PATENT SPECIFICATION

683,516

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COMPLETE SPECIFICATION

Process of Carrying Out Exothermic Catalytic Gas Reactions

We, METALLGESELLSCHAFT AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of 45, Bockenheimer Anlage, 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 process for carrying out exothermic catalytic gas reactions and especially for hydrogenating carbon monoxide to higher hydrocarbons.

When carrying out exothermic catalytic reactions between gases, large quantities of heat are liberated. If it is necessary for a favourable course of the reaction to confine the temperature range within narrow limits, the catalysts are disposed between heat-exchanging surfaces in such a way as to ensure the transmission of the heat of reaction, or a substantial part thereof, to a cooling liquid, particularly cooling water. For example in the production of higher hydrocarbons by the catalytic hydrogenation of carbon monoxide with the aid of cobalt or iron contact masses, the catalyst is accommodated in stationary layers between cooling elements lying close to one another. The cooling is effected by boiling water under pressure.

In the case of high velocity reactions, the conversion takes place mainly in the parts of the catalyst through which the gas flows first. The bulk of the heat of reaction is thus already liberated in those layers of the catalyst, while in the subsequent parts of the catalyst the degree of conversion of the gas becomes increasingly smaller. In order to avoid impairment of the catalyst or the possibility of undesired reactions by the suddenly liberated heat of reaction, the cooling of the reaction chamber must be so intense that even in the layers in which the maximum heat of reaction is liberated, said cooling is sufficient to keep the temperature below the permissible maximum. It is then unavoidable that in the parts of the catalyst in which the residual conversion of the gases should take place, i.e., in which the gases reacting with one another have only low concentrations, the withdrawal of heat becomes too great, so that in these parts of the reaction chamber the temperature falls progressively so that the rate of reaction soon becomes so slow so as virtually to cease. The utilisation of the catalyst and of the contact reactor is therefore incomplete.

Attempts have already been made to give the contact reactor a height of about 10 metres or more, in order to keep the boiling cooling medium in the lower part of the cooling chamber of the contact reactor under higher pressure than in the upper part thereof, thus making use of the hydrostatic pressure, to create in the lower part of the cooling chamber higher boiling temperatures than in its upper part. The attainable difference in temperature, even when using cooling media such as diphenyl—the boiling point of which varies to a greater extent with the pressure than the boiling point of water—is however very low, since the vapours rising in the cooling medium effect an equalisation of temperature.

The method of carrying out exothermic gas reactions in accordance with the present invention is effected in catalytic reactors in which the liberated heat of reaction is removed by heat exchange surfaces and is transmitted to an evaporating cooling medium contained in a chamber positioned within the reactor and in which the gaseous reactants are passed into the top and the reaction products withdrawn from the bottom of the reactor.

According to the present invention, in order to obtain reaction temperatures increasing from top to bottom of the reactor, a cooling medium comprising two or more organic liquid constituents

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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.

Thus, for example the boiling range is so selected that, on the gases passing through the catalyst from top to bottom, the temperature of the cooling medium in the lower part is kept at least more than 5° C., and advantageously more than 20° C., higher than in the uppermost part. This boiling range depends, in any individual case, on the particular reaction, on the extent of the desired reaction and on the optimum reaction temperature.

Mixtures of hydrocarbons are used for example as cooling media, in such a way that the heat of reaction is withdrawn by evaporation of the cooling agent, in the cooling chamber. The evaporation is carried out in such a manner that more or less extensive rectification of the cooling agent occurs. This rectification has the effect that in the lower layers, the evaporation of the cooling agent takes place at a higher temperature than in the upper layers.

The rectification of the cooling liquid mixture in the cooling chamber is, for example, produced by filling the cooling chamber with filling rings, spirals, balls or the like packings. A suitable number of grids or sieve trays may also be disposed one above the other. Finally in many cases the cooling chamber may also be designed as a rectification column with bubble trays and caps.

The rectification may be carried out in *per se* known manner, by introducing the liquid mixture continuously or intermittently into the cooling chamber, approximately at its mid-height, and withdrawing the lower boiling constituents of the liquid mixture from the top in the form of vapours and the higher boiling constituents in liquid form from the bottom of the cooling chamber. The rectification may however, also be varied in such a way that the liquid remains continuously or for a relatively long period of time in the cooling chamber, and that only the lower boiling constituents of the liquid are evaporated and are removed for example from the top of the cooling chamber in vapour form. Said lower boiling constituents are then condensed outside the cooling chamber, preferably whilst utilising their heat of condensation, for example for steam-raising and returned to the upper part of the cooling chamber at a suitable point.

As cooling medium for the catalyst use is made of mixtures of organic liquids, particularly of saturated hydrocarbons or hydrocarbon compounds, such as paraffins, diphenyl, or glycerine. For example the cooling medium may consist of hydrocarbon fractions whose boiling range is substantially greater and includes the necessary range of reaction temperatures, for example for reaction temperatures between 250° and 300° C. the boiling range might be from 150° C. to 450° C. or above. Paraffinic hydrocarbon fractions which contain relatively large amounts of C_{15}—C_{17} hydrocarbons may frequently also be used. The selection of the boiling range of the mixtures is determined by the particular reaction temperature and the design of the reaction chamber and also by the degree of rectification obtainable with the mixture. In the case of a small degree of rectification or corresponding distillative variation of temperature and concentration in the cooling chamber, a greater boiling range is selected than in the case of a greater degree of rectification. By this adjustment it is possible to make the cooling independent of the nature of the rectification. In addition, the cooling may be adjusted by the boiling curve of the cooling agent. For example, the reaction conditions in the contact reactor may first require a slow and then an increasingly faster increase of the cooling temperature. This requirement can also be easily complied with by using a cooling liquid mixture of suitable composition, for example, fractions af preferably saturated hydrocarbons or hydrocarbon compounds having a boiling curve which is flat at the beginning and rises sharply towards the end.

The same effect may be achieved by the selection of the packings in the cooling chamber, for example by varying the distance of the packings from one another or the size of the layer or layers of packing bodies.

If the boiling limits of the cooling liquid mixture are selected to be correspondingly wide, for example from 180 to 500° C., when using mixtures of paraffinic hydrocarbons as the cooling liquid for the catalytic hydrogenation of carbon monoxide to higher hydrocarbons, given sufficiently high cooling chambers and narrow cross-sections it is even possible to dispense with inserts in the cooling chamber. It is then sufficient to use only the difference in temperature, which for example is created by the constant return of the evaporated lower boiling and recondensed liquid constituents in the upper part of the cooling chamber.

The vapours of the cooling medium which escape from the cooling chamber may advantageously be used for steam raising by passing them through a heat exchanger in which boiling water is used as cooling medium. During the cooling the boiling water evaporates and is maintained under a certain pressure. If this pressure be altered, the temperature of the boiling water and simultaneously also the temperature of the condensing cooling medium will be altered. Thus, the temperature of the condensing cooling medium can be easily adjusted by varying the pressure under which the boiling water is maintained.

In order to enable the invention to be more readily understood, reference is made to the accompanying drawings which illustrate diagrammatically and by way of example various forms of apparatus suitable for carrying the same into practical effect, and in which:—

Fig. 1 is a vertical section of one form of contact reactor;

Figs. 2 and 3 show various forms of cooling chamber;

Fig. 4 is a vertical section of another form of contact reactor; and

Fig. 5 is a plan of Fig. 4.

Referring to Fig. 1, the reference numeral 1 denotes the jacket of the contact reactor, 2 the inlet and 3 the outlet for the gases, which flow through the tubes 4 filled with catalyst. These tubes are surrounded by the cooling medium, which occupies the space in the contact reactor which is not taken up by the tubes. In this cooling chamber are disposed sieve trays 5 which may be designed, as shown on an enlarged scale in Fig. 3, and be at different distances from one another. The cooling medium vapours leave the reactor through the connections 6, which lead into the annular pipe 7. From the annular pipe, the vapours pass through the pipe 8 into the heat exchanger 9, in which they condense and give up the heat thus liberated to water which enters the heat exchanger through the pipe 10 and leaves the heat exchanger as steam through the pipe 11. The cooling medium condensate returns from the heat exchanger 9 into the contact reactor 1 through a pipe 12.

If a sharper rectification is required, the cooling chamber may be designed in accordance with the principle illustrated in Fig. 2, in which trays 13 with caps 14 are disposed around the catalyst tubes 4. 15 are the overflows, which are advantageously placed at a high level, in order that the contact tubes may be bathed as evenly as possible by the cooling medium.

The invention may also be applied to so-called lamina reactors, which are used for the catalytic hydrogenation of carbon monoxide to hydrocarbons and, if desired, hydrocarbon compounds.

Laminar reactors consist, as is well known, of a rectangular container in which are inserted vertically a large number of sheets. Through these sheets (laminæ), which are at a distance of 9 mm. from one another, numerous pipes are passed, through which the cooling water flows. These pipes terminate outside the reactor in horizontal collecting pipes which in turn lead into vertical riser pipes at each end, so that four riser pipes, one at each corner of the reactor, are connected with a steam collector in such a manner that water continuously circulates through the cooling tubes and pipes.

The riser pipes on one side of the reactor are divided into compartments so that there is one compartment to each collector pipe. Said risers are not directly connected with the steam collector. The riser pipes on the other side of the reactor are advantageously filled with packing, sieve trays or the like. From each compartment of the subdivided riser pipes, a horizontal or slightly inclined, advantageously external, connecting pipe leads to those riser pipes connected with the steam collector.

The mode of operation is then as follows:—

The cooling agent is partially evaporated in the cooling pipes. The vapour evolved rises to the steam collector through the riser pipes connected thereto. The packing or the like prevents entrained liquid from being carried upward by the vapour so that equalisation of temperature between the upper and lower portions of the riser does not occur. The liquid thus retained by the packing flows back through the connecting pipes to the separate compartments of the subdivided riser pipes, keeping these continuously filled.

In Figs. 4 and 5, 21 denotes the shell of the reactor, 22 are the lamina sheets, and 23 the cooling pipes. The cooling pipes are coiled and end in collector pipes 24. The collector pipes 24 end at both ends in the riser pipes 25. The riser pipes on the reactor side L are subdivided by the partitions 26, whilst sieve trays 27 are disposed in the riser pipes on the reactor side R. 28 are the connecting pipes, which are guided from the riser pipes of one side of the reactor to those of the other side of the reactor. The riser pipes of one side of the reactor are connected by the pipes 29 to the steam collector 30. In the steam collector 30 are provided heat exchange tubes 31, which are in communication with the pipes 29, so that the oil vapours condense in the tubes 31. The heat of condensation is given up to water present in the steam collector 30, which is evaporated and taken off in the form of steam through the pipe 32. 33 is the water supply pipe to the steam collector; 34 is the inlet and 35 the outlet for the synthesis gases.

By the subdivision of the riser pipes on one side of the reactor, the connecting pipes 28 and, where fitted, the inserts or the like in the riser pipes on the other side of the reactor, and also by the cooling tubes, various superimposed compartments are created. In these the cooling medium can circulate independently. However, no permanent rapid mixing of the cooling media, which are contained in the various superimposed compartments, occurs. Owing to this fact and to the return of the cooling medium condensate from the steam collector, the effect is achieved that a kind of rectification of the cooling medium occurs in the riser pipes so that a higher boiling cooling medium composition obtains in the lower compartments than in the compartments lying thereabove. The reactor temperatures are likewise dependent on the cooling medium temperatures, so that the lower parts of the catalyst in the reactor work at higher temperatures than the upper parts. The effect is thereby achieved that the conversion in all parts of the catalyst, is approximately equal and the influence, which would be produced by the decreasing concentration of the reacting gases on the rate of reaction as they pass through the catalyst at the same temperature, is balanced by the increased rate of reaction due to the higher temperature.

EXAMPLE.

When producing hydrocarbons by the catalytic hydrogenation of carbon monoxide by the process of the present invention, there is used for the contact reactor, which may be designed as shown in the drawing, a cooling medium which boils between 190 and 250° C. and constitutes a mixture of saturated hydrocarbons with a high proportion of C_{11}, C_{12}, C_{13} and a smaller proportion of C_{14} hydrocarbons. As catalyst, use was made of a normal cobalt-thorium oxide catalyst composed of 100 parts of cobalt, 5 parts of thorium oxide, 8 parts of magnesium oxide, and 200 parts of kieselguhr.

The synthesis gas was a pressure gasification gas, which had been produced under a pressure of 20 atmospheres above atmospheric from brown coal and was composed of:—

CO_2	1.2%
CnHm	0.1%
CO	23.3%
H_2	54.6%
CH_4	18.6%
N_2	2.3%

The operation was carried out in one stage, with recycling of the synthesis gas, using 1 volume of fresh gas to 2 volumes of recycled gas. The gas issuing from the reactor, after separation therefrom of the valuable condensible reaction products and of water, was composed of:—

CO_2	7.2%
CnHm	0.5%
CO	1.0%
H_2	0.8%
CH_4	82.3%
N_2	8.2%

The temperature at the top of the contact reactor was 190° C. It rose to 210° C. at the bottom. The gas load of the catalyst was 300 cubic metres per cubic metre of catalyst per hour. The contact reactor worked at a gas pressure of 20 atms. The yield was 60% of gasoline, 25% of diesel oil, 12% of crude paraffin, and 3% of hard wax. The gas obtained, from which the lower benzines, principally those containing three or four carbon atoms had not been separated out, could advantageously be used as pipeline gas for long distance transmission or for use in the chemical industry, as its calorific value amounted to about 8000 cals. and its methane content was over 80%.

From the results hereinbefore set forth it can be seen that the catalyst in the hereindescribed process has worked up the gas to the extent of 99.5% conversion in a single stage operation, under a load of three times that usual in the normal Fischer-Tropsch synthesis.

What we claim is:—

1. A process of carrying out exothermic gas reactions and especially for hydrogenating carbon monoxide to higher hydrocarbons in catalytic reactors in which the liberated heat of reaction is removed by heat exchange surfaces and transmitted to an evaporating cooling medium contained in a chamber positioned within the reactor and in which the gaseous reactants are passed into the top and the reaction products are withdrawn from the bottom of the reactor, characterised in that in order to obtain reaction temperatures increasing from top to bottom of the 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.

2. Process as claimed in Claim 1, in which the boiling range of the cooling medium is so selected that the cooling medium temperature rises in passing from the gas inlet to the gas outlet of the contact reactor by more than 5° C., advantageously more than 20° C.

3. Process as claimed in Claim 1 or 2, in which substantially only the lower boiling constituents of the cooling medium are evaporated, and the vapours are condensed in a cooling chamber outside the reactor, for example by the use of boiling water as heat exchange medium and returned to the cooling medium in the upper part of the chamber containing the cooling medium and positioned within the reactor.

4. Process as claimed in any of Claims 1 or 2, in which the vapours evolved from the cooling medium are subjected to rectification in the chamber containing the cooling medium and positioned within the reactor.

5. Process as claimed in any of Claims 1 to 4, in which fractions of preferably saturated, hydrocarbons or hydrocarbon compounds having a boiling curve which is flat at the beginning and rises sharply towards the end and the boiling range of which is greater than and includes the necessary range of reaction temperature, are used as cooling media.

6. Process as claimed in Claim 3, in which when using boiling water as condensing medium for the vapours of the cooling agent the temperature of the cooling agent is adjusted by varying the pressure under which the boiling water is maintained.

7. Process as claimed in Claim 4, in which the cooling medium is introduced at the mid-height of the chamber containing the cooling medium and positioned within the reactor, the lower boiling constituents of the cooling medium are withdrawn in the form of vapour from the top, and the higher boiling constituents are withdrawn in liquid form at the bottom of said chamber containing the cooling medium within the reactor.

8. Process of carrying out exothermic gas reactions and especially for hydrogenating carbon monoxide to higher hydrocarbons, substantially as described.

Dated this 20th day of June, 1949.
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Fig. 1.

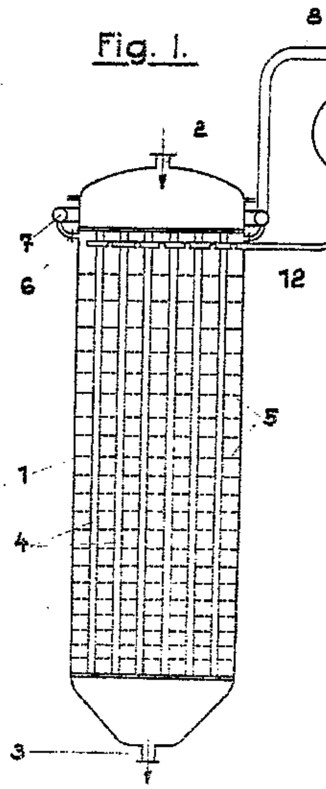


Fig. 2.

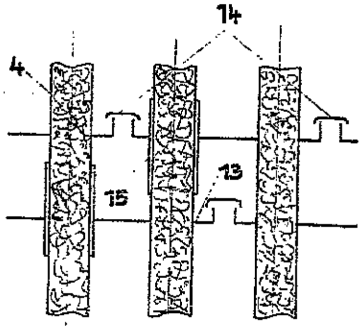
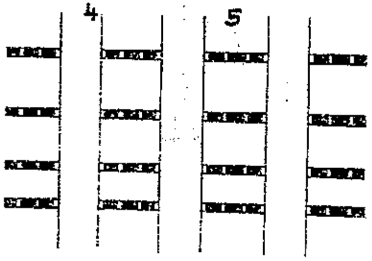
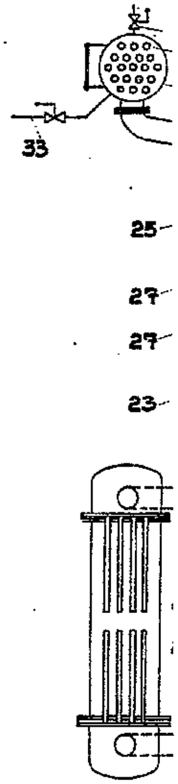


Fig. 3.





683,516 COMPLETE SPECIFICATION
2 SHEETS
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SHEETS 1 & 2

Fig. 4.

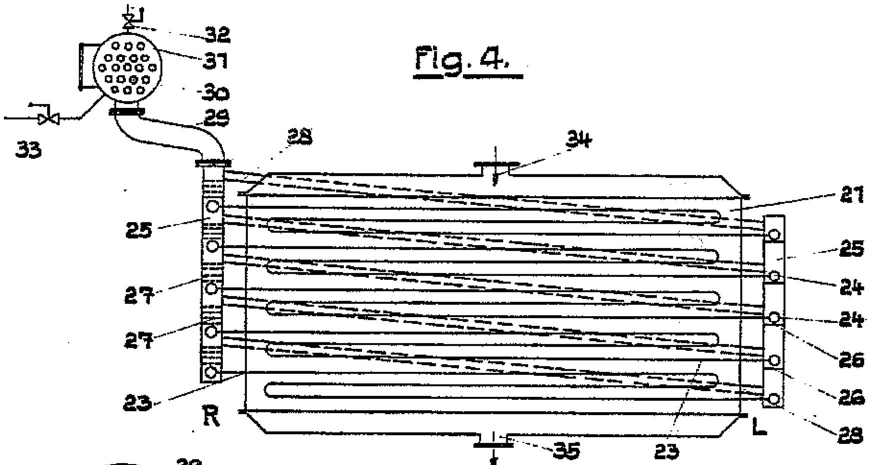
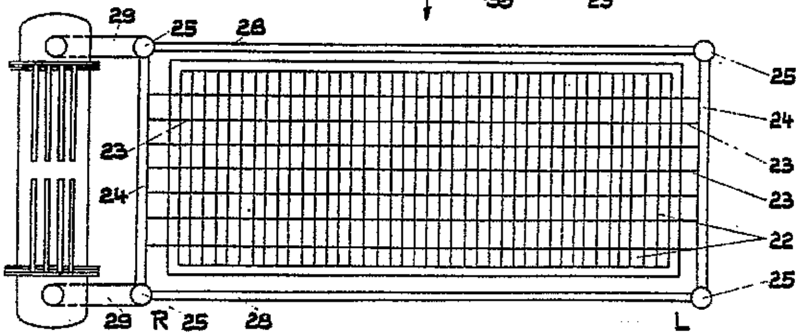


Fig. 5.



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SHEETS 1 & 2

Fig. 1.

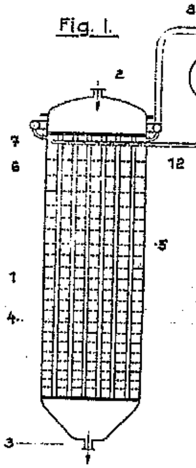

Fig. 2.

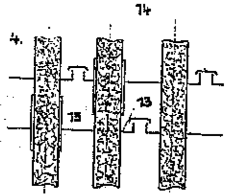

Fig. 3.

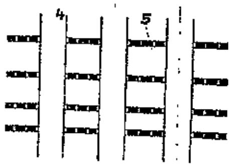

Fig. 4.

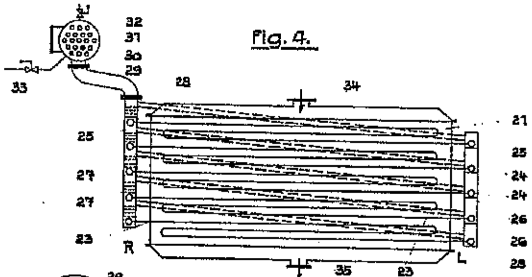

Fig. 5.