Modeling, simulation and analysis of a process for the production of crotonaldehyde

Andreas Scheithauer [a], Thomas Grützner [b], Daniel Zollinger [b], Erik von Harbou [a,*], Hans Hasse [a]

[a] Laboratory of Engineering Thermodynamics, University of Kaiserslautern, Erwin-Schrödinger-Strasse 44, 67663 Kaiserslautern, Germany
[b] Lonza AG, Rottenstrasse 6, 3930 Visp, Switzerland

ARTICLE INFO

ABSTRACT

Crotonaldehyde is an important intermediate in the chemical industry and usually produced from acetaldehyde in aqueous solution. Recently, new results on the reactions which yield crotonaldehyde from acetaldehyde have become available. It was shown that the formation of aldoxane from acetaldehyde and acetaldol, as well as the oligomer formation in the system acetaldehyde and water have to be taken into account. In the present paper, the established process for the production of crotonaldehyde is analyzed based on that new information. A model for the physico-chemical properties of the relevant mixtures is developed as well as an equilibrium stage based process model. The models are implemented in a steady state process simulation tool which is used for numerical studies of the process. The results provide unexpected insights in the process which contains distillations in which complex reactions occur. A conceptual process design is carried out applying a structured approach. The performance of the process is analyzed and potential for its optimization is discussed.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Crotonaldehyde (2-butenal) is an important intermediate in chemical industry and occurs in two stereoisomeric forms, cis- and trans-crotonaldehyde. Trans-crotonaldehyde is the predominant form (>95 %) [1]. Crotonaldehyde is used for the production of many products. The most important one is sorbic acid which is mainly used as preservative in foods, cosmetics and pharmaceuticals [2]. Another one is 2,3,6-trimethylphenol, which is a starting material for vitamin E production and serves as a comonomer for the production of crotonic acid copolymers which are used in various applications [1]. Crotonaldehyde can be also produced from other educts than acetaldehyde [3] and from acetaldehyde in gas phase [4–10]. These processes are not discussed here.

In the literature, the production of crotonaldehyde from aqueous acetaldehyde has until recently been considered as a simple two step reaction [1]: in the first step, the "aldol addition", which is carried out in basic medium, acetaldehyde is converted to acetaldol. In the second step, the "dehydration", acetaldol forms crotonaldehyde by elimination of water. The aldol addition has been subject of

many studies in literature, e.g. [11–17], and so has the dehydration [18–20].

In previous work of our group [21], it was shown, that the simple two-step picture of crotonaldehyde production in literature is an oversimplification. At the conditions encountered in the crotonaldehyde production, aldoxane is the main intermediate of the aldol addition whereas acetaldol is hardly present. The importance of the intermediate aldoxane, which is formed in a reaction of acetaldehyde with acetaldol, had been overlooked. Furthermore, poly(oxymethylmethylene) glycols, which are oligomers formed from acetaldehyde and water, are present and should be considered. Recently, new data on the equilibria [22] and kinetics [23] of these reactions have become available. Experience with the design of processes in which mixtures of formaldehyde and water occur, which are chemically closely related to the mixtures of acetaldehyde and water which are considered here, shows that the process design should be based on the knowledge of the true speciation of the studied mixtures [24–29].

In the present work, the new information presented in [21], [22], and [23] is used for an analysis of the established production process of crotonaldehyde. That process is described in [1] and discussed in more detail below. There are also many patents related to the production of crotonaldehyde, some of which are briefly discussed in [30].

* Corresponding author.
E-mail address: erik.vonharbou@mv.uni-kl.de (E. von Harbou).

A model for the physico-chemical properties of the relevant mixtures is developed as well as an equilibrium stage based process model. The models are implemented in a steady state process simulation tool which is used for numerical studies. The description of the crotonaldehyde production process provided here is considerably more detailed and realistic than that from previous work with respect to process description [1] or kinetic models [11,12,15,18,19], which were based on the oversimplified reaction scheme. The results from the present study provide unexpected insights in the process. A conceptual process design is carried out applying a structured approach. The performance of the process is analyzed and potential for its optimization is discussed.

2. Reaction system

In the aldol addition reaction, acetaldehyde (AA) is converted to acetaldol (ADL):
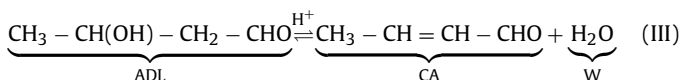
$$\underbrace{2CH_3-CHO}_{AA} \overset{OH^-}{\rightleftharpoons} \underbrace{CH_3-CH(OH)-CH_2-CHO}_{ADL} \qquad (I)$$
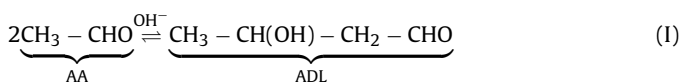
Reaction (I) occurs in basic media. In a subsequent reaction, acetaldol reacts with acetaldehyde to aldoxane (ALX):

$$\underbrace{CH_3-CHO}_{AA} + \underbrace{CH_3-CH(OH)-CH_2-CHO}_{ADL} \rightleftharpoons \underbrace{C_6H_{12}O_3}_{ALX} \qquad (II)$$
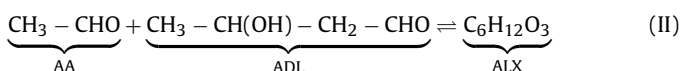
Reaction (II) occurs at all pH values.

Acetaldol (ADL) forms crotonaldehyde (CA) by elimination of water:

$$\underbrace{CH_3-CH(OH)-CH_2-CHO}_{ADL} \overset{H^+}{\rightleftharpoons} \underbrace{CH_3-CH=CH-CHO}_{CA} + \underbrace{H_2O}_{W} \quad (III)$$
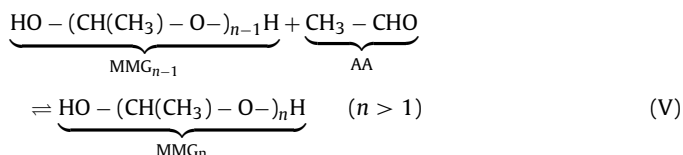
Reaction (III) is catalyzed by acids.

Industrial processes for the production of crotonaldehyde from acetaldehyde exploit the Reactions (I–III) in the following way: in a first step, at basic conditions and temperatures between about 290 and 310 K Reactions (I and II) occur simultaneously. At these conditions the chemical equilibrium of Reaction (II) is far on the aldoxane side [21]. Then the pH-value is shifted to acidic conditions, so that only Reactions (II and III) can occur. In order to recycle all unreacted acetaldehyde (and, thereby, to enrich acetaldol for conversion to crotonaldehyde), the cleavage of aldoxane (the reverse reaction of Reaction (II)) has to be enforced, because acetaldehyde is chemically bound in that high boiling component. The conditions in the reactive distillation column support the reverse reaction, as

acetaldehyde is removed by distillation when it is continuously drawn off in the top stream. Acetaldol then reacts to crotonaldehyde via Reaction (III). The role of aldoxane in the process has been elucidated only recently [21]. In previous works it had been mentioned only as a side product [31–34].

In mixtures of acetaldehyde and water poly(oxymethylmethylene) glycols (MMG) are formed. The first member of the homologous series is 1,1-ethanediol (MMG_1) and formed in the reaction of acetaldehyde (AA) with one water (W) molecule:

$$\underbrace{CH_3-CHO}_{AA} + \underbrace{H_2O}_{W} \rightleftharpoons \underbrace{HO-(CH(CH_3)-O-)H}_{MMG_1} \qquad (IV)$$
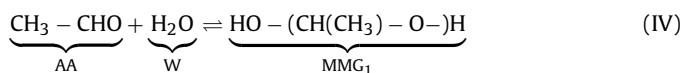
The formation of the higher oligomers ($MMG_{n>1}$) can be described as follows:

$$\underbrace{HO-(CH(CH_3)-O-)_{n-1}H}_{MMG_{n-1}} + \underbrace{CH_3-CHO}_{AA}$$
$$\rightleftharpoons \underbrace{HO-(CH(CH_3)-O-)_nH}_{MMG_n} \qquad (n>1) \qquad (V)$$

The poly(oxymethylmethylene) glycols are not stable as pure substances.

Some literature studies [35–38] report on the formation of paraldol (PADL). It is formed in a reaction of two acetaldol (ADL) molecules:

$$\underbrace{2CH_3-CH(OH)-CH_2-CHO}_{ADL} \rightleftharpoons \underbrace{C_8H_{16}O_4}_{PADL} \qquad (VI)$$
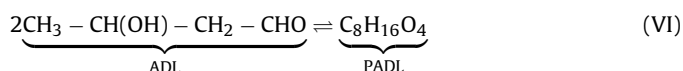
In the process studied here, the formation of paraldol (PADL) is unlikely [21] and, therefore, it is not considered in the present work.

Throughout the present work overall concentrations (mole or mass fractions) $\tilde{x}_i$ are distinguished from true concentrations x_i. The overall concentrations are those that are obtained when all poly(oxymethylmethylene) glycols are split into acetaldehyde and water. They are known e.g. from a gravimetric preparation of samples or conventional GC analysis. It is disregarded in which chemical form the educts water and acetaldehyde are present in the reaction mixture. True concentrations are, on the contrary, those related to the true speciation of the mixture, including the poly(oxymethylmethylene) glycols. They can, e.g. be obtained by NMR spectroscopy.

In the production of crotonaldehyde (CA) from acetaldehyde (AA) the formation of various side-products is possible [39]. The most important one is 2,4-hexadienal (HEX) [40–43], but also paraldehyde [44], dimeric crotonaldehyde [41,45], 2,4,6-octatrienal,
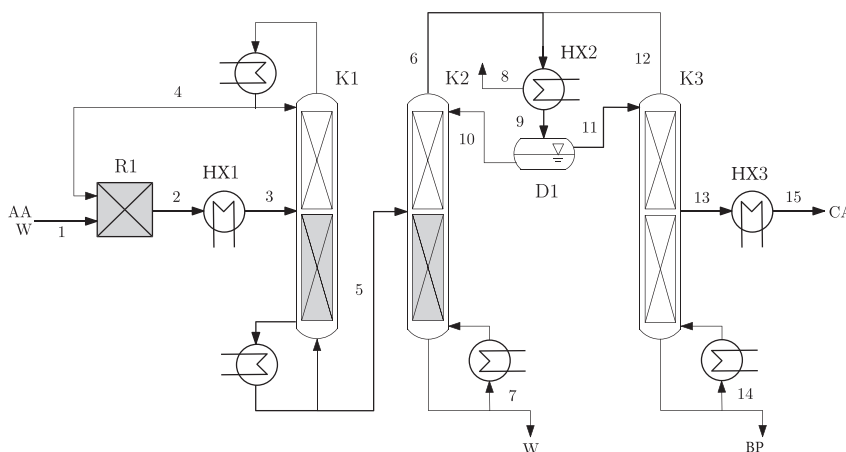

Fig. 1. Process flowsheet of the state-of-the-art process for the production of crotonaldehyde from acetaldehyde [1] with abbreviations for the apparatus and stream names as used in the present work.