

PROCESS FOR THE CHEMICAL CONVERSION OF A GASEOUS FEED INTO AN
AT LEAST PARTLY LIQUID PRODUCT

The invention relates to a process for the chemical conversion of a gaseous feed into an at least partly liquid product.

5 In known processes wherein (partly) liquid products are prepared at the conditions prevailing in the reaction zone, in most cases gravity flow of the liquid products towards the bottom of said zone is employed to collect and remove said products.

10 A problem associated with such processes is that the pressure drop over the reaction zone is usually relatively large, especially when the reaction zone is filled with particulate (catalyst) material, which makes it unattractive to apply relatively high space velocities in said zone. Moreover, temperature control in case of exothermic reactions is sometimes difficult, unless special measures are taken to prevent this; one of such measures comprises
15 carrying out the process in a plurality (sometimes even more than 1000) of tubular reaction zones.

Surprisingly, it has now been found that the afore-mentioned problems can be overcome by applying a radial flow regime inside the preferably substantially cylindrical reaction zone of a
20 normally substantially vertically extending reactor, notwithstanding the presence of liquid product therein, and removing liquid- and gaseous product (including unconverted gaseous feed) together from the reaction zone.

The invention therefore relates to a process for the
25 chemical conversion of a gaseous feed into an at least partly liquid product which comprises introducing the gaseous feed into at least one reaction zone comprising at least one catalyst bed and which reaction zone is maintained at conversion conditions, allowing said feed to flow with regard to the central axis of the
30 reaction zone substantially radially inwards to a product

collection zone, arranged substantially centrally inside the reaction zone around the central axis, and removing liquid- and gaseous product together from the reaction zone through the collection zone.

5 Processes and apparatuses in which a radial flow is maintained in the reaction zone are known for gas phase reactions such as the preparation of methanol or low-boiling hydrocarbons from synthesis gas.

10 A major advantage of the process according to the invention is that the temperature inside the reaction zone can be optimally controlled by passing the gaseous feed with a relatively high velocity through said zone, which now becomes attractive because the pressure drop over the reaction zone is relatively low. Consequently, recycling of liquid product through the reaction zone(s)
15 as sometimes applied in order to maintain temperature stability therein, in particular when the process is highly exothermic, is not necessary.

20 Furthermore, it now becomes feasible to operate a process in which liquid product is formed in stacked reaction zones without incurring excessive pressure drop over the zones, due to the fact that the length of the flow paths through the reaction zones remains substantially equal independent of the number of said zones.

25 The process according to the invention is carried out in such a manner that the gaseous feed flows inwardly towards the product collection zone arranged substantially centrally inside the reaction zone(s); this set-up is chosen because the volume of gas flowing towards the collective zone diminishes with the gradual formation of liquid products resulting in a decrease in
30 space velocity, which decrease is at least partly compensated by the decreasing area through which the gas flows towards the central collection zone.

 The radial flow velocity of the combined gaseous feed and -product stream is preferably maintained at a value sufficient to

allow at least a major part (i.e. more than 50% by weight, and most preferably substantially all) of the liquid product to be removed from the reaction zone(s) by said stream in order to avoid non-radial flow therein.

5 The present process is particularly suited for catalytic (especially exothermic) conversions, in which case the reaction zone(s) contain(s) at least one catalyst bed. It is also possible to carry out the process in a plurality of stacked catalyst beds which may contain the same or different catalysts. Moreover, each
10 catalyst bed may contain at least two (e.g. annular) zones comprising the same or different catalysts.

Heat produced in the catalyst bed(s) can be removed in some cases simply by maintaining in the reaction zone(s) an adequate space velocity of the gaseous feed. However, in many cases it will
15 be highly desirable to incorporate at least one heat exchange zone in the reaction zone(s), preferably in the form of heat exchange tubes through which a cooling fluid (e.g. water and/or steam) is led.

The radial flow pattern in the reaction zone(s) results in
20 excellent heat transfer to the heat exchange zones even at relatively low gas velocities, in particular when heat exchange tubes are arranged in the reaction zone(s) substantially parallel to a central, preferably perforated, collection tube, more particular when the heat exchange zones are arranged in concentric rings.

25 It is particularly preferred to use one or more heat exchange means situated in a concentric ring or a number of concentric rings around the central supply or collection tube in the form of helical wound tubes or tube bundles, each tube bundle comprising two or more helical wound tubes of substantially the same dimensions.
30 Thus, the cooling medium flows via one or more helical patterns situated concentrically around the central supply or collection tube, each pattern containing one or more helixes. When two or more concentric tubes or tube bundles are used, the screw-direction of the helixes of two adjacent tubes or tube bundles is preferably
35 opposite to each other. When two or more tube bundles are used it is preferred to use an increasing number of helical wound tubes in

bundles situated at a larger distance from the central tube, and to maintain substantially the same length for each tube.

The helical flowing pattern of the cooling medium enables the ratio heat-exchanger surface/reactor volume to be varied over a large range. The tube diameter may be varied as well as the distance between two layers of tubing in both the axial and the radial direction. The diameter of the cooling tubes is suitably chosen between 4 and 55 mm, especially between 10 and 35 mm. The distance between two adjacent rings of tubes or tube bundles (distance in the radial direction) is suitably chosen between 10 and 50 mm, especially between 15 and 25 mm, and the distance between two adjacent coils lying in a concentric ring (distance in the axial direction) is suitably chosen between 10 and 200 mm, especially between 10 and 50 mm. The helical wound tube bundles make it possible to use hemispheric tube sheet designs, thus avoiding the less suitable flat tube sheets.

Heat transfer in the reaction zone(s) can be further improved by arranging screens of (e.g. wire mesh) around a group of heat exchange tubes, which are preferably arranged in at least one concentric ring around the collection tube, in order to keep the space between adjacent tubes free from catalyst particles; as a result tube spacing can be much closer than without the application of screens. Of course, the openings in said screens should be small enough to prevent catalyst particles or other particulate contact material present in the reaction zone(s) from passing through a screen.

In addition, or as alternative, to the afore-mentioned screens the heat exchange tubes can be provided with fins (e.g. extending radially, tangentially or spirally from their outer surface) in order to improve heat transfer from the reaction zone to the cooling fluid.

As a result of improved heat transfer, in the present process the number of heat exchange tubes can be kept relatively small, thus allowing a relatively large amount of catalyst to be packed in a given volume of the reaction zone(s).

The heat exchange tubes are preferably spaced in such a manner in the reaction zone(s) that an optimal temperature profile for a particular reaction is attained therein in radial direction.

Moreover, each group (e.g. concentric ring) of heat exchange tubes is preferably in communication with separate cooling fluid in- and outlet means which can be operated independently of other groups of heat exchange tubes in order to attain optimal control over the temperature profile in the reaction zone(s).

Water is usually used as cooling medium. Preferably the water evaporates at least partially in the tubes. This enables the heat of reaction to be removed from the reaction zone by producing steam. Other cooling media as organic compounds, for instance biphenyl thermal oils, or liquid metals may also be used.

The process according to the invention is particularly suitable for converting a synthesis gas feed (at least partly) into hydrocarbons, preferably having at least 10 carbon atoms per molecule; most preferably paraffinic hydrocarbons having at least 20 carbon atoms per molecule are thus prepared.

The synthesis gas feed referred to hereinabove contains as major components hydrogen and carbon monoxide; in addition said feed may contain carbon dioxide, water, nitrogen, argon and minor amounts of compounds having 1-4 carbon atoms per molecule such as methane, methanol or ethene.

The synthesis gas feed can be prepared in any manner known in the art e.g. by means of steam/oxygen gasification of a hydrocarbonaceous material such as brown coal, anthracite, coke, crude mineral oil and fractions thereof, and oil recovered from tar sand and bituminous shale. Alternatively, steam methane reforming and/or catalytic partial oxidation of a hydrocarbonaceous material with an oxygen-containing gas can be applied to produce synthesis gas excellently suitable for use in the process according to the invention.

The present process is preferably carried out at a temperature from 100-500 °C, a total pressure from 1-200 bar abs. and a space velocity from 200-20,000 m³ (S.T.P.) gaseous feed/m³ reaction

zone/hour. Particularly preferred process conditions for the preparation of hydrocarbons include a temperature from 150-300 °C, a pressure from 5-100 bar abs. and a space velocity from 500-5000 m³ (S.T.P.) gaseous feed/m³ reaction zone/hour. The expression "S.T.P." as referred to hereinbefore means Standard Temperature (of 0 °C) and Pressure (1 bar abs.). In case synthesis gas is employed as gaseous feed, the H₂/CO molar ratio therein is preferably from 0.4-4 and most preferably from 0.8-2.5.

Suitable catalysts for the preparation of (paraffinic) hydrocarbons from synthesis gas contain at least a metal (compound) from Group 8 of the Periodic Table of the Elements, preferably a non-noble metal, in particular cobalt, optionally in combination with a noble metal e.g. ruthenium, on a refractory oxide carrier such as silica, alumina or silica-alumina, in particular silica. Furthermore, the catalysts preferably contain at least one other metal (compound) from Group 4b and/or 6b, most preferably chosen from the group consisting of zirconium, titanium and chromium. The catalysts preferably contain from 3-60 parts by weight of cobalt, optionally 0.05-0.5 parts by weight of ruthenium, and from 0.1-100 parts by weight of other metal(s) per 100 parts by weight of carrier.

The metals may be incorporated into the catalyst by means of any method known therefor in the art, such as (gas) impregnation (e.g. in the form of chlorides or carbonyls), ion-exchange, kneading or precipitation. Kneading and impregnation are preferred methods, the latter in particular for the incorporation of cobalt. The resulting catalyst composition is preferably calcined at temperatures from 350-700 °C after each impregnation or kneading step.

The catalysts are preferably employed in the present process in the form of spherical, cylindrical or lobed particles with a diameter from 0.1-15 mm, and in particular from 0.5-5 mm. The catalyst particles can be prepared by means of any method known in the art, such as pressing or extruding of powdery catalyst material, if desired together with a binder material. Catalyst spheres, in particular silica-containing spheres, are suitably prepared by means of the "oil-drop" method whereby said spheres are formed as

drops of a silica gel which are solidified while falling in an oil bath.

5 The catalyst present in the reaction zone(s) may be kept in contact with liquid product in case relatively heavy paraffins (with more than 20 carbon atoms per molecule) are synthesized with the present process in order to avoid the formation of carbonaceous deposits on the catalysts. Liquid redistribution means (e.g. in the form of trays or layers of material having a relatively low permeability for liquid and/or gas) can be arranged inside the reaction zone(s) in order to promote substantially horizontal radial flow patterns in the particulate catalyst mass and the desired optimal contact with liquid product. Furthermore, an oriented packing of non-spherical catalyst can be employed to promote radial flow in the reaction zone.

15 Furthermore, the invention relates to liquid products whenever prepared by a process as described hereinbefore.

20 In addition, the invention relates to an apparatus whenever used for carrying out the process as described hereinbefore which apparatus comprises a housing having gaseous feed inlet means and product outlet means and enclosing at least one reaction section which is in communication with the feed inlet means and via collection means with the product outlet means, which collection means are arranged substantially centrally inside the reaction section(s) around the central axis such that a substantially radial flow pattern can be maintained in said section(s).

25 The apparatus can furthermore contain catalyst supply- and removal means communicating with the reaction section(s). The product outlet means are suitably in communication with gas/liquid separation means arranged in the bottom section of the housing below the reaction section(s), which separation means are in communication with the collection means. The upper section of the housing (above the reaction section(s)) is suitably provided with a steam drum which is in communication with the outlets of cooling tubes which are preferably arranged inside the reaction section(s) as discussed hereinbefore. The other previously discussed preferred

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features of the process according to the invention are also applicable to said apparatus.

A preferred embodiment of the apparatus according to the invention is shown schematically in Figures 1 and 2 in which reference numerals relating to corresponding parts are the same.

In Figure 1 a longitudinal section of the present apparatus as shown.

Figure 2 represents a cross section at AA¹ of the apparatus as depicted in Figure 1.

The apparatus as schematically shown in Figures 1 and 2 comprises a housing (1) having gaseous feed inlet means (2) (depicted as a ring-shaped manifold provided with a plurality of nozzles (3) for optimal feed distribution) and product outlet means (4) connected to a perforated central collection tube (5) which is closed at its upper end (6). Reaction section (7) is laterally enclosed by a cylindrical wall section (8) provided with openings for the passage of gaseous feed therethrough. Reaction section (7) can be filled with catalyst via catalyst supply means (9) in the form of a frusto-conical section arranged in the upper section (10) of housing (1). The bottom section (11) of reaction section (7) is frusto-conically shaped for easy catalyst withdrawal and connected to tubular catalyst withdrawal means (12) which are provided with a (e.g. rotary) catalyst valve (13). Section (7) is furthermore provided with a plurality of heat exchange (cooling) tubes (14) which are arranged in concentric rings, each ring of tubes being connected to separate inlet means (15, 16) and outlet means (17, 18) for optimal temperature regulation inside reaction section (7).

Heat exchange tubes (14) may have been manufactured from straight tubes as indicated in the drawing. In a preferred embodiment these heat exchangers are in the form of a helical wound tube or tube bundle.

C L A I M S

1. Process for the chemical conversion of a gaseous feed into an at least partly liquid product which comprises introducing the gaseous feed into at least one reaction zone comprising at least one catalyst bed and which reaction zone is maintained at
5 conversion conditions, allowing said feed to flow with regard to the central axis of the reaction zone substantially radially inwards to a product collection zone arranged substantially centrally inside the reaction zone around the central axis, and removing liquid- and gaseous product together from the reaction
10 zone through the collection zone.
2. Process according to claim 1, wherein the reaction zone(s) contain(s) a heat exchange zone.
3. Process according to claim 2, wherein heat is removed from the reaction zone by a cooling medium which flows via one or more
15 helical patterns situated concentrically around the central supply or collection tube, each pattern containing one or more helixes.
4. Process according to claim 3, wherein the cooling medium flows via two or more concentric helical patterns wherein the
20 screw-directions of adjacent helical patterns are opposite to each other.
5. Process according to claim 3 or 4, wherein the cooling medium flows via two or more concentric helical patterns wherein an increasing number of helixes is used in the helical
25 patterns which are situated at a larger distance from the central tube, and which helixes have substantially the same length.
6. Process according to any one of the preceding claims wherein the radial flow velocity of the combined gaseous feed and
-product stream is maintained at a value sufficient to allow at
30 least a major part of the liquid product to be removed from the reaction zone(s) by said stream.



* C L M S *



7. Process according to any one of the preceding claims wherein a synthesis gas feed is converted into hydrocarbons, preferably having at least 10 carbon atoms per molecule.
8. Process according to any one of the preceding claims which
5 is carried out at a temperature from 100-500 °C, a total pressure from 1-200 bar abs. and a space velocity from 200-20,000 m³ (S.T.P.) gaseous feed/m³ reaction zone/hour.
9. Process for a chemical conversion of a gaseous feed into an at least partly liquid product substantially as described
10 hereinbefore.
10. Liquid products whenever prepared by a process according to any one of the preceding claims.
11. Apparatus whenever used for carrying out the process according to any one of claims 1-9 which comprises a housing
15 having gaseous feed inlet means and product outlet means and enclosing at least one reaction section which is in communication with the feed inlet means and via collection means with the product outlet means, which collection means are arranged substantially centrally inside the reaction section(s) around the
20 central axis such that a substantially radial flow pattern can be maintained in said section(s).
12. Apparatus according to claim 11, wherein the reaction section(s) contain(s) one or more heat exchange means situated in a concentric ring or a number of concentric rings around a
25 central supply or collection tube in the form of helical wound tubes or tube bundles, each tube bundle comprising two or more helical wound tubes of substantially the same dimensions.
13. Apparatus according to claim 12, comprising two or more concentrical tubes or tube bundles wherein the screw-direction of the helixes of two adjacent tubes or tube bundles is opposite to
30 each other.
14. Apparatus according to claim 12 or 13, comprising two or more concentrical tube bundles wherein an increasing number of helical wound tubes is used in bundles situated at a larger
35 distance from the central tube.
15. Apparatus for a chemical conversion of a gaseous feed into an at least partly liquid product substantially as described hereinbefore.