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CATALYTIC HYDROGENATION OF CARBON MONOXIDE
WITH INDIRECT HEAT EXCHANGE COOLING
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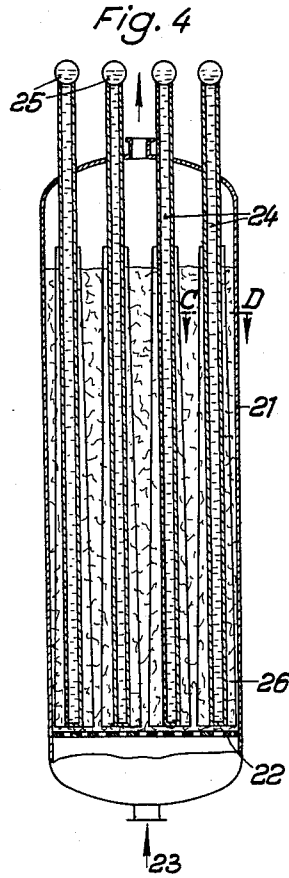
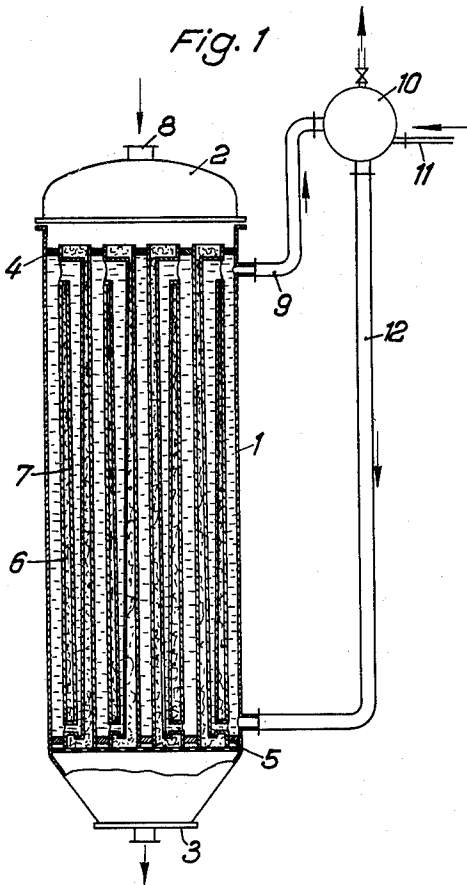


Fig. 2

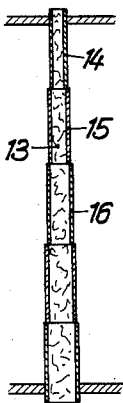


Fig. 3

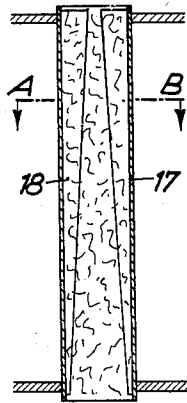


Fig. 6 (C-D)

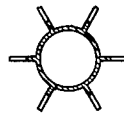
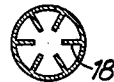


Fig. 5
(A-B)



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CATALYTIC HYDROGENATION OF CARBON MONOXIDE WITH INDIRECT HEAT EXCHANGE COOLING

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6 Claims. (Cl. 260—449)

This invention relates to temperature-gradient in connection with uniformly boiling coolants.

The catalytic treatment of gases, containing carbon monoxide and hydrogen, into higher hydrocarbons, may be conducted so that larger or smaller quantities of hydrocarbon derivatives containing oxygen are obtained, e. g. alcohols, fatty acids or the like. When proceeding in the conventional manner using the contact process with rigidly arranged catalysts, only quantities of 0.15 to 0.2 ton of the higher hydrocarbons and, under certain conditions other compounds containing oxygen are obtained per m³ of catalyst per day. In the above method the catalysts are placed in thin layers of 7.5 to 10 mm. thickness between cooled heat exchange surfaces (laminated ovens) or in tubes of 10–15 mm. diameter, or in the annular space between two telescoped tubes with a distance of about 10 mm. between the inner and outer tube. The cooling process in these methods had to be made especially effective in order to dissipate the generated reaction heat. Usually this was done by using boiling water under pressure. The use of larger contact layers was impossible because this would have produced excessive temperatures of the contact layers which would have resulted in side reactions, such as formation of large quantities of methane, separation of carbon and damage to the catalysts. The cooling with boiling water under pressure resulted in nearly constant reaction temperatures of the gases passing through the contact oven.

One object of this invention is increasing the yield in the synthesis of higher hydrocarbons using uniformly boiling coolants in the contact process. This and further objects will become apparent from the following description read in conjunction with the drawings in which:

Fig. 1 shows apparatus which can be used for the process according to the invention.

Fig. 2 shows another form of a contact tube which may be used in accordance with the invention.

Fig. 3 illustrates another form of a contact tube.

Fig. 4 is a vertical cross section of a contact oven with a suspended contact.

Fig. 5 shows another form of construction of the apparatus which may be used for the process in accordance with the invention.

Fig. 6 shows still another form of the apparatus which may be used for the process according to the invention.

It has now been found according to the invention that when using high gas velocities of more than .5 and suitably more than 2–10 m. per second at a temperature of zero degrees centigrade at a pressure of 760 mm. Hg. and relatively large thicknesses of contact layers of more than 15 mm. and preferably 20–50 mm. in thickness, a cooling medium of a constant or nearly constant boiling point can be used if the cross sections of the contact layers perpendicular to the direction of the gas flow in the direction of the path of the gas through the contact are increased in size. The great thicknesses of the contact layers permit, at the same time, a simple construction of the apparatus

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and a comparatively easy exchange of the contact. In the contact layers, which lie at the gas entry and which have a smaller cross section than those that follow, the velocity of the gases is greater than in the later ones. The consequence is a greater heat transfer rate and, thus, a better dissipation of the heat of reaction near the gas entry. Besides, here the heat transfer areas which enclose the catalyst are larger in proportion to the quantity of the catalyser than in the contact portions following, and thus effect an additional increase in the dissipation of the heat of reaction. On the other hand, the formation of heat for a certain specific catalysing effect is smaller at the gas entry and near this point because of the small quantities of the catalyst present, and the time of contact of the reacting gas with the catalyst is shorter due to the high velocity of the gas so that the synthesis of the gases and the heat of reaction remain lower at this point than on the succeeding passages of the gases through the catalyst. These conditions under which the reaction in the catalyser layer at the gas entry takes place result in a small difference of temperature between the reacting gases and the cooling medium.

On the succeeding path of the gas through the contact, on which the cross sections of the contact gradually or at intervals increase, the gas velocity and thus the rate of heat transfer decrease gradually, and the heat exchange surfaces which enclose the catalyser decrease in proportion to the quantity of the catalyser. Correspondingly, the difference in temperature between the gas in the catalyser or the catalyser space and the cooling medium increases gradually along the path of the gas. With the temperature of the cooling medium remaining constant, constantly increasing temperatures of reaction in the catalyser are obtained. With increasing cross sections of the catalyser layers the generation of heat at the catalyser increases further and the gas conversion is increased through the longer contact of the gas with the catalyser, which result in a further steady increase of the temperatures of reaction without requiring an analogous increase in the temperature of the cooling medium.

The result of the increasing temperatures of reaction along the path of the gas is that the specific conversion of carbon monoxide and hydrogen is kept at a constant rate in all parts of the catalyser or can be regulated according to other requirements, thus eliminating the harmful effect which the decreasing concentration of carbon monoxide and hydrogen produces in the lower layers of the catalyser. If, e. g. in a double tube oven the distance between the inner tube and the outer tube is increased from 10 mm. at the top of the oven to 25 mm. at the bottom, the temperature of reaction at a carbon monoxide-hydrogen conversion rate of 60%, increases approximately 15 or 20° during the passage of the gas from the top to the bottom through the contact. The contact will work faultlessly if the gas velocities are kept so high that due to the turbulent flow, a good dissipation of the heat of reaction and an equalization of temperatures in the contact is effected. In this process water can be used as a cooling medium. Other fluids with a constant boiling point, such as diphenyl, diphenyl oxide, hydrocarbons, silicons, mercury and the like, may also be used. The new process can be applied with or without circulation of the reacting gases. The variation of the quantity of the circulating gas down to working without any circulating gas offers the possibility to regulate the change of the flow velocity of the gases in the contact layer in the direction of the gas flow in the most effective manner, e. g., if a larger difference between the flow velocity at the gas entrance and the gas egress is desired, one can work with small quantities of circulating gas or without any circulation. In that case, the reaction produces a strong contraction of the gas so that this

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contraction also produces a decrease of the flow velocity and, thus, of the heat transfer rate and a longer stay of the gas in the contact. Thus, through a change of the circulating gas quantity, a change of the difference of temperature between the entering and emerging gas is also obtained.

The heat transfer through the heat exchange surfaces may be further reduced in the lower part of the contact oven by providing for the heat exchange surfaces a material with a lower coefficient of heat conductivity or insulating material, e. g. incrustations at the heat exchange surfaces. One can also, as is well known, when using tube or double tube ovens, make the diameter of the tubes or the outer tubes in the lower part of the oven larger than in the upper part.

The process according to the invention permits the use of increasing temperatures in the contact, independent of the direction of the gas flow. For instance, while passing the gases in the direction from the bottom to the top through the contact, one can keep the temperatures at an increasing rate from the bottom to the top, but it is necessary to apply the methods described above, which produce these differences in temperature, in reverse, e. g. the cross sections of the contact layers must increase in size from the bottom to the top while the gas velocities and the specific size of the heat exchange surfaces must be reduced from the bottom toward the top. This possibility is of importance especially when working with catalysers kept in suspension since this process is applicable only when the gas flows from the bottom to the top.

The contact oven according to Fig. 1 consists of a pressure tank 1, which is provided with a top cover 2 and a bottom 3. The contact tubes 6 are welded into the tube plates 4 and 5. The contact tubes 6 have on the inside concentrically arranged conical or graduated tubes 7, whose diameter decreases from the top to the bottom. The tubes 6 and 7 are connected in such a manner that the cooling water, which occupies the space between the pressure tank 1 and the contact tube 6, can also circulate through the concentrically arranged inner tubes 7. The catalyser is placed in the annular space between the tubes 6 and 7 in layers which increase in size toward the bottom. The gas to be synthesized enters into the contact oven through the upper sleeve 8 and is converted at the catalyser. As the layers increase in size, the gas velocity decreases and the time of contact between the gas and the catalyser increases, the temperature of reaction rises. The heat of reaction is transferred to the boiling cooling water, the steam generated is carried off through the connecting pipe 9 and the steam accumulator 10. The cooling medium circulates back into the contact oven through the connecting pipe 12 together with the water flowing in through the pipe 11.

Fig. 2 illustrates another form of a contact tube. The contact tube 13 consists of several pieces of tube 14, 15, 16 of different diameters and different lengths, which are welded together and, thus, have different cross sections of the layers.

Fig. 3 illustrates a contact tube 17 in which the surfaces that carry the heat off are varied by welded-on ribs 18 whose height decreases toward the bottom and in this manner also effect a variation in the thickness of the layer.

Fig. 4 is a contact oven designed for working with suspended catalysers. It consists of a pressure tank 21 in which the catalyser is placed over the grating 22. The gas to be synthesized enters the contact oven through the lower sleeve 23. The gas velocity is maintained high enough to keep the catalyser in suspension. The generated heat of reaction is transferred to the boiling cooling water in the cooling tubes 24 which extend into the catalyser space, and the steam generated is carried off through the collecting pipes 25. The cooling tubes 24 are provided with welded-on ribs whose height decreases from the bottom toward the top. Through this arrange-

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ment, the heat transfer surface in the lower part is increased and the thickness of the layer is decreased so that increasing temperatures of reaction from the bottom toward the top can be obtained.

The following examples are given by way of illustration and not limitation:

Example 1

Hydrocarbon synthesis is carried out in a contact oven 3 m. in diameter and 1.5 m. high in which the catalysers are arranged stationary in tubes. The contact oven contains 3100 tubes, each measuring 6 m. between top and bottom and having an inside diameter of 20 mm. at the top which increases to an inside diameter of 40 mm. at the bottom. This contact oven will take 15 m.³ of catalysers. The contact oven has a capacity of 15,000 Nm.³ of the synthesis gas/hour under a pressure of 20 atm. and of 37,500 Nm.³/hour of return gas. The gas velocity, based on the free cross section of the contact tubes and standard conditions (0° and 760 mm. Hg), is 13.3 m./sec. in the contact tubes at the entry and 3.55 m./sec. when leaving the oven. The heat transfer rate thus decreases from 538 kcal./m.²/hr./° C. at the upper end of the oven to 165 kcal./m.²/hr./° C. at the lower end of the oven while the heat transfer surface between the catalyser and the boiling cooling water, based on the same catalyser quantity, decreases by approximately 100%. With a temperature of 240° of the boiling cooling water surrounding the contact tubes, a temperature of reaction of 243° is observed where the gas enters the contact tubes, which by our invention increases to 263° when the gas leaves the contact tubes. The production of hydrocarbons by this contact oven is approximately 40 tons per day.

Example 2

A contact oven with contact tubes of 74 mm. inside diameter is used. Inside of these contact tubes there are concentrically arranged tubes whose outside diameter of 44 mm. at the top is reduced to 24 mm. at the bottom. The heights of the layers in the contact tubes obtained in this manner are 15 mm. at the top and 25 mm. at the bottom in the annular cross section perpendicular to the axis. 1070 contact tubes, each 6 m. high, are built into a contact oven which has a diameter of 3 m. The contact oven holds 21 m.³ of the catalyser. It will be filled with 21,000 Nm.³/hour of synthesis gas under a pressure of 20 atm. and 52,500 Nm.³/hour of circulating gas. The gas velocity, with reference to the free cross section of the contact tube, under standard conditions (0° and 760 mm. Hg) is 7 m./sec. at the top and diminishes to 5 m./sec. at the bottom. This reduces the heat transfer rate from 249 kcal./m.²/hr./° C. at the top of the oven to 139 kcal./m.²/hr./° C. at the bottom of the oven. The heat transfer surface diminishes by 17% from the top to the bottom while, under equal specific contact loads, the heat generated at the top is 40% less than at the bottom. At a temperature of the cooling medium, boiling water, of 240°, the temperature of reaction at the oven entrance in the layers of 15 mm. thickness is 250° which increases to 265° at the oven exit with a thickness of the layer of 25 mm. The yield of the contact oven is 58 tons of hydrocarbons per day.

Example 3

A contact oven with a diameter of 3.5 m. contains 5000 tubes of an inside diameter of 31 mm. and 10 m. in length, which have a capacity of about 46 m.³ of the catalyser. The contact oven is loaded with 46,000 Nm.³/hour of synthesis gas and with 115,000 Nm.³/hour of circulating gas under a gas pressure of 20 atm. The outside of the contact tubes at the upper end is covered with an insulating layer of 1 mm. in thickness. The insulating layer is enlarged toward the bottom and has a thickness of 4 mm. at the lower end. Coatings of enamel, silicates or other insulating materials can be used. The

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insulation can also be accomplished by placing another tube which is conically enlarged toward the bottom over the contact tube so that there is an annular space of 1 mm. radial inside diameter between the two tubes at the top which gradually increases to 4 mm. at the bottom. The annular space is connected in one place with the gas space or the steam space of the contact oven which forms the upper part of the space for the cooling medium. In this case, the gas space or the steam-filled annular space, whose inside diameter increases from 1 mm. to 4 mm., makes the insulation.

The heat transfer rate, which would amount to 444 kcal./m.²/hour/° C. on a non-insulated tube, is reduced by the insulation at the gas entry at the top to 235 kcal./m.²/hour/° C. and by the stronger insulation at the gas exit at the bottom to 90 kcal./m.²/hr./° C. With a temperature of the cooling medium of 220°, temperatures of reaction of 233° at the gas entry and 253° at the gas exit are obtained. With insulating layers made still thicker, the temperature of the cooling medium may be further reduced even at higher temperatures of reaction, the result of which is lower pressures of the cooling medium if boiling water is used for cooling. The gas conversion amounts to 60% of the CO+H₂ injected, and the yield of the contact oven is 90 tons of hydrocarbons per day.

Example 4

1200 double tubes, each 10 m. long, are built into a contact oven of a diameter of 3.5 m. Each double tube consists of an outside tube with an inside diameter of 82.5 mm. and an inside tube, which has an outside diameter of 30 mm. and is connected with the space containing the cooling medium. 6 longitudinal ribs, 10 m. in length, are welded on each inside tube distributed in equal distances from each other around the perimeter. The height of the ribs is 26 mm. at the top where the gas enters and gradually decreases to 5 mm. at the bottom where the gas passes out. The heat transfer area on the gas side is thereby reduced by 50% from the gas entry to the gas exit. The contact capacity of the oven is 53 m.³. With a load of 53,000 Nm.³/hour of synthesis gas under a pressure of 20 atm. and 53,000 Nm.³/hour of circulation gas, at a temperature of 220° of the cooling medium, the temperature of reaction at the gas entry is 234° and at the gas egress 262°. The yield of the contact oven is 100 tons of hydrocarbons per day.

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I claim:

1. In the production of hydrocarbons and hydrocarbon derivatives by catalytic carbon monoxide hydrogenation, the improvement which comprises passing synthesis gas at a velocity of at least about 0.5 meter per second through a substantially confined longitudinally extending fixed bed of particled catalyst of a cross-sectional mean bed thickness in excess of 10 millimeters, and increasing from end to end in the direction of gas flow, and cooling said catalyst with a coolant of a substantially constant boiling point in substantially indirect heat exchange relation to the outside of said bed.

2. Improvement according to claim 1 in which said catalyst bed is substantially vertically arranged and in which said synthesis gas is passed substantially downwardly therethrough.

3. Improvement according to claim 1 in which said mean thickness is at least 15 millimeters and in which said bed is defined by a substantially columnar body of said catalyst.

4. Improvement according to claim 1 in which said mean thickness is about 20 to 50 millimeters and in which said bed is defined by a substantially columnar body of said catalyst.

5. Improvement according to claim 1 in which said synthesis gas is passed at a velocity substantially between 2 and 20 meters per second.

6. Improvement according to claim 1 in which there is substantially maintained a temperature difference between catalyst and coolant substantially of about 10 to 50° C. at the widest catalyst bed section in heat exchange relation with said coolant.

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