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(54) Regeneration process for a Fischer-Tropsch catalyst

(57) Process for the regeneration of a catalyst used for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, comprising the steps of:

(i) washing the catalyst with hydrocarbons;
(ii) drying the washed catalyst;
(iii) treating the dried catalyst at elevated temperature with a gas containing about 0.1-3 % by vol oxygen.

The washing may occur in two stages, the first at 100-170°C being with paraffin, the second at 20-90°C being with naphtha or hexane.

The oxygen in stage (iii) may be diluted with nitrogen.

Specified catalyst components are cobalt with ruthenium on a carrier of silica and/or alumina. Zr, Ti or Cr may be included, singly or in combination.

Regeneration process for a Fischer-Tropsch catalyst

The invention relates to a regeneration process of a catalyst used for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen.

The preparation of hydrocarbons from a carbon monoxide and hydrogen mixture by contacting this mixture at elevated temperature and pressure with a specific catalyst is known in the literature as the Fischer-Tropsch hydrocarbon synthesis process. Dependent on the type of Fischer-Tropsch catalyst used a great variety of hydrocarbons can be synthesized, comprising branched and unbranched paraffins and olefins as well as oxygen containing organic compounds. Recently new catalysts were developed to synthesize relatively heavy paraffins having more than 20 carbon atoms per molecule which in a subsequent step can be very selectively hydrocracked to hydrocarbon mixtures of which the boiling range lies substantially between about 150 and 360°C. These middle distillates have excellent combustion properties.

During the regeneration of a catalyst the reaction products, particularly the very heavy paraffins, and carbonaceous deposits should be removed from the catalyst surface.

DE-B-1,017,151 discloses a method for the regeneration of a Fischer-Tropsch catalyst, in which the catalyst is subjected to an in-situ extraction using diesel oil and a gasoline fraction, in that order. The extraction results in a removal of the heavy paraffins, but carbonaceous deposits are retained and accumulate further during the subsequent catalytic preparation of hydrocarbons. Furthermore the activity of the catalyst and the operation time until the next extraction regeneration are reduced.

The spent catalyst may be regenerated by oxidation with oxygen. However, direct admission of air sets the catalyst on fire when a temperature of about 180°C is reached.

Lowering the amount of oxygen in the regeneration gas decreases the maximum temperature reached during burning. Due to the heat generated during the oxidation heavy paraffines adhered to the catalyst are evaporated and condensed on colder parts of the reactor leading to a blocking of the gas pipes.

The object of the invention is a regeneration process in which heavy paraffins and carbonaceous deposits are removed from the catalyst, whereas the aforementioned drawbacks are avoided.

Therefore the process of the present invention for the regeneration of a catalyst used for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, comprises the steps of:

(i) washing the catalyst with hydrocarbons;
(ii) drying the washed catalyst;
(iii) treating the dried catalyst at elevated temperature with a gas containing about 0.1-3 % by vol oxygen.

Preferably the extraction of heavy paraffins comprises two washing steps. In the first washing step using a first hydrocarbon the heavy paraffins are washed off, while the catalyst is impregnated with this first hydrocarbon. Then a second hydrocarbon is substituted for the first hydrocarbon, which second hydrocarbon is more easily removed during the subsequent drying treatment.

In order to maximize the extraction of heavy paraffins with the first hydrocarbon a hot first hydrocarbon is used, of which the temperature is in the range from about 100-170°C, preferably from about 120-150°C. An example of the first hydrocarbon is kerosine.

The extend of the substitution of the second hydrocarbon for the first hydrocarbon in the catalyst and the time necessary for a optimal substitution are reduced when in the washing step (ib) the temperature of the second hydrocarbon is in the range from about 20-90°C, preferably 25-80°C. Examples of the second hydrocarbon are naphtha, and hexane.

The catalyst apt for regeneration in the process of the present invention is used for the catalytic conversion of a gas mixture comprising carbon monoxide and hydrogen, into hydrocarbons. This gas mixture is normally referred to a synthesis gas and comprises next to the major compounds carbon monoxide and hydrogen minor amounts of carbon dioxide, water, nitrogen, argon and compounds having 1-4 carbon atoms per molecule such as methane, methanol and ethane.

Catalysts to be regenerated contain at least a metal (compound) from Group VIII 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 or alumina. Furthermore, the catalysts preferably contain at least one other metal (compound) from Group IVb and/or VIb, most preferably chosen form 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 carrier particles can be prepared by means of any method known in the art, such as pressing or extruding of powdry catalyst material, if desired together with a binder material. Catalyst carrier 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. Alumina based carriers are preferably made by extrusion.

Experiment

A spent Fischer-Tropsch catalyst was extracted with kerosine (120°C) and with naphtha (80°C). Then the catalyst is dried with nitrogen (16 hours, 80°C) resulting in the almost complete removal of naphtha.

After the extraction treatment about 90% of the catalyst contaminants consisting essentially of heavy paraffins, were removed.

Finally the remaining catalyst contaminants were removed by burning off using nitrogen comprising 1% by vol oxygen.

Claims

1. Process for the regeneration of a catalyst used for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, comprising the steps of:

(i) washing the catalyst with hydrocarbons;
(ii) drying the washed catalyst;
(iii) treating the dried catalyst at elevated temperature with a gas containing about 0.1-3 % by vol oxygen.

2. Process as claimed in claim 1, wherein said gas used in step (iii) contains 0.5-1.1 % by vol oxygen.

3. Process as claimed in claim 1 or 2, wherein step (i) comprises the steps of:

(ia) washing the catalyst with a first hydrocarbon; and
(ib) washing the catalyst with a second hydrocarbon.

4. Process as claimed in claim 3, wherein in the washing step (ia) the temperature of the first hydrocarbon is in the range from about 100-170°C, preferably from about 120-150°C.

5. Process as claimed in claim 4, wherein the first hydrocarbon comprises kerosine.

6. Process as claimed in claim 3-5, wherein in the washing step (ib) the temperature of the second hydrocarbon is in the range from about 20-90°C, preferably 25-80°C.

7. Process as claimed in claim 6, wherein the second hydrocarbon is selected from the group consisting of naphtha, and hexane.

8. Process for the regeneration of a catalyst as claimed in claim 1, substantially as described hereinbefore.

9. Process for the preparation of hydrocarbons by reaction of hydrogen and carbon monoxide comprising the use of a catalyst regenerated according to a process as claimed in any one or more of the claims 1-8.

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(54) Production of synthesis gas

(57) A process for the production of synthesis gas characterized by:

(a) partially oxidizing a carbonaceous fuel using air or oxygen enriched air,

(b) reacting carbon monoxide contained in the stream from step (a) with steam, to convert the majority of the carbon monoxide to carbon dioxide and hydrogen,

(c) passing the stream from step (b) through a permeable membrane separation device in which the carbon dioxide and hydrogen largely permeates through whilst the nitrogen does not

(d) utilizing a catalyst to cause combustible compounds present in the non-permeate stream (c) to react exothermally to raise the temperature of the stream.

The stream from step (d) may be expanded to gain shaft horsepower.

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SPECIFICATION

Synthesis gas production using air

This invention relates to the production of a synthesis gas containing predominantly carbon dioxide and hydrogen, from a carbonaceous fuel.

Currently synthesis gas is usually produced either by partially oxidizing fuel using oxygen, or alternatively the fuel is reacted with steam in a tubular steam reformer.

This invention describes the use of air or oxygen enriched air to partial oxidise the fuel. In this document, oxygen enriched air is air containing up to 80% oxygen.

The invention comprises partially oxidizing the fuel with air, or oxygen enriched air, utilising technology such as that developed by Texaco Development Corporation. The resulting gas mixture contains hydrogen, nitrogen, carbon monoxide and lesser amounts of carbon dioxide and methane. To this gas is added water (steam). This may take the form of a liquid water quench, which quench washes out particulate matter arising from the fuel oxidized. However, the water may simply be added after the gas is cooled, where cooling may entail raising of steam. Alternatively or additionally steam may be added with fuel to the partial oxidation reactor.

The steam-containing mixture is passed to a carbon monoxide shift reactor unit which may employ both high temperature and low temperature shift catalysts.

The effluent from the shift unit may be cooled to remove water vapour but is passed to a permeable membrane unit from which a nitrogen containing stream (the non permeate) is obtained. This stream also contains a significant amount of carbon monoxide and methane together with some hydrogen. In the permeable membrane unit most of the hydrogen and carbon dioxide permeates through the membrane there- by separating these components from bulk of the nitrogen. This separated stream forms the synthesis gas.

Between the effluent of the partial oxidation reactor and prior to the permeable membrane device there may be an expander from which shaft horse power may be gained.

The permeable membrane unit may comprise a number of units connected in series or parallel. A number of permeate take off points may be used, streams from such points may be fed to various stages of a syngas compressor thereby saving syngas recompression power. The permeable membrane device may itself include recycling streams.

Some of the permeate streams may be recycled back to the shift unit.

The non permeate stream from the permeable membrane device contains not only nitrogen but also combustible compounds—carbon monoxide, methane and hydrogen, but in amounts which may well not sustain a flame. In order to utilise their energy value air, or oxygen enriched air, may for example, be taken from the compressor supplying the partial oxidation reactor and combined with the stream. This stream is then passed through a catalytic oxidation unit to raise it temperature prior to expansion to gain shaft horse power. There may be more than one catalyst/expansion stage.

Additionally any carbon oxides and hydrogen may be catalytically reacted to methane to raise the temperature of the stream.

In certain circumstances the fron end of the flowsheet might be enhanced by the addition of the following. Having compressed air it is passed through permeable membrane separation device to gain two streams. The non permeate nitrogen enriched stream is substantially at the compressor out-put pressure. This stream may be heated and expanded to gain shaft power. The oxygen enriched stream is fed to the partial oxidation unit in, the manner described above.

Advantages of this flowsheet are the removal of the need for a tubular steam reformer and oxygen plant.

The syngas comprises predominantly carbon dioxide and hydrogen. These may be reacted together to produce a stream containing carbon monoxide, water and hydrogen. The water may be condensed out before the other gases are fed to a synthesis unit.

The syngas produced by this invention may be utilised in the production e.g. of alcohols, Fischer-Tropsch type of synthesis or other chemicals e.g. ethylene oxide, methyl tertiary butyl ether (MTBE), acetic acid.

In this application there is provided an invention which is a process for the production of synthesis gas characterized by:

(a) partially oxidizing a carbonaceous fuel using air or oxygen enriched air,

(b) reacting carbon monoxide contained in the stream from step (a) with steam, to convert the majority of the carbon monoxide to carbon dioxide and hydrogen,

(c) passing the stream from step (b) through a permeable membrane separation device in which the carbon dioxide and hydrogen largely permeates through whilst the nitrogen does not

(d) utilizing a catalyst to cause combustible compounds present in the non-permeate stream from stream (c) to react exothermically to raise the temperature of the stream.

The stream from (d) may be expanded to gain shaft horsepower and the permeate stream from step (d) may be used to produce alcohol, MTBE, ethylene oxide, acetic acid.

CLAIMS

1. A process for the production of synthesis gas characterized by

(a) partially oxidizing a carbonaceous fuel using air or oxygen enriched air,

(b) reacting carbon monoxide contained in the stream from step (a) with steam, to convert the majority of the carbon monoxide to carbon dioxide and hydrogen,

(c) passing the strean from stop (b) through a permeable membrane separation device in which the carbon dioxide and hydrogen largely permeates through whilst the nitrogen does not

(d) utilizing a catalyst to cause combustible compounds present in the non-permeate stream from stream (c) to react exothermically to raise the temperature of the stream.

2. A process as described in claim 1 wherein the stream from step (d) is expanded to gain shaft horsepower.

3. A process as described in claim 1 wherein the permeate stream from step (d) is used to produce alcohol, MTBE, ethylene oxide, acetic acid.

4. A process substantially as herein before described.

5. Products made by the process of this invention.

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