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(54) Shut-down process for a Fischer-Tropsch reactor, and said reactor

(57) A process for the shut-down of a reactor for the preparation of an at least partly liquid hydrocarbonaceous product by a catalytic reaction of carbon monoxide with hydrogen at elevated temperature and pressure and using a catalyst, which reactor is provided with cooling means and with means to recycle gas through the catalyst for temperature equalizing of the catalyst, comprising the steps of:

(i) interrupting the feed of synthesis gas;

(ii) depressurizing the reactor downstream of the catalyst, and providing the reactor upstream of the catalyst with inert gas; and

(iii) cooling the catalyst to ambient conditions.

The reactor may have spherical bodies containing a pressurised gas (eg H_2) above the catalyst bed, which bodies release the gas when the pressure in the reactor drops.

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SHUT-DOWN PROCESS FOR A FISCHER-TROPSCH REACTOR, AND SAID REACTOR

The invention relates to a shut-down process for a reactor used for the preparation of an at least partly liquid hydrocarbonaceous product by a catalytic reaction of carbon monoxide with hydrogen at elevated temperature and pressure using a Fischer-Tropsch catalyst, and to a reactor specifically designed for carrying out this shut-down process.

Processes for the preparation of an at least partly liquid hydrocarbonaceous product by catalytic reaction of carbon monoxide with hydrogen (for instance synthesis gas) are well known. This reaction is highly exothermic and conventional cooling means are used for the removal of heat from the reaction zone. Additionally such a reactor is provided with means to recycle gas through the catalyst for equalizing the temperature in the catalyst bed. Preferably such a reactor is also provided with means to recycle the hydrocabonaceous product through the catalyst for equalizing the temperature of the catalyst bed, and further to avoid the formation of hydrocarbonaceous deposists on the catalyst.

When this reactor is to be shut-down the supply of carbon monoxide and hydrogen is interrupted. In the dome-like reactor space above the catalyst bed a large amount of reactant gas mixture present, and passes therethrough at a relatively low velocity. The reaction heat is insufficiently removed and hot spots are formed in the catalyst bed. These hot spots result in a deterioration of the performance of the catalyst.

The invention has for its object to provide a shut-down process which does not result in a deterioration of the performance of the catalyst and includes a passivation thereof.

The invention relates to a process for the shut-down of a reactor for the preparation of an at least partly liquid hydrocarbonaceous product by a catalytic reaction of carbon monoxide with hydrogen at elevated temperature and pressure and using a catalyst, which reactor is provided with cooling means and with means to recycle gas through the catalyst for temperature equalizing of the catalyst, comprising the steps of:

(i) interrupting the feed of synthesis gas;

(ii) depressurizing the reactor downstream of the catalyst, and providing the reactor upstream of the catalyst with inert gas; and

(iii) cooling the catalyst to ambient conditions.

Accordingly after the interruption of the supply of carbon monoxide and hydrogen (primary synthesis gas as well as recycled synthesis gas), a gas stream through the catalyst bed is maintained at a sufficient velocity, which gas stream becomes more and more inert by the increasing proportion of inert gas. The supply of inert gas is maintained until the catalyst is cooled down to ambient conditions. Then the catalyst can be unloaded and exposed to air without any further precautions.

When the reactor is provided with means to recycle liquid product through the catalyst, the process comprises further between step (ii) and step (iii) the step (iia) of cooling the catalyst to a temperature slightly above the solidification temperature of the liquid product; and (iib) of interrupting the recycling of the liquid product, so that initially the liquid product recycling is used for the cooling and temperature levelling and deposits of solidified hydrocarbons are avoided.

Since hydrogen is available in large amounts in the plant in which the reactor is used, hydrogen is preferably used as inert gas.

In order to reduce the amount of the reactant gas mixture in the dome-like space above the catalyst bed, it is advantageous to arrange spherical bodies in the reactor

space above the catalyst.

When the inert spherical bodies contain hydrogen releasable therefrom when the pressure in the reactor falls below the working pressure, hydrogen is automatically released in the reactor space above the catalyst when during the shut-down operation the supply of carbon monoxide and hydrogen is interrupted.

Hydrogen for use during the shut-down process is accumulated in or on the inert bodies during the normal operation of the reactor, when according to a first embodiment the inert spherical bodies comprise an interfacial membrane permeable to hydrogen and impermeable to carbon monoxide, or according to a second embodiment the inert spherical bodies comprise material hydrogen absorbs on under reaction conditions and desorbs from under shut-down conditions.

The invention relates further to a reactor suitable for carrying out the shut-down process, comprising a reactor housing provided with at least one catalyst section containing catalyst, which section is in communication with inlet means for synthesis gas, with product outlet means, with means for recycling gas, with means for depressurizing the catalyst section, arranged downstream of the catalyst section and with means for supplying inert gas to the catalyst section, arranged upstream from the catalyst section.

Finally the invention relates to a reactor for the preparation of at least partly liquid hydrocarbonaceous product in a convertor reactor, by catalytic reaction of carbon monoxide with hydrogen at elevated temperature and pressure, which reactor is provided with inlet means for synthesis gas, and product outlet means, wherein inert, spherical bodies are arranged in the reactor space above the catalyst.

The shut-down process according to the invention is particularly suitable for a reactor in which sythesis gas is converted into hydrocarbons, preferably having at least 10 carbon atoms per molecule; more preferably paraffinic hydrocarbons having at least 20 carbon atoms per molecule.

Normally synthesis gas is used as the gas feed for the

reactor. Synthesis gas contains as major compounds hydrogen and carbon monoxide; in addition it may contain carbon dioxide, water, nitrogen, argon and minor amounts of compounds having 1-4 carbon atoms per molecule, such as methane, methanol and ethene.

The synthesis gas is prepared in any matter known in the art, for instance by means of steam/oxygen gasification of hydrocabonaceous 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 hydrocabonaceous material with an oxygen-containing gas may be used to produce synthesis gas.

The process conditions in the reactor for the preparation of the at least partly liquid hydrocabonaceous product are: a temperature from 100-500°C, a total pressure from 1-200 bar abs. and a space velocity from 200-20,000 m^3 (S.T.P.) gaseous feed/m^3 reaction zone/hour. Preferred process conditions include a temperature from 150-300°C, a pressure from 5-100 bar abs. and a space velocity from 500-5000 m^3 (S.T.P.) gaseous fee/m^3 reaction zone/hour. The expression "S.T.P." as referred to hereinbefore means Standard Temperature (0°C) and Pressure (1 bas abs.). The molar ratio of hydrogen to carbon monoxide is normally 0.4-4 and preferably from 1.8-2.5.

Suitable catalysts for the preparation of (paraffinic) hydrocarbons from the synthesis gas contain at least a metal (compound) from Group VIII of the Periodic Table of Elements, preferably a non-noble metal, in particular cobalt, optionally in combination with a noble metal for instance ruthenium, on a refractory oxide carrier such a silica, alumina or silica-alumina, preferably silica. Furthermore these catalysts preferably contain at least one other metal (compound) form Group IVb and/or VIb of the Periodic Table of Elements. This metal or compound is preferably chosen from the group consisting of zirconium, titanium and chromium. The catalysts contain preferably from 3-60 parts by

weight 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 inert spherical bodies present in the dome-like reactor space above the catalyst bed may consist of a spherical ceramic scale filled with pressurized gas, which scale collapses when the pressure in the reactor drops below the operation pressure.

If hydrogen is used as inert gas, a supply of hydrogen may be automatically formed during the normal operation of the reactor. According to a first embodiment a supply of hydrogen is formed by diffusion of hydrogen into an inert spherical body through a semi-permeable membrane which is permeable to hydrogen and impermeable to other components of the synthesis gas. According to another embodiment of such a supply for hydrogen the inert spherical bodies consist at least partly of a material on which hydrogen is absorbed with preference over other components of the synthesis gas mixture. A nickel-samarium alloy may be used as an absorbent metal material.

If the reactor is provided with a liquid product recycling circuit, it is preferred that the inert spherical bodies are supported on a netting separating the dome-like reactor space from the catalyst bed.

Claims

1. Process for the shut-down of a reactor for the preparation of an at least partly liquid hydrocarbonaceous product by reaction of carbon monoxide and hydrogen at elevated temperature and pressure and using a catalyst, which reactor is provided with cooling means and with means to recycle gas through the catalyst for equalizing the temperature of the catalyst, comprising the steps of:

(i) interrupting the feed of synthesis gas;

(ii) depressurizing the reactor downstream of the catalyst, and providing the reactor upstream of the catalyst with inert gas; and

(iii) cooling the catalyst to ambient conditions.

2. Process as claimed in claim 1, wherein the reactor is provided with means to recycle liquid product through the catalyst, comprising between step (ii) and step (iii):

(iia) cooling the catalyst to a temperature slightly above the solidificatior temperature of the liquid product; and

(iib) interrupting the recycling of the liquid product.

3. Process as claimed in claim 2, wherein in step (iia) the catalyst is cooled to about 160-200°C.

4. Process as claimed in claim 1-3, wherein in step (ii) nitrogen gas is used as inert gas.

5. Process as claimed in claim 1-3, wherein in step (ii) hydrogen is used as inert gas.

6. Process as claimed in claim 1-5, wherein inert, spherical bodies are arranged in the reactor space above the catalyst.

7. Process as claimed in claim 5 and 6, wherein the inert spherical bodies contain hydrogen releasable therefrom when the pressure in the reactor falls below the working pressure.

8. Process as claimed in claim 7, wherein the inert

spherical bodies comprise an interfacial membrane permeable to hydrogen and impermeable to carbon monoxide.

9. Process as claimed in claim 7, wherein the inert spherical bodies comprise material which absorbs hydrogen under reaction conditions and desorbs it under shut-down conditions.

10. Process as claimed in claim 1-9, wherein inert, spherical bodies are arranged in the reactor space under the catalyst.

11. Reactor suitable for carrying out the shut-down process according to any of the preceding claims 1-10, comprising a reactor housing provided with at least one catalyst section containing catalyst, which section is in communication with inlet means for synthesis gas, with product outlet means, with means for recycling gas, with means for depressurizing the catalyst section, arranged downstream of the catalyst section and with means for supplying inert gas to the catalyst section, arranged upstream from the catalyst section.

12. Reactor as claimed in claim 11, wherein inert, spherical bodies are arranged in the reactor space above the catalyst.

13. Reactor as claimed in claim 11 or 12, wherein the inert spherical bodies contain hydrogen releasable therefrom when the pressure in the reactor falls below the working pressure.

14. Reactor as claimed in claim 13, wherein the inert spherical bodies comprise an interfacial membrane permeable to hydrogen and impermeable to carbon monoxide.

15. Reactor as claimed in claim 11-14, wherein the inert spherical bodies comprise material which absorbs hydrogen under reaction conditions and desorbs it under shut-down conditions.

16. Reactor as claimed in claim 11-15, wherein inert, spherical bodies are arranged in the reactor space under the catalyst.

17. Reactor for the preparation of at least partly

liquid hydrocarbonaceous product in a convertor reactor, by catalytic reaction of carbon monoxide with hydrogen at elevated temperature and pressure, which reactor is provided with inlet means for synthesis gas, and product outlet means, wherein inert, spherical bodies are arranged in the reactor space above the catalyst.

18. Reactor as claimed in claim 17, wherein the inert spherical bodies contain hydrogen releasable therefrom when the pressure in the reactor falls below the working pressure.

19. Reactor as claimed in claim 18, wherein the inert spherical bodies comprise an interfacial membrane permeable to hydrogen and impermeable to carbon monoxide.

20. Reactor as claimed in claim 17-19, wherein wherein the inert spherical bodies comprise material which absorbs hydrogen under reaction conditions and desorbs from under shut-down conditions.

21. Reactor as claimed in claim 17-20, wherein inert, spherical bodies are arranged in the reactor space under the catalyst.

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