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PATENT SPECIFICATION

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3627

PROVISIONAL SPECIFICATION

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

We, MICHAEL STEINSCHLAEGER, of no nationality, and OVERSEAS FINANCE & COMMERCE (LONDON) LIMITED, a British Company, both of Market Buildings, 29, Mincing Lane, London, E.C.3, 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 voume 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 special 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 mixing water gas with coke oven gas and a gas containing hydrogen and methane produced by heating the waxy residue deposited on the catalysts in the Fischer-Tropsch process with hydrogen or gases containing the same, heating the gas mixture thus obtained in the presence of a nickel or cobalt catalyst to produce an oil and a gas rich in methane and subjecting the said gas to heating with steam to produce a gas mixture containing carbon monoxide and hydrogen. Preferably water gas is added to this mixture to produce a gas mixture containing carbon monoxide and hydrogen so that the proportion of hydrogen to carbon monoxide is between about 1.8 and 2.0 volumes of hydrogen per volume of carbon monoxide. The amount of water gas to be added will in general be between 10% and 100% of the volume of the gas to which it is added the exact amount added being dependent upon the working conditions employed in the various steps of the process.

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

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

A coal having an ash content of about 7%, a sulphur content of about 1.3% and containing about 28% of volatile constituents was coked and yielded 75% of coke calculated as dry coke on dry coal, the gas yield being 355 cubic metres per ton of dry coal and having a calorific value of about 4670 calories per cubic metre. The gas after treatment for the removal of organic and inorganic sulphur compounds had the following composition:

$CO=6\%$; $H_2=56.0\%$; $CH_4=26\%$; $C_nH_m=2.0\%$; $CO_2+N_2=10.0\%$.

Part of the coke obtained from the coal was subjected to the water gas reaction and it was found that 0.55 kgms. of dry coke yielded 1 cubic metre of blue water gas which after treatment for the removal of organic and inorganic sulphur compounds had the following composition:—

[*Price 1/-*]

$CO=40.7\%$; $H_2=51.0\%$; $CH_4=0.3\%$; $CO_2+N_2=8.0\%$

1,000,000 cubic metres of blue water gas of the composition described above were mixed with 550,000 cubic metres of coke oven gas of the composition mentioned above and with 70,000 cms. of a gas consisting of 86% hydrogen, 12% methane and 2% carbon dioxide + nitrogen obtained by treating a waxy material obtained in the Fischer-Tropsch process and deposited on the catalyst by passing thereover a gas containing 98% of hydrogen and obtained from the blue water gas in known manner. Thereby there were produced 1,627,000 cubic metres of a gas hereinafter referred to as Synthesis Gas I of the following composition:

$CO=27.2\%$; $H_2=54.3\%$; $CH_4=9.5\%$: $CO_2+N_2=8.2\%$; $C_nH_m=0.7\%$

The synthesis Gas I was then passed over a cobalt catalyst activated with thorium and mixed with a kieselguhr carrier at a temperature of 160—220° C. yielding per cubic metre of Synthesis Gas I 97 grams of primary products and 0.4 cubic metres of residual gas hereinafter referred to as Residual Gas I. It will thus be seen that a contraction in volume of 60% has taken place.

The Residual Gas I had the following composition:

$CO=18.0\%$; $H_2=25.0\%$; $CH_4=35.0\%$; $CO_2+N_2=20.5\%$; $C_nH_m=2.0\%$

The residual gas I was then mixed with steam in the proportion of 0.5—0.9 kgm. of steam per cubic metre of gas and the mixture heated in the presence of a nickel-molybdenum sulphide catalyst at a temperature of between 800—900° C. There is thereby obtained per cubic metre of Residual Gas I 2.22 cubic metres of a gas of the following composition:

$CO=24.0\%$; $H_2=64\%$; $CH_4=1.0\%$; $CO_2+N_2=11.0\%$

1,440,000 cubic metres of this gas were then mixed with 720,000 cubic metres of blue water gas of the composition described above and there was then obtained 2,160,000 cubic metres of a gas (Synthesis Gas II) of the following composition:

$CO=29.7\%$; $H_2=59.7\%$; $CH_4=0.8\%$; $CO_2+N_2=9.8\%$

This gas which had a low content of sulphur, i.e, about $\frac{1}{9}$ of the sulphur content of Synthesis Gas I and contains about 90% of reactive constituents is suitable for use in the Fischer-Tropsch process. By subjecting it to the Fischer-Tropsch process about 140 grams of primary products are obtained per cubic metre of gas.

If the large coke obtained in the coking of the coal is used for the production of the blue water gas the smaller coke may be used for heating the coke oven plant.

The residual gas obtained after the Synthesis Gas II has been subjected to the Fischer-Tropsch process (Residual Gas II) may also be used for heating the coke oven plant, the plant employed in treating the Residual Gas I with steam and for heating the plant employed in the sulphur purification and it is then found that the coal consumption is about 3.45 tons of coal per ton of primary products produced. The expression " primary products " does not include the oil yield in the coke oven plant.

This consumption of coal is very low and cannot even be approached by any of the processes hitherto known. If a different process is employed, for treating the methane with steam or if a different type of coal is used the coal consumption would differ slightly.

The process of the present invention has a number of advantages for example: (1) low consumption of coke and coke oven gas and therefore low consumption of coal (2) by regulating the addition of the gas rich in hydrogen and methane the proportion of carbon monoxide to hydrogen in Synthesis Gas I can be adjusted exactly irrespective of the nature of the composition of the coke oven gas. (3) no coke or coke oven gas remains so that the products consist only of the primary products of the synthesis and the by-products of the coking process, the only waste being the coke ash. (4) it is not necessary to work up the Synthesis Gas I so extensively which is advantageous, because the Synthesis Gas I is not so rich in reactive constituents and not so free from sulphur as the Synthesis Gas II, so that poisoning of the catalyst in the Fischer-Tropsch process is reduced (5) not such a large quantity of catalyst is required in the utilisation of the Synthesis Gas II in the Fischer-Tropsch process as would be required if some other gas were treated because the Synthesis Gas II is rich in reactive constituents and has a very low sulphur content.

Dated this 5th day of July, 1939.

ELKINGTON & FIFE,
Consulting Chemists & Chartered Patent Agents,
20 to 23, Holborn, London, E.C.1.
Agents for the Applicants.

COMPLETE SPECIFICATION

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

We, MICHAEL STEINSCHLAEGER, of no nationality formerly of Russian Nationality, of 50, Portsea Hall, Connaught Square, London, W.2, formerly of Market Buildings, 29, Mincing Lane, London, E.C.3, and OVERSEAS FINANCE & COMMERCE (LONDON) LIMITED, a British Company, of Market Buildings, 29, Mincing Lane, London, E.C.3, 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, or similar process such as the Fischer-Pichler Process, all of which are hereinafter referred to for the sake of brevity as 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 special 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 process comprises mixing water gas with coke oven gas and a gas containing hydrogen and methane produced by heating the waxy residue deposited on the catalysts in the Fischer-Tropsch process with hydrogen or gases containing the same, heating the gas mixture thus obtained in the presence of a nickel or cobalt catalyst to produce an oil and a gas rich in methane and subjecting the said gas to heating with steam to produce a gas mixture comprising substantially carbon monoxide and hydrogen. Preferably water gas is added to this mixture to produce a gas mixture containing carbon monoxide and hydrogen so that the proportion of hydrogen to carbon monoxide is between about 1.6 and 2.0 volumes of hydrogen per volume of carbon monoxide. The amount of water gas to be added will in general be between 10% and 100% of the volume of the gas to which it is added the exact amount added being dependent upon the working conditions employed in the various steps of the process.

The cobalt or nickel 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.

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

A coal having an ash content of about 7%, a sulphur content of about 1.3% and containing about 28% of volatile constituents was coked and yielded 75% of coke calculated as dry coke on dry coal, the gas yield being 355 cubic metres per ton of dry coal and having a calorific value of about 4670 calories per cubic metre. The gas after treatment for the removal of organic and inorganic sulphur compounds had the following composition:—

$CO=6\%$; $H_2=56.0\%$; $CH_4=26.0\%$; $C_nH_m=2.0\%$; $CO_2+N_2=10.0\%$.

Part of the coke obtained from the coal was subjected to the water gas reaction and it was found that 0.55 kgms. of dry coke yielded 1 cubic metre of blue water gas which after treatment for the removal of organic and inorganic sulphur compounds had the following composition:—

$CO=40.7\%$; $H_2=51.0\%$; $CH_4=0.3\%$; $CO_2+N_2=8.0\%$

1,000,000 cubic metres of blue water gas of the composition described above were mixed with 550,000 cubic metres of coke oven gas of the composition mentioned above and with 70,000 cubic metres of a gas consisting of 86% hydrogen, 12% methane and 2% carbon dioxide + nitrogen obtained by treating a waxy material obtained in the Fischer-Tropsch process and deposited on the catalyst by passing thereover a gas containing 98% of hydrogen and obtained from the blue water gas in known manner. Thereby there were produced 1,627,000 cubic metres of a gas hereinafter referred to as Synthesis Gas I of the following composition:

$CO = 27.2\%$; $H_2 = 54.3\%$; $CH_4 = 9.5\%$;
$CO_2 + N_2 = 8.2\%$; $C_nH_m = 0.7\%$.

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—220° C. yielding per cubic metre of Synthesis Gas I 97 grams of primary products and 0.4 cubic metres of residual gas hereinafter referred to as Residual Gas I. It will thus be seen that a contraction in volume of 60% has taken place.

The Residual Gas I had the following composition:

$CO = 18.0\%$; $H_2 = 25.0\%$; $CH_4 = 35.0\%$;
$CO_2 + N_2 = 20.5\%$; $C_nH_m = 2.0\%$

The Residual Gas I was then mixed with steam in the proportion of 0.5—0.9 kgm. of steam per cubic metre of gas and the mixture heated in the presence of a nickel-molybdenum sulphide catalyst at a temperature of between 800—900° C. There is thereby obtained per cubic metre of Residual Gas I 2.22 cubic metres of a gas of the following composition:

$CO = 24.0\%$; $H_2 = 64.0\%$; $CH_4 = 1.0\%$;
$CO_2 + N_2 = 11.0\%$

1,440,000 cubic metres of this gas were then mixed with 720,000 cubic metres of blue water gas of the composition described above and there was then obtained 2,160,000 cubic metres of a gas (Synthesis Gas II) of the following composition:

$CO = 29.7\%$; $H_2 = 59.7\%$; $CH_4 = 0.8\%$;
$CO_2 + N_2 = 9.8\%$

This gas which had a low content of sulphur, i.e. about $\frac{1}{3}$ of the sulphur content of Synthesis Gas I and contains about 90% of reactive constituents is suitable for use in the Fischer-Tropsch process. By subjecting it to the Fischer-Tropsch process about 140 grams of primary products are obtained per cubic metre of gas.

If the large coke obtained in the coking of the coal is used for the production of the blue water gas the smaller coke may be used for heating the coke oven plant.

The residual gas obtained after the Synthesis Gas II has been subjected to the Fischer-Tropsch process (Residual Gas II) may also be used for heating the coke oven plant, the plant employed in treating the Residual Gas I with steam and for heating the plant employed in the sulphur purification and it is then found that the coal consumption is about 3.45 tons of coal per ton of primary products produced. Alternatively the Residual Gas II after removal of carbon dioxide may be heated with steam in the presence of a nickel catalyst at a temperature of 800° C. and mixed with blue water gas to produce a Synthesis Gas III of the following composition:

$CO = 29.0\%$; $H_2 = 58.0\%$;
$CO_2 + N_2 + CH_4 = 13.0\%$.

This Synthesis Gas may be used in the same manner as Synthesis Gases I and II. In this case the consumption is 0.9 cubic metres of coke oven gas + 3.45 cubic metres of blue water gas per kgm. of primary products. The expression "primary products" does not include the oil yield in the coke oven plant but merely includes the products obtained in the synthesis.

This consumption of coal is very low and cannot even be approached by any of the processes hitherto known. If a different type of coal is used the coal consumption would differ slightly.

The blue water gas may be replaced wholly or in part by water gas obtained by the complete gasification of coal i.e. a process in which coal itself is subjected to the water gas reaction. If the blue water gas is wholly replaced in the process of the Example by water gas obtained by the complete gasification of a South Wales medium coking coal a consumption of 0.47 cubic metres of coke oven gas and 2.8 kg. of coal is necessary per kg. of primary products.

The process of the present invention has a number of advantages for example: (1) low consumption of coke and coke oven gas and therefore low consumption of coal (2) by regulating the addition of the gas rich in hydrogen and methane the proportion of carbon monoxide to hydrogen in Synthesis Gas I can be adjusted exactly irrespective of the nature of the composition of the coke oven gas, (3) no coke or coke oven gas remains so that the products consist only of the primary products of the synthesis and the by-products of the coking process, the only waste being the coke ash, (4) it is not necessary to work up the Synthesis Gas I so extensively which is advantageous, because the Synthesis Gas I is not so rich in reactive constituents and not so free from sulphur as the Synthesis Gas II, so that poisoning of the catalyst in the Fischer-Tropsch process is reduced, (5) not such a large quantity of catalyst is required in the utilisation of the Synthesis Gas II in the Fischer-Tropsch process as would be required if some other gas were treated because the Synthesis Gas II is rich in reactive constituents and has a very low sulphur content.

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 a gas mixture containing carbon monoxide and hydrogen suitable for use in the Fischer-Tropsch synthesis which comprises mixing water gas with coke oven gas and a gas containing hydrogen and methane produced by heating the waxy residue deposited on the catalysts in the Fischer-Tropsch process with hydrogen or gases containing the same, heating the gas mixture thus obtained in the presence of a nickel or cobalt catalyst to produce an oil and a gas rich in methane, and subjecting the said gas to heating with steam to produce a gas mixture comprising substantially carbon monoxide and hydrogen.

2. A process as claimed in claim 1 wherein the amount of water gas added is between 10 and 100% of the volume of the gas to which it is added.

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

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 synthesis when produced by the process claimed in any one of the preceding claims.

Dated this 3rd day of August, 1940.

ELKINGTON & FIFE,
Consulting Chemists & Chartered Patent Agents,
20 to 23, Holborn, London, E.C.1,
Agents for the Applicants.

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