

PATENT SPECIFICATION



Application Date: July 5, 1939.

No. 19624 39.

575,378

Complete Specification Left: Aug. 3, 1940.

Complete Specification Accepted: Feb. 15, 1946.

3634

PROVISIONAL SPECIFICATION

A Process for the Synthetic Production of Hydrocarbon Oils

We, MICHAEL STEINSCHLAEGER, of no nationality, and Overseas Finance & Commerce (London) Limited, a British Company, both of Market Buildings, 29, 5 Mincing Lane, London, E.C.3, do hereby declare the nature of this invention to be as follows:—

This invention relates to the manufacture of hydrogarbon oils from coal

ture of hydrocarbon oils from coal. In the processes which are at present employed for the manufacture of hydro-carbon oils from coal such as the Fischer Tropsch or other synthetic process it has been found to be desirable to produce a 15 product having a high clefine content. This is of importance because in the case of the lower boiling products which are used as fuels in internal combustion engines, a high olefine content results in a 20 high octane number of the furl whilst in the products of higher boiling point the presence of a high content of olefines euables them to be used for the production of a good yield of satisfactory lubricating oils. Hitherto however, the manufacture of a product containing a high content of olefines from coal has required a higher consumption of coal than in the manufacture of products not containing 30 such a high content of oleflues. Thus for example when employing a gas containing equal volumes of hydrogen and carbon monoxide a product can be produced containing about 55% of ofefines but this pro-35 cess necessitates a high consumption of coal. If on the other hand the consumption of coal is reduced by using a gas containing two volumes of hydrogen per volume of carbon monoxide according to 40 the Fischer Tropsch process a low boiling product is obtained which only contains about 30% of elefines and a higher boiling product in the lubricating oil range which contains an even smaller proportion of 45 olefines.

The object of the present revention is to overcome this drawback and to manufacture a product containing a high content of oleffings with a low consumption of coal.

According to the process of the present invention for the manufacture of hydrocarbon oils containing a high content of olefines, water gas is heated in the pres-

[Price 2]-]

ence of a cobalt, nickel or iron catalyst preferably at a temperature of between 55 160 and 250° C. and the residual gas, after carbon dioxide has been removed therefrom, is mixed with a gas having a high hydrogen content such as coke oven gas which has been reacted at an elevated 60 temperature with steam to increase the proportion of hydrogen and/or water gas which has been treated at an elevated temperature with steam preferably in the presence of a cobalt catalyst at 400—100° 65 C. to increase the proportion of hydrogen and preferably also with a gas rich in hydrogen and methane obtained by passing a gas rich in hydrogen over the residue deposited on a nickel, 70 cobalt or iron catalyst in a previous operation. The gas mixture thus obtained is then heated in the presence of a cobalt, nickel or iron catalyst preferably at a temperature between 160 and 75 250° C.

The cobalt or nickel catalyst employed may if desired be activated with an activator such as thoria and the iron catalyst may be activated with an activator such as 80 copper and the catalysts may be mixed with a carrier such as kieselguhr, magnesia or silica.

The following examples illustrate how the process of the invention may be 85 carried into effect:—

1. A coal having an ash content of about 7%, a sulphur content of about 1.3% and containing about 23% of volatile constituents was coked and yielded 90 75% of coke calculated as dry coke on dry coal, the gas yield being 355 cubic metres per ton of dry coal and having a calorific value of about 4670 calories per cubic metre. The gas after treatment for the 95 removal of organic and inorganic sulphur compounds had the following composition:—

 $\begin{array}{cccc} CO = 6\% \; ; & H_2 = 56.0\% \; ; & CH_1 = 26\% \; ; \\ C_1H_{10} = 2.0\% \; ; & CO_2 + N_3 = 10.0\% \; . \end{array}$

Part of the coke obtained from the coal was subjected to the water gas reduction and it was found that 0.55 kgms, of dry coke yielded 1 cubic metre of blue water gas which after treatment for the removal 105 of organic and inorganic sulphur com-

pounds had the following composition:-00=40.7%; $H_z=51.6\%$ $^{\circ}H_z=0.3\%$; $CO_2+N_2=8.0\%$.

1,000,000 cubic metres of blue water gas 5 free from sulphur and of the composition described above were passed over a cobalt cutalyst activated with thoria at a temperature of between 160° C. and 250° C. This produced 104 tons of products rich in 10 olefines and 400,000 cubic metres of residual gas of the following composi-

 $\begin{array}{c} \text{CO=52\%}: & \text{H}_{\text{a}}=19\%; \\ \text{CO}_{\text{a}}=12.5\%: & \text{and} & \text{N}_{\text{a}}=7.5\%. \end{array}$ CH, - 9%;

The carbon dioxide was washed out of this gas and 360,000 cubic metres of gas were obtained having the following composition :-

CO = 58%; $H_2 = 21\%$; $CH_1 = 9\%$; $CO_2 = 2.5\%$ and $N_2 = 8.5\%$. This gas was then mixed with 640,000 cubic metres of a gas obtained by heating coke oven gas of the composition described above which had been freed from organic 25 and inorganic sulphur compounds with steam at a temperature of 800 to 900° C. in the presence of a nickel-molybdenum sulphide entalyst and 80,000 cubic metres of a gas consisting of 86% of hydrogen, 30 12% of methane and 2% of earbon dioxide and nitrogen and obtained by treating the waxy material deposited on the cobalt cutalyst mentioned above by passing thereover a gas containing 98% of 35 hydrogen and obtained from the blue water gas in known manner. 1.080.000 cubic metres of synthesis gas of the following composition were thereby obtained:-

CO = 29.2%; $H_2 = 58.4\%$; $CH_1 = 4.6\%$;

 $CO_0 + N_2 = 8.0\%$.

This gas was passed over a cobalt catalyst activated with thoria and yielded 140 grams of liquid products per cubic metre of synthesis gas. The process described in this example requires a consumption of 2.5 tons of coke +1.2 cubic metres of coke oven gas per ton of primary product, the olefine content of the primary product ob-50 tained in this manner was about 27% more than when using a synthesis gas in which the proportion of CO to H₂ is as 1:2. If the admixture of coke oven gas treated with steam is reduced it is pos-55 siblo to raise the olefine content still further.

2. If no coke oven gas is obtainable the process may be economically carried out in the following manner, 1,000,000 cubic 60 metres of blue water gas of the composi-tion described above were passed over a cobalt entalyst activated with thoria at a temperature of between 160° C and 250° C., and 104 tons of products rich in ole-65 fines were produced as well as 400,000

cubic metres of residual gas. After washing out the carbon dioxide 360,000 cubic metres of gas of the following composition remained:-

CO = 58%; $H_2 = 21\%$; $CH_4 = 10\%$; 70

 $CO_{2} + N_{2} = 11.0\%$.

This residual gas which is substantially free from earbon dioxide is mixed with 360,000 cubic metres of a gas obtained by heating blue water gas of the composition 75 described above with steam at a temperature of from 400 to 500° C, in the presence of a cohalt catalyst and substantially removing the COs formed. The gas thus obtained from the blue water gas has the 80 following composition:— C0=8.1%; $H_2=92\%$; $CH_1=0.3\%$; $CO_2+N_2=4.5\%$.

The residual gas was also mixed with 40,000 cabic metres of a gas having the 85

composition:

 $H_2=86\%$; $CH_4=12\%$; $CO_2+X_2=2\%$ and obtained by treating the waxy material deposited on the cobalt catalyst mentioned above by passing thereover a gas 90 containing 98% of hydrogen and obtained from the blue water gas in known manner. A synthetic gas of the following composition was obtained:

CO=29%; $H_{z}=58\%$; $CH_{z}=4.5\%$; 95

 $CO_2 + N_2 = 9.5\%$.

This process results in a consumption of 3.75 tons of coke per ton of primary product. The olefine content of the products of the two stages taken together is about 100 33% higher than in products obtained from a synthesis gas in which the proportion of CO to H₂ is as 1:2.

3. In order to obtain a product with

about 50% more clefines (than from a syn. 105 thesis gas in which the proportion of CO to H₂ is as 1 to 2) 360,000 cubic metres of residual gas, free from CO, and otherwise of the composition mentioned in Example 1, was mixed with 380,000 cubic metres 110 of a gas prepared from coke oven gas by treatment with steam as described in Example I and 40,000 cubic metres of gas originating from the waxy material deposited on the catalyst as described in 115 Example 2 and a synthesis gas was obtained containing CO=84.0% and $H_2 = 51.5\%$. This synthesis gas was treated as described in the preceding Ex-This process involved a con- 120 sumption of about 3.1 tons of coke and 1.05 cubic metres of coke oven gas per ton of primary products containing a high

olefine content. Dated this 5th day of July, 1939. ELKINGTON & FIFE, Consulting Chemists and Chartered Patent Agents. 20 to 28, Holborn, London, E.C.1.

Agents for the Applicants,

COMPLETE SPECIFICATION

A Process for the Synthetic Production of Hydrocarbon Oils

We, MICHAEL STEINSCHLAEGER, of no nationality, formerly of Russian Nationality, of 50, Portsea Hall, Counaught Square, London, W.2, formerly of Market 5 Buildings, 29, Mineing Lane, London, E.C.3, and Overseas Finance & Cou-MERCE (LONDON) LAMITED, a British Company, of Market Buildings, 29, Mineing Laue, London, E.C.3, do hereby declare 10 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 synthetic

15 production of hydrocarbon oils from coal. In the processes which are at present employed for the synthetic production of hydrocarbon oils from coal such as the Fischer-Tropsch or like synthetic process it has been found to be desirable to produce a product having a high elefine con-tent. This is of importance because in the case of the lower boiling products. which are used as fuels in internal com-25 bustion engines, a high olefine content results in a high octane number of the fuel

whilst in the products of higher hoiling point the presence of a high content of olefines enables them to be used for the 30 production of a good yield of satisfactory lubricating oils. Hitherto, however, the manufacture of a product containing a high content of olefines from coal has required a higher consumption of coal than 35 in the manufacture of products not con-

taining such a high content of olefines. Thus for example when employing a gas containing equal volumes of hydrogen and carbon monoxide a product can be pro-40 duced containing about 55% of olefines but this process necessitates a high con-sumption of coal. If on the other hand the consumption of coal is reduced by

using a gas containing two volumes of 45 hydrogen per volume of carbon monoxide according to the Fischer-Tropsch process a low boiling product is obtained which only contains about 30% of olefines and a higher boiling product in the lubricating

50 oil range which contains an even smaller proportion of elefines.

The object of the present invention is to overcome this drawback and to manufacture a product containing a high con-55 tent of olefines with a low consumption of

According to the process of the present invention for the manufacture of hydrocarbon cils containing a high content of 60 olefines, water gas, blue water gas or water gas obtained by the complete gasification

of coal or mixtures thereof is heated in the presence of a cobalt, nickel or iron catalyst preferably at a temperature of he-tween 160 and 250° C. and the residual 65 gas, after carbon dioxide has been removed therefrom is mixed with a gas having a high hydrogen content such as coke oven gas which has been reacted at an elevated temperature with steam to in- 70 erease the proportion of hydrogen and/or water gas which has been treated at an elevated temperature with steam in the presence of a cobalt, nickel or iron catalyst at 400—500° C to increase the proportion 75 of hydrogen preferably after removal of carbon dioxide and preferably also with a gas rich in hydrogen and methane obtained by passing a gas rich in hydrogen over the residue deposited on a nickel, 80 cobalt, or iron catalyst in a previous opera-The gas mixture thus obtained is then heated in the presence of a cobalt, nickel or iron catalyst preferably at a temperature between 160 and 250° C.

The cobalt iron or nickel catalyst employed may if desired be activated with an activator such as thoria and the iron catalyst may be activated with an activator such as copper and the catalysts may 90 be mixed with a carrier such as kieselguhr, magnesia or silica.

The following examples illustrate how the process of the invention may be carried into effect :-

1. A coal having an ash content of about 7%, a sulphur content of about 1.3% and containing about 28% of vota-tile constituents was coked and yielded 75% of coke calculated as dry coke on dry 100 coal, the gas yield being 355 cubic metres per ton of dry coal and having a calorific value of about 4670 calories per cubic metre. The gas after treatment for the removal of organic and inorganic sulphur 105 compounds had the following composition:

 $C_{3}H_{44} = 2.0\%$; $H_{2} = 56.0\%$; $CH_{4} = 26.0\%$; $C_{3}H_{44} = 26.0\%$; $C_{3}H_{4} = 10.0\%$.

Part of the coke obtained from the coal 110 was subjected to the water gas reduction and it was found that 0.55 kgms. of dry coke yielded I cubic metre of blue water gas which after treatment for the removal of organic and inorganic sulphur com- 115

pounds had the following composition:— C0=40.7%; $H_2=51.0\%$ $CH_1=0.3\%$; $CO_2+N_2=8.0\%$.

1,000,000 cubic metres of blue water gas free from sulphur and of the composition 130 described above were passed over a cobalt catalyst activated with thoria at a tem-

perature of between 160° C, and 250° C. This produced 104 tons of products rich in olefines and 400,000 cubic metres of residual gas of the following composi-

CO = 52.0% $H_a19.0\%$; $CH_4 = 9.0\%$; $CO_2 = 12.5\%$ and $N_2 = 7.5\%$.

The carbon dioxide was washed out of this gas and 360,000 cubic metres of gas 10 were obtained having the following composition:

CO=58.0%; H₂=21.0%; CH₄=9.0%; CO₂ = 2.5% and N₂ = 8.5%. This gas was then mixed with 640,000 15 cubic metres of a gas obtained by heating coke oven was of the composition described above which had been freed from organic and inorganic sulphur compounds with steam at a temperature of 800 to 900° C. 20 in the presence of a nickel-molybdenum sulphide catalyst and 80,000 cubic metres of a gas consisting of 86% of hydrogen, 12% of methane and 2% of carbon dioxide and nitrogen and obtained by treat-25 ing the waxy material deposited on the cobalt catalyst mentioned above by passing thereover a gas containing 98% of hydrogen and obtained from the blue water gas in known manner. 1,080,000 water gas in known manner. 30 embic metres of synthesis gus of the fol-low composition were thereby obtained:

CO = 29.2%; $H_2 = 58.4\%$; $CH_1 = 4.6\%$;

 $CO_2 + N_2 = 8.0\%$.

This gas was passed over a cobalt cata-35 lyst activated with thoria and yielded 140 grams of liquid products per cubic metre of synthesis gas. The process described in this example requires a consumption of 2.5 tons of coke +1.2 cubic metres of coke 40 oven gas per ton of primary product, the olefine content of the primary product obtained in this manner was about 27% more than when using a synthesis gas in which the proportion of CO to H2 is as 45 1:2. If the admixture of coke oven gus treated with steam is reduced it is possible to mise the olefine content still further.

2. If no coke oven gas is obtainable the process may be economically carried out in the following manner, 1,000,000 cubic metres of blue water gas of the composition described above were passed over a cobalt catalyst activated with thoria at a 55 temperature of between 160° C and 250° C., and 104 tons of products rich in olefines were produced as well as 400,000 cubic metres of residual gas. After washing out the carbon diccide 360,000 cubic

60 metres of gas of the following composition remained:

60 = 58.0% $H_2 = 21.0\%$ $CH_1 = 10.0\%$; $CO_2 + N_2 = 11.0\%$.

This residual gas which is substantially 65 free from carbon dioxide is mixed with

360,000 cubic metres of a gas obtained by heating blue water gas of the composition described above with steam at a tempera-ture of from 400 to 500° C. in the presence of a cobalt catalyst and substantially 70 removing the CO. formed. The gas thus obtained from the blue water gas has the following composition:— C0 = 3.1%; $H_2 = 92.0\%$; $CH_4 = 0.3\%$; $CO_2 + N_2 = 4.5\%$.

The residual gas was also mixed with 40,000 cubic metres of a gas having the composition:

 $CH_4 = 12.0\%$; $CO_2 + N_2 =$ $H_2 = 86.0\%$; $CH_1 = 12.0\%$; $CO_2 + N_2 = 2.0\%$ and obtained by treating the waxy 80 material deposited on the cobalt catalyst mentioned above by passing thereover a gas containing 98% of hydrogen and obtained from the blue water gas in known manner. A synthetic gas of the following 85

olefine content.

composition was obtained:— CO = 29.0%; $H_2 = 58.0\% \cdot CH_4 = 4.5\%$; $CO_2 + N_2 = 9.5\%$.
This process results in a consumption of 3.75 tons of coke per ton of primary pro- 90 duct. The olefine content of the products of the two stages taken together is about 33% higher than in products obtained from a synthesis gas in which the proportion of CO to H₂ is as 1:2.

3. In order to obtain a product with about 50% more olefines (than from a synthesis gas in which the proportion of CO to H₂ is as 1 to 2) 360,000 cubic metres of residual gas, free from CO: and otherwise 100 of the composition mentioned in Example 1, was mixed with 380,000 cubic metres of a gas prepared from coke oven gas by treatment with steam as described in Example 1 and 40,000 cubic metres of gas 105 originating from the waxy material de-posited on the catalyst as described in Example 2 and a synthetic gas was obtained containing CO=34.0% and H₂=51.5%. This synthesis gas was 110 treated as described in the preceding Examples. This process involved a consumption of about 8.1 tons of coke and 1.05 cubic metres of roke oven gas per ton

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we 120 claim is:-

1. A process for the synthetic production of hydrocarbon oils containing a high content of olefines which comprises heating water gas, blue water gas or water gas 125 obtained by the complete gasification of coal or a mixture thereof in the presence of a cobalt, nickel or iron catalyst preferably at a temperature of between 160 and 250° C., removing carbon dioxide there-130

of primary products containing a high 115

from and mixing the residual gas with a gas having a high hydrogen content such as coke oven gas which has been reacted at an elevated temperature with steam to increase the proportion of hydrogen and/or water gas which has been treated at an elevated temperature with steam in the presence of a cobalt, nickel or iron catalyst at 400 to 500° C, to increase the proportion of hydrogen preferably after removal of curbon diexide and preferably also with a gas rich in hydrogen and methane obtained by passing a gas rich in hydrogen over the residue deposited on 15 a nickel, cobalt or iron catalyst in a previous operation, and thereafter heating the gas mixture thus obtained in the presence of cobalt, nickel or iron catalyst preferably at a temperature between 160 and 20 250° C.

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 for the synthetic production of hydrocarbon oils containing a high content of olefines substantially as described with reference to the examples given.

4. Hydrocarbon oils containing a high 30 content of oleffines when manufactured by the process claimed in any one of the preceding claims.

Dated this 3rd day of August, 1940.
ELKINGTON & FIFE,
Consulting Chemists and Chartered
Patent Agents,
20 to 23, Helborn, London, E.C.1,
Agents for the Applicants.

Printed for H.M. Stationery Office by Multi Machine Plates, Ltd.,—1951. Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,

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