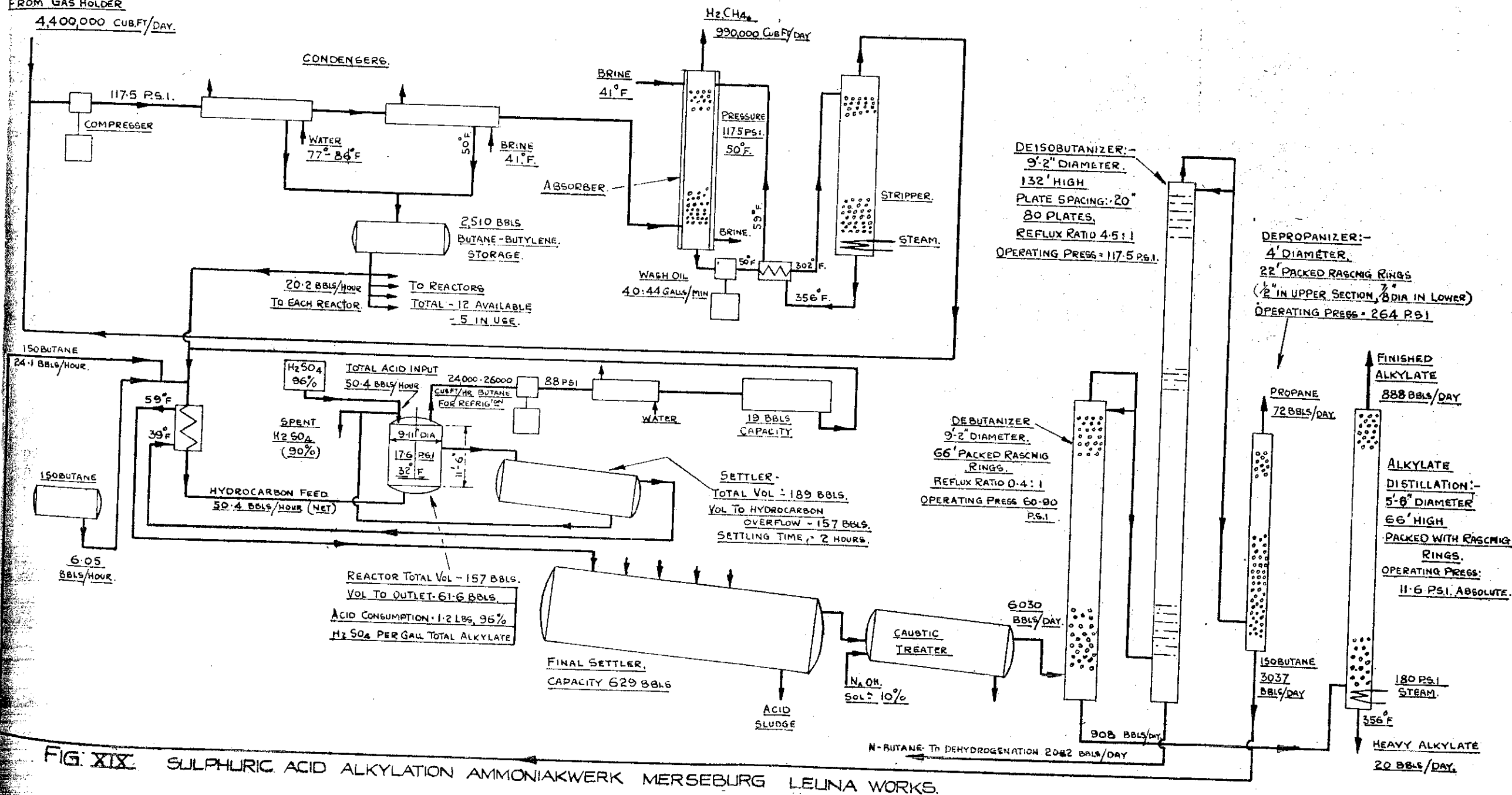


FIG. XIX. SULPHURIC ACID ALKYLATION AMMONIAKWERK MERSEBURG LEUNA WORKS.

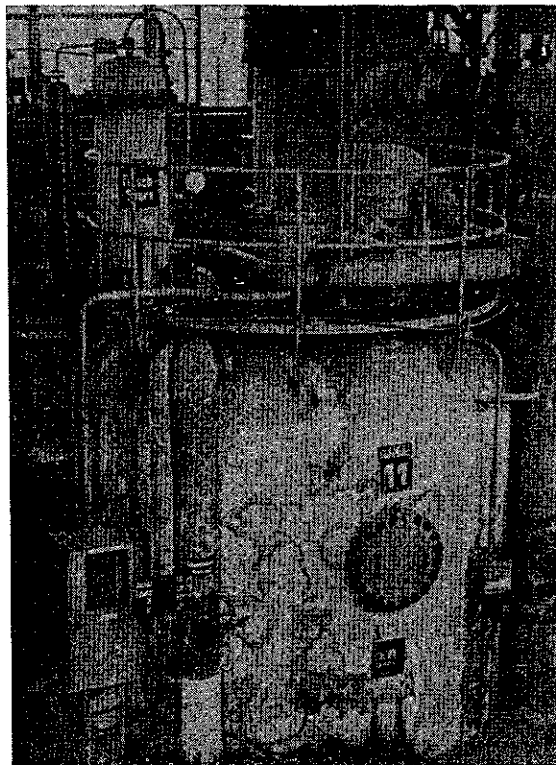


FIGURE XXII

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. Stratz, and are given in Table VIII. The photographs were taken by J. P. Jones.

TABLE VIII

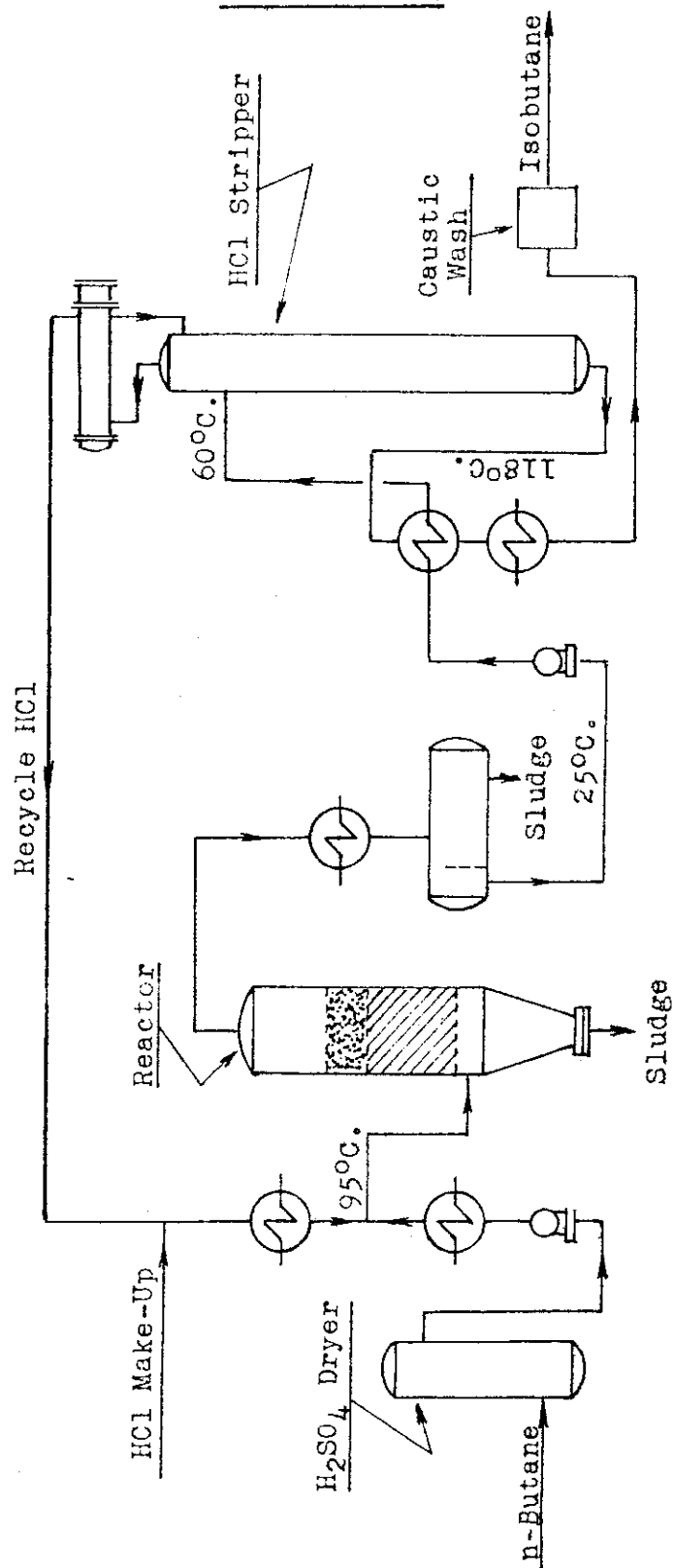
Operation	High pressure steam (176-220 psi), lbs/barrel of Alkylate.	Low pressure steam (37 psi) lbs/barrel of Alkylate.	Power high voltage KWH/barrel of Alkylate	Low voltage KWH/barrel of Alkylate	Circulating water gals/barrel of Alkylate	Make up water gals/barrel of Alkylate.	Fuel Gas BTU/barrel of Alkylate	Labour	
								Foremen	Lab. Technician
Dehydrogenation	-	320	-	11.1	646	-	937,000	14	
Compression of dehydrogenated gas and absorption unit	35	-	23.2	1.4	2,530	-	-		35
Alkylation, including Refrigeration.	1,225**	-	-	8.2	3,840	-	-	3	20
Butane-isobutane separation, Depropanizer	-	1,100	-	2.7	3,840	27	-		
Debutanizing of Alkylate, distillation of alkylate	302	382	18.5*	2.7	3,840	27 147*	-	4	1
TOTAL	1,562	1,802	41.7	26.1	14,696	201	937,000	11 +3 14	1 machinists

\*\* for butane refrigeration

\* for water circulation



FIG. XXIII



FLOW DIAGRAM - BUTANE ISOMERIZATION PROCESS



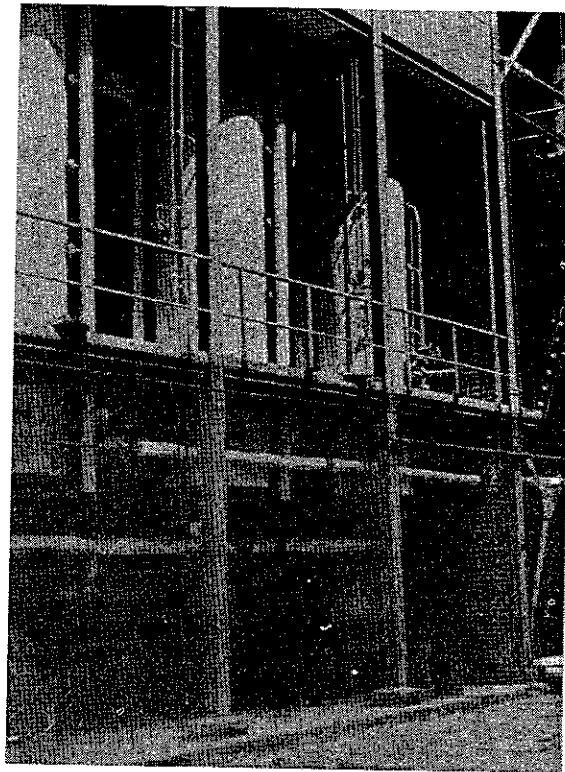


FIGURE XXIV