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PATENT SPECIFICATION

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3622

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 coke oven gas with steam at a temperature of 1200 to 1500° C. without a catalyst, or from 800 to 900° C. in the presence of a nickel or iron catalyst, mixing the gas thus produced with blue water gas in such proportion as to produce a gas containing carbon monoxide and hydrogen in a proportion suitable for use in the Fischer-Tropsch process, heating the mixture thus produced in the presence of a cobalt, nickel or iron catalyst at a temperature between 160 and 250° C. to produce oils and a gaseous product, mixing the gaseous product with steam and heating to a temperature of between 1200 and 1500° C. without a catalyst or to a temperature of between 800 and 906° C. with a nickel or iron catalyst and mixing the product with blue water gas in such a proportion as to form a gas containing hydrogen and carbon monoxide in a proportion suitable for use in the Fischer-Tropsch process.

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 examples illustrate how the process of the invention may be carried into effect.

1. 475,000 cubic metres of coke oven gas having the following composition:— $CO=7.0\%$, $H_2=54.0\%$, $CH_4=29.0\%$, $C_nH_m=3.6\%$; $N_2=4.4\%$ and $CO_2=2.0\%$, were mixed with steam in the proportion of 0.5 kgm. of steam per cubic metre of gas, and the mixture heated in the presence of a nickel catalyst (containing 10% by weight of magnesium oxide) at a temperature of 820° C. There was thereby obtained per cubic metre of coke oven gas 2.10 cubic metres of a gas of the following composition:—$CO=17.0\%$, $H_2=75.0\%$, $CH_4=2.5\%$, $N_2=3.2\%$ and $CO_2=2.3\%$.

1,000,000 cubic metres of this gas were then mixed with 1,500,000 cubic metres of blue water gas of the following composition:—CO=40.7%, H_2=51.0%, CH_4=0.3%, CO_2=5.0%, and N_2=3.0%, and there was thus obtained 2,500,000 cubic metres of a gas, hereinafter referred to as Synthesis Gas I, of the following composition:—CO = 31.0%, H_2 = 61.0%. CH_4 = 1.0%, CO_2 = 4.3%, and N_2= 2.7%.

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 to 220° C., yielding per cubic metre of Synthesis Gas I 112 gms. of primary products and 0.34 cubic metres of residual gas, hereinafter referred to as Residual Gas I. It will thus be seen that a contraction in volume of 66% took place. The Residual Gas I had the following composition:—CO=25.0%, H_2=40.0%, CH_4=15.0%, CO_2=12.6% and N_2=7.4%.

The Residual Gas I was then freed from carbon dioxide by washing with an aqueous solution containing a mixture of alkylolamine bases, and mixed with steam in the proportion of 0.25 kgm. of steam per cubic metre of gas and the mixture heated in the presence of a nickel catalyst at a temperature of 820° C. There was thereby obtained per cubic metre of Residual Gas I 1.53 cubic metres of a gas of the following composition:—CO=26.0%, H_2=64.0%, CH_4=1.0% and CO_2+N_2=9.0%.

1,145,000 cubic metres of this gas were then mixed with 485,000 cubic metres of blue water gas of the above-mentioned composition and there was thus obtained 1,630,000 cubic metres of a gas hereinafter referred to as Synthesis Gas II of the following composition:—CO = 30.4%, H_2=60.2%, CH_4=0.8% and CO_2+N_2= 8.6%.

By subjecting the Synthesis Gas II to the Fischer-Tropsch process about 140 gms. of primary products and 0.25 cubic metres of residual gas can be obtained per cubic metre of Synthesis Gas II. This residual gas, which is hereinafter referred to as Residual Gas II. may 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 sulphur purification, and it is then found that the coal consumption is about 3.75 tons of coal per ton of primary products produced.

2. 495,000 cubic metres of coke oven gas having the following composition:—CO=7.0%, H_2=54.0%, CH_4=29.0%, C_nH_m=3.6%, N_2=4.4% and CO_2=2.0% were mixed with steam in the proportion of 1.3 kgm. of steam per cubic metre of gas, and the mixture heated without a catalyst at 1450° C. There was thus produced 1,000,000 cubic metres of a gas of the following composition:—CO=21.0%, H_2=66.0%, CH_4=1.6% and CO_2+N_2= 11.4%. which was then mixed with 800,000 cubic metres of blue water gas of the following composition:—CO=40.7%, H_2=51.0%, CH_4=0.3%, CO_2=5.0% and N_2=3.0% and there was obtained 1,800,000 cubic metres of a gas hereinafter referred to as Synthesis Gas I^1 of the following composition:—CO=29.7%, H_2=59.3%, CH_4=1.0% and CO_2+N_2=10.0%.

The Synthesis Gas I^1 was passed over a cobalt catalyst activated with thoria and mixed with a kieselguhr carrier at a temperature of 160 to 220° C., yielding per cubic metre of Synthesis Gas I 103 gms. of primary products and 0.34 cubic metre of residual gas hereinafter referred to as Residual Gas I^1. It will thus be seen that a contraction of 66% had taken place. The Residual Gas I^1 had the following composition: — CO=24.0%, H_2=32.0%, CH_4=15.0% and CO_2+N_2=29.0%.

The Residual Gas I^1 (612,000 cubic metres) was then mixed with steam in the proportion of 0.6 kgm. of steam per cubic metres of gas and the mixture heated in the absence of catalysts at a temperature of 1450° C. There was thereby obtained 870,000 cubic metres of gas having the following composition: — CO=27.0%, H_2=46.0%, CH_4=0.7% and CO_2+N_2= 26.3%. This was mixed with 720,000 cubic metres of blue water gas of the above-mentioned composition and 350,000 cubic metres of converted blue water gas of the following composition:—CO= 4.0%, H_2=91.0%, CH_4+N_2=3.5% and CO_2=1.5% obtained by heating blue water gas with steam at 450° C. and washing with an aqueous solution containing a mixture of alkylolamine bases to remove carbon dioxide. There is thus obtained 1,940,000 cubic metres of a gas hereinafter referred to as Synthesis Gas II^1 of the following composition:—CO=28.0%, H_2=56.0%, CH_4=0.5% and CO_2+N_2= 15.5%.

By subjecting the Synthesis Gas II^1 to the Fischer-Tropsch process about 129 gms. of primary products and 0.30 cubic metres of residual gas can be obtained per metre of Synthesis Gas II^1. This residual gas, which is hereinafter referred to as Residual Gas II^1, may be used for heating the coke oven plant, the plant employed in treating the Residual Gas I^1 with steam and for heating the plant employed in sulphur purification, and it is then found that the coal consumption is about 3.8 tons per ton of primary products produced.

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 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 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 coke oven gas with steam at a temperature of 1200 to 1500° C. without a catalyst, or from 800 to 900° C. in the presence of a nickel or iron catalyst, mixing the gas thus produced with blue water gas in such proportion as to produce a gas mixture containing carbon monoxide and hydrogen in a proportion suitable for use in the Fischer-Tropsch process, heating the mixture thus produced in the presence of a cobalt, nickel or iron catalyst at a temperature between 160° and 250° C. to produce oils and a gaseous product, mixing the gaseous product with steam and heating to a temperature of between 1200 and 1500° C. without a catalyst or to a temperature of between 800 and 900° C. with a nickel or iron catalyst and mixing the product thus obtained with blue water gas in such a proportion as to form a gas containing hydrogen and carbon monoxide in a proportion suitable for use in the Fischer-Tropsch process.

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 examples illustrate how the process of the invention may be carried into effect:—

1. 475,000 cubic metres of coke oven gas having the following composition:—$CO=7.0\%$, $H_2=54.0\%$, $CH_4=29.0\%$, $C_nH_m=3.6\%$, $N_3=4.4\%$ and $CO_2=2.0\%$, were mixed with steam in the proportion of 0.5 kgm. of steam per cubic metre of gas, and the mixture heated in the presence of a nickel catalyst (containing 10% by weight of magnesium oxide) at a temperature of 820° C. There was thereby obtained per cubic metre of coke oven gas 2.10 cubic metres of a gas of the following composition:—$CO=17.0\%$, $H_2=75.0\%$, $CH_4=2.5\%$, $N_2=3.2\%$ and $CO_2=2.3\%$.

1,000,000 cubic metres of this gas were

then mixed with 1,500,000 cubic metres of blue water gas of the following composition:—$CO=40.7\%$, $H_2=51.0\%$, $CH_4=0.3\%$, $CO_2=5.0\%$, and $N_2=3.0\%$, and there was thus obtained 2,500,000 cubic metres of a gas, hereinafter referred to as Synthesis Gas I, of the following composition—$CO = 31.0\%$, $H_2 = 61.0\%$, $CH_4=1.0\%$, $CO_2=4.3\%$ and $N_2=2.7\%$.

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 to 220° C., yielding per cubic metre of Synthesis Gas I 112 gms. of primary products and 0.34 cubic metres of residual gas, hereinafter referred to as Residual Gas I. It will thus be seen that a contraction in volume of 66% took place. The Residual Gas I had the following composition:—$CO=25.0\%$. $H_2=40.0\%$, $CH_4=15.0\%$, $CO_2=12.6\%$ and $N_2=7.4\%$.

The Residual Gas I was then freed from carbon dioxide by washing with an aqueous solution containing a mixture of alkylolamine bases, and mixed with steam in the proportion of 0.25 kgm. of steam per cubic metre of gas and the mixture heated in the presence of a nickel catalyst at a temperature of 820° C. There was thereby obtained per cubic metre of Residual Gas I 1.53 cubic metres of a gas of the following composition:—$CO=26.0\%$, $H_2=64.0\%$, $CH_4=1.0\%$ and $CO_2+N_2=9.0\%$.

1,145,000 cubic metres of this gas were then mixed with 485,000 cubic metres of blue water gas of the above-mentioned composition and there was thus obtained 1,630,000 cubic metres of a gas hereinafter referred to as Synthesis Gas II of the following composition:—$CO = 30.4\%$, $H_2=60.2\%$, $CH_4=0.8\%$ and $CO_2+N_2=8.6\%$.

By subjecting the Synthesis Gas II to the Fischer-Tropsch process about 140 gms. of primary products and 0.25 cubic metres of residual gas can be obtained per cubic metre of Synthesis Gas II. This residual gas, which is hereinafter referred to as Residual Gas II, may 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 sulphur purification, and it is then found that the coal consumption is about 3.75 tons of coal per ton of primary products produced.

2. 495,000 cubic metres of coke oven gas having the following composition:—$CO=7.0\%$, $H_2=54.0\%$, $CH_4=29.0\%$, $C_nH_m=3.6\%$, $N_2=4.4\%$ and $CO_2=2.0\%$ were mixed with steam in the proportion of 1.3 kgm. of steam per cubic metre of gas, and the mixture heated without a catalyst at 1450° C. There was thus produced 1,000,000 cubic metres of a gas of the following composition:—$CO=21.0\%$, $H_2=66.0\%$, $CH_4=1.6\%$ and $CO_2+N_2=11.4\%$, which was then mixed with 800,000 cubic metres of blue water gas of the following composition:—$CO=40.7\%$, $H_2=51.0\%$, $CH_4=0.3\%$, $CO_2=5.0\%$ and $N_2=3.0\%$ and there was obtained 1,800,000 cubic metres of a gas hereinafter referred to as Synthesis Gas I^1 of the following composition:—$CO=29.7\%$, $H_2=59.3\%$, $CH_4=1.0\%$ and $CO_2+N_2=10.0\%$.

The Synthesis Gas I^1 was passed over a cobalt catalyst activated with thoria and mixed with a kieselguhr carrier at a temperature of 160 to 220° C., yielding per cubic metre of Synthesis Gas I 103 gms. of primary products and 0.34 cubic metre of residual gas hereinafter referred to as Residual Gas I^1. It will thus be seen that a contraction of 66% had taken place. The Residual Gas I^1 had the following composition: — $CO=24.0\%$, $H_2=32.0\%$, $CH_4=15.0\%$ and $CO_2+N_2=29.0\%$.

The Residual Gas I^1 (612,000 cubic metres) was then mixed with steam in the proportion of 0.6 kgm. of steam per cubic metres of gas ond the mixture heated in the absence of catalysts at a temperature of 1450° C. There was thereby obtained 870,000 cubic metres of gas having the following composition: — $CO=27.0\%$, $H_2=46.0\%$, $CH_4=0.7\%$ and $CO_2+N_2=26.3\%$. This was mixed with 720,000 cubic metres of blue water gas of the above-mentioned composition and 350,000 cubic metres of converted blue water gas of the following composition:—$CO=4.0\%$, $H_2=91.0\%$, $CH_4+N_2=3.5\%$ and $CO_2=1.5\%$ obtained by heating blue water gas with steam at 450° C. and washing with an aqueous solution containing a mixture of alkylolamine bases to remove carbon dioxide. There is thus obtained 1,940,000 cubic metres of a gas hereinafter referred to as Synthesis Gas II^1 of the following composition:—$CO=28.0\%$, $H_2=56.0\%$, $CH_4=0.5\%$ and $CO_2+N_2=15.5\%$.

By subjecting the Synthesis Gas II^1 to the Fischer-Tropsch process about 129 gms. of primary products and 0.30 cubic metres of residual gas can be obtained per metre of Synthesis Gas II^1. This residual gas, which is hereinafter referred to as Residual Gas II^1, may be used for heating the coke oven plant, the plant employed in treating the Residual Gas I^1 with steam and for heating the plant employed in sulphur purification, and it is then found that the coal consumption is about 3.8 tons per ton of primary products produced.

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 coke oven gas with steam at a temperature of 1200 to 1500° C. without a catalyst, or from 800 to 900° C. in the presence of a nickel or iron catalyst, mixing the gas thus produced with blue water gas in such proportion as to produce a gas mixture containing carbon monoxide and hydrogen in a proportion suitable for use in the Fischer-Tropsch process, heating the mixture thus produced in the presence of a cobalt, nickel or iron catalyst at a temperature between 160 and 250° C. to produce oil and a gaseous product, mixing the gaseous product with steam and heating to a temperature of between 1200 and 1500° C. without a catalyst or to a temperature of between 800 and 900° C. with a nickel or iron catalyst and mixing the product with blue water gas in such a proportion as to form a gas containing hydrogen and carbon monoxide in a proportion suitable for use in the Fischer-Tropsch process.

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 Examples 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, 1944.
ELKINGTON & FIFE,
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20 to 23, Holborn, London, E.C.1,
Agents for the Applicant.

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