

# ALIEN PROPERTY CUSTODIAN

## ART OF CARRYING OUT EXOTHERMIC REACTIONS

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No Drawing. Application filed January 10, 1941

The present invention relates to the art of carrying out exothermic reactions in the gaseous or vaporous phase.

In exothermic catalytic reactions it is often very important to carry away the heat of reaction formed as quickly as possible; in particular when the reaction is carried out in the presence of a catalyst an even small increase of the temperature beyond the desired height may affect the activity of the catalyst or may cause undesired side reactions.

An example of such reactions is the conversion of carbon monoxide with hydrogen to form hydrocarbons containing more than one carbon atom in the molecule. Several proposals have already been made for carrying away the excess of heat evolved during this reaction, for example by indirect heat exchange relation with vaporizing water surrounding the catalyst space or by passing the reaction gases so rapidly through the catalyst space that the heat evolved is carried away by the gases and cooling the gases before they enter again the catalyst space, or by carrying out the conversion in the liquid phase, preferably in the so-called proper oil, i. e. a portion of the liquid products formed in the reaction, or also by rinsing the catalyst with a liquid medium, if desired while simultaneously cooling the reaction space by indirect heat exchange relation. These operations may be carried into effect on a technical scale, but nevertheless their applicability is restricted. When carrying out the conversion while cooling by indirect heat exchange relation with a cooling liquid or while working in the liquid phase, the velocity of flow of the gases cannot be increased beyond a definite value, and when carrying away the heat by rapidly passing the gases through the catalyst space, the catalyst layers cannot be chosen too high, if the recycling of the gases shall not require too much energy.

It has also been proposed to render the cooling of the gases more effective by increasing their capacity of taking up heat by the addition of suitable substances, as for example by adding hydrocarbon vapors. However, the effect attained in this manner in respect of the maintenance of constant temperatures is only small.

I have now found that with exothermic catalytic reactions effected in the gaseous or vaporous phase, an increase of the temperature beyond the desired height may be avoided by introducing into the catalyst space during the conversion, preferably in a finely dispersed state,

a liquid, the boiling point of which, under the pressure of the gases or vapors prevailing in the reaction space, is lower than the temperature to be attained by this cooling step, and which liquid has been preheated to this boiling point or to a higher temperature. The said liquid may also be supplied in admixture with other liquids which have a higher boiling point and remain liquid also after the introduction into the catalyst space. Examples of such liquid mixtures are in particular hydrocarbon oils of which only a lower boiling fraction is vaporized in the catalyst space. In this manner any overheating may be avoided even in large catalyst spaces.

Further cooling means, as for example indirect heat exchange relation through the walls of the catalyst space or rapid recycling of the gases with intermediate cooling, are not necessary when operating in the said manner. However, if for any reason it is desired to supply only small amounts of liquid, for example in order to keep the amount of the added liquid in the gases or vapors only low, also further cooling means may be provided.

The said cooling operation may be employed for very different exothermic catalytic reactions, for example for the preparation of oxygen-containing organic compounds, in particular alcohols, from carbon monoxide and hydrogen and especially for the hydrocarbon synthesis from carbon monoxide and hydrogen. The cooling effect attained by the added liquid is the greater the larger is the amount of liquid with reference to the amount of gas. When carrying out strongly exothermic reactions, as for example the synthesis of hydrocarbons from carbon monoxide and hydrogen, the finely dispersed liquid is preferably added already into the first part of the catalyst space, where usually the largest amount of heat is evolved. The fine dispersion of the added liquid effects an instantaneous vaporization of the small liquid particles or a disruption thereof, if they contain higher boiling portions. The step of preheating the liquids before adding them into the reaction space is an essential feature of my present process, which involves particular advantages over the addition of liquids not having been preheated. This preheating step has the effect that the liquid particles are vaporized or disrupted instantaneously after their introduction into the catalyst space, in particular when the liquid is present in the form of a fine dispersion. This causes a very rapid cooling of the entire reaction space without single places thereof being cooled too strongly, as may occur

when adding liquids which have not been previously heated. The suitability of the said preheated liquids for the purpose in consideration is obviously very surprising, since it should have been expected that the step of preheating the cooling liquids before their introduction is disadvantageous and counteracts the desired cooling effect. But this is not the case apparently due to the fact that the heat necessary for vaporizing the liquids is considerable, especially with water.

Very different cooling liquids may be employed which are suitably selected according to the nature of the gases or vapors to be cooled. For example, when reacting gases or vapors free from oxygen, liquid hydrocarbons or liquid oxygen-containing organic compounds, such as for example alcohols, or mixtures of the said liquids, are useful. In some cases water or mixtures of water with other liquids may be employed. In many cases the liquids formed in the reaction itself or portions thereof may be added. The degree of the cooling effect may be regulated according to desire by varying the amount of the added liquid.

The cooling liquid added need not be liquid under ordinary conditions, but also normally solid substances come into consideration if they are liquid after preheating and are vaporized at least partly, under the conditions of the reaction as is the case for example with naphthalene.

Even such liquids may be employed as undergo a chemical change during their passage through the catalyst space, as for example by hydrogenation, splitting (cracking) or polymerization. Thus strongly unsaturated compounds may be introduced which in the presence of hydrogen are converted into less strongly unsaturated compounds; again, oxygen-containing compounds may be added which in the course of the reaction are reduced to a higher or lower degree.

As mixtures of liquids inhomogeneous mixtures, as for example mixtures of liquid hydrocarbons and water, also come into consideration.

The liquid is advantageously introduced directly before the catalyst, but the addition and the dispersion may also be effected at some distance from the catalyst layer if it is secured that a substantial part of the liquid is evaporated not before the catalyst layer, so that the desired cooling effect extends over the whole layer of the catalyst. The fine dispersion of the liquid is preferably produced by introducing the liquid through fine nozzles, but also other devices, such as for example porous plates, through which the liquid is pressed, may be employed.

In many cases it may be desirable to supply the

liquid at several places into the catalyst space, as for example at intervals following one another in the direction of the gas stream. This modification of the process is especially advantageous if the gases are passed through high catalyst layers.

If the conversion is effected in several stages, the liquid may be added to each stage or also to only one or several stages. The supply to the first stage is especially useful, since generally in this stage the largest amount of heat is evolved.

It has already been proposed to cool hot gases, which are subjected to exothermic reactions in several stages, after their issue from the single stages by the addition of preheated liquids being evaporated in the said gases. However, in this operation the gases are only cooled in the intermediate spaces between the single conversion stages, whereas in the present process the cooling is effected mainly in the catalyst space, i. e. during the conversion itself.

The following example will further illustrate the nature of the present invention, but the invention is not restricted to this example.

#### Example

A catalyst essentially comprising iron which is suitable for the synthesis of hydrocarbons from carbon monoxide and hydrogen is filled into the tubes of a tubular furnace. Thereupon, a mixture of carbon monoxide and hydrogen is passed through these tubes (which are surrounded by a vaporising cooling liquid) at 280° C., under a pressure of 20 atmospheres and with a velocity of flow of 1000 volumes per volume of catalyst and per hour. Part of the liquid hydrocarbons formed in this treatment is introduced, after compressing to 40 atmospheres and heating to 320° C., into the catalyst space through nozzles arranged above this space. In this manner it is attained that the temperature in the catalyst space does not rise beyond 285° C. Even after working for months the catalyst does not show any deposition of carbon or reduction of its activity.

When, however, the operation is effected without the addition of preheated liquid hydrocarbons, the catalyst becomes inactive after 20 days under the same conditions of temperature and pressure, even when employing a velocity of flow of only 600 volumes of gas per volume of catalyst and per hour, since carbon is deposited on the catalyst by reason of local overheating. The yield of liquid hydrocarbons reckoned on the amount of gas supplied is not greater in this case than when carrying out the conversion with an addition of preheated liquids.

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