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THE DEHYDROGENATION OF BUTANE (PROPANE) IN A TUBULAR FURNACE  
WITH A SOLID-BED CATALYST

Butane dehydrogenation is carried out on a commercial scale in a tubular furnace which is heated from the outside and through which the catalyst is passed continuously. In a separate regenerator the catalyst is regenerated by burning off the carbon deposit. The residence time of the catalyst in the dehydrogenation reactor is, on the average, four hours (corresponding to the catalyst life).

The basic disadvantages inherent in this method of operation are described in the following paragraphs but it must be mentioned that nevertheless this seemed to be the only feasible method up to now.

1. The catalyst is temperature sensitive and is very active at low temperatures (which should be maintained because of the yield) unless it is exposed to higher temperatures at various times during the operation. If this has occurred the catalyst must be operated at this higher temperature if it is desired to maintain the previous rate of conversion because on returning to the lower temperature at which the catalyst had been used before it had been superheated, a noticeable decrease of the conversion will be found. When the catalyst moves through the reactor it always comes in contact with spots of higher temperature at the wall of the reactor and at the end of the catalyst tube and in this way is inactivated for the zones which are maintained at the normal temperature of operation. This results in a decrease in conversion. The consequence is that the operating temperature of the reactor must be raised rapidly which, again, results in a decrease of the yield. A temperature of 1,076°F. must not be exceeded because of the strongly increased rate of cracking at this temperature and this necessitates that continuously much new catalyst has to be added resulting in high catalyst consumption. When a solid-bed catalyst would be used these disadvantages would disappear since the individual catalyst particles always remain in place which makes it possible to operate for prolonged periods at lower temperatures since the catalyst activity does not decrease as quickly. This would lead to higher conversion and yields as well as lowered catalyst consumption.

2. In the course of passing the catalyst through the reactor an average operating temperature establishes itself and the freshly-added catalyst is run immediately at some higher temperature, although it would give the desired conversion already at lower temperatures. In a solid-bed reactor the catalyst could always be operated at the lowest possible temperature.

3. In the moving catalyst process the requirements as to shape and mechanical strength of the catalyst are high (spheres resistant to attrition). These requirements could be made less stringent when a solid-bed is used. It has been proposed recently by Dr. Conrad from Oppau to operate the butane dehydrogenation process using a solid-bed in several unheated, shell-type reactors insulated at the inside and provided with intermediate preheaters. This type of operation has become possible because in the meantime dehydrogenation catalysts have been developed which can operate at such low temperatures that the reasons which up to now have prohibited this type of operation are no longer valid. In this type of process in which the heat necessary for the dehydrogenation is introduced in the preheater, the catalyst temperature drops between the gas inlet and exit by about 100 to 250°F. in each reactor of a four-stage unit.

This means that in the direction of decreasing reaction velocity (due to the approach of equilibrium), the temperature also decreases and consequently if the temperature in the center of the reactor is close to the optimum working temperature, it is too high in the first part and too low in the last part of the reactor. Subdivision into many stages avoids this disadvantage. In the intermediate preheaters the olefinic gas must always be reheated and this would lead to cracking at the temperatures required for operation with the catalysts known up to now. However, using the newly developed catalysts which can operate at 982° - 1,040°F. instead of the previous operating temperature of 1,076 - 1,112°F. the new method of operation would seem to be advantageous. Operation of a commercial unit would be similar to the low-pressure dehydrogenation used in the manufacture of high-octane motor fuel.

All considerations which led to the use of tubular furnaces heated from the outside in the dehydrogenation process would be applicable to the operation of the butane dehydrogenation with a solid-bed catalyst. Consequently, experiments were made in pilot units comparing operations with a solid-bed catalyst with those using a moving catalyst. The following conditions were chosen; Space velocity 1,700 to 1,800; temperature, 986°F. which was slowly raised according to the conversion obtained; on-stream period - 4 hours. A sample of catalyst 6530 from the butane dehydrogenation plant was used. The butane used originated from the hydrogenation unit and was washed free from olefins. Olefin-free n-butane from the bottoms of the butane splitter of the butane dehydrogenation unit did not show any difference as compared to the butane from the hydrogenation.

The following table shows the results of the two experiments and indicates clearly the advantage of operations with a solid catalyst bed. The experiments showed the considerable importance of the presence of water in the reaction mixtures with respect to the activity of the catalyst. The detrimental effects of water can be clearly seen from the record of the hydrogen formed during the reaction which is given in the following diagram. It can be seen that the conversion decreases by about 2 to 3% when fresh catalyst is introduced into the reactor. It slowly increases again to fall as soon as fresh catalyst is again introduced. The explanation of this unexpected phenomenon is the fact that the catalyst cools off during the transport from the regenerator and picks up moisture from the air; moisture is thereby introduced into the reactor resulting in decreased conversion. In order to show this effect more clearly, fresh catalyst was introduced into the reactor as fast as possible with nitrogen as flushing gas and the unit was operated stationary with this catalyst (solid-bed). As can be seen from the diagram, the conversion slowly increases with increasing dryness of the catalyst until it reaches a maximum and then decreases again due to carbon deposition on the catalyst. The dotted line indicates the theoretical curve which is almost reached in the solid-bed experiment in which contact of catalyst and air during regeneration does not take place. This indicates the advantage of the solid-bed process as compared to the moving catalyst process. On the other hand, the alternating reduction and oxidation operations in the same reactor require special construction materials. The experiments were carried out at temperatures up to 1,040°F. in a reactor made of FF6N steel. The catalyst which was removed after the solid-bed experiments showed a deposit of iron oxide which, however, did not have any catalytic effect (200 hours operating time). The ratio of on-stream time to regeneration time was 1:1 at 986°F. and 1:2 at 1,040°F. However, it is possible that more favorable ratios of on-stream time to regeneration time can be reached in commercial practice.

Temperature	988°F. *)			1004°F.			1022°F.			1040°F.			1058°F.			1076°F.		
	Hours of Dehydrogenation	% Conversion	% Yield	Hours	% Conversion	% Yield	Hours	% Conversion	% Yield	Hours	% Conversion	% Yield	Hours	% Conversion	% Yield	Hours	% Conversion	% Yield
Moving Catalyst	4	7-8	76	8	14-16	83	4	14	81.5	8	16	84	12	15-16		8	15-16	
Solid-bed Catalyst	48	27-28	91	24	26	90	44	26	89	76	27-28	89	Experiment discontinued; catalyst still active.					

Carbon deposition on the catalyst was in both cases 2 - 3% (calculated on the basis of butane reacted).

\*) The operating temperature was raised in both cases only when the conversion decreased noticeably.

