

# ALIEN PROPERTY CUSTODIAN

## PREPARATION OF CROTONALDEHYDE

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No Drawing. Application filed August 20, 1940

The present invention relates to improvements in the preparation of crotonaldehyde. In particular it relates to the crotonisation of acetaldo1 by the action of heat on crude acetaldo1 solutions as obtained in the aldolisation of acetaldehyde.

It is an object of this invention to provide a practical, economical and commercially applica- 5 ble method for the preparation of crotonaldehyde in a continuous process. It has been known for some time that crotonaldehyde may be prepared by introducing aldol into a boiling dilute acid solution and removing the decomposition prod- 10 ucts substantially as fast as formed. In order to promote the expulsion of the decomposition products it has also been proposed to carry out the crotonisation under sub-atmospheric pressure while using lower temperatures. The decompo- 15 sition products of the crotonisation consist substantially of crotonaldehyde and water, provided that the aldol used was free from other constituents. In practice, the decomposition products are admixed with acetaldehyde which is always present in the crude aldol usually employed in the preparation of crotonaldehyde. Hence, during the step of condensing crotonalde- 20 hyde and water from the vapors distilling off from the crotonising vessel, care has to be taken that the acetaldehyde is also condensed. When operating under normal pressure, the condensa- tion of acetaldehyde requires a cooling medium of low temperature. In a vacuum process, it becomes necessary to use brine in order to avoid substantial losses of acetaldehyde.

We have now found that the crotonisation of crude aldol may be carried out with excellent yields in a very simple manner, by exposing the liquid aldol to the action of heat in a crotonising vessel under superatmospheric pressure. Generally speaking, the pressure used may only be, from 0.5 to 2 atmospheres in excess of atmospheric pressure, though higher pressures may likewise be employed.

In preparing crotonaldehyde according to our invention, crude aldol as obtained by treating acetaldehyde with aqueous alkaline solutions may be admixed continuously with an agent promot- 45 ing the splitting off of water and be pressed into a fractionating device kept under superatmospheric pressure. The crotonisation products obtained (including acetaldehyde) are separated by fractional distillation under superatmospheric pressure, the crotonisation thus taking place dur- 50 ing the fractionation.

Crude aldol may also be introduced continu- ously into a still connected with a fractionating

column kept under superatmospheric pressure, the still being charged with an aqueous solution of a crotonising agent. This solution is heated to a temperature enabling the crotonisation prod- 5 ucts to be distilled off. The speed of distillation is so chosen that the concentration of the croton- ising solution remains substantially constant dur- ing the process. The vapors emerging from the solution consisting substantially in an azeotropic mixture of crotonaldehyde and water and in ac- 10 etaldehyde are separated in the single constitu- ents by means of the fractionating column and obtained in the liquid form. The acetaldehyde obtained may again be used for preparing aldol.

The crotonising agent may be added to the crude aldol before it is introduced into the re- 15 action vessel.

According to our invention it is possible to con- dense the acetaldehyde distilling off together with crotonaldehyde and water simply by means 20 of water of ordinary temperature as cooling me- dium, whereas when working under normal or subatmospheric pressure, special cooling agents are necessary. It is surprising that the speed of crotonisation is not affected by working under superatmospheric pressure and that the croton- 25 aldehyde formed does not undergo any side-re- actions.

The following example will further serve to illustrate the nature of our invention, but the in- 30 vention is not restricted to this example. The parts are by weight.

### Example

A solution of 5 parts of primary sodium phos- 35 phate in 100 parts of water is kept boiling in a distillation still provided with a fractionating apparatus under a pressure of 0.8 in excess of atmospheric pressure. 160 parts of a mixture of aldol and acetaldehyde, containing 76 parts of aldol, per hour are introduced into the still. A mixture of water, crotonaldehyde and acetalde- 40 hyde distills off at the same rate. There are obtained 60 parts of crotonaldehyde per hour, and 84 parts of acetaldehyde per hour, the latter being condensed at 35° C by means of water of 25° C as the cooling agent. Crotonaldehyde and water leave the fractionating device in the liquid form. The acetaldehyde is led back for aldolisa- 50 tion.

The primary sodium phosphate in the above process may be replaced by other electrolyte so- lutions exerting a from acid to neutral reaction. There may be used, for example, diluted mineral acids, organic acids or salt solutions having a

from acid to neutral reaction. Preferably, the crotonisation should be carried out in an aqueous solution having a pH-value within the range from 2 to 7. In order that this range is maintained during crotonisation, it is preferable to use electrolyte solutions which have a buffering action within that range. The preparation of such buffering solutions is generally known; we prefer to use, for example, primary and secondary alkali

metal phosphates or mixtures thereof or these phosphates admixed with small amounts of free phosphoric acid, or potassium biferate or, in case the aldol used has already a weakly acid reaction, sodium acetate.

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