VIII. CATALYTIC CRACKING.

Introduction

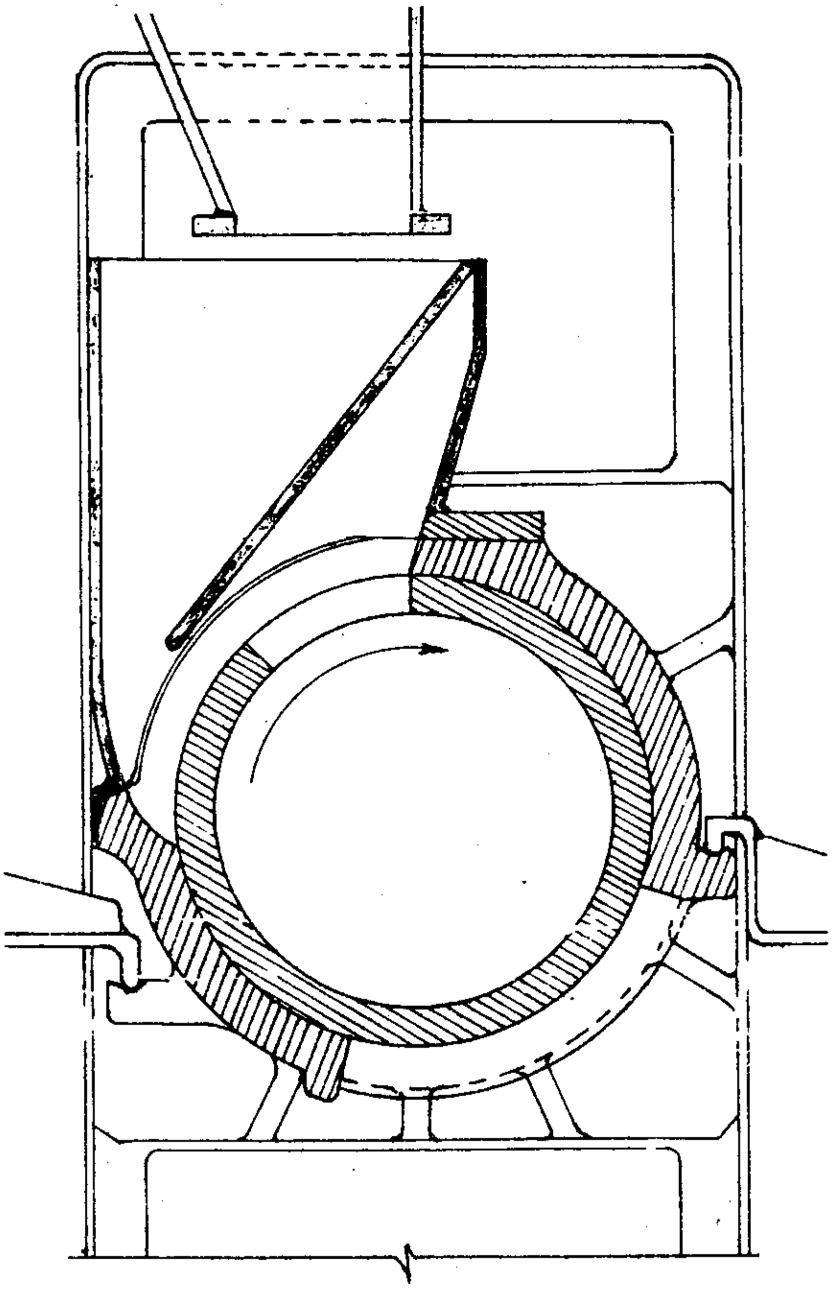
Catalytic cracking was not being employed on any appreciable scale in Germany. Experimental work was being carried out at Leuna on a catalytic process similar to the TCC process, using a silica alumina catalyst, and there was a pilot unit of 20 litres catalyst capacity which could process 12 litres of 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. IV.

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 reactangular 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

FIG. XVI



CATALYST VALVE - CATALYTIC CRACKING UNIT 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 antimony electrode. The temperature during the precipitation is allowed to rise to 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°.

The silica gel is then produced by heating to 70-80°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 ¼ 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°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.%
C_3-C_4	14 wt.%
C_5-165°C.	30-33 wt.%
Coke	5%
Residue	45-48%

The C_3-C_4 fraction contains 60% C_3 and 40% C_4, 75% of the C_4 cut being isobutane. The C_5-165°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% C_5-165°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.

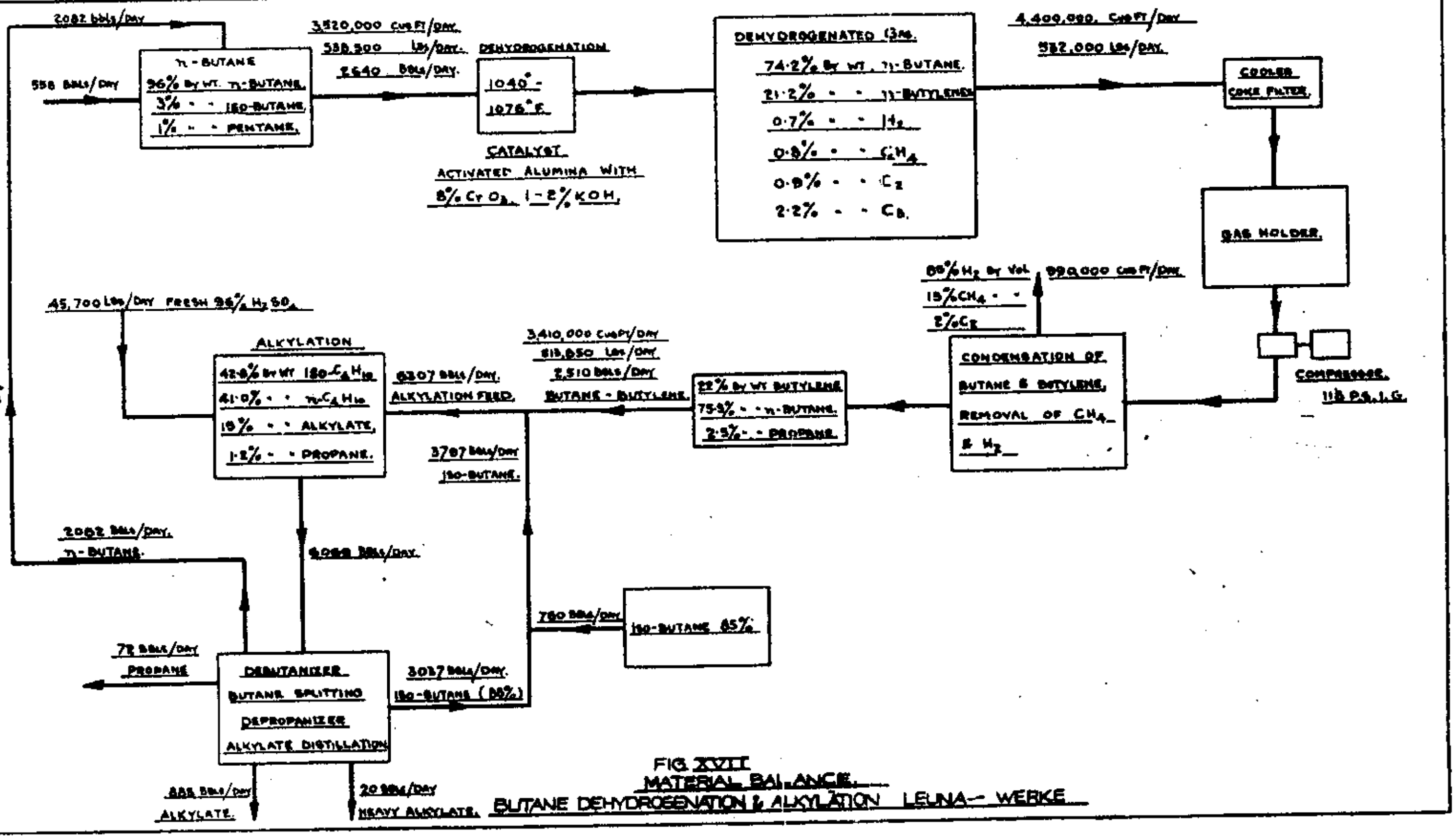


FIG. XVII
MATERIAL BALANCE.
BUTANE DEHYDROGENATION & ALKYLATION LEUNA - WERKE