Pressure-swing or extraction-distillation for the recovery of pure acetonitrile from ethanol ammoxidation process: A comparison of efficiency and cost

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ARTICLE INFO

ABSTRACT

Acetonitrile is increasingly used as solvent for the fine chemicals and pharmaceutical industries. Ethanol ammoxidation has been proposed as an alternative way for its production starting from a renewable source. This process leads to a complex mixture of products, which needs an optimized separation train to maximize the recovery and purity of acetonitrile. Pressure swing distillation, operated at 7 and 10 bar, has been compared as for feasibility and economic impact with the extractive distillation using dichloromethane as entrainer. The pressure swing option led to higher CH_3CN recovery (95.5%) with respect to extractive distillation (92.1%), irrespectively from the operating pressure. Furthermore, the pressure swing option allowed to tune more easily product purity by adding or removing trays in the stripping section of the high pressure column, leaving water as the only impurity. Similar results were obtained when operating the pressure swing between 1 and 7 bar or 1 and 10 bar, but the operation at 10 bar was characterised by lower installation and operating costs, thus it was considered as optimal. The same economical evaluation was carried out for the extractive distillation option, which revealed more expensive with respect to pressure swing. Different energy integration options have been also compared.

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1. Introduction

Acetonitrile is used for the synthesis of pharmaceutical products, e.g. Vitamin B1 and sulfapyrimidine, as intermediate to produce pesticides, for the manufacturing of flame retardant agents and as a reacting intermediate for recrystallisation. It is also widely applied as polar aprotic solvent, e.g. for the purification of butadiene, and for the production of synthetic fibers and paints. It is used as extraction solvent for fatty acids from animal and vegetable oil and as entrainer for distillation in the petrochemical industry, besides a broad use as mobile phase for HPLC analysis (AAVV, 1991).

Its US production in 2014 is reported between 4.5 and 22.5 kton (Anon, 2017) and is substantially bound to that of acrylonitrile (Sohio process through propylene ammoxidation), where acetonitrile is a byproduct (2–3 wt%), although many acrylonitrile plants do not even have a specific recovery unit for acetonitrile and thus it is incinerated. This production route determined a considerable shortage of acetonitrile in 2008–2009, partly due to the suspension of acrylonitrile

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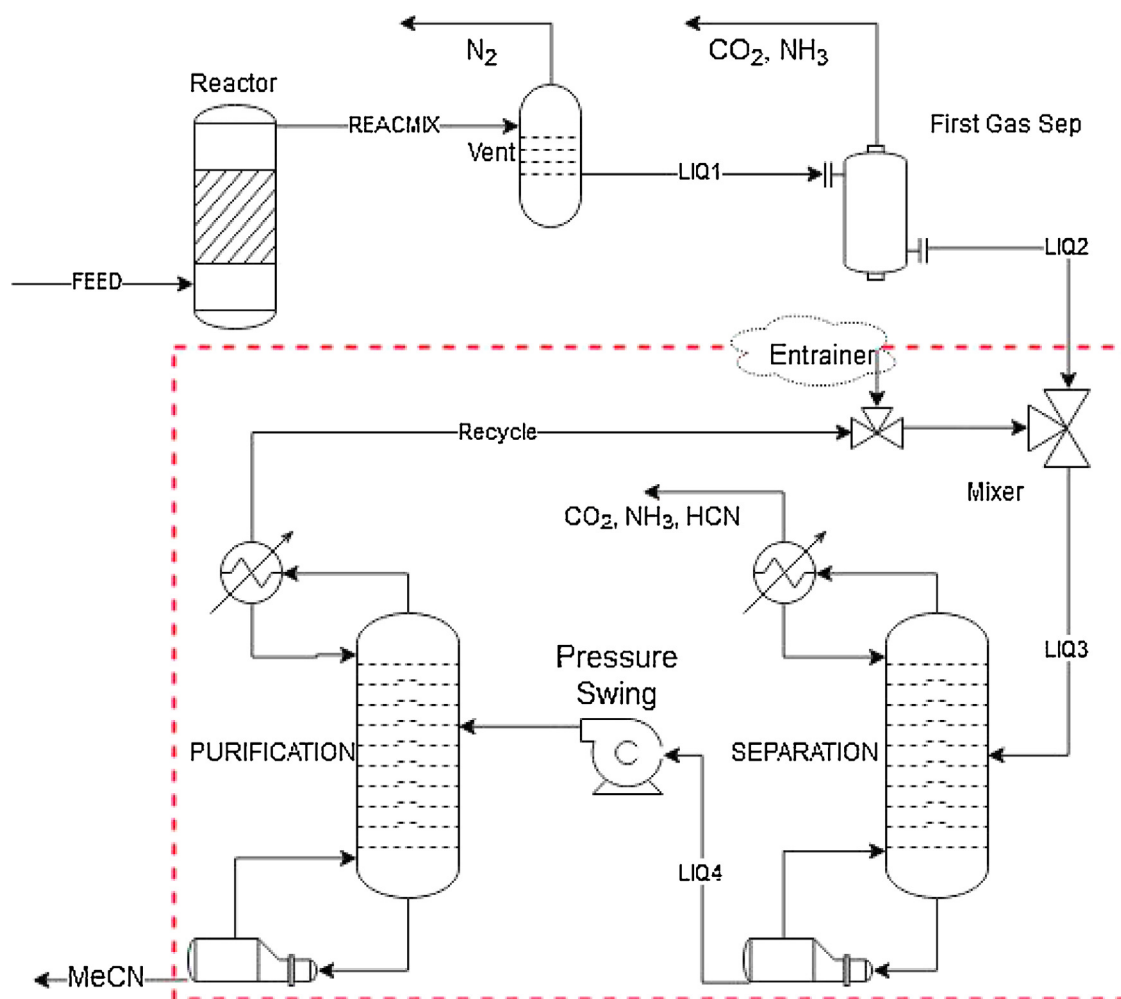 E-mail address: ilenia.rossetti@unimi.it (I. Rossetti).

Fig. 1 – PFD of the acetonitrile production plant by ammoxidation of ethanol. The part dealt with in the present paper is enclosed in the red rectangle. The 'ENTRAINER' makeup stream is pertinent to the reference DCM case, while it is not needed if the PS strategy is adopted. By contrast, in this latter case a pump is placed between the columns. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

manufacturing during Olympiads in China, and partly to the world crisis, which limited acrylonitrile consumption. This suggested the development of independent processed for the production of acetonitrile, e.g. by ammoxidation of ethylene or ethanol. Given the increasing availability of ethanol and its classification as renewably produced chemical, the latter production route is particularly interesting, but it implies the development of a fully integrated catalytic process (Eshelman and Delgass, 1994; Folco et al., 2017; Hamill et al., 2015; Hummel et al., 1993). In addition, the purification strategies for acetonitrile recovery have been designed up to now relying on the existing acrylonitrile process, or based on model binary/ternary mixtures. Thus, also its recovery and purification have to be newly optimised considering the real mixture composition outflowing from the ammoxidation reactor. Therefore, if renewable ethanol is used as raw material, either of first or (even better) second generation, an improved environmental footprint is expected for this process with respect to those relying on fossil resources. Life Cycle Assessment (LCA analysis) of the full flowsheet is currently in progress to quantify this point.

Ethanol ammoxidation occurs according to the following reaction, where ethanol is usually the limiting reactant:

$$CH_3CH_2OH + O_2 + NH_3 (+N_2) \rightarrow CH_3CN + 3H_2O (+CO/CO_2$$

$$+ HCN + CH_2CH_2 + N_2) \tag{R1}$$
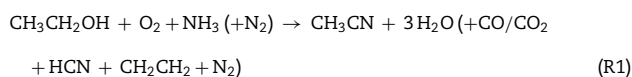
The product stream, therefore, includes some condensable species (mainly water and CH_3CN, which form a minimum boiling azeotrope at constant pressure) and many uncondensable products, with the addi-

tion of unreacted ammonia and oxygen. Among the gases, some are also partially soluble in the acetonitrile/water mixture (predominantly, CO_2, NH_3 and HCN).

Different strategies can be used to resolve binary azeotropic mixtures, as recently reviewed by Shen et al. (2016), which mainly include extractive or azeotropic distillation with a homogeneous or heterogeneous entrainer, or pressure swing distillation. The resolution of acetonitrile-containing mixtures by different strategies, including pressure swing, has been addressed in some papers (Zhu et al., 2016; Wang et al., 2016a; Sazonova et al., 2015; Huang et al., 2008; Luyben, 2017; Repke et al., 2005; Luo et al., 2016), however only some of the deal with the acetonitrile/water system.

Nevertheless, most of these investigations approach model binary mixtures, while examples of synthesis of a fully integrated separation strategy for pure acetonitrile recovery from a real reactor effluent mixture are actually lacking. Recently, we compared different homogeneous and heterogeneous entrainers for the separation of a product mixture deriving from a real acetonitrile production plant (Tripodi et al., n.d.).

The aim of this work is therefore to propose an optimized strategy to maximize the recovery and purity of acetonitrile, with the minimum purity goal of 99.9% required by its application as solvent. A pressure swing distillation option, with different operating pressures, has here been compared with extractive distillation with dichloromethane as entrainer. This latter solution indeed has been often proposed to resolve water-based azeotropes.

After a preliminary feasibility assessment, based on the thermodynamic properties of the mixture, the full purification train has been