

PROCESS FOR PRODUCING LIQUID HYDROCARBONS
FROM A HYDROCARBONACEOUS FEED

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

5 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.

10 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 in the hydrocarbon synthesis step.

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

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.

20 The invention therefore relates to a 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;
- 25 (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;
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- (iii) separating carbon dioxide from heating gas used 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).

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 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 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 step (i) (which comprises carbon monoxide and hydrogen and, in addition, usually smaller amounts of carbon dioxide, 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).

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 wherein reformer product gases emanating from e.g. reformer tubes filled with catalyst particles, are mixed with an 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 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 preferably from 4000-6000 l(S.T.P.)/l 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.

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.

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, 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 normally liquid hydrocarbons produced in step (iv).

5 Due to the usually higher temperature of the oxidation zone, compared with the reforming zone, the conversion of any remaining 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
10 separate stream, to protect burners in said oxidation zone 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 employed
15 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 according to the invention is usually gaseous and if liquid, should, of course, be
20 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 at least partly desulphurized (before
25 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 the reforming zone(s)
30 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.
35 Preferably all the carbon dioxide thus removed is combined with the

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total hydrocarbonaceous feed after the, optional, desulphurization step. Alternatively, the carbon dioxide removed in step (iii) may be separated into two feed streams, one of which is combined with the feed stream for step (i), the other one is combined with the feed stream for step (ii). Furthermore, additional amounts of carbon dioxide from extraneous sources can be used.

In step (iv) of the process according to the present 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 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 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 fractions (having a boiling range from about 150-360 °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 less suited, in particular when the hydrocarbon synthesis is carried out in a single stage. A part of the product gas obtained in step (iv) is preferably expanded (e.g. in a turbo-expander) and/or combusted (e.g. in the combustion chamber of a gas turbine) to 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 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 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 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 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 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 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 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 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 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 the liquid hydrocarbon synthesis and/or hydrodesulphurization of hydrocarbonaceous feed, if required.

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In case gas with a H_2/CO molar ratio above the preferred range from 1.0-2.5 (in particular 1.25-2.25) 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 "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 feed pressure; alternatively, hydrogen is recovered by means of semi-permeable membranes wherein hydrogen with a relatively high purity is recovered at a low pressure and the remainder of the stream has a pressure substantially equal to the feed 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 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 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 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 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 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 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 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 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 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.
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 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 carrier. The reformer product is partially oxidized in oxidation zone (11) 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 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 Mmol/day of normally liquid hydrocarbons (stream (17)) and a product gas stream (18).



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1. Process for producing liquid hydrocarbons from a hydrocarbonaceous feed which comprises the following steps:
 - 5 (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
10 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 used in step (ii);
 - 15 (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
 - 20 (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).
- 25 2. Process according to claim 1 wherein the total reformer product obtained in step (i) is subjected to 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 claims wherein product gas obtained in step (iv) is applied in step (ii).
- 30 5. Process according to claim 4 wherein a part of the product gas obtained in step (iv) is expanded and/or combusted to provide power for compressing and/or separating from air the oxygen-containing gas applied in step (ii).



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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).
- 5 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).
- 10 8. Process according to any of the preceding claims wherein step (iv) is carried out as a 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.
- 10 10. Process substantially as described hereinbefore with reference to the Example.
11. Liquid hydrocarbons prepared by a process according to any of the preceding claims.
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