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(54) PROCESS FOR THE SYNTHETIC MANUFACTURE OF HYDROCARBON OILS

(54) PROCÉDE POUR LA FABRICATION SYNTHÉTIQUE D'HUILES D'HYDROCARBURES

Publication number(72) Inventors (Country): MICHAEL STEINSCHLAEGER (Not Available)(73) Owners (Country): MICHAEL STEINSCHLAEGER(71) Applicants (Country):(74) Agents:(45) Issued on: Dec. 28, 1954(22) Filed on:(43) Laid open on:(52) Canadian Class (CPC): 260/678.7(51) International Class (IPC): N/APatent Cooperation Treaty (PCT): No(30) Application priority data: NoneAvailability of Patent: N/ALanguage of Filing: Unknown

ABSTRACT:

CLAIMS: Show all claims

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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This invention relates to a process for the manufacture of hydrocarbon oils and is particularly concerned with the production of products rich in olefines.

Primary products obtained by the Fischer-Tropsch or like processes from gases containing CO and H₂ in ratios varying between 1 : 1.5 and 2 : 1 by volume are rich in valuable olefines. On the other hand the yield of primary products rich in olefines per cubic metre of gas used in comparison with the yields obtained in the synthesis processes using gases having a ratio of CO : H₂ = 1 : 2 by volume is low. Consequently a high consumption of fuels, high cost of production and high capital expenditure for the plant are involved.

An object of the present invention is to overcome these drawbacks.

The present invention provides a process for the production of hydrocarbon oils water gas (which expression as used herein includes blue water gas or water gas obtained by the complete gasification of coal or a gas obtained by decomposing a hydrocarbon-containing gas with steam and/or carbon dioxide) (Synthesis Gas I) freed from sulphur and other undesirable constituents and containing CO and H₂ in a ratio varying between 1 : 1.5 and 2 : 1 by volume is heated in the presence of a cobalt, nickel or iron catalyst at a temperature of between 150 and 250°C. at atmospheric or increased pressure to produce primary products rich in olefines and a Residual Gas I, which Residual Gas I is then mixed with gaseous or liquid hydrocarbons (which expression as used herein includes gases, vapours or liquids containing the same) and treated (according to the nature of the Synthesis Gas II required) with carbon dioxide and/or steam with or

without partial or complete removal of carbon dioxide in the presence of a catalyst or without a catalyst at a temperature of between 800 and 1500° C. to produce a Synthesis Gas II which is then heated in the presence of a cobalt, nickel or iron catalyst at a temperature of between 150 and 250° C. at atmospheric or increased pressure to produce further primary products rich in olefines and a Residual Gas II.

Coke oven gas or other gaseous or liquid hydrocarbons used for the production of Synthesis Gas II are freed from sulphur and other undesirable constituents before being mixed with the Residual Gas I. Instead of mixing the above mentioned gases with the Residual Gas I water gas or converted water gas (i.e. water gas treated with steam at a temperature of between 400 and 500° C.) (with or without partly or completely washing out carbon dioxide) or a mixture thereof may be mixed with the Residual Gas I which has in this case been treated with carbon dioxide and/or steam.

The present invention also includes a process for the production of hydrocarbon oils which comprises heating water gas (Synthesis Gas I) freed from sulphur and other undesirable impurities and containing CO and H₂ in a ratio varying between 1 : 1.5 and 2 : 1 by volume in the presence of a cobalt, nickel or iron catalyst at a temperature of between 150 and 250° C. at atmospheric or increased pressure to produce primary products rich in olefines and a Residual Gas I, dividing the Residual Gas I into two parts, mixing the first part with gaseous or liquid hydrocarbons and treating the mixture with carbon dioxide and/or steam at a

temperature of between 500 and 1500°C. to produce a Synthesis Gas II', treating the second part with carbon dioxide and/or steam at a temperature of between 500 and 1500°C., mixing the product with water gas and/or water gas which has been treated with steam at a temperature of between 400 and 500°C. to produce a Synthesis Gas II'', mixing the Synthesis Gas II' with the Synthesis Gas II'' to produce a Synthesis Gas II, and heating the Synthesis Gas II in the presence of a cobalt, nickel or iron catalyst at a temperature of between 150 and 250°C. at atmospheric or increased pressure to produce further primary products rich in olefines and a Residual Gas II.

The amount of the gases other than Residual Gas used is dependent on the composition of the Synthesis Gases required. The Residual Gas II obtained may be treated in the same or a similar way as the Residual Gas I, thus obtaining Synthesis Gas III. This procedure may be repeated until the amount of the inert gas in the last obtained Residual Gas is so high that the gas is practically useless for production of synthesis gases or primary products. The last residual gas and fuels of low calorific value are used for heating purposes.

The composition of the Synthesis Gases I, II, etc., can be varied according to the primary products which are required and according to the catalysts used.

The following example in which the percentages are by volume illustrates how the process of the invention may be carried into effect:

The composition of the Synthesis Gas I was CO = 41.0%,
H₂ = 51.0%, CH₄ = 1.0%, N₂ = 2.0%, CO₂ = 5.0%.

1,000,000 Cubic metres of the Synthesis Gas I was heated in the presence of a cobalt catalyst at 180° C. A contraction of 40% by volume took place and a yield of 51 gms. of primary products rich in olefines was obtained per cubic metre of Synthesis Gas I employed. The Residual Gas I amounted to 600,000 cubic metres. The composition of the Residual Gas I was CO = 46.0%, H₂ = 32.0%, CH₄ = 10.4%, N₂ = 3.3%, CO₂ = 5.5%.

The 600,000 cubic metres of Residual Gas I were mixed with 50,000 cubic metres of coke oven gas of the following composition: CO = 7.0%, H₂ = 54.0%, CH₄ = 30.0%, C_nH_m = 3.0%, CO₂ = 3.0%, N₂ = 3.0%. The composition of the mixture was CO = 42.9%, H₂ = 33.7%, CH₄ = 12.0%, C_nH_m = 0.3%, N₂ = 3.3%, CO₂ = 7.9%.

After addition of 130,000 kgs. of steam the mixture was heated at 1000° C. in the presence of a nickel catalyst and the treated gas amounting to 660,000 cubic metres (Synthesis Gas II) had the following composition: CO = 40.4%, H₂ = 50.6%, CH₄ = 0.7%, N₂ = 2.5%, CO₂ = 5.8%. After heating the Synthesis Gas II in the presence of a cobalt catalyst at 180° C. 59 metric tons of primary products rich in olefines and 530,000 cubic metres of Residual Gas II of the following composition were obtained: CO = 42.5%, H₂ = 35.0%, CH₄ = 7.0%, N₂ = 4.1%, CO₂ = 11.4%. After removal of the Carbon dioxide the remaining 470,000 cubic metres of carbon dioxide-free Residual Gas were mixed with 50,000 cubic metres of coke oven gas of the aforesaid composition and the mixture was treated with steam at 1000° C. in the presence of a nickel catalyst thus obtaining a Synthesis Gas III amounting to 660,000 cubic metres of the following composition: CO = 42.0%,

$H_2 = 53.3\%$, $CH_4 = 0.6\%$, $N_2 = 3.5\%$, $CO_2 = 0.4\%$. This gas was treated in the same way as Synthesis Gas I and II and a Residual Gas III was obtained. The process was continued in a similar manner until a Residual Gas V was produced.

This last Residual Gas V amounting to 265,000 cubic metres had the following composition: $CO = 41.5\%$, $H_2 = 40.0\%$, $CH_4 = 8.3\%$, $N_2 = 9.5\%$, $CO_2 = 2.7\%$.

The total production was 225 metric tons of primary products rich in olefines.

The water gas consumption was 1,000,000 cubic metres. The coke oven gas consumption was 175,000 cubic metres. The heat necessary for the treatment of the mixture amounted after deducting the potential heat of the Residual Gas V to 500,000,000 K. Cal., or the consumption of:

- (a) Water gas per kg. of primary products rich in olefines was 4.45 cubic metres
- (b) Coke oven gas per kg. of primary products rich in olefines was 0.78 cubic metres
- (c) Heat per kg. of primary products rich in olefines was 2,200 K. Cal.

in the form of producer gas, blast furnace gas or other gases of low calorific value.

If it is desirable to use more coke oven gas so as to use coke and coke oven gas in the same proportion as the coking coal used in the coke oven plant is delivering, the initial Synthesis Gas I can be made partly from coke and partly by decomposing coke oven gas with carbon dioxide.

Using natural gas as a source for production of Synthesis Gases the following results can be achieved as seen from the Table:

Composition of the natural gas: $CH_4 = 90.0\%$, $C_2H_6 = 8.0\%$, $CO_2 + N_2 = 2.0\%$.

TABLE

Synthesis Gas No.	1	2	3	4
1. Production of Synthesis Gas from	Natural gas treated with CO ₂ in the presence of a catalyst at 1000°C.	Residual Gas I + natural gas with steam in the presence of a catalyst at 1000°C.	Residual Gas II + natural gas with steam in the presence of a catalyst at 1000°C.	Residual Gas III + natural gas with steam in the presence of a catalyst at 1000°C.
2. Synthesis Gas, cubic metres	1,000,000	810,000	670,000	510,000
3. Used Residual Gas, cubic metres	-	300,000	405,000	355,000
4. Used natural gas	200,000	50,000	45,000	50,000
5. Composition of Synthesis Gas CO + H ₂ %	46 + 51	45.5 + 51.5	44.8 + 51.8	45 + 51
6. Composition of Residual Gas CO + H ₂ %	-	56 + 32	56 + 32	54 + 32
7. Yields of primary products rich in olefines	92	75	62	47

Consumption of natural gas per kg. of primary products:

1. For Synthesis Gas production, 1.36 cubic metres.
2. For heating purposes, 0.64 cubic metres.

Total consumption per kg. of primary products rich in olefines:

2.0 cubic metres.

Having thus described my invention, I claim:

1. A process for the production of hydrocarbon oils which comprises heating water gas (Synthesis Gas I) freed from sulphur and other undesirable impurities and containing CO and H₂ in a ratio varying between 1 : 1.5 and 2 : 1 by volume in the presence of a cobalt, nickel or iron catalyst at a temperature of between 150° and 250° C. at atmospheric or increased pressure in a vessel to produce primary products rich in olefines and a Residual Gas I, mixing the Residual Gas I with gaseous or liquid hydrocarbons and treating the mixture with carbon dioxide or steam or a mixture of carbon dioxide and steam at a temperature of between 800° C. and 1500° C. to produce a Synthesis Gas II, and heating the Synthesis Gas II in a second and separate vessel in the presence of a cobalt, nickel or iron catalyst at a temperature of between 150° and 250° C. at atmospheric or increased pressure to produce further primary products rich in olefines and a Residual Gas II.

2. A process for the production of hydrocarbon oils which comprises heating water gas (Synthesis Gas I) freed from sulphur and other undesirable impurities and containing CO and H₂ in a ratio varying between 1 : 1.5 and 2 : 1 by volume in the presence of a cobalt, nickel or iron catalyst at a temperature of between 150° and 250° C. at atmospheric or increased pressure to produce primary products rich in olefines and a Residual Gas I, dividing the Residual Gas I into two parts, mixing the first part with gaseous or liquid hydrocarbons and treating the mixture with carbon dioxide or steam or a mixture of carbon dioxide and steam at a temperature of between 800° and 1500° C. to produce a Synthesis Gas II', treating the second part with carbon dioxide or steam or a

mixture of carbon dioxide and steam at a temperature of between 800° and 1500° C., mixing the product with water gas or water gas which has been treated with steam at a temperature of between 400° and 500° C. or a mixture of water gas and water gas which has been treated with steam at a temperature of between 400° and 500° C. to produce a Synthesis Gas II', mixing the Synthesis Gas II' with the Synthesis Gas II'' to produce a Synthesis Gas II, and heating the Synthesis Gas II in the presence of a cobalt, nickel or iron catalyst at a temperature of between 150° and 250° C. at atmospheric or increased pressure to produce further primary products rich in olefines and a Residual Gas II.

3. A process as claimed in either of the preceding claims 1 or 2 wherein the Residual Gas II is mixed with gaseous or liquid hydrocarbons and the mixture is treated with carbon dioxide or steam or a mixture of carbon dioxide and steam at a temperature of between 800° and 1500° C. to produce Synthesis Gas III which is thereafter heated in the presence of a cobalt, nickel or iron catalyst at a temperature of between 150° and 250° C. at atmospheric or increased pressure to produce further products rich in olefines and a Residual Gas III.

4. A process as claimed in either of the preceding claims 1 or 2 wherein the Residual Gas II is treated with carbon dioxide or steam or a mixture of carbon dioxide and steam at a temperature of between 800° and 1500° C., the product is mixed with water gas or water gas which has been treated with steam at a temperature of between 400° and 500° C. or a mixture of water gas and water gas which has been treated with steam at a temperature of between 400° and 500° C. to produce Synthesis Gas III which is thereafter heated in the presence of a

cobalt, nickel or iron catalyst at a temperature of between 150° and 250° C. at atmospheric or increased pressure to produce further primary products rich in olefines and a Residual Gas III.

5. A process as claimed in either of the preceding claims 1 or 2 wherein the Residual Gas II is divided into two parts, the first part is mixed with gaseous or liquid hydrocarbons and the mixture treated with carbon dioxide or steam or a mixture of carbon dioxide and steam at a temperature between 800° and 1500° C. to produce a Synthesis Gas III', and the second part is treated with carbon dioxide or steam or a mixture of carbon dioxide and steam at a temperature of between 800° and 1500° C. and the product mixed with water gas or water gas which has been treated with steam at a temperature of between 400° and 500° C. or a mixture of water gas and water gas which has been treated with steam at a temperature of between 400° and 500° C. to produce a Synthesis Gas III'', the Synthesis Gas III' is mixed with the Synthesis Gas III'' to produce a Synthesis Gas III which is thereafter heated in the presence of a cobalt, nickel or iron catalyst at a temperature of between 150° and 250° C. at atmospheric or increased pressure to produce further primary products rich in olefines and a Residual Gas III.

6. A process as claimed in claim 1 wherein the treatment with carbon dioxide or steam or a mixture of carbon dioxide and steam is effected in the presence of a catalyst.

7. A process as claimed in either of the preceding claims 1 or 2 wherein carbon dioxide is partly or completely removed from the mixture of Residual Gas I and gaseous or liquid hydrocarbons.

8. A process as claimed in claim 2 wherein carbon dioxide is partly or completely removed from the water gas or the water gas which has been treated with steam or the mixture of water gas and water gas which has been treated with steam before its addition to the Residual Gas I.