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STUDY OF THE ECO-EFFICIENCY OF ACRYLONITRILE PRODUCTION PROCESSES

Danyelle Soares Bastião
danyellesoares@id.uff.br
Fluminense Federal University –
UFF, Niterói, Rio de Janeiro, Brazil

Igor Nardi Caxiano
igornardi@id.uff.br
Fluminense Federal University –
UFF, Niterói, Rio de Janeiro, Brazil

Diego Martinez Prata
pratadiego@gmail.com
Fluminense Federal University –
UFF, Niterói, Rio de Janeiro, Brazil

ABSTRACT

Highlights

Simulation of acrylonitrile production processes.
Simulation of utilities for more realistic results.
Analysis of the gain in eco-efficiency considering five eco-indicators.
The process with partial condensation step proved to be the most sustainable option.

Objective

To evaluate the gain in eco-efficiency by introducing a partial condensation step in the conventional acrylonitrile production process.

Methodology

The conventional and modified acrylonitrile production process, as well as the associated utilities plant, was simulated computationally using the UniSim Design Suite R390.1 software. Based on the results, five eco-indicators were developed (water, fuel and energy consumption, CO_2 emission and liquid effluent generation), which were simultaneously evaluated through the Eco-efficiency Comparison Index of the considered processes.

Results

The modification of the conventional process of acrylonitrile production, from the introduction of a partial condensation stage with the main purpose of reducing the consumption of process water, resulted in a 76% increase in eco-efficiency, considering the eco-indicators used in the study. The reduction in water consumption was evidenced by the calculation of the corresponding eco-indicator, which was 47% lower for the modified process.

Limitations of research

Eco-efficiency was evaluated, disregarding social and safety factors. In addition, the few data provided on the process and scaling of recovery section equipment, by the reference authors, limited the comparison of results.

Practical implications

The paper presents a practical example of the use of eco-indicators in the analysis of the increase of eco-efficiency by the modification of industrial processes, mainly for the reduction of water consumption. Although the modification evaluated in this work has been implemented in an acrylonitrile production plant, the methodology can be applied in a similar way to other industrial processes.

Originality

The present work shows a quantitative evaluation of the gain in eco-efficiency (notably with regard to water consumption) by the introduction of a partial condensation stage in the conventional acrylonitrile production process.

Keywords: Acrylonitrile; Eco-indicators; Eco-efficiency; Computer Simulation.

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1. INTRODUCTION

Acrylonitrile is an organic compound mainly used in the manufacture of acrylic fibers for the textile industry and in the production of polymers such as ABS plastic (Acrylonitrile Butadiene Styrene). This compound is still used as an intermediate in the manufacture of nitrile rubbers, resins and various thermoplastics (Licht *et al*., 2016; Guerrero-Pérez *et* Bañares, 2015).

In 2015 alone, world production of acrylonitrile totaled more than 6 million tons (Qin, 2015). Much of this production comes from industrial routes using the Sohio process, based on the reaction of oxygen and ammonia (or ammoxidation) with propylene, in the presence of a suitable catalyst. This process has been used on a large scale since 1960 – when it replaced the production process from acetylene and hydrogen cyanide (HCN), used by IG Farben – due to its better economic and environmental performance and the greater availability of propylene (Hansora, 2013; Grasselli, 2002). Although there are proposals in the literature for alternative routes of acrylonitrile production, they are not significantly competitive. Production from biomass, for example, has lower conversions and the origin of the raw material limits the use of the final product, as well as lower energy efficiency (Grasselli *et* Trifirò, 2016). Propane ammoxidation is the most commonly used alternative route. However, this should continue because of the low efficiency of the catalytic systems used, which reduce the environmental performance of the process (Cespi *et al*., 2014).

A characteristic of the production of acrylonitrile by the Sohio process is the high consumption of process water and the consequent high generation of liquid wastes, which must be treated before disposal to avoid contamination of water and soil. Alternatives for this treatment present in the literature include the combined use of aerobic and anaerobic treatment processes and of bioreactor with activated sludge immobilized by water-based polyurethane (Dong *et al*., 2017; Na *et al*., 2016). The process also generates gaseous streams that must be treated for the removal of toxic nitriles and acrolein (Dimian *et* Bildea, 2008).

These environmental impact factors, coupled with the high water and energy consumption for the production of acrylonitrile, make it interesting from a sustainability point of view to develop new technologies or modifications in existing plants to reduce the environmental impacts associated with the process, notably by reducing the use of process water, effluent generation and gaseous emissions. An alternative for the reduction of tailings generation as unwanted products is the modification of the design specifications of the reaction section, as emphasized by Hopper *et al*. (1993) and Shadiya *et al*. (2012). For the reduction in water consumption, Dimian et Bildea (2008) suggest the implementation of a partial condensation stage followed by a three-phase decanter, similar to Wu's (1980) proposal.

Sustainable development and the search for strategies to make production processes more eco-efficient is an issue frequently addressed in the chemical and petrochemical industries. In this context, several methods were proposed to quantify sustainability in the industrial sector (Azapagic *et* Perdan, 2000). One of these proposed concepts was the eco-indicators, commonly defined by the ratio between an environmental variable and an economic variable (UNCTAD, 2004). The methodology of the Eco-efficiency Comparison Index (ECI), in turn, was proposed by Pereira *et al*. (2014; 2018) with the objective of simultaneously using a set of eco-indicators to compare and quantify the sustainability gains of actions proposed and implemented in a petrochemical industrial process at different time periods (before, during and after the modifications). This same methodology can also be applied to compare different industrial technologies and, in this way, determine quantitatively which one presents greater eco-efficiency, as already done in the literature (Mangili *et al*., 2018; Junqueira *et al*., 2018). Given that eco-efficiency is useful to enterprises because it allows associating environmental and economic performance (Müller *et al.*, 2015), this methodology can help in the decision-making task, defining modifications in the existing production routes (energy integration, catalyst substitution, etc.) or in the process, still in the conceptual design phase, which presents the best eco-efficiency.

Considering the commercial importance of acrylonitrile and the characteristics of the environmental impacts resulting from its production process, the present work aimed to evaluate the relative Eco-efficiency of production routes proposed by Dimian *et* Bildea (2008), namely: conventional process; and process modified by the introduction of a partial condensation stage, aiming at the reduction of water consumption by the process. The eco-indicators of water, fuel and energy consumption, CO_2 emissions and generation of liquid effluents were calculated for the processes studied, using the methodology of the ECI to determine quantitatively whether the suggested modification is in fact able to reduce considerably the environmental impacts of the production of acrylonitrile.

2. ACRYLONITRILE PRODUCTION PROCESS

In this work the process of acrylonitrile production from propylene was studied, as presented by Dimian *et* Bildea (2008). The authors based on the Sohio process, as well as on technologies employed industrially in compound synthesis and the purification processes involved, to develop a plant with a capacity of 120,000 t/year of acrylonitrile that would be used in the manufacture of polymers. Figure 1 shows the process flow diagram.

The process has three feed streams at 623.15 K and 222.9 kPa: propylene (C_3H_6) at 340 kmol/h; ammonia (NH_3) at 408 kmol/h; and air containing 646 kmol/h of oxygen and 2584 kmol/h of nitrogen. The acrylonitrile (AN) is produced in a fluidized bed reactor from the ammoxidation reaction of the propylene in the gas phase, according to Equation 1. Due to the exothermic character of the reaction, the reactor is cooled with water by means of serpentines, forming vapor of high pressure.

$$C_3H_6 + NH_3 + 1{,}5\ O_2 \rightarrow C_3H_3N + 3\ H_2O \quad (1)$$

The catalysts most used in the acrylonitrile production process are based on metallic mixtures of bismuth and molybdenum oxides, supported or not, which allow the conversion of about 80%. Other commercially available catalysts are produced from antimony and strontium oxides (Brazdil, 2017). The mixture of oxygen to the other reagents is carried out in suitable configurations directly in the reactor due to its explosive character (Jordan, 1989) and to the characteristics of the reaction mechanism, in which ammonia chemisorption is a fundamental factor. The absence of NH_3 in the active sites of the catalyst favors the occurrence of unwanted reactions of propylene with oxygen, reducing the conversion of propylene to the desired product and making it difficult to recover (Pudar *et* Goddard, 2015; Dimian *et* Bildea, 2008).

Table 1 shows the main reactions that occur in the reactor and their respective conversions. The first reaction corresponds to the main acrylonitrile formation reaction (C_3H_3N), while the others are unwanted parallel reactions of acetonitrile formation (C_2H_3N or ACN), hydrogen cyanide (HCN), CO_2, acrolein (C_3H_4O or ACR) and succinonitrile ($C_4H_4N_2$ or SCN), respectively.

Table 1. Reactions in propylene ammoxidation reactor for the production of acrylonitrile

Reaction	Conversion
$C_3H_6 + NH_3 + 1{,}5\ O_2 \rightarrow C_3H_3N + 3\ H_2O$	0.801
$2\ C_3H_6 + 3\ NH_3 + 3\ O_2 \rightarrow 3\ C_2H_3N + 6\ H_2O$	0.021
$C_3H_6 + 3\ NH_3 + 3\ O_2 \rightarrow 3\ HCN + 6\ H_2O$	0.027
$C_3H_6 + 4{,}5\ O_2 \rightarrow 3\ CO_2 + 3\ H_2O$	0.107
$C_3H_6 + O_2 \rightarrow C_3H_4O + H_2O$	0.027
$C_3H_3N + HCN \rightarrow C_4H_4N_2$	0.005

Source: Dimian *et* Bildea (2008)

The reactor effluent is cooled with water in the HX1 cooler and subjected to an acid quench in which NH_3 is neutralized with 40% H_2SO_4 solution. The tail stream of this process may contain polymers and other condensable and soluble materials (Godbole, 2000) and should be routed to an appropriate treatment system where it is possible to recover the ammonium sulphate formed as a by-product marketed for the manufacture of fertilizers. The resulting vapor phase is cooled with water in the HX2 cooler and then sent to the acrylonitrile absorber tower operating at 162.1 kPa and using the process water at 278.15 K as the solvent (stream 17 from the bottom of the desorbing column). The light organic compounds, nitrogen, carbon oxides and unreacted propyl-

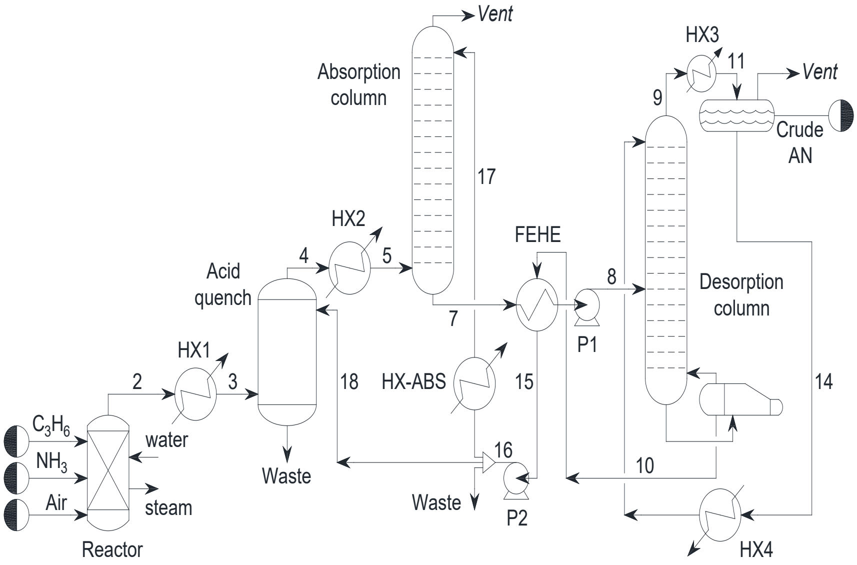

Figure 1. Flow diagram of the acrylonitrile production process

Source: Made from Dimian *et* Bildea (2008)

*AN - acrylonitrile

ene are removed in a gas stream (vent) and sent for treatment. Load losses of 9.7 and 20.7 kPa were assumed in the heat exchangers HX1 and HX2, respectively.

The liquid stream from the absorber is cooled in the FEHE exchanger (which uses only process streams for which a pressure drop of 34.5 kPa has been established), subsequently pressurized in the pump P1 at 152 kPa and introduced into the desorption column. The upper column vessel is a decanter with aqueous phase recycling, and the acrylonitrile recovered in the organic phase is referred to further purification processes, which were not addressed in this work. The bottom product of the nonabsorbent, consisting mainly of water, cools the effluent from the absorption column, and is subsequently pressurized in the P2 pump to 206.7 kPa. Then one part is discarded and another part is reused in the acid quench and in the absorption column, in which case it has previously been cooled with water in the HX-ABS cooler, in which the loss of charge is 34.5 kPa.

A modification of the acrylonitrile production process, according to Dimian *et* Bildea (2008), was proposed by the authors themselves based on a technology patented by Wu (1980). In this configuration, the reactor effluent is partially condensed at 283.15 K after the quench, and then sent to the three-phase decanter (inserted in the process), in which approximately 50% of the acrylonitrile is recovered in an organic phase which is directed to the steps of purification together with the crude acrylonitrile obtained at the end of the process. The vapor phase is pressurized in the compressor K1 at 450 kPa, cooled in the AC air cooler to 293.15 K and subsequently sent to the absorption column which, in the modified process, operates at 450 kPa. The aqueous phase, in turn, is pressurized in the P1 pump to 202.6 kPa and mixed with the bottom outlet of the absorber for the recovery of acrylonitrile.

Figure 2 shows the flowchart of the acrylonitrile production process with the described modification, with changes (in red) being highlighted in relation to the conventional process. In this work, the operating conditions of the modified process quench remained the same as those used in the conventional process. It should be noted that the configuration of the pumps has been modified to meet the new operating conditions.

According to Wu (1980), the technology is capable of increasing the recovery efficiency of acrylonitrile, in addition to reducing the initial capital investment (even with the acquisition of a compressor, because the dimensions of the columns and heat exchangers can be reduced) and the operational costs of the process, mainly related to the burning of fuel in the boiler of the utilities. The modification of the process was proposed by Dimian *et* Bildea (2008) with the main objective of reducing the total water consumption of the plant. The possibility of reducing environmental impacts through this technology will be evaluated quantitatively with the calculation of eco-indicators and the methodology of ECI.

3. UTILITIES PLANT

Due to the thermal exchange processes present in the acrylonitrile production plant, an auxiliary utility plant is necessary for the supply of cooling water and heating steam to the process. In order to obtain more realistic results for water and energy consumption in the eco-efficiency analysis, a utility plant for the acrylonitrile production

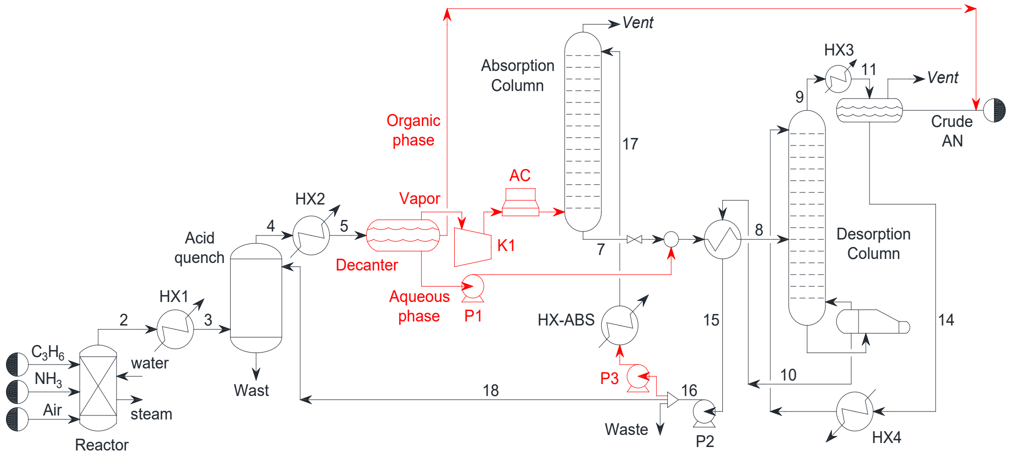

Figure 2. Production process of acrylonitrile with partial condensation

Source: Made from Dimian *et* Bildea (2008) process was developed based on the cooling water and heating vapor systems presented by Turton *et al.* (2012) and Boyd (2011), respectively. Its flowchart is shown in Figure 3.

It was considered that the cooling water is inserted in the processes at 303.15 K and leaves at 318.15 K (Turton *et al.*, 2012), being reused by means of an open recirculation refrigeration system. For the heating processes, low pressure steam (LPS) is formed at 408.15 K and 308.2 kPa in a boiler from water at 303.15 K and atmospheric pressure, according to the heuristics presented by Seider *et al.* (2009). According to the authors, it was considered that cooling the reactor with water generates high pressure steam (HPS) at 527.59 K and 4228 kPa.

Although the utilities plant used to recycle cooling water and condensate from the heating processes, losses of the treatment of the water supplied to the boiler and by drag and evaporation in the cooling tower, in addition to the purges present in the tower and the boiler, make it necessary to introduce a replacement or makeup stream, responsible for the water consumption to supply the demand of the thermal exchange processes present in the production of acrylonitrile. The energy consumption of utility equipment is also accounted for in the energy consumption eco-indicator, as well as the water loss streams in the liquid phase are used to calculate the effluent generation eco-indicator. It was considered that the steam generated in the cooling of the reactor is exported, for economic purposes, and should be reduced of the total water consumption of the plant.

Table 2 shows the heuristics related to water losses used in the utility plant and their respective references.

Table 2. Expressions for calculating eco-indicators

Process	Loss	Reference
Drag (cooling Tower)	0.2%	Walas (1990)
Evaporation (cooling tower)	2.68%	Walas (1990)
Loss of treatment (boiler water)	1%	Turton et al. (2012)
Non-condensed losses	20%	Boyd (2011)
Purge in the tower	3%	Walas (1990)
Purge in the boiler	1%	Seneviratne (2007)

Source: Authors

4. ECO-INDICATORS AND ECO-EFFICIENCY COMPARISON INDEX

As defined by BASF (2018), the eco-efficiency analysis aims to harmonize the economy and ecology, which involves conducting a comprehensive study of alternative solutions to include a total cost determination and the calculation of the ecological impact. This analysis allows the competitive delivery of goods and services at the same time as the environmental impacts are progressively reduced (Verfaillie *et* Bidwell, 2000). Thus, Eco-efficiency is a very useful concept for industrial enterprises to help make decisions related to the choice of projects and implementation of process modifications, since it allows the joint evaluation of environmental impacts and economic performance (Müller *et al.*, 2015).

In this context, eco-indicators are tools that allow quantification of the eco-efficiency of an industrial route and, in this way, verify whether new processes or technologies can add value to the enterprise, increasing its performance. According to the United Nations Conference on Trade and

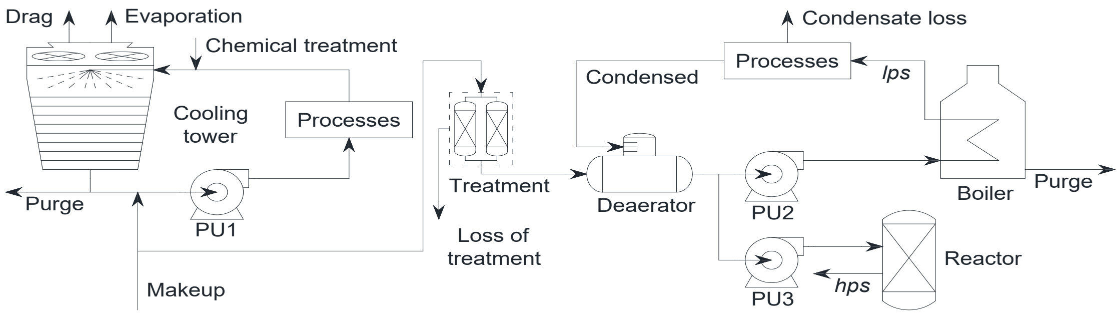

Figure 3. Utility plant for the acrylonitrile production process

Source: Elaborated from Turton *et al.* (2012) and Boyd (2011)

Development (UNCTAD, 2004), an eco-indicator is expressed by the ratio of an environmental variable (such as water consumption, CO_2 emissions or effluent generation) and an economic variable or net revenue), according to Equation 2.

$$\text{Eco-Indicator} = \frac{\text{Environmental variable}}{\text{Economic variable}} \qquad (2)$$

In the form presented by Equation 2, the analysis considers the lowest values of eco-indicators as the best results obtained, usually employing the rate of production as the economic variable. The definition of eco-indicator as the inverse ratio (economic variable by environmental variable) is also used in the literature, according to the definition presented by Verfaillie *et* Bidwell (2000), where the objective of the analysis becomes the highest values of the indicators, with net revenue as an economic variable.

However, the analysis of a single eco-indicator is generally not sufficient for assessing eco-efficiency, given the variety of environmental impacts associated with industrial plants. A proposed solution to quantitatively compare the economic and environmental performance of processes is the methodology of the Eco-efficiency Comparison Index or ECI, proposed by Pereira *et al.* (2014; 2018). The methodology initially consists of the simultaneous evaluation of a set of Eco-Indicators for the processes under study, whose values are normalized by division by the highest value of their respective category. The normalized values of the eco-indicators are used for the elaboration of radar charts for each process, as shown in Figure 4 for a hypothetical case.

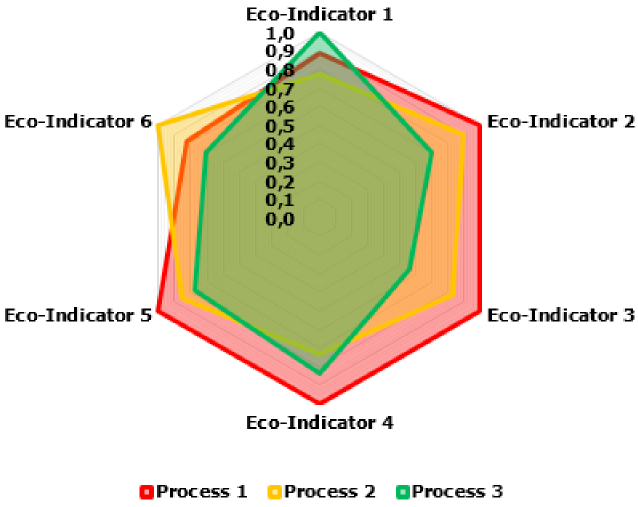

Figure 4. Radar charts for comparing the eco-efficiency of hypothetical processes

Source: Authors

The eco-efficiency of the processes is compared by calculating the area of each radar chart, using the Law of Sines according to Equation 3 (Pereira *et al.*, 2018).

$$S = \frac{1}{2} \cdot \text{sen}\left(\frac{2 \cdot \pi}{n}\right) \cdot \left(EI_1 \cdot EI_n + \sum_{i=1}^{n} EI_i \cdot EI_{i+1}\right) \qquad (3)$$

In which,

S: chart area

n: number of evaluated eco-indicators

EI: standard values of eco-indicators

By the methodology, the process whose radar graph has the smallest area is the most eco-efficient among the studied processes, since the definition of eco-indicators according to Equation (2) is used. The ECI is calculated by means of Equation 4 (Pereira *et al.*, 2018), and its value presents the percentage gain in eco-efficiency in relation to the less eco-efficient process.

$$ICE = \left(1 - \frac{S}{S^*}\right) \cdot 100 \qquad (4)$$

In which,

ECI: Eco-efficiency Comparative index

S: chart area

S*: graph area of the largest area among the processes

The methodology initially consists of the simultaneous evaluation of a set of eco-indicators for the processes under study, whose values are normalized by division by the highest value of their respective category. The normalized values of the eco-indicators are used for the elaboration of radar charts for each process, as shown in Figure 4 for a hypothetical case.

In a similar way, the ECI methodology was used in the work of Junqueira *et al.* (2018) to compare six cumene production processes (using conventional technologies, transalkylation, energy integration, split column, reactive column and double effect distillation) in relation to seven Eco-Indicators (consumption of raw material, fuel, water and energy, CO_2 emissions, specific cost of production and generation of effluents). The authors concluded that the processes with intensification show a gain of up to 79.2% in eco-efficiency over the conventional process.

In the present work, the ECI methodology was used to evaluate the water savings and the possible reductions in environmental impacts by modifying the acrylonitrile production process with the partial condensation stage, and the eco-indicators of water consumption, fuel and energy, CO_2 emissions and generation of liquid effluents to represent the eco-efficiency of the process.

5. METHODOLOGY

Computational simulations were performed in Honeywell's UniSim Design Suite R390.1 software, in the steady state. The acrylonitrile production process was specified based on the data of process streams, operating conditions and dimensions of the equipment as described in the work of Dimian *et* Bildea (2008), using the UNIQUAC--RK thermodynamic model. For simplicity, the sulfuric acid stream required by acid quench was disregarded in the simulation. The utility plan, in turn, was specified with the heuristics presented in the previous sections, using the thermodynamic model UNIQUAC.

The results obtained were used to calculate the Eco-Indicators of water, fuel and energy consumption, CO_2 emission and generation of liquid effluents by means of the expressions presented in Table 3.

The economic variable chosen was the recovery rate of acrylonitrile, which corresponds to the mass flow rate of the substance in the raw stream sent to the purification processes. The volumetric flow rates considered in the eco-indicators of water consumption and effluent generation were obtained with the simulations of the main process and the utility plant.

The consumption of energy by combustion comes from the boiler of the utility plant, where it was considered, for a more conservative scenario, the burning of natural gas at an efficiency of 80% (Seider *et al.*, 2009). The amount of natural gas used by the equipment was determined considering a minimum calorific value of 48 GJ/kg for the fuel used (IPCC, 2006). For the consumption of electrical energy, it was considered that the pumps and compressors operate with 75% efficiency (Walas, 1990).

The emissions of CO_2 by combustion were determined by means of the conversion factor for natural gas of 0.0561 (IPCC, 2006); for the indirect emissions by consumption of electric energy, in turn, the conversion factor used was of 0.0258 , corresponding to the average emission factor for the year 2017 in Brazil (MCTIC, 2018).

The values of the eco-indicators for the original process and the modified with the partial condensation step are finally used to quantitatively compare the two processes using the ECI methodology.

6. RESULTS

Table 4 presents the results obtained by computational simulation for the main process streams of the acrylonitrile production plant without the partial condensation stage (conventional process). The results are compared with the data presented by Dimian *et* Bildea (2008) by means of respective relative deviations.

It can be seen from the data in Table 4 that the simulation in the UniSim was satisfactory, since results similar to those reported by the reference authors were obtained, with the largest deviations observed in components with very low molar fluxes. It is important to note that some of the small deviations are related to the fact that the work of Dimian *et* Bildea (2008) disregarded the formation reaction of succinonitrile from acrylonitrile and HCN (according to the last reaction shown in Table 1). In addition, the authors used Aspen Plus software in computer simulation, while the present work used UniSim, whose parameters of thermodynamic models and numerical solution strategies, including tolerances for convergence, may be different.

Table 3. Expressions for calculating eco-indicators

Eco-indicator	Expression	Unit
Water consumption	$EI_{H_2O} = \frac{\textit{Makeup} - \text{Vapor exportado}}{\text{Taxa de recuperação de AN}}$	$m^3{}_{H_2O}/t_{AN}$
Fuel consumption	$EI_C = \frac{\text{Gás natural consumido}}{\text{Taxa de recuperação de AN}}$	kg_{GN}/t_{AN}
Energy consumption	$EI_E = \frac{\text{Energia (elétrica + combustão)}}{\text{Taxa de recuperação de AN}}$	GJ/t_{AN}
CO2 Emission	$EI_{CO_2} = \frac{\text{Emissões (combustão + indiretas)}}{\text{Taxa de recuperação de AN}}$	t_{CO_2}/t_{AN}
Effluent generation	$EI_{ef} = \frac{\text{Purga}_{(\text{refrigeração+caldeira})} + \text{Perdas}_{(\text{processos+rejeitos})}}{\text{Taxa de recuperação de AN}}$	$m^3{}_{ef}/t_{AN}$

Source: Authors

Table 4. Results of computational simulation

	Stream 5			Stream 7			Crude AN		
	D&B	**UniSim**	**Deviation (%)**	**D&B**	**UniSim**	**Deviation (%)**	**D&B**	**UniSim**	**Deviation (%)**
				Molar flow (kmol/h)					
C_3H_6	5.78	5.78	-	4.6E-3	2.3E-2	-400.0	1.1E-3	1.1E-3	-
O_2	26.35	26.18	0.6	4.9E-3	2.0E-2	-314.9	1.8E-4	1.8E-4	-
N_2	2584	2584	-	0.252	1.017	-303.1	5.5E-3	5.5E-3	-
NH_3	-	-	-	-	-	-	-	-	-
CO_2	109.14	109.15	0.0	0.54	0.50	7.5	0.277	0.277	-
HCN	27.54	26.18	4.9	27.54	26.16	5.0	26.93	26.15	2.9
AN	272	271	0.5	271.0	271.1	-0.1	271.0	271.0	-
ACR	9.18	9.18	-	9.04	9.14	-1.1	9.03	9.03	-
ACN	10.71	10.74	-0.2	10.71	12.38	-15.6	10.45	10.45	-
H_2O	993.47	993.55	0.0	10999	10929	0.6	49.4	49.4	-
SCN	-	1.36	-	-	15.96	-	-	-	-
Total	4038	4037	2.5E-2	11318	11265	0.5	367.1	366.3	0.2
T (K)	303.15	303.15	-	301.15	297.20	1.3	303.15	303.15	-
P (kPa)	172.3	172.3	-	162.1	162.1	-	152.0	152.0	-

Source: Dimian *et* Bildea (2008); authors

The simulation of the process with the partial condensation step was performed as described by the authors of reference, aiming at obtaining the same crude acrylonitrile stream from the original process. For this process stream, the simulation obtained divergences with respect to the results presented by Dimian *et* Bildea (2008) only in the molar flow of HCN (of 26.0 kmol/h) and in the presence of small amount of succinonitrile (1.28·10-4 kmol/h). This is again due to the fact that the formation reaction of the latter compound is disregarded in the authors' work.

In Figure 5 a comparison of the water utilization in m^3/h by equipment is presented by the conventional and unmodified acrylonitrile production process with the partial condensation step. Note that the modified one presents a considerable reduction in the water consumption for practically all the equipment, and the increase in the use of water by the HX2 cooler is explained due to the partial condensation of the reactor effluent in this equipment.

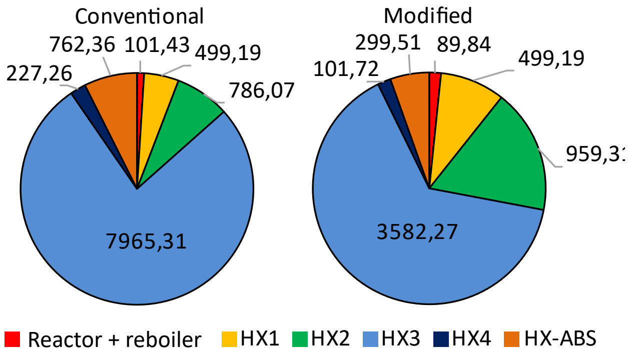

Figure 5. Use of water in m^3/h by equipment in both processes

Source: Authors

Table 5 presents the results for the water consumption and steam flow exported in both processes, as well as the resulting values for the water consumption eco-indicator.

Table 5. Results for the eco-indicator of water consumption

	Volumetric flow ()	
	Conventional	**Modified**
Makeup for the cooling system	133.4	104.2
Makeup for steam generation	580.1	309.4
Exported steam	79.7	79.7
Total ()	633.8	333.9
Recovered acrylonitrile (tAN/h)	14.4	14.4
Eco-indicator of water consumption ()	44.1	23.2

Source: Authors

The results of Table 5 demonstrate that the modification of the conventional process reduces the amount of makeup required by utility plant systems, resulting in a reduction of 299.9 m^3/h or 47% of the water consumption in the plant. It should be noted that the amount of exported steam generated by the reactor cooling does not change, since there was no change in the operating conditions for the reaction.

Figure 6 shows the quantitative contribution by source of water loss in the utility plant for both processes, as well as the corresponding portions of the effluent generation, considering, in a more conservative scenario, the total abstraction of the liquid streams, which are referred for treatment and subsequent disposal. It is noted that the losses for the modified process are lower than the conventional losses in all categories and that, in both cases, the purge stream in the cooling tower is the main contributor to water consumption, followed by losses by evaporation occurring on the same equipment.

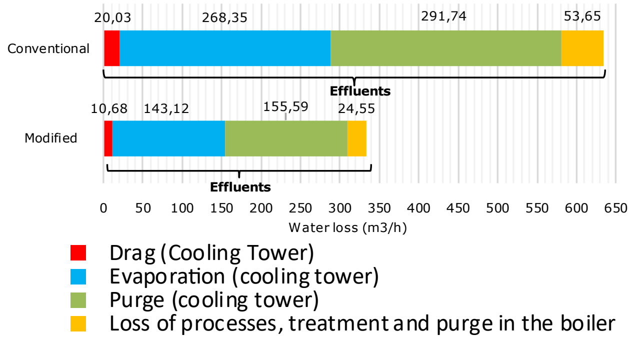

Figure 6. Sources of water loss

Source: Authors

In the conventional and unmodified process, the combustion of natural gas in the utility plant boiler is responsible for 99% and 96% of the total energy consumption, respectively, with the remainder coming from the use of electric energy. Figure 7 shows the sources of electricity consumption.

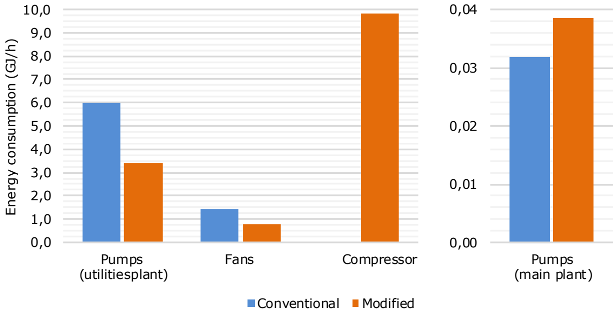

Figure 7. Electric power consumption

Source: Authors

It should be noted that, although the modified process shows a reduction in consumption from the utilities equipment, pump consumption in the main plant is higher than for the conventional process. This is due to the addition of pump P3 and the new configuration of this equipment, in order to take into account the new operating conditions of the process in order to introduce the partial condensation stage. The K1 compressor and the AC air cooler added contribute considerably to the energy consumption; however, this effect is offset by the reduction of total energy consumption by 439 GJ/h or 54% relative to the conventional process.

Figure 8 shows the CO_2 emissions in the conventional and unmodified processes by each source. Again, the introduction of the compressor results in an increase in indirect CO_2 emissions from the consumption of electricity, but the lower consumption of fuel by the boiler allows the total emissions to be reduced by 24.8 t_{CO_2}/h o or 54% relative to the conventional process.

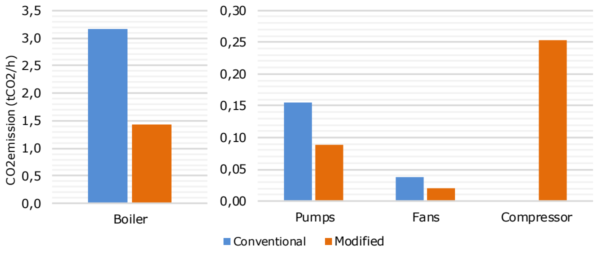

Figure 8. Sources of CO_2 emission

Source: Authors

The eco-indicators of water, fuel and energy consumption, CO_2 emission and generation of liquid effluents were calculated from the results of the simulations according to the expressions presented in the methodology. Table 6 shows the values of the eco-indicators for the two processes, as well as their respective normalized values.

Table 6. Calculated Eco-indicators and normalized values

Category	Eco-Indicator		Normalized value	
	Conventional	Modified	Conventional	Modified
Water consumption (M^3H_2O/t_{AN})	44.07	23.24	1.00	0.53
Fuel consumption (kg_{GN}/t_{AN})	1.17	0.53	1.00	0.45
Energy consumption (GJ/tAN)	56.79	26.28	1.00	0.46
CO2 Emission (t_{CO2}/t_{AN})	3.17	1.44	1.00	0.46
Effluent generation (m3ef/tAN)	25.44	13.97	1.00	0.55

Source: Authors

With the normalized values of the eco-indicators, it was possible to construct the radar charts for the processes (Figure 9). The area of the graphs allowed evaluating quantitatively the processes through the ECI, whose results are presented in Table 7.

According to the results presented previously, the introduction of the partial condensation step in the acrylonitrile production process considerably reduces the water consumption by the plant. This reduction in consumption directly affects the other eco-indicators evaluated, and its effects on eco-efficiency are easily observed in the results of Table 7, which shows that the modified process is 76% more eco-efficient than the conventional acrylonitrile production process.

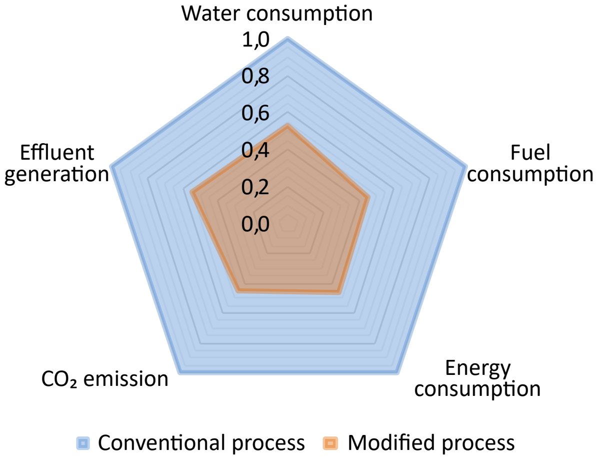

Figure 9. Radar Charts for the Eco-efficiency Comparison Index

Source: Authors

Table 7. Results of the Eco-efficiency Comparison Index

Eco-indicator x Eco-indicator	Conventional	Modified
Water consumption x Fuel consumption	1.00	0.24
Fuel consumption x Energy consumption	1.00	0.21
Energy consumption x CO2 emission	1.00	0.21
CO2 emission x Generation of effluents	1.00	0.25
Generation of effluents x Water consumption	1.00	0.29
Sum	5.00	1.20
Chart area	2.38	0.57
Eco-efficiency Comparison Index		76%

Source: Authors

7. CONCLUSIONS

The computational simulation of the acrylonitrile production process was satisfactory, since the results obtained presented small deviations from the data of the reference authors, justified by the difference between the software used and the inclusion of the succinonitrile formation reaction, which is more reliable to the actual process. The results of the simulations of the conventional and modified processes, as well as of the utilities plant, provided the necessary information for the calculation of the five eco-indicators proposed for the eco-efficiency analysis.

The calculated values for the eco-indicators and the result of the ECI methodology demonstrated that the process modification reduced environmental impacts in all categories, causing the recovery of acrylonitrile by the process with partial condensation step to show an improvement of 76% in the eco-efficiency of the process, adding value to the process. Notably, the introduction of the partial condensation stage considerably reduced the total water consumption of the process, resulting in savings of 47% or 299.9 . These observations could be made due to the practicality of the calculation of eco-indicators and the comparative analysis made possible by the ECI methodology. The method used in this work, although considering the results of computational simulation to analyze an acrylonitrile production process, can be applied to other processes, including using real data.

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