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COMPLETE SPECIFICATION.

Process for Producing a High Grade Gas Rich in Hydrogen.

We, VEREINIGTE STAHLWERKE AKTIENGESELLSCHAFT, a German Company, of 67/69, Breitestrasse, Düsseldorf, Germany, Assignees of ERNST HERMANN SCHULZ and FRANZ EISENSTECKEN, citizens of the German Republic, of 72, Kronprinzenstrasse, Dortmund, and 9, Delbrückplatz, Essen-West, respectively, Germany, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

It has already been proposed to transform hydrocarbons with the aid of water vapour, carbonic acid gas or air into mixtures of carbonic oxide and hydrogen by firing or passing them over contact-substances. Thus, according to a well known process gas mixtures containing hydrocarbons are transformed into mixtures of water gas in the presence of a quantity of oxygen and air which is insufficient to cause complete combustion, the gases resulting from this reaction, after having been cooled, being converted with water vapour and the carbonic acid gas formed removed in well known manner. The main purpose of this treatment of hydrocarbons effected according to known methods is to produce hydrogen, mixtures of hydrogen and nitrogen or water gas for use in the synthetic production of ammonia or methanol. With this use the residue of methane that is still present in spite of repeated conversions apparently does not interfere. If, however, by means of such a gas, mixture reducing processes, e.g. the extraction of metals from oxide ores, are to be carried out, the ore, or the oxidised or oxide-containing metal, will be reduced; at the same time, however, by the action of the methane contained in the gas mixture, carbonisation will take place to such a degree as to make a special treatment of the product thus obtained indispensable.

It is the object of the present invention to provide a process for converting distillation gases, hydrocarbons or gas mixtures containing hydrocarbons into a gas rich in hydrogen, which, being free from hydrocarbons, is eminently suitable for the purpose of reducing oxide ores, oxides, or metals containing oxides. In carrying out the process the starting gases are passed over catalysers together with superheated steam at a temperature of 1000° C. or more. Particularly suitable catalysers are iron, cobalt, nickel, chromium, aluminium, manganese, copper, vanadium, tungsten, as well as their alloys one with another. Preferably the reaction is carried out in a channel of refractory material which is heated by means of an external source. In this connection carborundum proves to be a particularly valuable material, exercising at the same time an exceedingly beneficial catalytic influence on the process. The arrangement may be modified, as by disposing tubes of heat-resisting material in a channel lined with refractory material. Into these tubes the catalyser will be introduced and the gases under treatment will pass therethrough. By such an arrangement the heating surface and the contact-substance supplement one another as far as their respective actions are concerned. In order to compensate for the decrease in strength of the refractory material which occurs in consequence of the high temperatures employed, the tubes may be disposed on supports of refractory material. The tubes must not be supported over their entire surface, but at several spaced points only, the size of the separating spaces depending upon the temperatures employed and the nature of the material. These tubes are heated from the outside and their supports may be arranged in such a way as positively to impose a circuitous or other path upon the combustion gases, that is to say, for example, the tubes may be supported in jackets of refractory material each formed with a helical passage extending from end to end around the tube or formed by a helically disposed length of the material surrounding each tube and carried in a suitable framework, or the tubes may be supported on longitudinally and radially disposed lengths of the material which may be interrupted and may break joint.

For the purpose of generating the tem-

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perature suitable for bringing about the reaction the heat may be produced in the space where the reaction takes place as by making use of the inductive action of an electric current of high tension or frequency either by directly connecting the catalyser to the source of electric current or by arranging in the reaction-space suitably shaped metallic bodies which first of all serve to receive the electric energy inductively and to pass it on as heat to the catalysers. Such bodies must have as large a superficial area as possible. The small tubular bodies known as "Raschig" rings have been found to answer well. Good results have also been secured with metal turnings. For the purpose of obtaining a larger throughput the starting substances are preferably pre-heated without causing an essential change to take place in the composition of the starting mixture. The heat necessary for the pre-heating operation may be advantageously derived from the waste gases generated in the course of the process. The starting material, before being introduced into the reaction space, will be freed from sulphur compounds in well known manner.

By means of the new process a gas perfectly suitable for reaction purposes is produced from distillation gases, hydrocarbons or gas mixtures containing hydrocarbons. As compared with mixtures obtained by known processes the new gas is advantageously characterised by the entire absence of hydrocarbons. The carbonic oxide produced, on account of its degree of concentration, has also a beneficial action upon the reaction process. The mixture obtained according to the new process represents not only a suitable reducing agent, but is also well adapted for the production of pure hydrogen or mixtures of nitrogen and hydrogen for synthetically producing ammonia and methanol.

EXAMPLE.

50 cbm of coke gas (of a composition comprising about 2.6% CO_2, 2.2%, heavy hydrocarbons 1.0% O_2, 6.6% CO, 22.4% CH_4, 58.7% H_2 and 12.1% N_2) are passed together with 12 kg of superheated water vapour over an activated chromium-aluminium compound contact at a temperature of 1100° C. A gas is produced having about the following composition: 20% CO, 71% H_2 and 9% N_2.

No claim is made per se to the details of construction of the apparatus as hereinbefore described, nor to the use of the particular catalysers that are herein mentioned.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for producing a high grade gas rich in hydrogen from distillation gases, hydrocarbons and mixtures of gases containing hydrocarbons, which gas is suitable for the reduction of oxide ores, iron oxides and iron-containing oxides, characterised by the fact that the gases from which the said gas is produced are passed at a temperature of 1000° C. or more, together with superheated steam, over metallic catalysts, so that practically only nitrogen and carbon monoxide are present together with the hydrogen in the gas produced, substantially as hereinbefore described.

2. Process according to claim 1, characterised by the fact, that iron, cobalt, nickel, chromium, aluminium, manganese, copper, vanadium, tungsten, as well as their alloys one with another are employed as catalysers.

3. Process according to claims 1 and 2, characterised by the fact that the reaction is carried out in a channel of refractory material such as carborundum, heated from outside.

4. Process according to claims 1 and 2, characterised by the fact that the reaction mixture is passed through metallic tubes embedded into a channel lined with refractory material in which they are surrounded by the combustion gases.

5. Process according to claim 4, characterised by the fact that the tubes are mounted on supports of refractory material.

6. Process according to claim 5, characterised by the fact that the tubes are supported at several points, the size of the spaces between these points depending upon the temperatures employed and the nature of the material.

7. Process according to claim 5, characterised by the fact that the supports are disposed relatively to the tubes in such a way as positively to direct the combustion gases.

8. Process according to claims 1 and 2, characterised by the fact that the heat necessary for heating the catalyser and for carrying through the reaction is generated in the reaction space proper, e.g. by the inductive action of an electric current of high tension or frequency.

9. Process according to claim 8, characterised by the fact that the catalyser itself receives the electric energy thereby being heated to the desired temperature.

10. Process according to claims 1, 2 and 3, characterised by the fact that in the reaction space suitably shaped metallic bodies are arranged which are capable of

receiving the electric energy and passing it on to the catalyser and the reaction mixture in the form of heat.

11. Process according to claims 1 and 2, characterised by the fact that the starting substances are preheated without causing an essential change in the starting mixture.

12. Process according to claim 11, characterised by the fact that the heat necessary for preheating is derived from the waste gases generated in the course of the process.

13. Process according to claims 1 and 2, characterised by the fact that the starting substances, before being introduced into the reaction space, are freed from sulphur compounds.

Dated this 3rd day of July, 1929.

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Reference has been directed, in pursuance of Section 7, Sub-section 4, of the Patents and Designs Acts, 1907 to 1921, to Specifications Nos. 274,610, 163,703 and 401/1911.

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