PATENT SPECIFICATION

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COMPLETE SPECIFICATION

A Process for the Catalytic Hydrogenation of Carbon Monoxide

...GESELLSCHAFT ... appreciably to influence the CO/H_2 consump- ... yield of synthesis

ERRATA

SPECIFICATION No. 787,122

Page 2, line 42, *after* "was" *insert* "then"
Page 2, line 51, *for* "feed" *read* "fresh"
Page 2, line 53, *for* "feed" *read* "fresh"

THE PATENT OFFICE,
21st April, 1958.

ously carried out in several stages, ... to the high space velocity then used, the CO/H_2 consumption ratio may be substantially adjusted to the $CO—H_2$ 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 multi-stage process has hitherto not been used, because in this case the CO/H_2 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/H_2 ratio is 3:2, because thereby it is possible to obtain the same yields of hydrocarbons containing 3 or more carbon atoms in the molecule as well as a high efficiency of the catalyst.

Although in the hydrogenation of carbon monoxide in a liquid medium, it is not possible

quantity of fresh synthesis gas, ... CO conversion is obtained while less methane and less carbon are formed. If the process 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 hydrocarbons containing 3 or more carbon atoms in the molecule. Moreover, the efficiency of the catalyst is reduced by the increased formation of carbon.

The term "fresh synthesis gas" is to be understood as denoting a gas mixture containing carbon monoxide and hydrogen, in which carbon monoxide and hydrogen together form more than 50% by volume of the gas mixture. The ratio of $CO:H_2$ in the fresh synthesis gas will be within the limits known in the synthesis of hydrocarbons from carbon monoxide and hydrogen in the presence of an iron catalyst.

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A Process for the Catalytic Hydrogenation of Carbon Monoxide

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, a German Company, of Homberg/Niederrhein, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

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.

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/H_2 consumption ratio may be substantially adjusted to the $CO—H_2$ 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 multi-stage process has hitherto not been used, because in this case the CO/H_2 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/H_2 ratio is 3:2, because thereby it is possible to obtain the same yields of hydrocarbons containing 3 or more carbon atoms in the molecule as well as a high efficiency of the catalyst.

Although in the hydrogenation of carbon monoxide in a liquid medium, it is not possible appreciably to influence the CO/H_2 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 multi-stage operation the yield of hydrocarbons having 3 or more carbon atoms in the molecule, may be increased to 165—185 grams per normal cubic metre of $CO+H_2$, and the efficiency of the catalyst may be substantially increased by first operating the reactors in parallel for more than six hours, preferably for more than twelve hours, for example, for 24—72 hours, with fresh synthesis gas at a load of less than 3 normal litres of $CO+H_2$ per gram of Fe per hour, the load of fresh gas being increased continuously or at intervals as the CO-conversion and synthesis gas contraction increases, up to 3 normal litres of $CO+H_2$ per gram of Fe per hour, the reactors being only then changed to multi-stage 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 fresh synthesis gas, an increased CO conversion is obtained while less methane and less carbon are formed. If the process 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 hydrocarbons containing 3 or more carbon atoms in the molecule. Moreover, the efficiency of the catalyst is reduced by the increased formation of carbon.

The term "fresh synthesis gas" is to be understood as denoting a gas mixture containing carbon monoxide and hydrogen, in which carbon monoxide and hydrogen together form more than 50% by volume of the gas mixture. The ratio of $CO:H_2$ in the fresh synthesis gas will be within the limits known in the synthesis of hydrocarbons from carbon monoxide and hydrogen in the presence of an iron catalyst.

It has been found to be particularly advantageous to start the catalyst first with a load of 0.8—1.2 normal litres of $CO+H_2$ per gram of Fe per hour, and to increase the load of fresh synthesis gas continuously or at intervals to 2—2.7 normal litres of $CO+H_2$ per gram of Fe per hour as the conversion of CO and the gas contraction increases.

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°—500° C., preferably at a temperature within the range 250°—400° 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 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.

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 charged 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. The precipitate was impregnated with K_2CO_3, dried for 12 hours at 350° C. whilst air was passed over it, and ground in a ball mill with crude scale paraffin wax (Paraffingatsch), the suspending medium. The two reactors were heated to 280° C. while nitrogen was passed through the catalyst suspension. When the temperature of 280° C. was reached, the gas passed through the reactors was changed to feed synthesis gas ($CO:H_2=3:2$). The load amounted to 1 normal litre of feed 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° C. the two reactors were connected in series, that is to say, the synthesis was changed to multi-stage operation. The load of reactor I (stage I) was increased to 6 normal litres of synthesis gas (approximately 5.4 normal litres of $CO+H_2$). 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 is fairly constant at 95%.

In spite of the increased CO conversion, the formation of methane did not increase, so that an average yield of 169—172 grams of hydrocarbons containing 3 or more carbon atoms per molecule per normal cubic metre of $CO+H_2$ was obtained, an increase in yield of roughly 4%—5% over that obtained during operation of the reactors in parallel. 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.

In the interval between the 429th and the 453rd hour on stream, 171.2 grams of organic compounds containing three or more carbon atoms in the molecule and of the composition given below, were obtained per normal cubic metre of $CO+H_2$:—

	Grams
C_3+C_4 hydrocarbons	44.2
C_5 hydrocarbons and higher hydrocarbons boiling below 200° C.	89.5
Hydrocarbons boiling in the range 200°—300° C.	21.3
Hydrocarbons boiling above 300° C.	14.5
Alcohols	1.7
	171.2

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 centimeters 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 in parallel with a load of fresh synthesis gas of 1.1 normal litres, corresponding approximately to 1.0 normal litres of $CO+H_2$ ($CO:H_2=3:2$), 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 synthesis gas, equivalent to approximately 2.3 normal litres of $CO+H_2$, 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 conditions, while the temperature was slowly reduced. When the temperature in the catalyst suspension was 215° C. at the gas inlet and 252° C. at the gas outlet, the reactors were connected in series, that is to say, the synthesis was changed to multi-stage operation. Reactor I (stage I) was charged with 10 normal litres of fresh synthesis gas, equivalent to approximately 9 normal litres of $CO+H_2$, 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 CO_2 scrubbing tower (hot K_2CO_3 solution) and a condenser into reactor II (stage II) in which all of the carbon monoxide except for approximately 20%, was converted. The tail gas of the second stage was similarly passed through a CO_2 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 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 hydrocarbons containing 3 or more carbon atoms in the molecule 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.

In the interval between the 424th and 448th hour on stream, 180.7 grams of synthesis products having the composition given below were obtained per normal cubic metre of $CO+H_2$:—

	Grams
C_3+C_4 hydrocarbons	38.6
C_5 hydrocarbons and higher	
Hydrocarbons boiling below 200° C.	101.5
Hydrocarbons boiling in the range 200°—300° C.	21.7
Hydrocarbons boiling above 300° C.	17.1
Alcohols	1.8
	180.7

What we claim is:—

1. A process for carrying out the hydrogenation of carbon monoxide in the presence of an iron catalyst suspended in a liquid medium in two or more reactors, in which the process is first started with the reactors connected in parallel for a period of more than 6 hours using fresh synthesis gas at a load of less than 3 normal litres of $CO+H_2$ per gram of Fe per hour, increasing the fresh synthesis gas load continuously or at intervals to a value not exceeding 3 normal litres of $CO+H_2$ per gram of Fe per hour as the CO conversion and the synthesis gas contraction respectively increase, and thereafter passing the fresh synthesis gas through the several reactors in series to convert the process into one of multi-stage operation.

2. A process according to Claim 1, in which the load of fresh synthesis gas in increased after converting the process to multi-stage operation.

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 any one of the preceding claims, in which the reactors are connected in parallel for a period within the range 24—72 hours.

5. A process according to any one of the preceding claims, in which the catalyst is first started with from 0.8 to 1.2 normal litres of $CO+H_2$ per gram of Fe per hour, the load being increased at intervals or continuously to a value within the range 2—2.7 normal litres of $CO+H_2$ per gram of Fe per hour as the CO conversion increases and before the change-over to multi-stage operation.

6. A process according to any one of the preceding claims, in which a precipitated catalyst is used, the catalyst having been dried at a temperature in the range 200°—500° C. whilst a gas, such as air, was passed over it, to such a degree that it contains less than 0.3% by weight of water.

7. A process according to Claim 6, in which the drying of the precipitated catalyst was effected at a temperature in the range 250°—400° C.

8. A process according to Claim 6 or Claim 7, in which the precipitated catalyst was dried to bring its content of water to less than 0.1% by weight.

9. A process according to any one of the preceding claims, in which the temperature in the catalyst suspension increases upwardly in the direction of flow of the gases, to the extent of from 20° C. to 100° C.

10. A process according to Claim 9, in which the temperature in the catalyst suspension increases to the extent of from 30° C. to 60° C.

11. A process according to any one of the preceding claims, in which the carbon dioxide is removed from the synthesis gas between the individual stages during multi-stage operation.

12. A process according to Claim 11, in which the carbon dioxide is removed by scrubbing with a hot, aqueous solution of potassium carbonate.

13. A process for the hydrogenation of carbon monoxide in multi-stage operation in the presence of an iron catalyst suspended in a liquid medium, substantially as hereinbefore described.

14. A process for the hydrogenation of carbon monoxide, substantially as hereinbefore described in Example 1 or Example 2.

15. Hydrocarbons whenever obtained by the process claimed in any one of the preceding claims.

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