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(54) **Process for producing liquid hydrocarbons from a hydrocarbonaceous feed**

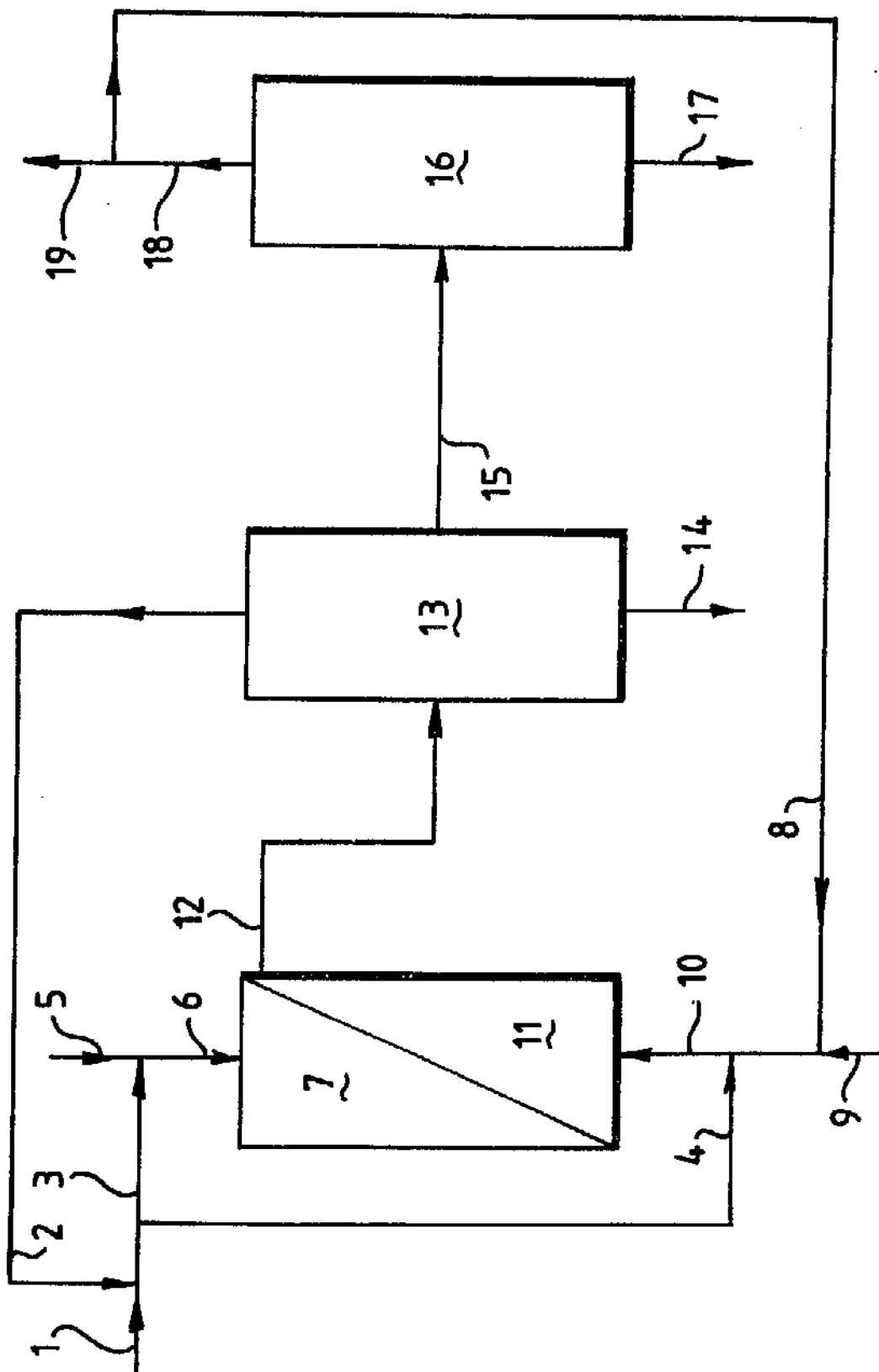
(57) Process for producing liquid hydrocarbons from a hydrocarbonaceous feed which comprises the following steps:

- (i) catalytically reforming at least part of the hydrocarbonaceous feed at elevated temperature and pressure with steam in at least one reforming zone;
- (ii) heating the reforming zone(s) by means of a carbon dioxide-containing heating gas comprising a product obtained by partial oxidation of reformer product obtained in step (i) or of a remaining part of the hydrocarbonaceous feed or of a mixture thereof with an oxygen-containing gas in an oxidation zone;
- (iii) separating carbon dioxide from heating gas obtained in step (ii);
- (iv) catalytically converting at least part of the reformer product obtained in step (i) and/or gas obtained after separating off carbon dioxide in step (iii) at elevated temperature and pressure into normally liquid hydrocarbons; and
- (v) combining at least part of the carbon dioxide obtained in step (iii) with hydrocarbonaceous feed for at least one of steps (i) and (ii).

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SPECIFICATION

Process for producing liquid hydrocarbons from a hydrocarbonaceous feed

5 The invention relates to a process for producing liquid hydrocarbons from a hydrocarbonaceous feed and to liquid hydrocarbons thus obtained.

10 It is known to produce liquid hydrocarbons by converting a hydrocarbonaceous feed (e.g. natural gas) into synthesis gas (which comprises hydrogen and carbon monoxide) and catalytically converting synthesis gas into liquid and gaseous hydrocarbons.

15 However, the preparation of synthesis gas requires a relatively large energy input and in many cases, in particular when partial oxidation is the preparation method applied, adjustment of the CO/H₂ ratio in the gas to be applied to the hydrocarbon synthesis step.

20 Moreover, substantial amounts of carbon-containing material are usually not converted into the desired normally liquid hydrocarbons.

25 It has now been found that liquid hydrocarbons can be produced with a very efficient use of energy and materials by means of an integrated process.

The invention therefore relates to a process for producing liquid hydrocarbons from a hydrocarbonaceous feed which comprises the

30 following steps:

(i) catalytically reforming at least part of the hydrocarbonaceous feed at elevated temperature and pressure with steam in at least one reforming zone;

35 (ii) heating the reforming zone(s) by means of a carbon dioxide-containing heating gas comprising a product obtained by partial oxidation of reformer product obtained in step (i) or of a remaining part of the hydrocarbonaceous feed or of a mixture thereof with an oxygen-containing gas in an oxidation zone;

40 (iii) separating carbon dioxide from heating gas obtained in step (ii);

(iv) catalytically converting at least part of the reformer product obtained in step (i) and/or gas obtained after separating off carbon dioxide in step (iii) at elevated temperature and pressure into normally liquid hydrocarbons; and

45 (v) combining at least part of the carbon dioxide obtained in step (iii) with hydrocarbonaceous feed for at least one of steps (i) and (ii).

A major advantage of the process according to the invention is that carbon dioxide which has been separated in step (iii) from heating gas obtained in step (ii) is recycled and combined with

50 hydrocarbonaceous feed in order to attain optimal use of carbon-containing streams.

Another major advantage of the present process is that the reforming zone(s) is (are) heated in step (ii) by means of a heating gas produced and further

80 applied in the process itself, thereby avoiding the use of extraneous heat sources and making the process more energy efficient than non-integrated processes.

Preferably, the total reformer product obtained in

85 step (i) (which comprises carbon monoxide and

hydrogen and, in addition, usually smaller amounts of carbon monoxide, steam and/or unconverted hydrocarbons) is subjected to partial oxidation in step (ii), most preferably together with the remaining part of the hydrocarbonaceous feed which has not been catalytically reformed in step (i).

70 In order to attain optimal use of the heat produced by the aforementioned partial oxidation of reformer product, the oxidation- and reforming zones are preferably integrated into one reactor, for instance the one as described in German patent application 3244252, wherein reformer product gases emanating from e.g. reformer tubes filled with catalyst particles, are mixed with an

75 oxygen-containing gas and, optionally, hydrocarbonaceous feed and/or recycle gases, and the resulting heating (combustion) gas is directed along the outside of said reformer tubes.

In step (i) of the process according to the invention

85 various reforming catalysts can be suitably applied, such as catalysts containing one or more metals from Group 8 of the Periodic Table of the Elements, preferably nickel, on a support (e.g. alumina, silica and/or combinations thereof). Step (i) is suitably carried out at a temperature from 500-1100 °C, preferably from 500-1000 °C, and a pressure from 3-100 bar, and preferably from 15-40 bar. The space velocity of gaseous hydrocarbonaceous feed and steam combined is suitably from 1000-8000, and

90 preferably from 4000-6000 1 (S.T.P)/1 catalyst/hour.

The percentage of hydrocarbonaceous feed which is converted in step (i) of the process according to the invention is suitably from 50-99% by weight and preferably from 80-95% by weight.

100 The catalytic reforming of step (i) may be carried out in a fixed-, moving- or fluidized bed of catalyst particles; fixed beds of catalyst particles placed inside a plurality of reformer tubes are preferably employed.

105 As oxygen-containing gas for use in step (ii) air can be employed. Preferably, however, an oxygen-containing gas with a higher oxygen-content than air is employed, in particular substantially pure oxygen i.e. oxygen gas which contains less than 0.5% by volume of contaminants such as nitrogen and argon; the presence of the latter inert gases is undesirable because it leads to a gradual build-up of such gases in the system.

Step (ii) of the process according to the present invention is preferably carried out non-catalytically at substantially the same pressure as step (i), in order to enable the afore-described integration of oxidation- and reforming zones. The temperature of the heating gas produced in step (ii) is, of course,

115 preferably somewhat higher than the temperature inside the reforming zone(s) which are to be heated; suitable heating gas temperatures range from 500-1500 °C, preferably from 700-1200 °C.

In particular when a relatively high percentage of hydrocarbonaceous feed has been converted in step (i), a remaining part of hydrocarbonaceous feed is preferably applied in step (ii) together with the total reformer product of step (i) and at least part of the product gas (e.g. containing unconverted feed gas and lower olefinic compounds) separated off from

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normally liquid hydrocarbons produced in step (iv).

Due to the usually higher temperature of the oxidation zone, compared with the reforming zone, the conversion of any remaining

5 hydrocarbonaceous feed will be even higher than attained in step (i), even if steam is introduced into the oxidation zone together with reformer product, with the oxygen containing gas or as a separate stream, to protect burners in said oxidation zone

10 from overheating.

Moreover, relatively cold hydrocarbonaceous feed and/or other feed streams can be applied for temperature regulation purposes in step (ii). The amount of additional hydrocarbonaceous feed

15 employed in step (ii) is preferably between 0 and 100% by volume, and most preferably between 10 and 80% by volume, of the amount of hydrocarbonaceous feed employed in step (i).

The hydrocarbonaceous feed for the process 20 according to the invention is usually gaseous and if liquid, should, of course, be different from the liquid hydrocarbons produced. Preferably it comprises methane e.g. in the form of natural gas. In case a feed with a relatively high sulphur-content (e.g. in the form of hydrogen sulphide and/or organic sulphur compounds) is employed, such a feed is preferably 25 at least partly disulphurized (before being catalytically reformed) e.g. in the presence of hydrogen with a catalyst comprising at least one metal (compound) from Group 6 and/or 8 of the Periodic Table of the Elements on a refractory carrier such as a nickel/molybdenum/alumina catalyst.

At least part, and preferably substantially all, of the carbon dioxide present in the heating gas with which 35 the reforming zone(s) have been heated in step (ii) is removed in step (iii) by means of e.g. liquid absorption (with e.g. organic amines), adsorption on molecular sieves or membranes. Steam is suitably removed simultaneously with carbon dioxide and may be re-used after reheating. Preferably all the carbon dioxide thus removed is combined with the total hydrocarbonaceous feed after the, optional, desulphurization step. Alternatively, different 40 amounts of carbon dioxide, varying from 0-100% by volume of carbon dioxide removed in step (iii), are combined with feed streams for step (i) and step (ii); furthermore, additional amounts of carbon dioxide from extraneous sources can be used.

In step (iv) of the process according to the present 50 invention a hydrogen- and carbon monoxide-containing gas (obtained in step (i) and/or (iii)) is converted in one or more stages at least partly into normally liquid hydrocarbons in the presence of a Fischer-Tropsch type of catalyst which preferably 55 comprises at least one metal (compound) from Group 4b, 6b and/or 8, such as zirconium, chromium, iron, cobalt, nickel and/or ruthenium, on a carrier.

In some cases a single-stage liquid hydrocarbon synthesis is preferred; as a result a product gas 60 comprising relatively large amounts of lower olefinic compounds (and unconverted feed gas), is thereby produced. In addition to normally liquid hydrocarbons such as gasoline (having a boiling range from about 40-150 °C) and/or middle distillate 65 fractions (having a boiling range from about 150-350

°C).

As mentioned hereinbefore, at least part of the product gas from step (iv) is preferably applied in step (ii) rather than in step (i) for which it is usually 70 less suited, in particular when the hydrocarbon synthesis is carried out in a single stage. A remaining part of product gas obtained in step (iv) is preferably expanded in a turbo-expander and/or combusted (e.g. in the combustion chamber of a gas turbine) to 75 provide power for compressing and/or separating from air the oxygen (-containing) gas applied in step (ii).

Step (iv) of the process according to the invention can also advantageously be carried out as a 80 two-stage liquid hydrocarbon synthesis in which at least part of the normally liquid hydrocarbons obtained in the first stage is catalytically hydrocracked in the second stage.

In the first stage of such a two-stage synthesis 85 preferably a class of catalysts is applied by means of which a product is obtained containing a relatively small amount of olefinic and oxygen-containing organic compounds and a relatively large amount of unbranched paraffins boiling above the middle 90 distillate boiling range. The first stage is preferably carried out at a temperature of 125-350 °C, in particular 175-275 °C and a pressure from 5-100 bar, and in particular from 10-75 bar.

In the second stage of the two-stage synthesis 95 preferably at least the fraction of the first stage product boiling above the middle distillate boiling range is then hydrocracked into middle distillates having a considerably improved pour point, compared with middle distillates obtained in a 100 single-stage synthesis.

It is particularly preferred to submit the total normally liquid product (the fraction containing molecules having at least five carbon atoms) of the first stage to the second stage in order to improve the 105 quality of the lighter hydrocarbons (e.g. gasoline and kerosene fractions) which are present therein.

In case the first stage product still contains sufficient unconverted hydrogen for carrying out the second stage, both stages can be advantageously 110 carried out in series-flow, without separation or addition of components in between both stages, at substantially the same pressure in both stages. The temperature in the second stage is preferably from 200-450 °C and in particular from 250-350 °C. In the 115 second stage preferably a catalyst is used which contains at least one noble metal from Group 8 (in particular platinum and/or palladium) on a carrier (in particular silica-alumina). Preferably such catalysts contain 0.1-2% by weight, and in particular 0.2-1% by 120 weight, of noble metal(s).

Hydrogen-containing gas is preferably recovered from product gas obtained in at least one of steps (i)-(iv) of the process according to the invention in order to provide hydrogen for the second stage of 125 the liquid hydrocarbon synthesis and/or hydrodesulphurization of hydrocarbonaceous feed, if required.

In case gas with a H₂/CO molar ratio above the preferred range from 1.0-2.5 (in particular 1.25-2.25) 130 for feed to be applied in step (iv) is obtained after

separating off carbon dioxide in step (iii), hydrogen is preferably recovered from said gas in order to lower the H_2/CO ratio therein.

- Hydrogen is preferably recovered by means of
 5 "pressure swing adsorption", using molecular
 sieves wherein components other than hydrogen are
 selectively adsorbed at a higher pressure and
 desorbed at a lower pressure, thereby producing the
 hydrogen at a pressure substantially equal to the
 10 feed pressure; alternatively, hydrogen is recovered
 by means of semi-permeable membranes wherein
 hydrogen with a relatively high purity is recovered at
 a lower pressure and the remainder of the stream
 has a pressure substantially equal to the feed
 15 pressure.

The invention will be elucidated by means of the
 Figure in which a preferred embodiment of the
 process is schematically depicted (without ancillary
 equipment such as pumps and valves being
 20 indicated).

- A hydrocarbonaceous feed is introduced through
 line (1), combined with carbon dioxide-containing
 gas recycled through line (2) and split into streams
 (3) and (4); stream (3) is combined with steam
 25 introduced through line (5) and led via line (6) (and
 optionally a heat exchanger; not shown in the
 Figure) to reforming zone (7) wherein step (i) of the
 process according to the invention is carried out.
 Stream (4) is combined with product gas containing
 30 unconverted synthesis gas and lower olefinic
 compounds recycled through line (8) and with
 substantially pure oxygen gas (originating from an
 air separation plant which is not depicted in the
 Figure) introduced via line (9); the gas mixture thus
 35 obtained is led via line (10) to oxidation zone (11) in
 which said gas mixture is combined with reformer
 product emanating from reforming zone (7) and
 partially oxidized to provide heating gas with which
 the reforming zone is heated in step (ii) of the
 40 process according to the invention.

Heating gas obtained in step (ii) is led via line (12)
 to carbon dioxide separation unit (13) (step (iii)) from
 which the total amount of recovered carbon
 dioxide-containing gas is recycled (step (v)) through
 45 line (2) to the hydrocarbonaceous feed. Water is
 removed from unit (13) through line (14) and
 reheated in the utilities section (not shown in the
 Figure) of the process to produce steam.

- The gas obtained after separating off carbon
 50 dioxide in step (iii) is introduced through line (15)
 into hydrocarbon synthesis unit (16) (step (iv)),
 optionally via a hydrogen removal unit (not shown in
 the Figure) from which hydrogen for use in unit (16)
 and/or hydrodesulphurization of the
 55 hydrocarbonaceous feed can be obtained. Normally
 liquid hydrocarbons are removed from unit (16) via
 line (17) whereas product gas is removed via line (18)
 and led partly via line (19) as fuel gas to a gas turbine
 driving an air separation compressor (not shown in
 60 the Figure); the remaining part of the product gas is
 recycled via lines (8) and (10) to oxidation zone (11).

The invention is further illustrated by the following
 Example.

65 Example

In a process set-up substantially as depicted in the
 Figure a natural gas feed stream (1) comprising 137
 Mmol (= 10^6 mol)/day methane and 3 Mmol/day
 nitrogen is combined with 61 Mmol/day of carbon
 70 dioxide (stream (2)) and 205 Mmol/day of steam
 (stream (5)) and introduced into reforming zone (7)
 which is operated at a temperature of 900 °C and a
 pressure of 25 bar abs. and wherein the feed is
 contacted with a catalyst comprising Ni on Al_2O_3 as
 75 carrier. The reformer product is partially oxidized in
 oxidation zone (7) with 76 Mmol/day of substantially
 pure oxygen (stream (9)) and subsequently led to
 unit (13) in which the afore-mentioned 61 Mmol/day
 of carbon dioxide (stream (2)) is removed. The
 80 resulting substantially carbon dioxide-free gas
 stream (15) comprises 245 Mmol/day of hydrogen,
 136 Mmol/day of carbon monoxide, 3 Mmol/day of
 nitrogen and 10 Mmol/day of steam, and is
 converted in hydrocarbon synthesis unit (16) into 7
 85 Mmol/day of normally liquid hydrocarbons (stream
 (17)) and a product gas stream (18).

CLAIMS

- 90 1. Process for producing liquid hydrocarbons
 from a hydrocarbonaceous feed which comprises
 the following steps:
 (i) catalytically reforming at least part of the
 hydrocarbonaceous feed at elevated temperature
 95 and pressure with steam in at least one reforming
 zone;
 (ii) heating the reforming zone(s) by means of a
 carbon dioxide-containing heating gas comprising a
 product obtained by partial oxidation of reformer
 100 product obtained in step (i) or of a remaining part of
 the hydrocarbonaceous feed or of a mixture thereof
 with an oxygen-containing gas in an oxidation zone;
 (iii) separating carbon dioxide from heating gas
 obtained in step (ii);
 105 (iv) catalytically converting at least part of the
 reformer product obtained in step (i) and/or gas
 obtained after separating off carbon dioxide in step
 (iii) at elevated temperature and pressure into
 normally liquid hydrocarbons; and
 110 (v) combining at least part of the carbon dioxide
 obtained in step (iii) with hydrocarbonaceous feed
 for at least one of steps (i) and (ii).
2. Process according to claim 1 wherein the total
 reformer product obtained in step (i) is subjected to
 115 partial oxidation in step (ii) together with the
 remaining part of the hydrocarbonaceous feed.
3. Process according to claim 1 or 2 wherein
 substantially pure oxygen gas is applied in step (ii).
4. Process according to any of the preceding
 120 claims wherein product gas obtained in step (iv) is
 applied in step (ii).
5. Process according to claim 4 wherein at least
 part of the product gas obtained in step (iv) is
 expanded and/or combusted to provide power for
 125 separating and/or compressing the oxygen gas.
6. Process according to any of the preceding
 claims wherein hydrogen-containing gas is
 recovered from product gas obtained in at least one
 of steps (i)-(iv).
- 130 7. Process according to claim 6 wherein at least

part of the recovered hydrogen-containing gas is combined with hydrocarbonaceous feed and/or applied in step (iv).

8. Process according to any of the preceding claims wherein at least part of the normally liquid hydrocarbons obtained in step (iv) are catalytically hydrocracked.

9. Process substantially as described hereinbefore with particular reference to the Example and the drawing.

10. Liquid hydrocarbons prepared by a process according to any of the preceding claims.