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PROCESS FOR THE PRODUCTION OF NITROGEN-HYDROGEN MIXTURES

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3 Claims. (Cl. 23—7)

This invention relates to a process for producing nitrogen-hydrogen mixtures by splitting hydrocarbons by means of steam and air.

It is known that hydrocarbons are converted into carbon monoxide or carbon dioxide and hydrogen respectively by passing the gases with the addition of steam at an increased temperature over catalytically acting substances. Likewise is known the splitting of hydrocarbons by means of oxygen, using air, for instance.

For splitting up hydrocarbons by means of steam a large amount of heat is required in consequence whereof the use of the well-known method of splitting by steam alone is of secondary importance in industrial exploitation.

It has been found that, when splitting hydrocarbons, say, of lighting gas, by means of air at a higher temperature, a liberation of carbon takes place at those sections of the apparatus where the mixture of gas and air is heated to the requisite reaction temperature.

This drawback is obviated if the heating is effected in a high-grade steel tube or such tubes which are either empty or provided with a filling of metal pieces. The surprising discovery was made that by this method the separation of carbon always incident to the superheating of the gases, even in the presence of steam and air, is rendered harmless, as the stream of gases carries these undesired carbon particles away with it right into the sphere of the catalytic reaction, i. e. into the reaction vessel. Here, then, the precipitated carbon is gasified by means of steam and air, especially by the first of these substances. Another advantage obtained by such metal-filled tubes is the excellent heat transmission.

When the process was developed it was discovered that, owing to the large amount of heat transmitted to the reaction mixture through the reaction-vessel walls, the retorts are subjected to so heavy strains as to undergo deformations or to fail in other ways. When utilizing heat-resisting alloys, especially for somewhat large containers, it is difficult to conduct the heat through right into the central portion without jeopardizing the mass by overheating.

It is, therefore, good practice to adopt double-walled vessels of annular cross-section, as retorts of circular or oval section have proved unable to stand the stresses when the heat transmission is to be uniform throughout and right into the centre. On the other hand, when using double-walled cylinders, the heat is uniformly transmitted into the annulus from all sides and the thickness of the layer is reduced with the result of better heat transmission.

A further improvement in the development of the process consists in working in two stages differing from one another in heat effect in such a way that in the first stage carried out at a lower temperature an endothermic reaction is generated, while in the second stage an exothermic reaction is produced.

Steam and air need not be added simultaneously; if, first, only steam and lighting gas are passed, say, over nickel charged on magnesite, an enrichment with hydrogen takes place in the gas-mixture above the catalytically acting substance as part of the methane and the whole of the heavy hydrocarbons have already entered into reaction at a comparatively low temperature. So, for instance, it was observed that the passage over nickel at 850° C. and a space velocity of 1: 1000 caused 25 to 30 per cent. of the existing methane to be converted into carbon monoxide and carbon dioxide.

According to this invention, the air necessary for the complete splitting-up of methane is only supplied just before or at that moment in which the gas mixture is admitted to the second stage, whereby it is useful to have the air, prior to its admission, pre-heated to the reaction temperature. If, now, in the second stage, the steam-containing gas air-mixture is passed over the nickel at an increased temperature, a part of the first-stage products, inter alia the excess of hydrogen evolved, is oxidized to water. The amount of heat liberated thereby is sufficient to heat the steam-containing mixture of gas and air to a temperature ensuring a perfect conversion of the methane into carbon monoxide and hydrogen. Therefore, supposing good insulation, the second stage can be carried out without additional external heating. Thus, for instance, with lighting or coke-oven gas of normal composition and with steam and air without any special addition of pure oxygen, one can manage, according to this invention, to introduce at once into the mixture the nitrogen necessary for the ammonia synthesis, which result, in the case of standard coke-oven gas, can be brought about neither by air alone nor by steam alone.

I am aware of the fact that it is known to convert carbon monoxide into carbon dioxide by means of steam in the presence of a catalyzator, and to cause thereafter the absorption of said carbon dioxide, and I therefore do

not claim either of these procedures singly or in combination with one another, in that my invention relates to a process for the production of nitrogen-hydrogen in which said conversions are merely steps in a particular succession (not alternation) of phases or stages, which succession constitutes the invention proper.

I thus claim:—

1. A process for the production of nitrogen-hydrogen mixtures by first splitting in known manner hydrocarbons by means of steam and air in the presence of catalytically acting substances, converting thereafter the carbon monoxide of the gas mixture so obtained to carbon dioxide by passing this gas mixture over a catalytically acting substance in the presence of steam, and finally causing absorption of the carbon dioxide, said process of producing nitrogen-hydrogen mixtures consisting therein that it is carried out in two stages, the first of which constitutes the endothermic part of the process and consists in converting only a part of the hydrocarbon with the aid of steam chiefly into carbon monoxide by means, and with the consumption, of heat, and the second of which constitutes the exothermic part of the process and in which air is added in order to convert the remaining hydrocarbons also chiefly to carbon monoxide, substantially as set forth.

2. A process for the production of nitrogen-hydrogen mixtures by first splitting in known manner hydrocarbons by means of steam and air in the presence of catalytically acting substances, converting thereafter the carbon monoxide of the gas mixture so obtained to carbon dioxide by passing this gas mixture over a catalytically acting substance in the presence of steam, and finally causing absorption of the carbon dioxide, said process of producing nitrogen-hydrogen mixtures consisting therein that it is carried out in two stages, the first of which constitutes the endothermic part of the process and consists in converting only a part of the hydrocarbon with the aid of steam chiefly into carbon monoxide by means, and with the consumption, of heat, and the second of which constitutes the exothermic part of the process and in which air is added in order to convert the remaining hydrocarbons also chiefly to carbon monoxide the amount of air in said second stage being so chosen that after the ensuing catalytic conversion of the carbon monoxide to carbon dioxide and after the absorption of the carbon dioxide (CO_2), as well as of other impurities perhaps present, the nitrogen and the hydrogen are present approximately in the ratio of 1: 3.

3. A process for the production of nitrogen-hydrogen mixtures by first splitting in known manner hydrocarbons by means of steam and air in the presence of catalytically acting substances converting thereafter the carbon monoxide of the gas mixture so obtained to carbon dioxide by passing this gas mixture over a catalytically acting substance in the presence of steam, and finally causing absorption of the carbon dioxide, said process of producing nitrogen-hydrogen mixtures consisting therein that it is carried out in two stages the first of which is carried out in a two-fold enclosed cylindrical reaction space and constitutes the endothermic part of the process and in which only a part of the hydrocarbons together with steam is chiefly converted into carbon monoxide by means, and with the consumption of heat, and the second of which constitutes exothermic part of the process and in which air is added in order to convert the remaining hydrocarbons also chiefly to carbon monoxide, substantially as set forth.

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