PATENT SPECIFICATION

690,925

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Index at acceptance:—**Classes 1(i)**, F3a1x; **and 2(iii)**, B1g.

2257

COMPLETE SPECIFICATION

Method of Producing Hydrocarbons and Oxygenated Derivatives thereof

We, METALLGESELLSCHAFT AKTIENGESELLSCHAFT, a Corporation organised under the Laws of Germany, of 45, Bockenheimer Anlage, Frankfurt-on-the-Main, Germany, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a method of producing hydrocarbons and oxygenated derivatives thereof.

When carrying out catalytic gas reactions with high heat of reaction, large amounts of heat are liberated, which are removed by heat exchange surfaces, in order to prevent an excessive increase of the reaction temperature. If a narrow temperature range is desirable or necessary for a favourable reaction, the catalysts are disposed in thin layers between heat exchange surfaces to ensure the removal of the heat of reaction. For example, in the production of higher hydrocarbons and oxygen-containing hydrocarbon compounds by hydrogenation of carbon monoxide, catalyst layer thicknesses of about 7 to 10 mm. are necessary. As a result of this requirement, great difficulties are encountered in the construction of the contact reactors. In particular, very large amounts of iron must be used for the contact reactor. In the synthesis of hydrocarbons by the catalytic hydrogenation of carbon monoxide at normal pressure, contact reactors are thus used which, for a yield of about 1.8 to 2 tons per day of hydrocarbons, require 35 tons of iron, and for carrying out this process under pressure the weight of the reactor unit for the same output rises to about 40 to 60 tons.

The filling and emptying of these contact reactors presents great difficulties. In order to obtain outputs at least to some extent practicable in large scale operation, layer heights of 2.5 to 4.5 metres must be used, so that the removal of catalyst from such layers becomes very difficult.

As is known, a chemical reaction proceeds more slowly, the farther advanced the conversion of the reactants. In a contact reactor in which the catalyst is accommodated between cooling surfaces in thin elongated layers for example in tubes externally surrounded by boiling water, the rate of conversion of the gas mixture passed therethrough is greater at the points of entry into the elongated layer, and decreases in the proportion to which the gas has flowed through the catalyst layer. The temperature of the cooling medium is so adjusted that optimum reaction conditions prevail as the gas enters the catalyst, for example, such conditions as will result in maximum yields with low formation of methane in the synthesis of hydrocarbons. The temperature of the cooling medium is thus sharply limited. Since the cooling medium is at all points at approximately the same temperature, the rate of reaction falls to the extent to which the concentration of the reactants falls in passing through the catalyst. Towards the end of the path of the gas, the reaction practically comes to a standstill.

In known processes however the temperatures of the individual catalyst grains are not equal across any cross-section of the catalyst layer. A catalyst grain near the centre of the layer must overcome a greater resistance to the passage of heat than that from a catalyst grain adjacent the cooling surface.

It has been found that the difference in temperature between the catalyst grains of the same catalyst layer cross-section decreases, as a certain high gas load of the catalyst is reached. The velocity of the gas passing through the catalyst then becomes so high that owing to turbulence in the gas the removal of heat from the central catalyst grain becomes approximately as good as that from

the catalyst grains or particles lying nearer the cooling surfaces. The load at which this phenomenon occurs is, depending on the nature of the catalyst, about 5 times or more the catalyst loading hitherto employed.

The present invention accordingly provides a method of producing hydrocarbons and oxygenated hydrocarbons by hydrogenation of carbon monoxide in catalytic reactors, in which the reactant gases are passed longitudinally through thin elongated stationary layers of the catalyst, each of which layers is disposed between or enclosed by heat exchange surfaces which are indirectly cooled by a cooling medium, characterised in that for the purpose of improving the transfer of heat to the cooling medium, such gas velocities in the catalyst chamber are selected, as amount to more than 0.5 metre per second, and preferably between 2 and 10 metres per second, (when referred to 0°C. and 760 mm Hg pressure and to the free cross-sectional area of the catalyst space e.g. an empty tube, before being charged with catalyst) while using catalyst layers the thickness of which is more than 15 mm., and preferably 20 to 50 mm. and while maintaining temperature differences between the catalyst chamber and cooling medium of over 10°C. and preferably up to 50°C.

In the process of the present invention also, the boiling temperature of the cooling medium is advantageously increased from the gas inlet to the gas outlet of the contact reactor, such increase amounting for example to more than 5°C. and advantageously to more than 20°C.

This can be achieved for example, by the method described in our specification No. 683,516 in accordance with which in order to obtain reaction temperatures increasing from top to bottom of a catalytic reactor, a cooling medium comprising two or more organic liquid constituents having different boiling points is used, the boiling range of which cooling medium is substantially greater than and includes the necessary range of reaction temperature.

Such an evaporation in which the lower boiling liquids are first evaporated, causes a distillative alteration of the concentration of the cooling medium in the contact reactor to take place in such a manner that the lower boiling constituents accumulate at the top and the higher boiling constituents at the bottom of the contact reactor. The temperature at the bottom of the contact reactor thus becomes higher than at the top, and by a suitable choice of the composition of the cooling medium, which can easily be determined by means of experiments, and by a suitable construction of the contact reactor, it becomes possible for each part of the contact to be at the respective optimum temperature. If the gas flows from top to bottom through the catalyst, the temperatures along the path of the gas can now be so adjusted that they correspond at all points to the optimum reaction temperatures necessitated by the altered concentration of the reactants. The same effect in relation to the temperature distribution in the cooling medium may also be obtained by other means, for example by passing a boiling cooling medium through the cooling chamber, counter-current to the gas passing through the contact reactor, resistances being interposed in the path of the cooling medium, so that the boiling cooling medium undergoes a definite loss of pressure and a corresponding alteration of the boiling temperatures on its passage through the cooling chamber. A uniform conversion may also be obtained by passing a non-boiling cooling medium through the cooling chamber concurrently with the gas, said cooling medium moving at such a speed that its temperature increases from the inlet to the outlet by the desired increase of the reaction temperature.

The uniform conversion effects a uniform loading of all parts of the catalyst and a uniform heat generation throughout the entire path of the gas. The reaction temperature at the end of the reaction is so maintained that the rate of the reaction slightly increases or decreases from the beginning to the end of the path of the gas.

Attempts have already been made to give the contact reactor a height of about 10 metres or more, in order, by making use of the hydrostatic head, to create higher boiling temperatures in the lower part of the cooling chamber than in its upper part. The attainable difference in temperature was however very low, even when using cooling media such as diphenyl, (the boiling point of which varies more greatly with the pressure than the boiling point of water) because the vapours rising in the cooling medium effect an equalisation of temperature.

The velocity of flow of the reacting gases through the catalyst was at the same time increased, due to the fact that per volumetric unit of catalyst the same conversion was obtained as with shorter catalyst tubes. However, such high gas velocities as those prescribed by the present invention, and which lie in the range of turbulent flow, have not hitherto been employed. It has also not yet been realised that any particular advantages could be obtained thereby.

In contradistinction to the foregoing known processes, the present invention aims at increasing the conversion to any desired extent within reasonable limits.

In the known hydrogenation of carbon monoxide into higher hydrocarbons, in which the catalyst is disposed in tubes or double tubes, the speed of flow of the reacting gases in the catalyst amounts at most to about 0.1 metre per second (when referred to 0°C. and

760 mm Hg pressure and to the free cross-sectional area of the catalyst space before being charged with catalyst). If on the other hand, in accordance with the present invention, the speed of flow is raised advantageously up to from 2 to 10 metres per second, or even higher, then because of the resultant turbulent gas movements, the rate of removal of heat from the catalyst grains to the walls of the tubes is substantially accelerated, and the temperature within such cross-sections becomes very uniform. The temperature at the centre of the cross-section is approximately the same as that at the edge of the cross-section. In addition, the high speed of flow of the reacting gases, in conjunction with the uniform temperatures obtained within the catalyst cross-sections, effects a more uniform distribution of the conversion and of the temperature along the gas path.

On the other hand, the high gas velocities result in a correspondingly increased conversion per unit of weight of catalyst. Accordingly, a substantially greater reaction heat is liberated per unit weight of catalyst and per unit period. In order to transfer this larger amount of heat through the walls of the reaction chamber to the cooling agent, a correspondingly greater temperature difference between the catalyst in the reaction chamber and the coolant is therefore also necessary. This greater difference in temperature cannot, however, now result in any damage to the catalyst, since the temperature of the catalyst is very uniform and dangerous hot spots no longer occur. In this method of operation also, the reaction temperature can be varied as desired, by varying the boiling temperature of the coolant.

By virtue of the great increase of the gas velocity, according to the present invention, with a uniform gas conversion throughout the entire length of the path of the gas through the catalyst, the effect is thus achieved that the increase of the rate of conversion is no longer limited by the withdrawal of heat. The limitations are on the contrary to be found in the reactivity of the catalyst.

The increase of speed may be achieved, for example when the catalyst is accommodated in tubes, by incorporating in the tubes baffle members, guide plates, deflector plates or helical windings, by which the rectilinear flow of the gases is suppressed and the gases are forced to travel a substantially longer path through the catalyst. This arrangement can be applied when the catalysts are not disposed in or between tubes or coaxial tubes but, for example, are disposed stationarily between heat exchanger plates or in any other known manner. Inserts which produce constrictions and enlargements thus effecting a rapid change of speed, which can be increased until pulsating flow is obtained, and which by destruction of the laminar boundary layers at the heat exchange surfaces, effect an improvement of the transfer of heat, and also permit a great increase in the output of catalyst reactors.

It is advantageous to increase the catalyst layer to more than 5 metres in depth, for example to a depth 10 to 20 metres. The use of greater layer thicknesses in accordance with the present invention also ensures easy removal of spent catalyst from the contact space and thus permits the construction of substantially larger catalyst reactor units.

The inserts used to increase the gas velocities are advantageously designed according to the invention as heat exchange surfaces. This can be achieved, for example, by using spirally wound fins on the tubes around or through which the cooling medium flows, or by welding the guide or deflector plates and baffle members to the heat exchange surfaces.

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

Fig. 1 is an elevation in section of a contact reactor; and

Figs. 2 to 5 are sections through various forms of catalyst and cooling tube.

The catalyst reactor shown in Fig. 1 consists of a jacket 1, and tubes 2 containing the catalyst and fastened, for example welded, into tube plates 3 and 4. 5 and 6 denote the end covers.

The synthesis gas enters the reactor at 7 and flows through the catalyst contained in the tubes 2. Said gas is deflected therein by the helically wound inserts 8, which are so shaped that the path of the gas through the catalyst becomes as long as possible. In order that the conversion may remain approximately equal over the entire path of the gas through the catalyst, the pitch of the helical inserts 8 is steeper at the bottom than at the top. The gas leaves the catalyst reactor at 9.

In the cooling medium chamber of the reactor are provided sieve plates 10 which serve to increase the difference in temperature which arises between the highest and lowest points of the cooling chamber by the greater evaporation of the lower boiling constituents of the liquid when using as cooling medium liquid mixtures, the components of which have different boiling points. The cooling medium vapours which are formed in the cooling system pass through the pipe 11 into the heat exchanger 12, in which they are condensed. The condensate flows through the pipe 13 back into the upper part of the cooling medium chamber. In the heat exchanger 12 the vapours of the cooling medium give up their heat of condensation,

for example to water which is admitted at 14 and passes out at 15 in the form of steam.

In the embodiment shown in Fig. 2, the cooling surfaces 2 are provided with guide plates 16, which cause the gas to follow a zig-zag path through the catalyst.

In the construction shown in Fig. 3, similar guide plates 17 are fixed to the cooling tubes in a coaxial tube reactor, the catalyst being accommodated in the annular space between the outer tube 28 and the inner tube 18. The inner tube 18 is in communication at top and bottom with the cooling medium space 19, so that it is also filled with cooling medium.

A coaxial tube reactor is likewise used, in the embodiment shown in Fig. 4 in which the gas is led downwardly through the catalyst. The inner tube 20 is however tapered progressively in the downward direction. In the uppermost part of the catalyst tube larger cooling surfaces, on the one hand, and smaller catalyst thicknesses, on the other hand, are thereby achieved than in the lower part thereof. Accordingly, in the upper part of the tube there results not only greater cooling, but also a higher gas velocity than in the part lying therebeneath.

In the embodiment shown in Fig. 6, the catalyst is contained in the space between coaxial tubes. The outer tube 21 may have smooth walls or else be equipped with built-in inserts. The inner tube 22 has constrictions 23 and enlargements 24. This has the effect that the gas velocity in the catalyst lying between the two tubes increases and decreases several times. A pulsating flow results which loosens the layers of gas in the immediate proximity of the catalyst and the heating surfaces and still further improves the transfer of heat.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A method of producing hydrocarbons and oxygenated hydrocarbons by hydrogenation of carbon monoxide in catalytic reactors, in which the reactant gases are passed longitudinally through thin elongated stationary layers of the catalyst, each of which layers is disposed between or enclosed by heat exchange surfaces which are indirectly cooled by a cooling medium, characterised in that for the purpose of improving the transfer of heat to the cooling medium, such gas velocities in the catalyst chamber are selected, as amount to more than 0.5 metre per second, and preferably between 2 and 10 metres per second, (when referred to 0°C. and 760 mm. Hg pressure and to the free cross-sectional area of the catalyst space before being charged with catalyst) while using catalyst layers the thickness of which is more than 15 mm., and preferably 20 to 50 mm. and while maintaining temperature differences between the catalyst chamber and cooling medium of over 10°C. and preferably up to 50°C.

2. Method as claimed in Claim 1, in which when the catalyst layers are enclosed by tubular heat exchange surfaces, the length of the layer of catalyst amounts to more than 5 metres and preferably between 10 and 20 metres.

3. Method as claimed in Claim 1 or 2, in which the gas velocities are attained by means of accelerating members such as baffle members, guide plates, deflector plates or helical windings disposed in the catalyst layers.

4. Method as claimed in any of Claims 1 to 3, in which the temperature of the cooling agent is increased in the direction from the gas inlet to the gas outlet of the catalyst reactor, for example by the method described in Specification No. 683,516, said increase preferably amounting to more than 5°C. and advantageously to more than 20°C.

5. Method as claimed in any of Claims 1 to 4, in which the velocity of the flow of gas through the upper part of the catalyst layers is kept higher than that in the lower part of said catalyst layers.

6. Method as claimed in any of Claims 1 to 5, in which a pulsating gas flow is maintained by a series of constrictions and widenings of the cross-section of the catalyst chamber in the direction of the gas flow.

7. Method as claimed in any of Claims 1 to 5, in which the gas is led downwardly through thin vertical catalyst layers extending lengthwise along cooling surfaces cooled by boiling liquids and in which the cross-sectional area of the spaces in which the catalyst is disposed increases in the direction of the gas flow.

8. Method as claimed in Claim 7, in which the vertical catalyst layers have an annular cross-section which is defined externally by a cylindrical tube and internally by a downwardly tapering tube.

9. Method as claimed in Claim 8, in which the diameter of the inner tube decreases from above to below uniformly or stepwise.

10. Method of producing hydrocarbons and oxygenated derivatives thereof, substantially as described with reference to the accompanying drawings.

Dated this 20th day of June, 1949.
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690,925 COMPLETE SPECIFICATION
1 SHEET

Fig. 1.

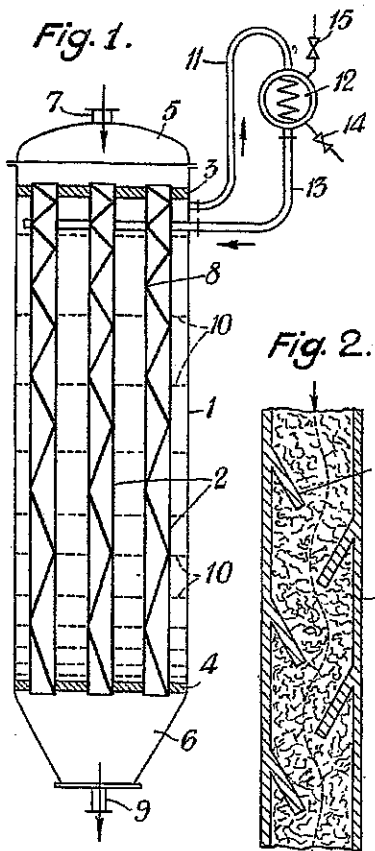

Fig. 2.

Fig. 3.

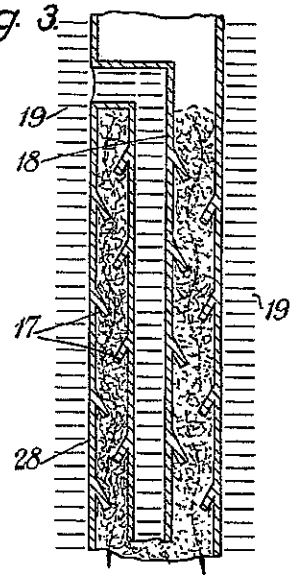

Fig. 4.

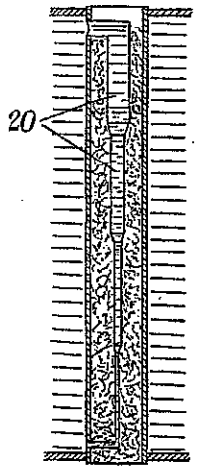

Fig. 5.