A newly designed process for the production of acetonitrile from renewable sources

Ilenia Rossetti[1]*, Antonio Tripodi[1], Daniele Cespi[2,3], Fabrizio Passarini[2], Fabrizio Cavani[2], Gianguido Ramis[4]

1 Chemical Plants and Industrial Chemistry Group, Dip. Chimica, Università degli Studi di Milano and INSTM Unit Milano-Università, via C. Golgi 19, Milan, Italy; 2 Dip. Chimica Industriale "Toso Montanari", Università di Bologna, Viale del Risorgimento 4, Bologna; 3 Environmental Management and Consulting (EMC) Innovation Lab S.r.l., Viale Italia 29, 47921 Rimini (Italy); 4 Dip. Ing. Chimica, Civile ed Ambientale, Università degli Studi di Genova and INSTM Unit Genova, P.le Kennedy 1,Genoa, Italy

**Corresponding author: ilenia.rossetti@unimi.it*

Highlights

- New plant for the production of acetonitrile from ethanol, designed from the grass roots.
- The plant layout includes optimized separation of the complex products mixture.
- Process intensification by valorisation of all the byproducts (incl. CO_2) and heat integration.
- Life cycle assessment of the whole plant layout.

1. Introduction

The chemical importance of acetonitrile comes from its very particular polarity, affinity with both organic liquids and water and relatively high boiling point. Its main use is as a solvent for pharmaceutical and laboratory applications (nearly 70%) [1], but is also used in the extractive separation of butadiene from C_4 alkanes and in other similar processes.

Acetonitrile is mainly a byproduct of the acrylonitrile synthesis (6 Mton in 2010) and its yield depends on how the main process is operated. This intrinsic dependence is the underlying reason for the recognized mismatch between its demand and availability worldwide.

More recently, routes to acetonitrile as the main reaction product have been sought [1] and an efficient atom-economy could be achieved by using C_2 substrates, such as ethanol, ethane and ethylene. In brief, all these reactions are characterized by the alkylation of ammonia. Ethanol as a reactant is a promising alternative being a renewable resource, readily available from established fermentation processes and usable for this process without particular purification requirements.

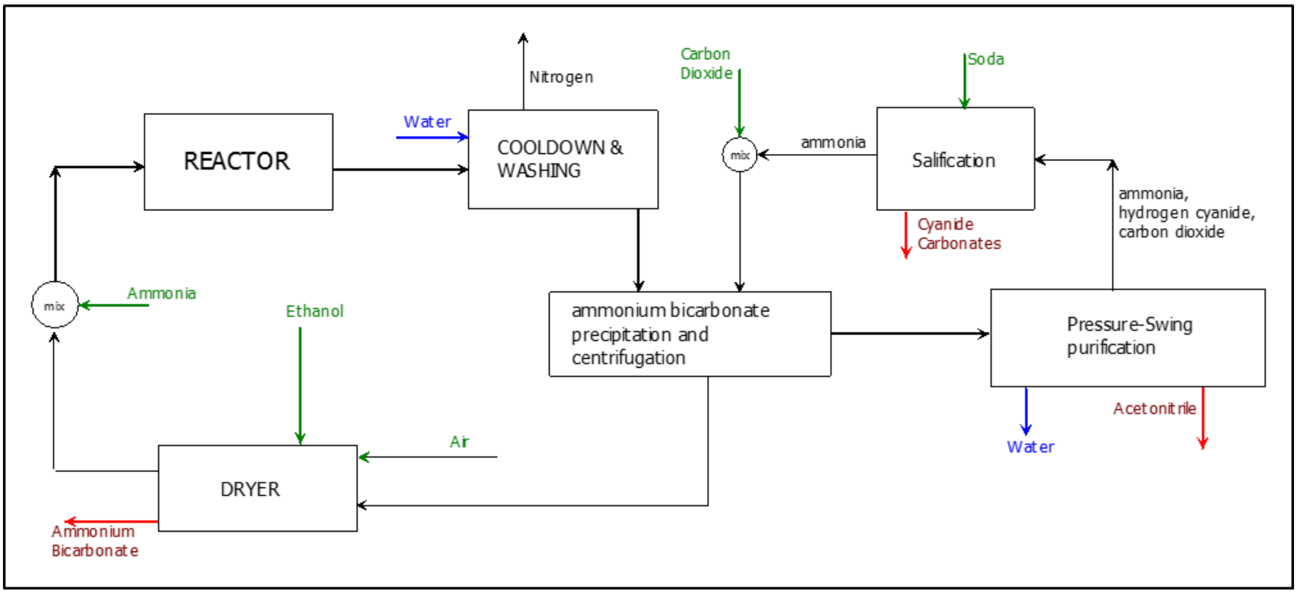
A new fully integrated ethanol-to-acetonitrile production plant has been designed here from the grass roots. The system is designed to produce acetonitrile on a pilot scale (10 kg/h) from ethanol, ammonia and air (ammoxidation). Besides the reaction section, the full separation train for pure acetonitrile recovery (> 99%) has been optimized and integrated with the recovery of all the byproducts (CO_2, HCN) and unreacted NH_3. The recovery and valorisation of the marketable byproducts (cyanide salts and NH_4HCO_3) is also discussed. Finally, the process consumes more CO_2 than what constitutes the reactor byproduct, allowing the further sequestration of this greenhouse gas.

2. Methods

The overall process design has been carried out using the software Aspen PLUS® V 8.8, with the APV88 and NISTV88 components databanks for components properties. The thermodynamic system used is the ENRTL (Electrolyte Non Random Two Liquids) to compute the non-ideality in the liquid phase. It was chosen since salts are present overall the process and it allows to model their thermodynamic properties in a more reliable way than NRTL. The Redlich-Kwong equation of state was used to model non-ideality for the gaseous phase. Some species were also treated as Henry components (properties from the same databases) to account for their solubility.

3. Results and discussion

After selecting the most appropriate thermodynamic package to correctly compute phase equilibria and the relative duties, a new integrated process has been designed as conceptually sketched in the Figure. Basically, ethanol, ammonia and air are mixed in the reactor, which operates according to the specifications experimentally derived in a previous work [2]. The product mixture is composed of unreacted and newly formed N_2, NH_3, HCN, CO_2, CH_3CN and H_2O. All the byproducts are separated by washing and precipitation as marketable NH_4HCO_3 (even using additional CO_2 as external input) and NaCN. The separation of the former salt is accomplished straigforwardly by using ethanol, which recovered in the drier, thus achieving preheating and partial vaporisation of the reactant and its mixing with air. Further heat recovery is allowed between the reactor fedd/products lines (not drawn). Finally, the separation of pure acetonitrile is accomplished by pressure swing distillation, for intensified resolution of the azeotrope [3]. 92% recovery of the produced acetonitrile (99.5% purity) is the final yield of the process, which includes marketable byproducts, heat recovery options and further CO_2 sequestration.



4. Conclusions

A process for acetonitrile production through ethanol ammoxidation has been designed on a pilot-plant scale. This represents a fully new process, with complete materials recovery, that allows the independent production of acetonitrile exploiting renewable sources. We consider the relatively low ammonia consumption, the full byproducts recovery and marketability and the close connection between the process sections as the most promising features of this newly designed plant.

In order to evaluate the potential benefits of the bio-based synthesis of acetonitrile a Life Cycle Assessment (LCA) approach was applied by comparing the environmental scores of the renewable route with those achieved by the traditional fossil-based pathway. A cradle to gate perspective, from raw material extraction up to the acetonitrile production, has confirmed the lower impacts in terms of resources depletion and environmental burdens for the innovative and renewable synthetic process.

References

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Keywords
Acetonitrile; Life cycle assessment; Pressure swing distillation; Plant design.