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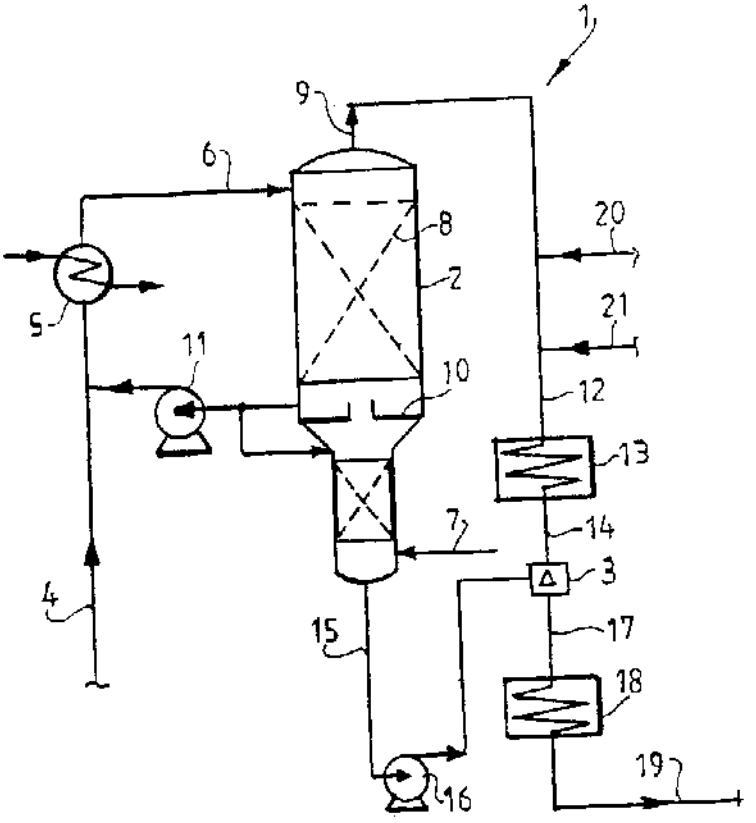
(54) Process and installation for the preparation of hydrocarbons

(57) Process for the preparation of C_5^+-hydrocarbons, which process comprises the following steps:

i) catalytically reforming C_4^--hydrocarbons with steam to synthesis gas at elevated temperature and pressure;
ii) catalytically converting synthesis gas into hydrocarbons at elevated temperature and pressure, using a Fischer-Tropsch catalyst;
iii) partly evaporating at (2) process water (4) obtained in step ii), at elevated pressure using a hot gaseous medium (7);
iv) additionally heating at (13) the gaseous mixture obtained in step iii);
v) injecting at (3) at least part of the remaining process water into the heated gaseous mixture; and
vi) using the gaseous mixture (19) as a feed for steam reforming of step i).



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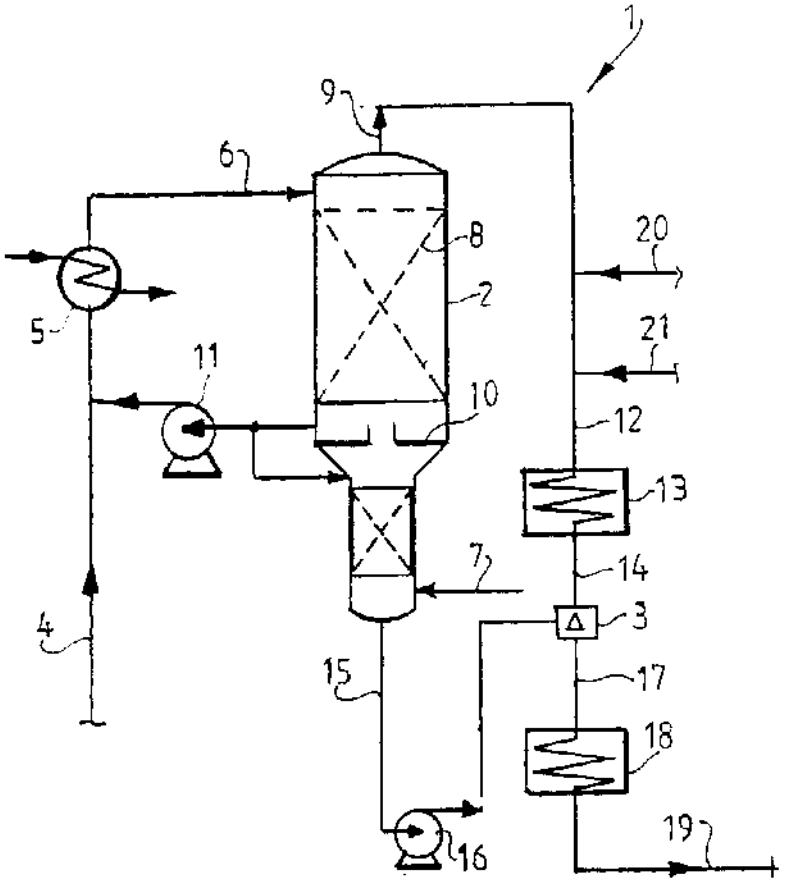
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PROCESS AND INSTALLATION FOR THE PREPARATION OF HYDROCARBONS

The present invention relates to a process and to installation for the preparation of hydrocarbons by steam reforming natural gas to synthesis gas which is subsequently converted into hydrocarbons.

During the catalytical conversion of synthesis gas into hydrocarbons, process water is formed, which is contaminated with oxygenates comprising for instance formalydehyd, acetaldehyd, propionaldehyd, butyraldehyd, valeraldehyd, methanol, ethanol, propanol-1, butanol-1, acetic acid, formic acid. These contaminants do not allow the disposal of untreated process water into the environment. Since conventional methods for the generation of process steam for use in steam reforming of natural gas by means of boiling against process gas and furnace fluegas both originating from the steam reforming reaction, require relatively pure water, the process water contaminated with oxygenates cannot be used in the conventional steam generating process.

It has been found that process water formed as a by-product in the catalytical conversion of synthesis gas into hydrocarbons, can be recycled as steam containing the oxygenates in gas form. The vaporization of the process water is performed in two stages. A first stage in which more volatile oxygenates are vaporized with most of the water, and a second stage in which the less volatile oxygenates and the remainder of the water are flash vaporized into superheated steam containing the more volatile oxygenates.

In the steam reforming process these oxygenates are reformed into suitable products. Accordingly a built-up of oxygenates in the recycle-circuit is avoided.

Therefore the invention relates to a process for the preparation of C_5^+-hydrocarbons, comprising the following

steps:

i) catalytically reforming C_4^--hydrocarbons with steam to synthesis gas at elevated temperature and pressure;

ii) catalytically converting synthesis gas into hydrocarbons at elevated temperature and pressure, using a Fischer-Tropsch catalyst;

iii) partly evaporating process water obtained in step ii), at elevated pressure using a hot gaseous medium;

iv) additionally heating the gaseous mixture obtained in step iii);

v) injecting at least part of the remaining process water into the heated gaseous mixture; and

vi) using the gaseous mixture as a feed for steam reforming of step i).

A major advantage of the process according to the invention is that in this process, process water containing oxygenates as impurities is used as a gaseous feed in the first stage of this process, avoiding costs for the purification and disposal of the process water.

C_5^+-hydrocarbons comprise five or more carbon atoms, C_4^--hydrocarbons comprise one to four inclusive carbon atoms.

Preferably the C_4^--hydrocarbons mentioned under i), more preferably natural gas, is used as the hot gaseous medium for the evaporation of the contaminated process water, so that the CO/H_2 ratio is readily controlled in dependence of the amount of process water to be recycled.

The optimal steam to carbon ratio of the feed for the conversion process is 4 or higher. For an optimal adjustment of this ratio it is preferred to have provisions to the optimal addition of steam and carbondioxide to the gaseous mixture in which the remaining process water is injected.

Another aspect of the invention relates to an installation for the preparation of hydrocarbons using the process described hereinbefore. This installation comprises:

a reformer reaction for catalytically reforming natural gas with steam to synthesis gas, having inlet means for natural gas and for steam, and outlet means for synthesis gas;

a converter reactor for catalytically converting synthesis gas into hydrocarbons, having inlet means for synthesis gas connected with the synthesis gas outlet means of the reformer reactor, outlet means for hydrocarbons, and outlet means for process water;

a saturator having inlet means connected with the process water outlet means of the converter reactor, inlet means for a hot gaseous medium, outlet means for a gaseous mixture comprising evaporated process water connected via an inlet pipe with a heating unit, and outlet means for the remainder of the process water; and

an injector unit having inlet means connected with the heating unit, inlet means for process water connected with the process water outlet of the saturator, and outlet means connected with a recycling pipe connected with the reformer reactor.

Finally the invention relates to hydrocarbons prepared according to the process of the invention.

In step (i) of the process according to the invention natural gas is reformed to synthesis gas at a temperature from 500-1100°C, preferably from 500-1000°C, and at a pressure from 3-100 bar, preferably from 15-40 bar, using a conventional reforming catalyst, such as one or more metals of Group VIII of the Periodic Table of Elements, preferably nickel, on a support, such as alumina, silica and or combinations thereof. The space velocity of the combined feed consisting of natural gas, steam and recycled oxygenates is 100-8000, preferably from 4000-6000 liters (S.T.P.)/l catalyst/hour.

The synthesis gas formed in step (i) contains as major components hydrogen and carbon monoxide; in addition carbondioxide, water, nitrogen, argon and impurities herein referred to as oxygenates, compounds having 1-4 carbon atoms per molecule, such as formalydehyd, acetaldehyd, propionaldehyd, butyraldehyd, valeraldehyd, methanol, ethanol, propanol-1, butanol-1, acetic acid, formic acid.

In step (ii), the Fischer-Tropsch hydrocarbonsynthesis

reaction, synthesis gas is converted in one or more stages into normally liquid hydrocarbons, using a Fischer-Tropsch type of catalyst which preferably comprises at least one metal (compound) of Group IVB, VIB and/or VIII of the Periodic Table of Elements, such as zirconium, chromium, iron, cobalt, nickel and/or ruthenium, applied on a support.

Step (ii) is preferably carried out at a temperature from 100-500°C, at a pressure from 1-200 bar and a space velocity from 200-20.000 m^3 (S.T.P.) gaseous feed/m^3 reaction zone/hour.

The annexed drawing shows the single figure of the saturator of the installation according to the invention, in which process water contaminated with oxygenates is evaporated in two stages and recycled in gas form to the reformer reactor.

The single figure shows a section 1 of the installation for the preparation of hydrocarbons, comprising a saturator 2 and an injector unit 3 for the evaporation of process water contaminated with oxygenates and originating from the convertor reactor and the evaporated product is recycled to the reformer reactor.

The process water contaminated with oxygenates is supplied via the pipe 4, heated in a heat convertor 5, and supplied to the top of the saturator 2 via process water inlet means 6. Hot natural gas is supplied to the bottom of the saturator 2 via natural gas inlet means 7.

The saturator 2 is of a conventional type, comprising a packed bed of ceramic saddles over which process water trickles downwardly in countercurrent relation to upwardly moving hot natural gas. The top effluent comprising steam and the more volatile oxygenates, leaves the saturator via the outlet means 9. The outlet means 9 are connected with an inlet pipe 12 of a heat exchanger 13. The heated top effluent is supplied to the injector unit 3 via its inlet means 14.

Via the bottom outlet means 15 of the saturator 2 and a compressor 16 pressurized bottom effluent, comprising the remainder of the process water and the less volatile oxyge-

nates is supplied to the injector unit 3 in which it is flash vaporized in the super heated top effluent. The outlet means 17 of the injector unit 3 are via an additional heat convertor 18 connected with a recycling part 19 feeding steam and gaseous oxygenates to the reformer reactor.

The surplus of process water is collected on a collecting ring 10 and after compression in a compressor 11 fed to the pipe 4.

For the adjustment of the steam to carbon ratio of the feed for the reformer reactor carbon dioxide and/or steam can optionally be supplied to the top effluent via the pipes 20, 21 respectively.

Heat for heating the process water in the heat convertor 5 originates from the steam reforming reaction, whereas heat supplied to the heat converters 13 and 18 originates from the converting reaction.

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Claims

1. Process for the preparation of C_5^+-hydrocarbons, which process comprises the following steps:

i) catalytically reforming C_4^--hydrocarbons with steam to synthesis gas at elevated temperature and pressure;

ii) catalytically converting synthesis gas into hydrocarbons at elevated temperature and pressure, using a Fischer-Tropsch catalyst;

iii) partly evaporating process water obtained in step ii), at elevated pressure using a hot gaseous medium;

iv) additionally heating the gaseous mixture obtained in step iii);

v) injecting at least part of the remaining process water into the heated gaseous mixture; and

vi) using the gaseous mixture as a feed for steam reforming of step i).

2. Process as claimed in claim 1, wherein the hot gaseous medium contains C_4^--hydrocarbons.

3. Process as claimed in claim 1, wherein the hot gaseous medium contains natural gas.

4. Process as claimed in claim 1-3, wherein steam is added to the gaseous mixture which is subsequently heated in step (iv).

5. Process as claimed in claim 1-4, wherein carbondioxide is added to the gaseous mixture.

6. Process as claimed in claims 1-5, wherein natural gas, steam and/or carbon dioxide are/is added in an amount such that the steam to carbon ratio of the recycled gaseous mixture is equal to or larger than 4.

7. Process for the preparation of hydrocarbons according to claim 1, substantially as described hereinbefore, with particular reference to the example and the drawing.

8. Hydrocarbons whenever prepared according to a process as described in any of the preceeding claims.

9. Installation for the preparation of hydrocarbons comprising:

- a reformer reactor for catalytically reforming natural gas with steam to synthesis gas, having inlet means for natural gas and for steam and outlet means for synthesis gas;

- a converter reactor for catalytically converting synthysis gas into hydrocarbons, having inlet means for synthesis gas connected with the synthesis gas outlet means of the reformer reactor, outlet means for hydrocarbons and outlet means for process water;

- a saturator having inlet means connected with the process water outlet means of the convertor reactor, inlet means for a hot gaseous medium, outlet means for a gaseous mixture comprising evaporated process water connected via an inlet pipe with a heating unit, and outlet means for the remainder of the process water; and

- an injector unit having inlet means connected with the heating unit, inlet means for process water connected with the process water outlet of the saturator and outlet means connected with a recycling pipe connected with the reformer reactor.

10. Installation as claimed in claim 9, wherein a feeding pipe for steam is connected with the inlet pile of the heating unit.

11. Installation as claimed in claim 9 or 10, wherein a feeding pipe for carbon dioxide is connected with the inlet pipe of the heating unit.

12. Installation for the preparation of hydrocarbons substantially as described hereinbefore with particular reference to the example and the drawing.