

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF BUTADIENE

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No Drawing. Application filed August 11, 1939

The synthesis of butadiene, C_4H_6 , has attained today a remarkable importance owing to its use in the manufacture of synthetic rubber.

The processes heretofore employed for the manufacture of butadiene starting from alcohol and aldehyde offer, however, many inconveniences, owing to the low industrial yield obtainable, the high cost of the raw materials and the difficulty of obtaining butadiene in a very pure state.

Attempts for the manufacture of butadiene from a less expensive raw material, e. g. from butylenes C_4H_8 , obtained as by-products from petroleum cracking, had not heretofore given industrially interesting results, owing to difficulties in the separation of butylenes from butadiene as a consequence of the low yields obtained and owing to the poisoning of the catalysts after a short time of working.

We have now found a continuous process whereby it is possible to obtain a high yield in butadiene from butylenes and particularly from alpha-butylene, completely avoiding the above mentioned inconveniences. In what follows the expression "butylene" will mean chiefly alpha- or Δ .1-2. butylene, but also beta- or Δ .2-3-butylene in both its cis- and trans-forms, and/or mixings of two or of all these of the above named.

The mentioned process consists in the catalytic dehydrogenation of butylene on dehydrogenating catalysts, e. g. on nickel deposited on a suitable support, in the presence of a substance which by its presence promotes the dissociation of butylene in hydrogen and butadiene and prevents the deposition of the elementary carbon and/or of other organic substances on the catalyst:

We have found that it is possible to carry out said process by mixing with butylene, before entering the reaction oven, a given quantity of carbon dioxide, the presence of which promotes the reaction:



This effect is due to many reasons: first because the carbon dioxide causes a diminution of the partial pressure of the single components which take part in the reaction and it is known that a diminution of pressure favours the reactions which take place with an increase of volume. Further the carbon dioxide helps to prevent the formation of free carbon which, if deposited on the catalyst, would quickly poison it by reacting with it forming carbon monoxide.

The influence of carbon dioxide is, however, much greater than that which could be foreseen on the ground of the above considerations.

In fact, an addition of steam would also be sufficient to obtain from said points of view an effect similar to that given by carbon dioxide, but this is practically not the case. This is due, partially at least, to the fact that carbon dioxide takes part in the reaction either reacting directly with butylene according to the equation:



or through its reaction with hydrogen,



thus promoting the reaction of dehydrogenation of butylene.

While the kinetic mechanism of reaction is not yet fully explained, the remarkably advantageous action of carbon dioxide can be explained only by admitting its activating action on the dehydrogenating catalyst, or its participation to an intermediate reaction which is kinetically more speedy.

As catalysts, besides nickel, may be used other elements belonging to the same group and possessing a dehydrogenating activity. Should it be desired to avoid the use of more costly metals, good results may be obtained by the use of catalysts obtained by the dispersion upon porous supports, like alumina or silica or better bentonite, of finely divided nickel obtained, e. g. by reduction of reducible nickel salts as basic carbonate, oxalate, hydroxide, and the like, which have been precipitated on the support itself. The temperature of dehydrogenation may vary within broad limits but the best results are obtained at temperatures ranging between $500^\circ + 700^\circ$ C and preferably between $500^\circ + 600^\circ$ C.

For instance a mixing consisting of equal volumes of alpha-butylene and carbon dioxide is led at $500^\circ - 600^\circ$ C through a catalyst layer consisting of bentonite on which 5% of nickel is deposited, and, after separation of carbon dioxide and of the gases more difficult to condense, yields a mixing containing about equal volumes of butylene and butadiene and even, when the speed of passage on the catalyst is low, more butadiene than butylene.

The carbon dioxide, separated by means of suitable solvents, may be returned in circulation while the separation of butylene and butadiene may be obtained by condensation.

The separation of butylene from butadiene may be carried out by fractionating solution by means of suitable solvents following known methods; the separated butylene may be returned in circulation and converted into butadiene. It is

also possible to obtain by a single operation a yield so high, to render it possible the separation of butylene from the formed butadiene, by polymerization of butadiene e. g. with sodium, thus directly obtaining synthetic rubber of good quality.

By thus operating and by returning in circulation the unaltered butylene, it has been possible to obtain yields in butadiene which in the total are higher than 80% of the butylene employed.

The above mentioned process may be applied not only in the case of butylene coming from cracking gases, but also in the case of butylene, or mixings of butylenes, obtained by other ways e. g. butylene obtained by dehydration of butyl-alcohol, also butylene obtained as a by-product in the manufacture of butadiene obtained by processes based on the catalytic decomposition of mixings of alcohol and acetic aldehyde on alumina or other catalysts.

In fact, following the last mentioned process a quantity of butylene which corresponds to 20+30% of the butadiene produced, is obtained as a by product.

The recovering of said butylene and its transformation in butadiene by the process hereinbefore disclosed, allows to increase by 20% the total output of butadiene without increasing the consumption of raw materials, alcohol and aldehyde.

It is further possible to use alpha-butylene obtained from normal butyl alcohol by a reaction which may be carried out with practically quantitative yields i. e., by dehydration of said normal butyl alcohol on catalysts mainly consisting of alumina or of caolin. The butylalcohol may have been obtained by hydrogenation of aldol.

Besides alpha-butylene, beta-butylene or mixings of both may be used, because during the dehydrogenation of beta-butylene a migration of the pre-existing double bond takes place.

The dehydrogenation reaction of the butylenes is endothermal and the heat of reaction must be supplied from the outside by heating the reaction chamber with hot gases or by indirect or direct heating of the catalyst or of the reacting gases by means of electric resistences. As the reaction is reversible, it is useful that the reaction gases leave the catalyst at the highest temperature of the cycle and be at once cooled down.

It is also possible, in order to avoid the need of addition of heat from the outside which is expensive owing to the high reaction temperature, to carry out a partial combustion inside the reaction chamber of the hydrogen coming from the dehydrogenation of butylene. For this purpose it is sufficient to mix carbon dioxide with the small quantity of oxygen, or air required to develop by burning a quantity of heat capable to balance the heat absorbed by the reaction of dehydrogenation and to bring the reacting gases to the reaction temperature.

In order to diminish the latter mentioned amount of heat it is useful to pre-heat the gases which enter in the reaction chamber, by utilizing the heat possessed by the gases issuing from the reaction chamber itself. In this case small quantities of oxygen or air, substantially lower than the lowest limit of explosion of the mixing, are sufficient to maintain stationary the temperature of the catalyst without addition of heat from the outside.

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