PATENT SPECIFICATION

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3623

PROVISIONAL SPECIFICATION

A Process for the Production of Gas Mixtures containing Carbon Monoxide and Hydrogen

I, MICHAEL STEINSCHLAEGER, of no nationality, formerly of Russian nationality, of 50, Portsea Hall, Connaught Square, London, W.2, do hereby declare the nature of this invention to be as follows:—

This invention relates to the production of gaseous mixtures containing carbon monoxide and hydrogen suitable for use in the Fischer-Tropsch process.

In order to carry out the Fischer-Tropsch process in the most satisfactory manner the proportion of hydrogen to carbon monoxide should be between about 1.8 and 2.0 volumes of hydrogen per volume of carbon monoxide.

Gases occurring in nature or artificially produced do not have the desired composition because they are usually rich in carbon monoxide. It is therefore necessary to apply particular processes in order to obtain gases rich in hydrogen, which are then mixed with gases rich in carbon monoxide.

When coal is coked, coke and coke oven gas are obtained. Water gas, a gas rich in carbon monoxide, may be obtained from the coke, and a gas rich in hydrogen may be produced from the coke oven gas by heating it with steam. If these gases are mixed a synthesis gas is obtained containing $CO:H_2$ in the proportion of 1:2. This process has the drawback that the coke being formed during coking and gasification is never completely used up and consequently the coal consumption is too high.

It is an object of the present invention to overcome the aforesaid drawback and produce a gas mixture which can be satisfactorily utilised in the Fischer-Tropsch process in a cheap and efficient manner or to produce a gas mixture which by the mere addition of water gas will contain hydrogen and carbon monoxide in the correct proportions.

With this object in view, the process of the present invention for the production of a gas mixture containing carbon monoxide and hydrogen suitable for use in the Fischer-Tropsch synthesis comprises heating a mixture of blue water gas, hydrogen and coke oven gas in the presence of a cobalt or nickel catalyst, at a temperature between 160 and 250° C. to produce an oil and a residual gas, which gas is then heated at a temperature between 1200 and 1450° C. and the product mixed with blue water gas and a gas which has been obtained by heating blue water gas with steam at a temperature between 400 and 550° C. and then separating carbon dioxide. This produces a gas which is suitable for use in the Fischer-Tropsch synthesis, that is to say it contains between about 1.8 and 2.0 volumes of hydrogen per volume of carbon monoxide.

The cobalt, nickel or iron catalyst employed may, if desired, be activated with an activator such as thoria, and the catalyst may be mixed with a carrier such as kieselguhr, magnesia or silica.

All the gases employed in the process should be purified so that they contain not more than 0.4 gms. of total sulphur per 100 cubic metres of gas.

The following example illustrates how the process of the invention may be carried into effect.

930,000 cubic metres of blue water gas, 500,000 cubic metres of coke oven gas and 100,000 cubic metres of hydrogen are mixed together to form 1,530,000 cubic metres of a gas hereinafter referred to as Synthesis Gas I having the following composition:— $CO=27.1\%$, $H_2=54.3\%$, $CH_4=10.4\%$, $C_nH_m=1.1\%$, $CO_2=3.7\%$ and $N_2=3.4\%$. The Synthesis Gas I was then passed over a cobalt catalyst activated with thoria and mixed with a kieselguhr carrier at a temperature of 160 to 220° C. and there was obtained per cubic metre of Synthesis Gas I a yield of 96 gms. of primary products and 0.4 cubic metre of residual gas, hereinafter referred to as Residual Gas I. The treatment of 1,530,000 cubic metres of Synthesis Gas I thus produced 612,000 cubic metres of Residual Gas I of the following composition:—$CO=17.0\%$, $H_2=24.0\%$, $CH_4=38.0\%$, $C_nH_m=3.0\%$ and $C_2+N_2=18.0\%$.

The Residual Gas I was then heated with steam in the proportion of 1.0 kgm. of steam per cubic metre of Residual Gas I at a temperature of 1400° C. without a catalyst, and there was obtained per cubic metre of Residual Gas I 2.2 cubic metres of a gas of the following composition:— $CO=27.0\%$, $H_2=57.1\%$, $CH_4=1.4\%$, $CO_2=3.5\%$ and $N_2=11.0\%$. There was thus produced 1,345,000 cubic metres of gas, which was then mixed with 575,000 cubic metres of blue water gas and 175,000 cubic metres of a gas obtained by heating blue water gas with steam at 450° C. and then washing out the carbon dioxide by means of an aqueous solution containing a mixture of alkylolamine bases. This produces 2,095,000 cubic metres of a gas hereinafter referred to as Synthesis Gas II of the following composition:—$CO=29.0\%$, $H_2=58.0\%$, $CH_4=1.0\%$ and $CO_2+N_2=12.0\%$.

This gas can be subjected to the Fischer-Tropsch process and it then yields 140 gms. of primary products per cubic metre. The coal consumption is 3.55 tons per ton of primary products.

Dated this 10th day of May, 1940.
ELKINGTON & FIFE,
Consulting Chemists and Chartered Patent Agents,
20 to 23, Holborn, London, E.C.1,
Agents for the Applicant.

COMPLETE SPECIFICATION

A Process for the Production of Gas Mixtures containing Carbon Monoxide and Hydrogen

I, MICHAEL STEINSCHLAEGER, of no nationality, formerly of Russian nationality, of 50, Portsea Hall, Connaught Square, London, W.2, 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:—

This invention relates to the production of gaseous mixtures containing carbon monoxide and hydrogen suitable for use in the Fischer-Tropsch process.

In order to carry out the Fisher-Tropsch process in the most satisfactory manner the proportion of hydrogen to carbon monoxide should be between 1.8 and 2.0 volumes of hydrogen per volume of carbon monoxide.

Gases occurring in nature or artificially produced do not have the desired composition because they are usually rich in carbon monoxide. It is therefore necessary to apply particular processes in order to obtain gases rich in hydrogen, which are then mixed with gases rich in carbon monoxide.

When coal is coked, coke and coke oven gas are obtained. Water gas, a gas rich in carbon monoxide, may be obtained from the coke, and a gas rich in hydrogen may be produced from the coke oven gas by heating it with steam. If these gases are mixed a synthesis gas is obtained containing $CO:H_2$ in the proportion of 1:2. This process has the drawback that the coke being formed during coking and gasification is never completely used up and consequently the coal consumption is too high.

It is an object of the present invention to overcome the aforesaid drawback and produce a gas mixture which can be satisfactorily utilised in the Fischer-Tropsch process in a cheap and efficient manner or to produce a gas mixture which by the mere addition of water gas will contain hydrogen and carbon monoxide in the correct proportions.

With this object in view the present invention provides a process for the production of a gas mixture containing carbon monoxide and hydrogen suitable for use in the Fischer-Tropsch synthesis which comprises heating a mixture of blue water gas, hydrogen and coke oven gas in the presence of a cobalt, or nickel catalyst, at a temperature between 160 and 250° C. to produce an oil and a residual gas, which gas is then heated with steam at a temperature between 1200 and 1450° C. and the product mixed with blue water gas and a gas which has been obtained by heating blue water gas with steam at a temperature between 400 and 550° C. and then separating carbon dioxide. This produces a gas which is suitable for use in the Fischer-Tropsch synthesis, that is to say it contains between about 1.8 and 2.0 volumes of hydrogen per volume of carbon monoxide.

The cobalt, nickel or iron catalyst employed may, if desired, be activated with an activator such as thoria and the catalyst may be mixed with a carrier such as kieselguhr, magnesia, silica, pumice or aluminium earths.

All the gases employed in the process should be purified so that they contain not more than 0.4 gms. of total sulphur per 100 cubic metres of gas.

The following example illustrates how the process of the invention may be carried into effect:

930,000 cubic metres of blue water gas, 500,000 cubic metres of coke oven gas and 100,000 cubic metres of hydrogen are mixed together to form 1,530,000 cubic metres of a gas hereinafter referred to as Synthesis Gas I having the following composition:— $CO=27.1\%$, $H_2=54.3\%$, $CH_4=10.4\%$, $C_nH_m=1.1\%$, $CO_2=3.7\%$ and $N_2=3.4\%$. The Synthesis Gas I was then passed over a cobalt catalyst activated with thoria and mixed with a kieselguhr carrier at a temperature of 160 to 220° C. and there was obtained per cubic metre of Synthesis Gas I a yield of 96 gms. of primary products and 0.4 cubic metre of residual gas, hereinafter referred to as Residual Gas I. The treatment of 1,530,000 cubic metres of Synthesis Gas I thus produced 612,000 cubic metres of Residual Gas I of the following composition:—$CO=17.0\%$, $H_2=24.0\%$, $CH_4=38.0\%$, $C_nH_m=3.0\%$ and $C_2+N_2=18.0\%$.

The Residual Gas I was then heated with steam in the proportion of 1.0 kgm. of steam per cubic metre of Residual Gas I at a temperature of 1400° C. without a catalyst, and there was obtained per cubic metre of Residual Gas I 2.2 cubic metres of a gas of the following composition:— $CO=27.0\%$, $H_2=57.1\%$, $CH_4=1.4\%$, $CO_2=3.5\%$ and $N_2=11.0\%$. There was thus produced 1,345,000 cubic metres of gas, which was then mixed with 575,000 cubic metres of blue water gas and 175,000 cubic metres of a gas obtained by heating blue water gas with steam at 450° C. and then washing out the carbon dioxide by means of an aqueous solution containing a mixture of alkylolamine bases. This produces 2,095,000 cubic metres of a gas hereinafter referred to as Synthesis Gas II of the following composition:—$CO=29.0\%$, $H_2=58.0\%$, $CH_4=1.0\%$ and $CO_2+N_2=12.0\%$.

This gas can be subjected to the Fischer-Tropsch process and it then yields 140 gms. of primary products per cubic metre.

The coal consumption is 3.55 tons per ton of primary products.

The expression "primary products" as used herein means hydrocarbons containing three or more carbon atoms in the molecule obtained in the synthesis and does not include the oil yield in the coke oven plant.

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. A process for the production of a gas mixture containing carbon monoxide and hydrogen suitable for use in the Fischer-Tropsch synthesis which comprises heating a mixture of blue water gas, hydrogen and coke oven gas in the presence of a cobalt or nickel catalyst, at a temperature between 160 and 250° C. to produce an oil and a residual gas, which gas is then heated with steam at a temperature between 1200 and 1450° C. and the product mixed with blue water gas and a gas which has been obtained by heating blue water gas with steam at a temperature between 400 and 550° C. and then separating carbon dioxide.

2. A process as claimed in claim 1 wherein the cobalt, nickel or iron catalyst is activated with an activator such as thoria.

3. A process as claimed in claim 1 or 2 wherein all the gases employed in the process are purified so that they contain not more than 0.4 gms. of total sulphur per 100 cubic metres of gas.

4. A process for the production of a gas mixture containing carbon monoxide and hydrogen suitable for use in the Fischer-Tropsch synthesis substantially as described with reference to the Example given .

5. Gas mixtures containing carbon monoxide and hydrogen suitable for use in the Fischer-Tropsch process when produced by the process claimed in any one of the preceding claims.

Dated this 12th day of May, 1941.

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