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Procedure For The Performance Of Carbon Monoxide Hydrogenation Using Contacts Slurried In A Fluid Medium
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Economic processing of catalytic carbon monoxide hydrogenation in the fluid phase presents substantial difficulties. Thus, for instance, it is impossible to carry out a fluid phase benzene synthesis in one step in a correspondingly high, agitated container. As soon as a higher degree of conversion is to be achieved in this form of processing, unacceptable high quantities of methane occur. No better result is obtained even when, in the place of agitators, very high fluid columns are used in which the contact is slurried while the carbon monoxide-hydrogen mixture enters at the bottom of the fluid column. It has been observed that by increasing the fluid column from, for example, 3 m to between 4 to 9 m, only a minimal increase of the conversion can be achieved.

Numerous serial steps have already been used when working in the fluid catalyst phase. In this process, columns were used that are equipped with submerged, bell or sieve bottoms, applications in which the fluid contact phase, without including the foam layer, was only a few centimeters high. More or less satisfactory reactions, however, could only be achieved with this method if work was carried out with a very large apparatus, which was very difficult to handle and technically monitor.

It has been found that the catalytic fluid phase carbon monoxide hydrogenation can be carried out in a very simple and economical manner if synthesis gases containing carbon monoxide and hydrogen flow, in a highly dispersed separation, in a stepped manner through fluid columns of only 20 to 50 centimeters height arranged in series and, if plates of ceramic material that have been sintered in accordance with the discovery are used for the distribution of the gases. Particularly useful are fluid columns of approximately 90 cm height arranged in series. In this method of working, no, or at least no complete, separation of the entering synthesis products is necessary. For example, use is made of porous clay plates, which, with a gas flow per hour of 7 l per cm² have a pressure resistance of 600 to 2000 mm water column. These types of sintered plates are arranged in a column above each other and form the border surfaces of the individual synthesis steps. The gas is separated from the fluid before the next base and distributed again by the next higher sinter plate.

The technical success achieved in this manner is made clear by the following comparison figures.

In an intermediate hydrocarbon mixture of a suitable boiling range made of cobalt catalyst slurry contained in a 3 m high pipe of 25 mm clear width with, a suitable heating arrangement, such as a water jacket and which is heated to around 190°, a carbon monoxide - hydrogen mixture, was introduced from below with the aid of a sintered porcelain plate at 10 at. pressure. This resulted in approximately 50 to 60 % conversion of CO/H₂ mixture to substantially normally fluid hydrocarbon substances. As soon as the increase in temperature had improved the extent of the conversion, there occurred very quickly a fast increase of methane formation, which made the synthesis operation completely uneconomical.

In a second example, the reaction pipe used was divided by several sinter plates into individual sections whereby there was a fluid column of 90 cm above each sinter plate in which the required catalyst quantity was in suspension. Above this, there was a gas space of approximately 10 cm height and then a new sinter plate, which again distributed the gas mixture in a highly dispersed manner. In this manner the above-mentioned 3 m long pipe was divided into three synthesis sections. The catalyst composition and the type of fluid used for the slurry were the same as in the first case. There were also no differences between the synthesis temperatures, the gas pressures and contact loads.

In contrast to the first experiment, the introduced carbon monoxide - hydrogen gas mixture with the sectioned contact tube could be transformed to over 90 % whereby the formation of methane was less than 5 % of the transformed carbon monoxide.

Particularly advantageous results are achieved when the temperature in the individual gas distribution steps is kept low enough so that not more than about 1 % in each step of the transformed, carbon monoxide is changed to methane. Under these circumstances a substantially increased contact load is achieved than is technically possible today within the framework of carbon monoxide hydrogenation. Whilst with the fixed catalysts an hourly loading of approximately 1 standard cubic meter synthesis gas per kilogram of contact metal content is used and it is assumed that with multi-step synthesis in general one counts on 0.60 standard cubic meter per kilogram of cobalt, then with the fluid phase carbon monoxide hydrogenation under highly dispersed gas distribu-

tion, the contact loads in the individual steps can be selected to be approx 2 to 7 times higher.

Thus, in the example of the second case mentioned, with the three conversions steps with 90 % conversion and a total of less than 5 % methane formation, 1.6 standard cubic meter synthesis gas per 1 kilo of cobalt were transformed per hour.

Because of the consumption of carbon monoxide, the usual gas volume contraction took place in the individual synthesis steps. If, despite this, the same gas velocity is to be maintained in all the contact steps, which is necessary because the contact is otherwise insufficiently agitated and the danger exists that it will settle on the bottom, then either the throughput section of the serially arranged synthesis sections must be reduced in steps or the throughput gas volume must be correspondingly increased.

If the contact tube cross section in the first step is, for instance, 50 cm² and if there is a 50 per cent restriction in this step then the fluid cross section in the second step only requires to be 25 cm² whilst the third and fourth steps only require 12.5 cm² and 6.25 cm² respectively. With this method, without significant methane formation and with the help of four steps, one can achieve more than 90 % transformation. In this way, approximately 19 g of fluid and easily liquefiable products are attained per standard cubic meter of synthesis ideal gas (CO + H₂).

Instead of stepped cross section reductions one can also achieve constancy of the gas velocity by other methods, as well, for example by mixing in vaporizable fluids or by a stepwise circulation arrangement of the synthesis gases that increases with progressing restriction.

The simultaneous mixing in of vaporizable fluids, for instance, easily boiling hydrocarbons or water, has the special advantage that, in this manner, the heat quantity produced in the contact slurry can be dispersed very intensively. For instance, by spraying and simultaneous vaporizing hexane almost exactly as much hexane steam is produced as corresponds to the reduction of the carbon monoxide-hydrogen volume. Similar conditions can be achieved with steam. The use of evaporating water is especially advantageous as this cooling medium possesses a high evaporation

temperature and is not soluble in the generated hydrocarbons.

It is insignificant whether the sprayed-in fluid whose quantity depends transformation level, synthesis pressure and synthesis temperature, produces more gas when evaporating than corresponds to the reduction of volume by contraction. An increase in the gas velocity improves the contact slurry and is very desirable.

If work is carried out by adding gas volume by means of sprayed-in vaporizable fluids, then the synthesis can be carried out in steps without any operational difficulties by means of a column whose individual bases consist of sinter plates and which are spaced at a distance of about 100 cm from each other. The gas enters into each column division through the sintered plates from below, passes through the fluid and comes into intensive contact with the contact slurry. At the same time, so much easily boiling, hydrocarbons or steam is sprayed into the individual steps that, with the occurring evaporation heat, constancy of temperature is insured. Without cooling, the gas then passes through the next sinter plate into the following synthesis step.

If, instead of direct cooling by means of vaporizable fluids, work is carried out by indirectly acting cooling jackets or with cooling pipes in the catalyst slurry or other forms of cooling surface, or if the gases are allowed to flow through corresponding cooling arrangements between the individual steps, then it is necessary to equalize the synthesis gas contraction by passing through partial circuit guides of the gases. The extent of the cycling arrangement must be enlarged in the direction of the serially arranged steps, proportionate with the increasing contraction in order to ensure sufficient contact slurring by increasing the gas velocity in the upper steps. Further details can be taken from the following example.

Embodiment Example

The carbon monoxide hydrogenation was performed at 181-183° in a contact tube of 25 mm ID and 3 m height that was divided into three sections of 1 m length by sinter plates. Heating was achieved by means of a heating jacket that was heated to 190°. Each step was filled with contact slurry that contained 18 grams of contact in 340 grams diesel oil so

that a gas space of 10 cm height remained in each section.

At a pressure of 10 atmospheres, 27 l per hour of a carbon monoxide-hydrogen mixture with 8 l CO, 16 l H₂ and 3 l N₂ was introduced into the first step and distributed at high dispersion through the sinter plate. This resulted in a 50 % transformation. Subsequently, the gas volume consisted of the 19 l and contained 4 l CO, 8 l H₂, 3 l N₂ and 4 l steam. As cross section of the synthesis apparatus was the same in all three sections, the gas volume was supplemented to 27 l by introducing 8 l steam, distributed again at high dispersion through a further a further sinter plate, and introduced into the second step. Here again the result was a 50 % conversion so that with two steps a 75 % transformation was attained. From the second step, there flowed per hour 2 l CO, 4 l H₂, 3 l N₂ and 14 l water steam or a total of 23 l. After mixing in 4 l water steam, the gas volume of 27 l was a fed through the third sinter plate. The third step resulted in a transformation of 60 %.

In three steps, a total of 90 % conversion was attained whereby the methane formation did not exceed 1 to 2 %. Per standard cubic meter synthesis gas 190 g of fluid and easily liquefiable products were produced.

PATENT CLAIMS:

1. Process for the performance of carbon monoxide hydrogenation using contact slurries in a fluid medium especially over nickel, cobalt, or iron catalysts in several steps at temperatures of between 150 to 280° at near atmospheric or up to 50 atmospheres increased pressure, high catalyst loading and highly dispersed distribution of the synthesis gas within the fluid medium, characterized in that the gases are distributed in a highly dispersed manner through sintered plates of ceramic material.
2. Process in accordance with claim 1, characterized in that the gas velocity in all steps is kept almost even, for instance by the application of stepwise smaller throughput cross-sections of the serially arranged steps or mixing-in of vaporizable fluids (e.g. of easily boiling hydrocarbons or water) or by a cycling arrangement of synthesis gases in the individual steps.