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(54) PROCESS FOR THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE

(54) PROCEDE POUR L'HYDROGENATION CATALYTIQUE D'OXYDE DE CARBONE

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The invention relates to a process for the catalytic hydrogenation of carbon monoxide, and particularly to a method of carrying out such a process in stages and in a liquid medium in the presence of an iron catalyst.

It is an object of the invention to provide a process for increasing the yield and for increasing the efficiency of the catalyst when the hydrogenation of carbon monoxide is carried out in a liquid medium in the presence of an iron catalyst.

10 It is known that the hydrogenation of carbon monoxide in the presence of an iron catalyst in the gaseous phase is most advantageously carried out in several stages, because, due to the high space velocity then used, the CO/H₂ consumption ratio may be substantially adjusted to the CO-H₂ ratio in the fresh gas, so that the yield may be substantially increased. In contrast therewith, when the hydrogenation of carbon monoxide is carried out in a liquid medium, the stage-wise process has hitherto not
20 been used, because in this case the CO/H₂ consumption ratio cannot be appreciably influenced by an increased velocity of the gas, and because, when synthesis gases rich in carbon monoxide are used, it is possible to obtain in a single stage the same yields as are obtained in several stages in a synthesis carried out in the gaseous phase with water gas or synthesis gases rich in hydrogen. It has been found that it is particularly advantageous to use a gas in which the CO/H₂ ratio is 3 : 2, because thereby it is possible to obtain the yields
30 referred to of useful hydrocarbons as well as a high efficiency of the catalyst.

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Although in the hydrogenation of carbon monoxide in a liquid medium, it is not possible appreciably to influence the CO/H₂ consumption ratio and thus the total yield of synthesis products by carrying out the process in stages, it has been found, according to the invention, that in stage-wise operation the yield of useful hydrocarbons, that is to say of hydrocarbons having 3 or more carbon atoms in the molecule, may be increased to 165 - 185 grams per normal cubic metre of CO + H₂, and the efficiency of the catalyst may be substantially increased by first operating the synthesis reactors in parallel for more than six hours, preferably for more than twelve hours, for example, for 24-72 hours, with fresh gas at a load of less than 3 normal litres of CO + H₂ per gram of Fe per hour, the load of fresh gas being increased continuously or in stages as the CO-conversion and/or synthesis gas contraction increases, up to 3 normal litres of CO + H₂ per gram of Fe per hour, the synthesis reactors being only then switched to stagewise operation, while, if necessary, increasing the load of synthesis gas still further. As a result of the catalyst being initially loaded with but a small quantity of synthesis gas, an increased CO conversion is obtained while less methane and less carbon are formed. If the catalyst is not started in accordance with the invention, but is at once started with the synthesis reactors connected in series, higher temperatures are necessary to obtain equally high CO-conversions. As a result, an increased formation of methane and an increased separation of carbon will occur at the expense of the yield of useful synthesis products. Moreover,

the efficiency of the catalyst is reduced by the increased formation of carbon.

It has been found to be particularly advantageous to start the catalyst first with a load of 0.8 - 1.2 normal litres of $\text{CO} + \text{H}_2$ per gram of Fe per hour, and to increase the load of fresh gas continuously or in stages to 2 - 2.7 normal litres of $\text{CO} + \text{H}_2$ per gram of Fe per hour as the conversion of CO and/or the gas contraction increases.

10 The strongest effect in the process according to the invention may be obtained by using a precipitated catalyst which has been dried at a temperature within the range $200^\circ - 500^\circ\text{C}$, preferably at a temperature within the range $250^\circ - 400^\circ\text{C}$, by means of a gas, such as air, the drying being carried out to such an extent that the catalyst contains less than 0.3 %, preferably less than 0.1 %, of water.

Moreover, a rise in temperature, of from 20°C to 100°C , preferably of from 30°C to 60°C , in the catalyst suspension in the upward direction, that is to say, in
20 the direction of the flow of synthesis gas, has an extremely advantageous effect on the efficiency of the catalyst and the formation of unsaturated hydrocarbons.

In the process according to the invention it has been found to be advantageous to remove the carbon dioxide, in whole or in part, from the synthesis gas between the stages. For this purpose it is advantageous to use a hot solution of K_2CO_3 for the reason that hydrocarbons are not washed out by the use of such a solution.

30 The process according to the invention is

illustrated by the following Examples:-

EXAMPLE 1

Two synthesis reactors having a length of 5 metres and an internal diameter of 5 centimetres were each filled with 4.5 kilograms of a 10 % catalyst suspension. The catalyst used, which, in addition to iron, only contained 0.2 % of Cu and 0.4 % of K_2CO_3 , was precipitated with ammonia from an iron nitrate/copper nitrate solution, impregnated with K_2CO_3 , dried for 12 hours at $350^\circ C$ while air was passed over it, and ground in a ball mill together with crude scale paraffin wax (Paraffingatsch). The two reactors were heated to $280^\circ C$ while nitrogen was passed through the catalyst suspension. When the temperature of $280^\circ C$ was reached, the gas passed through the reactors was changed to synthesis gas ($CO : H_2 = 3 : 2$). The load amounted to 1 normal litre of synthesis gas, which corresponded approximately to 0.9 normal litres of $CO + H_2$, per gram of Fe per hour. Over the first 4 hours, the gas load was increased continuously, in accordance with the CO conversion and the synthesis gas contraction, to 2.4 normal litres of synthesis gas (approximately 2.2 normal litres of $CO + H_2$) per gram of Fe per hour. After 3 hours on stream, a CO conversion of 90 % was attained. With this load, the two reactors continued to be operated for a further 48 hours while the temperature was reduced. When the temperature had dropped to $250^\circ C$, the two reactors were connected in series, that is to say, the synthesis was changed to stage-wise operation. The load of reactor I (stage I) was increased to 6 normal litres of synthesis gas

(approximately 5.4 normal litres of $\text{CO} + \text{H}_2$). After having been cooled to room temperature, the tail gas of stage I was passed through reactor II (stage II). The synthesis temperature was controlled in such manner that 60 % - 65 % of the carbon monoxide in the synthesis gas was converted in the first stage, and 30 % - 35 % of the carbon monoxide was converted in the second stage, so that the total conversion of carbon monoxide was fairly constant at 95 %.

10 In spite of the increased CO conversion, the formation of methane did not increase, so that an average yield of 169 - 172 grams of useful hydrocarbons per normal cubic metre of $\text{CO} + \text{H}_2$ was obtained, which equals an increase in yield of roughly 4 % - 5 %. The efficiency of the catalyst in the first stage was about 800 grams, and that of the second stage 500 grams, of hydrocarbons per gram of Fe, so that the efficiency of the catalyst of the first stage had risen by 300 grams of hydrocarbons per gram of Fe.

20 Example 2 shows that it is also possible to increase the catalyst efficiency of the subsequent stages.

EXAMPLE 2

Three synthesis reactors each having a length of 6 metres and an internal diameter of 5 centimetres were charged with the same catalyst as that used in Example 1. The reactors were heated in such manner that the temperature in the catalyst suspension was 235°C at the gas inlet and 282°C at the gas outlet. At this temperature, the three reactors were first started with
30 a load of fresh gas of 1.1 normal litres, corresponding

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approximately to 1.0 normal litres of CO + H₂
(CO : H₂ = 3 : 2) per gram of Fe per hour. During the
first six hours, the gas load was continuously increased
in accordance with the CO conversion and the synthesis gas
contraction respectively, to 2.5 normal litres of fresh
gas, equivalent to approximately 2.3 normal litres of
CO + H₂ per gram of Fe per hour. A CO conversion of
over 90 % was thus obtained after five hours. The three
reactors were operated for a further 48 hours under these
10 conditions, while the temperature was slowly reduced.
When the temperature in the catalyst suspension was 215^oC
at the gas inlet and 252^oC at the gas outlet, the reactors
were connected in series, that is to say, the synthesis was
changed to stagewise operation. Reactor I (stage I)
was charged with 10 normal litres of fresh gas, equivalent
to approximately 9 normal litres of CO + H₂, per gram of
Fe per hour. The CO conversion amounted to approximately
45 %. The tail gas of the first stage was then passed
through a CO₂ scrubbing tower (hot K₂CO₃ solution) and a
20 condenser into reactor II (stage II) in which all of the
carbon monoxide except for approximately 20 %, was con-
verted. The tail gas of the second stage was similarly
passed through a CO₂ scrubber and a condenser to be
immediately thereafter substantially completely converted
in the third reactor (stage III), the total CO conversion
being from 97 % to 99 %.

Particularly striking features of the hydrogenation
of carbon monoxide in the liquid phase carried out in
accordance with the invention, are the constancy of
30 the synthesis temperature, the unusually high CO

conversion of an average of 98 % with a low methane formation, and the long active life and efficiency of the catalyst even in the subsequent stages.

The average yield of useful hydrocarbons (C_3+) amounts to 178 - 182 grams per normal cubic metre of $CO + H_2$, the efficiency of the catalyst being approximately 1200 grams of hydrocarbons per gram of Fe in the first stage and approximately 1050 grams per gram of Fe in the second stage. In the third stage, the efficiency is lower. However, the catalyst is still not exhausted.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A process for the hydrogenation of carbon monoxide, which comprises passing a fresh synthesis gas containing carbon monoxide and hydrogen in synthesis proportions upwardly through a suspension of an iron catalyst in a liquid medium under synthesis conditions of temperature and pressure, the catalyst suspension being contained in two or more reactors connected in parallel and through which the fresh synthesis gas is passed for at least 6 hours at a rate of less than 3 normal litres of CO + H₂ per gram of total iron in the catalyst per hour, continuously or otherwise increasing the space velocity of the fresh synthesis gas to a value not exceeding 3 normal litres of CO + H₂ per gram of total iron per hour as the CO conversion and/or the gas contraction increases, and thereafter passing the gas through the several reactors in series to convert the process into one of multi-stage operation.

2. A process for carrying out the hydrogenation of carbon monoxide in two or more reactors in the presence of an iron catalyst suspended in a liquid medium, in which the reactors are first brought on-stream by being connected in parallel for more than 6 hours, using fresh synthesis gas at a space velocity of less than 3 normal litres of CO + H₂ per gram of Fe per hour,

increasing the space velocity of the fresh synthesis gas continuously or in stages up to a value not exceeding 3 normal litres of CO + H₂ per gram of Fe per hour as the CO conversion and the synthesis gas contraction respectively increase, and thereafter switching the reactors to stage-wise operation during which the synthesis gas is passed through the several reactors in series, if necessary with further increase in the space velocity of the synthesis gas.

3. A process according to claim 1 or claim 2, in which the reactors are connected in parallel for more than 12 hours,

4. A process according to claim 1 or claim 2, in which the reactors are connected in parallel for a period within the range 24 - 72 hours.

5. A process according to claim 1 or claim 2, in which the catalyst is first brought on-stream with from 0.8 to 1.2 normal litres of CO + H₂ per gram of Fe per hour, the space velocity being increased in stages or continuously to a value within the range 2 - 2.7 normal litres of CO + H₂ per gram of Fe per hour before the change-over to stage-wise operation is effected.

6. A process according to claim 1 or claim 2, in which a precipitated catalyst is used, the catalyst having been dried at a temperature in the range 200° - 500°C in a stream of gas, such as air, to such a degree that it contains less than 0.3% by weight of water.

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7. A process according to claim 1 or claim 2, in which a precipitated catalyst is used, the precipitated catalyst having been dried at a temperature in the range 250° - 400°C in a stream of gas, such as air, until its water content is less than 0.3% by weight.

8. A process according to claim 1 or claim 2, in which a precipitated catalyst is used, the precipitated catalyst having been dried at a temperature in the range 250° - 400°C in a stream of gas, such as air, to bring its content of water to less than 0.1% by weight.

9. A process according to claim 1 or claim 2, in which the temperature in the catalyst suspension increases upwardly in the direction of flow of the synthesis gas, to the extent of from 20°C to 100°C .

10. A process according to claim 1 or claim 2, in which the temperature in the catalyst suspension increases upwardly in the direction of flow of the synthesis gas, to the extent of from 30°C to 60°C .

11. A process according to claim 1 or claim 2, in which carbon dioxide is removed from the synthesis gas between the individual stages during the stage-wise operation.

12. A process according to claim 1 or claim 2, in which carbon dioxide is removed, by scrubbing with a hot, aqueous solution of potassium carbonate, from the synthesis gas between the

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individual stages during the stage-wise operation.

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