#### PATENT SPECIFICATI

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### PROVISIONAL SPECIFICATION No. 8440 A.D. 1940.

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

I, MICHAEL STEINSCHLAEGER, of no ationality, formerly of Russian nationality, formerlynationality, of 50, Portsea Hall, Connaught Square, London, W.2, do hereby 5 declare the nature of this invention to be as follows:-

This invention relates to the production ot gaseous mixtures containing carbon monoxide and hydrogen suitable for use 10 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 15 1.8 and 2.0 volumes of hydrogen per volume of carbon monoxide.

Gases occurring in nature of artificially produced do not have the desired composition because they are usually rich in carbon monoxide. It is therefore neces-20 carbon monoxide. sary 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 30 by heating it with steam. If these gases are mixed a synthesis gas is obtained containing CO: H, in the proportion of 1:2, This process has the drawback that the coke being formed during coking and 35 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 40 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 45 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 earhon monoxide and hydrogen suitable for use 50 in the Fischer-Tropsch synthesis comprises heating coke with at least 150%, for example 200% of the theoretical amount of steam required for the water gas reaction, at a temperature of between 55 900 and 1100° C., to produce a gas containing more hydrogen and carbon dioxide than is normally present in blue water gas, preferably removing carbon dioxide from the said gas, mixing the residue with 60 coke oven 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 65 presence of a cobalt, nickel or iron catalyst at a temperature between 160 and 250° C., to produce oils and gaseous products rich in methane, and heating the said gaseous products with steam at a tem- 70 perature between 800 and 900° C. in the presence of a nickel or iron catalyst 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 80 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 200% of the theoretical proportion of steam required 90 for the blue water gas reaction at a temperature of 950° C. and there was thus produced a gas having the following composition: -CO = 36.0%,  $H_2 = 53.0\%$ ,  $CH_4 = 1.0\%$ ,  $CO_2 = 7.0\%$  and  $N_3 = 3.0\%$ . This 95 gas, was washed with a

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containing a bases mixture of alkylolcarbon to remove dioxide and a gas was obtained having the following composition:—CO=38.4%, 5 H<sub>2</sub>=56.4%, CH<sub>4</sub>=1.0%, CO<sub>2</sub>=1.0% and N<sub>2</sub>=3.2%. 1,000,000 cubic metres of this gas was mixed with 500,000 cubic metres of a coke oven gas having the following composition:—C0=7.0%, H<sub>2</sub>=54.0%, 10 C<sub>n</sub>H<sub>m</sub>=3.6%, CH<sub>s</sub>=29.0%, N<sub>2</sub>=4.4% and C0=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: -C0 = 27.5%, 15 H<sub>2</sub>=55.3%, CH<sub>4</sub>=10.4%, C<sub>n</sub>H<sub>m</sub>=1.2% and CO<sub>2</sub>+N<sub>2</sub>=5.6%. The Synthesis Gas I was then passed over a cobalt entalyst activated with thoria and mixed with a kieselguhr carrier at a temperature of 20 160-220° C. and there was obtained per cubic metre of Synthesis Gas I a yield of 70 gms. of primary products and 0.5 cubic metre of residual gas hereinafter referred to as Residual Gas I. It will thus be seen 25 that a contraction of volume of 50% took place. The Residual Gas I had the following composition: -CO = 31.5%,  $H_2 = 82.9\%$ ,  $CH_4 = 32.0\%$ ,  $C_nH_{nr} = 2.4\%$  and  $CO_2 + N_2 = 11.2\%$ . The Residual Gas 30 I was then mixed with steam in the proportion of 0.56 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 35 temperature of 800° C. There was thus

composition: -CO = 24.0%. 67.0%,  $CH_1 = 1.0\%$  and  $CO_2 + N_2 = 8.0\%$ . 1,610,000 cubic metres of this gas were 40 then mixed with 1,000,000 cubic of blue water gas and there was thus obtained 2,610,000 cubic metres of a gas hereinafter referred to as Synthesis Gas II of the following composition:—CO=30.5%, 45 H<sub>2</sub>=61.0%, CH<sub>3</sub>=0.7% and CO<sub>2</sub>+N<sub>2</sub>-7.8%. By subjecting this Synthesis Gas II to the Rischer-Tropsch process about 140 gms. of primary products and 0.25 cubic metre of residual gas can be obtained per 50 cubic metre of gas.

The residual gas hereinafter referred to as Residual Gas II obtained after the Synthesis Gas II has been subjected to the Fischer-Tropsch process (the composi- 55 tion of the Residual Gas II was as follows:—CO=21.0%,  $H_2=34.0\%$ ,  $CH_4=14.0\%$ , and  $CO_2+N_2=81.0\%$ ) may be used for heating the coke oven plant, the plant employed in treating the Residual III. dual Cas I with steam and for heating the plant employed in the sulphur purification and it is then found that the coal consumption is about 3.6 tons of coal per ton of primary products produced. The expression "primary products" does not include the oil yield in the coke oven plant.

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. 8441 A.D. 1940.

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

I, MICHAEL STEINSCHLAEGER, of no ationality, formerly of Russian of 70 nationality, formerly of Russian nationality, of 50, Portsea Hall, Con-naught Square, London, W.2, do hereby declare the nature of this invention to be as follows:--

obtained per cubic metro of Residual Gas I 2,15 cubic metres of a gas of the follow-

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-80 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 90 are then mixed with gases rich in carbon monaxide.

When coal is coked, coke and coke oven gas are obtained. Water gas, a gas rich in carbon monoxide, may be obtained from 95 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<sub>2</sub> in the proportion of 1:2, 100 This process has the drawback that the coke being formed during coking and

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gasification is never completely used up and consequently the coal consumption is

too high.

It is an object of the present invention 5 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 10 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 15 of a gas mixture containing carbon monoxide and hydrogen suitable for use in the Fischer-Tropsch synthesis comprises heating coke with at least 150%, for example 200% of the theoretical amount

20 of steam required for the water gas reaction, at a temperature of between 900 and 1000° C., to produce a gas containing more hydrogen and carbon dioxide than is normally present in blue water gas, prefer-25 ably removing carbon dioxide from the said gas, mixing the residue with coke oven gas in such proportion as to produce

a gas containing carbon monoxide and hydrogen in a proportion suitable for use 30 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 gaseous products 35 rich in methane, and heating the said gaseous products with steam at a temperature between 1200 and 1500° C. in the absence of a catalyst to produce a gas which on admixture with normal blue

40 water gas and a gas obtained by heating normal blue water gas with steam in the presence of a cobalt or ninkel catalyst at a temperature of between 400 and 550° C. and then separating carbon dioxide is suit-45 able for use in the Fischer-Tropsch

process,

The cobalt, nickel or iron catalyst employed may, if desired, be activated with an activator such as theria and the 5() 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 processes of the invention may be carried into effect:

Coke was treated with 175% of the theoretical proportion of steam required for the blue water can reaction at a temperature of  $950^{\circ}$  C. and there was thus produced a gas having the following 65 composition:—CO = 36.0%,  $H_a = 58.0\%$ ,

 $CH_4 = 1.0\%$ ,  $CO_2 = 7.0\%$  and  $N_2 = 3.0\%$ . This gas was washed with water under pressure to remove carbon dioxide and a gas was obtained having the following composition: -400 - 38.4%,  $H_2 = 56.4\%$ , 70  $\text{CH}_{2}=1.0\%$ ,  $\text{CO}_{2}=1.0\%$  and  $\tilde{N}_{2}=3.2\%$ . 1,000,000 cubic metres of this gas was mixed with 500,000 cubic metres of a coke oven gas having the following composition:—CO=7.0%,  $H_2=54.0\%$   $C_nH_m=753.6\%$ ,  $CH_4=29.0\%$ ,  $N_2=4.4\%$  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 = 27.5%,  $H_2 = 55.3\%$ , 80  $CH_4 = 10.4\%$ ,  $C_nH_m = 1.2\%$  and  $CO_2 + N_2 = 5.6\%$ . 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. 85 and there was obtained per cubic metre of Synthesis Gas I a yield of 70 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 90 contraction of volume of 50% took place. The Residual Gas I had the following composition:—CO=21.5%. H<sub>2</sub>=32.9%, CH<sub>4</sub>=32.0%, C<sub>5</sub>H<sub>20</sub>=2.4% and CO<sub>5</sub>N<sub>2</sub>=11.2%. The Residual Gas I was then 95 mixed with steam in the proportion of 1.10 kgm; of steam per cubic metre of gas and the mixture heated in the absence of a catalyst-at-a-temperature of 1250° C. There was thus obtained a gas of 100 the following composition:—CO=27.5%,  $H_2=59.6\%$ ;  $CH_4=32.0\%$ ,  $C_5H_m=2.4\%$  and  $CO_2+N_3=11.2\%$ . The Residual Gas I was then mixed with steam in the proportion of 1.10 kgm. of steam per cubic 105 metre of gas and the mixture heated in the absence of a catalyst at a temperature of 1250° C. There was thus obtained a gas of. the following composition:—CO = 27.5%,  $H_2 = 59.0\%$ ;  $CH_4 = 1.2\%$  and 110  $CO_2 + N_4 = 12.3\%$ , 1,510,000 cubic metres of this gas were then mixed with 700,000 cubic metres of blue water gas and 170,000 cubic metres of a gas obtained by heating blue water gas with steam in the presence 115 of a nickel catalyst at 450° O. and then separating carbon dioxide by treatment with an aqueous solution containing a mixture of alkylolamine bases, and there was thus obtained 2,380,000 cubic metres 120 of a gas hereinafter referred to as Synthesis Gas II of the following composition: -C0=29.7%,  $H_z=59.3\%$ ,  $CH_z=0.9\%$ ,  $CO_z+N_z=10.1\%$ . By subjecting it to the Fischer-Tropsch process about 140 125 gms. of primary products and 0.25 cubic metres of residual gas can be obtained per cubic metre of gas.

The residual gas hereinafter referred as Residual Gas II obtained after the Syn. 130 thesis stas II has been subjected to the Fischer-Tropsch process 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 the sulphur purification and it is then found that the coal consumption is about 3.8 tons of coal per ton of primary products produced. The expression

" primary products" does not include the 10 oil yield in the coke oven plant.

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 STEINSCHLARGER, of no nationality, formerly of Russian nationality, of 50, Portsea Hall, Containing the Landson, 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 state
20 ment:—

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

25 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 30 volume of carbon monoxide.

(Jases occurring in nature or artificially produced do not have the desired composition because they are usually rich in earbon 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 40 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 45 mixed a synthesis gas is obtained containing CO: H<sub>2</sub> 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 con-50 sequently the coal consumption is too

high.
Specification No. 513,778 describes a process for the production of gaseous mixtures containing carbon monoxide and 55 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 coal distillation gases and the resulting mixture is passed over a 60 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 65 bricks, yielding a gas consisting principally of a mixture of rarbon 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 80 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 coke with at least 85 150%, for example 200% of the theoretical amount of steam required for the water gus reaction, at a temperature of between 900 and 1100° C., to produce a gas containing more hydrogen and 90 carbon dioxide than is normally present in blue water gas, preferably removing carbon dioxide from the said gas, mixing the residue with coke oven gas in such proportion as to produce a gas containing 95 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 100 between 160 and 250° C., to produce oils and gaseous products rich in methane, and heating the said gaseous products with steam at a temperature between 800 and 900° C, in the presence of a nickel or iron 105 catalyst 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 heating coke with at least 150%, for example 10 200% of the theoretical amount of steam required for the water gas reaction, at a temperature of between 900 and 1000° C., to produce a gas containing more hydrogen and carbon dioxide than is normally. 15 present in blue water gas, preferably removing carbon dioxide from the said gas, mixing the residue with coke oven gas in such proportion as to produce a gas containing carbon monoxide and hydrogen 20 in a proportion suitable for use in the Fischer-Tropsch process, heating mixture thus produced in the presence of a cobalt, nickel or iron catalyst at a temperature between 160 and 250° C., to pro-25 duce oils and gaseous products rich in methane, and heating the said gaseous products with steam at a temperature between 1200 and 1500° C. in the absence of a catalyst to produce a gas, mixing said gas with normal blue water gas and a gas obtained by heating normal 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 35 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 em-

The cobalt, nickel or iron catalyst em-40 ployed 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.

45 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 50 the process of the invention may be

carried into effect:

1. Coke was treated with 200% of the theoretical proportion of steam required for the blue water gas reaction at a temperature of 950° C, and there was thus produced a gas having the following composition:—CO=36.0%, H<sub>2</sub>=53.0%, CH<sub>4</sub>=1.0%, CO<sub>2</sub>=7.0% and N<sub>2</sub>=3.0%. This gas was washed with a solution containing a mixture of alkylolamine bases to remove carbon dioxide and a gas was obtained having the following composition:—CO=38.4% H<sub>2</sub>=56.4%, CH<sub>4</sub>=1.0%, CO<sub>2</sub>=1.0% and N<sub>4</sub>=3.2%. 65 1.000,000 cubic metres of this gas was

mixed with 500,000 cubic metres of a coke oven gas having the following composition: -C0=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 70 1500,000 and in the second results of the sec 1,500,000 cubic metres of a gas hereinafter referred to as Synthesis Gas I of the following composition: -C0 = 27.5%,  $H_2 = 55.3\%$ ,  $CH_4 = 10.4\%$ ;  $C_nH_m = 1.2\%$  and  $CO_2 + N_2 = 5.6\%$ . The Synthesis Gas 75 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 80 70 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 85 the following composition:—C0=21,5%,  $H_2=32.9\%$ ,  $CH_4=32.0\%$ ,  $C_nH_m=2.4\%$  and  $CO_2+N_2=11.2\%$ . The Residual Gas I was then mixed with steam in the proportion of 0.56 kgm. of steam per cubic 90 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 800° C. There was thus obtained per cubic metre of Residual 95 Gas I, 2.15 cubic metres of a gas of the following composition: -CO = 24.0%,  $\text{H}_z = 67.0\%$ ,  $\text{CH}_z = 1.0\%$  and  $\text{CO}_z + \text{N}_z = 8.0\%$ . 1,610,000 cubic metres of this gas were then mixed with 1,000,000 cubic 100 metres of blue water gas and there was thus obtained 2,610,000 cubic metres of a gas hereinafter referred to as Synthesis Gas II of the following composition:— CO = 30.5%,  $H_2 = 61.0\%$ ,  $CH_4 = 0.7\%$  and 105  $CO_2 + N_2 = 7.8\%$ . By subjecting this Synthesis Gas II 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 residual gas hereinafter referred to as Residual Gas II obtained after the Syithesis Gas II has been subjected to the Fischer-Tropsch process (the composition of the Residual Gas II was as follows:— 115 CO=21.0%, H<sub>2</sub>=34.0%, CH<sub>4</sub>=14.0%, and CO<sub>2</sub>+N<sub>2</sub>=31.0%) 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 the sulphur purification and it is then found that the coal consumption is about 3.6 tons of coal per ton of primary products—products—The expression primary products—The expression primary products—The expression

oil yield in the coke oven plant.

2. Coke was treated with 175% of the theoretical proportion of steam required for the blue water gas reaction at a temperature of 950° C, and there was thus 180

produced a gas having the following composition: -C0 = 36.0%,  $H_2 = 53.0\%$ ,  $CH_4 = 1.0\%$ ,  $CO_2 = 7.0\%$  and  $N_2 = 3.0\%$ . This gas was washed with water under pressure to remove carbon dioxide and a gas was obtained having the following composition:—C0 = 38.4%,  $H_z = 56.4\%$ ,  $CH_4 = 1.0\%$ ,  $CO_2 = 1.0\%$  and  $N_2 = 3.2\%$ . 1,000,000 cubic metres of this gas was 10 mixed with 500,000 cubic metres of a coke oven gas having the following composition: CO = 7.0%,  $H_2 = 54.0\%$ ,  $C_nH_m = 3.6\%$ ,  $CH_1 = 29.0\%$ ,  $N_2 = 4.4\%$  and  $CO_2 = 3.6\%$ 2.0% . There was thus produced  $1,500,\bar{0}00$ 15 metres of a gas hereinafter referred to as Synthesis Gas I<sup>1</sup> of the following composition: -CO = 27.5%, H<sub>2</sub> = 55.3%, CH<sub>3</sub> = 10.4%, C<sub>2</sub>H<sub>m</sub> = 1.2% and CO<sub>2</sub> + N<sub>3</sub> = 5.60 MeV. Centhesis Gas I<sup>1</sup> one than 5.6%. The Synthesis Gas I1 was then 20 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<sup>1</sup> a yield of 70 gms, of primary products and 0.5 cubic metre of residual gas hereinafter referred to as Residual Gas I1. It will thus be seen that a contraction of volume of 50% took place. The Residual Gas II had the following so composition:—CO = 21.5%, H<sub>2</sub> = 32.9%, CH<sub>1</sub> = 32.0%, C<sub>n</sub>H<sub>m</sub> = 2.4% and CO<sub>2</sub> + N<sub>2</sub> = 11.2%. The Residual Gas I<sup>2</sup> was then mixed with steam in the proportion of 1.10 kgm. of steam per cubic metre of gas 35 and the mixture heated in the absence of and the mixture heated in the absence of a catalyst at a temperature of 1250° C. There was thus obtained a gas of the following composition: —CO = 27.5%, H<sub>2</sub>=59.0%, CH<sub>4</sub>=1.2%, and CO<sub>2</sub>+N<sub>2</sub>=40 12.3%. 1.510,000 cubic metres of this gas were then mixed with 700,000 cubic metres of blue, water case and 170,000 metres of blue water gas and 170,000 cubic metres of a gas obtained by heating blue water gas with steam in the presence 45 of a nickel catalyst at 450° C. and then separating carbon dioxide by treatment with an aqueous solution containing a mixture of alkylolamine bases, and there was thus obtained 2,380,000 cubic metres was thus obtained 2,550,000 cubic metres
50 of a gas hercinafter referred to as
Synthesis Gas II<sup>1</sup> of the following
composition:—C0=29.7%. H<sub>2</sub>=59.3%,
CH<sub>4</sub>=0.9%: and CO<sub>2</sub>+N<sub>3</sub>=10.1%. By
subjecting it to the Fischer-Tropsch process about 140 gms. of primary products
and 0.25 cubic matra of residual cas can and 0.25 cubic metre of residual gas can be obtained per cubic metres of gas. The residual gas hereinafter referred to as Residual Gas 11 obtained after the 60 Synthesis Gas III has been subjected to the Fischer-Tropsch process may be used for heating the coke oven plant, the plant

comployed in treating the Residual Gas It with steam and for acating the plant com-

65 ployed in the sulphur purification and it-

is then found that the coal consumption is about 3.8 tons of coal per ton of primary products produced. The expression "primary products" as used herein means hydrocarbons containing three or more 70 carbon atoms in the molecule obtained in the synthesis and does not include the oil yield in the coke oven plant.

By the term "coke" as used herein is

By the term "coke" as used herem is to be understood all types of coke including coke made from coal by either high temperature or low temperature carbon-

isotion and petroleum coke.

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

1. A process for the production of a gas mixture containing carbon monoxide and 85 hydrogen suitable for use in the Fischer-Tropsch synthesis which comprises heating coke with at least 150%, for example 200% of the theoretical amount of steam required for the water gas reaction, at a 90 temperature of between 900 and 1100° C., to produce a gas containing more hydrogen and carbon dioxide than is normally present in blue water gas, preferably removing carbon dioxide from the said gas, 95 mixing the residue with coke oven 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 mix- 100 ture thus produced in the presence of a cohalt, nickel or iron catalyst at a temperature between 180 and 250° C. to produce oils and gaseous products rich in methane, and heating the said gaseous 105 products with steam at a temperature be-tween 800 and 900° C. in the presence of a nickel or iron catalyst to produce a gas which on admixture with normal blue water gas is suitable for use in the 110 Fischer-Tropsch process.

-2.  $\Lambda$  process for the production of a gus mixture containing carbon monoxide and hydrogen suitable for use in the Fischer-Tropsch synthesis which comprises heat- 115 ing coke with at least 150%, for example 200% of the theoretical amount of steam required for the water gas reaction, at a temperature of between 900 and 1000° C., to produce a gas containing more hydrogen 120 and carbon dioxide than is normally present in blue water gas, preferably removing carbon dioxide from the said gas, mixing the residue with coke oven gas in such proportion as to produce a gas con- 125 taining 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 tem- 130 573,928

perature between 160 and 250° C. to produce oils and gaseous products rich in methane, and heating the said gaseous products with steam at a temperature 5 between 1200 and 1500° C. in the absence

between 1200 and 1500° C. in the absence of a catalyst to produce a gas, mixing said gas with normal blue water gas and a gas obtained by heating normal blue water gas with steam in the presence of a cobalt or nightly catalyst at a temporary of he

10 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 15 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.

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

5. A process for the production of a gas mixture containing carbon monoxide and hydrogen suitable for use in the Fischer-Tropach synthesis substantially as described with reference to the Examples 30 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 35 of the preceding claims.

of the preceding claims.

Dated this 12th day of May, 1941.

ELKINGTON & FIFE,

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Patent Agents,

20 to 23, Holbern, London, E.C.1,

Agents for the Applicant.

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7