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PROCESS FOR THE MANUFACTURE OF BUTADIENE FROM BUTANE OR BUTANE CONTAINING GASES

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It is known that by the catalytic dehydrogenation of butane, gases containing butylene and butadiene are obtained.

It is also known, as disclosed in a prior Patent by the same Applicants, that the best yields in the dehydrogenation of butylene into butadiene are obtained when working in the presence of carbon dioxide.

When, however, butane is used as a starting material it is very difficult to directly obtain a high yield of transformation in butadiene, except when working at very high temperatures at which, owing to secondary reactions, remarkable losses occur.

The reason of the low yield is due to the fact that, owing to the law of mass action, the hydrogen molecule which is formed in the dehydrogenation of butane into butylene opposes to the further dehydrogenation of butylene into butadiene.

A process whereby it is possible to obtain high yields in the transformation of butane into butadiene, would offer a remarkable interest owing to the important use that butadiene may find in the manufacture of polymers useful in the synthetic rubber industry.

By this invention it is possible to obtain high yields of transformation, preventing that a remarkable loss of substances in secondary reactions may occur.

This invention consists in the dehydrogenation of butane in the presence of carbon dioxide at relatively low temperatures e. g. 500° C+600° C.

Under these conditions the dehydrogenation is only partial, but losses owing to secondary reactions are avoided.

Afterwards, the reaction products, consisting of a gaseous mixture of: unaltered butane, butylene, butadiene, hydrogen, carbon dioxide, carbon oxide and water vapors, are cooled, eventually compressed, and both temperature and pressure respectively are fixed in a manner that practically all the butadiene, butylene and butane may separate in the liquid state, while hydrogen and carbon oxide separate in the gaseous state.

The carbon dioxide remains partially dissolved in the mixture of liquid hydrocarbons while partially remains in the residual gases and may eventually be separated from the latter and recovered by means of suitable solvents according to the known methods.

The mixture thus obtained consisting of butane, butylene and butadiene, eventually supplied with further carbon dioxide, is again passed at slightly higher temperatures (about 600° C+650° C) upon a dehydrogenating catalyst, so that the butane still present and the butylene previously formed may be further dehydrogenated into butadiene.

When it is desired to obtain a mixture much enriched with butadiene, a third treatment may be effected after the new separation of hydrogen and other difficult condensable gases.

By this process it is possible to obtain a production of gases much enriched with butadiene which may directly be employed for the manufacture of polymers of butadiene or which may be utilized for the manufacture of pure butadiene e. g. by a fractionated absorption according to a prior patent by the same applicants.

In any case if butadiene is used in the manufacture of synthetic rubber by polymerization (e. g. with sodium or in emulsion e. g. with styrol), the butylenes and eventually the butane accompanying it and which do not polymerize, may after polymerisation be recovered as gases and treated again in order to be dehydrogenated into butadiene.

This process may be applied not merely to butane but also to mixtures of butane and butylene coming from the liquefaction and rectification of gases coming from the stabilisation of gasolines obtained by cracking or hydrogenation, or even to butylene resulting as a by-product in the manufacture of synthetic rubber or obtained by dehydratation of butyl-alcohol.

Further, the process may be applied to the fraction C_4 obtained by distillation and rectification of hydrocarbons obtained from water gas through the Fischer's synthesis effected at temperature and pressure higher than the usual.

E. g. the hydrocarbons obtained by synthesis from carbon oxide and hydrogen by reaction upon catalysts made of cobalt at a temperature higher than 200° C, contain remarkable proportions (eventually higher than 20%) of butane and butylene. Said fractions, separated from the other hydrocarbons and dehydrogenated in the presence of carbon dioxide upon a dehydrogenating catalyst (e. g. consisting of reduced nickel on a backing or bentonite) according to the process disclosed may supply, after two or three treatments, a mixture enriched with butadiene which may be used in the manufacture of synthetic rubber. Thus it is possible to obtain about 30 grs. of butadiene from 1 cm. of water gas and further 100 grs. of hydrocarbons resulting as by-products in the synthesis of water gas after the separation of the fraction C_4.

Said yields are of interest and afford to carry out the industrial production of synthetic rubber

using as a starting material water gas obtained from the gasyfication of poor fuels.

When the recovery of hydrogen coming from the dehydrogenation of butane is not deemed of interest, a small quantity of air or oxygen may eventually be added to the mixture of butane and carbon dioxide.

In such a case, by using catalysts affording the selective combustion of hydrogen, to which purpose the metals of the eighty group of the periodic system are capable of acting, the yield of each single operation of dehydrogenation may be improved and consequently by only one or two operations of dehydrogenation a product enriched with butadiene can be obtained.

The latter method must however be effected in the presence of well determined quantities of air in order to avoid the formation of explosive mixtures or anyhow secondary reactions.

To said purpose the quantity of oxygen present in the mixture must be lower than that which is required for the complete combustion of the hydrogen coming from the dehydrogenation of butane into butadiene.

When butane is obtained from water gas by the Fischer's synthesis under a pressure of 10–20 atm., the dehydrogenation of butane may be effected by utilizing the carbon dioxide coming from the washing under pressure of the water gas in order to purify it from the carbon dioxide always therein present.

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