PATENT SPECIFICATION

689,214

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Index at acceptance:—**Classes 1(i),** F3a1(a: x); **and 2(iii),** B1g.

COMPLETE SPECIFICATION

Method of Producing Hydrocarbons

We, RUHRCHEMIE AKTIENGESELLSCHAFT, a body corporate organised under the Laws of Germany, of Oberhausen-Holten, Germany, and LURGI GESELLSCHAFT FÜR WÄRMETECHNIK m.b.H., a body corporate organised under the Laws of Germany, of 17 to 19, Gervinusstrasse, Frankfurt-on-the-Main, 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:—

This invention relates to a method of producing hydrocarbons.

In the catalytic working-up of gases containing carbon monoxide and hydrogen into higher hydrocarbons (which may also be so conducted that more or less large amounts of oxygen-containing hydrocarbon derivatives for example alcohols, fatty acids, or the like, are obtained) hitherto catalyst outputs of only about 0.15 to 0.2 tons of higher hydrocarbons and, where applicable, oxygen-containing compounds per cubic metre of catalyst per day have been attained in the case of stationary catalysts.

The catalysts were accommodated in thin layers of a thickness of 7.5 to 10 mm. between indirectly cooled heat exchange surfaces (lamellar reactors) or in tubes of 10 to 15 mm. in diameter or in the annular space of double tubes with a distance of about 10 mm. between the inner and outer tubes. The cooling had to be particularly effective in order to be able to remove the reaction heat produced. It was usually effected with boiling water under pressure. The use of catalyst layers of greater thicknesses was not possible, because excess temperatures would otherwise have occurred in the catalyst layers, which would have given rise to subsidiary reactions, such as high methane production, a separation of carbon, and injury to the catalysts. Cooling with boiling water under pressure had the result that the reaction temperatures on the path of the gases through the catalyst reactors were almost constant at all points.

In the specification of Application No. 683,516 there has been described a method of carrying out catalytic gas reactions, the application of which to the synthesis of higher hydrocarbons provides a substantial increase of the catalyst output. Mixtures of two or more organic liquids having different boiling temperatures, which partly evaporate in the cooling medium chamber of the catalyst reactor, are used as cooling medium. The vapours are condensed, and the condensate is returned to the surface or near the surface of the cooling medium into the catalyst reactor. The method permits the adjustment of rising temperatures in the cooling medium space, from top to bottom. It is thus possible, in the synthesis of hydrocarbons in which the carbon monoxide-hydrogen concentration progressively decreases from the inlet to the outlet of the gas, to keep the reaction of carbon monoxide and hydrogen on the passage of the gases through the catalyst, at all points, quantitatively constant, or to guide the same in accordance with other considerations, by maintaining reaction temperatures rising from the gas inlet to the gas outlet. Whereas when using cooling by means of boiling water only the uppermost catalyst layers work, with increasing reaction temperatures all the catalyst layers are uniformly effective, so that a substantial increase of the output of the catalyst reactor and an increase of the gas throughput are obtained.

If furthermore in this process, described in the aforesaid specification use is made of high rates of flow of the gases, of over 0.5 and conveniently over 2 to 10 metres per second, referred to 0° C. and

760 mm. mercury, and to the free cross-section of the catalyst space, the catalyst can be disposed with layer thicknesses of more than 15 mm., and advantageously 20 to 50 mm. Through the high gas velocity the heat produced at the catalyst core is rapidly removed, so that overheating cannot occur. In addition, the high gas velocities have the effect that a turbulent flow is obtained, which results in a uniform distribution of temperature over the entire cross-section of the catalyst. In consequence, working with great differences of temperature between the catalyst and the cooling agent of between 10 and 50° C. is possible, whereby an increase of the removal of heat from the catalyst to the cooling agent is obtained.

It has now been found that when using high gas velocity and catalyst layers of substantial thicknesses, it is possible to use a cooling medium with a constant or substantially constant boiling temperature, if the catalyst layer cross-sections increase perpendicular to the direction of flow of the gas in the direction of the path of the gas through the catalyst. The great catalyst layer thickness then simultaneously permit a simple structural formation of the apparatus and relatively easy replacement of the catalyst. In the catalyst layers lying at the gas inlet and having a smaller cross-section than the subsequent ones, there is a greater gas velocity than in the last ones. This results in a greater coefficient of heat transfer and hence better removal of heat of reaction near the gas inlet. In addition, the heat removal surfaces enclosing the catalyst are larger in relation to the amount of catalyst than in the following catalyst parts, and additionally increase the removal of the heat of reaction. On the other hand, the generation of heat for a specific catalyst output is smaller in consequence of the small amounts of catalyst at and near the gas inlet, and in consequence of the high gas velocity, the time of contact of the reaction with the catalyst is shorter, so that the gas reaction and the heat of reaction remain lower there than on the remainder of the path of the gases through the catalyst. These conditions under which the reaction proceeds in the catalyst layer lying at the gas inlet lead to a low difference of temperature between the reaction gas and the cooling medium.

On the remainder of the path of the gas through the catalyst, on which the catalyst cross-sections increase gradually or by stages, the gas velocity and hence the coefficient of heat transfer gradually become smaller; similarly, the heat exchange surfaces surrounding the catalyst decrease in relation to the amount of catalyst. Accordingly, the difference in temperature between the gas contained in the catalyst, or the catalyst space, and the cooling agent becomes increasingly greater along the path of the gas. Given equal temperature of the cooling medium, therefore, constantly increasing reaction temperatures are therefore obtained in the catalyst. With increasing catalyst layer cross-sections, moreover, the generation of heat at the catalyst increases, and the gas reaction is increased through the longer time of contact of the gas with the catalyst, which results in a further constant rise in the reaction temperatures, without a similar rise in the temperature of the cooling medium being necessary.

Through the rising reaction temperatures along the path of the gas, the effect is achieved that the specific reaction of carbon monoxide and hydrogen in all parts of the catalyst can be kept equally great or can be adjusted according to other advantageous considerations, and the disadvantageous influence caused by the decreasing concentration of carbon monoxide and hydrogen in the lower catalyst layers is eliminated. If, for example, in a double tube reactor the distance between the inner tube and the outer tube is allowed to increase from 10 mm. at the top end of the reactor to 25 mm. at the bottom end of the reactor, the reaction temperature increases, with a carbon monoxide-hydrogen reaction of 60% of the amount present on the path of the gas from top to bottom through the catalyst, by about 15 to 20° C. The catalyst works perfectly under these conditions if such high gas velocities are maintained that in consequence of the turbulent flow a good removal of the heat of reaction and an equalisation of temperature in the contact occurs. Water can be used as cooling medium in this arrangement. However, other liquids having a uniform boiling point, such as diphenyl, diphenyl oxide, hydrocarbons, silicones, mercury or the like can also be used.

In the hereindescribed process it is possible to work with or without recycling of the reaction gases. The variation of the amount of recycled gas, down to working without recycled gas, then permits the variation of the speed of flow of the gases in the catalyst layer in the direction of the gas path to be adjusted to the optimum. If, for example, it is desired to have a great difference between the speed of flow at the gas inlet and that at the gas outlet, it is possible to work with low amounts of recycled gas or without recycled gas. Through the reaction a great contraction of gas is then brought about, so that this contraction also contributes to the reduction of the rate of flow and hence of the transfer of heat and to the increasing of the time of stay of the gas in the catalyst. Through a variation of the amount of recycled gas a variation of the difference in temperature between the gas inlet and the gas outlet is thus also achieved.

The passage of heat through the heat exchange surfaces can also be further reduced in the bottom part of the catalyst reactor by providing therein for the heat exchange surfaces a material having a lower thermal conductivity, or insulation, for example by means of incrustations on the heat-exchange surfaces. As is known *per se*, when using tube or double-tube reactors, the tubes or the outer tubes respectively can also be made with a larger diameter in the bottom part of the reactor than in the upper part.

The process according to the present invention permits the adjustment of rising temperatures in the catalyst, independently of the direction of the flow of gas. Thus, for example, when passing the gases through the catalyst in the direction from bottom to top, it is also possible to increase the temperatures from bottom to top, and it is then only necessary to apply conversely the previously described measures which produce these differences in temperature, for example to increase the catalyst layer cross-sections from bottom to top and to decrease the gas speeds and the specific size of the heat exchange surfaces from bottom to top. This possibility is particularly of importance when working with catalysts in suspension, since that method entails the flow of gas from bottom to top.

Certain embodiments of apparatus which are suitable for use in carrying out the invention are illustrated diagrammatically and by way of example in the accompanying drawings, in which:—

Fig. 1 shows a catalyst reactor with stationary catalyst and Fig. 4 a catalyst reactor with catalyst in suspension, in vertical section. Details of these reactors are shown in Figs. 2, 3, 5 and 6.

The catalyst reactor illustrated in Fig. 1 consists of a pressure vessel 1, which is provided with an upper lid 2 and a base 3. Catalyst tubes 6 are welded in the tube bases 4 and 5. The catalyst tubes 6 contain in their interior coaxially disposed conical or stepped tubes 7, the diameter of which decreases from top to bottom. The tubes 6 and 7 are connected together in such a manner that the cooling water, which is located between the pressure container 1 and the catalyst tubes 6, can also circulate through the coaxially disposed inner tubes 7. The catalyst is arranged in the annular space between the tubes 6 and 7, with a layer thickness increasing in the downward direction. The synthesis gas passes through the upper branch 8 into the catalyst reactor and is reacted on the catalyst. With increasing layer thickness, the reduction of the speed of the gas, and the increase of the time of stay of the gas on the catalyst, the reaction temperature rises. The heat of reaction is given up to the boiling cooling water, and the resulting steam is withdrawn through the connecting pipe 9 and the steam collector 10. The cooling water circulates back into the catalyst reactor with the water fed in through the pipe 11, through the connecting pipe 12.

In Fig. 2 is shown another shape of a catalyst tube. The catalyst tube 13 consists of several lengths of tubing 14, 15, 16 . . , of different diameters and different lengths, which are welded together and thus provide different layer cross-sections.

Fig. 3 shows a catalyst tube 17 in which the heat-removing surfaces are modified by welding-on ribs 18 of a height decreasing in the downward direction, whereby a variation of the layer thickness is likewise achieved.

The catalyst reactor illustrated in Fig. 4 serves for working with catalysts in suspension. It consists of the pressure vessel 21, in which the catalyst is disposed over the grid 22. The synthesis gas passes into the catalyst reactor through the bottom branch 23. The gas velocity is kept so high that the catalyst remains in suspension. The reaction heat evolved is given up through the cooling tubes 24 projecting into the catalyst space to the boiling cooling water contained therein, and the resulting steam is taken off through the collector pipes 25. The cooling tubes 24 are provided with welded-on ribs 26, the height of which decreases from bottom to top. The heat exchange surface is thereby increased in the bottom part and the layer thickness reduced, so that reaction temperatures rising from bottom to top can be obtained.

The following Examples will serve to illustrate the invention.

EXAMPLE 1.

This Example relates to a hydrocarbon synthesis in a catalyst reactor having a diameter of 3 metres and a height of 7.5 metres, and in which the catalysts are disposed stationarily in tubes. The catalyst reactor contains 3.100 tubes having a length of 6 metres between the tube bases and with an inside diameter of 20 mm. at the top, increasing to an inside diameter of 40 mm. at the bottom. This catalyst reactor holds 15 cubic metres of catalyst. The catalyst reactor is charged with 15,000 cubic metres (at normal temperature and pressure) of synthesis gas per hour, at a pressure of 20 atmospheres, and with 37,500 cubic metres (at normal temperature and pressure) of recycled gas per hour. The gas velocity, referred to the free catalyst tube cross-section and to normal conditions (0° and 760 mm.Hg), amounts in the catalyst tubes to 13.3 metres per second at the reactor inlet and 3.55 metres per second at the reactor outlet. The coefficient of heat transfer is thereby reduced from 538 Kcal per square metre per hour per degree Centigrade at the top end of the reactor to 165 Kcal per square metre per hour per degree Centigrade at the bottom end of the reactor, while the heat exchange surface between the catalyst and the boiling cooling water, referred to the same amount of catalyst is reduced by about 100%. With a cooling medium temperature of the boiling water surrounded the catalyst tubes of 240° C., a reaction temperature of 243° C. is adjusted at the entry into the catalyst tubes, and in accordance with the invention this increases at the gas outlet in the catalyst tubes to 263° C. The production of hydrocarbons of this catalyst reactor amounts to about 40 tons of hydrocarbons per day.

Example 2.

A catalyst reactor with catalyst tubes having an inside diameter of 74 mm. is used. In the contact tubes are disposed coaxial tubes the diameter of which decreases from 44 mm. external diameter to 24 mm. external diameter in the downward direction. The layer thicknesses thereby obtained in the catalyst tubes amount to 15 mm. at the top and 25 mm. at the bottom in the annular cross-section at right-angles to the axis. In a catalyst reactor having a diameter of 3 metres 1070 catalyst tubes of a height of 6 metres are accommodated. The catalyst capacity of the catalyst reactor amounts to 21 cubic metres, and the catalyst reactor is charged with 21,000 cubic metres (at normal temperature and pressure) per hour of synthesis gas, under a pressure of 20 atmospheres, and 52,500 cubic metres (at normal temperature and pressure) of recycled gas per hour. The gas velocity, referred to the free catalyst tube cross-section and referred to normal condition (0° C. and 760 mm. Hg), amounts to 7 metres per second at the top and at the bottom falls to 5 metres per second. The coefficient of heat transfer is thereby reduced from 249 Kcal per square meter per hour per degree Centigrade at the top end of the reactor to 139 Kcal per square metre per hour per degree Centigrade at the bottom end of the reactor. The heat removal surface is reduced from top to bottom by 17%, while with the same specific catalyst charge the generation of heat is smaller by 40% at the top than at the bottom. With a cooling medium temperature in the boiling water of 240°, a reaction temperature of 250° is adjusted at the reactor inlet in the layers of 15 mm. thickness, and with increasing catalyst layer thickness at the reactor outlet, with a thickness of 25 mm., this increases to 265°. The output of the catalyst reactor amounts to 58 tons of hydrocarbons per day.

Example 3.

A catalyst reactor having a diameter of 3.5 metres contains 5000 tubes having an inside diameter of 31 mm., and in which, over a length of 10 metres, about 46 cubic metres of catalyst can be accommodated. The catalyst reactor is charged with 46,000 cubic metres (at normal temperature and pressure) of synthesis gas per hour and with 115,000 cubic metres (at normal temperature and pressure) of recycled gas per hour, under a gas pressure of 20 atmospheres. The catalyst tubes are covered on the outside at the top end with an insulating layer of a thickness of 1 mm. The insulating layer increases from top to bottom and at the bottom end is about 4 mm. in thickness. Enamel coats or coatings of silicones or other insulating material may be used. The insulation can also be obtained by drawing over the catalyst tube a second tube flaring conically in the downward direction, so that between the two tubes there is formed an annular space having a radial inside width of 1 mm. at the top, increasing to 4 mm. at the bottom. The annular space is in communication with the gas space or the steam chamber forming the uppermost part of the cooling medium space in the catalyst reactor, at one point. In this case the annular space filled with gas or steam, and the inside width of which increases from 1 mm. to 4 mm., forms the insulation.

The coefficient of heat transfer, which at the non-insulated tube would amount to 444 Kcal per square metre per hour per degree Centigrade, is reduced by the insulation at the top, at the gas inlet, to 235 Kcal per square metre per hour per degree Centigrade and at the bottom, at the gas outlet, owing to the thicker insulation to 90 Kcal per square metre per hour per degree Centigrade. With a cooling medium temperature of 220° C., reaction temperatures are obtained at 233° C. at the gas inlet and 253° C. at the gas outlet. With still thicker insulation layers, the cooling medium temperature can be further reduced even at higher reaction temperatures, whereby when cooling with boiling water, lower cooling medium pressures are obtained. The gas reaction amounts to 60% of the $CO + H_2$ introduced and the output of the catalyst reactor is 90 tons of hydrocarbons per day.

EXAMPLE 4.

In a catalyst reactor having a diameter of 3.5 metres, 1200 double tubes of a length of 10 metres are accommodated. Each double tube consists of an outer tube of an inside diameter of 82.5 mm. and an inner tube of an outside diameter of 30 mm. connected to the cooling medium space. On each inner tube are welded six longitudinal ribs of a length of 10 metres uniformly distributed over the periphery. The height of the ribs amounts at the top at the gas inlet, to 26 mm. and decreases in the downward direction towards the gas outlet to 5 mm. The heat transfer surface on the gas side is thereby reduced from the gas inlet towards the gas outlet by 50%; the catalyst capacity of the reactor amounts to 53 cubic metres. With a load of 53,000 normal cubic metres per hour of synthesis gas, with a pressure of 20 atmospheres, and 53,000 normal cubic metres per hour of recycled gas, and with a cooling medium temperature of 220° C., the reaction temperature is 234° C. at the gas inlet and 262° C. at the gas outlet. The output of the catalyst reactor is 100 tons of hydrocarbons per day.

What we claim is:—

1. A method of producing hydrocarbons, and if desired oxygen-containing hydrocarbon derivatives, by the catalytic hydrogenation of carbon monoxide using gas velocities of over 0.5 metres per second referred to 0° C. and 760 mm. of mercury in the catalyst and catalyst layer thicknesses of more than 10 mm., characterised in that a cooling medium having a constant or substantially constant boiling temperature is used and that the temperature difference between the catalyst and the cooling medium along the path of the gas through the catalyst is caused to vary continuously or in stages, that the variation in the temperature difference between the catalyst and cooling medium is effected by increasing the cross-section of the catalyst layers in the direction of flow of the gas and/or by reducing the heat exchange surfaces in the direction of flow of the gas and/or by reducing the heat transfer through the heat exchange surfaces in the direction of flow of the gas by insulating said surfaces, especially on the cooling medium side.

2. Method as claimed in Claim 1, in which a part of the gas leaving the synthesis is recycled to the synthesis after partial or complete separation of the reaction products therefrom.

3. Method as claimed in Claim 1 or 2, in which differences in temperature at the gas outlet, between the catalyst and cooling medium of between 10° and 50° C. are maintained.

4. Method as claimed in any of Claims 1 to 3, applied to catalysts held in suspension, characterised in that the gases are conducted in the direction from bottom to top through the catalyst space and the temperature in the catalyst space is kept lower at the bottom than at the top.

5. Method as claimed in any of Claims 1 to 4, in which the height of the catalyst-containing tubes is between 6 and 10 metres.

6. Method of producing hydrocarbons, substantially as described with reference to the accompanying drawings and to the foregoing Examples.

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Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

689,214 COMPLETE SPECIFICATION
1 SHEET
This drawing is a reproduction of the Original on a reduced scale.

Fig. 1

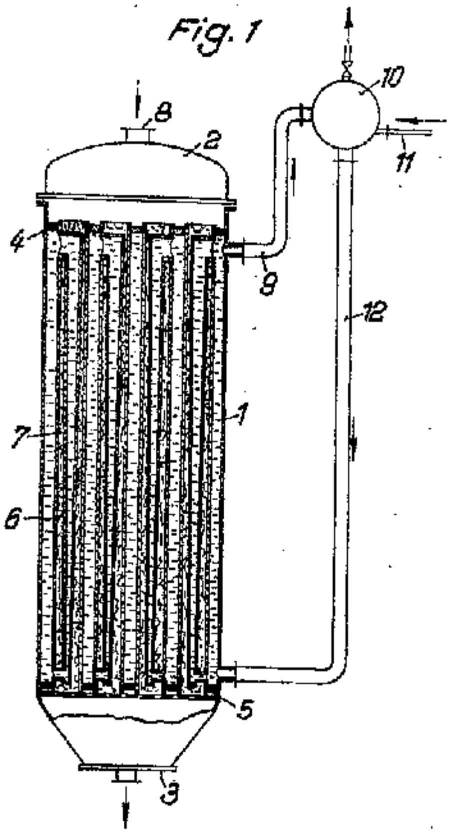

Fig. 4

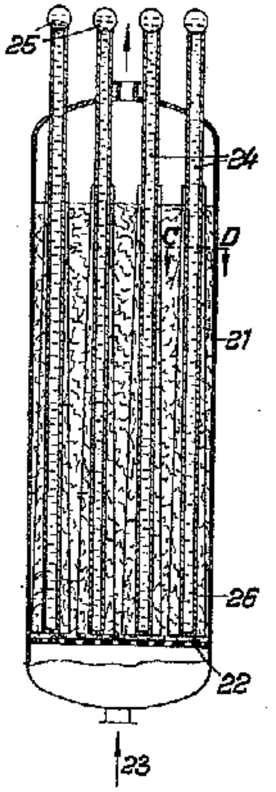

Fig. 2

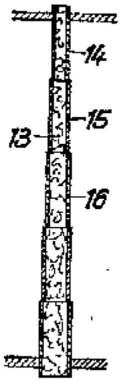

Fig. 3

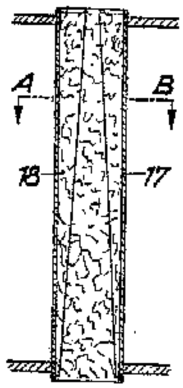

Fig. 6 (C-D)

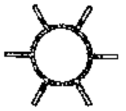

Fig. 5
(A-B)

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COMPLETE SPECIFICATION

Method of Producing Hydrocarbons

PATENTS ACT, 1949

SPECIFICATION NO. 689,214

Reference has been directed, in pursuance of Section 8 of the Patents Act, 1949, to Patent No. 690,985.

THE PATENT OFFICE,
30th November, 1953

DB 37883/1(2)/3537 150 11/53 R

producing hydrocarbons.

In the catalytic working-up of gases containing carbon monoxide and hydrogen into higher hydrocarbons (which may also be so conducted that more or less large amounts of oxygen-containing hydrocarbon derivatives for example alcohols, fatty acids, or the like, are obtained) hitherto catalyst outputs of only about 0.15 to 0.2 tons of higher hydrocarbons and, where applicable, oxygen-containing compounds per cubic metre of catalyst per day have been attained in the case of stationary catalysts.

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lyst reactor, are used as cooling medium. The vapours are condensed, and the condensate is returned to the surface or near the surface of the cooling medium into the catalyst reactor. The method permits the adjustment of rising temperatures in the cooling medium space, from top to bottom. It is thus possible, in the synthesis of hydrocarbons in which the carbon monoxide-hydrogen concentration progressively decreases from the inlet to the outlet of the gas, to keep the reaction of carbon monoxide and hydrogen on the passage of the gases through the catalyst at all points, quantitatively constant, or to guide the same in accordance with other considerations, by maintaining reaction temperatures rising from the gas inlet to the gas outlet. Whereas when using cooling by means of boiling water only the uppermost catalyst layers work, with increasing reaction temperatures all the catalyst layers are uniformly effective, so that a substantial increase of the output of the catalyst reactor and an increase of the gas throughput are obtained.

If furthermore in this process, described in the aforesaid specification use is made of high rates of flow of the gases, of over 0.5 and conveniently over 2 to 10 metres per second, referred to 0° C. and