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PATENT SPECIFICATION

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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 5 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

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 or artificially produced do not have the desired composition because they are usually rich in car-20 hon 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 30 by heating it with steam. If these guses . are mixed a synthesis gas is obtained containing CO: H_a in the proportion of 1:2. This process has the drawback that the coke being formed during coking and gasi-35 fication is never completely used up and. consequently the coal consumption is too high.
It is an object of the present invention

to overcome the uforesaid 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 contain 45 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 mon-50 oxide and hydrogen suitable for use in the

Fischer-Tropsch synthesis comprises heat ing a coke oven gas with steam at a tem-

perature of 1200 to 1500° C, without a catalyst, or from 800 to 900° C, in the presence of a nickel or iron catalyst, mix- 55 ing 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 mix 60 ture 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 heat- 65 ing 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 pro- 70 portion 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 em- 75 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 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 85 the process of the invention may be

carried into effect.

1. 475,000 cubic metres of coke oven gas having the following composition:- $\overset{\text{CO}}{\text{CO}} = 7.0\%, \quad \overset{\text{H}_2}{\text{H}_2} = 54.0\%, \quad \overset{\text{CH}_4}{\text{CH}_4} = 29.0\%, \quad 90$ $\overset{\text{C}_3}{\text{C}_3} \overset{\text{H}_3}{\text{H}_3} = 3.6\%, \quad \overset{\text{N}_3}{\text{N}_3} = 4.4\% \quad \text{and} \quad \overset{\text{CO}_2}{\text{C}_3} = 2.0\%, \quad \overset{\text{N}_3}{\text{N}_3} = 4.4\% \quad \overset{\text$ 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% 95 by weight of magnesium oxide) at a temperature of \$20° 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%, H₂=75.0%, 100 CH₂=2.5%, N₂=3.2% and CO₂=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 composi-

[Price 1/-]

tion: --CO = 40.7%, H₂ = 51.0%, CH₄ = 0.3%, CO₅ = 5.0%, and N₂ = 3.0%, and N₃ = 3.0%, and N₄ = 3.0%, and N₅ = 3 there was thus obtained 2,500,000 cubic metres of a gas, hereinafter referred to as 5 Synthesis Gas I, of the following composition:—CO = 31.0%, H₂ = 61.0%. CH₄ = 1.0%, CO₂ = 4.3%, and N₄ = 2.7%.

The Synthesis Gas I was then passed

10 over a cobalt catalyst activated with theria 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 15 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:—C0 = 25.0%. $CH_a = 15.0\%$, $CO_s = 12.6\%$

20 H₂=40.0%, 0 and N₂=7.4%.

The Residual Gas I was then freed from carbon dioxide by washing with an aqueous solution containing a mixture of 25 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 20 thereby obtained per cubic metre of Residual Gas I 1.53 cubic metres of a gas of the following composition: CO = 26.0%, $H_2 = 64.0\%$, $CH_2 = 1.0\%$ and $CO_2 + N_3 = 9.0\%$. $CH_{\bullet}=1.0\%$ and

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 herein-

40 after referred to as Synthesis Gas II of the following composition: -CO = 30.4%, $H_2 = 60.2\%$, $CH_4 = 0.8\%$ and $CO_4 + N_2 = 30.2\%$ 8.6%.

By subjecting the Synthesis Gas II to 45 the Fischer-Tropsch process about 140 gms. of primary products and 0.25 cabic metres of residual gas can be obtained per cubic metre of Synthesis Gas II.

residual gas, which is hereinafter referred 50 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

55 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 ionowing composition.—
60 CO=7.0%. H₂=54.0%, CH₄=29.0%;
C₁H_m=3.6%. N₂=4.4% and CO₂=2.0% as having the following composition: were mixed with steam in the proportion of 1.3 kgm, of steam per cubic melre of gas, and the mixture heated without a

catalyst at 1450° C. There was thus pro-65 duced 1,000,000 cubic metres of a gas of the following composition: -C0 = 21.6%, $H_2 = 66.0\%$, $CH_4 = 1.6\%$ and $CO_2 + N_2 = 11.4\%$. which was then mixed with 800.000 cubic metres of blue water gas of 70 the following composition: -C0 = 40.7%. $H_a\!=\!51.0\%$, $CH_a\!=\!0.3\%$, $CO_a\!=\!5.0\%$ and $N_a\!=\!3.0\%$ and there was obtained 1,800,000 cubic metres of a gas hereinafter referred to as Synthesis Gas I¹ of the following 75 composition: —CO=29.7%, H₂=59.3%, CH₂=1.0% and CO₂+N₂=10.0%.
The Synthesis Gas I¹ 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 I¹. It will thus be seen that 85 a contraction of 06% had taken place. The Residual Gas I' had the following composition: — CO=24.0%, $H_2 = 32.0\%$

CH₄=15.0% and $CO_2 + N_2 = 29.0\%$. The Residual Gas I¹ (612,000 cubic 90 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 95 870,000 cubic metres of gas having the following composition: — CO = 27.0%, $II_2 = 46.0\%$, $CH_4 = 0.7\%$ and $CO_2 + N_2 = 0.7\%$ 26.8%. This was mixed with 720,000 cubic metres of blue water gas of the 100 above-mentioned composition and 350,000 cubic metres of converted blue water gas of the following composition:—CO=4.0%, $H_z=91.0\%$, $CH_z+N_z=3.5\%$ and $CO_z=1.5\%$ obtained by heating blue 105 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 herein 110 after referred to as Synthesis Gas II1 of the following composition: —CO=28.0%, $H_4=56.0\%$, $CH_4=0.5\%$ and $CO_2+N_2=$ 15.5%.

By subjecting the Synthesis Gas II1 to 115 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 III. This residual gas, which is hereinafter referred to as 120 Residual Gas III, 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 125 found that the coal consumption is about 3.8 tons per ton of primary products produced.

中央集份 92. J.

Dated this 10th day of May, 1940.

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

COMPLETE SPECIFICATION -

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

nationality, formerly of Russian nationality, of 50, Portsea Hall, Connaught Square, London, W.2, do hereby declare 5 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

10 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 15 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 20 produced do not have the desired composition because they are usually rich in carbon monoxide. It is therefore necessary to apply particular processes in orderto obtain gases rich in hydrogen, which 25 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 30 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: II, in the proportion of 1:2. 35 This process has the drawback that the coke being formed during coking and gasi-. fication 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 . 45 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 in-50 vention provides a process for the production of a gas mixture containing carbon monoxide and hydrogen suitable for use in

I. MICHAEL STEINSCHLABGER, of no the Fischer-Tropsch synthesis which comprises heating a coke oven gas with steam at a temperature of 1200 to 1500° C. with 55 out 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 mon- 60 oxide 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 be-tween 1200 and 1500° C. without a catalyst or to a temperature of between 800 70 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 76 use in the Pischer-Tropsch process.

The cobalt, nickel or iron catalyst employed may, if desired, be activated with an activator such as thoriz and the catalyst may be mixed with a carrier such as 80 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 35 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 90 as having the following composition:-were mixed with steam in the proportion of 0.5 kgm. of steam per cubic metre of 95 gas, and the mixture heated in the presence of a nickel catalyst (containing 10% by weight of magnesium oxide) at a temperature of \$20° C. There was thereby obtained per cubic metre of coke oven gas 100 2.10 cubic metres of a gas of the following composition: -CO = 17.0%, $H_z = 75.0\%$, $CH_z = 2.5\%$, $N_z = 3.2\%$ and $CO_z = 2.3\%$.

1,000,000 cubic metres of this gas were

13. 5 m/4 10 mg.

- / (Magg) - (Mg/)

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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%, H₂ = 61.0%, CH₄=1.0%, CO₂=4.3% and N₂=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 1112 15 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 20 the following composition: -C0 = 25.0%. $\rm H_2\!=\!40.0\%$, $\rm CH_4\!=\!15.0\%$, $\rm CO_2\!=\!12.6\%$ and $\rm N_2\!=\!7.4\%$.

The Residual Gas I was then freed from

carbon dioxide by washing with an 25 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 80 at a temperature of 820° C. There was thereby obtained per cubic metre of Residual Gas I I.53 cubic metres of a gas of the following composition:—CO = 26.0%, $H_2 = 64.0\%$, $CH_2 = 1.0\%$ and $85 CO_2 + N_2 = 9.0\%$.

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 40 1,630,000 cubic metres of a gas hereinafter referred to as Synthesis Gas II of the following composition: —CO = 30.4%, $\rm H_2=60.2\%$, $\rm CH_4=0.8\%$ and $\rm CO_2+N_2=$ 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. 50 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 em-

55 ployed 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

60 gas having the following composition:—
CO=7.0%, H₂=54.0%, CH₄=29.0%,
C_nH_m=3.6%, N₄=4.4% and CO₂=2.0%
were mixed with steam in the proportion of 1.3 kgm, of steam per cubic metre of 65 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 $CO_2 + N_2 = 1.6\%$ $H_2=00.0\%$, $CH_4=1.0\%$ and $CO_2+N_2=11.4\%$, which was then mixed with 70 800,000 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 1,800,000cubic metres of a gas hereinafter referred 75 to as Synthesis Gas I of the following composition:—CO=29.7%, $H_z=59.3\%$, $CH_z=1.0\%$ and $CO_z+N_z=10.0\%$.

The Synthesis Gas I' was passed over a cobalt catalyst activated with thoria and 80 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 I2. It will thus be seen that a contraction of 66% had taken place. The Residual Gas I had the following composition: — CO=24.0%, H₂=32.0%, CH₄=15.0% and CO₂+N₂=29.0%.

The Residual Gas I (612.000 cubic metres) and the minutes of the composition of

metrcs) 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 95 of 1450° C. There was thereby obtained 870,000 cubic metres of gas having the following composition: — CO = 27.0%, H₂=46.0%, CH₄=0.7% and CO₅+N₅=26.3%. This was mixed with 720,000 100 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%, H₂=91.0%, CH₄+N₂=3.5% and 105 CO₂=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 110 1.940,000 cubic metres of a gas hereinafter referred to as Synthesis Gas III of the following composition: -CO = 28.0%, $H_1 = 56.0\%$, $CH_2 = 0.5\%$ and $CO_2 + N_2 = 0.5\%$ 15.5%.

By subjecting the Synthesis Gas III 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 II². This residual 120 gas, which is hereinafter referred to as Residual Gas III, 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 em- 125 ployed 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 " 130

 $p_{ijkl}(\hat{\phi})$ waste. 1,171.3 7.43 11.7

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 5 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

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 heat-15 ing a coke oven gas with steam at a temperature of 1200 to 1500° C. without a satalyst, 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 25 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 30 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 35 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 40

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 45 100 cubic metres of gas.

4. Λ process for the production of a gas mixture containing carbon monoxide and hydrogen suitable for use in the Fischer-Tropsch synthesis substantially as de- 50 scribed with reference to the Examples

given. 5. Gas mixtures containing carbon monexide and hydrogen suitable for use in the Fischer-Tropsch process when pro- 55 duced by the process claimed in any one of the preceding Claims.

Dated this 12th day of May 1944. ELKINGTON & FIFE, Consulting Chemists and Chartered Patent Agents, 20 to 23. Holborn, London, E.C.I, Agents for the Applicant.

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