

Dehydrogenation of n-Butane at Leuna

Two catalysts have been developed. Catalyst 5530 is based on non-peptized aluminate alumina whereas catalyst 3675 is based on peptized alumina. Both catalysts contain 10% Cr_2O_3 and 2% K_2O .

The catalysts were tested in laboratory reactors of a diameter of 0.65" and a catalyst volume of 1.52 cu. in. The experiments were continued for 400 hours at a space velocity of 1000:1. Catalyst 5530 gave a n-butane conversion of 30% with a yield of 88 to 90% and a carbon deposit of 1% calculated on the n-butane charge. Catalyst 3675 gave a conversion of 33% with a yield of 92 to 94% and the same amount of carbon deposit as the other catalyst.

When working with catalyst 5530 the temperature must be raised to 1,040°F. after 80 to 90 hours of dehydrogenation, whereas with catalyst 3675 the temperature will have to be raised to about 1,040°F. only after 300 hours, which is of importance with respect to the yield.

In pilot plant tests using a gas heated reactor of 0.93" diameter, a yield of 81 to 82% at a conversion of 25 to 27% was obtained with catalyst 3675 at a space velocity of 650 to 700:1. The loss by attrition was very low and amounted to only 0.2 to 0.25% per pass of catalyst in continuous operation.

For commercial operation a conversion of 25% and a yield of 80% at a space velocity of 650:1 is assumed for catalyst 5530, whereas for catalyst 3675 a conversion of 25% and a yield of 86 to 88% with a space velocity of 800:1 is considered.

Analysis of the butylene obtained by dehydrogenation showed that it consisted of 43% alpha and 57% beta butylene which corresponds to the figures calculated from the theoretical equilibrium.

The isomerization of n-butane is operated with a conversion of 30% and a yield of 95 to 98%. The catalyst consumption amounts to 0.5 to 0.7% based on the isobutane produced, provided that the butane feed is free of olefins and higher hydrocarbons. The water content should not exceed 0.02% by weight. The HCl content of the reactor feed amounts to 10 to 15%. The reactor for the isomerization is of the shell type and is operated at 212°F. and 235 psi. at a space velocity of 3 volumes of feed (liquid) per volume of catalyst charge. Aluminum chloride containing iron is used as catalyst which is preferable to iron-free catalyst because it is considerably more active. Tests with a reactor of 1.6' diameter and a catalyst bed height of 3.3' with a height of packed space of 6.6' showed temperature differences between 10 and 20°F. between the reactor inlet and the zone of highest temperature (in the lowest catalyst layer, above the packed space). The temperature of the center of the reactor is 2 to 4°F. higher than the temperature of the catalyst at the reactor wall. This indicates that shell-type reactors of any diameter desired can be used for isomerization.

Leuna Works - June 18, 1942.

Development of Butane Dehydrogenation in Leuna (T52 Process)

End of 1934	First experimental work on the dehydrogenation of isobutane with the intention to manufacture iso-octane by polymerization of the isobutylene produced. Catalysts used: Heavy metal sulphide and activated charcoal.
End of 1934	Cr ₂ O ₃ catalyst, additions of BaCl ₂ .
Middle of 1936	Pilot plant experiments. It was decided to build a semi-commercial plant as the last step in the studies leading to the design of an iso-octane manufacturing plant at Leuna.
Middle of 1937	Starting-up of the semi-commercial unit. Activated charcoal was used as catalyst since the oxide catalyst could not be made on a commercial scale and the necessity of adding barium chloride resulted in difficulties with construction materials.
End of 1938	Installation of a sluicing device in the large dehydrogenation reactor and work with moving catalyst (activated charcoal). The first data were assembled for the construction of a large-scale unit.
End of 1939	Improvements in the mechanical strength of the catalyst, especially the shaping into spheres (Giulini alumina with Cr ₂ O ₃). This made possible the use of the sluicing process.
February 4, 1939	Order by the German government agency for the construction of a butane dehydrogenation plant.
Middle of 1939	The operation of the dehydrogenation reactor was changed to short on-stream periods (4 to 8 hours) and high space velocity.
End of 1940	The butane dehydrogenation unit in Leuna was started up. The development of the isobutane dehydrogenation process was carried out with continuous exchange of experience with the contract partners in the United States; Dr. Ringer acted as intermediary. The change from long to short on-stream time was based on American suggestions and this resulted in better utilization of the catalyst at higher space velocity and higher conversion.

Isomerization of Normal Butane

1936	Start of the experimental work on the isomerization of n-butane to isobutane in order to increase the quantity of isobutane required for the manufacture of iso-octane.
Middle of 1939	Work on isomerization intensified because of the further developments of the work on alkylation (WS ₂ or AlCl ₃ catalyst).

Polymerisation

- Middle of 1936** Work was started on the polymerisation of isobutylene using a two-stage sulphuric acid process.
- 1938** Development of a one-stage sulphuric acid process. The experimental work was based to a large extent on American experiences which were transmitted to us.
- April, 1939** Preparation of a phosphoric acid-asbestos catalyst for the polymerization with a solid-bed catalyst (2,940 psi).
- 1938 to 1939** Testing of all three polymerization processes in technical units and testing of all stages of the process for the production of butylene.

Development of Alkylation at Louma (AT 244 Process)

- 1936** First publications on alkylation in the foreign literature.
- 1937** Publication of patents on alkylation (Shell, Anglo-Iranian, Standard Oil).
- Middle of 1938** Dr. Ringer points out the work done in the United States and suggests to take up this work at Louma.
- September - October, 1938** Start of experimental work on the alkylation of isobutane with isobutylene.
- November, 1938** First I. G. patent application on alkylation.
- Spring, 1939** Small pilot plants for alkylation were operated. This appeared to be a way to reduce the equipment needed for dehydrogenation and eliminate hydrogenation of iso-octane.
- August, 1939** Alkylation of isobutane with n-butylene instead of iso-butylene. This permits to double the production of iso-octane from the butane available without the necessity of isomerization of n-butane.
- 1939 to 1941** Change-over of the experimental work on dehydrogenation using n-butane instead of isobutane. Development of a specific dehydrogenation catalyst for n-butane.
- Fall, 1939** Experimental results as well as information from the United States make it advisable to plan an alkylation unit to replace the process of iso-octane manufacture by polymerization and hydrogenation.
- December, 1939** Start of a semi-technical unit using the process developed at Louma which deviates from the process used in the United States.

February, 1940 First samples of alkylate are tested by the German Air Ministry.
End of 1940 Final decision on the alkylation project.
March, 1941 A large-scale unit (62.5 bbls. per day) is operated to obtain final design data.

Work on Isomerization

1939 to 1941 The work on high-pressure isomerization with WS_2 as catalyst was discontinued and processes for low-pressure using $AlCl_3$ were developed. The isomerization process finally developed is different from the Shell process, both with respect to the kind of catalyst used and the details of operation.

MEMORANDUM ON THE PROJECTED PLANT FOR THE MANUFACTURE
OF BUTYLENE BY CHLORINATION OF BUTANE
FOLLOWED BY DEHYDROCHLORINATION.

Leuna - June 8 - 10, 1942.

For the chlorination step the heating surfaces shall be designed on the basis that the heat of reaction liberated during chlorination is 630 B. t. u. per pound of chlorine reacted which corresponds to 480 B. t. u. per pound of butylchloride.

The dehydrochlorination is to be carried out without catalyst at 842°F. and a pressure of 264 psig. in a reactor with a heating surface of 1,941 square feet. The design of the reactor is based on the assumption that for splitting off of HCl, 224 B. t. u. per pound of butylchloride are required. This is based on a specific heat of 0.79 B. t. u. per pound for liquid and 1.58 B. t. u. per pound for gaseous butylchloride. The latter value seems rather low. Based on laboratory experiments, the residence time should be 1 to 5 seconds in the dechlorination step. The conversion is 65%, and can be raised to 90% but in this case by-products are formed due to undesired side reactions.