

VIII. CATALYTIC CRACKING.

Introduction

Catalytic cracking was not being employed on any appreciable scale in Germany. Experimental work was being carried out at Leuna on a catalytic process similar to the TCC process, using a silica alumina catalyst, and there was a pilot unit of 20 litres catalyst capacity which could process 12 litres of oil per hour. A larger unit (at Deuben near Zeitz) was essentially complete, and was designed to process 1,000 litres of oil per hour. The Deuben plant has not been in operation, however. It was also planned to build a commercial unit as part of an underground aviation gasoline plant near Nordhausen. A sketch of the proposed reactor-regenerator set up is attached as Fig. XV.

Reaction Conditions

The regenerator is mounted above the reactor so that the regenerated catalyst is fed to the reactor by gravity. Spent catalyst from the bottom of the reactor is elevated to the top by means of an open bucket elevator. The main regeneration zone consists of an air-catalyst exchanger device where the air for regeneration passes through the inside of rectangular plate sections and is preheated by the catalyst passing on the outside. The preheated air from this section then passes up to the top of the regenerator in an outside duct, and then passes down through the catalyst and leaves the regenerator through a collecting device below the air preheater section. The object of the air preheater section, in addition to that of heat economy, is to control the temperature of regeneration so as not to exceed 550°C . Below the regenerating zone, the catalyst is cooled with recirculated inert gas and then passes through a feeder into the reaction zone. Oil enters the reactor about the middle of the reactor through a distributor and passes upward through the top half of the catalyst bed and leaves through a collecting device. In the bottom half of the reactor, the catalyst is stripped with inert gas and then discharged through a second feeder similar to the one located between the regenerator and the reactor. No steam stripping is used anywhere in the system as it was thought to be detrimental to catalyst activity.

The catalyst feeder mechanism or valve consists of concentric cylinders, the inner cylinder being rotated so that on each revolution, the cylinder is filled with catalyst in an upward position, and the catalyst discharged in a downward position. Apparently, this feeder had not been used on any commercial unit and it was not known what trouble would be encountered with erosion by the catalyst dust. A detail drawing of this feeder was obtained. A cross-section is attached as Fig. XVI.

Catalyst

The catalyst used is a silica alumina catalyst, nine parts of silica to one part of alumina. The catalyst particles are white to yellow round granules with an apparent density of 0.7 and a crushing strength of 10-30 kg.

The alumina for the catalyst is prepared by dissolving technical aluminum oxide in 25% sodium hydroxide solution in the proportions of 1 mol. of Al_2O_3

to 1.5 mols of Na_2O . The solution contains 300 gr. of Al_2O_3 per litre. Water is added to the solution equivalent to one-third of the final total volume. To this solution is added 45% nitric acid while maintaining a pH of 6-7 anti-mony electrode. The temperature during the precipitation is allowed to rise about 50°C . The precipitate is filtered and the cake is washed either in a filter press or by decantation until the wash water is clear of nitrate ion. The alumina is then dried to a 30% water content by heating at 120°C .

Silica gel is prepared by mixing a water glass solution containing 27% SiO_2 with a specific weight of 1.333 with 2N sulphuric acid at a pH of 3-4 and a temperature of $10-15^\circ$.

The silica gel is then produced by heating to $70-80^\circ\text{C}$. The gel is then broken into pieces of 3-5 cm. size and washed with water by decantation until the wash water is free of sulphate ion. The wash water is either distilled water or steam condensate with 2-3 degrees hardness. 100 kg. of gel require approximately 40 cu.m. of wash water. The gel is then dried at 120°C . to 30% water content, powdered in a vibrating mill to a particle size of 90% through a sieve having 10,000 openings per square cm.

The aluminum hydroxide is kneaded with sufficient water to produce a plastic mass containing 50-60% solids, and then peptized with sufficient 45% nitric acid to convert 10% of the material to aluminum nitrate. The silica gel is then added to this peptized aluminum hydroxide and the mass kneaded for 6-10 hours. The catalyst is then pressed and transferred to a candy-making machine (Frankoma) and formed into spheres of about 1-4 inch diameter. The spheres are dried at 120°C . and then calcined at 450°C . for 4 hours.

An alternative method of catalyst preparation consists of mixing the gels, both containing about 30% water, in a mixer and then kneading them with water for 1 to 3 hours. No nitric acid is used in this preparation to peptize the aluminum oxide.

The catalyst is said to be amorphous since X-ray pictures show a general dark field with a few weak and unclear lines principally from crystalline aluminum oxide. If the catalyst is calcined for a longer period of time at 550°C ., the X-ray pictures show definite evidence of recrystallization of the alumina.

Products

A typical pilot plant operation cracking a light Hannover gas oil of $165-350^\circ\text{C}$. boiling range at a space velocity of 0.6 volumes of oil per volume of catalyst per hour, and a residence time of one hour gave the following results:

Dry gas	3 wt.%
$\text{C}_3\text{-C}_4$	14 wt.%
$\text{C}_5\text{-}165^\circ\text{C}$.	30-33 wt.%
Coke	5%
Residue	45-48%

The $\text{C}_3\text{-C}_4$ fraction contains 60% C_3 and 40% C_4 , 75% of the C_4 cut being isobutane. The $\text{C}_5\text{-}165^\circ\text{C}$. gasoline fraction contained 5-8 wt.% olefins, 25%

aromatics and 67-70% paraffins and naphthenes. The octane number of this fraction with 0.12% by volume of TEL was 90-92 MM.

Catalyst Life

Catalyst life tests in a 1.2 litre catalyst testing apparatus indicated that the catalyst life decreased from a yield of 30% C₅-165°C. fraction to a 25% yield in 6-9 months. The oil used for these catalyst life tests was a 200-400°C. mixed base gas oil from the Vienna district.

Pilot plant tests were also made on cracking a brown coal middle oil and a hard coal middle oil. The highest rich-rating gasoline was made from hard coal middle oil. The lowest rating was obtained from cracking gas oil, and the brown coal middle oil gave an intermediate result.

Hydrogenation of Product

Experiments were conducted in the laboratory on hydrogenating the residue from the catalytic cracking unit using a catalyst containing equal molecular proportions of nickel oxide and tungstic acid at a temperature of 400 C. under 200 atms. pressure with 2000 litres of hydrogen per litre of charge. A second catalyst was also tried which contained 10% tungstic acid on activated alumina at 450°C., but this catalyst produced considerable cracking. 5-8% gasoline with a low octane number was obtained. With the nickel oxide-tungstic oxide catalyst, no cracking was obtained. The catalytic cracking of this hydrogenated residue, which was more paraffinic than the original charge, produced results similar to those obtained on the fresh charge.

Some work has been done on the cracking of pure normal decane, normal decene and decalin. It was found that decalin was the easiest to crack, normal decane being the most difficult and normal decene intermediate. There was little difference in the refractivity of the normal decene and the decalin, however.

Conclusions

Apparently the Germans had not been doing any work on a fluid type catalytic cracking process, and are not, at the present time, very familiar with handling any sort of catalytic process in which the catalyst is used for short periods and then regenerated. The proposed catalytic cracking unit for Nordhausen is apparently the first attempt by them to employ a catalytic process of this type. It is doubtful if anything new is to be learnt from the Germans on catalytic cracking of gas oil, with the presumable exception of their low-temperature regeneration of catalysts. The low temperature regeneration apparently gives considerably longer catalyst life, but this of course has not been proven by commercial operation.

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. Giesen, Dr. Hanisch and Dr. Strätz. Dr. Giesen 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 catalysts. 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 2,640 bbls./day of n-butane (96%) to the dehydrogenation reactor yielding, after proper separation, 2,510 bbls. of a butane/butylene mixture (535 bbls. n-butylenes, 1,905 bbls. n-butane, 72 bbls. propane) as alkylation feed stock. The total amount of iso-butane (85%) charged to the alkylation step was 3,797 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 90% 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 downward 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 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

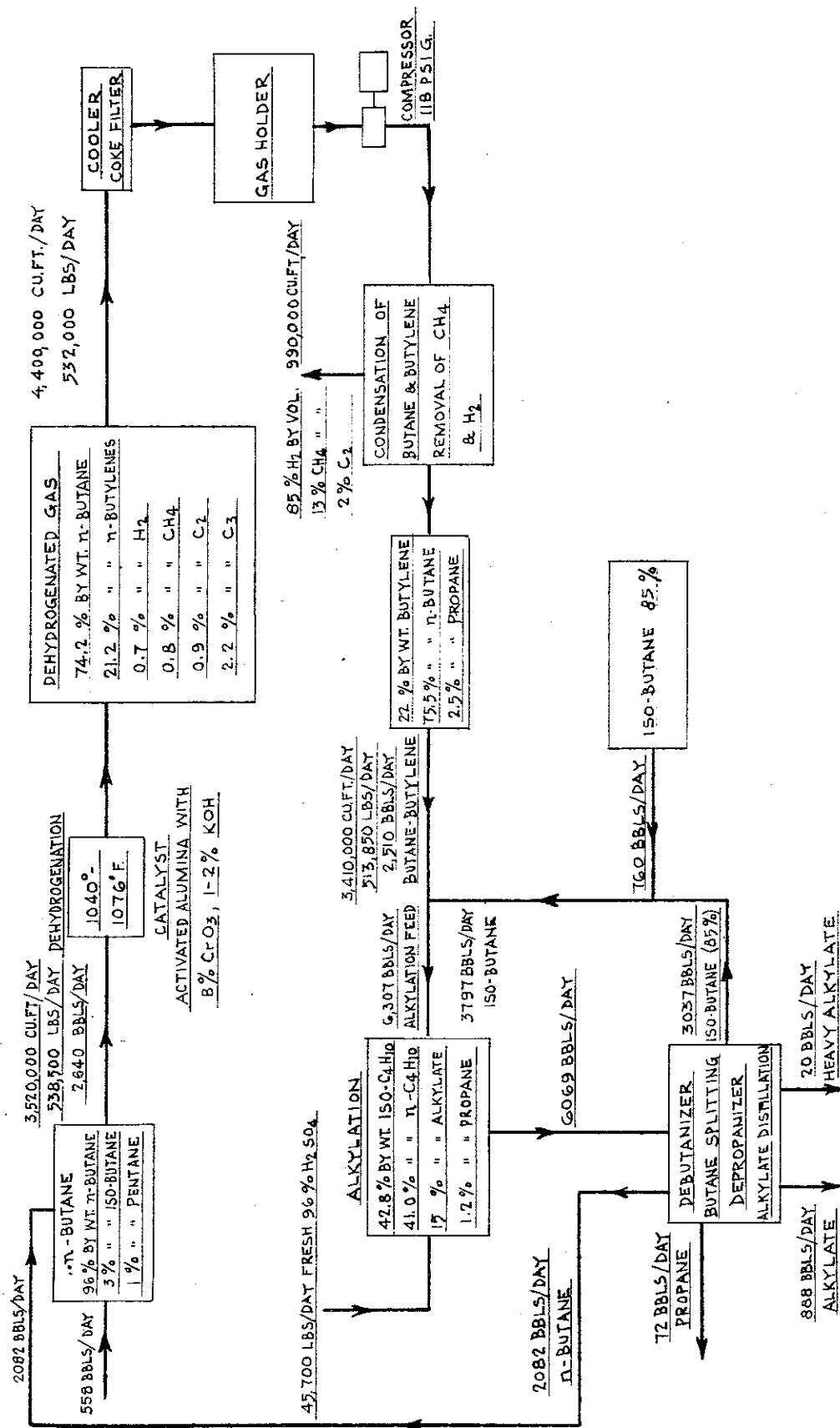


FIGURE XVII.- MATERIAL BALANCE - BUTANE DEHYDROGENATION & ALKYLATION LEUNA - WERKE

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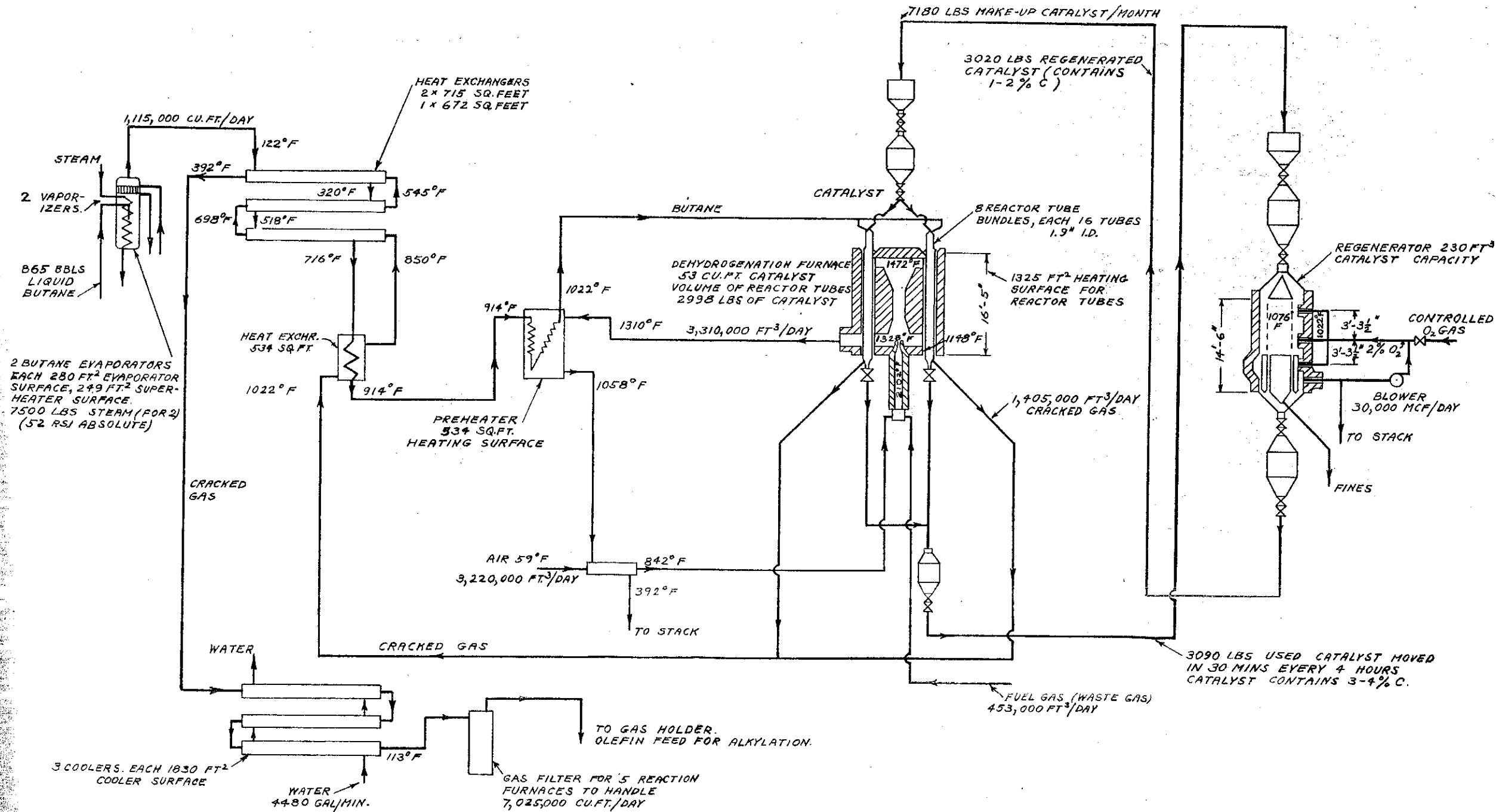


FIGURE XVIII-BUTANE DEHYDROGENATION LEUNA WORKS AMMONIAKWERKE MERSEBURG.

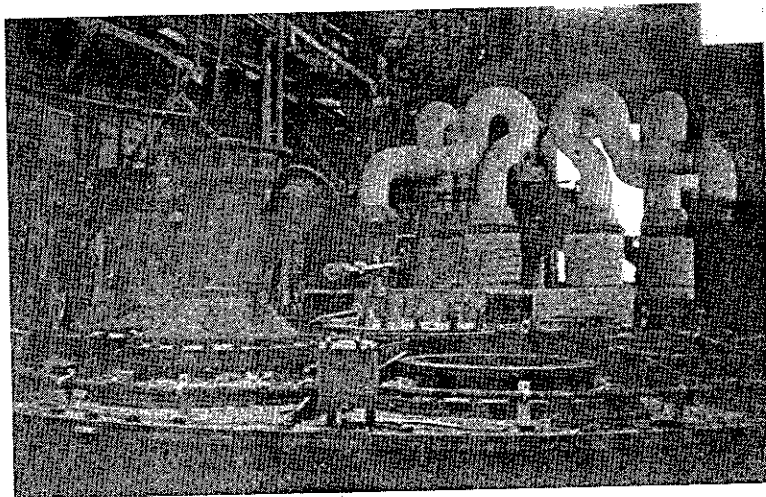


FIGURE XX

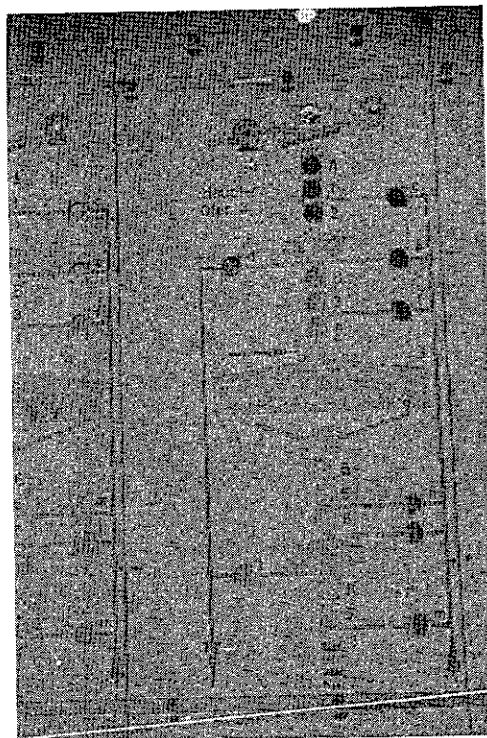


FIGURE XXI

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 shown 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 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 "