[Second Edition.]

PATENT SPECIFICATION

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3625

PROVISIONAL SPECIFICATION.

Improvements in or relating to Processes for the Production of Mixtures of Hydrocarbons containing a High Proportion of Olefines from Carbon Monoxide and Hydrogen.

We, LONDON TESTING LABORATORY LIMITED, a British Company, of 81, Cannon Street, London, E.C.4, and MICHAEL STEINSCHLAEGER, of no nationality, of the aforesaid Company's address, do hereby declare the nature of this invention to be as follows :—

This invention relates to a process for obtaining mixtures of hydrocarbons containing a high proportion of olefines from carbon monoxide and hydrogen.

Water gas prepared by the action of steam on red-hot coke consists principally of carbon monoxide and hydrogen in the relative proportions of approximately 1:1.25. If this water gas is passed over a cobalt catalyst under suitable conditions a number of olefines are formed and these unsaturated hydrocarbons are very suitable for conversion by further treatment into lubricants or high quality fuels suitable for use in internal combustion engines and the like. This process, however, suffers from the disadvantage that only a low yield of hydrocarbons is obtained although the proportion of olefines is high. It is the chief object of this invention to enable an increased yield of hydrocarbon products rich in olefines to be obtained.

According to the invention, a gaseous mixture, such as water gas, containing carbon monoxide and hydrogen is passed first over a cobalt catalyst thereby producing a proportion of hydrocarbons after which it is passed over an iron catalyst whereby a further yield of hydrocarbons is obtained. According to a further feature of the invention the gaseous mixture, after passing over the cobalt catalyst, is mixed with additional gas, which may be water gas, containing carbon monoxide and hydrogen, the quantity of additional gas being such that the proportion by volume of carbon monoxide to hydrogen in the resultant mixture is 2:1 and 3:2. The carbon dioxide and hydrocarbons produced in the first reaction may be removed before the mixing with the additional gas is effected.

The gas mixture is preferably passed over the catalysts under an increased pressure but the reactions may be effected at atmospheric pressure or even at reduced pressure.

The invention will be more fully described with reference to the following example in which there is used as a starting material water gas produced from coke and having the following composition by volume:

Carbon dioxide, CO_2	4.5%
Carbon monoxide, CO	40.0%
Hydrogen, H_2	50.0%
Methane, CH_4	0.5%
Nitrogen, N_2	5.0%

One thousand cubic metres of this gas are passed over a cobalt catalyst. Reaction takes place and a gas is obtained containing a small proportion of hydrocarbons and considerable quantities of carbon dioxide which latter is removed by washing with water under pressure. The gas before and after the removal of the carbon dioxide has the following compositions:

	Composition of gas before removal of CO_2	Composition of gas after removal of CO_2
Carbon dioxide, CO_2	24.0%	2.5%
Carbon monoxide, CO	45.0%	58.0%
Hydrogen, H_2	15.0%	19.0%
Methane, CH_4	4.0%	5.0%
Nitrogen, N_2	10.0%	13.0%
Hydrocarbons, C_nH_m	2.0%	2.5%

[*Price* 1/-]

The volume of the gas before washing is 850 cubic metres, while after washing it is 273 cubic metres.

To the washed gas there is added two thirds of its volume, i.e. 182 cubic metres, of water gas giving a mixture containing 51% of carbon monoxide and 32% of hydrogen. This mixture is then passed over an iron catalyst at a pressure of 10 atmospheres and this gives a further yield of hydrocarbons and more particularly of olefines.

The process of the invention enables good yields of hydrocarbons and more particularly of olefines to be obtained, since the reaction which takes place in the presence of an iron catalyst yields products richer in olefines than are obtained with a cobalt catalyst, while it is possible to adjust the proportion of carbon monoxide and hydrogen to the optimum value. This is particularly advantageous when water gas is used as the starting material, since the proportions of carbon monoxide and hydrogen in this gas are not the best for the efficient production of hydrocarbons.

Dated this 18th day of February, 1938.

HASELTINE, LAKE & CO.,
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Agents for the Applicants.

COMPLETE SPECIFICATION.

Improvements in or relating to Processes for the Production of Mixtures of Hydrocarbons containing a High Proportion of Olefines from Carbon Monoxide and Hydrogen.

We, LONDON TESTING LABORATORY LIMITED, a British Company, of 81, Cannon Street, London, E.C.4, and MICHAEL STEINSCHLAEGER, of no nationality, of the aforesaid Company's address, 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 invention relates to a process for obtaining mixtures of hydrocarbons containing a high proportion of olefines from gaseous mixtures containing carbon monoxide and hydrogen.

Water gas prepared by the action of steam on red-hot coke consists principally of carbon monoxide and hydrogen in the relative proportions of approximately 1:1.25. It is known that if this water gas is passed over a cobalt catalyst under suitable conditions a number of olefines are formed and these unsaturated hydrocarbons are very suitable for conversion by further treatment into lubricants or high quality fuels suitable for use in internal combustion engines and the like. This process, however, suffers from the disadvantage that only a low yield of hydrocarbons is obtained although the proportion of olefines is high. It is the chief object of this invention to enable an increased yield of hydrocarbon products rich in olefines to be obtained.

According to the invention a gaseous mixture, such as water gas, containing carbon monoxide and hydrogen is passed first over a cobalt catalyst at a temperature of 180°—210° C. and substantially atmospheric pressure thereby producing a yield of hydrocarbons after which it is passed over an iron catalyst at a temperature of 200—240° C. and a pressure of 0—10 atms. whereby a further yield of hydrocarbons is obtained.

The olefine content of the products of the two catalytic stages depends upon the pressure at which the synthesis is carried out, the pressure being adjusted to give the maximum yield of olefines. The higher olefine yield is due to the higher yield of hydrocarbons as compared with the use of cobalt catalyst alone.

A particularly suitable catalyst for the first catalytic stage is a cobalt-thorium-kieselguhr catalyst in the ratio 100:18:100, while a particularly suitable catalyst for the second catalytic stage is an iron-copper catalyst containing iron and copper in the ratio of 20:1.

According to a further feature of the invention the gaseous mixture, after passing over the cobalt catalyst, may be mixed with additional gas, such as water gas, containing carbon monoxide and hydrogen, the quantity of additional gas being such that the proportion by volume of carbon monoxide to hydrogen in the resultant mixture is between 2:1 and 3:2. The carbon dioxide and hydrocarbons produced in the first reaction may be removed before the addition of further gas.

The invention will be more fully described with reference to the following example in which there is used as a starting material water gas produced from coke and having the following composition by volume:

Carbon dioxide, CO_2	4.5%
Carbon monoxide, CO	40.0%

Hydrogen, H_2 - - -	50.0%
Methane, CH_4 - - -	0.5%
Nitrogen, N_2 - - - -	5.0%

1000 cubic metres of this gas are passed over a cobalt-thorium-kieselguhr catalyst containing cobalt, thorium and kieselguhr in the ratio 100:18:100, at a temperature of 208° C. and substantially atmospheric pressure. Reaction takes place and a gas is obtained containing a small proportion of hydrocarbons and considerable quantities of carbon dioxide which latter is removed by washing with water under pressure.

The volume of the gas before washing is 350 cubic metres, while after washing and removing the hydrocarbons by means of a carbon adsorption plant, it is 273 cubic metres. The 1000 cubic metres of water gas passed over the cobalt catalyst yield 80 grammes of hydrocarbon products per cubic metre, containing 53% of olefines.

To the washed gas there is added two thirds of its volume, i.e. 182 cubic metres, of water gas giving 455 cubic metres of a mixture containing 51% of carbon monoxide and 32% of hydrogen. This mixture is then passed over an iron-copper catalyst, containing iron and copper in the ratio of 20:1, at a pressure of 10 atmospheres and a temperature of 235° C. and this gives a further yield of hydrocarbons and more particularly of olefines. The 455 cubic metres of gas passed over the iron catalyst give a yield of 90 grammes of hydrocarbon products per cubic metre, containing 45% of olefines. Thus, 1182 cubic metres of water gas yield a total of 120.950 grammes of hydrocarbon products containing 38% of olefines.

The process of the invention thus enables good yields of hydrocarbons and more particularly of olefines to be obtained, since the reaction which takes place in the presence of an iron catalyst yields products richer in olefines than are obtained with a cobalt catalyst, while it is possible to adjust the proportion of carbon monoxide and hydrogen to the optimum value. This is particularly advantageous when water gas is used as the starting material, since the proportions of carbon monoxide and hydrogen in this gas are not the best for the efficient production of hydrocarbons.

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 the production of mixtures of hydrocarbons containing a high proportion of olefines which comprises passing a gaseous mixture containing carbon monoxide and hydrogen over a cobalt catalyst at a temperature of 180—210° C. and substantially atmospheric pressure thereby producing a yield of hydrocarbons and then passing the resulting gaseous mixture over an iron catalyst at a temperature of 200—240° C. and a pressure of 0—10 atmospheres whereby a further yield of hydrocarbons is obtained.

2. A process according to claim 1, in which water gas is used as the initial gaseous mixture containing carbon monoxide and hydrogen.

3. A process according to claim 1 or claim 2, in which the carbon dioxide and hydrocarbons formed during the first catalytic stage are removed before the gases are passed to the second stage.

4. A process according to any of claims 1 to 3, in which the carbon dioxide produced during the first catalytic stage is removed by washing with water under pressure before the gases are passed to the second catalytic stage.

5. A process according to any of the preceding claims, in which the gaseous mixture after passage over the cobalt catalyst is mixed with additional gas containing carbon monoxide and hydrogen.

6. A process according to claim 5, in which the additional gas is water gas.

7. A process according to claim 5 or claim 6, in which the quantity of additional gas added is such that the proportion by volume of carbon monoxide to hydrogen in the resultant gaseous mixture is betwen 2:1 and 3:2.

8. A process for the production of mixtures of hydrocarbons containing a high proportion of olefines substantially as hereinbefore described.

9. Mixtures of hydrocarbons containing a high proportion of olefines when prepared by a process according to any of the preceding claims.

Dated this 17th day of February, 1939.

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