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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in or relating to Exothermic Synthesis Under Pressure.

We, COMPAGNIE DE BETHUNE, of Bully les Mines, Pas de Calais, France, a body corporate organized under the laws of France, 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 has reference to exothermic synthesis under very high pressures.

One of the principal difficulties in connection with exothermic synthesis (with diminution of volume) from gaseous bodies under very high pressure, consists in the elimination of the calories freed by the reaction.

In order to operate under several hundreds of atmospheres, it is essential to give the walls of the reaction tubes such thickness that even when employing a metal which is a good conductor of heat, the quantity of calories radiated during a given time will usually be less than that which the reaction releases. If the reaction takes place at a high temperature it will also be necessary for the preservation of the reaction tubes not to have a too sharp temperature drop between the internal and external walls, thus making it necessary to jacket the tubes externally. The insulating jacket obviously reduces loss of heat by radiation.

However, if the calories set up by the reaction are not either dissipated or absorbed, the temperature of the gaseous mixture rises abnormally in the apparatus where the reaction occurs. It affects the output and often deteriorates the catalysing apparatus employed as well as the catalytic material.

These rises in temperature are one of the reasons for which it is often necessary to reduce, reluctantly, the pressure at which it is necessary to work; at the same time the rate of combination of the bodies produced is reduced, and one is obliged to maintain the temperature at a suitable figure, to the detriment of the output.

More particularly the synthesis of methyl alcohol from carbon monoxide and hydrogen or from gaseous mixtures containing CO and H_2 requires the range of temperatures to be kept as low as possible. Any rise in temperature has not only the objection of reducing the rate of combination into alcohol between CO and H_2 (according to the laws of displacement of equilibrium) but also the objection of orientating the action towards the formation of other valueless products such as carbonic acid or methane.

If one compares this synthesis with that of ammonia, it is seen that the former releases 27.2 calories per gramme-molecule of CH_3OH, that is to say, for 3 molecular volumes of reaction gases (1 CO and $2H_2$), whilst the latter only releases 24.2 calories per 2 gramme-molecules of NH_3, that is to say for 4 molecular volumes of reaction gases ($1N_2$ and $3H_2$).

The synthesis of methyl alcohol relatively to the volume of reaction gases, therefore releases $\frac{27.2 \times 4}{24.2 \times 3} = 1.5$ times more heat.

If one attempts to effect the synthesis of methyl alcohol by employing very high pressures similar to certain processes of ammonia synthesis, one will soon be stopped by the enormous heat disengaged, for with very high pressures, the rate of combination is particularly high.

From what precedes, it is clear that the realisation of the synthesis of methyl alcohol at high pressure is practically impossible, or at least one cannot get from it all the results sought unless one cools by some means the zone of reaction.

For the reasons explained above one cannot count on radiation to get rid of the calories.

The present invention has for its object to cool the reaction zone in the catalytic synthesis of methyl alcohol under pressure starting from CO and H_2 by absorbing the disengaged calories proportionally in the interior of the zone of reaction. To this end the process according to the invention consists essentially in injecting into the reaction zone a liquid whose presence is harmless to the synthesis of the alcohol, and in propor-

tions such that its heating and above all its vaporisation in the middle of the reaction zone absorbs the excess of reaction calories.

If the liquid product has a high latent heat of vaporisation its passage from liquid to vapour or gas will require a large quantity of calories which will be furnished by the exothermic reaction itself and so will prevent any undue rise in temperature. At the outlet to the catalytic apparatus the liquid element will be re-condensed by cooling of the gases, and be separated along with the distillation of the alcohol produced by the reaction. This liquid product, it is important to remark, operates by the heat necessary to its vaporisation; it should not be in any manner considered as a dilutant added to the gases to limit the release of calories by diminution of the rate of reaction. On the contrary, as it will only be necessary to inject a relatively small quantity of a liquid having a high latent heat of vaporisation, the occurrence of dilution will be negligible relatively to the amount of the lowering of the temperature of the action, which in itself augments the output.

Amongst the liquids that it is possible to choose, water is that which gives the best results. Its heat of vaporisation is high. It is also found on the one hand that the addition of water is not harmful to the operation of the reaction, and on the other hand that if it diminishes by an amount which in any case is quite small, the rate of reaction that it would have been possible to reach under the same pressure and temperature without water injection, it augments in fact the effective output, for without it the temperature could not have been kept so low in the reaction zone that the combination rate will retain a sufficient value. Finally, water presents this advantage that once in the gaseous state, it checks the reaction of the formation in the gaseous mixture of methane; thus

$$CO + 3H_2 = CH_4 + H_2O.$$

This parasitic reaction is very objectionable because taking place in a zone of temperature hardly any higher than that corresponding to the synthesis of the alcohol, it releases still more heat than the reaction of the synthesis and consequently tends to raise the temperature still more rapidly.

The quantity of water to inject is indicated by observation of the temperatures, the rate of the reaction, the analysis of the gases, etc. It is always very small. The introduction of water into the catalytic apparatus can be effected in any convenient manner.

By way of example, the means indicated in the annexed drawing may be adopted. In this drawing:

1 is the catalysing tube, and 2 the cartridge containing the catalyst. The gases, carbon monoxide and hydrogen, for the synthesis of the alcohol enter by 3, circulate by tube 1 and cartridge 2 and traverse the latter from top to bottom, being cooled at the outlet of the tube in the refrigerator or condenser 4, which may lead into a collector 5.

The cooling water is injected into the upper part of the tube by a pump or any other suitable means so that it is brought into effective contact with the gases and the catalyst. Any other suitable means, however, might alternatively be adopted.

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 process for the synthesis of methyl alcohol under high pressure, starting with gaseous mixtures containing carbon monoxide and hydrogen, in which the undue rise of temperature is prevented by injection into the reaction zone, of a liquid whose presence does not harm the synthesis and which is employed in the proportion necessary to obtain the desired temperature and which becomes vaporised by absorbing part of the heat released by the reaction, substantially as described.

2. In the synthesis of methyl alcohol the use of water as the injected liquid for the cooling of the reaction zone, substantially as described.

3. An apparatus for synthesis under pressure according to Claim 1, said apparatus being constructed and arranged substantially as described with reference to the drawing.

Dated this 10th day of January, 1928.

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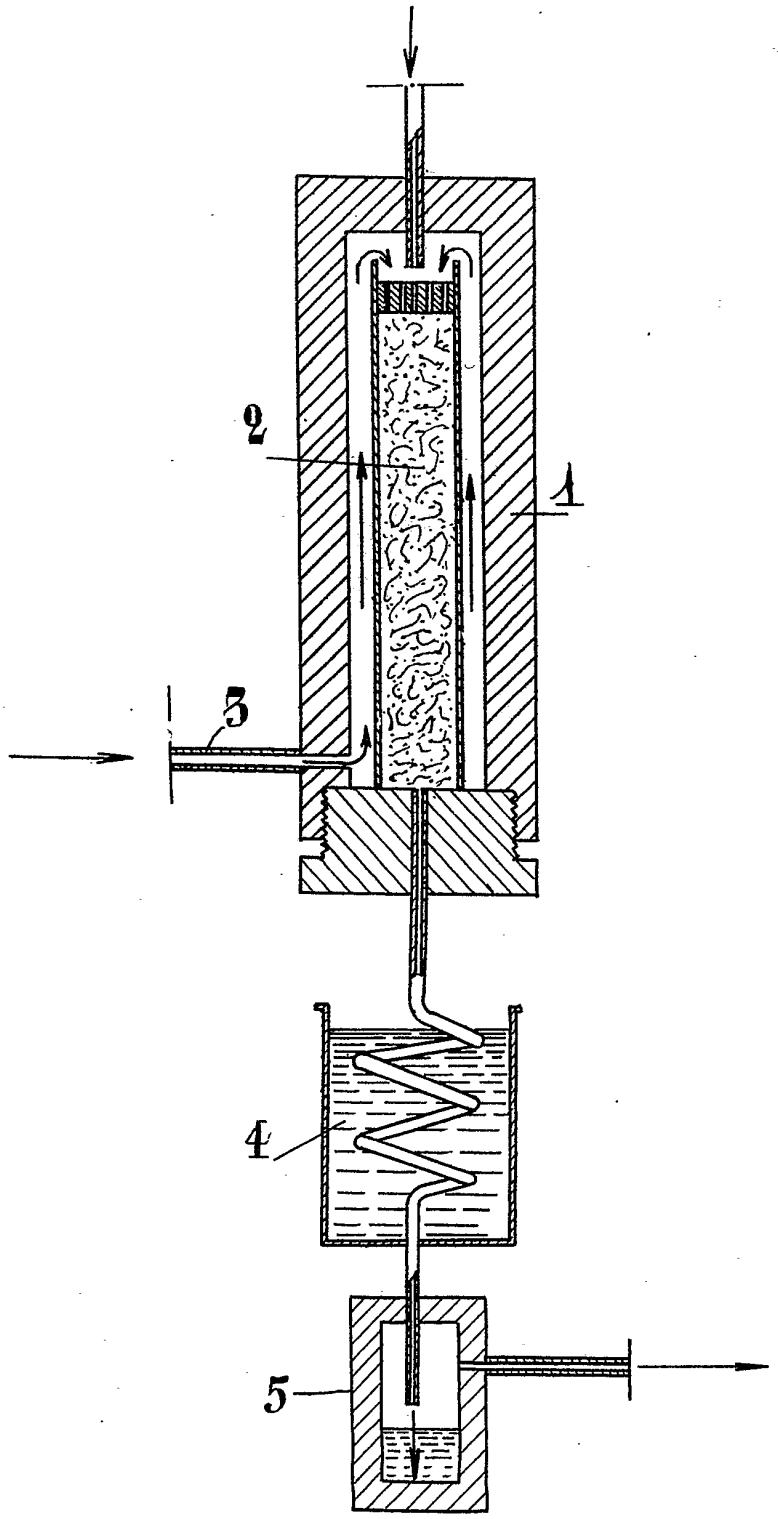

[This Drawing is a reproduction of the Original on a reduced scale.]

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