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ENVIRONMENTAL ANALYSIS OF THE MALEIC ANHYDRIDE PRODUCTION PROCESS

Patrick Vaz Mangili[1] – patrickmangili@gmail.com
Rafael Oliveira dos Santos[1] – ro_santos@id.uff.br
Igor Nardi Caxiano[1] – igornardi@id.uff.br
Lizandro de Sousa Santos[1] – lizandrosousa@id.uff.br
Diego Martinez Prata[1] – pratadiego@gmail.com
[1] Universidade Federal Fluminense, Department of Chemical and Petroleum Engineering – Niterói, RJ, Brazil

Abstract. *Maleic anhydride is a chemical product with a large range of application, such as an intermediate for the production of resins, polymers, varnishes and paints. As awareness about environmental impacts rises, industries seek to develop more efficient and sustainable processes. In this study, two different maleic anhydride production processes (via oxidation of benzene and via oxidation of n-butane) are compared in terms of their ecological performances. The environmental comparison, in turn, was carried out through the Eco-efficiency Comparison Index method by estimating five different categories of eco-indicators, namely raw materials consumption, energy use, CO_2 emissions, water consumption and wastewater generation. For the case analyzed, the butane technology showed to be the most environmentally attractive, since it's about 54% more eco-efficient than the benzene process.*

Keywords: *Process Simulation, Eco-efficiency, Eco-indicators, MAN.*

1. INTRODUCTION

Maleic anhydride (MAN) is a chemical product associated with a broad market due to its application as an intermediate for the production of unsaturated polyester resins, polymers, varnishes and paints, among several other commodities. In 2015, the global capacity of MAN production amounted to 2800 million metric tons (Mestl et al., 2016). Furthermore, the world demand for MAN is expected to reach US$4.11 billion by 2024, being the Central Europe, Latin America and Asia markets the most accountable for such growth (Grand View Research, 2016). Nowadays, MAN can be manufactured from two different gas-phase technological processes, namely the oxidation of benzene and the oxidation of n-butane.

Eco-efficiency relates the environmental impacts of processes to its economic performance. This analysis is generally performed based on the quantitative evaluation of the process eco-indicators, which are represented by a relationship between an environmental variable, such as atmospheric emissions, and an economic variable, for example production rate or net profit (Mangili et al., 2018).

This paper aims to compare environmental performances of both technologies for MAN manufacture. In this regard, raw material consumption, energy use, CO_2 emissions, water consumption and wastewater generation were chosen as eco-indicators, which were then normalized and grouped through the Eco-efficiency Comparison Index (ECI) method (Pereira et al., 2018), in order to obtain the eco-efficiency of both processes.

2. LITERATURE REVIEW

This section presents the literature review regarding the MAN synthesis processes and the importance of environmental analysis for the industry.

2.1 Maleic Anhydride Production

Maleic anhydride can be manufactured by two different process routes. The selective oxidation of benzene induces the loss of two carbon atoms, thus decreasing mass yield and resulting in the formation of heavy by-products such as phthalic anhydride and benzoquinone. In the oxidation of n-butane, in turn, lighter by-products such as acetic and formic acids are obtained (Centi et al., 2001).

The main reaction for the MAN production from benzene oxidation, achieved by using a vanadium-molybdenum catalyst, is described in Eq. (1).

$$C_6H_6 + 4.5O_2 \rightarrow C_4H_2O_3 + 2CO_2 + 2H_2O \tag{1}$$

In the oxidation of n-butane, the reaction, as shown in Eq. (2), is carried out using a vanadium-phosphorus catalyst.

$$C_4H_{10} + 3.5O_2 \rightarrow C_4H_2O_3 + 4H_2O \tag{2}$$

Both technologies also differ from each other in terms of operating conditions that depend on several factors such as feedstock conditions, process design, etc. The reactor type may be of fixed, fluidized or moving bed. MAN recovery can be performed in either aqueous or organic phase, whereas its purification may be carried out through either azeotropic distillation or thin-film evaporation (Baerns, 2004).

2.2 Utility Plants

The utility plants are responsible for providing auxiliary services which are necessary for the continuous operation of a considerable number of industrial processes. Utilities such as electricity, fuel gas, process and cooling water, steam, compressed air and inert gases are generally supplied in a central site facility inside the plant (Towler & Sinnot, 2013).

Considering both of MAN production processes, the utilities plants for steam generation and cooling water, needed to attain a better overview of the consumption of water and the energy costs, were simulated.

2.3 Environmental Analysis

The evaluation of the environmental impacts of chemical plants has become indispensable in process design. For this purpose, the use of the eco-indicators is an important tool when measuring the sustainability of an industrial process. The eco-indicator is generally defined by a ratio of an environmental variable and an economical variable, usually related to the production (Siitonen et al, 2010).

Therefore, the evaluation of the eco-indicators complements the traditional techno-economic analysis of process design, helping in decision making. The determination of a single indicator is not sufficient to assert which technology has the highest environmental performance, since most indicators are calculated independently of one another. For this reason, the eco-indicators were then quantitatively compared by means of the Eco-efficiency Comparison Index (ECI) method, originally proposed by Pereira et al. (2018). The ECI is intended to jointly evaluate process indicators in order to define the most eco-efficient.

3. METHODOLOGY

This section discloses the methodology used for simulating the benzene and n-butane MAN production processes and the utility systems, as well as for determining the eco-indicators and the eco-efficiency.

3.1 Process Simulation

Both processes, as well as the utility plants, were simulated using the software UniSim® Design Suite R390.1 from Honeywell. The processes were simulated under steady-state conditions by using the Non-Random Two Liquid (NRTL) thermodynamic model (enthalpy, phase equilibrium, etc.).

Regarding the utility plants simulation, a set of heuristics were utilized in order to describe the water losses inside the cooling water and steam generation plants. The heuristics utilized in this work are described in Table 1.

Table 1 – Heuristics for the Utility Plants.

Utility Plant	**Parameter**	**Value**
Cooling Water	Drift and Evaporation Losses	3%
	Blowdown Losses	0.3%
Steam Generation	Condensate Return	80%
	Blowdown Losses	3%

References: Turton et al. (2012), Towler & Sinnot (2013) and Smith (2005).

3.2 Eco-efficiency

The eco-indicators were determined through the guidelines provided by Mangili and coworkers (2018) and the equations utilized are described in Table 2. The production rate of MAN (t/h) was considered as the economic variable. It was assumed that pumps and compressors operate with electricity at 75% efficiency, heaters and reboilers operate with steam generated in the utility plant's boiler and condensers and coolers operate with cooling water generated in the utility plant.

Table 2 – Eco-indicators equations.

Indicator	Formula	Unit
Raw material consumption	$E_{RM} = \frac{\text{Total mass flow rate of raw materials}}{\text{Total mass flow rate of MAN product}}$	t_{RM} / t_{MAN}
Energy use	$E_E = \frac{\text{Total electricity and thermal energy consumed}}{\text{Total mass flow rate of MAN product}}$	GJ / t_{MAN}
CO_2 emissions	$E_C = \frac{\text{Indirect, Combustion and Fugitive Emissions}}{\text{Total mass flow rate of MAN product}}$	t_{CO_2}/ t_{MAN}
Water consumption	$E_W = \frac{\text{Cooling water and Steam generation Systems' make-up}}{\text{Total mass flow rate of MAN product}}$	m_w^3/ t_{MAN}
Wastewater generation	$E_{WW} = \frac{\text{Blowdown losses from utilities plant}}{\text{Total mass flow rate of MAN product}}$	m_{ef}^3/ t_{MAN}

The raw material consumption eco-indicator was calculated considering the main feed streams of the processes. The CO_2 fugitive emissions were estimated by considering total combustion of gases. The energy to CO_2 emission conversion factors utilized for both combustion and indirect emissions are presented in Table 3. The value of 0.0227 tCO_2/GJ corresponds to the average CO_2 emissions related to electricity generation in Brazil for the year of 2017.

Table 3 - Conversion factors for indirect CO_2 emissions.

Parameter	Conversion Factor		Reference
Electricity to CO_2	0,0227	tCO_2/GJ	MCTIC(2018)
Energy to CO_2 (Natural Gas Basis)	0,0561	tCO_2/GJ	IPCC (2006)

For the water consumption and wastewater generation eco-indicators, the data was obtained from the utilities plant simulation, considering the water makeup stream for the cooling water and steam generation system and the water losses in the blowdown of the cooling tower and boiler. The five eco-indicators were then utilized in the ECI method, following the same procedure applied by Mangili et al. (2018) and Pereira et al. (2018).

4. PROCESS DESCRIPTION

The benzene and butane technologies for MAN manufacture studied in this work are based on the works of Turton et al. (2010) and Frank (1975), respectively. The butane process was scaled-up in order to match both plant capacities and thus allow a fair comparison regarding the processes’ environmental impacts.

4.1 Benzene Technology

The process flow diagram for the MAN production technology via benzene oxidation is illustrated in Fig. 1.

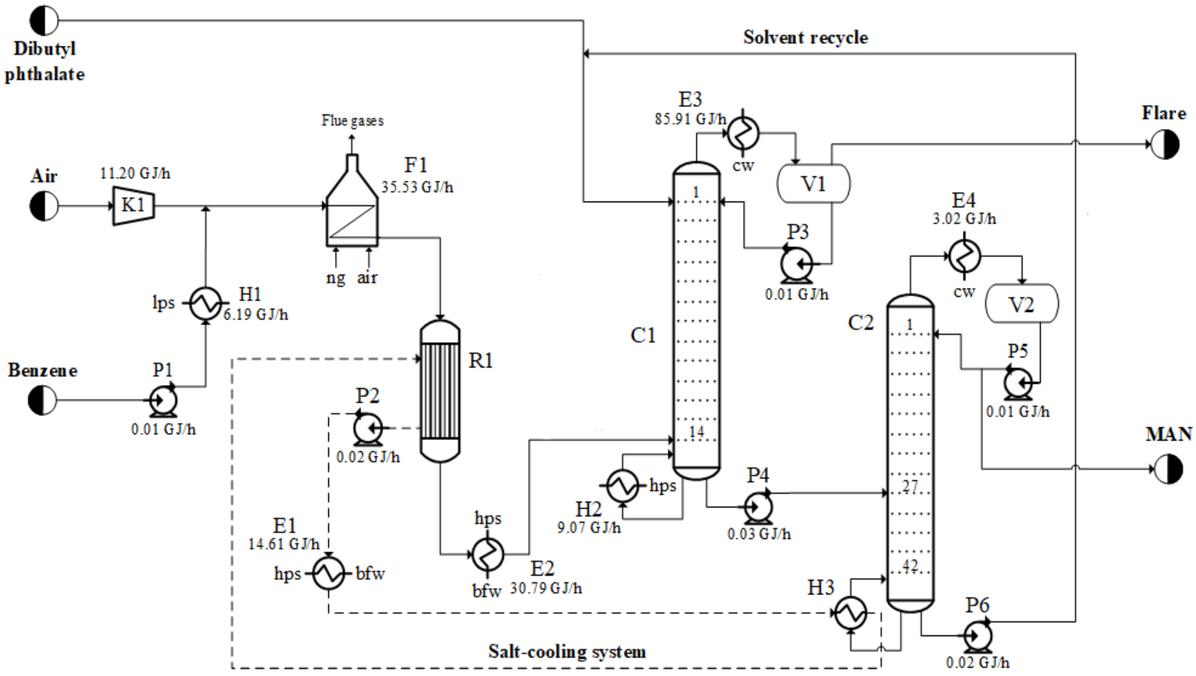

Figure 1 – MAN production process via oxidation of benzene.

Fresh benzene at 42.3 kmol/h is pressurized and mixed with 2790.0 kmol/h of compressed air from compressor K1. The resulting mixture is heated to 460.0° C prior to being fed to a tubular reactor R1, composed of 12,100 catalyst-filled tubes with 20 ft length and 1 in diameter. The reaction kinetics are modeled in accordance to Turton et al. (2010).

It should be noted that reactor R1 is cooled through a molten salt-cooling system, which is integrated to distillation column C2's reboiler. This system was not simulated due to the software limitations regarding the simulation of solid components. However, since Turton et al. (2010) provided the information about Pump P2 and cooler E1, these equipment were taken into account.

The reactor product is cooled down and fed to the bottom of an absorption column C1 having 14 sieve plates, full-reflux condenser and reboiler. A dibutyl phthalate stream, used as solvent for recovering MAN, is fed to the top of C1. The absorber's top product consisting of unreacted components and combustion gases is sent to the flare.

The bottom product of the column C1, which contain solvent and recovered MAN, is taken to the distillation column C2, from which MAN is obtained as distillate with a purity of 94.7 mol %. C2's bottom product, comprised of dibutyl phthalate, is recycled to the top of the absorption column.

4.2 Butane Technology

The process flow diagram for the MAN production technology via n-butane oxidation is illustrated in Fig. 2.

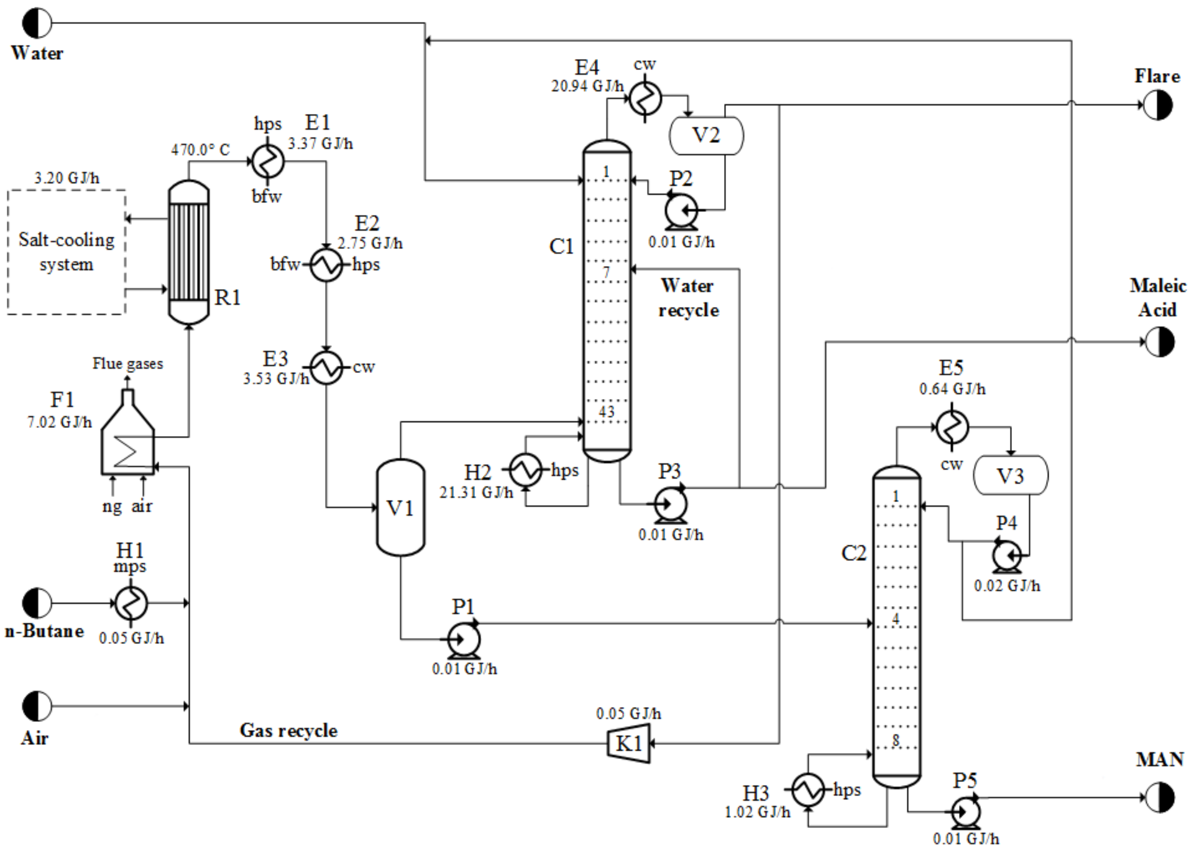

Figure 2 – MAN production process via oxidation of n-butane.

Fresh n-butane at 50.0 kmol/h is heated to 25.0° C and mixed with 323.3 kmol/h of air and a compressed gas recycle stream from the absorption section. The resulting mixture is heated to 420.0° C prior to being fed to a tubular reactor R1 having 15,000 1-in diameter, 16-ft length catalyst-filled tubes. The tubular reactor proposed by the reference was simulated as a conversion reactor since the patent provided the conversion factors for n-butane to MAN, CO and CO_2 (60%, 25% and 15%, respectively).

Similar to the benzene process, the reactor R1 is cooled through a salt-cooling system, which was not simulated. However, since the simulation provided the value of the required energy to cool down the reactor, we used said value to estimate the amount of bfw used to cool the molten salt.

The reactor product is cooled down after passing through a series of three coolers prior to being sent to a flash vessel V1. The bottom product is sent to the distillation column C2, from which water is retrieved as distillate and recycled to the absorption column and MAN is obtained at the bottom with a purity of 99.9 mol %.

V1's top product, containing unreacted components and combustion gases is sent to the bottom of an absorption column C1, whose top section is fed by a water make-up stream. C1's bottom product is then divided into a water recycle stream, which is sent back to the 7th stage of the absorber, and a maleic acid product. C1's top product, in turn, is divided into a gas recycle stream, which is pressurized in compressor K1 and sent back to the feed section, and an off-gas stream, sent to the flare.

4.3 Utilities Plant

The utilities plant was designed to allow a more realistic estimation of the water consumption and wastewater generation from both technologies. Its flowsheet is illustrated in Figure 3.

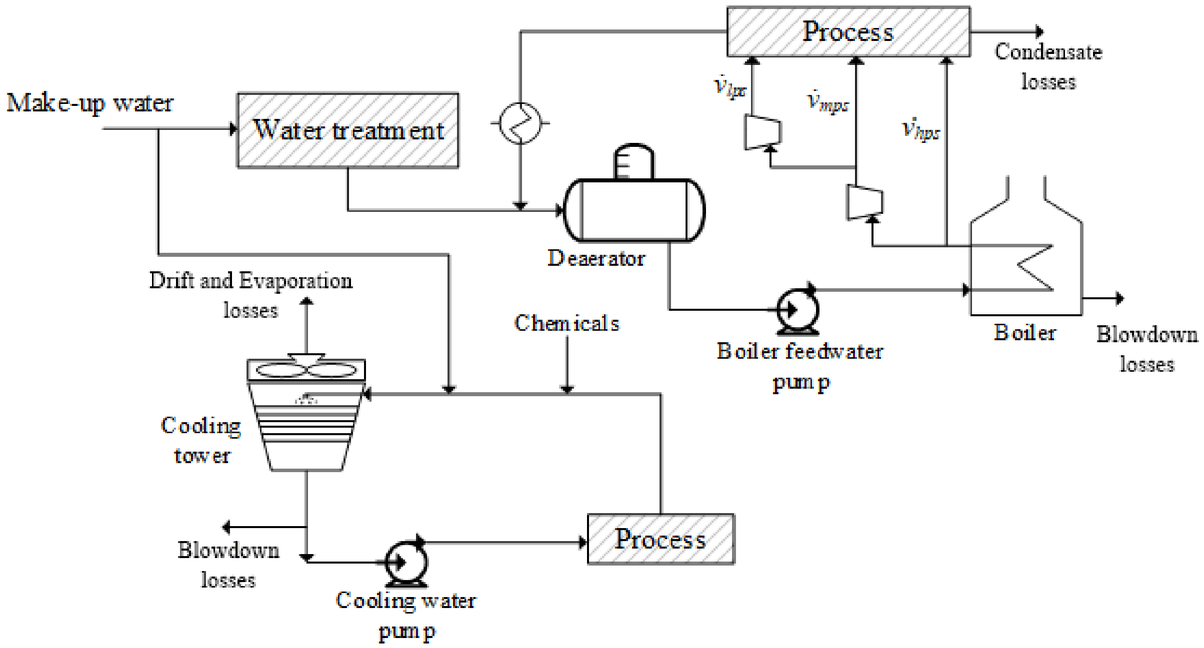

Figure 3 – Utility system.

The cooling water (CW) is sent to the coolers and condensers in the main plant and then is mixed with a water make-up stream and recycled to the cooling tower, where the water is cooled down by an induced draft system. Subsequently, the cooled water is pressurized and sent back to the process. Cooling water supply and return temperatures were assumed to be 30° C and 45° C, respectively (Turton et al., 2010).

In the boiler, high-pressure steam (HPS) is generated and used to generate medium-pressure steam (MPS) and low-pressure steam (LPS). The different types of steam are then sent to the heaters and reboilers in the main plant. The returning condensate is mixed with a make-up water stream and sent to a deaerator. Then, the boiler feed water (BFW) is sent back to the boiler. A blowdown is done before the boiler in order to avoid accumulation of solids or contaminants in the cycle. Boiler feed water supply temperature was considered to be 130° C (Tvedt and Holloway, 1997).

The low, medium and high pressure steams conditions used here were taken from Seider et al. (2009) and are shown in Table 4.

Table 4 – Steam parameters.

Steam	**Supply temperature (° C)**	**Pressure (bar)**
Low pressure	135.0	3.10
Medium pressure	185.5	11.35
High pressure	254.0	42.38

5. RESULTS

This section presents the results obtained for the main streams of the process' simulation, as well as for the eco-indicators and the ECI method.

5.1 Main Stream Results

The results for the benzene process and butane process main streams are shown in Table 5 and Table 6, respectively.

Table 5 – Results for the main stream of the benzene process.

Stream	Benzene	Air	Dibutyl phthalate	Flare	MAN
Molar Flow (kmol/h)	42.3	2790	0.1	2797.6	27.6
Temperature (°C)	30	30	320	260	190.1
Pressure (bar)	1.0	2.8	1.0	2.1	0.7
Molar Fraction					
C_6H_6	1.000	0.000	0.000	0.002	0.000
CO_2	0.000	0.000	0.000	0.046	0.000
O_2	0.000	0.210	0.000	0.132	0.000
N_2	0.000	0.790	0.000	0.788	0.000
H_2O	0.000	0.000	0.000	0.032	0.000
Dibutyl phthalate	0.000	0.000	1.000	0.000	0.000
MAN	0.000	0.000	0.000	0.000	0.947
Quinone	0.000	0.000	0.000	0.000	0.015
Maleic Acid	0.000	0.000	0.000	0.000	0.038

Table 6 – Results for the main stream of the butane process.

Stream	n-Butane	Air	Water	Flare	MAN	Maleic Acid
Molar Flow (kmol/h)	50.0	323.3	63.86	372.1	21.36	47.2
Temperature (°C)	14.0	25.0	45.0	124.3	198.6	83.6
Pressure (bar)	1.7	1.7	1.0	1.0	1.0	1.0
Molar Fraction						
C_4H_{10}	1.000	0.000	0.000	0.068	0.000	0.000
CO_2	0.000	0.000	0.000	0.042	0.000	0.000
O_2	0.000	0.210	0.000	0.000	0.000	0.000
N_2	0.000	0.790	0.000	0.610	0.000	0.000
H_2O	0.000	0.000	1.000	0.280	0.000	0.000
MAN	0.000	0.000	0.000	0.000	0.999	0.000
Maleic Acid	0.000	0.000	0.000	0.000	0.001	1.000

The total production rate, which corresponds to the mass flow rate of stream "MAN", can be obtained from the results described in Table 5 and 6, that is, 2.40 t/h for the benzene process and 2.20 t/h for the butane process.

5.2 Environmental Analysis Results

The results for the five eco-indicators obtained for both process are described in Table 7.

Table 7 – Eco-indicators results.

Process	**Benzene technology**	**Butane technology**
Raw materials eco-indicator, t_{RM}/t_{MAN}	1.36	1.39
Energy use eco-indicator, GJ/t_{MAN}	34.78	17.86
CO_2 emissions eco-indicator, t_{CO_2}/t_{MAN}	4.12	3.05
Water use eco-indicator, $m^3{}_W/t_{MAN}$	11.13	9.31
Wastewater eco-indicator, $m^3{}_{ef}/t_{MAN}$	19.12	11.72

The results show that the butane technology has the lowest eco-indicators for all categories evaluated, except for the raw material consumption indicator. Its lower energy consumption mainly relates to the higher energy required by the fired heater to heat the reactor feed, thus increasing both the energy use and consequently the CO_2 emissions indicators due to the combustion of natural gas. The lower water consumption of the butane process can be mainly related to the lower thermal requirements of the absorption column when compared to the columns of the benzene technology.

The indicators shown in Table 7 were normalized by dividing them by the highest value in the same category, as suggested by Pereira et al. (2018). The qualitative analysis was then performed by plotting the normalized values in a pentagon-shaped radar-type chart, as shown in Figure 7.

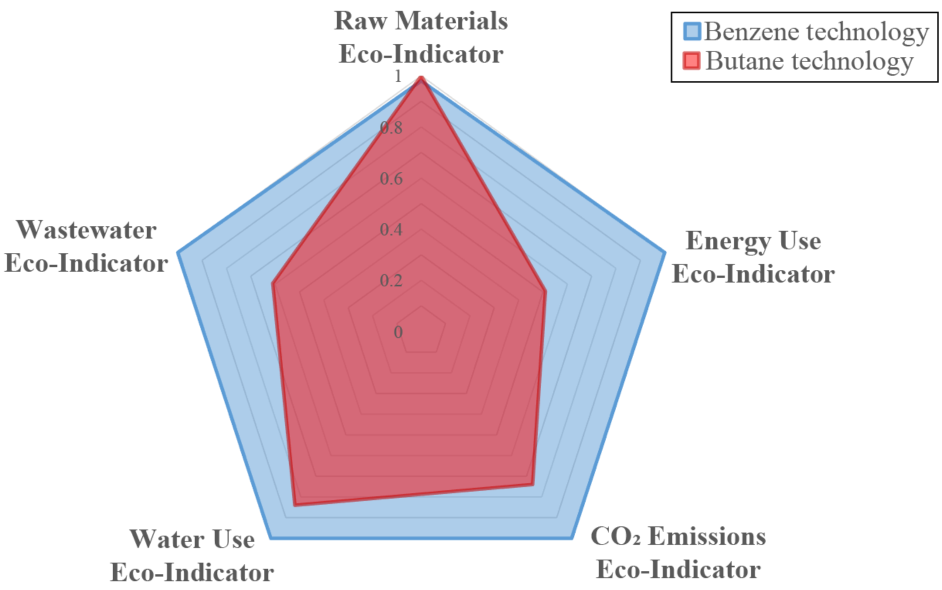

Figure 4 – Qualitative ECI.

The quantitative evaluation was carried out by summing up the area of each minor triangle calculated with the Law of Sines, from which we note that the butane process is approximately 54% more ecologically efficient than the benzene process.

6. CONCLUSIONS

The comparison between the benzene and butane technologies for MAN production studied in this work demonstrated that the process from butane is 54% more environmentally attractive than benzene process. The results showed that, for 1 ton of MAN produced, the butane process consumes approximatively 48% less energy, emits 26% ton CO_2 less and consumes 16% less water than the butane process.

In this regard, process simulation was shown to be a convenient technique for estimating the environmental footprint of industrial processes. In addition, with basis on the results provided in this paper, future studies on MAN production may be developed in order to perform thermal integration and design new MAN purification methodologies for reducing ecological impacts.

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