

PATENT SPECIFICATION.



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COMPLETE SPECIFICATION.

Method for Simultaneously Synthesizing Methanol and Liquid Hydrocarbons.

I, GEORGES PATART, 60, rue Spontini, Paris, France, a citizen of the French Republic, 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 gas mixtures which are subjected to a catalytic treatment for the synthetic manufacture of methanol and the homologous alcohols consist essentially of oxides of carbon and hydrogen. It has already been observed that said mixtures may also contain saturated hydrocarbons (such as methane) which may wholly or partially replace hydrogen in the gas mixture. In my prior Specification No. 247,178, I have indicated that, if a relatively large amount of ethylene or its homologues (about 10 to 40% of the total volume of gas mixture) is added to the mixture, this ethylene will condense into a mixture of liquid hydrocarbons which are partially saturated, without offering prejudice to the production of methanol from the other components of the initial mixture.

It has been already proposed to manufacture oxygenated organic compounds by a process which consists in subjecting to the action of a methanol forming catalyzer, a gas mixture formed of mixtures of industrial gases such as water gas, coal gas, coke oven gas or low temperature carbonisation gas. In this known process, said industrial gases must be purified in order to remove unsaturated or aromatic hydrocarbons, while methane hydrocarbons remain in the mixture, they being considered not injurious.

In my Specification No. 247,178, I have already mentioned the utilisation of ethylene which is contained in coal dis-

tilation gas at the rate of 2 to 3%, amount which is then increased to 10 to 40% before subjecting the gas mixture to the catalysis.

The process forming the subject of the present invention consists in subjecting to the action of a methanol-forming catalyzer, a mixture of water-gas with a gas from the distillation of coal, in substantially equal parts by volume, both gases having their normal industrial composition whereby the mixture contains ethylene.

The gas mixtures consist exclusively of the gases from the distillation of coal of the current varieties and water gas. Both the illuminating gas or coke oven gas and the water gas have not been subjected to any more important purifying operations than those in normal use for illuminating gas and, hence, the coal distillation gas contains ethylenic compounds.

These two gases are mixed in about equal proportions, but these may vary according to the composition of the gases. The synthesis takes place at the maximum pressure, and is continued, by successive circulations, upon the catalyzer and subsequent condensations, until the production of the liquid has fallen to a rate which is considered insufficient. The following example will illustrate the manner in which the operation may be performed:

EXAMPLE:

By mixing equal parts of Paris city gas as commonly used, and of industrial water gas, there is obtained a gas mixture having the following composition: CO₂, 3 per cent.; O₂, 0.6 per cent.; C₂H₄, 1.4 per cent.; CO, 26 per cent.; H₂, 54 per cent.; CH₄, 8.9 per cent.; N₂, 6 per cent.

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This gas mixture is treated as follows: The said mixture is circulated for eight hours in a closed circuit, and at a pressure of 150—250 atm., upon a catalyzer consisting of a mixture of zinc oxide and chromium oxide obtained by reducing agglomerated basic chromate of zinc, and which is maintained at 300 degrees C.; the part of the gas entering into the reaction is periodically replaced by a like amount from the initial gas mixture; in these circumstances, I collect a homogeneous liquid by condensation with cooling, while maintaining the pressure. The said liquid, when diluted with water, will separate into two layers. The upper layer, consisting of hydrocarbons, represents some 2.5 per cent. of the total volume; the lower layer consists of methanol in the practically pure state, diluted with water.

On the other hand, the final composition of the circulated gas is as follows: CO_2 , 1.2 per cent.; O_2 , 0 per cent.; C_2H_4 , 2.2 per cent.; CO , 27.2 per cent.; H_2 , 16.7 per cent.; CH_4 , 27.3 per cent.; N_2 , 25.4 per cent.

From the above composition, it will be seen that the percentage of nitrogen, which latter may be considered as inert, is more than four times larger than initially. On the contrary, the percentage of ethylene is only 60% larger than initially. This relatively small proportion of ethylene in the final mixture shows that an important portion of ethylene has been condensed into liquid hydrocarbons, simultaneously with the hydrogenation of carbon oxides into methanol. Moreover, by comparing the initial and final percentage of methane it will be seen that more than 25 per cent. of the methane enters into the reaction but it has been ascertained that the methane is converted into methanol and does not contribute to the hydrocarbon production.

It has been further observed that towards the end of the operation, and during the last hour of operation, the production of methanol is scarcely reduced, whilst the partial pressure of hydrogen in the gas mixture subjected to catalysis is hardly over 34 atm. So that when operating at a total pressure of 800—1000 atm. the operation can be continued with a satisfactory output until the percentage of hydrogen in the mixture is reduced to 4 or 5 per cent.

The residual gas may be allowed to expand, with production of cold, by any known process, so as to liquefy the methane contained in the residual gas, whilst the other components of this gas remain in the gaseous state.

The methane may be separately collected and partially burned with practically pure oxygen as stated in my Specification No. 247,176 entitled: "Method for the utilisation of methane", which produces a mixture containing substantially 4 volumes of hydrogen for 2 volumes of carbon monoxide, this mixture being added to the original gas mixture in order to be again subjected to the catalytic action.

As to the part of the residual gas mixture which has not been liquefied, and which consists almost exclusively of hydrogen, nitrogen and carbon monoxide, the hydrogen can be separated therefrom by means known per se, and this hydrogen may also be added to the gas mixture concerned in the reaction. I am thus enabled, after the continuous operation has lasted for a stated time to much reduce the use of water gas in the preparation of the initial gas mixture.

As to the liquid product obtained by condensation the pressure being still maintained, it consists of slightly hydrated methanol having hydrocarbons in solution; it may be employed without further treatment for heating purposes or for carburization; in other cases the hydrocarbons can be separated therefrom by decantation, after adding water, and the aqueous solution of methanol when distilled, will furnish pure methyl alcohol.

The above described process affords the following advantage: The coal distillation gas and the water gas used as starting material need not be purified to a larger extent than usually, whereby the cost of the methanol obtained is materially reduced. Besides, the non saturated hydrocarbons contained in said gases will be condensed into liquid hydrocarbons of great commercial value. Although the percentage of non saturated hydrocarbons in the initial mixture is relatively low, the amount of hydrocarbons obtained is sufficient to render the process very economical.

A process of manufacturing methanol or other oxygen containing organic compounds has been already claimed, which resides in the catalytic treatment of illuminating gas used alone, freed from sulphur compounds and benzene hydrocarbons and having about the composition:—50 per cent. hydrogen, 30 per cent. methane, 12 per cent. carbon monoxide, 4 per cent. ethylene and 4 per cent. nitrogen; said illuminating gas is passed over a contact mass at 400 degrees Centigrade and 800 atmospheres pressure. I do not claim this process as my invention.

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:—

- 5 1. Method for simultaneously synthesizing methanol and liquid hydrocarbons which consists in subjecting to the action of a methanol forming catalyzer, a mixture of water-gas with a gas from the
10 distillation of coal, in substantially equal parts, by volume, both gases having their normal industrial composition, whereby the mixture contains ethylene.
- 15 2. Method according to Claim 1 which further consists in effecting an incom-

plete combustion of the methane contained in the residual gas, the mixture of hydrogen and carbon oxides contained in the residual gas and produced by said
20 combustion of the methane being partially substituted for the initial source of hydrogen and carbon oxides in the gas mixture under treatment.

- 25 3. Method for simultaneously synthesizing methanol and liquid hydrocarbons substantially as described.

Dated this 28th day of January, 1926.

MARKS & CLERK.

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