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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in and relating to the Production of Gaseous Mixtures suitable for the Synthesis of Hydrocarbons, Methanol, and other Oxy-organic Compounds.

I, GIULIO NATTA, of 19, Via Rugabella, Milan, Italy, an Italian Subject, 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:—

The present invention is for an improved production of gaseous mixtures comprising carbon monoxide and hydrogen suitable for the synthesis of hydrocarbons, methanol and other oxy-organic compounds.

For the synthesis of methanol and other organic substances by catalytic action under pressure, it is generally necessary, in order to obtain good yields and a continuous circulation of the gaseous masses, to employ the gaseous mixtures in as pure a state as possible. The condensation of inert gases and waste of energy for their compression and circulation is so avoided. Further the life of the catalysts is thus prolonged.

The methods which have been used up to the present for the preparation of mixtures of carbon monoxide and hydrogen and which are based on the use of water gas and on the enrichment of the latter with hydrogen, can hardly give very pure mixtures of carbon monoxide and hydrogen unless resource be had to costly and complex methods of purification. In the manufacture of water gas it is difficult to separate completely the gas of the air phase from that of the steam phase, and the gas thus remains contaminated with nitrogen. This last takes no part in the synthesis of organic substances under pressure, and it accumulates during the process in the circulating gases which have to be discharged from time to time, and so interrupts the operation.

Enrichment of water gas with hydrogen in order to obtain a mixture containing two or more molecules of hydrogen for each molecule of carbon monoxide, demands a noteworthy production of hydrogen, either derived from water gas itself or from the electrolytic method. These processes require a delicate and costly plant, and a great consumption of electric energy.

The process of the present invention gives readily, and without the use of catalysts or electrolytic hydrogen, mixtures of carbon monoxide and hydrogen in the pure state in the requisite proportion needed for the synthetic manufacture e.g. methyl alcohol.

In the manufacture of water gas by passing oxygen and steam over incandescent carbon in special generators, the following reactions take place:—

(1) $2C + O_2 = 2CO + 58.000$ calories
(2) $C + O_2 = CO_2 + 97.000$ calories
(3) $2CO + O_2 = 2CO_2 + 136.000$ calories
(4) $C + CO_2 = 2CO - 39.000$ calories
(5) $C + H_2O = CO + H_2 - 39.300$ calories
(6) $C + 2H_2O = CO_2 + 2H_2 - 39.600$ calories.

The reactions which lead to the formation of CO require temperatures higher than those at which CO_2 is formed. Many of the processes proposed up to the present for the preparation of water gas with oxygen demand high temperatures to increase the proportion of carbon monoxide and thus give gases of superior combustible power. In these cases the generator allows of rapid production, but there are inconveniences such as the formation of clinker and the attack or corrosion of the refractory linings. In the process of the present invention, the temperatures of the generator are maintained low so that there is generally produced the following reaction:—

(7) $5C + 2O_2 + 4H_2O = 3CO_2 + 2CO + 4H_2 + 76.000$ calories.

The heat developed is quite sufficient to maintain the temperature of the generator at the point at which the reaction takes place. The mixture thus obtained contains two molecules of hydrogen per molecule of carbon monoxide and, after removal of the carbon dioxide, may be employed in the synthesis of methyl alcohol and other oxygenated organic compounds. The elimination of the carbon dioxide is easily effected and without notable waste of energy, seeing that during the compression of the gases before

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their conduction to the synthesis tower, the carbon dioxide may be dissolved in water and the energy of expansion of the so dissolved CO_2 recovered.

By preheating the mixture of oxygen and water vapour by the heat of the gases issuing from the generator, the following reaction can also be obtained:—

(8) $3C+O_2+3H_2O=2CO_2+CO+3H_2+19.000$ calories.

After eliminating the carbon dioxide, a gas is thus obtained which is still richer in hydrogen and which may be employed in the synthesis of hydrocarbons. By reason of the energy of the combustion with oxygen, it is very difficult to keep the temperature within the limits of 700—750° C. between which the reaction indicated under (7) above takes place. To obtain the reaction indicated under (8) above, it is necessary to keep to even lower temperatures.

The process of this invention renders it possible to keep within the said limits of temperature and to obtain a gas whose composition corresponds to the reactions indicated, the velocity of gas in the generator being maintained low and the concentration of oxygen being reduced by an excess of water-vapour. In order to regulate the generator temperature, on which the composition of the gas depends, especially as regards the ratio (hydrogen : carbon monoxide), the temperature of the gas entering the generator may be modified, either by preheating more or less by the heat of the issuing gases or by cooling the generator itself with water instead of steam.

Whilst at temperatures from 900° to 1000° C. a gas may be obtained containing from 4 to 8 per cent of carbon dioxide and over 65 per cent of carbon monoxide, by working at temperatures between 700 to 750° C, with oxygen and water-vapour (for example, steam) in the proportions of one volume of oxygen to two volumes of water-vapour, a gas is produced, by using the process just described, containing 30—35 per cent of CO_2 about 20 per cent of CO, and 40—45 per cent of hydrogen. This mixture, more particularly suitable for the production of alcohols, such as methanol, contains at the most from 1—1.5 per cent of uncombined oxygen, and it is practically free from nitrogen, the slight traces of which may be regarded either as a chemical component of the coke, or (when wood-carbon is employed) as absorbed from the air by the carbon. This process permits of the application, for the synthetic manufacture of alcohols and of other organic products of high value, of the oxygen which forms a by-product in the electrolytic manufacture of hydrogen, and which, for the greater part, has not hitherto been utilised.

Moreover, the process of the present invention offers the great advantage over the other known processes based on the enrichment with hydrogen of ordinary water gas obtained according to the reaction :—

$$CO+H_2O=CO_2+H_2$$

that it does not require costly apparatus, high working costs or the employment of catalysts. The process also permits of the obtention of a purer gas, whilst the utilisation of the heat of the generator is better and the carbon monoxide as well as the hydrogen are produced in the desired proportion but in larger volume and with a notably lower consumption of carbon.

This process may also be used in the preparation of hydrocarbons such as methane. By working the generator at lower temperature (not exceeding about 700° C.) and preheating the oxygen and the water vapour which are in the proportions of 1 volume of oxygen to three volumes of water vapour (for example, steam), to substantially the desired reaction temperature, the optimum being about 600° C, it is possible to obtain gaseous mixtures which contain three volumes of hydrogen per volume of carbon monoxide. From this mixture, by the known catalytic reaction :

$$CO+3H_2=CH_4+H_2O$$

it is possible, after elimination of the carbon dioxide, to obtain methane of a high grade of purity. In order to accelerate the working of the generator and to obtain more easily a high hydrogen and carbon dioxide content, it is advisable not to work the generator at reduced pressure, and it may be advantageous to employ a pressure much higher than the ordinary pressure but for practical purposes such pressure should be limited to pressure below 15—20 atmospheres, the oxygen and steam being introduced at such high pressure. Part of the heat of reaction in the generator itself is utilised under the form of compression work. In fact, the increase in volume which the gases undergo during the reaction in the generator economises the work that would be required to compress the gases from the ordinary pressure to that which corresponds to the pressure in the generator. Moreover, a higher pressure favours the formation of carbon dioxide instead of carbon monoxide, because all the reactions which lead to the formation of the former take place with little or no variation of volume, while the reactions which lead to the formation of CO take place with a large increase of volume.

It has already been proposed (British Patent Specification No. 304,760) to pass

mixtures of oxygen and steam in excess over semi-coke for the purpose of obtaining a gas richer in hydrogen than in carbon monoxide and utilisable as a combustible. No broad claim is made herein to the production of carbon monoxide-hydrogen mixtures richer in hydrogen than in carbon monoxide. The present invention depends upon operating in the presence of carbon practically free from volatile impurities, at a maximum temperature of substantially 750° C with so proportioned an initial gas mixture containing steam and oxygen as to yield a mixture for organic syntheses wherein there are at least two volumes of hydrogen for every volume of carbonic oxide.

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

1. For organic syntheses, for example, of hydrocarbons, methanol and like oxy-organic compounds, the manufacture of a gaseous mixture of carbon monoxide, carbon dioxide and hydrogen containing at least substantially two volumes of hydrogen for each volume of carbon monoxide, by passing a mixture comprising oxygen and water-vapour (for example, steam) in the proportion of not more than substantially one volume of oxygen to substantially two volumes of the water-vapour over carbon substantially free from volatile impurities at a re-action temperature not exceeding about 750° C., substantially as described.

2. A process according to Claim 1, wherein a mixture of substantially one volume of oxygen and two volumes of water-vapour (for example, steam) is passed over the carbon while the temperature is maintained between approximately 700° to 750° C., for the purpose of obtaining a gaseous mixture which, free from carbon dioxide, is composed of substantially two volumes of hydrogen to one volume of carbon monoxide, suitable for the manufacture of methanol.

3. A process according to Claim 1, wherein a mixture of substantially one volume of oxygen and three volumes of water-vapour (for example, steam) is passed over the carbon while the temperature is maintained below about 700° C., for the purpose of obtaining a gaseous mixture which, freed from carbon dioxide, is composed of substantially three volumes of hydrogen to one volume of carbon monoxide, suitable for the manufacture of hydrocarbons.

4. A process according to any of the preceding Claims wherein the gaseous mixture passed over the carbon is introduced into the reaction-sphere at a pressure higher than the atmospheric pressure.

5. A process according to any of the preceding claims wherein the necessary reaction temperature is regulated by varying the preheating of the gaseous mixture led to the carbon.

6. A process according to any of the preceding claims Nos. 1 to 4, wherein the necessary reaction temperature is regulated by introducing into the reaction sphere suitable quantities of water in place of the corresponding quantities of steam.

7. A process according to Claim 5, wherein the preheating of the gaseous mixture led to the carbon is effected by the heat of the gases withdrawn from the reaction-sphere.

8. The improved process for the manufacture of gaseous mixtures for organic syntheses, substantially as hereinbefore set forth.

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