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2607

COMPLETE SPECIFICATION.

Method for the Simultaneous Manufacture of Methyl Alcohol and Liquid Hydrocarbons by Synthesis.

I, GEORGES PATART, 50, 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:—

It is a known fact that if gaseous mixtures composed of carbon oxides and hydrogen (or hydrocarbons rich in hydrogen), are subjected, at high pressure and temperature, to the action of suitable catalyzers, hydrocarbons or oxygenated derivatives of the hydrocarbons, such as alcohols, aldehydes, ketones, organic acids and the like are synthesized. By this process, liquid hydrocarbons can be obtained only by incorporating into the gas mixture a proportion of carbon monoxide which exceeds the proportion of hydrogen entering into the reaction either alone or in combination in the state of gaseous hydrocarbons, and in this event, the oxygenated compounds which are simultaneously obtained will form a very complex mixture, from which it is practically impossible to separate the component parts.

On the contrary, compounds which are soluble in water (with the exclusion of all hydrocarbons) and chiefly practically pure methyl alcohol are principally obtained by the utilisation—in the presence of suitable catalyzers—of gas mixtures wherein hydrogen preponderates relatively to carbon monoxide, for instance of mixtures containing carbon monoxide and hydrogen in the proportion of 1 to 2. Saturated gaseous hydrocarbons, rich in hydrogen, may be contained in the gas mixture and even replace part or all of the hydrogen, but it has been hitherto considered that the non-saturated and the aromatic hydrocarbons should be removed from the gas mixture before subjecting the latter to catalytic action.

But I have found—according to the present invention—this remarkable fact that, starting with a gas mixture in which the hydrogen and carbon monoxide are contained in the proportion of 2 to 1, and even in a higher ratio, if I introduce into the same a considerable proportion (10 to 40 per cent.) of ethylene or its homologues, and if the gas mixture thus containing a hydrocarbon is subjected to catalysis under pressure in the same conditions as the mixture composed solely of hydrogen and carbon monoxide —in the case in which only pure methyl alcohol is to be produced—I obtain in these new conditions a condensation product, from the gases which have been subjected to catalysis, consisting of a liquid which separates by its own means into two superposed layers, whereof the upper layer consists of a mixture of liquid hydrocarbons and the lower layer consists of methyl alcohol in a practically pure state, as if two reactions had taken place simultaneously with and independently of each other, one reaction consisting in the polymerisation (or condensation) of the ethylene into the state of liquid hydrocarbon, and the other reaction consisting solely in the formation of methyl alcohol at the expense of the carbon monoxide and the hydrogen. I even observe that the output of each of these reactions carried out at the same time upon a common catalyzer and at the same temperature and under a partial pressure which is necessarily reduced, is equal and even superior to what could be had by carrying out each of these two reactions, independently of one another, in the respective special conditions which are the most favorable to each of them, and that the purity of the products thus simultaneously obtained will not be affected.

As a rule, I obtain the best results as concerns the total output by operating under the conditions such as pressure, temperature, nature of the catalyzer and the like, which offer the maximum out-

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put and purity in synthesizing exclusively methyl alcohol from a gas mixture free from hydrocarbons. But in certain cases, I may depart from these conditions in order to obtain a particular increased output, or to obtain a determined quality of liquid hydrocarbons produced by the reaction. The operating pressure should be as high as possible and the temperature as low as possible.

The proportion of ethylene (or its homologues) which may be used in the gas mixture is about 10 to 40%. As a rule, I prefer to operate between 15 and 35 per cent., the remainder of the gas mixture consisting of hydrogen and of carbon monoxide in ratios variable between 10 and 1.5 to 1.

EXAMPLE:

I circulate, in a closed circuit, at 150—250 atm. pressure, a gas mixture containing (by volume) 23 per cent. of ethylene, 22 per cent. of carbon monoxide, 49.3 per cent. of hydrogen, 1.2 per cent. of carbon dioxide, 0.5 of oxygen and 4 per cent. of nitrogen upon a catalytic mass consisting of a basic chromate of zinc which is formed into grains by agglomeration and is preliminarily reduced in the reaction chamber itself by a current of pure hydrogen or by the gas mixture which is to be treated. The temperature of the reaction chamber is maintained at about 300 degrees C. The gas mixture, which is cooled in a certain part of the circuit, is partly condensed into a liquid which separates by its own means into two layers. The upper layer—which represents about $^1/_4$ of the total amount of the liquid—consists solely of a mixture of hydrocarbons showing the fluorescence which characterises the major part of the petroleum products; its specific gravity is 0.735 at 15 degrees C. This product when simply filtered, constitutes an excellent fuel for internal combustion engines such as aeroplane or motor vehicle engines. The lower layer, whose specific gravity is 0.805 at 15 degrees C., is almost entirely distilled over between 66 and 68 degrees C. and consists of methyl alcohol in a practically pure state, which holds in solution only traces of hydrocarbons and very small quantities of aldehydes or higher alcohols which can be eliminated by a single distilling operation.

Even after a continuous operation for several days, no carbon deposit is formed upon the catalyzer nor in the reaction chamber.

During the continuous circulation upon the catalyzer, the composition of the gas mixture will not appreciably change as concerns ethylene, hydrogen and carbon monoxide, if due care is taken to replace by a portion of initial mixture the fraction of the gas mixture combined and eliminated in the liquid state. Only very small quantities of saturated gaseous hydrocarbons will be produced, these consisting chiefly of ethane, and they can be discharged concurrently with nitrogen, when the amount of this latter which accumulates in the circuit is such that it must be discharged.

The process according to the invention thus offers a simple and practical means for the synthetic manufacture of liquid fuel for internal combustion engines, by the utilisation of ethylene which is contained in coal distillation gas at the rate of 2 to 3 per cent., the amount of ethylene being increased to the proportions of about 10 to 40% by mixing the coal, before the distillation, with heavy petroleum oils or the residues of their distillation. Ethylene may also be obtained from the gases produced by cracking heavy petroleum oils, or by treating in like manner vegetable oils or fish oils with or without catalytic action. In the case in which—due to special economic conditions—ethyl alcohol extracted from vegetable raw material should be cheaper than gasoline it may be preferable to specially produce the ethylene by the catalytic dehydration of this ethyl alcohol, thus converting ethyl alcohol into petrol products by catalytic action. The ethylene employed in the method according to this invention may be mixed with other gases such as nitrogen, methane or other saturated hydrocarbons which are periodically eliminated together with the nitrogen which accumulates in the circuit.

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. Method for the simultaneous production of methanol and liquid hydrocarbons which consists in subjecting to the action of a methanol forming catalyzer, under high pressure and temperature, a gas mixture containing in addition to carbon monoxide and hydrogen, ethylene or its homologues in the proportion of about 10 to 40% of the total volume of gas mixture.

2. Method for the simultaneous production of methanol and liquid hydrocarbons substantially as described.

Dated this 28th day of January, 1926.

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