



Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec



Alternative integrated distillation strategies for the purification of acetonitrile from ethanol ammoxidation

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ARTICLE INFO

Article history:

Received 19 August 2017
Received in revised form 13 September 2017
Accepted 2 October 2017
Available online xxx

Keywords:

Acetonitrile
Distillation
Azeotrope separation
Process simulation
Thermodynamic models

ABSTRACT

The feasibility and performance of different strategies to purify a complex mixture of H₂O/CH₃CN/NH₃/HCN from bioethanol ammoxidation are compared. Dichloromethane as entrainer is taken as a base case and compared with more sustainable molecules, such as ethyl acetate (EA), ethylene glycol (EG) and glycerol (G). The thermodynamic behavior of the homogeneous or heterogeneous mixtures is first discussed. Then, the separation and purification section is designed accordingly. To yield high-purity acetonitrile a low-boiling entrainer (EA) is preferable. If economic issues prevail, then EG grants a lighter sizing of the equipment and lower heat duties. Similar recoveries of acetonitrile, ranging from 90 (EG and G) to 92% (DCM and EA) were achieved when comparing the different entrainers. Higher purities are obtained with the lower-boiling additives with respect to acetonitrile, leading to purity >99.99% for DCM and EA, >99.6% for EG and >99% for G.

This acetonitrile purification section is part of a full integrated plant, newly designed for the production of this commodity from renewable sources, since no commercial examples of bioethanol-to-acetonitrile plants are disclosed in the literature.

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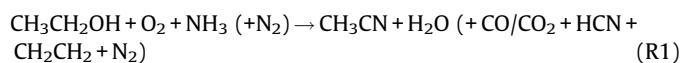
Introduction

Acetonitrile (CH₃CN, MeCN) is a hugely used solvent for pharmaceutical synthesis and analytical procedures, due to its peculiar polarity properties ([1,2] and references therein). It can be used, for the same reason, also as a homogenous entrainer both in industrial [3,4] or in fine-chemistry processes [5], and as a special solvent for novel electrochemical processes [6]. Another reason of its widespread use is its ready availability as a byproduct of the large-scale acrylonitrile production [1], but alternative routes having acetonitrile itself as the main product would make it possible to meet its increasing demand independently [7] from acrylonitrile. Recently, indeed, a concerning acetonitrile shortage (and increase of price) was observed due to diminishing production of acrylonitrile in 2008 [7].

Important side-products are ammonia, a reagent used in excess in the classical acrylonitrile process and also for this new process for the direct synthesis of acetonitrile, and hydrogen cyanide: they

are found also when acetonitrile is obtained as a byproduct from modified ammonia or Fischer-Tropsch full-scale reactors [8,9]. Therefore, the acetonitrile purification strategy has to be carefully and realistically designed also taking into account these compounds, which is commonly not done in the literature. Furthermore, if innovative processes are developed, e.g. using renewable raw materials as a way to exploit an integrated biorefinery, new intensified strategies to improve acetonitrile recovery and purity have to be proposed: the already well-known [10] separation procedures are no more directly applicable or, at least, they should be newly adapted to the current stream compositions.

The conversion of bio-ethanol and ammonia in presence of air (ammoxidation of ethanol, R1) is of growing interest, thanks to the low cost and large-scale availability of these reactants and to the very promising selectivity of dedicated catalysts [11,12]. However, in this case the reaction mixture contains also a large excess of nitrogen (since oxygen is usually supplied as air to guarantee the economic sustainability of the process), water, CO₂ and, to a lower extent, ethylene.



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<https://doi.org/10.1016/j.jiec.2017.10.003>

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Therefore, the scope of this work is to compare several advanced strategies to purify a stream of acetonitrile produced by ethanol-ammoxidation with a 7 wt% V_2O_5/TiO_2 catalyst [12], which yields a reaction mixture different from the already established ones (at least on an industrial scale) and representative of processes based on bio-ethanol for the production of acetonitrile [13]. A pilot scale plant has been here considered, sized on ca. 10 kg/h acetonitrile production.

An overview of the full ethanol-to-acetonitrile process that we have newly designed from the grass root is reported in Fig. 1. Ethanol (limiting reactant), ammonia and air are fed to a catalytic reactor operating under the optimised conditions reported in Ref. [12], so to accomplish full ethanol conversion. A first rough separation recovers most unreacted air and CO_2 , and is essentially accomplished through simple flash blocks. The liquid mixture includes the acetonitrile, water (which form an azeotrope, Fig. S1) and dissolved NH_3 and HCN. The further separation of ammonia and hydrogen cyanide yields a H_2O/CH_3CN azeotropic mixture to be resolved [14–17].

This work focuses on the description of the last blocks ('PURSTAGE' and 'SEPSTAGE', preceded by the CO_2 'FLASH' of Fig. 1), so the reference feed stream is 'LIQMIX2'. The ammonia separated at each stage can be either recycled into the reactor or valued as a marketable byproduct (ammonium bicarbonate), depending on the overall economy of the process. The same holds for HCN, which is a marketable product, usually in the form of salt. Thus, this paper widens the scope of similar ones, which mainly focus of the water–acetonitrile azeotrope resolution, since it evaluates azeotropic or extractive distillation options in a real pilot scale plant, including other impurities, which may affect final product purity and equilibrium calculations.

The purification strategy for this new process, essentially different from the acrylonitrile route to acetonitrile, has to be specifically designed. Therefore, in this work different acetonitrile purification options are compared, namely homogenous and heterogeneous distillation by using different entrainers: ethyl acetate, ethylene glycol, glycerol (paragraph "Alternative

entrainers"). They will be considered as "greener" alternative solutions with respect to a base case consisting in the straightforward azeotrope resolution with dichloromethane (DCM), which is comprehensively described in paragraph "Process and methods". Besides the specific discussion on the azeotropic/extractive distillation, the attention will be focused on the optimisation of the upstream strategy for each case (removal of volatile components), which may introduce important purity/stability issues during the final acetonitrile purification steps. Some preliminary options for process intensification are discussed in paragraph "Process intensification". Finally, paragraph "Complementary considerations" includes a detailed discussion of the thermodynamic models used and on their possible failures to describe phase equilibria for some options, and more specific design issues. These latter points were indeed addressed at first, but they are detailed in the last paragraph for the interested readers, only. Flowsheets and stream tables are reported in the main text, while ancillary information is reported in Supplementary information.

Process and methods

Aspen Plus[®] V8.8 (Aspen Technology Inc.) has been used for process simulation, with the APV88 PURE32 databank. The thermodynamic data needed were retrieved or derived from the Aspen Database and compared with available literature data for consistency. A base-check comparing the saturation pressure of the H_2O/CH_3CN mixture yields a maximum standard deviation of 1.38 kPa (at a mean bubble pressure of 37.51 kPa) between the three different models commonly used (UNIQUAC, NRTL-RK, UNIFAC – with the first two in very good agreement). The greatest difference between the models and the data amounts to 2.53 kPa at 36.92 kPa. Details are reported in the Supplementary information, particularly in Fig. S9. In general, UNIQUAC works well for the H_2O/CH_3CN azeotrope and much better than UNIFAC with the EA/CH_3CN azeotrope [14–17].

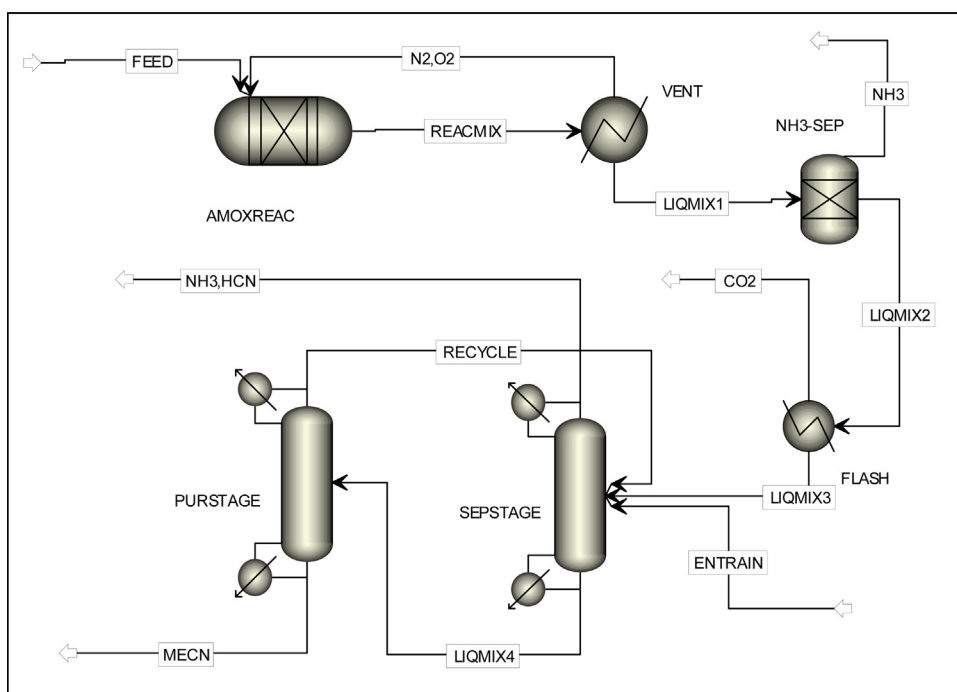


Fig. 1. Block scheme of the bioethanol-to-acetonitrile process. This work focuses on the description of the last blocks ('PURSTAGE' and 'SEPSTAGE', preceded by the CO_2 'FLASH'), so the reference feed stream is 'LIQMIX2'. The 'ENTRAIN' stream is actually a make-up. The compressor on air recycle to the reactor is not included.

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