PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

405

Treating Coke Oven Gas.

We, COMPAGNIE DE BETHUNE, of Bully-les-Mines, (Pas-de-Calais), France, a French Corporate Body, 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 object of this invention is a new and useful process for preparing nitrogen, carbonic oxide and hydrogen in view of simultaneous synthesis of Ammonia and of methyl alcohol from coke oven gases of which the following is a true, clear, and complete specification.

Persons skilled in the art are aware that coke oven gas is nowadays an important raw material in the synthetic ammonia industry. Coke oven gas usually contains about 50% of hydrogen.

Many processes have been proposed for extracting and utilizing the said hydrogen, and the present invention relates exclusively to coke oven gas that has been so treated and having a hydrogen content more nearly in the region of 10%.

In such residual gases there remains a variously proportioned mixture of methane, of ethylene, of propylene, of ethane, of carbonic oxide, of carbonic anhydride, of nitrogen and also of a little residual hydrogen. Some of those gases may, however, have been partly or totally separated in view of other manufacturings or else for requirements of a technical order.

According to our invention, we prepare from dehydrogenated coke oven gas by a process of partial combustion with air, a mixture of carbon monoxide, hydrogen and nitrogen which is adapted to be directly manufactured after removal of unsaturated hydrocarbons and CO_2, into methyl alcohol and ammonia on addition of further quantities of pure hydrogen to complete the requisite amount.

Those skilled in the art know the general phenomenon that if hydrocarbons are burnt in a quantity of air insufficient for complete combustion, the resulting mixture includes nitrogen, carbon monoxide, hydrogen and water vapour, together with a little carbon dioxide. The carbon monoxide content of the mixture is, however, usually too high for the mixture to be used directly for ammonia synthesis, and it is thus necessary to get rid of it. This is generally accomplished by the action of steam on the gaseous mixture in the presence of catalysts or by combustion with additional air. Whatever means is employed, the elimination of the CO in the form of CO_2 is very costly.

In the process according to the present invention, utilizing dehydrogenated coke oven gas as a starting material, all the carbon monoxide contained in the gaseous mixture is allowed to remain, and it is only necessary to remove the valueless carbon dioxide and water vapour which moreover are formed only in small quantities.

Now we have discovered that by means of a partial combustion carried out with a largely insufficient amount of air, and furthermore conducted under carefully-regulated conditions, it is possible to obtain from the residual gases proceeding from the manufacture of hydrogen from coke oven gases a lean gas very rich in nitrogen, containing 15% to 20% hydrogen, 10% to 15% carbon monoxide and CO_2 lying between 4% and 5% which is easily removable, but free from hydrocarbons, except for small traces which are removed by metallic catalysts.

It is a characteristic of the present invention that the CO_2 content is maintained between 4% and 5% during the partial combustion as will be hereinafter described.

The elimination of the carbon dioxide is done by washing with ammonia solution; on the other hand the whole of the carbon monoxide remains in the gaseous mixture to be used in the synthesis of methyl alcohol, so that the purification which is consequently greatly simplified is confined to the elimination of the hydrocarbons and carbon dioxide.

As a matter of fact, the residual gases forming the starting material may be likened, to some extent, to a fuel which the problem is to transform into another combustible gaseous mixture through in-

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complete combustion, as is done with coal or coke in gas generators. The resulting lean gas will, however, be richer in hydrogen than a lean coal or coke producer gas, owing to the substantial amount of hydrocarbons and, more particularly of methane existing in the initial mixture. Said hydrocarbons would normally, under the influence of heat, decompose into carbon and hydrogen, but experiments have shown that if only a part of the hydrogen is oxidised and if another part thereof remains in a free state, the whole of the carbon is, on the contrary, transformed into carbon monoxide, a small fraction of said carbon monoxide being in its turn oxidised as CO_2.

Were operations conducted without precautions, there would, besides, be found traces of oxides of nitrogen, to an amount, however, which would appear less heavy than in the case of complete combustion.

We have discovered that the formation of oxides of nitrogen in the course of incomplete combustion can be avoided by operating under certain conditions hereinafter described but that, per contra, there remain in the gases small traces of unsaturated hydrocarbons, especially of acetylenic hydrocarbons, which are equally detrimental to ammonia catalysis; and which we have been able to rid of through dissociation at a high temperature in the presence of iron, chromium or nickel turnings or, better still, of an alloy made up of these three metals. Once the conditions for correct manufacturing of the gaseous mixture rich in nitrogen are achieved, we find ourselves in the presence of nitrogen, of hydrogen and of carbon monoxide.

Hydrogen is then added in such proportions that the hydrogen content of the final mixture is twice that of the carbon monoxide contained therein, and three times that of the nitrogen according to the symbols.

$$\begin{gathered} CO+2H_2 \text{ and} \\ N_2+3H_2 \end{gathered}$$

The syntheses of methyl alcohol + ammonia are afterwards carried out by following known processes:

Nitrogen and hydrogen are suitable for ammonia synthesis, and the carbon monoxide can be eliminated by already known processes through transforming the greater part thereof into methyl alcohol which is condensed, and the remainder into methane, a gas which has practically no action on ammonia catalysis, contrary to what occurs with unsaturated hydrocarbons.

We will now describe the process and the plant for performing the same which are the objects of our invention, by referring to the sole Figure of the drawing appended hereto.

The residual gas after the removal of hydrogen from coke oven gas and blown by compressor 1 is mixed with a proper amount of air blown by compressor 1^1, and the mixture is injected into a tower or gas generator 2, filled with refractory material broken in small bits, and maintained at a high temperature by the reaction itself. The supply rate of the gaseous mixture is so adjusted that combustion takes place without any flaming at the gas generator inlet and continues chiefly in the interstices of the refractory material with which the latter is furnished.

The hot gases pass next into tower 3 containing Fe, Ni or Cr turnings, or alloys thereof, and are here subjected to the catalytic reaction intended to destroy all traces of unsaturated hydrocarbons.

The gases are then cooled by means of water sprinkling in a scrubber 4, after which they pass into another scrubber 5, sprinkled with an ammonia solution. A last washing with purified water in a tower 6 dissolves the traces of ammonia carried by the gas.

A pump 7 circulates the ammonia solution which passes through a trough 8 whereinto fresh solution is fed in a continuous manner while the used solution is drained, also continuously, at any point of the circuit. Combustion is controlled mainly by regulating the relative proportions of gas and of air, and the temperature inside the gas generator so as not to produce oxides of nitrogen. Experience has shown between what limits it is necessary to confine the temperature. Near the bottom of the refractory bricks, the temperatures should not be allowed to fall lower than 1200° C. so that the hydrocarbons are practically all dissociated. For this purpose, we have but to avoid exceeding in the gases issuing from the combustion tower a maximum CO_2 content which will vary according to the composition of the initial gas, the rate of supply of the gas, and incidental variations as by heat losses from conduction and radiation, but will always be about 4 or 5% (analysis effected after steam condensation). In practice it is sufficient to take tests from time to time to ascertain the CO_2 content, and control the supplies of gas and air accordingly.

For example, with an initial gas composed as follows:

CO_2	0
O_2	2.4
C_nH_m	0.7
CO	7.5
H_2	10.4
CH_4	65
N_2	14
	100.00

the temperature is kept below 1300° C. on maintaining the CO_2 content below 4.7%. When the reaction is so conducted that the CO_2 content remains between 4.4 and 4.7% (corresponding to the two extremes of temperature 1200° C. and 1300° C.) the following final gaseous mixture has been obtained:

CO_2	4.6
O_2	0
C_nH_m	small traces
CO	11.8
H_2	16
CH_4	0
N_2	67.6
	100.00

The mixture contains no trace of oxygenized nitrogen compounds.

The traces of unsaturated hydrocarbons, and especially of acetylenic hydrocarbons, that may exist in the gas after combustion are eliminated by catalytic destruction at a high temperature in the presence of iron or nickel or chromium turnings, or, preferably, in the presence of an alloy made up of these three metals.

The gases are deprived of their CO_2 contents through washings with an ammonia solution and next with purified water in order to dissolve the ammonia carried along. The gases are then fit to be mixed with the hydrogen intended for the direct synthesis of methyl alcohol and ammonia, in which process the final mixture is compressed to 900 atmospheres and passes, at a suitable temperature, to a first catalyst which produces the synthesis of methyl alcohol.

$$CO + 2H_2 = CH_3OH.$$

Next, after the condensation and extraction of the methyl alcohol, the mixture, still subjected to the same pressure, passes to the apparatus for the ammonia synthesis preferably by the Claude process.

The combustion in the gas generator 2 at the proper temperature at the base of the refractory bricks is insured by maintaining the CO_2 content in the final gas between 4% and 5% corresponding to a temperature not exceeding 1300° C. The upper limit, however, is obviously of more importance than the lower, for if this upper limit is passed one runs the risk of producing oxides of nitrogen, whilst on falling below the lower limit only saturated hydrocarbons are introduced which play but an inert part in the reaction and which when present in small quantities diminish only slightly the yield of the catalyst. Thus, the combustion is effected by endeavouring in practice to keep below the maximum limit set by the conditions of the moment; consequently the CO_2 content will be maintained closer to the lower than the upper limit, so as not to be taken by surprise in the event of an untimely increase in the rate of combustion.

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 mixture of hydrogen nitrogen and CO from dehydrogenated coke oven gas suitable for direct synthesis of alcohol and ammonia consisting in effecting the incomplete combustion of said gas so that the CO_2 content is maintained between 4% and 5% so that oxides of nitrogen are not produced, and thereafter eliminating unsaturated hydrocarbons and CO_2.

2. A process according to Claim 1, in which the products of combustion are freed from traces of unsaturated hydrocarbons contained therein through hot catalytic destruction in the presence of iron, nickel or chromium, or of an alloy made up of these three metals, and, on the other hand, from CO_2 by washing by means of an ammonia solution.

3. The use of the gaseous mixture according to any of the foregoing claims for direct synthesis of methyl alcohol and of ammonia.

4. The improved process for producing a mixture of hydrogen, nitrogen and carbon monoxide substantially as described.

Dated this 22nd day of June, 1929.

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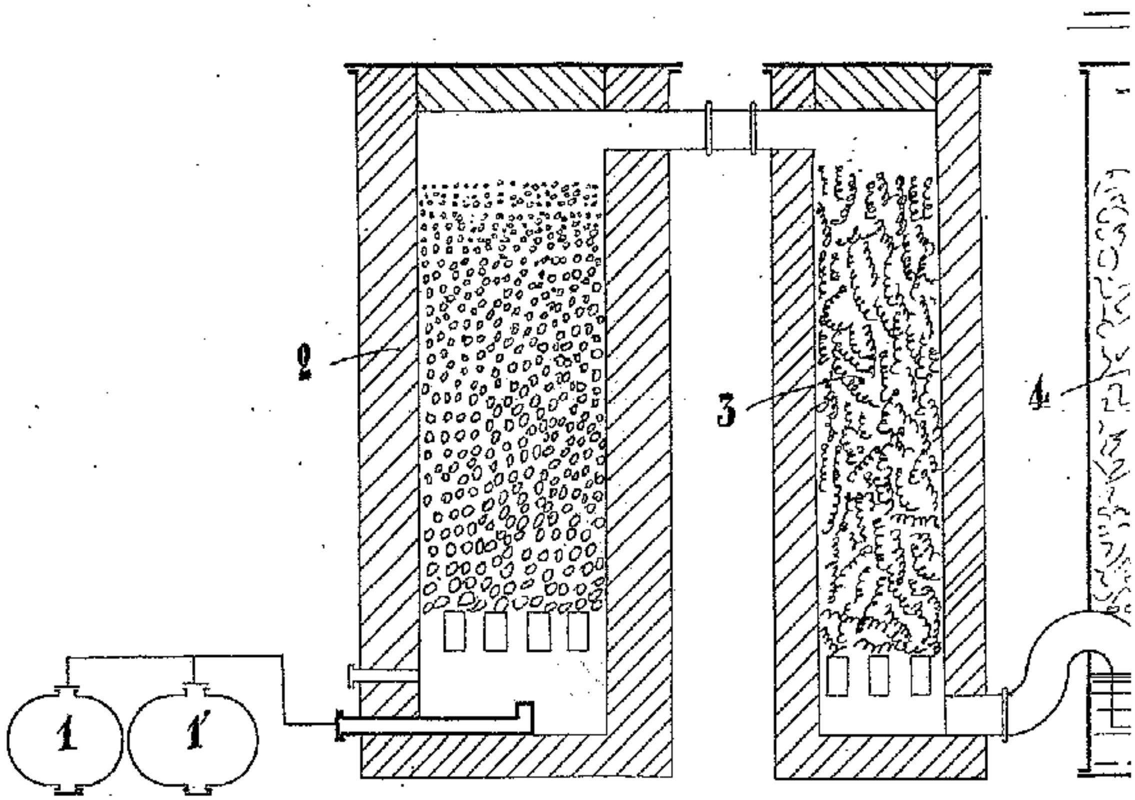
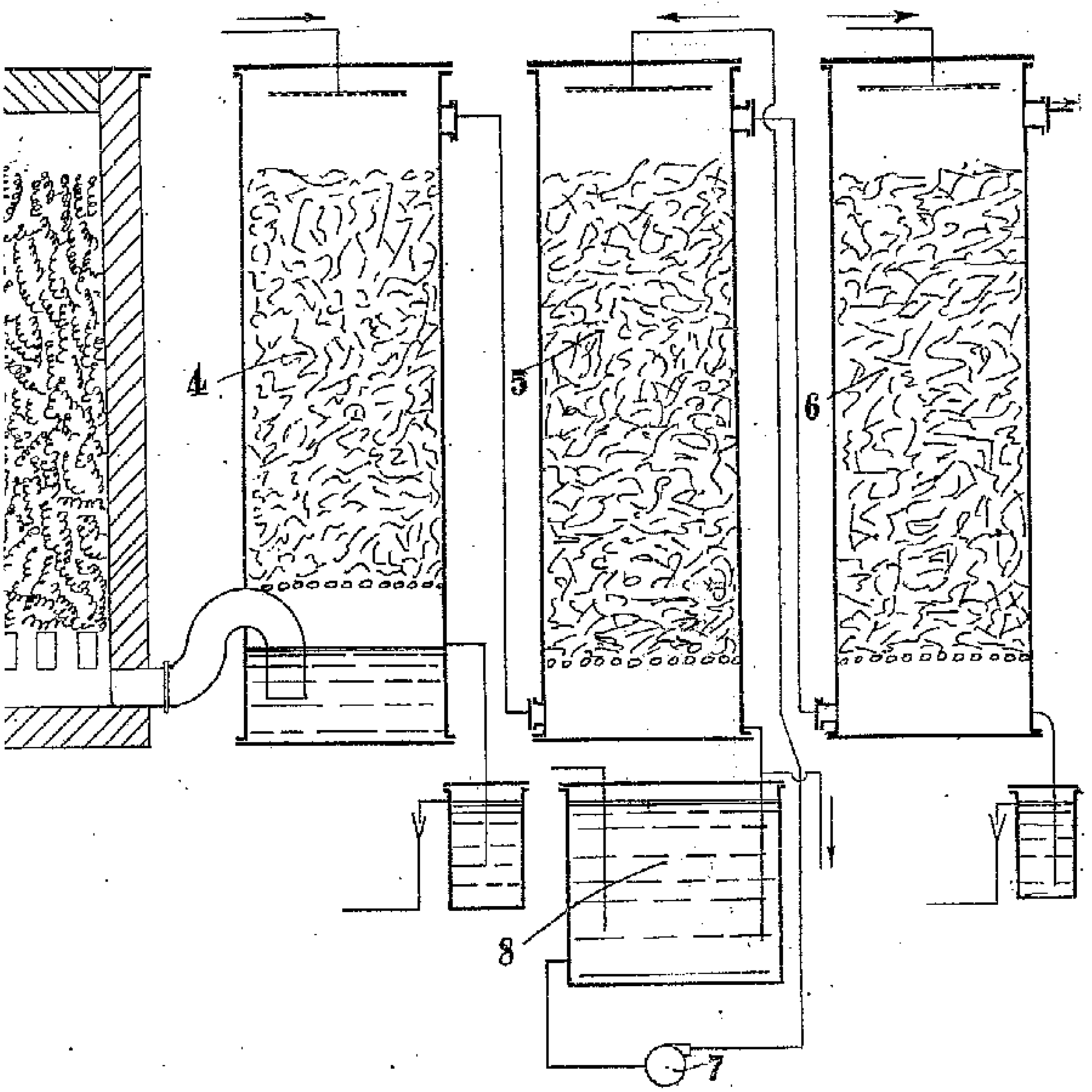
[This Drawing is a reproduction of the Original on a reduced scale]





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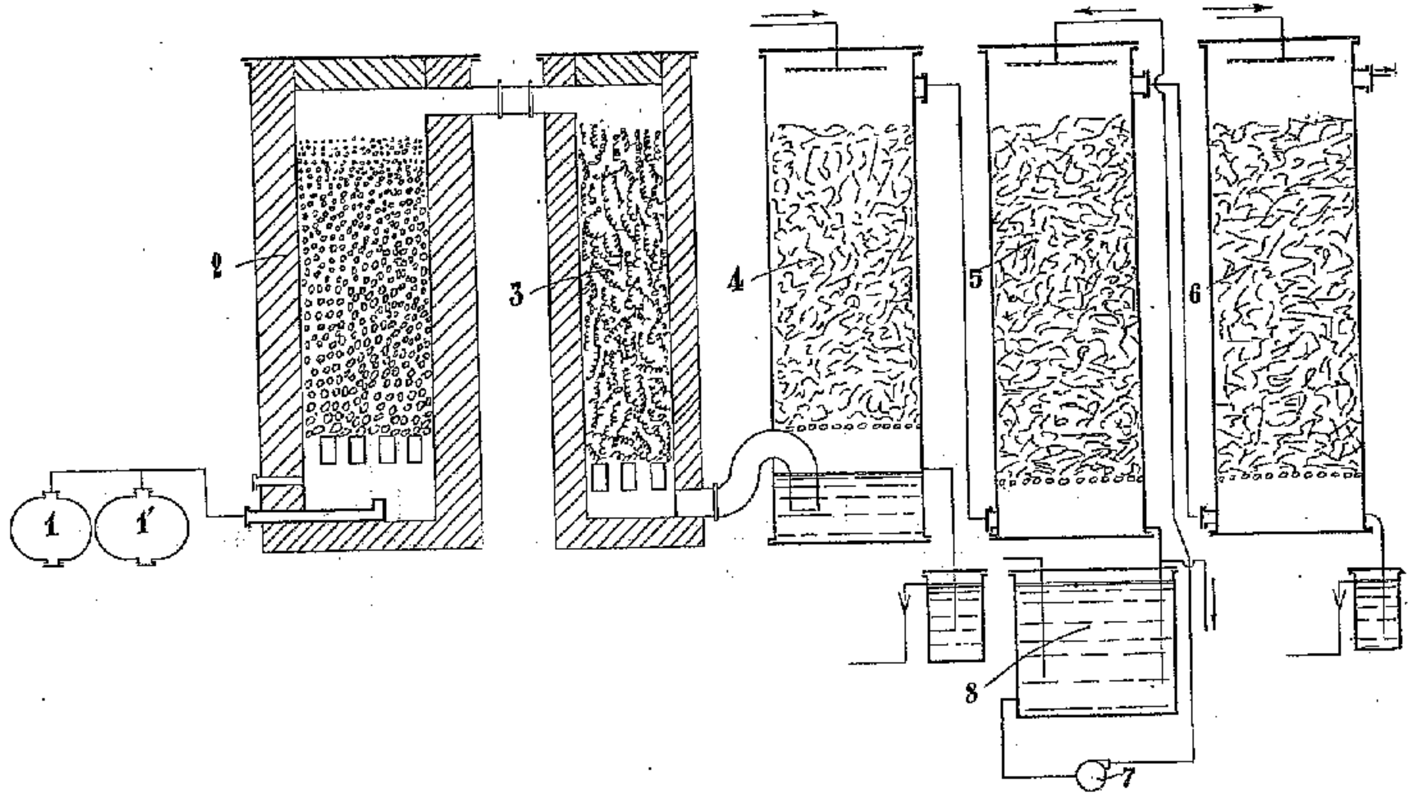

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