PATENT SPECIFICATION

Application Date: May 10, 1940. No. 8442/40. **573,924**

" " May 10, 1940. No. 8443/40.

One Complete Specification left (under Section 16 of the Patents and Designs Acts, 1907 to 1939): May 12, 1941.

Specification Accepted: Dec. 13, 1945.

3621

PROVISIONAL SPECIFICATION
No. 8442 A.D. 1940.

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 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 normal blue water gas with coke oven gas in such proportion as to produce a gas containing carbon monoxide and hydrogen in a proportion suitable for the Fischer-Tropsch synthesis, heating the mixture thus produced in the presence of a cobalt, nickel or iron catalyst at a temperature of 160—250° C., to produce oils and gaseous products rich in methane, and heating the said gaseous products with steam in the presence of a nickel or iron catalyst at a temperature of between 800 and 900° C. to produce a gas which on admixture with normal blue water gas is 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 example illustrates how the process of the invention may be carried into effect:—

Coke was treated with steam in the proportion normally used in the blue water gas reaction (i.e. 1.4 kgms. of steam per kgm. of coke) at a temperature of 1100° C. and there was thus produced a gas having the following composition:— $CO=40.7\%$, $H_2=51.0\%$, $CH_4=0.3\%$ and $CO_2+N_2=8.0\%$. 1,000,000 cubic metres of this gas was then mixed with 500,000 cubic metres of coke oven gas having the following composition:—$CO=7.0\%$, $H_2=54.0\%$, $C_nH_m=3.6\%$, $CH_4=29.0\%$, $N_2=4.4\%$ and $CO_2=2.0\%$. There was thus produced 1,500,000 cubic metres of a gas hereinafter referred to as Synthesis Gas I of the following composition:— $CO=29.3\%$, $H_2=51.7\%$, $CH_4=10.0\%$, $C_nH_m=1.2\%$ and $CO_2+N_2=7.8\%$. The Synthesis Gas I was then passed over a cobalt catalyst activated with thoria and

[Price 1/-]

mixed with a kieselguhr carrier at a temperture of 160—220° C., and there was obtained per cubic metre of Synthesis Gas I a yield of 58 gms. of primary products and 0.5 cubic metre of residual gas, hereinafter referred to as Residual Gas I. It will thus be seen that a contraction of volume of 50% took place. The Residual Gas I had the following composition:— CO=20%, H_2=29.0%, CH_4=33.0%, C_nH_m=2.4% and CO_2+N_2=15.6%.

The Residual Gas I (750,000 cubic metres) was then mixed with steam in the proportion of 0.575 kgm. of steam per cubic metre of gas and the mixture heated in the presence of a nickel catalyst (containing 10% by weight of magnesia) at a temperature of 800° C. 1,650,000 cubic metres of a gas was obtained of the following composition: CO=21.0%, H_2=65.0%, CH_4=1.0% and CO_2+N_2=10.0%. This gas was then mixed with 1,000,000 cubic metres of blue water gas and there was thus obtained 2,650,000 cubic metres of a gas, hereinafter referred to as Synthesis Gas II, of the following composition:—CO=30.2%, H_2=60.0%, CH_4=0.8% and CO_2+N_2=9.0%. By subjecting it to the Fischer-Tropsch process, about 140 gms. of primary products and 0.25 cubic metre of residual gas can be obtained per cubic metre of gas. The coal consumption was 3.77 tons of coal per ton of primary products obtained.

Dated this 10th day of May, 1940.

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

PROVISIONAL SPECIFICATION
No. 8443 A.D. 1940.

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 mixing normal blue water gas with coke oven gas in such proportion as to produce a gas containing carbon monoxide and hydrogen in a proportion suitable for the Fischer-Tropsch synthesis, heating the mixture thus produced in the presence of a cobalt, nickel or iron catalyst at a temperature of 160—250° C., to produce oils and gaseous products rich in methane, and heating the said gaseous products with steam in the absence of a catalyst at a temperature of between 1200 and 1500° C. to produce a gas which in admixture with suitable proportions of blue water gas and a gas which has been obtained by heating blue water gas with steam in the presence of a cobalt or nickel catalyst at a temperature of between 400 and 550° C. and then separating carbon dioxide yields a product 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 example illustrates how the process of the invention may be carried into effect.

Coke was heated with steam in the proportion normally used in the blue water gas reaction (i.e. 1.4 kgm. of steam per kgm. of coke) at a temperature of 1100° C. and there was produced a gas having the following composition:—$CO=40.7\%$, $H_2=51.0\%$, $CH_4=0.3\%$ and $CO_2+N_2=8.0\%$. 1,000,000 cubic metres of this gas was then mixed with 500,000 cubic metres of coke oven gas having the following composition:—$CO=7.0\%$, $H_2=54.0\%$, $C_nH_m=3.6\%$, $CH_4=29.0\%$, $N_2=4.4\%$ and $CO_2=2.0\%$. There was thus produced 1,500,000 cubic metres of a gas hereinafter referred to as Synthesis Gas I of the following composition:—$CO=29.3\%$, $H_2=51.7\%$, $CH_4=10.0\%$, $C_nH_m=1.2\%$ and $CO_2+N_2=7.8\%$. 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 58 gms. of primary products and 0.5 cubic metre of residual gas, hereinafter referred to as Residual Gas I, and having the folowing composition:—$CO=20.0\%$, $H_2=29.0\%$, $CH_4=33.0\%$, $C_nH_m=2.4\%$ and $CO_2+N_2=15.6\%$. It will thus be seen that a contraction of volume of 50% took place. The Residual Gas I (750,000 cubic metres) was then mixed with steam in the proportion of 1.4 kgm. of steam per cubic metre of gas and the mixture heated to 1400° C. in the absence of a catalyst. There was obtained 1,580,000 cubic metres of a gas of the following composition:—$CO=27.6\%$, $H_2=57.3\%$, $CH_4=0.6\%$ and $CO_2+N_2=14.5\%$. This was then mixed with 510,000 cubic metres of blue water gas and 125,000 cubic metres of a 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 a gas of the following composition:—$CO=29.0\%$, $H_2=58.0\%$, $CH_4=1.0\%$ and $CO_2+N_2=12.0\%$ which is suitable for use in the Fischer-Tropsch synthesis. By this means the consumption of coal amounts to 3.8 tons per ton of primary products.

Dated this 10th day of May, 1940.

ELKINGTON & FIFE,
Consulting Chemists & 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.

Specification No. 513,778 describes a process for the production of gaseous mixtures containing carbon monoxide and

hydrogen and suitable for conversion into hydrocarbons in which a gas mixture consisting principally of carbon monoxide and hydrogen for example water gas is mixed with cold distillation gases and the resulting mixture is passed over a catalyst for example a cobalt or nickel catalyst, producing gases rich in methane, these gases being then converted at 1400—1450° C. with steam in a decomposing plant lined with refractory bricks, yielding a gas consisting principally of a mixture of carbon monoxide and hydrogen.

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 cheaper and more efficient manner than by the process of the aforesaid Specification No. 513,778 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 mixing normal blue water gas with coke oven gas in such proportion as to produce a gas containing carbon monoxide and hydrogen in a proportion suitable for the Fischer-Tropsch synthesis, heating the mixture thus produced in the presence of a cobalt, nickel or iron catalyst at a temperature of 160—250° C. to produce oils and gaseous products rich in methane, and heating the said gaseous products with steam in the presence of a nickel or iron catalyst at a temperature of between 800 and 900° C. to produce a gas which on admixture with normal blue water gas is suitable for use in the Fischer-Tropsch process.

The present invention also 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 mixing normal blue water gas with coke oven gas in such proportion as to produce a gas containing carbon monoxide and hydrogen in a proportion suitable for the Fischer-Tropsch synthesis heating the mixture thus produced in the presence of a cobalt, nickel or iron catalyst at a temperature of 160—250° C., to produce oils and gaseous products rich in methane, and heating the said gaseous products with steam in the absence of a catalyst at a temperature of between 1200 and 1500° C. to produce a gas, mixing said gas with suitable proportions of blue water gas and a gas which has been obtained by heating blue water gas with steam in the presence of a cobalt or nickel catalyst at a temperature of between 400 and 550° C. and then separating carbon dioxide, the gases being mixed in such proportion that a product is obtained which is 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 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. Coke was treated with steam in the proportion normally used in the blue water gas reaction (i.e. 1.4 kgms. of steam per kgm. of coke) at a temperature of 1100° C. and there was thus produced a gas having the following composition:— $CO=40.7\%$, $H_2=51.0\%$, $CH_4=0.3\%$ and $CO_2+N_2=8.0\%$. 1,000,000 cubic metres of this gas was then mixed with 500,000 cubic metres of coke oven gas having the following composition: $CO=7.0\%$, $H_2=54.0\%$, $C_nH_m=3.6\%$, $CH_4=29.0\%$, $N_2=4.4\%$ and $CO_2=2.0\%$. There was thus produced 1,500,000 cubic metres of a gas hereinafter referred to as Synthesis Gas I of the following composition:—$CO=29.3\%$, $H_2=51.7\%$, $CH_4=10.0\%$, $C_nH_m=1.2\%$ and $CO_2+N_2=7.8\%$. 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., and there was obtained per cubic metre of Synthesis Gas I a yield of 58 gms. of primary products and 0.5 cubic metre of residual gas, hereinafter referred to as Residual Gas I. It will thus be seen that a contraction of volume of 50% took place. The Residual Gas I had the following composition:— $CO=20.0\%$, $H_2=29.0\%$, $CH_4=33.0\%$, $C_nH_m=2.4\%$ and $CO_2+N_2=15.6\%$.

The Residual Gas I (750,000 cubic metres) was then mixed with steam in the proportion of 0.575 kgm. of steam per cubic metre of gas and the mixture heated in the presence of a nickel catalyst (containing 10% by weight of magnesia) at a temperature of 800° C. 1,650,000 cubic metres of a gas was obtained of the following composition:— $CO=24.0\%$, $H_2=65.0\%$, $CH_4=1.0\%$ and $CO_2+N_2=10.0\%$. This gas was then mixed with 1,000,000 cubic metres of blue water gas and there was thus obtained

2,650,000 cubic metres of a gas, hereinafter referred to as Synthesis Gas II, of the following composition:—CO=30.2%, H_2=60.0%, CH_4=0.8% and CO_2+N_2=9.0%. By subjecting it to the Fischer-Tropsch process, about 140 gms. of primary products and 0.25 cubic metre of residual gas can be obtained per cubic metre of gas. The coal consumption was 3.77 tons of coal per ton of primary products obtained.

2. Coke was heated with steam in the proportion normally used in the blue water gas reaction (i.e. 1.4 kgm. of steam per kgm. of coke) at a temperature of 1100° C. and there was produced a gas having the following composition:—CO=40.7%, H_2=51.0%, CH_4=0.3% and CO_2+N_2=8.0%. 1,000,000 cubic metres of this gas was then mixed with 500,000 cubic metres of coke oven gas having the following composition: CO=7.0%, H_2=54.0%, C_nH_m=3.6%, CH_4=29.0%, N_2=4.4% and CO_2=2.0%. There was thus produced 1,500,000 cubic metres of a gas hereinafter referred to as Synthesis Gas I^1 of the following composition:—CO=29.3%, H_2=51.7%, CH_4=10.0%, C_nH_m=1.2% and CO_2+N_2=7.8%. The Synthesis Gas I^1 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^1 a yield of 58 gms. of primary products and 0.5 cubic metre of residual gas, hereinafter referred to as Residual Gas I^1, and having the following composition:—CO=20.0%, H_2=29.0%, CH_4=33.0%, C_nH_m=2.4% and CO_2+N_2=15.6%. It will thus be seen that a contraction in volume of 50% took place. The Residual Gas I^1 (750,000 cubic metres) was then mixed with steam in the proportion of 1.4 kgm. of steam per cubic metre of gas and the mixture heated to 1400° C. in the absence of a catalyst. There was obtained 1,580,000 cubic metres of a gas of the following composition: CO=27.6%, H_2=57.3%, CH_4=0.6% and CO_2+N_2=14.5%. This was then mixed with 510,000 cubic metres of blue water gas and 125,000 cubic metres of a 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 a gas of the following composition:—CO=29.0%, H_2=58.0%, CH_4=1.0% and CO_2+N_2=12.0% which is suitable for use in the Fischer-Tropsch synthesis. By this means the consumption of coal amounts to 3.8 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 mixing normal blue water gas with coke oven gas in such proportion as to produce a gas containing carbon monoxide and hydrogen in a proportion suitable for the Fischer-Tropsch synthesis, heating the mixture thus produced in the presence of a cobalt, nickel or iron catalyst at a temperature of 160—250° C. to produce oils and gaseous products rich in methane, and heating the said gaseous products with steam in the presence of a nickel or iron catalyst at a temperature of between 800 and 900° C. to produce a gas which on admixture with normal blue water gas is suitable for use in the Fischer-Tropsch process.

2. 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 normal blue water gas with coke oven gas in such proportion as to produce a gas containing carbon monoxide and hydrogen in a proportion suitable for the Fischer-Tropsch synthesis, heating the mixture thus produced in the presence of a cobalt, nickel or iron catalyst at a temperature of 160—250° C. to produce oils and gaseous products rich in methane, and heating the said gaseous products with steam in the absence of a catalyst at a temperature of between 1200 and 1500° C. to produce a gas, mixing said gas with blue water gas and a gas which has been obtained by heating blue water gas with steam in the presence of a cobalt or nickel catalyst at a temperature of between 400 and 550° C. and then separating carbon dioxide, the gases being mixed in such proportion that a product is obtained which is suitable for use in the Fischer-Tropsch process.

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

4. A process as claimed in any one of the preceding claims wherein all the

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

5. 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.

6. 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.

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

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1946. Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 1s. 0d. each (inland) 1s. 1d. (abroad) may be obtained.