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PRODUCTION OF UNSATURATED HYDROCARBONS

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1 Claim. (Cl. 260—170)

The present invention relates to improvements in the production of unsaturated hydrocarbons, in particular by heat-treatment of saturated hydrocarbons in the presence of steam.

The conversion of saturated gaseous or vaporous hydrocarbons (hereinafter referred to as "saturated vaporized hydrocarbons") into unsaturated hydrocarbons in the presence of steam, which is carried out at temperatures between 600° and 900° C. is an endothermic reaction. For this conversion usually from 0.5 to 2 volumes, preferably about 1 volume, of steam are allowed to react with one volume of hydrocarbons. In order to carry the reaction out continuously on a technical scale it is necessary to employ reaction vessels, as for example tubes, which are heated externally, as for example by combustion gases. In order to obtain the greatest possible efficiency and in order to utilize the heat content of the reacted gases to the greatest possible extent for the preheating of fresh gases it is very important to have a wall material which has a good heat conductivity, which is readily worked and which is not fragile. Furthermore, this wall material should not cause undesirable side reactions, as for example the formation of carbon black.

We have now found that in carrying out the said reaction practically, readily accessible and readily worked wall materials answer the purpose by carrying out the reaction in externally heated apparatus constructed of iron containing less than 2 per cent of nickel (by which term for the purpose of the present invention also steels containing less than 2 per cent of nickel are meant) of which the heated sides are wholly or partly provided with a coating of very heat-resisting steels, i. e. steels which are stable to oxidizing heating gases having a temperature of up to 900° or 1000° C., especially chromium nickel steels. For example ordinary iron tubes, contrary to expectation, are only slightly attacked at temperatures of about 750° C. by the mixtures of the vaporized hydrocarbons and steam. The commercial chromium steels or steels containing aluminium, in so far as they contain less than 2 per cent of nickel behave even more satisfactorily. Since iron and also the said steels are not sufficiently stable to oxidizing heating gases at high temperatures, they are provided according to the present invention on their heated sides, in so far as is necessary, with a coating of steels stable at high temperatures, as for example chromium nickel steels with a high content of nickel (as for example the steel known as "NCT 3" and containing 20 per cent of nickel). The employment of such steels as the inner wall material for the reaction vessels is objectionable, however, because steels containing large amounts of nickel readily give rise to the deposition of carbon black and occasionally promote catalytically other undesirable side reactions such as the formation of carbon monoxide and hydrogen from hydrocarbons. The coating of steels stable at high temperatures may be produced for example by inserting in a tube of Nicrotherm steel a tube of iron or chromium steel (containing less than 2 per cent of nickel) care being taken by pressing or rolling that the junction is as tight as possible. A tube of chromium steel may also be provided externally with a coating of nickel, a diffusion of the nickel into the outer layers of the tube being brought about by heating to high temperatures so that a high percentage nickel steel is formed at the outside. Other known methods may also be employed.

The apparatus for the preheating of the mixture of gas and steam (preferably with the aid of the heat content of the reacted gas) may be constructed for example of iron or chromium steel containing little or no nickel and without any protective coating.

According to the present invention, olefines may be produced continuously from paraffinic hydrocarbons, as for example from waste hydrogenation gases and cracking gases. The employment of steam causes no appreciable additional expenditure because the heat necessary for the heating of the steam may be recovered to a great extent by heat-exchange and the heat-exchanger may consist of relatively cheap material. When large amounts of hydrogen sulphide are present in the gases to be converted, it is preferable to remove them before the reaction. The stability of the apparatus is thus increased and furthermore no undesirable by-products containing sulphur are formed.

The following example will further illustrate the nature of this invention but the invention is not restricted to this example.

Example

40 liters of gas containing about 95 per cent of saturated hydrocarbons (30 per cent of C_2H_6, 60 per cent of C_3H_8 and 5 per cent of C_4H_{10}) as well as a little hydrogen and nitrogen, together with 40 grams of steam are passed per hour through a tube of ordinary iron having an internal diameter of 2.5 centimeters and a length of 60 centimeters the said tube being surrounded

by a heat-resistant chromium nickel steel tube 2 millimeters in thickness. The tube is heated externally by heating gases so that in the neighbourhood of the gas outlet the temperature in the interior is 770° C. A gas is obtained which contains from 30 to 35 per cent of olefines (from 20 to 25 per cent of C_2H_4 and 10 per cent of C_3H_6) 15 per cent of methane and from 20 to 25 per cent of hydrogen and also higher paraffin hydrocarbons. After using the tube for 8 days no deposition of carbon or attack on the tube can be detected.

What we claim is:—

In the conversion of a saturated gaseous hydrocarbon into unsaturated hydrocarbons by heat-treatment at a temperature between 600° and 900° C. in the presence of steam, the step of heating the said saturated gaseous hydrocarbons together with steam to the said temperature in a space confined by a chromium steel containing less than 2 per cent of nickel.

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