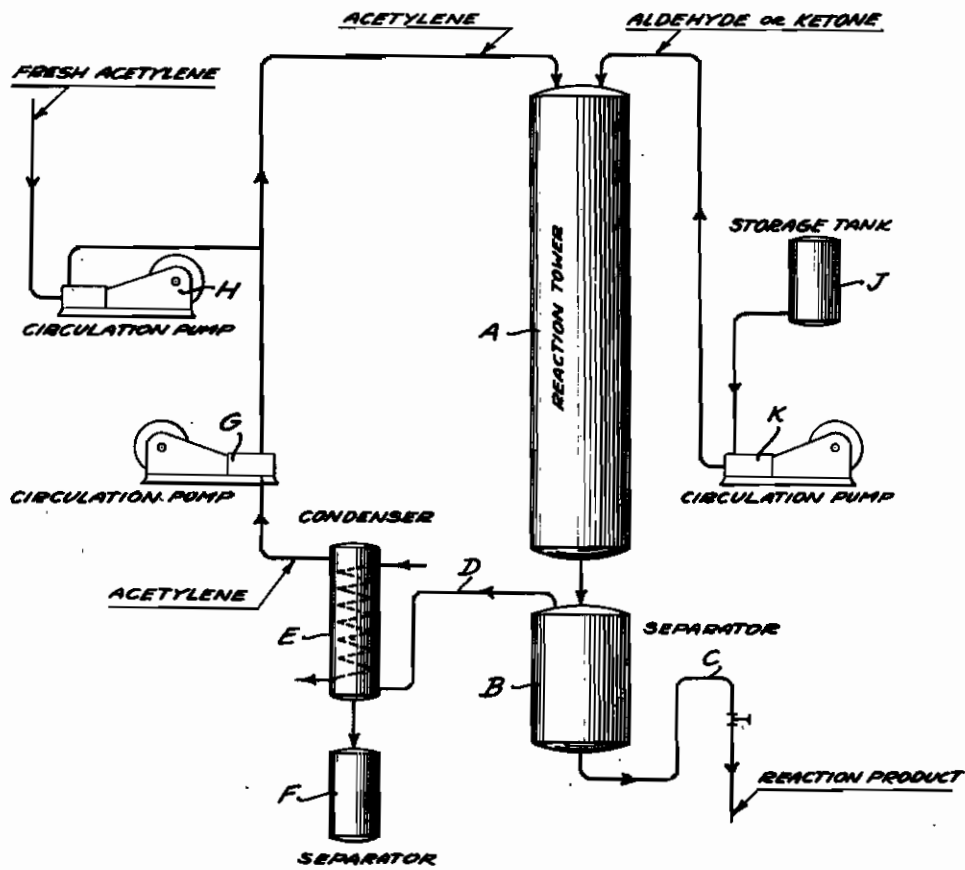


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PROCESS FOR THE PRODUCTION OF ALCOHOLS
OF THE ACETYLENE SERIES
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ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF ALCOHOLS OF THE ACETYLENE SERIES

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The present invention relates to a process for the production of alcohols of the acetylene series.

We have found that alkinols, i.e. alcohols of the acetylene series, may be obtained in an especially advantageous manner by causing to flow aldehydes or ketones in the liquid state, which term wherever used herein shall also include aldehydes and ketones in the dissolved state, together with an excess of acetylene through a reaction vessel charged with an acetylide of a heavy metal of the 1st and 2nd group of the periodic system or with such compounds of these metals as are capable of forming acetylides by reaction with acetylene, separating from the excess of acetylene leaving the reaction room the vaporous substances contained therein and recycling the acetylene into the reaction room.

The reaction may be carried out with aliphatic aldehydes of saturated or unsaturated nature, for example with formaldehyde, acetaldehyde or crotonaldehyde, and also with araliphatic or aromatic aldehydes, such as benzaldehyde. Suitable ketones are, for example, aliphatic ketones, such as acetone or methylethylketone, and hydroaromatic or araliphatic ketones, such as cyclohexanone or acetophenone.

As catalysts there may be used the acetylides of the heavy metals of the 1st and 2nd group of the periodic system and in particular the acetylides of metals of the Group I a of that system and of mercury, copper acetylide being the preferred catalyst. While the heavy metal acetylides may be prepared per se, it is also possible to allow them to be formed in the course of the reaction itself from heavy metal compounds capable of forming the acetylides. Such compounds are, for example, salts of the said heavy metals, for example, cupric phosphate and acetate, cuprous or cupric chloride, ammoniacal copper sulphate or silver nitrate or mercury chloride or mixtures of these salts, if necessary in the presence of compounds capable of binding acids. Such compounds are, for example, the salts of alkali and earth alkali metals and of magnesium with weak acids, for example, the formates, acetates, carbonates and bicarbonates. There may also be used earth alkali metal hydroxides, such as barium or calcium hydroxide, and other weakly basic substances, such as zinc oxide, zinc carbonate, alkali metal phosphates and silicates. Solutions or suspensions of these compounds may be used. The catalyst may, for example, be dispersed in the aldehyde or ketone as a powder or may be rigidly arranged in the form of small pieces or deposited on a carrier. As carriers

silica gel or another inert carrier may be used, for example aluminium oxide, Fuller's earth, aluminium silicate, active charcoal or coke.

Catalysts suitable in the present reaction may be obtained, for example, in the following way (parts by weight):

(1) 4.5 parts of 20 per cent aqueous ammonia are added to a solution of 2 parts of crystallized cupric chloride in 100 parts of water. Acetylene is led into the solution thus obtained at ordinary temperature while stirring for 50 minutes. The precipitated cupric acetylide is filtered off by suction and washed with water.

(2) A solution of 30 parts of cuprous chloride in 20 parts of 20 per cent aqueous ammonia solution is diluted with 2000 parts of water and acetylene is led in while stirring after the addition of 50 parts of fuller's earth. The resulting precipitate is washed with water.

(3) A mixture of 40 parts of cuprous chloride and 40 parts of basic magnesium carbonate is suspended, while stirring in a solution of 2 parts of silver nitrate in 150 parts of water, the suspension being treated with acetylene at 70° C until the original pale yellow color has been converted into a dark red-brown. The mixture of silver and copper acetylene compounds thus obtained may be used as such or after bringing it onto pumice stone.

It should be understood that other methods for preparing the catalysts may be used with the same results.

Among solvents and diluents adapted for the purpose of our present invention we may mention in particular water, alcohols, ethers or mixtures thereof and hydrocarbons. When starting from aldehydes or ketones which are liquid under the reaction conditions, the solvent or diluent may entirely be dispensed with. When reacting aldehydes we prefer to use a weakly acid or neutral reaction, while when starting from ketones the reaction liquid may as well be alkaline. Generally speaking the hydrogen ion concentration is advantageously kept between about pH=2.5 and pH=12, in order to avoid a splitting of the acetylene alcohols and the decomposition of the catalyst.

The reaction is carried out at elevated temperatures, preferably between about 60° and 160° C, temperatures between 90° and 140° C being the most suitable ones.

According to our invention the alcohols of the acetylene series may be prepared continuously or discontinuously. Thus, acetylene may be introduced into a reaction tower charged with the

catalyst from below and passed through a downward stream of liquid or dissolved aldehyde or ketone. The trickling method may be used with special advantage: The liquid or dissolved aldehyde or ketone, for example an aqueous solution of formaldehyde, is caused to trickle at say from 60 to 110° C over a catalyst rigidly arranged in the reaction tower while an excess of acetylene is led in at the bottom of the tower. Instead in countercurrent the acetylene may, however, be led in the same direction as the liquid aldehyde or ketone through the reaction room. Superatmospheric pressure of say, for example, from 2 to 20 atmospheres, and, instead of pure acetylene, dilute acetylene from any source, for example acetylene in dilution with hydrogen, carbon monoxide or carbon dioxide, methane or steam, may be employed.

The heat resulting in the highly exothermic reaction causes the aldehyde or ketone and/or the solvent used in dissolving the aldehyde or ketone to be partially evaporated. The vapor thus formed, the quantity of which is a function of the partial pressure at the reaction temperature, leaves the reaction vessel together with the unconverted acetylene. On cooling, the acetylene is freed from the vapors contained therein and is returned into the reaction vessel.

By the constant discharge of acetylene saturated with vapors, the temperature in the reaction vessel may be easily so controlled that, even in the case of high throughputs, reaction vessels of a very great inner diameter may be employed. This control of the temperature prevents the catalyst to be decomposed by overheating by the heat evolved in the reaction even in the middle of the reaction space where an outside cooling is not or but difficultly possible, and thus prevents the yield to be unfavorably affected. The degree of evaporation and the temperature in the reaction vessel depend on the quantity of the acetylene circulated through it. The solvent, the pressure and the speed of the acetylene are preferably so chosen that the temperature of the catalyst or the temperature in the neighbourhood of the catalyst does not considerably exceed 160° C; as stated above, it is preferable to keep the temperature within a range of from 90 to 140° C.

Depending on the reaction conditions, the nature of the initial materials and the catalyst, mono- or divalent alcohols of the acetylene series or mixtures thereof are obtained. From acetylene and formaldehyde there may thus be obtained either propargyl alcohol or butine-2-diol-1.4 or their mixtures. Such mixtures may easily be separated, whereupon the monohydric alcohols of the acetylene series, for example, the propargyl alcohol, may be returned into the reaction vessel, where it is wholly or partially converted into the dihydric alcohol. When the monohydric alcohol has a low boiling point, it may wholly or partially be removed by the acetylene gas from which it may be separated by condensation together with the solvent and initial material before the acetylene is led back into the reaction vessel.

One embodiment of the present invention will be more fully illustrated by way of the following Example for the preparation of butine-2-diol-1.4 from acetylene and aqueous formaldehyde by the

trickling method; it is to be understood, however, that our invention is not restricted to the said Example.

Example

A vertical pressure-tight tube of alloy steel of 400 millimeters inner diameter and 12000 millimeters length is charged with 1400 liters of silica gel on which copper oxide has been deposited. This catalyst is prepared by soaking the silica gel twice with a saturated solution of basic copper carbonate in concentrated aqueous ammonia, drying and heating the grains to 400° C. During the course of the reaction the copper oxide is converted into copper acetylide. 650 kilograms of a 30 per cent aqueous solution of formaldehyde, preheated to 50 to 60° C, are allowed to trickle down through the tube in the course of an hour, while 300 cubic meters of acetylene (measured at 0° C and 760 millimeters) are simultaneously led in at the top of the tube. The pressure in the tube amounts to 5 atmospheres. The unconverted acetylene is pumped round in a cycle and the acetylene consumed by the reaction is continuously replenished. After a short time a temperature of from 100° to 120° C is set up in the main reaction zone of the tube. The reaction mixture leaving the tower is passed through a pressure-tight separator, where the aqueous solution of butine-2-diol-1.4 is separated from the acetylene and vaporized substances which are led into a cooler where they are cooled down to 40° C. In a separator connected with the cooler about 120 kilograms of water are collected per hour containing some propargyl alcohol and methanol. From the aqueous solution of butine-2-diol-1.4 the pure butine-2-diol-1.4 may be isolated, for example, by evaporating the water. The yield amounts to 96 per cent (percentage with reference to the formaldehyde employed). The acetylene and, if desired, the propargyl alcohol are returned into the reaction tube.

The present invention will be further described with reference to the accompanying drawing which diagrammatically shows an apparatus suitable for use in carrying out the reaction in accordance with our present invention.

From the storage tank J the aqueous solution of formaldehyde is conveyed to the reaction tower A by pump K, while acetylene is simultaneously pumped in at the top of tower A. The bottom end of the tower communicates with a pressure tight separator B, where the liquid reaction product and the gas are separated. The aqueous solution of butine-diol is withdrawn through line C, whereas the acetylene and the steam (together with some methanol and propargyl alcohol) are passed to cooler E through line D. The water, methanol and propargyl alcohol are collected in separator F connected with the cooler E. The acetylene is passed to the circulating pump G and returned into the reaction tower. By the pump H fresh acetylene is pressed into the system at the rate at which it is used up during the reaction.

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