Acetonitrile from bio-ethanol ammoxidation: process design from the grass-roots and life cycle analysis

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ABSTRACT

The growing interest for new routes to obtain acetonitrile led to the development of catalysts active towards the ammoxidation of various substrates. Among these, a C2 molecule such as ethanol represents a good choice in terms of atom economy and, being renewable, sets the basis for a

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long-term sustainable process. This paper describes a fully integrated, newly designed process for the production of acetonitrile from bioethanol, currently not present in the literature. The target is the production and purification of 10 kg/h of acetonitrile, unit of production used for calculations, obtained from ethanol, ammonia and air as raw materials. All the by-products, mainly ammonium bicarbonate and sodium cyanide, are considered marketable chemicals and represent an added value, instead of a disposal issue. Their optimized recovery is included in this flowsheet as a basis for the future economic assessment of the system. The process consumes CO_2 without its direct emission. In principle, all the carbon atoms and 90% of the nitrogen atoms are turned into reaction products and the main loss is gaseous N_2. The process design has been performed by means of the Aspen PLUS® process simulator, on the basis of literature data and other experimental results. In addition, to evaluate the potential benefits of the innovatiove bio-based route, a life cycle analysis was carried out including all the stages involved in the bio-acetonitrile production (from raw materials extraction up to the gate plant). The results were then compared with those achieved for the traditional fossil route (SOHIO process), showing a sensible decrease of the environmental burdens in terms of non-renewable resources and damages on ecosystems (*e.g.* toxicity, climate change, etc.). Finally, a simplified sensitivity analysis was carried out by substituting the starting raw material for the production of bio-ethanol (corn) with other conventionally used worldwide, such as sugarcane and wood. The latter option seems to make the system more competitive in terms of carbon neutrality, thanks to the usage of the residual lignocellulosic fraction available on market.

Introduction

The 1st principle of Green Chemistry[1] suggests to avoid waste by optimization of reaction or, when it is not possible to improve the whole process, by recovering and transforming the side streams into valuable added products. An interesting industrial example is represented by acetonitrile, which is mainly produced as byproduct from the acrylonitrile synthesis (≈6 Mtons in 2010 [2]).

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%) [3], but it is also adopted as extraction agent to separate butadiene from C4 alkanes [4], propylene and propane [5] and for cellular metabolome extraction[6].

However, acetonitrile's yield depends on how the main acrylonitrile process is operated. This intrinsic dependence represents the reason for the recognized mismatch between its demand and availability worldwide [7].

More recently, routes to acetonitrile as the main reaction product have been sought (tough important details such as the feedstock nature and consumption are anyway patented and undisclosed[3]) and an efficient atom-economy could be achieved by using C2 substrates.

Among these, ethanol (EtOH) ammoxidation is a promising alternative, since EtOH is a renewable resource, readily available from established fermentation processes [8] and usable for this process without particular purification requirements. Another crucial aspect is EtOH abundance and market estimated to be over 158×10^9 L [9] and 53,105.3 million US$ by 2025[10]. This led to different exemples of valorisation of ethanol for chemicals

production, such as its conversion to ethylene by dehydration over acidic catalysts[11,12] or its conversion to 1-butanol[13].

Besides interesting attempts to develop suitable catalysts, to date, no full description of a plant for acetonitrile production by ethanol ammoxidation is disclosed in the literature. Novel production processes can take advantage, nowadays, of computational calculation tools that can sensibly reduce the times of a preliminary feasibility study, leaving the further stages of development to cope with design details, after having sorted out less favourable options. In addition, computational studies can easily integrate a benign-by-design approach[14] by supporting synthetic chemists to focus the efforts on the most suitable solution. Thus, process simulation and life cycle analysis should accompany tightly the design of new and sustainable processes as tools to address decisions towards feasibility.

The conversion of ethanol (azeotropic purity) into acetonitrile is studied in this paper according to the experimental data summarized in the following section. A new fully integrated acetonitrile production plant has been designed from the grass roots. The system is suitable to produce acetonitrile (10 kg/h is taken as reference basis) from ethanol, ammonia and air. Besides the reaction section, the full separation train for pure acetonitrile recovery (> 99%) has been optimized as described elsewhere [15,16], and integrated with the recovery of all the by-products (CO_2, HCN) and unreacted ammonia. The recovery and valorisation of the marketable by-products (cyanide salts and NH_4HCO_3) is also discussed as one of the possible co-product recovery examples. The process consumes more CO_2 than what constitutes the reactor by-product, allowing a further sequestration of this greenhouse gas (GHG). Then, in order to support the design stage, a life cycle approach was also applied to verify the environmental performances of the whole system in terms of renewability and ecosystem burdens.

Background

As written above, acetonitrile is the major by-product of propylene ammoxidation to acrylonitrile[17]. The global acetonitrile market has grown at Compound Annual Growth Rate (CAGR) *ca.* 5% during 2009-2016, and is now close to 6.5 Mtons/year. Acetonitrile is isolated by distillation, and depending on the distillation capability, different acetonitrile qualities are obtained[3]. In 2008-2009, the chemical industry experienced a severe acetonitrile shortage[7,18], because several acrylonitrile plants were shut down, due to stagnation of fibers market. This made the industry aware of the fact that a dedicated process for the synthesis of acetonitrile is needed.

Possible routes for the synthesis of acetonitrile include:

(a) Reaction between CO, NH_3 and H_2[19,20];

(b) Hydrocyanation of methane with HCN, at 900 °C[21,22];

(c) Ethane or ethylene ammoxidation; catalysts for ethane ammoxidation include mixed Nb/Sb oxides, Nb-promoted Ni oxides and Co-exchanged zeolites. Because of the better yields obtained, ethane ammoxidation is the preferred route[18,23–28].

Recently Alzchem claimed to have started a gas-phase ammoxidation process for the production of acetonitrile.

Computational 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 [29]. Some species were also treated as Henry components (properties from the same databases) to account for their solubility.

The life cycle analysis was carried out using the SimaPro software (PhD version 8.4.0.0)[30] and its libraries. Among these, Ecoinvent (v.3.3)[31] represents one of the most consolidated and used databases worldwide. It is adopted by researchers to cover all the background data concerning raw materials extraction and refinery, energy and transportation, infrastructure, an all the auxiliary substances required to simulate the system under study.

In addition, several impact analysis methods were adopted. More details are reported in the last paragraph.

Process description

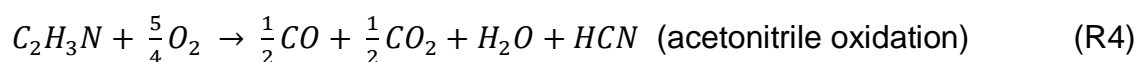### Conversion Data and Stoichiometry

The conceptual process layout is reported in Fig. 1, whereas the PFD is sketched in Fig. 2.

The alkylation of Ammonia with Ethanol (whose C-O bond is activated by the initial dehydrogenation or oxidation into acetaldehyde) and the further oxidation of the C-N into the nitrile group, has been studied by diverse groups on different catalysts[32–35]. The reaction is demonstrated at laboratory level. Nevertheless, process scale up to the pilot-plant or commercial scale has not been attempted yet. Furthermore, process design issues are still open and integrated processes are actually missing for this.

Plant design is here based on the data obtained by Folco et al. [36] on a Cs doped V_2O_5/TiO_2 catalyst. 3 moles of ammonia per mole of ethanol are used as feed and a byproduct distribution dominated by light gases (carbon mono- and di-oxide, thanks to the pronounced oxidative conditions adopted) rather than by high-boiling condensates is obtained.

The dataset is reported in Table 1. Though higher selectivities to acetonitrile were achieved by the same authors, the selected reaction conditions (320°C, atmospheric pressure, catalyst load of 0.8 g per cm^3/s of gas flow) were characterized by a relatively low temperature, very low ethylene and polycondensate yields, a small undesired combustion of ammonia, almost complete oxidation of CO to CO_2 and the complete consumption of the intermediately formed acetaldehyde. Furthermore, in order to simplify the already complex separation train, catalyst and conditions corresponding to full ethanol conversion were selected. Indeed, different operating conditions led to higher selectivity to acetonitrile, but with unreacted ethanol in the products stream. This would make the whole separation much more demanding and, overall, the purity of acetonitrile required by the market was not met.

The product distribution has then been rationalized with the following stoichiometry:

$C_2H_6O + O_2 + NH_3 \rightarrow C_2H_3N + 3H_2O$ (ethanol ammoxidation)   (R1)

$C_2H_6O \rightarrow C_2H_4 + H_2O$ (ethanol dehydration)   (R2)

$C_2H_6O + \frac{5}{2}O_2 \rightarrow CO + CO_2 + 3H_2O$ (ethanol oxidation)   (R3)

$C_2H_3N + \frac{5}{4}O_2 \rightarrow \frac{1}{2}CO + \frac{1}{2}CO_2 + H_2O + HCN$ (acetonitrile oxidation)   (R4)

$\frac{3}{4}O_2 + NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2O$ (ammonia oxidation)   (R5)

$CO + \frac{1}{2}O_2 \rightarrow CO_2$ (CO oxidation)   (R6)

where it is assumed that the heavy compounds generated (and for whom a brute formula is not available) are re-oxidized to CO_2. The molar flows were selected to

meet a model scale production target of 10 kg/h of acetonitrile, just as a basis for calculation.

The excess of oxygen needed in the adopted conditions has two drawbacks: i) the necessity to feed it as air, and then to design a reactor where the inert N_2 volumetric flow is as large as the flow of the reactants; ii) the undesired oxidation of acetonitrile into HCN. Nevertheless, once the HCN is neutralized and recovered as cyanide salts, it becomes a marketable byproduct itself [37].

On the other hand, the non-negligible N_2 flow has also at least three positive consequences: i) it increases the thermal inertia in the reactor, convenient when coping with an exothermal reaction network; ii) it reduces the relative volumetric flow increase, at constant temperature and pressure (any reaction above, except the last, produces more moles than it consumes), then keeping the pressure drops nearly constant; iii) it reduces the relative decrease of the excess reactants (oxygen and ammonia) concentration, keeping the kinetic conditions nearer to the laboratory ones (where the inert carrier is actually in large excess and ammonia and oxygen are in excess with respect to ethanol), meeting nearly the conditions in which kinetic testing was performed, for a more reliable prevision.

At this stage, the dataset available allows to select an appropriate operating window based on wide experimental design, but is not suitable to derive a robust kinetic model. Thus, the reactor only takes a picture of the inlet-outlet compositions, but it is not possible to carry out the optimisation of the process variables and reactor sizing.

Ammonia – Carbon Dioxide Process integration

The reaction, as outlined in the cited works, prescribe an excess of ammonia in the reactor feed. The substantial flow of this reactant still present at the reactor outlet

poses a serious recovery issue, due to its affinity both with nitrogen and acetonitrile (in the hot gas phase) and with water and acetonitrile (in the condensed liquid phase). The contemporary presence of CO_2, on the other hand, suggests different options for ammonia recovery. The first trivial route would be its separation and recycle. However, this relies on expensive cryogenic separation. Alternatively, CO_2 and NH_3 may react to form urea or can be used to produce ammonium bicarbonate (NH_4HCO_3). Both the latter can be viable alternatives, since the value of both chemicals is higher than that of ammonia. Ammonium bicarbonate and urea find application in the same fertilisers market, with cost ca. 0.18-0.22 USD/kg (with a more unstable quotation for urea). However, urea needs an additional plant that may be unfitted to the relatively small plant size typically expected for renewable-based processes, thus additional costs. By contrast, ammonium bicarbonate can be easily reacted and separated while cooling down the product mixture, envisaging lower capital costs.

From a sustainability point of view, the production of ammonium bicarbonate consumes one mole CO_2 per mole of NH_3, whereas halved amount of CO_2 is consumed to produce urea. On this basis, as will be discussed further in the following, the selection of ammonium bicarbonate as ammonia recovery co-product (maybe even the predominant one, from mass balances), allows to convert additional carbon dioxide with respect to the amount produced during the reaction. A rigorous comparison between the two routes needs the economic assessment and a further comparative life cycle assessment, which is out of the scope of this work. Thus in the following we consider only the ammonia recovery in form of ammonium bicarbonate. In this way, four process improvements are achieved at once: i) all the ammonia is converted into marketable products, rising its conversion from 30% (acetonitrile plus cyanides) to 96% (acetonitrile, cyanides and ammonium bicarbonate, what is left out

is the nitrogen generated from ammonia oxidation); ii) the further purification of acetonitrile is made easier; iii) the CO_2 emission from the reactor is fully brought to zero and, since additional CO_2 is consumed, the process is even more sustainable from this point of view; iv) the cryogenic separation of ammonia from N_2 (deriving from feeding air and produced during the reaction), preliminary to its possible recycle to the reactor, as alternative option, is avoided.

This two-process integration has been designed interposing, between the reaction and purification stages, a salt formation and precipitation section (as in the 'wet' ammonium bicarbonate process or in several later options for CO_2-NH_3 absorption [38–43]) with a main washing tower discharging the oversaturated solution into a decanter. A first centrifuge separates the suspension, then the ammonia still present is further precipitated blowing into the liquid an additional amount of carbon dioxide and separating through a second centrifuge.

Bicarbonate recovery

The ammonium bicarbonate salt exits from the centrifuges as a hydrated solid. It has to be dried in order to prevent its decomposition, mediated by water, into gaseous ammonia and CO_2 that, even at low temperatures, results into an appreciable material loss [44]. Moreover, the moisture discharged from the centrifuges along with the salt contains a small quantity of acetonitrile, which has to be recovered to improve process yield. Taking advantage of the salt being insoluble in alcohols [45], the slurry is first washed with ethanol, causing a 'chemical separation' of the moist salt from the water and so quenching the decomposition [44], allowing a safer warm-air drying.

The air current passed over the salt in the dryer recovers then the acetonitrile still absorbed in the solid plus the ethanol and the oxygen needed for the reaction, so the

dryer exhaust flow can be directly recycled to the reactor as part of the feed mixture, into which ammonia is then vaporized. In this way, the dryer heat input is also fully recovered to the process without any additional ethanol consumption.

In the present as for the washer and dryer, the saturation threshold of ammonium bicarbonate has been calculated on water as basis solvent, being this the default method of the software electrolyte-NRTL framework. This is a conservative approach. As a matter of fact, the salt solubility in a mixed solvent involving also ethanol and acetonitrile was lower, as confirmed experimentally in the bench-scale tests we carried out to find data to set these units.

The liquid mixture discharged by the centrifuges along with the ammonium salt has been fixed according to a series of experiments. After dissolving the salt in pure water or in a water-ethanol-acetonitrile mixture, the vials have been centrifuged and the solid filtered and left to dry at ambient temperature. Weighting the sample just after the filtration and after the drying we could quantify the humidity content of the centrifuged salt.

According to these tests, we could also specify the drier block as a "virtual evaporator" that actually eliminates all the species present as liquid in the stream, except for a residual mass fraction that can be set appropriately based on experiments. The acetonitrile recovery from the dried vapor is tuned accordingly.

Acetonitrile purification

Acetonitrile forms an azeotrope with water [46], thus, a dedicated purification strategy must be developed. The method chosen to purify the acetonitrile is the pressure swing distillation technique [47] and its application to this case is fully described elsewhere [16]. With respect to other purification strategies [15,48,49] this has appreciable

heat duties, but it does not require the addition of any other chemical (with their relative feed circuits, makeup costs and dedicated procedures).

The entire acetonitrile purification train consists of four blocks, *i.e.* two main columns, each of them preceded by two auxiliary turrets:

a) the first column is without condenser and discharges water excess in the bottom;

b) the second column performs the main task: it collects the acetonitrile-water binary azeotrope (at the 10 bar equilibrium composition) recycled from the other main tower, and produces a distillate where acetonitrile and water are at the atmospheric azeotrope ratio dumping all the remaining excess water in the bottoms;

c) the third turret separates hydrogen cyanide (plus residual ammonia and CO_2) from the acetonitrile-water binary liquid;

d) the fourth main column operates at 10 bar: at this pressure, the feed composition results poorer in water (33 mol%) than the equilibrium azeotrope is (48 mol%), so that pure acetonitrile can flow in the residues.

The operating pressure of the columns in the pressure swing loop was optimised in a previous work and resulted in a better separation with respect to lower pressure cases. On the other hand it avoid excessively high pressure, that would not add value for separation in spite of increasing capital and operating costs.

An intermediate "stabilising" column has been added just before the pump to the high pressure column in order to accomplish full gas recovery. In principle, this could be achieved with a partial condenser, but the liquid phase composition sent to the pump still contained dissolved gas when dealing with a simple once-through flash separation.

Hydrogen Cyanide separation

Being much more soluble than ammonium bicarbonate, ammonium cyanide cannot be precipitated at this stage, where a relatively large volume of water is still present. This gas is quenched into a sodium hydroxide bath (pH ≥13), where it turns into solvated sodium cyanide. The vapours released from this alkaline solution contain the residual ammonia, which can be recycled into the bicarbonate precipitation section, while the carbonate residues remain in the liquid phase as sodium carbonate. A further development of this work will account for the stepwise separation of the sodium salts, relying on the sensibly different solubility of NaCN with respect to Na_2CO_3. Also in this case, this difference is greatly enhanced by adding ethanol [45]. The reactions set used in this section is detailed in the Supplementary Information.

Results and discussion

The overall process balances are reported in Table 2 and Fig. 3.

Of 0.24 kmol/h of acetonitrile formed in the reactor according to reaction 1, 0.22 kmol/h are recovered with 99.5% purity. The higher loss takes place in the main precipitation column, which is indeed the more complex block calculated. The process takes place at low pressure to save compression costs, anyway the gaseous flow through the reactor is at 1 bar-gauge, in order to obtain some volume flow reduction. The pressure is reduced gradually within the salt-precipitation stage to the atmospheric level, because the pressure-swing technique takes advantage of the highest differential pressure available.

Mixture washing

Several preliminary calculations of the thermodynamic conditions for this stage have been done, to test the possibility to start the separation of the ammonia at this point:

the results achieved with a vapor-liquid separator indicated a low K_{vl} for ammonia due to its precipitation as NH_4HCO_3, but a higher K_{vl} for acetonitrile (Fig. 4), so the gas-liquid contact has been extended with a multiple-stages layout substituting the single-stage separator with a small plate column.

Along the four-trays of the washer, several functions are carried out at once: i) outflow of the non-condensable gases; ii) final cooling of the reaction products; iii) first precipitation of ammonium bicarbonate in the recirculated bottoms.

Most of the acetonitrile (4-5% on a molar basis) is lost at this stage, together with 1.2 mol% of the ammonia.

To lower the losses within a single block configuration we should have decreased the temperature even below this already low value. Additional stages purposely dedicated to the recycle of these species (e.g. intercooled compressors plus separators, or basic washings) may be further added on purpose, following economic evaluation.

We did not increase the water amount (that would lower the ammonia loss overhead) to precipitate more bicarbonate. A swell, we did not lower the temperature because the three cryogenic cycles currently under development are at present, designed at -15 or -20 °C.

Solid precipitation and handling

The solubility of ammonium bicarbonate depends from several equilibria besides the solid-liquid electrolytes distribution, plus the equilibria of repartition of ammonia and CO_2 between the liquid and the vapor phases. Given a mixture of water, ammonia and CO_2, the solid precipitate is coupled to the pH and depends essentially on the temperature: this is kept to -10 °C for the whole section (a less demanding condition

of 0°C is also foreseen for one block). Ice formation is neglected because of the high ionic strength of the solution and the presence of acetonitrile.

To model the separation of the salt from the liquid, two centrifuges based on the Stokes law (either with advancing screws or rotating discs) have been placed in the flowsheet (Fig. 2). Anyway, rather than calculating the solid separation as a consequence of the detailed mechanical parameters and the particle size distribution, we have chosen the more generic approach of specifying an overall salt separation efficiency and its gross moisture content.

The moisture content has then been specified in the block as 25% on a dry basis.

The salt precipitated corresponds then to the equilibrium condition (at -10 °C and pressure of 1.0 – 1.9 bar) for the ammonia exiting the reactor (0.706 kmol/h) plus that recovered from the Pressure Swing section (0.072 kmol/h) within the calculated water flows, *i.e.* 0.665 kmol/h of ammonium bicarbonate. The difference of 0.041 kmol/h is lost chiefly as gas from the washer block, then as a liquid trace in the alkaline bath, while the ammonium trapped within the salt is recovered as the moisture evaporates in the dryer.

Dryer specifications

According to the drying experiments performed, the dryer can be specified at a temperature as high as 40 °C. Since this temperature is sensibly higher than the ambient condition, the liquid evaporation can be considered complete, but the decomposition into ammonia and CO_2 is very slow when only little amount of water is present within the solid and, thus, it can be neglected. Indeed, the global block mass balance still takes into account all the water discharged from the centrifuges, but this liquid has to be thought as physically separated from the crystals by the action of ethanol. [15]

Pressure Swing distillation

The final acetonitrile purification via this technique is fully described elsewhere[15,16]. The role of the intermediate column PS3 and its specification are also explained in the dedicated work on separation by pressure swing[16].

The blocks specifications are reported in Table 3. The last column is sized so to work very close to the theoretical material solution of the azeotrope breaking:

$$\begin{cases} F \times x_{atm} = D \times x_{10} + B \times 0.995 \\ B \geq 0.22 \end{cases} \qquad \text{(E1)}$$

where B, F and D are the flows of acetonitrile in the column bottoms, feed and distillate, respectively, and its recovery and purity are set as process targets. x_{atm} and x_{10} are the molar azeotropic fractions at different pressures. The first three-columns joint operation is rather more complex, as it involves the treatment of a 5-species non-ideal mixture, so we refer the reader to the above cited papers for additional details. This plant section is the most demanding in energetic terms: it is then possible further and more detailed optimization and economic analysis.

Alkaline salts trap

Ammonia and CO_2 in equilibrium with the precipitated salt are expelled from the Pressure-Swing section, but their recovery and separation from HCN via distillation is scarcely feasible due to the very low bubble point of ammonia. It is more convenient to separate ammonia from HCN exploiting their opposite acid-base behaviour, even if this implies to treat the carbonates alongside the cyanides. This strategy has been adopted because: i) ammonia is a more valuable feedstock than CO_2, then its recovery has the priority, ii) carbonates and cyanides have quite different solubilities,

so their further solid-liquid separation should not be problematic, iii) the conversion of CO_2 into carbonates improves the carbon-recycle character of the process.

The alkaline bath pH (raised with sodium hydroxide) and temperature have been chosen so to maximize the recovery of ammonia while keeping all the cyanide within the solution.

Thermal duties and integration

The thermal needs and deliveries of the process are summarized in Table 4. The main issue of this design is the cryogenic temperature needed for an efficient ammonium bicarbonate precipitation. Several strategies are possible to meet this demand, as they will be developed and compared in a further work. At the moment, the most promising seems a simple compression-expansion cycle of a refrigerant mixture (it requires less heat than an adsorption cycle based upon rectification and is likely better suited for a possible scale up with respect to a heterogeneous-absorber machine).

Atom and CO_2 balances

As outlined in Fig. 3, the process relies on a tight atom economy, since the losses are within the 10% and are due mostly to the unavoidable ammonia undesired oxidation in the reactor. Considering that only a part of the carbon is fed as ethanol, the acetonitrile and bicarbonate yields with respect to this reactant becomes more balanced, *i.e.* the 48% (instead of 33%) and the 46% (instead of the 50%) respectively, while the cyanide represents *ca.* 6%.

The ammonium bicarbonate process is then not only effective to recover the ammonia, but also to turn the competitive combustion of ethanol into a still useful reaction with a marketable outcome. Of the total fed carbon atoms, 28% comes from

external CO_2, and this leaves the possibility to couple this process with other installations characterized by net positive CO_2 emissions.

Life cycle analysis

Life Cycle Assessment (LCA) methodology is a standardized approach based on ISO 14040 series[50,51], used by researchers and companies to support design of innovative products and systems. LCA is not new in the chemical sector. In previous studies, LCA has been applied to evaluate the production of acrylonitrile from propylene and propane to ammoxidation[52]. However, it is quite a versatile methodology, easily applied at both industrial[53] and laboratory scale[54,55]. In general, in the case of bio-chemicals is used to support decision making and marketing procedures. In fact, through a life cycle analysis and its holistic approach researchers are able to identify environmental criticalities of the innovative pathways and to propose valuable alternatives to the traditional routes. Its usage within the bio-based industry is strongly suggested by international literature[56] to estimate and compare environmental scores of chemicals from renewables with those achieved by fossil routes. In this case a *cradle to gate* perspective is usually recommended, since able to include in the model from raw materials extraction up to the synthesis of the target molecule. In the study, the LCA approach was used to compare the innovative bio-based acetonitrile route with the traditional pathway from oil (SOHIO process). Results from flowsheet simulation were used to fill in the inventory data for the bio-based acetonitrile. Table 5 collects the full inventory for the production of 1 kg of bio-acetonitrile (functional unit). On the other hand, the default process in Ecoinvent[31] library was used as a base to simulate the production of fossil acetonitrile from an average European plant based on SOHIO process (process name *Acetonitrile {RER}| Sohio process | Alloc*

Def, U). The SimaPro license[30] includes several standardized analysis methods, among which the Cumulative Energy Demand (CED) one (v 1.09)[57]. CED is in general defined as "*the entire demand, valued as primary energy, which arises in connection with the production, use and disposal of an economic good*"[58]. In this case, CED was used to identify the whole amount of resources utilized in the entire chain (raw materials and energy) and their origin (fossil or renewables). Table S1 in ESI shows the results from CED evaluation, in which resources consumption is expressed in terms of MJ eq. As depicted, bio-acetonitrile route is able to reduce the total amount of resources up to -33% if compared to the fossil one. In addition, given that CED is considered a valuable screening indicator of the overall impact of products[59,60], it was used to estimate a new and easy parameter called *renewability grade* of both routes to acetonitrile. The renewability grade represents the ratio between the renewables and the whole amount of resources used in the entire supply chain (from raw materials extraction up to the industrial gate). The scores, expressed in percentage of overall quantity, are reported in Fig. 5. As depicted, the renewability grade of the bio-based acetonitrile reaches 84%: more than four-fifths of the resources has renewable origin. These results seem impressive if compared with those of the fossil pathway for which the score is around 1% as a consequence of the lower grade of renewables used which are mainly concentrated in the production of energy (*e.g.* hydro-, solar- and wind-power, Table S1). This represents a further confirmation of the fact that the reduction in the use of fossil resources between two routes was evaluated around -89% (Table S1 in ESI).

The *renewability grade* was introduced since it is simple to estimate and quite useful when the bio-based sector is under study, to identify if the innovation is able to reduce the fossil dependence or not.

CED is usually considered a *single-issue analysis method*, since able to show the consumption of resources only. No information concerning negative implication on ecosystems are easily understandable. Therefore, in order to show these potential impacts the ReCiPe 2016 method was adopted[61]. The method expressed results in terms of 18 impact categories at midpoint level. Table 2 shows the trends of both routes using the characterization factors (*e.g.* kg of CO_2 eq. for the climate change). Among these, only 10 (the more relevant after a weighting analysis) were selected to be translated into a *single score* by using a common unit (millipoints, mPt). Results in the form of single score (Fig. 6) represent the cumulative impacts reached by both pathways to estimate the worst in terms of sustainability. A greater cumulative score means larger environmental burdens. On the contrary, lower mPt values indicate potential reduction of the impacts. As disclosed, the bio-based synthesis presents an inferior cumulative score than the fossil pathway mainly thanks to its renewability grade. The usage of bio-EtOH, in fact, leads the whole system to achieve lower burdens in terms of fossil dependence (*fossil depletion* category, -78%) and climate change (-64%). In addition, the avoided production of ammonium bicarbonate, sodium cyanide and sodium carbonate (all recovered as by-products in bio-refinery system) produces significant improvements in terms of human toxicity and metal depletion. In fact, both categories achieve negative results which means avoided impacts and, therefore, potential benefits on ecosystems. On the contrary, the categories directly linked to cultivation of biomass (such as land occupation and transformation) present worst results for the bio-based route if compared with those achieved by fossil pathway. These results are in line with our expectations. In fact, as already discussed in a recent publication[9], today the main source of EtOH is a dedicated crop such as corn. This scenario represents the actual situation on market

(*default bio-based scenario*) in which EtOH is 100% corn-based, derived from US production (worldwide leader). In order to investigate other primary sources for bio-acetonitrile, two further EtOH raw materials were evaluated: sugarcane and lignocellulosic biomass.

Results of this sensitivity analysis are collected in Fig. 7. The usage of dedicated sugarcane presents a dramatic increase of the environmental impacts for all the impact categories considered, if compared with the default bio-based scenario (*Bio-based acetonitrile, from corn EtOH*). In particular, the *Bio-based acetonitrile, from sugarcane EtOH* simulates the Brazilian situation (second major producer of EtOH), in which the main source is sugarcane. This alternative has negative effects on environment (=higher scores in mPt) for the categories of natural land transformation, terrestrial ecotoxicty, climate change, fossil fuel usage and land occupation. The main reason is the depletion of the natural forest as a consequence of the intensive cultivation of sugarcane and usage of fertilizers. Cumulative impact of the sugarcane-based scenario is far to be considered *carbon neutral* and/or comparable with the fossil route: +96% (see ESI, Table S2). On the other hand, second generation EtOH, which means ethanol from lignocellulosic fraction, seems to be more competitive. The *Bio-based acetonitrile, from lignocellulosic EtOH*, in fact, could reduce the overall impact of -73% if compared with the traditional process; and it seems only + 7% if compared with the default bio-based scenario (the main reason is the lower efficiency of transformation for lignocellulosic biomass → EtOH *vs.* corn → EtOH). However, the most interesting aspect is that the usage of residual lignocellulosic materials (*e.g.* bio-waste, such as residual wood fraction deriving from timber and prunes activities) leads the whole system to the carbon neutrality: climate change effects are negative (avoided impacts, see ESI Table S2).

Conclusions

A process for acetonitrile production through ethanol ammoxidation has been designed from the grass roots. This represents a fully new process, with complete materials recovery, that allows the independent production of acetonitrile exploiting renewable sources.

The process feasibility is proven even dealing with relatively low selectivity to acetonitrile (*e.g.* as low as 50%). The large excess of ammonia, needed to enhance the ammoxidation kinetics against the oxidation reactions, is fully recovered as marketable ammonium bicarbonate. Alternatives are possible, such as ammonia recovery as urea, but they should be carefully evaluated from the economic point of view. The resolution of the acetonitrile-water azeotrope has been designed so to accomplish the purification of a more complex mixture. Overall, a 92% recovery of the produced acetonitrile (99.5% purity) is the final yield. The flue gases recovery and valorisation is also possible with the addition of NaOH.

The simplified life cycle evaluation here was applied to support process development. LCA results confirm the reduction in the environmental burdens of the innovative bio-based route, compared to the traditional pathway from petroleum. However, the usage of non-dedicated crops is strongly recommended. In fact, despite the lower yield conversion, the lignocellulosic fractions deriving from residual woods seems the better way to fight climate change and to promote a lower carbon society starting from greener commodities.

Supplementary Information

The Supplementary Information file includes the reactions set for solids recovery; the phase diagram to describe equilibria in the washer and drier sections; Resources consumption and the sensitivity analysis of different routes to acetonitrile.

REFERENCES

(1)   Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press, Oxford, 1998.

(2)   Cespi, D.; Passarini, F.; Neri, E.; Vassura, I.; Ciacci, L.; Cavani, F. Life Cycle Assessment comparison of two ways for acrylonitrile production: The SOHIO process and an alternative route using propane. *J. Clean. Prod.* **2014**, *69*, 17–25.

(3)   Mcconvey, I. F.; Woods, D.; Lewis, M.; Gan, Q.; Nancarrow, P. The Importance of Acetonitrile in the Pharmaceutical Industry and Opportunities for its Recovery from Waste. *Org. Process Res. Dev* **2012**, *16* (4), 612–624.

(4)   Evans, B.; Hawkins, S.; Schulz ed., G. *Ullmann's Encyclopedy of Industrial Chemistry*; Evans, B., Hawkins, S., Schulz, G., Eds.; VCH, Weinheim, 1991.

(5)   Liao, B.; Lei, Z.; Xu, Z.; Zhou, R.; Duan, Z. New process for separating propylene and propane by extractive distillation with aqueous acetonitrile. *Chem. Eng. J.* **2001**, *84*, 581–586.

(6)   Rabinowitz, J. D.; Kimball, E. Acidic Acetonitrile for Cellular Metabolome Extraction from Escherichia coli. *Anal. Chem.* **2007**, *79* (16), 6167–6173.

(7)   Tullo, A. A SOLVENT DRIES UP. *Chem Eng News* **2008**, *86* (47), 2008.

(8)   Huang, H. J.; Ramaswamy, S.; Tschirner, U. W.; Ramarao, B. V. A review of separation technologies in current and future biorefineries. *Sep. Purif. Technol.* **2008**, *62* (1), 1–21.

(9)   Cespi, D.; Passarini, F.; Vassura, I.; Cavani, F. Butadiene from biomass, a life cycle perspective to address sustainability in the chemical industry. *Green Chem.* **2016**,

18, 1625 –1638.

(10)   Global Ethanol Market, By Process (Wet Milling, Dry Milling), Source (Natural

Source, Synthetic Source), End-Use Industry (Automotive, Alcoholic Beverages,

Pharmaceutical, Cosmetic), and Geography - Insights, Size, Share, Opportunity

Analysis, & Industry https://www.coherentmarketinsights.com/market-insight/ethanol-

market-276.

(11)   Rossetti, I.; Compagnoni, M.; Finocchio, E.; Ramis, G.; Di Michele, A.; Millot, Y.;

Dzwigaj, S. Ethylene production via catalytic dehydration of diluted bioethanol: a

step towards an integrated biorefinery. *Appl. Catal. B Environ.* **2017**, *210*, 407–420.

(12)   Rossetti, I.; Compagnoni, M.; De Guido, G.; Pellegrini, L.; Ramis, G.; Dzwigaj, S.

Ethylene production from diluted bioethanol solutions. *Canad. J. Chem. Eng.* **2017**,

95, 1752.

(13)   Michaels, W.; Zhang, H.; Luyben, W. L.; Baltrusaitis, J. Design of a separation

section in an ethanol-to-butanol process. *Biomass and Bioenergy* **2018**, *109*

(December 2017), 231–238.

(14)   Anastas, P. T.; Ferris, C. A. *Benign by design. Alternative synthetic design for

pollution prevention*; American Chemical Society, 1994; Vol. 577.

(15)   Tripodi, A.; Manzini, D.; Compagnoni, M.; Ramis, G.; Rossetti, I. Alternative

Integrated Distillation Strategies for the Purification of Acetonitrile from Ethanol

Ammoxidation. *J. Ind. Eng. Chem.* **2018**, *59*, 35–49.

(16)   Tripodi, A.; Compagnoni, M.; Ramis, G.; Rossetti, I. Pressure-swing or extractive

distillation for the recovery of pure acetonitrile from ethanol ammoxidation process: A

comparison of efficiency and cost. *Chem. Eng. Res. Des.* **2017**, *127C*, 92–102.

(17)   Cavani, F.; Centi, G.; Marion, P. Catalytic ammoxidation of hydrocarbons on mixed

oxides. In *Metal Oxide Catalysts*; Jackson, S. D., Hargreaves, J. S. J., Eds.; Wiley-

VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2009; pp 771–818.

(18) Rojas, E.; Guerrero-pérez, M. O.; Bañares, M. A. Direct ammoxidation of ethane : An approach to tackle the worldwide shortage of acetonitrile. *Catal. Commun.* **2009**, *10* (11), 1555–1557.

(19) Kim, K. N.; Lane, A. M. sorted by relevance | date The selective synthesis of acetonitrile from carbon monoxide, hydrogen, and ammonia over MO/SiO2. *J. Catal* **1992**, *137*, 127–138.

(20) Tatsumi, T.; Kunitomi, S.; Yoshiwara, J.; Muramatsu, A.; Tominaga, H. Synthesis of acetonitrile and related compounds from CO-H2-NH3 over Mo/SiO2. *Catal. Lett.* **1989**, *3*, 223–226.

(21) Krebaum, L. J. Preparation of acetonitrile. US 3129241, 1964.

(22) Sandner, W. J.; Fierce, W. L. Preparation of acetonitrile. CA 615929, 1961.

(23) Li, Y.; Armor, J. N. A Reaction Pathway for the Ammoxidation of Ethane and Ethylene over Co-ZSM-5 Catalyst. *J. Catal.* **1998**, *176*, 495–502.

(24) Li, Y.; Armor, J. N. Ammoxidation of ethane to acetonitrile. IV: substantial differences between Y and dealuminated Y zeolite. *Appl. Catal. A Gen. A* **1999**, *183*, 107–120.

(25) Sobalik, Z.; Belhekar, A. A.; Tvaru, Z.; Wichterlová, B. Metal ligand complexes in CoH–BEA relevant to ethane ammoxidation to acetonitrile: an FTIR study. *Appl. Catal. A Gen. A* **1999**, *188*, 175–186.

(26) Rojas, E.; Calatayud, M.; Banares, M.; Guerrero-Perez, O. Theoretical and Experimental Study of Light Hydrocarbon Ammoxidation and Oxidative Dehydrogenation on (110)-VSbO 4 Surfaces. *J. Phys. Chem. C* **2012**, No. 110.

(27) Bulánek, R.; Novoveská, K.; Wichterlová, B. Oxidative dehydrogenation and ammoxidation of ethane and propane over pentasil ring Co-zeolites. *Appl. Catal. A Gen.* **2002**, *235*, 181–191.

(28) Ayari, F.; Mhamdi, M.; Debecker, D. P.; Gaigneaux, E. M.; Alvarez-Rodriguez, J.;

Guerrero-Ruiz, A. Effect of the chromium precursor nature on the physicochemical and catalytic properties of Cr–ZSM-5 catalysts: Application to the ammoxidation of ethylene. *J. Mol. Catal. A Chem.* **2011**, *339*, 8–16.

(29) Chen, C.; Mathias, P. M. Applied Thermodynamics for Process Modeling. *AIChE J.* **2002**, *48* (2), 194–200.

(30) *PRé Consultants, SimaPro, PhD version 8.4.0.0, Amersfoort, The Netherlands*; 2018.

(31) *Ecoinvent Centre (formerly Swiss Centre for Life Cycle Inventories) Ecoinvent 3.3 Database*; 2016.

(32) Belov, V. V.; Markov, V. I.; Sova, S. B.; Golosman, E. Z.; Nechugovskii, A. I. New composite catalysts for the synthesis of acetonitrile from ethanol and ammonia, prepared using calcium aluminates (Talyum). *Russ. J. Appl. Chem.* **2016**, *89* (3), 414–420.

(33) Feng, C.; Zhang, Y.; Zhang, Y.; Wen, Y.; Zhao, J. Study on alumina-supported cobalt-nickel oxide catalyst for synthesis of acetonitrile from ethanol. *Catal. Letters* **2011**, *141* (1), 168–177.

(34) Hamill, C.; Driss, H.; Goguet, A.; Burch, R.; Petrov, L.; Daous, M.; Rooney, D. Mild temperature palladium-catalyzed ammoxidation of ethanol to acetonitrile. *Appl. Catal. A Gen.* **2015**, *506*, 261–267.

(35) Hu, Y.; Cao, J.; Deng, J.; Cui, B.; Tan, M.; Li, J.; Zhang, H. Synthesis of acetonitrile from ethanol via reductive amination over Cu/γ-Al2O3. *React. Kinet. Mech. Catal.* **2012**, *106* (1), 127–139.

(36) Folco, F.; Ochoa, J. V.; Cavani, F.; Ott, L.; Janssen, M. Ethanol gas-phase ammoxidation to acetonitrile. *Catal. Sci. Technol.* **2017**, *7*, 200–212.

(37) AAVV. *Cyanides of Hydrogen, Sodium and Potassium, and Acetone Cyanohydrin - I*;

ECETOC, 2007; Vol. JACC 53.

(38) Zhuang, Q.; Clements, B.; Li, Y. From ammonium bicarbonate fertilizer production process to power plant CO 2 capture. *Int. J. Greenh. Gas Control* **2012**, *10*, 56–63.

(39) Sutter, D.; Gazzani, M.; Mazzotti, M. A low-energy chilled ammonia process exploiting controlled solid formation for post-combustion CO 2 capture. *Faraday Discuss.* **2016**, *192*, 59–83.

(40) Gaspar, J.; Waseem, M.; Blaker, E.; Langseth, B.; Hansen, T.; Thomsen, K.; von Solms, N.; Fosbol, P. L. A Low Energy Aqueous Ammonia CO2 Capture Process. *Energy Procedia* **2014**, *63*, 614–623.

(41) Gazzani, M.; Sutter, D.; Mazzotti, M. Improving the efficiency of a chilled ammonia CO 2 capture plant through solid formation : a thermodynamic analysis. *Energy Procedia* **2014**, *63*, 1084–1090.

(42) Bak, C.; Asif, M.; Kim, W. Experimental study on CO2 capture by chilled ammonia process. *Chem. Eng. J.* **2015**, *265*, 1–8.

(43) Yildirim, Ö.; Kiss, A. A.; Hüser, N.; Leßmann, K.; Kenig, E. Y. Reactive absorption in chemical process industry: A review on current activities. *Chem. Eng. J.* **2012**, *213*, 371–391.

(44) Kuu, W.; Chilamkurti, R.; Chen, C. Effect of relative humidity and temperature on moisture sorption and stability of sodium bicarbonate powder. *Int. J. Pharm.* **1998**, *166*, 167–175.

(45) Lide ed., D. R. *"Physical Constants of Inorganic Compunds" in CRC Handbook of Chemistry and Physics*, 15th ed.; Lide, D. R., Ed.; CRC Press, 2005.

(46) Horsley, H. *Azeotropic Data*; American Chemical Society, 1973.

(47) Repke, J. U.; Forner, F.; Klein, A. Separation of homogeneous azeotropic mixtures by pressure swing distillation - Analysis of the operation performance. *Chem. Eng. Technol.* **2005**, *28* (10), 1151–1157.

(48)   Rodríguez-Donis, I.; Gerbaud, V.; Joulia, X. Entrainer Selection Rules for the Separation of Azeotropic and Close-Boiling-Temperature Mixtures by Homogeneous Batch. *Ind. Eng. Chem. Res.* **2001**, *40*, 2729–2741.

(49)   Li, J.; Yang, X.; Chen, K.; Zheng, Y.; Peng, C.; Liu, H. Sifting Ionic Liquids as Additives for Separation of Acetonitrile and Water Azeotropic Mixture Using the COSMO-RS Method. *Ind Eng Chem Res* **2012**.

(50)   *EN ISO 14040 Environmental Management, Life Cycle Assessment, Principles and Framework, International Organization for Standardization, Geneva, Switzerland.*; 2006.

(51)   *EN ISO 14044 Environmental Management, Life Cycle Assessment, Requirements and Guidelines, International Organization for Standardization, Geneva, Switzerland.*; 2006.

(52)   Cespi, D.; Passarini, F.; Neri, E.; Vassura, I.; Ciacci, L.; Cavani, F. Life Cycle Assessment comparison of two ways for acrylonitrile production: the SOHIO process and an alternative route using propane. *J. Clean. Prod.* **2014**, *69*, 17 – 25.

(53)   Cespi, D.; Cucciniello, R.; Ricciardi, M.; Capacchione, C.; Vassura, I.; Passarini, F.; Proto, A. Butadiene from biomass, a life cycle perspective to address sustainability in the chemical industry. *Green Chem.* **2016**, *18*, 4559–4570.

(54)   Ricciardi, M.; Passarini, F.; Vassura, I.; Proto, A.; Capacchione, C.; Cucciniello, R.; Cespi, D. Glycidol, a Valuable Substrate for the Synthesis of Monoalkyl Glyceryl Ethers: A Simplified Life Cycle Approach. *ChemSusChem* **2017**, *10*, 2291–2300.

(55)   Samorì, C.; Cespi, D.; Blair, P.; Galletti, P.; Malferrari, D.; Passarini, F.; Vassura, I.; Tagliavini, E. Application of switchable hydrophilicity solvents for recycling multilayer packaging materials. *Green Chem.* **2017**, *19*, 1714–1720.

(56)   Anastas, P. T.; Beach, E. S.; Kundu, S. Tools for Green Chemistry, Volume 10. In

Handbook of Green Chemistry Series; Wiley-VCH Verlag GmbH & Co. KGaA., 2017.

(57) Frischknecht, R.; Jungbluth, N.; Althaus, H.-J.; Bauer, C.; Doka, G.; Dones, R.; Hischier, R.; Hellweg, S.; Humbert, S.; Köllner, T.; et al. *Implementation of Life Cycle Impact Assessment Methods, ecoinvent report No. 3, v2.0, Swiss Centre for Life Cycle Inventories, Dübendorf*; 2007.

(58) *VDI – Verein Deutscher Ingenieure, VDI-richtlinie 4600: Cumulative energy demand, terms, defiitions, methods of calculation, Düsseldorf, Germany*; 1997.

(59) Huijbregts, M. A. J.; Rombouts, L. J. A.; Hellweg, S.; Frischknecht, R.; Hendriks, A. J.; Meent, D. Van De; Ragas, A. M. J.; Reijnders, L.; Struijs, J. Is cumulative fossil energy demand a useful indicator for the environmental performance of products? *Environ. Sci. Technol.* **2006**, *40*, 641–648.

(60) Wernet, G.; Mutel, C.; Hellweg, S.; Hungerbühler, K. The Environmental Importance of Energy Use in Chemical Production. *J. Ind. Ecol.* **2011**, *15*, 96–107.

(61) Huijbregts, A. M. *ReCiPe 2016 – A which comprises A harmonised life cycle impact assessment method at midpoint and endpoint level. RIVM (National Institute for Public Health and the Environment) Report, , the Netherlands (v. 1.00).*; 2016.

Acronyms, abbreviations and symbols

ENRTL	**E**lectrolytes **N**on-**R**andom **T**wo **L**iquids
MeCN	Acetonitrile, CH_3CN
NRTL	**N**on-**R**andom **T**wo **L**iquids
RADFRAC	**R**igorous **AD**sorption-**FRAC**tioning
T	**T**emperature

Flowsheets coding

Functional coding – section number – **block coding** – *block number*

Functional codes		Block type code	
		AA	Compressor
FR	Feed of Reagents	AP	Pump for Pressure rising
SB	Separation of By-products	CA	Column with Azeotropes
SP	Separation of Products	CM	Column with a Mixture of more than 2 specie
SV	Separation of Wastes	CV	Control Valve
TP	Transformation of Products	HB	Heat exchanger,Boiler
		HF	Heat exchanger,Furnace
		HX	Heat eXchanger, generic
		MJ	Mixing Junction
		PA	Tube at Atmospheric pressure
		PP	Tube under Pressure
		RK	Reactor in Kinetic conditions
		SA	Separation of Azeotropes
		SC	Separation Column
		SF	Separation via Flash
		SG	Separation by Gravity
		SJ	Splitting Junction
		SS	Separation of Solids

TABLES

Compound	Inlet Flow (kmol/h)	Conv. (%)	Sel. (%)	Flow (kmol/h)
C_2H_6O	0.5	100	-	0.0
H_2O	0.0	-	-	1.67
CH_3CN	0.0	-	48	0.24
NH_3	1.3	30	-	0.91
HCN	0.0	-	13	0.065
CO_2	0.0	-	38	0.39
CO	0.0	-	4	0.04
C_2H_4	0.0	-	2	0.01
N_2	6.9	-	12	6.94
O_2	1.7	52	-	0.7

Table 1: Activity data and input-output flows of the chemicals for the ethanol ammoxidation on a Cs-V/TiO_2 catalyst [36].

Material Inputs		Material Outputs	
Air	170 m^3/h	Acetonitrile	9 kg/h
Water	loss makeup < 2 l/h	Ammonium bicarbonate	52 kg/h
Carbon Dioxide	16 kg/h	Sodium Cyanide	3 kg/h
Ethanol (azeotrope)	23 kg/h	Sodium Carbonate	6 kg/h
Ammonia	18 kg/h	Flue gases	75 m^3/h
NaOH (solid)	13 kg/h	Water drainage	7 l/h

Table 2: Overall plant feeds and products balances.

Block	HEATER	PS2	PS3	PS4
Function	Mixture re-heating	Excess water discharge	Gases purification	Azeotrope breaking
Trays	6	15	25	18
Feed tray	1	7	5	10
Reflux ratio (mol/mol)	-	0.77	2.9	1.8
Bottoms rate (kmol/h)	1.23	0.47	0.60	0.22
T (head) (°C)	83	68	25	160
T (residues) (°C)	100	100	76	175
Pressure (bar-a)	1	1	1	10
Condenser duty (kW)	-	-6.8	-7.2	-5.7
Reboiler Duty (kW)	13.3	1.2	1.5	10.5
Split Fractions (B/F)				
Water	na	na	0.98	<0.01
Acetonitrile	0.00	0.00	0.98	0.55
volatiles	0.00	0.00	0.00	-

Table 3: Specifications and results of the Pressure-Swing section distillation columns. Negative duties stand for released (rather than absorbed) heat. 'B/F' stands for 'Bottoms to Feed ratio'.

Block	AUTOHX	REACTOR	WASHER	CO2INLET	HEATER	PS2		PS3		PS4		SALTBATH
Type	Heat Exchanger	Reactor	Washing column	Flash mixer	Tray reboiler	Column reboiler	Column condenser	Column reboiler	Column condenser	Column reboiler	Column condenser	Flash tank
Duty (kW)	14.9	-97.4	-62.4	-8.2	15.1	1.2	-6.8	1.5	-9.9	10.5	-7.0	-2.0
Notes	Feed-to-product exchange		Cryogenic section	Cryogenic section	Column without condenser							Alkaline bath, CN salification

Table 4: Duties report for the main process blocks (refer to Figure 2). The duties of additional heaters and coolers, here not shown for simplicity, have been lumped into the nearest main block's account.

Inventory flow	unit	amount
Input		
air	m^3	18.89
water	l	0.22
CO$_2$	kg	1.78
ethanol	kg	2.56
ammonia	kg	2.00
NaOH (solid)	kg	1.44
heating power	kWh	5.77
electric power	kWh	0.74
Output		
acetonitrile	kg	1.00
avoided products		
ammonium bicarbonate	kg	5.78
sodium cyanide	kg	0.33
sodium carbonate	kg	0.67
air emissions		
flue gases	m^3	8.33
water (gas)	kg	0.05
acetonitrile (gas)	kg	0.05
ammonia (gas)	kg	0.01
ethylene (gas)	kg	0.03
CO (gas)	kg	0.08
N$_2$ (gas)	kg	17.35
O$_2$ (gas)	kg	1.79
heating power	kWh	-22.50
water emissions		
water drainage	l	0.78

Table 5: Cradle to gate inventory for the production of 1kg of bio-based acetonitrile from EtOH ammoxidation.

Impact category	Unit	Bio-based acetonitrile, from corn EtOH	Fossil-based acetonitrile, from SOHIO process
Climate change	kg CO_2 eq	1.4E+00	3.8E+00
Ozone depletion	kg CFC-11 eq	1.4E-07	2.7E-07
Terrestrial acidification	kg SO_2 eq	4.7E-02	2.1E-02
Freshwater eutrophication	kg P eq	-1.1E-03	4.3E-04
Marine eutrophication	kg N eq	1.2E-02	1.5E-02
Human toxicity	kg 1,4-DB eq	-1.1E+01	6.1E-01
Photochemical oxidant formation	kg NMVOC	6.0E-02	8.6E-03
Particulate matter formation	kg PM10 eq	9.2E-03	5.1E-03
Terrestrial ecotoxicity	kg 1,4-DB eq	-1.4E-03	2.1E-04
Freshwater ecotoxicity	kg 1,4-DB eq	-1.1E+00	1.4E-02
Marine ecotoxicity	kg 1,4-DB eq	-2.2E-01	1.5E-02
Ionising radiation	kBq U^{235} eq	-5.2E-01	1.6E-01
Agricultural land occupation	m^2 yr	2.6E+00	9.6E-02
Urban land occupation	m^2yr	1.3E-01	7.8E-03
Natural land transformation	m^2	8.9E-04	4.8E-04
Water depletion	m^3	3.2E-01	6.6E-02
Metal depletion	kg Fe eq	-2.8E-01	1.1E-01
Fossil depletion	kg oil eq	5.1E-01	2.4E+00

Table 6: Results from cradle to gate analysis in terms of characterization factors per each impact category.
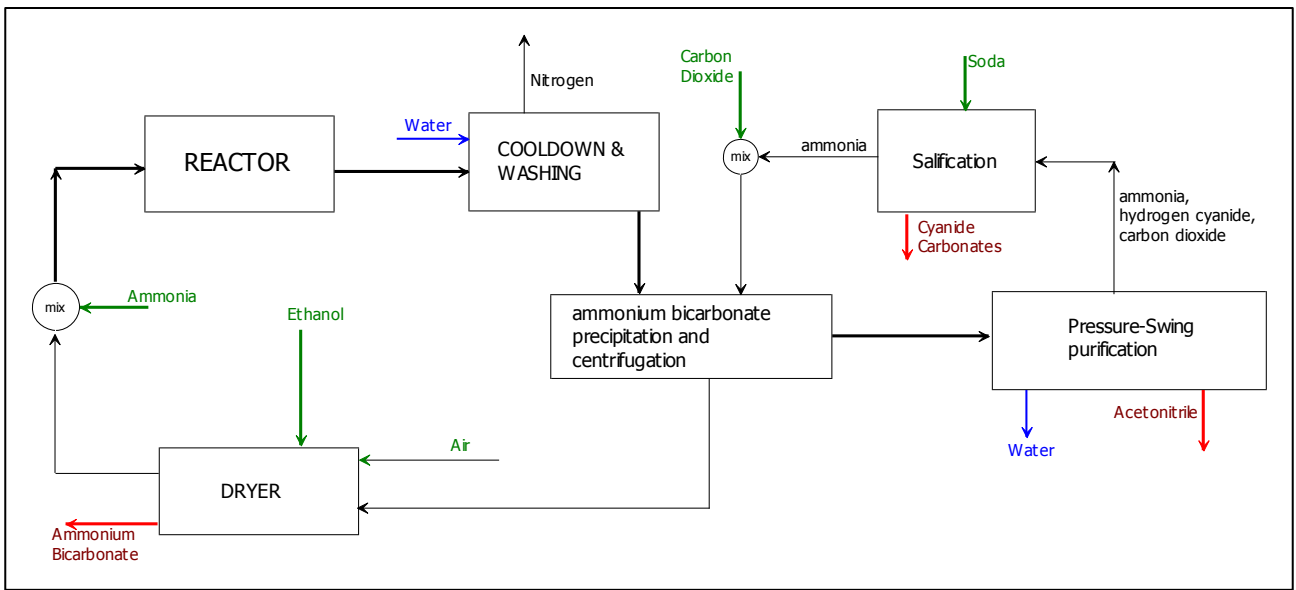
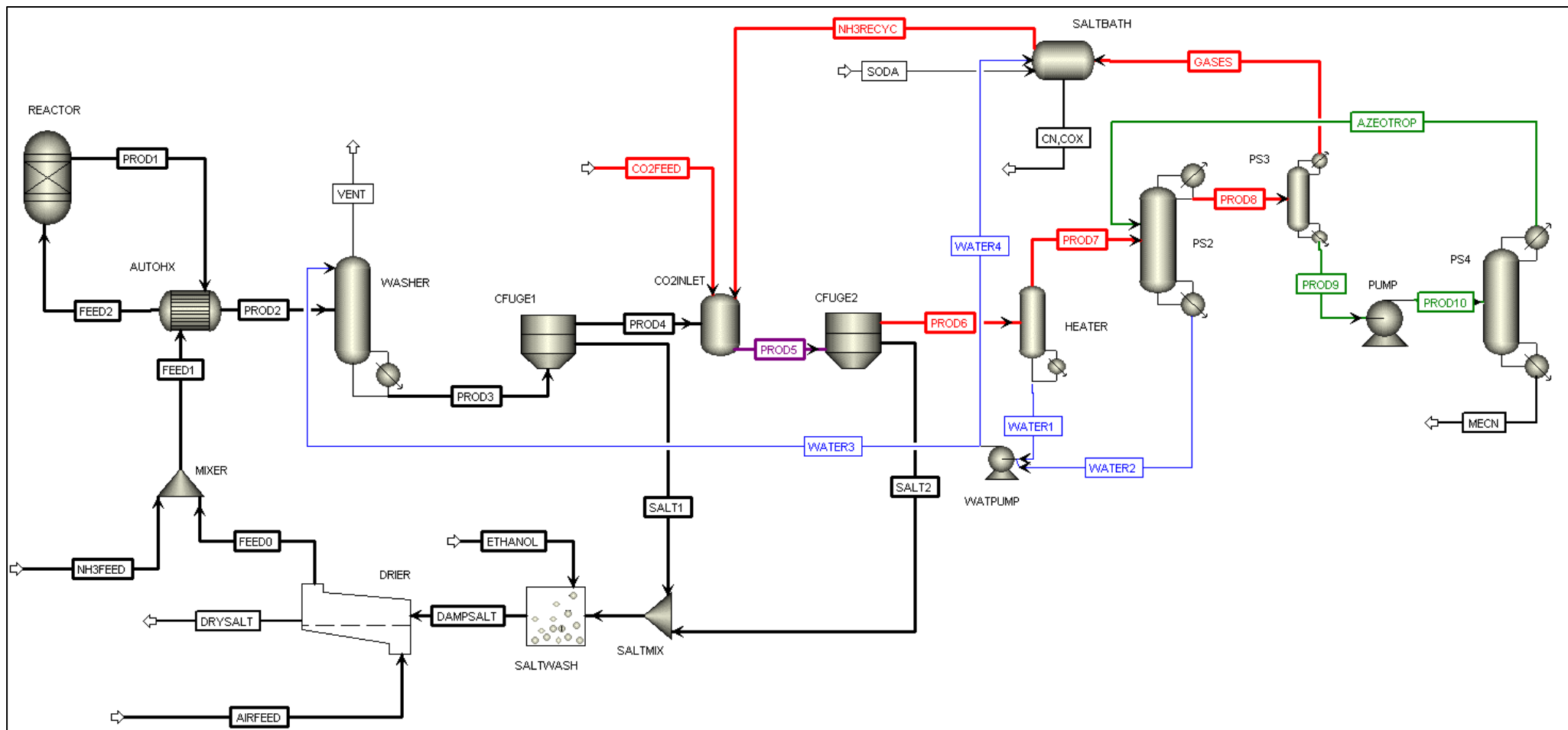# FIGURES

Figure 1: Process conceptual scheme.

Figure 2: Simplified full plant flowsheet, where the main material loops are more clearly distinguished. The feed line/reactor/solid handling loop encompasses all the blocks to the second centrifuge (starting from the left) but has no accumulation being always open to the 'PROD6' stream. The ammonia recycle is linked with the first at the key block 'CO2INELT', and has a potential build-up issue because the exiting flow (stream 'SALT2') depends not-linearly on the 'CO2FEED' input. The pressure-swing recycle encloses the last three columns (on the right) and its convergence depends on the purge stream 'GASES'. The water recycle is completely open via a (not drawn) drainage line just before the washer and an additional makeup line upstream the pump.
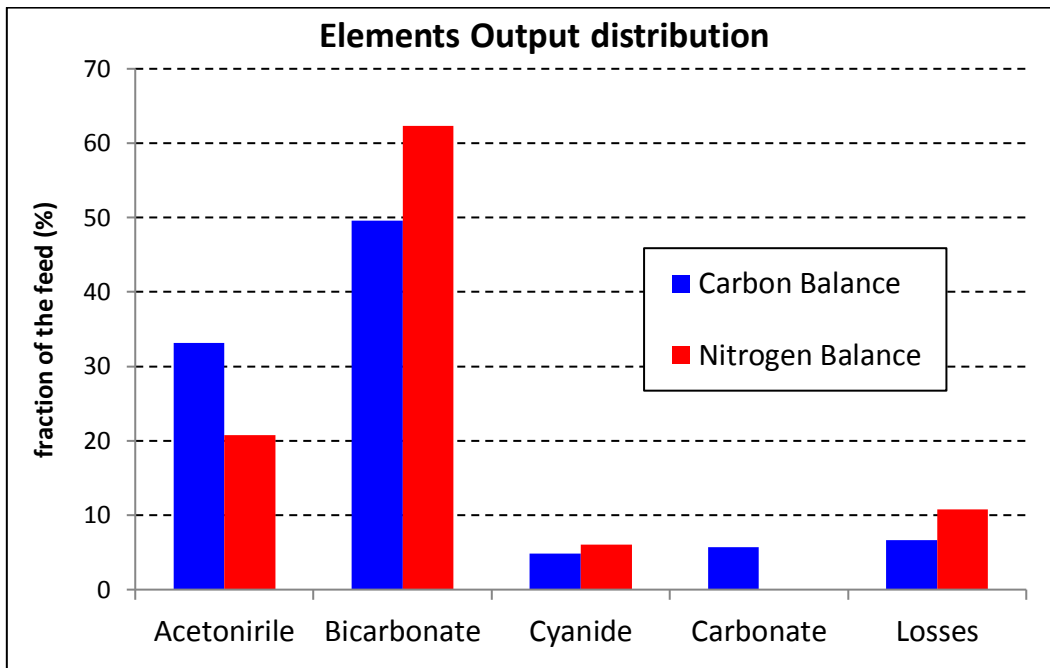
Figure 3: Overview of the atom economy for the process. The carbon fed as CO_2 instead of ethanol amounts to the 28% of the total moles, explaining the higher contribution of CO_2 to the balance, while all the reactive nitrogen comes from the ammonia.
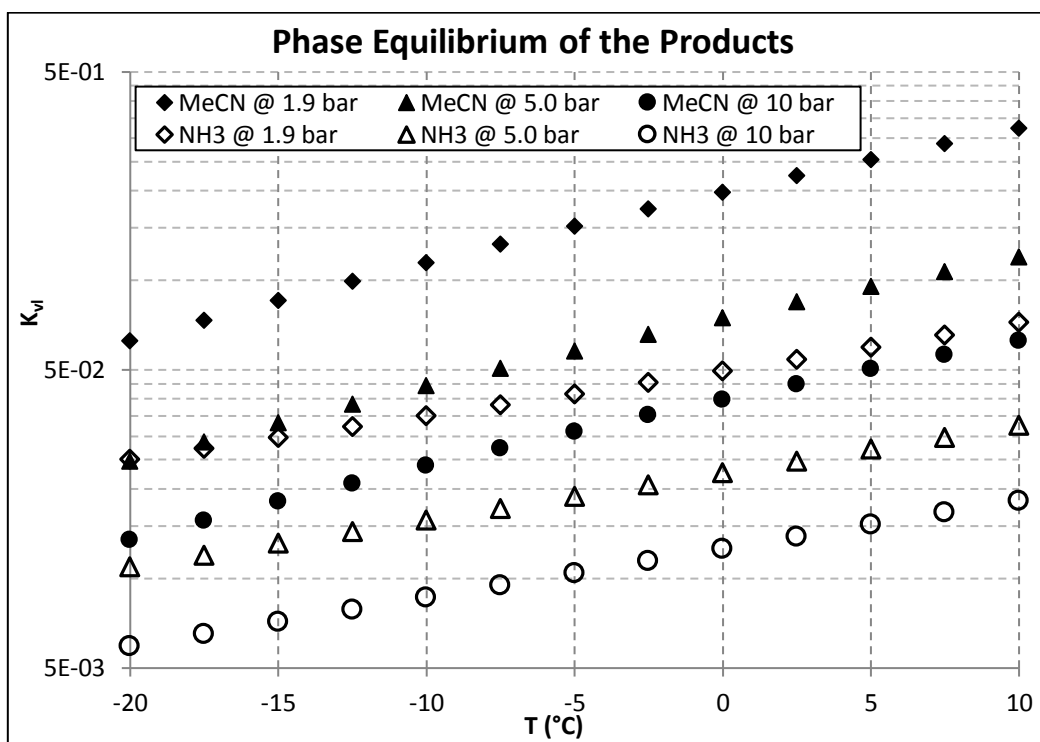

Figure 4: Analysis of the acetonitrile-ammonia distribution in the liquid/vapor phases of the product mixture cooled down at different temperatures and pressures. The partition of ammonia is calculated as the ratio:

$$NH_{3(g)}/\left(NH_{3(l)} + NH_{4(l)}^+ + NH_4HCO_{3(s)}\right) \text{ (mol/mol)}.$$
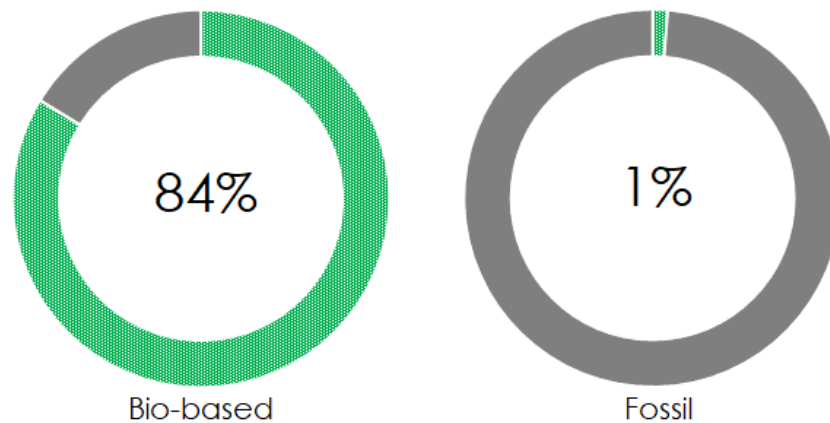
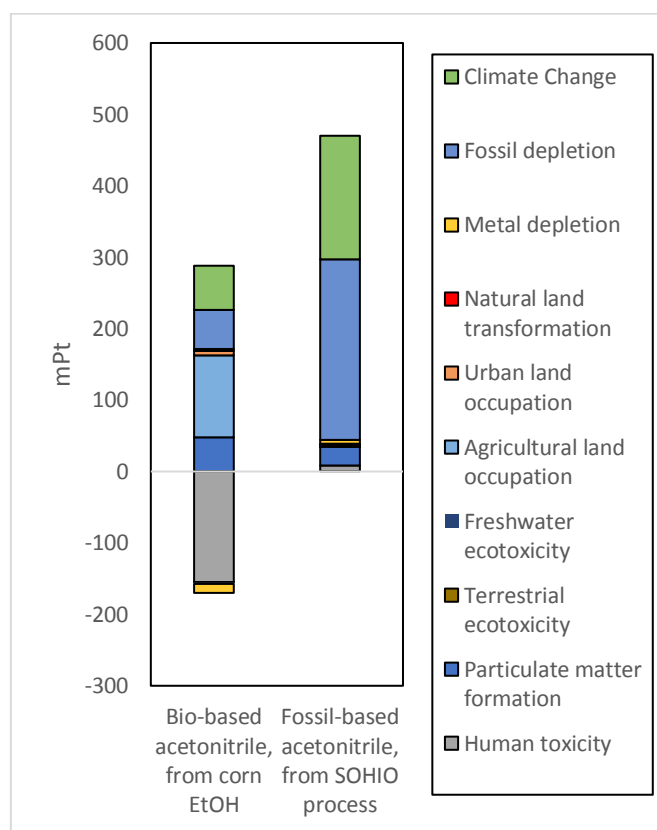**Figure 5:** Renewability grade (green) for the bio-based and fossil routes to acetonitrile.

Figure 6: Single score of the two alternative routes to acetonitrile, in terms of single score (i.e. cumulative impact).
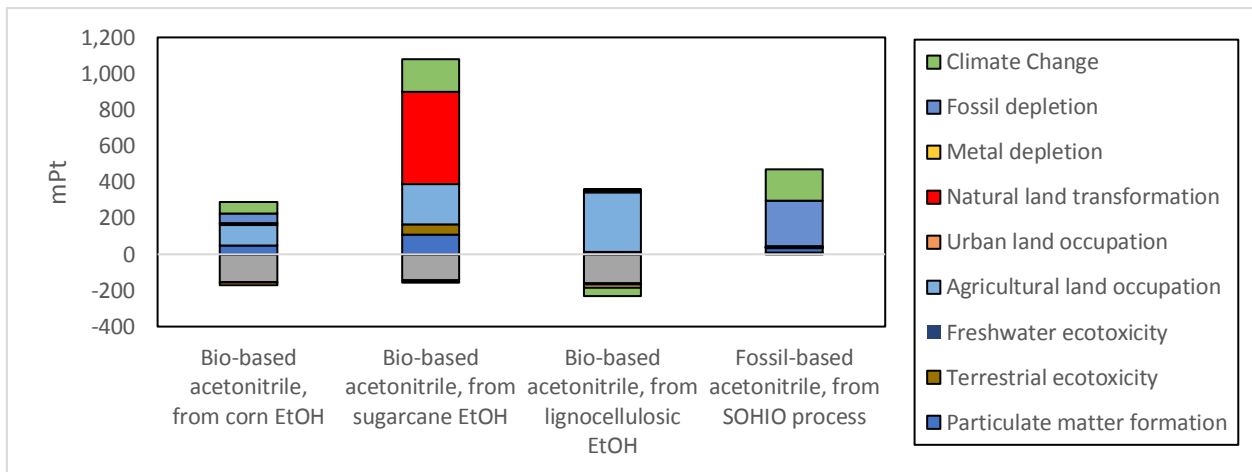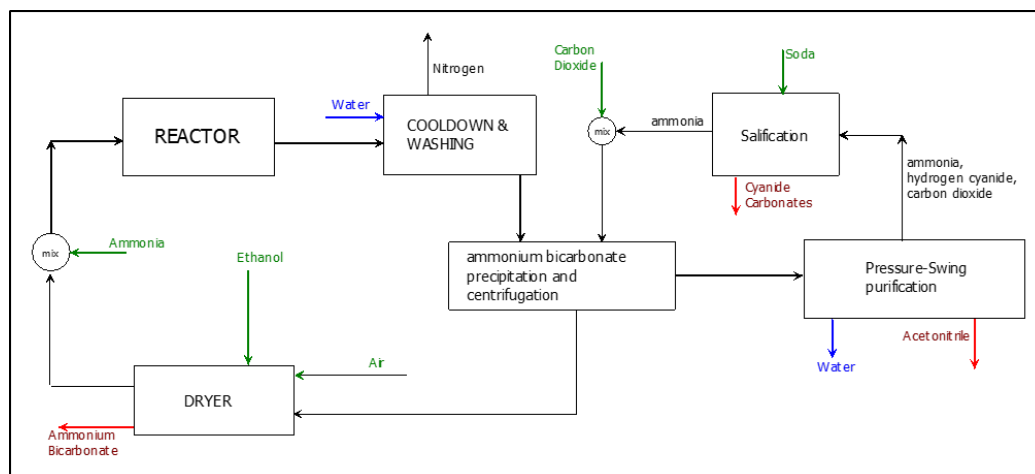
Figure 7: Sensitivity analysis of different routes to acetonitrile, cumulative scores (Pt).

For Table of Contents Use Only

Table of Contents

An integrated plant has been designed to produce acetonitrile by ammoxidation of ethanol. The sustainability of this approach is checked through life cycle assessment.

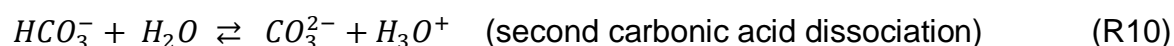**SUPPLEMENTARY INFORMATION**

Total 3 pages.

Page S2: reactions set for solids recovery;

Page S3: Table S1 - Resources consumption and Table S2 - Sensitivity analysis of different routes to acetonitrile

Reactions set for salts recovery

The acid-base and salt chemistry of the involved species is based on the following stoichiometry, applied to any liquid-phase stream (save where differently specified), whereas reactions 1-6 (in the main text) are confined within the reactor block:

$$H_2O + NH_3 \rightleftarrows OH^- + NH_4^+ \qquad \text{(NH}_3\text{ dissociation)} \qquad \text{(R7)}$$

$$H_2O + HCN \rightleftarrows H_3O^+ + CN^- \quad \text{(HCN dissociation)} \qquad \text{(R8)}$$

$$H_2CO_3 + H_2O \rightleftarrows HCO_3^- + H_3O^+ \quad \text{(first carbonic acid dissociation)} \qquad \text{(R9)}$$

$$HCO_3^- + H_2O \rightleftarrows CO_3^{2-} + H_3O^+ \quad \text{(second carbonic acid dissociation)} \qquad \text{(R10)}$$

$$HCO_3^- + NH_4^+ \rightleftarrows NH_4HCO_{3(s)} \quad \text{(ammonium bicarbonate precipitation)} \qquad \text{(R11)}$$

$$NaOH_{(s)} \rightarrow Na^+ + OH^- \quad \text{(NaOH dissociation)} \tag{R12}$$

$$2H_2O \rightleftarrows H_3O^+ + OH^- \quad \text{(water auto-protolysis)} \tag{R13}$$

where the formation of carbamates has been neglected, at this stage of process development, being at least one order of magnitude less concentrated with respect to the ammonium and bicarbonate ions [Mathias, P. M.; Reddy, S.; Connell, J. P. O. Quantitative Evaluation of the Aqueous-Ammonia Process for CO 2 Capture Using Fundamental Data and Thermodynamic Analysis. *Energy Procedia* **2009**, *1* (1), 1227–1234].

Type of resources consumed in MJ eq.	Bio-based acetonitrile	Fossil-based acetonitrile
Total	74.4	111.5
Non renewable, fossil	23.3	106.0
Non-renewable, nuclear	-11.3	4.1
Non-renewable, biomass	0.1	0.0
Total Non-renewable	12.1	110.1
Renewable, biomass	64.6	0.8
Renewable, wind, solar, geothermal	-0.7	0.1
Renewable, water	-1.6	0.5
Total Renewable	62.3	1.4

Table S1 Resources consumption of both routes expressed in MJ eq. Negative values represent benefits from product and energy recovery of the bio-refinery system.

Impact category	Bio-based acetonitrile, from corn EtOH	Bio-based acetonitrile, from sugarcane EtOH	Bio-based acetonitrile, from lignocellulosic EtOH	Fossil-based acetonitrile, from SOHIO process
Total	1.18 E+02	9.23 E+02	1.27 E+02	4.70 E+02
Climate Change	6.16E+01	1.80E+02	-4.70E+01	1.73E+02
Human toxicity	-1.55E+02	-1.42E+02	-1.59E+02	8.49E+00
Particulate matter formation	4.76E+01	1.10E+02	1.29E+01	2.62E+01
Terrestrial ecotoxicity	-4.64E-01	5.38E+01	-6.89E+00	7.14E-02
Freshwater ecotoxicity	-2.16E+00	-2.17E+00	-2.21E+00	2.63E-02
Agricultural land occupation	1.15E+02	2.23E+02	3.29E+02	2.56E+00
Urban land occupation	6.04E+00	1.21E+00	1.28E+01	3.59E-01
Natural land transformation	2.75E+00	5.11E+02	1.76E+00	1.43E+00
Metal depletion	-1.29E+01	-1.25E+01	-1.64E+01	5.10E+00
Fossil depletion	5.50E+01	7.29E-01	1.61E+00	2.52E+02

Table S2 Sensitivity analysis of different routes to acetonitrile, cumulative scores (Pt).