

# 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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## 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<sub>3</sub>CN 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

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extractive distillation option, which revealed more expensive with respect to pressure swing. Different energy integration options have been also compared.

*Keywords:* Acetonitrile; Distillation; Azeotrope separation; Pressure swing distillation; Green chemistry; ASPEN Plus; Process simulation; Extractive distillation; Cost analysis.

## **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 [1]. Its US production in 2014 is reported between 4.5 and 22.5 kton [2] 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 manufacturing during Olympiads in China, and partly to the world crisis, which limited acrylonitrile consumption. This suggested the development of independent processes 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 [3–6]. 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:



The product stream, therefore, includes some condensable species (mainly water and  $\text{CH}_3\text{CN}$ , which form a minimum boiling azeotrope at constant pressure) and many uncondensable products, with the addition of unreacted ammonia and oxygen. Among the gases, some are also partially soluble in the acetonitrile/water mixture (predominantly,  $\text{CO}_2$ ,  $\text{NH}_3$  and  $\text{HCN}$ ).

Different strategies can be used to resolve binary azeotropic mixtures, as recently reviewed by Shen et al. [7], 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 [8–14], however only some of them 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 [15].

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 designed and optimized for the different selected options. An energy integration analysis was also carried out, in order to save utilities and to optimise the thermal integration of the plant. Finally, the cost of the proposed strategies has been compared, assessing their specific impact on the acetonitrile production cost.

## **2 – Models and methods**

Process simulation was accomplished by using Aspen Plus<sup>®</sup> V9 (Aspen Technology Inc.), implementing the APV9 PURE35 databank. The thermodynamic data needed were found in the Aspen Database and compared with the available literature data for consistency. The thermodynamic model chosen is the Non Random Two Liquids (NRTL) model to compute the non ideality in the liquid phase, coupled with the Redlich-Kwong (RK) equation of state for the gas phase, which is often the first choice when the distillation of non-ideal mixtures is involved, provided that relatively low pressure is used [16]. Computations done with the UNIQUAC and UNIFAC models were also compared to check the consistency of the previsions, returning similar results. The maximum deviation with respect to the literature data reported by Villarman et al. [17] was 2.6 % for the calculation of acetonitrile partial pressure in mixture with water with the UNIQUAC package. The corresponding calculation of the activity coefficients at infinite dilution using the same model was 1.5 % different from the experimentally derived values.

The separation case here selected is based on experimental data collected for the production of acetonitrile by amoxidation of ethanol. The test reactor here considered [4] produces *ca.*10 kg/h of acetonitrile according to reaction R1 and is designed from the grass roots as a new pilot scale unit starting from experimental data collected on a micropilot scale equipment.

A first separation of inert Nitrogen (from air, used to supply O<sub>2</sub> in the feed, and in part produced as byproduct) and gaseous products is designed, according to the simplified block diagram of Fig. 1. This eliminates most of the volatile compounds, leaving a mixture of the following composition to be fed to the acetonitrile purification section highlighted in red in the same Fig. 1: acetonitrile (0.218 kmol/h), water (0.84 kmol/h), ammonia (0.117 kmol/h), CO<sub>2</sub> (0.09 kmol/h) and HCN (0.064 kmol/h).

## **2.1 - Preliminary Gas Separation**

Before the azeotrope resolution columns, either accomplished by extractive distillation or pressure swing, the mixture must be conditioned to eliminate the volatile components and excess water with respect to the azeotrope. Without this pretreatment, either purity/recovery goals were not achieved, or too expensive columns have to be designed.

To eliminate the gases, a flash unit was designed, followed by two-columns in series. This set of units accomplished the elimination of CO<sub>2</sub> (that can be captured), NH<sub>3</sub> (recycled to the reactor or recovered as salt to be valorized as fertiliser), and HCN (valorized as salt). These columns also allowed to concentrate the water/acetonitrile mixture towards the azeotropic composition. The process flow diagram is exemplified in Fig. 2.

According to such scheme, the flash drum (code SP-SF01) leads to CO<sub>2</sub> separation as gas and a distillation column (code SP-SC01) releases water as bottom product and a nearly azeotropic distillate. A second distillation column refines the elimination of CO<sub>2</sub>, NH<sub>3</sub> and HCN. To fully eliminate the latter compounds, at least 15 stages are needed in this block.

The goal of the separation is to maximize acetonitrile recovery, with a purity >99.9%. According to the specific acetonitrile purification strategy adopted, the gas-separation section described above can work independently upstream the purification blocks, or can be co-fed with the recycled streams.

## **3 – Pressure swing distillation**

### **3.1 – Pressure swing feasibility check**

The separation of the simple binary  $\text{CH}_3\text{CN}$ -Water mixture can be achieved by resolving the azeotrope through a differential pressure system [13]. The operating pressure indeed affects the composition of the azeotrope, allowing a straightforward separation [8,9,13,18–20]. For instance, pressure swing has been compared by Cao et al. as for costs and control options, also adopting a variable diameter column [21] and different feed temperature [22], for the following azeotropic mixtures: acetone-chloroform, acetone-methanol, methanol-chloroform, benzene-cyclohexane and isopropyl alcohol-diisopropyl ether. A simulated annealing algorithm was used to optimize the operating pressure minimizing the total annual costs (TAC) in the case of the pressure swing separation of the acetone-methanol system [23]. The attention was often focused on the control options of pressure swing systems [9,12,14,21,22,24–26], but only in some cases this strategy was adopted for the resolution of the acetonitrile/water system [9,11,13], and never as part of a fully integrated purification train as in the present case.

The thermodynamic foundation of this technique is presented in Fig. 3, which shows the binary equilibrium diagrams at variable pressure, while Fig. 4 reproduces the very basic equipment layout. Varying the pressure in the downstream column, the atmospheric azeotrope produced by the upstream block becomes a suitable feed to recover pure acetonitrile as bottom product, while the azeotrope (at composition imposed by the operating pressure) is recovered as distillate and recycled. Indeed, at sufficiently high operating pressure, the composition of the mixture to be separated lies on the  $\text{CH}_3\text{CN}$ -rich side of the azeotropic equilibrium diagram.

In order to set up the pressurized column operation, however, the mixture outflowing from the ammoxidation reactor has to be properly conditioned. Indeed, after the preliminary gross separation of the gaseous products and unreacted ammonia and oxygen, the residual carbon dioxide, ammonia and HCN, still present in the liquid phase have to be effectively removed, as described in the next section. This point represents a practical issue to be solved in the real process and has been insufficiently addressed previously in the literature.

### 3.2 Conditioning of the pressure swing feeding mixture

The residue volatile byproducts rise one major complication, since the pump may cavitate if fed with volatile components (unless the mixture is sub-cooled, which is practically unfeasible at its inlet composition). Moreover, with respect to the case of azeotropic/extractive distillation, the first column (SP01CM02 of Fig. 4a) has to be optimized [15].

Altogether, these issues led to arrange a first separation step that relies on a flash drum (which vents mainly CO<sub>2</sub>, stream SB02PA01) and a second venting stage atop the first column, with care for certain aspects: the first column (code SP02CM02, Fig. 4), that dumps most of the water (stream SB02PA02) while still venting CO<sub>2</sub> (stream SB02PA03), has been specified with a two-outlets (vapor and liquid) partial condenser in order to: *i*) retain the acetonitrile even when the distillate rate is slightly increased to enhance the overhead gas flow and *ii*) to avoid downstream separated cooling blocks, needed to align an only-vapor distillate to the second column operating temperatures; a second array of trays (SP02CA03 in the same Figure) discharges NH<sub>3</sub> and HCN in one step as head products: a condenser and a liquid reflux are needed (though this means to release heat at potentially low temperatures) to avoid losses of vaporised acetonitrile.

The boiling point of HCN is intermediate between that of NH<sub>3</sub> and that of the azeotrope, and it might split roughly equally between the distillate and the residue if the bottoms rate is not chosen carefully and the reflux ratio is not sufficient (*vide infra*).

In the subsequent pressure swing section, the atmospheric azeotrope, separated from the gases and the excess water, is routed to a pressurised column (SP02CA05) that lets pure acetonitrile out through the bottoms, giving back a diluted azeotrope (calculated at 7 bar(a)) to be recycled. The feeding temperatures are in accordance to the following criteria. Column 02: as low as 25 °C from the upstream CO<sub>2</sub> vent to avoid excessive loss of vaporised acetonitrile; Column 03: 20-25 °C from first column condenser for the same reason; Column 05: in the 70 – 80 °C range to grant feeding sufficient enthalpy.

The second gas-venting column is conceptually feasible, but being fed with an NH<sub>3</sub>:HCN ratio as low as 2, its preliminary design may not be simple since the use of ternary diagrams is only approximate. In turn, the already formed azeotrope between acetonitrile and water puts aside the heavy/light keys approach. Anyway, in spite of the different boiling point of NH<sub>3</sub> and HCN, their volatility is sufficiently different from that of the less volatile components, that they can be considered as one volatile pseudo-component. Indeed, the two volatiles can be approximated as one gaseous mixture, as the calculation of the simulated column confirms (Fig. 5; see also Table 1 for the preliminary mixture analysis). This block becomes critical for the overall assessment of the process, because it presents a potentially too low heat-release temperature (*ca.* 5 °C).

### **3.3 Pressure-swing resolution of the Water/CH<sub>3</sub>CN azeotrope**

Coming to the pressure-swing system, the pressure increment has been at first kept to 5 bar to check the feasibility of the technique even under a mild azeotrope-shift. The mass-balance of the recirculation has firstly been solved for the azeotrope composition at this pressure and the atmospheric one, then a further tuning of the columns performances led to shift the third column up to the 6.8-7 bar range to align its overhead CH<sub>3</sub>CN-Water mixture to the expected co-feed of the first column. This reassessment has greatly helped the tear convergence and, moreover, the removal of water residues from the product stream.

The process streams are reported in Table 2: the recovery of acetonitrile from the inlet stream amounts to more than 95%, in essentially pure form (>99.99%). An optimization of the whole set up has been carried out according to capital and operating costs (CAPEX and OPEX) evaluation (paragraph 6). The results reported in Table 2 are relative to the optimized configuration.

The gross flowrate of the recycled azeotrope, in turn, has been kept as low as possible in order to have leaner column designs. The heat duties of the various blocks are also presented in Table 3 for the optimized version, including the sensitivity analysis done on trays number and feed tray position based on cost analysis (*vide infra*). This solution allows to recover 95.5% of CH<sub>3</sub>CN, with a very high



purity. For instance, when decreasing the trays number of the stripping section of column SP01CA05 to 10 theoretical trays (keeping unaltered feed tray position), acetonitrile purity decreased down to 99.89% with a significant decrease of the equipment costs of this column. This represents an easily tunable option to set product purity depending to market requirement.

Pressure has been further increased to 10 bar, keeping unaltered the upstream options, except of course for the composition of the recycled stream. Higher separation efficiency was achieved, leading to 99.94% purity with 9 theoretical stages, only, for column SP01CA05, with the stream and block details reported in Table 3. The capital costs decrease when operating pressure swing at 10 bar due to the lower number of theoretical stages to achieve the desired acetonitrile purity and recovery. Higher OPEX are expected due to *ca.* double pump consumption and slightly higher duty demand for column SP01CA05. The detailed cost assessment, after heat integration, can allow to determine the most convenient operating pressure.

#### **4 Process optimisation**

Typically, a cross heat integration is used in the case of pressure swing distillation, by thermally coupling the condenser of the high pressure column and the reboiler of the low pressure one [11].

In the pressure-swing separation method the enthalpy content of the 7 bar or 10 bar distillate can be used to regenerate directly the feed stream to the first column: in this way the heat transfer from the hot stream to this column is the higher possible. Fig. 6 provides a visual check of this option. In principle, the recycle stream could also release energy, by pre-heating the feed to the pressurised column. However, also in this case, with the same overall heat balance, any real heat transfer would be inferior.

Notice that for the pressure swing case, whether column 2 operates slightly above or below the distillation boundary, column 3 has always a sufficient margin between its feed point and the 7 bar azeotrope (at least as a first approximation), so at this stage a further increase of pressure seems not needed. Care should be taken, however, since the column 3 behavior as actually calculated becomes

sensitive to tray number, feed tray and, moreover, to the calculated profile of CH<sub>3</sub>CN/Water volatility (Fig. 3), so for example it was hardly possible to obtain acetonitrile with purity >90% at less than 5.5 bar.

## 5 - Extraction with dichloromethane (DCM)

DCM is often used to separate water-containing azeotropes [10,27], thus it has been here applied as heterogeneous entrainer. The experimental data for the Water-CH<sub>3</sub>CN and Water-DCM azeotropes are reported in the literature [28,29] and confirm the ASPEN Plus<sup>®</sup> estimation.

The flowsheet of the proposed purification section is reported in Figure 7.

Also in this case, the mixture has to be conditioned in order to eliminate the volatile components. A first flash drum (SP01SF01) eliminates most CO<sub>2</sub> and NH<sub>3</sub>, while the column SP01SC01 eliminates excess water in the bottom with respect to the azeotrope. A further column completes the elimination of HCN and NH<sub>3</sub> leaving the water/CH<sub>3</sub>CN azeotrope as bottom product.

A liquid-liquid separator (SP01SE01) is used to separate acetonitrile from water with the addition of DCM as entrainer. The top aqueous phase is sent to a decanter, while the bottom organic phase is sent to a third column (SP01SA01) to purify CH<sub>3</sub>CN and recycle DCM. Indeed, according to the thermodynamic equilibria, a ternary mixture including DCM, water and CH<sub>3</sub>CN is distilled, leaving pure CH<sub>3</sub>CN as bottom product. According to this solution, a purity of 99.95% is achieved, with 92.1% recovery.

Equipment specifications are reported in Tables 3 and 4. The reflux ratios of the first columns can vary between 2 and 5 and a very sensitive parameter is the bottoms:feed ratio. By contrast, the third column operates with the lowest reflux ratio because the vaporised CH<sub>3</sub>CN interacts less with the gaseous DCM than with ammonia or HCN vapors. The complete mass-balance report is reported in Table 5.

The solvent used in the extractor is not pure, but it is recycled DCM [30]. The system design has been carried out based on the following considerations. Different runs were done by varying the DCM-

Acetonitrile ratio: the first with DCM equimolar with respect to the amount of acetonitrile to recover, then by increasing DCM with a 50% or 70% molar excess of DCM with respect to acetonitrile. The column specifications were set to obtain *ca.* 0.2 kmol/h of pure acetonitrile (purity >99.9%).

## **6 Comparison between the two purification strategies and economic analysis**

The two proposed purification strategies for acetonitrile lead to higher product recovery in the PS case, with a higher and easier tunable purity for the PS option, by simple addition of a few trays in the stripping section of the high pressure column, depending on market requirements. The heat flow in and out the equipment is higher for the PS case than for the DCM one. This is due to the higher CH<sub>3</sub>CN recirculation imposed for PS. On the other hand, a chemical compound has to be added for the DCM case. The latter is mostly recovered and recycled, imposing a very limited make up of entrainer (*ca.* 1 mol/h).

In particular, lower reflux and boilup ratios are calculated for the first column in the PS cases (block SP01CM02, Table 3) with respect to SP01SC01 of the DCM case (Table 4). In spite of a similar design of the second column for the PS and DCM cases, the last column has lower reflux and boilup ratios for both the PS flowsheets (SP1CA05, Table 3, similar at 7 and 10 bars) with respect to the DCM case (SP01SA01, Table 4).

Very low duty was calculated for the first column of the PS flowsheets, with as low as 10 theoretical stages. The same column for the DCM case was designed with only 7 trays, but it was characterized by higher duty. A smaller third column was designed when operating the PS at 10 bar (9 trays) with respect to the 7 bar option (14 trays), with similar duties. The design of this last section was instead more demanding for the DCM case, which needed an extractor and a 15 trays column, with a slightly higher duty.

Based on all these considerations and on the higher recovery of the PS option operated at 10 bar (>95% recovery vs. 92% of the DCM case), the most favorable case seems the pressure swing at 10 bar.

According to this basic comparison, a more detailed assessment of costs is needed to select and confirm the best option. A comparative analysis between three process layouts has been carried out. Sizing of equipment has been carried out by using heuristic rules conventionally reported in engineering handbooks [31–33]. Full equipment design details are reported in Tables S1-S3 of the Supplementary information, together with the general scheme used to size the columns (Fig. S1). If not else specified, carbon steel has been used as material for construction.

The equipment cost estimation is reported in Table 6. According to the proposed sizing, equipment cost has been calculated, together with the installed, operation and maintenance and overall capital. Valves and splits have been neglected. The calculation has been carried out considering construction from the grass roots, operation for 20 years, with 10 years depreciation (straight line), 8766 productive h/year. The heuristic rules have been based on general concepts outlined in the above mentioned references and on previous expertise of the group. In particular, the plant is fully new so a design from the grass roots is the only option available. Both 20 years operation and 10 years depreciation were selected as a very conservative case. Being the technology new, investors may better accept the risk if relatively rapid return of investment may be envisaged. Thus, every scenario represents a situation where longer operation induces almost pure earning. The productive h/year were selected as a continuous operation without shutdown, because this fully new process is not known for the moment. However, the same calculations relative to 8000 h/year operation increased the acetonitrile hourly production cost by *ca.* 3% in each case, without affecting the comparison between the cases. Taxes are accounted for 40 %/year, interests rate for 20 %/year and a salvage of 20 % of the initial capital costs is considered. The escalation is considered 5 %/year for capital costs, 3 % for labor/maintenance and utilities. The latter percentages were selected as typical items for South/Central European areas.

According to these assumptions, decreasing equipment costs are estimated in the order DCM > PS (7bar) > PS (10 bar), mainly due to less expensive columns design. Accordingly, decreasing capital costs (CAPEX) are estimated in the same order. Operating costs follow essentially the same order

due to the algorithms used, which correlate the estimation of labor and maintenance costs to the equipment costs. However, operating costs also include utilities, which are directly related to the efficiency of the different solutions and are expected to be different for the different options here proposed.

Utilities are detailed in Table 7. The comparison evidences that electricity consumption is slightly higher for the pressure swing options than for the DCM-based one, as expected due to the presence of an additional pump. However, by examining the breakdown of pumps consumption, the main contribution is due to column reflux pumps, so that the additional contribution to electricity consumption of the pump for pressure swing is limited.

Higher steam cost is observed for pressure swing operated at 10 bar with respect to 7 bar, due to the need of higher pressure steam for the higher temperature achieved in the reboiler of the high pressure column. However, both PS options allow to save both steam and cooling water with respect to the DCM solution.

## **CONCLUSIONS**

The separation and purification procedure to maximize acetonitrile recovery with purity > 99.9% has been described for a newly design process based on the ammoxidation of ethanol. The main issue in this separation is the resolution of the water/acetonitrile azeotrope, which has been here achieved by pressure swing distillation at different operating pressure and by using dichloromethane as heterogeneous entrainer. At difference with literature reports, the acetonitrile azeotropic separation has been inserted in the whole separation train, optimizing the overall separation section of a pilot scale plant, producing ca. 75 ton/year of pure acetonitrile.

With respect to the DCM case, pressure swing allowed to achieve higher CH<sub>3</sub>CN recovery (> 95%), with higher purity > 99.9%. In the case of pressure swing, the product purity can be effectively tuned by simply setting the number of trays in the stripping section of the high pressure column, achieving only residual water in the product.

Detailed equipment sizing and cost evaluation allowed to conclude that lower CAPEX and OPEX are associated with the pressure swing solution, especially when operated at 10 bar. The contribution of additional utilities for the pump feeding the high pressure column is negligible. Savings both in columns design and overall utilities are possible by selecting the pressure swing solution operated at 10 bar.

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### Acronyms, abbreviations and symbols

aq.	aqueous	org.	organic
AP	ASPEN Plus	RADFRAC	Rigorous Adsorption-FRActioning
HX	Heat eXchanger	RK	Redlich – Kwong
DCM	DiChloroMethane, CH <sub>2</sub> Cl <sub>2</sub>	T	Temperature
NRTL	Non-Random Two Liquids	UNIFAC	UNIQUAC Functional-group Activity Coefficient
P	Pressure	UNIFAC-LL	UNIFAC-Liquid-Liquid
PS	Pressure Swing	UNIQUAC	UNiversal QUAsi-Chemical

### Flowsheets coding

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

<b>Functional codes</b>		<b>Block type code</b>	
FR	Feed of Reagents	AP	Pump for Pressure rising
SB	Separation of Byproducts	CA	Column with Azeotropes
SP	Separation of Products	CM	Column with a Mixture of more than 2 specie
SV	Separation of Wastes	HB	Boiler
		HC	Cooler or condenser
		HX	Heat eXchanger, generic
		PA	Pipe at Atmospheric pressure
		PP	Pressurized Pipe
		SA	Separation of Azeotropes
		SC	Separation Column
		SF	Separation via Flash

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## TABLES

### AZEOTROPE SEARCH REPORT

Physical Property Model: NRTL-RK Valid Phase: VAP-LIQ

Component Name	Classification (respect to residues)	Temperature (°C)
WATER	Stable node	100.02
ACETONITRILE	Stable node	81.65
HYDROGEN CYANIDE	Unstable node	25.66
AMMONIA	Unstable node	-33.40
Mixture Investigated For Azeotropes At A Pressure Of 101325 Pa		
Number Of Components	Homogeneous Classification	Temperature (°C)
2	Saddle	76.55
Composition	mole/mole	mass/mass
WATER	0.327	0.176
ACETONITRILE	0.673	0.824

**Table 1:** Preliminary evaluation for the behavior of a mixture made of CH<sub>3</sub>CN – H<sub>2</sub>O – HCN – NH<sub>3</sub>.

Material streams										
Stream Name	SB01PA03	SB01PA08	SB01PA10	SB01PP09	SP01PA01	SP01PA02	SP01PA04	SP01PA05	SP01PP06	SP01PP07
Temperature (°C)	97.6	11.8	130.4	142.5	85.0	84.1	67.5	76.2	77.1	158.1
Pressure (bar)	1	1	1	7	1	1	1	1	7	7
Molar Vapor Fraction	0	1	1	1	0.83	0.88	1	0	0	0
Mole Fractions										
WATER	0.9932	0.0021	0.4525	0.4525	0.6231	0.5820	0.2086	0.2999	0.2999	3.41E-05
ACETONITRILE	0.0027	0.0285	0.5474	0.5474	0.1692	0.2603	0.4943	0.7001	0.7001	1.00E+00
HCN	0.0024	0.2110	0.0001	0.0001	0.0462	0.0350	0.0647	3.59E-05	3.59E-05	2.48E-09
AMMONIA	0.0018	0.4311	7.21E-11	7.22E-11	0.0923	0.0701	0.1321	4.79E-11	4.79E-11	2.40E-18
CO <sub>2</sub>	2.41E-07	0.3273	0.00E+00	0.00E+00	0.0692	0.0526	0.1003	5.39E-18	5.39E-18	0.00E+00
Mass Flow (kg/h)	14.75	7.88	12.63	12.63	31.25	43.88	29.13	21.25	21.25	8.62
Mole Flow (kmol/h)	0.815	0.275	0.413	0.413	1.300	1.713	0.898	0.623	0.623	0.210

**Table 2:** Stream report for the pressure-swing separation flowsheet, operated at 7 bar (trace threshold: default, convergence threshold:  $10^{-4}$ , tear threshold:  $10^{-3}$ ). Stream names refer to Fig. 4.

## Blocks balance report

Name	SP01CM02	SP01CA03	SP01CA05 (7 bar)	SP01CA05 (10 bar)	SP01HX01	SP01AP04 (7 bar)	SP01AP04 (10 bar)
<b>Theoretical trays number</b>	10 (7)	15 (5)	14 (5)	9 (3)	-	-	
<b>Pressure (bar)</b>	1	1	7	10	1	6 ( $\Delta$ P)	9 ( $\Delta$ P)
<b>Inlet Stream T (°C)</b>	84.1	67.5	77.2	77.6	85 (feed) 130.4 (recyc)	76.2	76.2
<b>Outlet Stream T (°C)</b>	67.5 (D) 97.6 (B)	11.8 (D) 76.2 (B)	142.5 (D) 158.1 (B)	157.6 (D) 176.1 (B)	84.1	77.1	77.6
<b>Reflux ratio</b>	1.0	5.5	0.7	0.7	-	-	-
<b>Boilup ratio</b>	0.16	1.4	4.6	4.9	-	-	-
<b>Required Heat (kW)</b>	1.52	8.24	7.3	7.4	-	-	-
<b>Released Heat (kW)</b>	-8.57	-14.17	-2.5	-2.4	-	-	-
<b>Heat Duty (kW) / Work</b>	-7.05	-5.93	4.8	5	-	0.012	0.026
<b>Heat recovery assumption</b>	Possibly 14 % of reboiler duty from 3 <sup>rd</sup> col. condenser	Possibly 20 % of reboiler duty from 3 <sup>rd</sup> col. condenser	Whole condenser duty to any cold stream	yes	yes	-	-

**Table 3:** Thermal and operating parameters for the blocks of the pressure swing section operated at 7 or 10 bar (or, as in the case of pumps, electrical work needed at 100% efficiency); the values are negative when the heat is released rather than required. The number in parentheses trays number indicate the feed stage. (\*) CO<sub>2</sub>, (\*\*) NH<sub>3</sub> and HCN.

Blocks balance report

Name	SP01SC01	SP01SC02	SP01SE01	SP01SA01	SP01SF01	SP01HX01	SP01SG01
Trays number	7 (1)	15 (3)	2	15 (10)	-	-	-
Inlet Stream T (°C)	20	56	25 (top-org) 25 (bot-aq)	28	25	75	40 (org) 26 (aq)
Outlet Stream T (°C)	71 (D) 100 (B)	22 (D) 75 (B)	26 (top-aq) 28 (bot-org)	40 (D) 81 (B)	20	25	25
Reflux ratio	2.5	5	-	1.4	-	-	-
Boilup ratio	0.76	1.6	-	5.7	-	-	-
Required Heat (kW)	5.7	5.3	-	10	na	0	0
Released Heat (kW)	-3.1(*)	-5.6	-	-9.6	-0.2	-0.4	-0.2
Heat Duty (kW)	5.7	-0.3	-	0.4	-0.2	-0.4	-0.2
Heat recovery assumption	no	no	no	no	-	no	no
Relevant Split Fractions (bottoms: feed)							
WATER	83 %	>99 %	28.8 % (**)	<0.1 %	>99 %	-	-
CH <sub>3</sub> CN	trace	98 %	99.3 %	71.3 %	95 %	-	-
DCM	-	-	99.8 %	<0.1 %	-	-	-
Gases	traces	<0.01 %	90.1 %	<0.0001 %	44.8 %	-	-

**Table 4:** Synthetic report of specifications, balances and heat duties for the process blocks of the DCM-separation flowsheet (Fig. 7). (\*) Being the first column without condenser, this released heat is computed as the cooling duty of the exchanger block HC01; (\*\*) for the extractor, the CH<sub>3</sub>CN-DCM rich phase is considered as 'bottoms'.

Stream Name	SP01PA 01	SP01PA 02	SB01PA 01	SP01PA 03	SB01PA 02	SP01PA 04	SP01PA 05	SS01PA 01	SP01PA 06	SP01PA 07	SP01PA 08	SB01PA 04	SB01PA 05	SB01PA 07
<b>Components Mole Frac (mol/mol)</b>														
WATER	0.623	0.709	0.02	0.293	1	0.293	0.399	0.007	0.399	0.063	0	0.976	0.089	0.024
CH <sub>3</sub> CN	0.169	0.184	0.064	0.448	0	0.448	0.601	0.034	0.601	0.421	1	0.019	0.172	0.184
HCN	0.046	0.047	0.039	0.115	0	0.115	0	0.425	0	0	0	0	0	0
AMMONIA	0.092	0.052	0.374	0.126	0	0.126	0	0.468	0	0	0	0	0	0
CO <sub>2</sub>	0.069	0.007	0.503	0.018	0	0.018	0	0.066	0	0	0	0	0	0
DCM	0	0	0	0	0	0	0	0	0	0.517	0	0.005	0.738	0.793
<b>Stream summary</b>														
Mole Flow (kmol/h)	1.3	1.137	0.163	0.468	0.67	0.468	0.342	0.126	0.342	0.676	0.203	0.107	0.473	0.441
Mass Flow (kg/h)	31.25	25.96	5.29	13.9	12.06	13.9	10.88	3.02	10.88	42.10	8.33	2.01	33.78	33.23
T (°C)	25	20	20	70.9	99.6	55.7	75.1	21.5	25	28.1	81.2	25.7	39.5	25
P (bar)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Vapor Frac	0.14	0.0	1.0	1.0	0.0	0.33	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0

**Table 5:** Stream report for the DCM-based case (tear tolerance:  $10^{-3}$ , others by default). Makeup stream FR01PA01 has zero flow and has been used only to help convergence.

Item	DCM	PS 7 bar	PS 10 bar
<b>Total Capital Cost [USD]</b>	6362460	5834690	5727380
<b>Total Operating Cost (USD/Year)</b>	1319810	1317460	1314790
<b>Total Utilities Cost (USD/Year)</b>	41923	41223	41709
<b>Desired Rate of Return (%/Year)</b>	20	20	20
<b>Equipment Cost (USD)</b>	278600	269000	250900
<b>Total Installed Cost (USD)</b>	1305300	1305300	1267600
<b>Productivity CH<sub>3</sub>CN (kg/h)</b>	8.32	8.62	8.616
<b>Purity CH<sub>3</sub>CN (%)</b>	> 99.95	>99.99	>99.99
<b>Impact on production cost (USD/kg)</b>	26.79	25.13	24.96

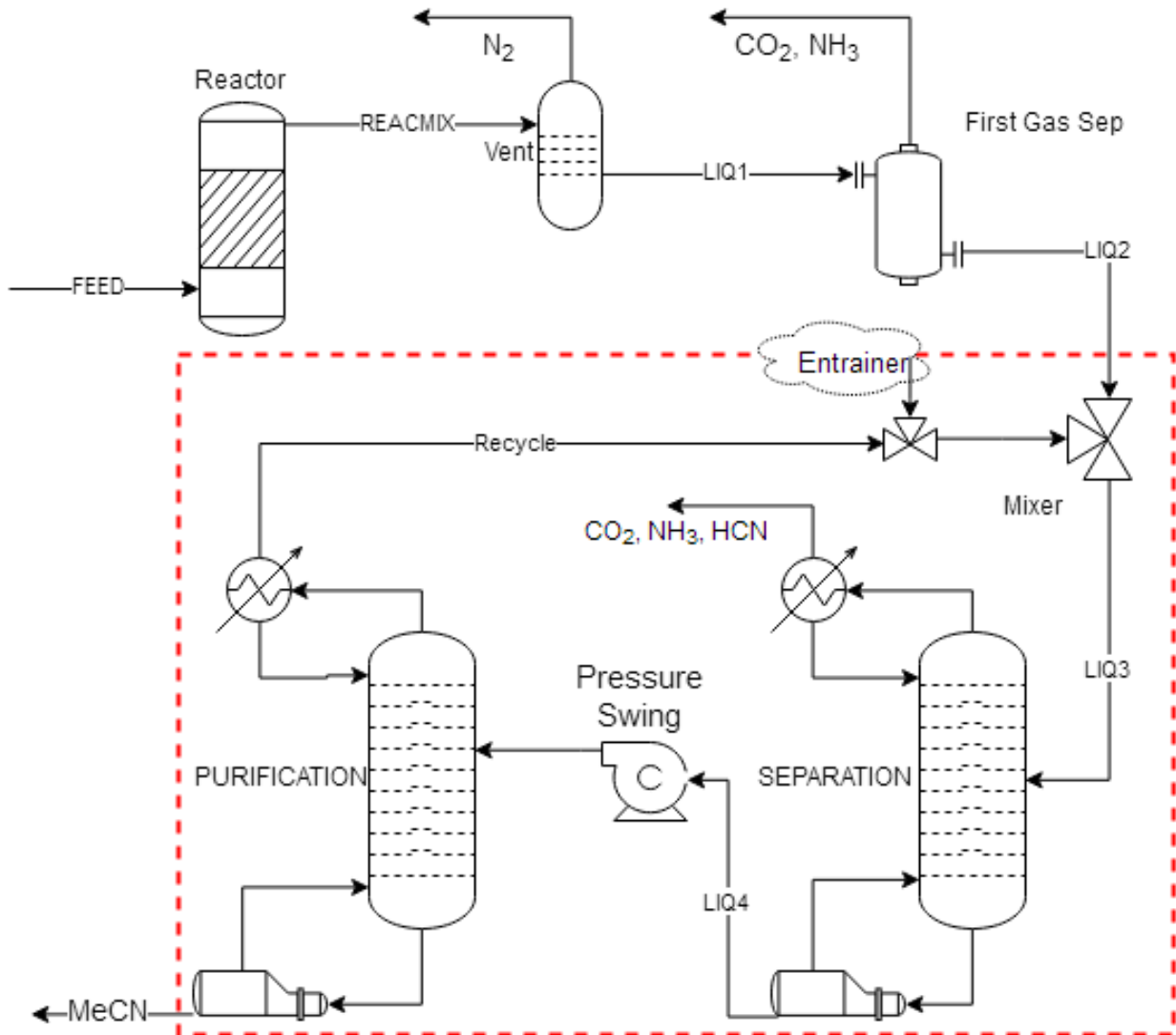
**Table 6:** Comparison of CAPEX and OPEX for the three solutions proposed. Unitary costs are provided by the 2017 updated version of ASPEN Economic Evaluator tool (V. 9).

	Utility	Fluid	Rate	Rate Units	USD/unit	USD/h
<b>DCM</b>	Electricity		52.507	kW	0.0775 /kWh	4.069
	Cooling Water	Water	1.01 x 10 <sup>6</sup>	m <sup>3</sup> /h	0.32 /m <sup>3</sup>	0.032
	Refrigerant - Freon 12	Refrigerant	121.8	kg/h	0.00019 /kg	0.023
	Steam @100PSI	Steam	36.6	kg/h	0.018 /kg	0.658
<b>PS 7 bar</b>	Electricity		52.693	KW	0.0775 /kWh	4.084
	Cooling Water	Water	0.859 x 10 <sup>6</sup>	m <sup>3</sup> /h	0.32 /m <sup>3</sup>	0.027
	Refrigerant - Freon 12	Refrigerant	309.3	kg/h	0.00019 /kg	0.058
	Steam @100PSI	Steam	29.7	kg/h	0.018 /kg	0.534
<b>PS 10 bar</b>	Electricity		52.693	KW	0.0775 /kWh	4.084
	Cooling Water	Water	0.851 x 10 <sup>6</sup>	m <sup>3</sup> /h	0.32 /m <sup>3</sup>	0.027
	Refrigerant - Freon 12	Refrigerant	309.6	kg/h	0.00019 /kg	0.058
	Steam @100PSI	Steam	16.9	kg/h	0.018 /kg	0.303
	Steam @165PSI	Steam	13.3	kg/h	0.021 /kg	0.286

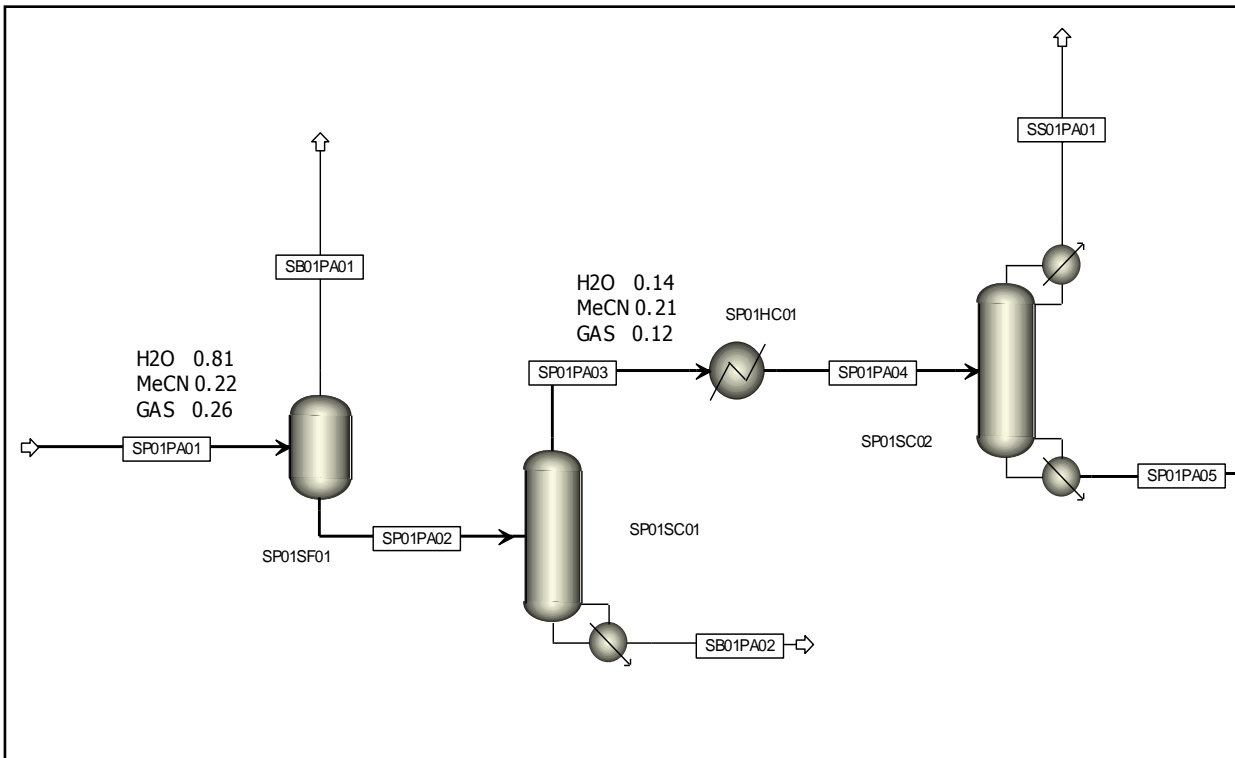
**Table 7:** Utilities consumption detail for the different separation options.



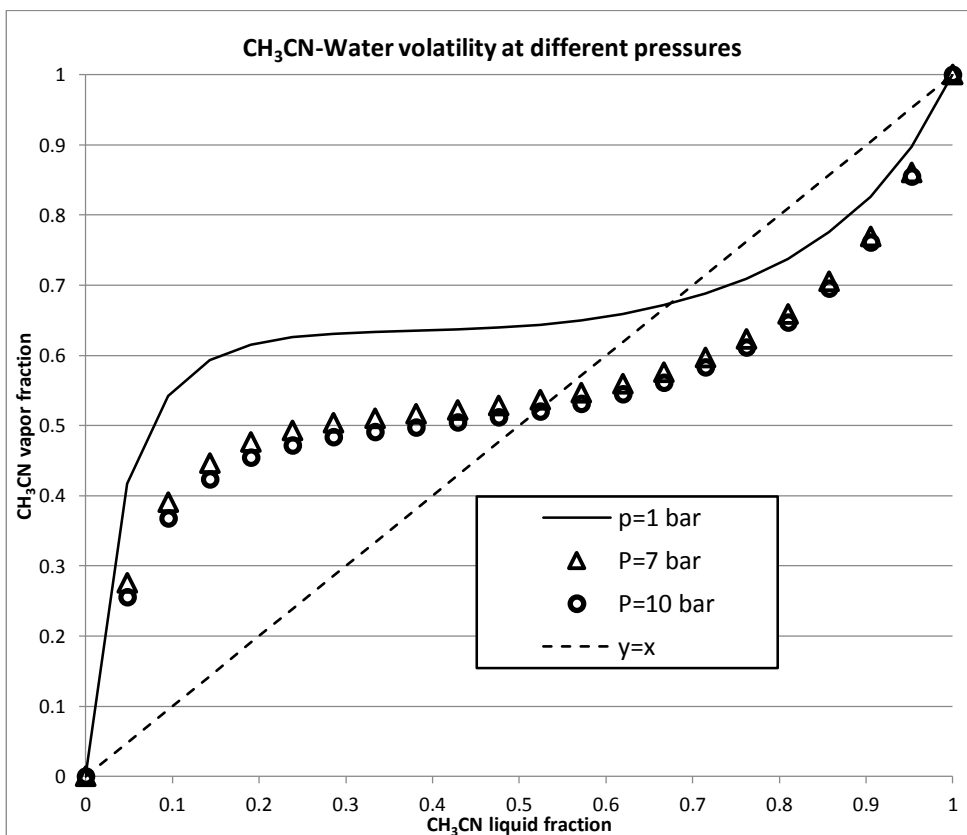
**FIGURES**



**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.

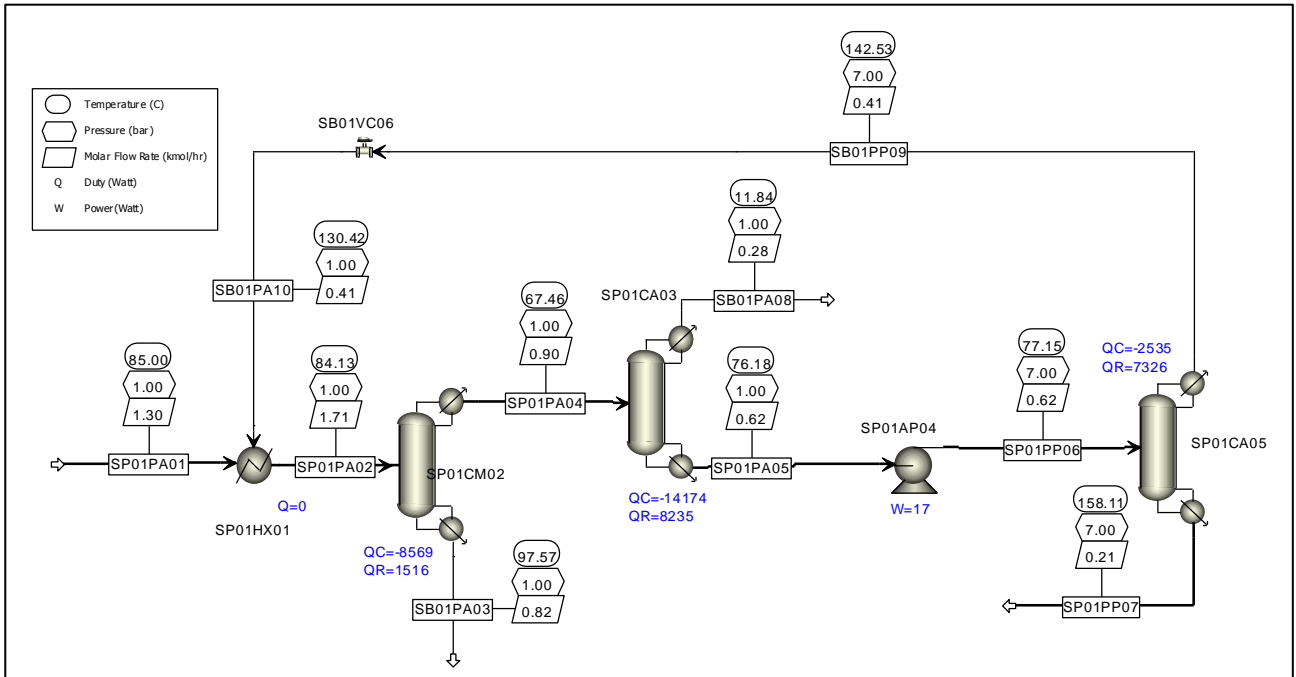


**Fig. 2:** Process flow diagram of the preliminary gas separation section.

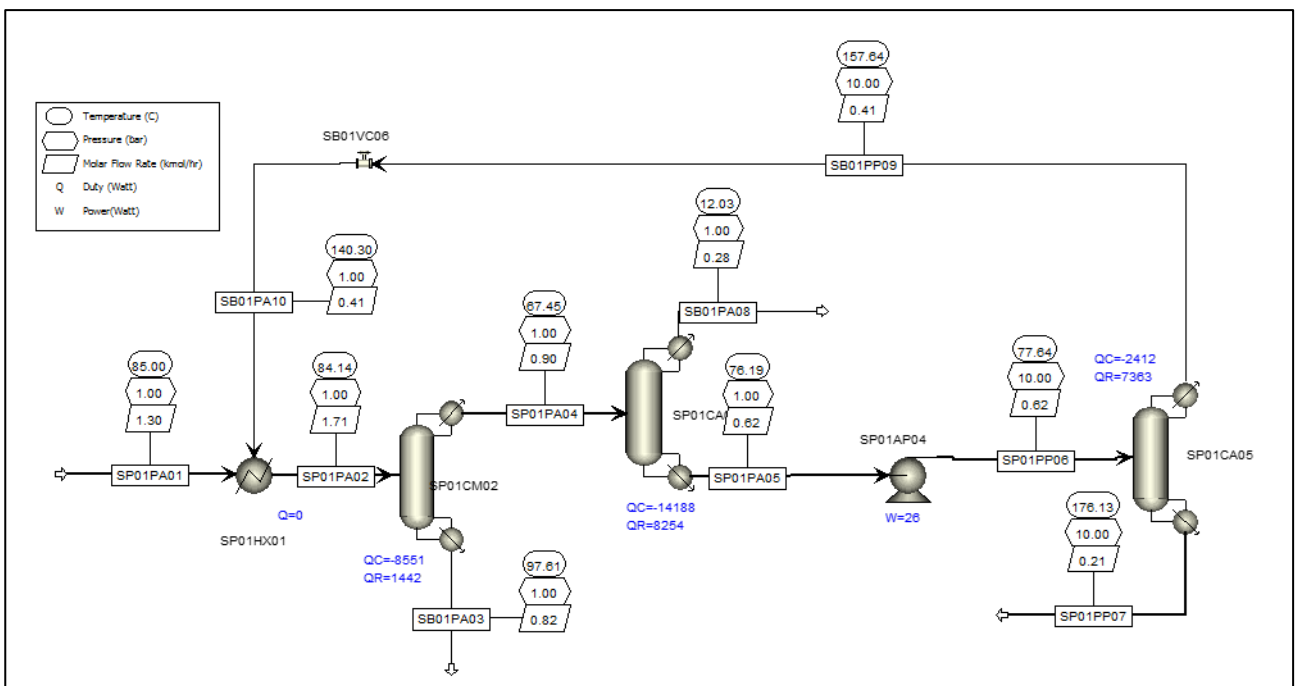


**Figure 3:** Vapor-liquid equilibria for the acetonitrile-water mixture at 1 bar (line), 5 and 7 bar (circles, squares) – the azeotropic fraction of CH<sub>3</sub>CN passes from 0.67 to 0.55 and less, and the CH<sub>3</sub>CN:water ratio from 2 to 1.2. Method: NRTL-RK.

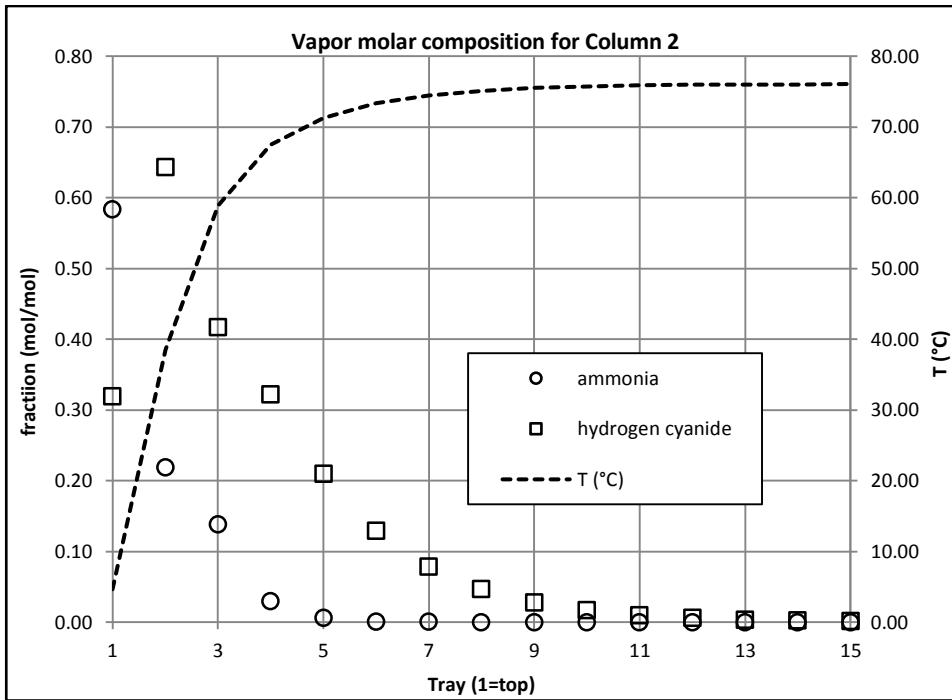
a)



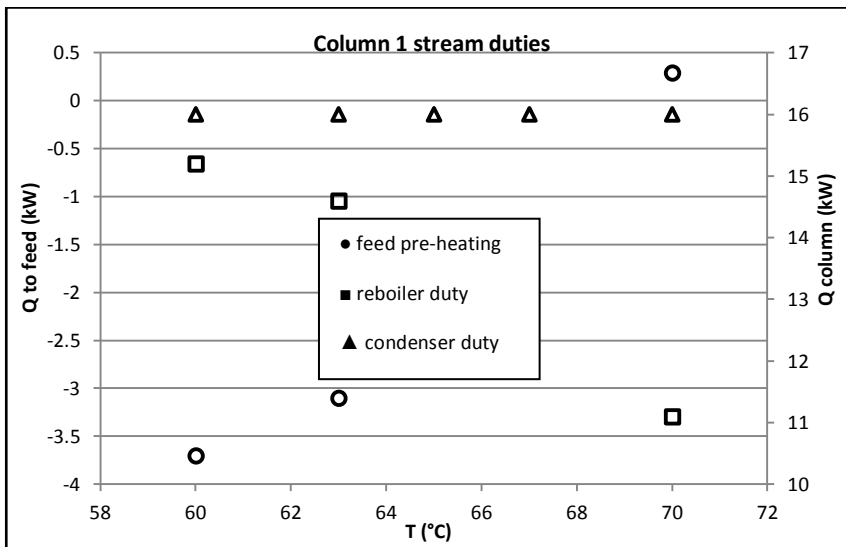
b)



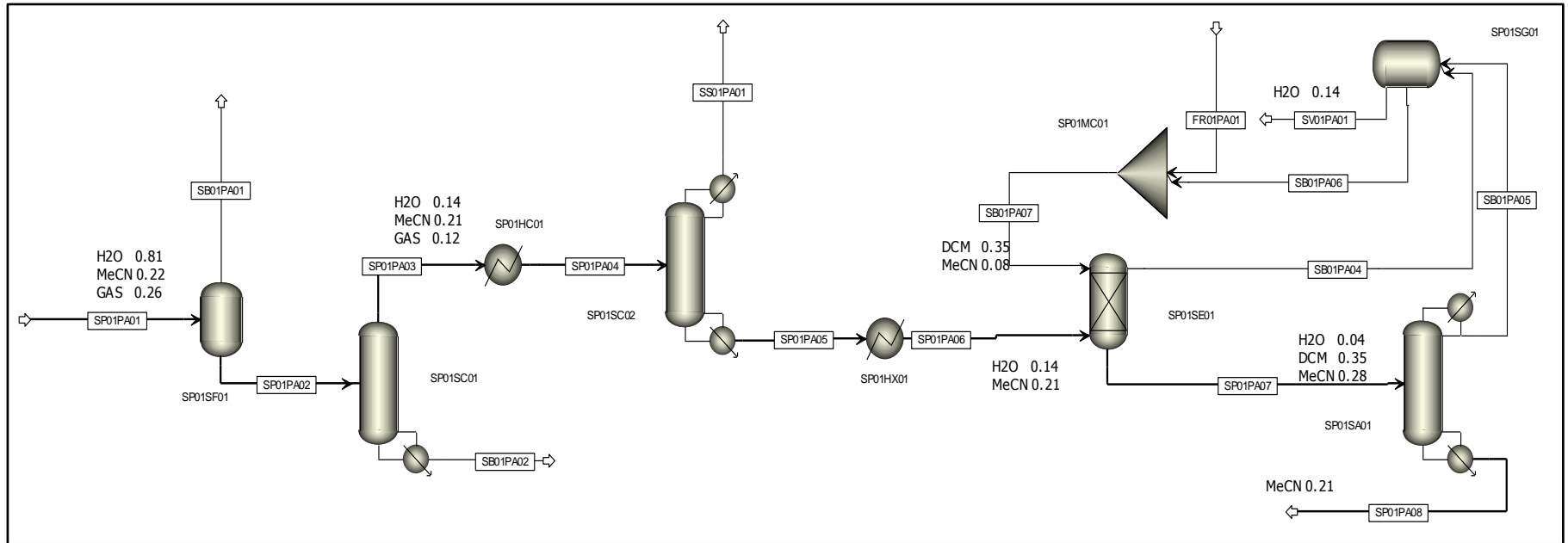
**Figure 4:** Process flow diagram for the separation of acetonitrile from water solvent and the volatile byproducts. The first two columns accomplish the discharge of excess water to produce a binary atmospheric azeotrope, but two blocks are needed to effectively purge the gases/volatile components having very different boiling points. The third column operates at higher pressure to recover pure acetonitrile as bottom product. Quoted cases for pressure swing at 7 bar (a) and 10 bar (b).  $Q_c$  = condenser duty (W),  $Q_R$  = reboiler duty (W),  $W$  = pump duty (W).



**Figure 5:** Rectification of HCN and NH<sub>3</sub> in the second column, following their different boiling points under the achieved temperature profile. The decrease of vaporised HCN fraction in the condenser is due to the abrupt decrease of the mixture boiling point determined by NH<sub>3</sub>: this makes the acid be more concentrated in the liquid.



**Figure 6:** Heat released from the recycled stream of the pressure swing scheme to the first column (left axis, circles: calculated as the duty required by pre-heater HX01 to grant the column feed temperature reported on the x-axis. Negative values mean that this heat is released rather than absorbed), resulting in a decrease of the required boiler duty (right axis, squares). The heat released from the condenser remains unchanged (right axis, triangles).



**Fig. 7:** Process flow diagram for the DCM-based separation option.