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COMPLETE SPECIFICATION.

A Method of Cooling Reactors for the Hydrogenation of Carbon Monoxide.

We, Ruhrchemie Aktiengesellschaft, of Oberhausen-Holten, Germany, a German joint-stock Company, 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:—

The catalytic hydrogenation of carbon monoxide, which results in the production of hydrocarbons and other compounds, is preferably carried out in such manner that the synthesis gases, that is carbon monoxide and hydrogen, are passed downwardly through the catalyst layers or columns present in the synthesis reactor. The direction of flow of the gases is appropriate in respect of synthesis products which are, in part, obtained in liquid form, but has the disadvantage that only in the upper catalyst layers does a lively gas conversion take place with intensive evolution of heat. In spite of the good circulation of an indirect cooling agent, the upper catalyst layers thus always have a somewhat higher temperature than the lower catalyst layers. As a result of this, the synthesis gases in the lower part of the reactor which are of lower concentration owing to the conversion which has already occurred in the upper part of the catalyst layers or columns, can be converted only to a slight extent. In fact it would be advantageous to make use of a lower temperature at the upper end of the catalyst filling, and an increased temperature at the lower end of the catalyst filling. In this way a uniform utilization of the catalyst and an appreciably higher reactor performance would be attained.

Attempts have already been made to achieve a higher synthesis temperature in the lower catalyst layers by the use of indirect cooling media consisting of a mixture of various high boiling hydrocarbons. By the use of mixtures of this kind an internal layering by fractionation develops in the cooling agent in the reactor, which is of such a type that the lower layers of liquid boil at a higher temperature than the upper layers. Since the reaction heat of the synthesis process is led off by the heat of vaporization taken up at the boiling temperature existing at the time, the catalyst can, in this way, be maintained in its various layers at different temperature levels.

This method of calalyst cooling with cooling temperatures dependent upon the height of the catalyst layer has, however, appreciable disadvantages. The recycling of the fractions vaporized off, with a hydrocarbon mixture not having a constant boiling point, presents difficulties in respect of maintaining the original layering. As soon as vortices occur within the cooling agent, for example because of too narrow transit cross sections, the desired technical operational temperature gradient within the cooling agent in the reactor can no longer be maintained. In order to avoid vortices it is necessary to operate with slow liquid circulation and reduced vaporization intensity.

It has been found that, when the synthesis gas is passed downwardly through the reactor, a catalyst temperature which rises in the direction of gas flow and which varies with the height of the catalytic material can be obtained with simplicity when a liquid cooling medium is used in indirect heat transfer relation with the catalyst, the cooling medium being a solution the solvent of which vaporizes under the conditions of the reaction and which consists of a single compound or of an azeotropic mixture, the solution being such that its boiling point varies with relatively small changes in the concentration of the solution so that in the lower layers of the

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cooling liquid within the synthesis reactor the boiling point is from 5°C. to 20°C. higher than in the upper layers of the cooling liquid. The positive temperature gradient in the catalyst, that is to say the temperature rise in the column or layer of catalyst in the direction of gas flow, is then dependent, at the same temperature, upon the type of cooling liquid present in the reactor. In spite of the fact that the boiling temperature increases from top to bottom, the medium vaporized off consists of an homogeneous liquid, or of a constant boiling liquid, the return of which to the reactor presents no difficulties.

The cooling medium or solution is provided around and/or within the catalyst.

The solutions used as cooling media contain osmotically working substances, that is to say, substances which alter the vapour pressure, and consequently the boiling temperature, of the solvent. At those places in the catalyst filling where an intensive heat development occurs, large amounts of the solvent are vaporized. The greater the quantity of solvent vaporized from solutions of this type, the greater their specific gravity and their boiling point. The portions of the solution the specific gravity of which has increased sink down within the cooling agent in the reactor, whilst the portions of the solution which are not so concentrated collect in the upper part of the cooling agent in the reactor. Thus a fractional layering takes place according to boiling points, and according to specific gravities, in which the higher boiling components remain at the bottom. In contrast to the boiling points of vaporizing homogeneous solvents, which depend hydrostatically upon the catalyst position, if solutions are used whose boiling point varies osmotically, that is to say, with the concentration of the solution, then the development of vortex movements within the cooling agent supply is prevented as far as possible.

The reaction heat developed during synthesis is of necessity carried off, in the lower catalyst layers, by the concentrated solution layers, at a higher temperature than in the upper part of the catalyst column. In this way a positive temperature gradient exists in the catalyst column, the temperature increasing uniformly in the direction of flow of the synthesis gas. The lower temperature maintained at the upper end of the catalyst filling serves to effect a reduced conversion of the fresh synthesis gases, whilst the higher temperature at the lower end of the catalyst filling enables a normal catalytic conversion of the synthesis gases, which are already partially exhausted, to be effected.

The solvent, preferably water, which is vaporized off from the solution used as cooling agent, is replaced by fresh solvent (fresh water), the fresh solvent being added from above to the cooling agent supply within the reactor. The fresh solvent dilutes the solution serving as cooling agent, first in its upper layers, and not until later does it reach the lower layers of the cooling agent in the reactor. In this way, the internal layering of the cooling agent column in the reactor, and consequently the gradient of the boiling temperatures, is maintained.

The solute is preferably non-volatile, or substantially non-volatile, under the conditions within the reactor.

The osmotic change of vapour pressure and boiling temperature in the cooling agent column is best realized by means of aqueous solutions of readily soluble inorganic or organic salts or bases. For this purpose, salts and compounds which suffer no change or decomposition at the temperatures in question, nor attack chemically the material of which the synthesis reactor is constructed, are preferably used. Particularly well suited are, for example, aqueous solutions of calcium chloride, magnesium chloride or sodium hydroxide; their solubility ratios are in such a range, that it is possible to obtain without difficulty, by differences in concentration, differences in temperature of up to 20°C. between the upper and lower layers of the cooling agent in the reactor. If use is made of salt solutions, then the work is carried out with the addition of appropriate corrosion-preventing substances, such as are commonly used for example with cooling brines.

What we claim is:—

1. A method of cooling and of maintaining a positive temperature gradient in the direction of gas flow in a substantially vertical layer or column of catalytic material in a reactor in which a synthesis gas comprising carbon monoxide and hydrogen is reacted by being passed downwardly through the catalytic material, which comprises providing a solution around and/or within the catalytic material and in indirect heat transfer relation therewith, the solution having a solvent component which is a single liquid compound or an azeotropic mixture and which vaporizes under the conditions within the reactor, the solution being such that its boiling point varies with relatively small changes in the concentration of the solution so that the boiling point of the lower layers of the solution is from 5°C. to 20°C. higher than the boiling point of the upper layers of the solution in the reactor.

2. A method according to Claim 1. in which the solute is substantially non-volatile under the conditions within the

reactor.

3. A method according to either of the preceding claims, in which the solution is an aqueous solution of a readily soluble organic or inorganic salt or base.

4. A method according to any one of the preceding claims, in which the solution is an aqueous solution of calcium chloride, magnesium chloride or sodium hydroxide.

5. A method of cooling reactors for the hydrogenation of carbon monoxide, substantially as hereinbefore described.

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EDWARD EVANS & CO.,
14-18, High Holborn, London, W.C.1.
Agents for the Applicants.

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