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AMENDED SPECIFICATION

Reprinted as amended under Section 11 of the Patents and Designs Acts, 1907 to 1939, in accordance with the Decision dated the fifth day of December, 1939, and the Supplementary Decision dated the twenty-ninth day of April, 1940, of the Superintending Examiner, acting for the Comptroller-General.

PATENT SPECIFICATION

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Complete Specification Accepted: Oct. 12, 1936.

3660

COMPLETE SPECIFICATION

Method of Increasing Yield in the Catalytic Synthesis of Aliphatic Hydrocarbons

We, STUDIEN- UND VERWERTUNGS-GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG, of Mülheim-Ruhr, Germany, a Company organised and existing under the laws of the German State, 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 known to produce aliphatic hydrocarbons synthetically by the use of catalysts from the oxides of carbon and from hydrogen. It has been found that if a gas mixture of suitable composition—for example a mixture of 1 part carbon monoxide and 2 parts hydrogen—can be passed once over a good contact substance at, for example, 190° C. and at not too high a velocity, all the carbon monoxide may be converted into hydrocarbons. When hydrocarbons having more than one carbon atom, particularly liquid hydrocarbons, are desired, the optimum temperature of working is known to be within about ±10° C. of 200° C.

We have now found that there is a much greater yield of aliphatic hydrocarbons which contain more than one carbon atom in the molecule (more particularly liquid hydrocarbons which readily volatilise), if the method is carried out at ordinary, or slightly increased, or slightly reduced, pressure, and at a temperature within the range of 180° to 200° C., in at least two stages and, in between, either the oil, that is to say, the liquid hydrocarbons produced by synthesis and having higher boiling points and a greater specific gravity than benzine, or the reaction water alone, or, in addition, benzine and the hydrocarbons that boil at a still lower temperature, are removed from the gas, care being taken during the early stages, by operating at suitably low temperatures within the specified range, or by maintaining a high velocity, or by having insufficient hydrogen, that is to say, by the use of a mixture of carbon monoxide and hydrogen containing less than two parts by volume but not less than one part by volume of hydrogen to one part by volume of carbon monoxide, or by any combination of these conditions, to ensure that the mixture of carbon monoxide and hydrogen present is not completely consumed but only to the extent of, for example, one-half or two thirds. By this means the generation of heat within the contact substance is clearly limited, and thus the consumption of the mixture of carbon monoxide and hydrogen is arrested in the direction of the undesirable formation of methane. If employing more than two stages, the process is carried out in the further stages in the same manner, that is, without complete consumption of the mixture of carbon monoxide and hydrogen, and only in the last stage is the residuum of carbon monoxide and hydrogen completely converted.

The present invention can be carried out as a cyclic process with one or more contact stages, the gases leaving the cycle, after removal of reaction products, being completely converted in a further stage.

EXAMPLE I.

12 litres of a gas mixture (one part of CO plus two parts of H_2) are passed every hour over a contact layer of a length of 90 cms. (12 grammes of cobalt) at a temperature of 190° C.; the product contains up to 110 grammes of benzine plus oil per cubic metre at normal temperature and pressure.

By using three contact layers of a

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length of 30 cms. (each layer 4 grammes of cobalt) disposed in parallel and passing over each contact layer 4 litres of gas per hour at a temperature of 190° C., the product again contains up to 110 grammes of benzine plus oil per cubic metre of gas at normal temperature and pressure.

If 12 litres of gas be passed every hour over the three contact layers of a length of 30 cms. (each layer 4 grammes of cobalt) in succession and, after passing each layer, the reaction products, oil plus benzine plus water be removed—the temperature of the layers being so selected that in each stage no more than one-third of the original carbon monoxide is converted—the product contains up to 120 grammes of oil plus benzine per cubic metre at normal temperature and pressure. The temperatures in the several stages may be, for example,

First stage, 182° C.
Second stage, 187° C.
Third stage, 193° C.

If 12 litres of gas be passed every hour over two contact layers of a length of 30 cms. (each layer 4 grammes of cobalt) disposed parallel to each other and the remainder of the gas is passed over a contact layer of a length of 30 cms. disposed to the rear of the other two contact layers, the temperature selected being such, for example, as 184° C. in the first stage and 195° C. in the second stage, so that in each layer approximately the same volume of carbon monoxide is converted and then oil, water and benzine are removed from behind each layer, the total product contains up to 130 grammes of benzine plus oil per cubic metre at normal temperature and pressure.

It is possible by this method to work with lower temperatures in the first stage, and as a result there is a better yield of liquid hydrocarbons at the expense of the gaseous hydrocarbons which are otherwise produced.

EXAMPLE II.

The temperature is not the same in all the various stages, but is lowest in the first stage and highest in the last, for example, 180° C. in the first stage, rising to about 200° C. in the last stage. The light benzine and the hydrocarbons which boil at a lower temperature are removed between the several stages, for example, by washing with cold oil, or by the use of active carbon, or by other methods.

EXAMPLE III.

The same procedure is followed as in Example II except that after each stage all the desired reaction products are removed, the oil being removed by washing with circulating washing oil having a temperature of over 100° C., the water by washing with water, the benzine by washing with cold oil, and the unsaturated gaseous hydrocarbons by washing with suitably concentrated sulphuric acid and the saturated gaseous hydrocarbons by treatment with active carbon.

EXAMPLE IV.

Complete conversion of the carbon monoxide in the early stages is avoided if an insufficient quantity of hydrogen is present, and after the different stages so much hydrogen, or gas containing a high percentage of hydrogen, be then added to the remaining gas, as will limit the conversion. Only before the last stage is the amount of hydrogen required for complete conversion added. The reaction products are removed between the several stages. The method of working Example IV is applicable when it is desired to secure as large a yield as possible of unsaturated hydrocarbons.

The process hereinbefore described and explained by means of Examples of increasing the yield of aliphatic hydrocarbons which contain more than one carbon atom in the molecule is carried out at atmospheric pressure or at slightly elevated or reduced pressures.

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 method of increasing the yield of synthetically produced aliphatic hydrocarbons having more than one carbon atom in the molecule, from the oxides of carbon and hydrogen by the use of catalysts, at ordinary pressure or at very slightly increased or reduced pressure and at a temperature within the range of 180° to 200° C., characterised in that mixtures of carbon monoxide and hydrogen which contain not less hydrogen than carbon monoxide are subjected to reaction conditions such that maximum conversion is at first avoided and the mixtures are at first only partly converted and subsequently, after completely or partially removing the condensible reaction products, the unconverted reaction gas is subjected to a final conversion, under reaction conditions such that maximum conversion is obtained after gas capable of reacting has, if required, been added.

2. A method according to Claim 1, characterised in that the incomplete conversion of the mixture of carbon monoxide and hydrogen is effected as a cyclic process involving one or more contact stages, the condensible reaction products being removed after each stage whereupon the

remaining gases are completely converted in a further stage only after having left the circuit.

3. A method according to Claim 1, substantially as hereinbefore described.

Dated this 9th day of April, 1935.

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Agents for the Applicants.

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