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PATENT SPECIFICATION

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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, 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 hydrocarbon oils from coal.

In the processes which are at present employed for the manufacture of hydrocarbon oils from coal such as the Fischer Tropsch or other synthetic process it has been found to be desirable to produce a product having a high olefine 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 high octane number of the fuel whilst in the products of higher boiling point the presence of a high content of olefines enables 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 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 produced containing about 55% of olefines but this process 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 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 oil range which contains an even smaller proportion of olefines.

The object of the present invention is to overcome this drawback and to manufacture a product containing a high content of olefines 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 presence of a cobalt, nickel or iron catalyst preferably at a temperature of between 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 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—500° 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, 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 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 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 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 volatile constituents was coked and yielded 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 removal of organic and inorganic sulphur compounds had the following composition:—

$CO = 6\%$; $H_2 = 56.0\%$; $CH_4 = 26\%$;
$C_nH_m = 2.0\%$; $CO_2 + N_2 = 10.0\%$.

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 of organic and inorganic sulphur com-

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pounds had the following composition:—
$CO = 40.7\%$; $H_2 = 51.0\%$ $CH_4 = 0.3\%$; $CO_2 + N_2 = 8.0\%$.

1,000,000 cubic metres of blue water gas free from sulphur and of the composition described above were passed over a cobalt catalyst activated with thoria at a temperature 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 composition:—
$CO = 52\%$; $H_2 = 19\%$; $CH_4 = 9\%$; $CO_2 = 12.5\%$ and $N_2 = 7.5\%$.

The carbon dioxide was washed out of this gas and 360,000 cubic metres of gas were obtained having the following composition:—
$CO = 58\%$; $H_2 = 21\%$; $CH_4 = 9\%$; $CO_2 = 2.5\%$ 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 and inorganic sulphur compounds with steam at a temperature of 800 to 900° C. 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 treating 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 cubic metres of synthesis gas of the following composition were thereby obtained:—
$CO = 29.2\%$; $H_2 = 58.4\%$; $CH_4 = 4.6\%$; $CO_2 + N_2 = 8.0\%$.

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 obtained in this manner was about 27% more than when using a synthesis gas in which the proportion of CO to H_2 is as 1:2. If the admixture of coke oven gas treated with steam is reduced it is possible 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 metres of blue water gas of the composition described above were passed over a cobalt catalyst activated with thoria at a 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 dioxide 360,000 cubic metres of gas of the following composition remained:—
$CO = 58\%$; $H_2 = 21\%$; $CH_4 = 10\%$; $CO_2 + N_2 = 11.0\%$.

This residual gas which is substantially 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 temperature of from 400 to 500° C. in the presence of a cobalt catalyst and substantially removing the CO_2 formed. The gas thus obtained from the blue water gas has the following composition:—
$CO = 3.1\%$; $H_2 = 92\%$; $CH_4 = 0.3\%$; $CO_2 + N_2 = 4.5\%$.

The residual gas was also mixed with 40,000 cubic metres of a gas having the composition:—
$H_2 = 86\%$; $CH_4 = 12\%$; $CO_2 + N_2 = 2\%$
and obtained by treating 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. A synthetic gas of the following composition was obtained:—
$CO = 29\%$; $H_2 = 58\%$; $CH_4 = 4.5\%$; $CO_2 + N_2 = 9.5\%$.

This process results in a consumption of 3.75 tons of coke per ton of primary product. 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 H_2 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 H_2 is as 1 to 2) 360,000 cubic metres of residual gas, free from CO_2 and otherwise 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 originating from the waxy material deposited on the catalyst as described in Example 2 and a synthesis gas was obtained containing $CO = 34.0\%$ and $H_2 = 51.5\%$. This synthesis gas was treated as described in the preceding Examples. This process involved a consumption 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 23, 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, Connaught Square, London, W.2, formerly of Market Buildings, 29, Mincing Lane, London, E.C.3, and Overseas Finance & Commerce (London) Limited, a British Company, of Market Buildings, 29, Mincing Lane, London, E.C.3, 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 synthetic 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 olefine 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 high octane number of the fuel whilst in the products of higher boiling point the presence of a high content of olefines enables 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 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 produced containing about 55% of olefines but this process 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 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 oil range which contains an even smaller proportion of olefines.

The object of the present invention is to overcome this drawback and to manufacture a product containing a high content of olefines 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, 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 between 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 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—500° C to increase the proportion 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, 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 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 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 volatile constituents was coked and yielded 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 removal of organic and inorganic sulphur compounds had the following composition:—

$CO = 6\%$; $H_2 = 56.0\%$; $CH_4 = 26.0\%$; $C_nH_m = 2.0\%$; $CO_2 + N_2 = 10.0\%$.

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 of organic and inorganic sulphur compounds had the following composition:—

$CO = 40.7\%$; $H_2 = 51.0\%$ $CH_4 = 0.3\%$; $CO_2 + N_2 = 8.0\%$.

1,000,000 cubic metres of blue water gas free from sulphur and of the composition described above were passed over a cobalt catalyst activated with thoria at a temperature 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 tht following composition:—

$CO=52.0\%$ $H_2$19.0%; $CH_4=9.0\%$; $CO_2=12.5\%$ and $N_2=7.5\%$.

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

$CO=58.0\%$; $H_2=21.0\%$; $CH_4=9.0\%$; $CO_2=2.5\%$ 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 and inorganic sulphur compounds with steam at a temperature of 800 to 900° C. 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 treating 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 cubic metres of synthesis gas of the follow composition were thereby obtained:—

$CO=29.2\%$; $H_2=58.4\%$; $CH_4=4.6\%$; $CO_2+N_2=8.0\%$.

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 obtained in this manner was about 27% more than when using a synthesis gas in which the proportion of CO to H_2 is as 1:2. If the admixture of coke oven gas treated with steam is reduced it is possible 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 metres of blue water gas of the composition described above were passed over a cobalt catalyst activated with thoria at a 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 dioxide 360,000 cubic metres of gas of the following composition remained:—

$CO=58.0\%$ $H_2=21.0\%$ $CH_4=10.0\%$; $CO_2+N_2=11.0\%$.

This residual gas which is substantially 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 temperature of from 400 to 500° C. in the presence of a cobalt catalyst and substantially removing the CO_2 formed. The gas thus obtained from the blue water gas has the following composition:—

$CO=3.1\%$; $H_2=92.0\%$; $CH_4=0.3\%$; $CO_2+N_2=4.5\%$.

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

$H_2=86.0\%$; $CH_4=12.0\%$; $CO_2+N_2=2.0\%$ and obtained by treating 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. A synthetic gas of the following composition was obtained:—

$CO=29.0\%$; $H_2=58.0\%$ · $CH_4=4.5\%$; $CO_2+N_2=9.5\%$.

This process results in a consumption of 3.75 tons of coke per ton of primary product. 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 H_2 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 H_2 is as 1 to 2) 360,000 cubic metres of residual gas, free from CO_2 and otherwise 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 originating from the waxy material deposited on the catalyst as described in Example 2 and a synthetic gas was obtained containing $CO=34.0\%$ and $H_2=51.5\%$. This synthesis gas was treated as described in the preceding Examples. This process involved a consumption 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.

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 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 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-

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 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, 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 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 content of olefines 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, Holborn, London, E.C.1,
Agents for the Applicants.

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