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Multi-criteria decision analysis for the selection of sustainable chemical process routes during early design stages

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ABSTRACT

Decision-making for sustainable design requires the evaluation of different options considering all sustainability dimensions simultaneously: economic, environmental and social. Each dimension has a specific relative importance, which depends on the process that is being assessed. The determination of the relative importance is not a simple task, principally, during early design stages when detailed information about the process is scarce, and when core decisions affecting the entire design are made. An example of this kind of decisions during early design stages is the selection of the chemical process route, which, once defined, provides the guidelines for the process design. The present study proposes a multi-criteria analysis based methodology to evaluate different chemical process route options under sustainability criteria and to guide the selection among them. The methodology uses normalized indicators to assess each sustainability dimension, and a multi-criteria analysis method (MCDA) to calculate the weights and influences between dimensions. Indicators, dimension weights and influences are integrated into the Sustainable Cumulative Index (SCI) that can be used to compare chemical process route options in sustainability terms and to support their selection. The proposed methodology is illustrated through the assessment and selection of a chemical process route to produce ethyl acetate.

1. Introduction

Currently, the application of sustainability principles in the chemical industry is a general concern. This is increasingly reflected in legal regulations and industrial practices, as well as in education and scientific fields. For example in Europe since 2007, the REACH regulation (Registration, Evaluation, Authorization and Restriction of Chemicals) places the responsibility on industries to manage risks from chemicals and to provide safety information on such substances (EC Environment, 2015). Similarly, the United States Environmental Protection Agency (EPA) is working to examine the scope of the chemicals included in the Toxics Release Inventory (TRI) program, providing communities with more information on the issue (EPA, 2015). Non-governmental institutions such as the International Organization for Standardization (ISO) have been supporting this trend by establishing requirements for environmental management in the ISO 14000 standard and for social

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Abbreviations: SCI, Sustainable Cumulative Index; MCDA, multi-criteria analysis method; IWF, integrated weighting factor; AHP, Analytic Hierarchy Process; DEMATEL, Decision-Making Trial and Evaluation Laboratory.

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responsibility in the ISO 26000. In the same direction, an increasing number of higher education institutions have incorporated the principles of sustainable development into their curricula, as analyzed by Lozano (2010, 2003).

Even if awareness of developing sustainable chemical processes has been a hot topic for some years, the industrial sector is still in search of practical tools to conduct systematic sustainability assessments of existing processing technologies as well as new ones (Othman et al., 2010). In general, the design task requires assessing different alternatives in order to decide which of the options constitutes the best choice according to an objective function (traditionally process economics). It is desirable that the decision-making process becomes rational and structured rather than intuitive or subjective. This can be difficult when analyzing chemical processes from an integrated sustainability approach, because it requires the simultaneous consideration of the economic, environmental, and social dimensions. This can be more demanding during early design stages, because the conceptual process is not defined and the main process variables are unknown. In this context, appropriate assessment methods for each dimension and tools to make decisions involving multiple conflictive objectives are needed.

There are several studies and methodologies that can be used to evaluate process design options in terms of sustainability. They differ in the assessment method used, the completeness (partial or integral sustainability), and the design stage in which they can be applied. Most methods can only be implemented during advanced design stages, when enough information is available to perform the material and energy balances for the entire process. Examples of these methods are life cycle assessment (LCA) for environmental impacts (Azapagic, 1999), quantitative risk assessment (QRA) for risk estimation (Arendt, 1990; Papazoglou et al., 2003), and the widely used qualitative methods such as failure mode and effects analysis (FMEA) and hazard and operability study (HAZOP) for reliability and safety analysis.

However, in order to obtain sustainable products, processes and plants, actions must be taken at the very early stages of the design process when the most important decisions are made (Banimostafa et al., 2012). During these stages, after product properties are established, possible chemical process routes are searched and screened, and only the most promising ones are further analyzed. The term chemical process route is used here according to the definition given by Edwards and Lawrence (1993): the raw material(s) and the sequence of chemical reaction steps that convert them to the desired product(s). A chemical process route can have more than one chemical reaction. According to Hassim and Edwards (2006) and Srinivasan and Nhan (2008), the choice of a chemical process route is one of the key decisions in early design stages. Its selection defines possible raw materials to be used in the process and their pretreatment (upstream operations), as well as reaction conditions (phase, type of catalyst, etc.), and it also constrains the design of the downstream operation. In this sense, it is important to avoid negative effects on sustainability dimensions by their systematic consideration from the beginning of the design process.

Several authors have suggested different sustainability indicators to measure the performance of alternatives in early design stages. Carvalho et al. (2008) presented a methodology to calculate the economic performance during the chemical process route selection. Their methodology, besides performing the cash flow analysis between input costs and revenues from product sales, considers side reactions, byproducts and energy costs. Similarly, some approaches have been proposed to measure the environmental impact of chemical process routes, which include, among others, the Environmental Hazard Index (EHI) proposed by Cave and Edwards (1997), the Waste Reduction algorithm (WAR) proposed by Young et al. (2000) and the environmental potential impact (EPI) proposed by Li et al. (2009). The social dimension can be quantitatively represented at the early design stage through safety and health indicators. Safety has been extensively studied because workers' lives depend on the establishment of safe conditions in chemical processing plants. Right decisions during early design stages can reduce or remove risks, which is called inherent safety design. Inherent safety assessment methods include the Inherent Safety Index (ISI and ISI2) referenced by Adu et al. (2008) and the Prototype Inherent Safety Index (PIIS) proposed by Edwards and Lawrence as reviewed by Rahman et al. (2005). Some approaches have been presented for occupational health indicators, which are perhaps less studied than any others, including the Process Route Healthiness Index (PRHI), the Inherent Occupational Health Index (Hassim and Edwards, 2006) and the graphical method to evaluate the inherent occupational health hazards (Hassim et al., 2013).

Two aspects have to be covered in order to apply indicators toward the calculation of an integrated sustainability assessment. First, it is necessary to standardize the indicators that describe each dimension, because they have different meanings, definitions and units. Second, the information given by all indicators has to be presented simultaneously so that decision-makers can visualize eventual trade-offs between alternatives and identify the best in terms of sustainability.

An interesting approach for accomplishing the first aspect was proposed by Srinivasan and Nhan (2008). They classified the indicators into those that are defined in an interval or ratio scale and are easy to normalize, and those that are not. For the latter they proposed normalization based on frequency distribution for common reactions, avoiding subjective scaling.

Concerning the second aspect, common approaches are the addition of normalized indicators without weighting (Srinivasan and Nhan, 2008), weighting them according to industrial practices (Sugiyama et al., 2006; Albrecht et al., 2010; Banimostafa et al., 2012) or weighting them in relation to local management policies (Tugnoli et al., 2008). Other approaches integrate the sustainability indicators using graphical representations or statistical techniques. Some authors proposed tools such as principal component analysis (PCA) (Sugiyama et al., 2006), sensitivity analysis and graphical multi-objective evaluation (Banimostafa et al., 2012). These methods allow process designers to identify key indicators, visualize trade-offs and provide information on the mutual dependence of different criteria, but are merely descriptive.

Another alternative to integrate the sustainability indices is the implementation of multi-criteria decision analysis (MCDA), which is addressed in the present study. The use of MCDA to solve sustainability problems was carried out by Othman et al. (2010), using Analytic Hierarchy Process (AHP) to support decision-making during chemical process design. It was also used by Santoyo-Castelazo and Azapagic (2014), who implemented MCDA for a sustainability assessment of energy systems. More cases where MCDA methods were applied to chemical engineering problems are listed in Table 1.

The choice of a particular MCDA method is strongly linked to the characteristics of the problem, the nature of available data, and the main goal. For the application of a specific MCDA method during early design stages, it should be considered that the relative importance of the sustainability dimensions could change from one chemical industry to another, and that there is a mutual relation among the different sustainability dimensions. In this regard, the present study proposes a methodology for chemical process route selection during early design stages that address these two aspects: the relative importance through the integration of the Analytic Hierarchy Process (AHP) and the interrelation between the dimensions by the Decision-Making Trial and Evaluation Laboratory (DEMATEL) (Chou et al., 2012; Abdullah and Zulkifli, 2015; Chou et al., 2010). The proposed methodology calculates an integrated sustainability index called Sustainable Cumulative Index (SCI) on the basis of normalized sustainability indicators using MCDA methods. Indicators assess the performance of alternatives in each dimension, while MCDA methods integrate assessments according to the specific characteristics of the process to be designed. The application of MCDA methods is normally based on the opinion of experts or in data analysis. In this case, we used the opinion of experts to formalize the technical knowledge that helps to define the importance and interrelation of criteria.

To illustrate this methodology, it was applied for the selection of the most sustainable chemical process route to produce ethyl acetate among four different alternatives. The integrated AHP-DEMATEL method was applied based on the opinion of two groups of decision-makers: experts from industry and academia and undergraduate students of chemical engineering. Although the methodology shown in this article was implemented in the selection of a chemical

Table 1 – Example of multi-criteria decision analysis (MCDA) methods applied to solve chemical engineering problems.

Subject	Method	Type of problem – stage	Reference
Increase productivity in the textile industry	MACBETH	Process design – process optimization	(Bana e Costa et al., 1999)
Hydrogen storage	MACBETH	Process design – storage	(Montignac et al., 2009)
Flood control	MACBETH	Process design –process control	(Bana e Costa et al., 2004)
Development of the control structure of an FCC unit	Rough sets	Process design –separation operations	(Mizsey and Kraslawski, 2006)
Optimization of a pulping process	Rough sets	Process design	(Thibault et al., 2003)
Energy planning	ELECTRE III	Plant design –conceptual engineering	(Georgopoulou et al., 1997)
Design of a distillation unit	PROMETHEE	Plant design – basic engineering	(Ramzan et al., 2009)
Treatment of waste water from the textile industry	PROMETHEE	Process design	(Aragonés-Beltrán et al., 2009)
Selection of technology to produce microalgae-based biodiesel	Weighting	Process design	(Torres et al., 2013)
Evaluation of hydrogen production methods	AHP	Process design	(Pilavachi et al., 2009)
Evaluation of biodiesel production methods	AHP	Process design	(Narayanan et al., 2007)

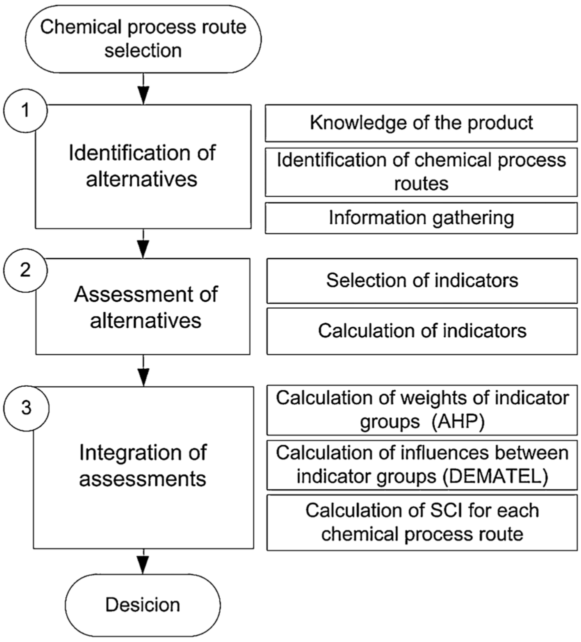

Fig. 1 – Methodology for chemical process route selection proposed in this study.

process route of a specific product, it is generic. Its structure, based on the steps shown in Fig. 1 (identification of alternatives, assessment through indicators and integration through MCDA methods), can be applied to the selection of chemical process routes for other types of products. Moreover, this approach can also be extended to aid decision-making for other choices made during early design stages, including those for the design of upstream and downstream operation.

2. Multi-criteria analysis based methodology for the selection of a sustainable chemical process route during early design stages

Fig. 1 shows a diagram of the methodology for the selection of chemical process routes proposed in this study. It comprises three main stages: identification and characterization of alternatives, assessment of alternatives through sustainability indicators, and integration of assessments in the Sustainable Cumulative Index (*SCI*) by the MCDA methods.

2.1. *First stage: Identification of alternatives*

During the first stage, the product is completely characterized (properties, specifications, prices, legal framework, etc.), chemical process routes are identified and studied (for example, through thermodynamic and kinetics analysis), and the information needed to calculate the indicators is gathered. This information includes economic, safety, occupational health and environmental properties of the compounds, and operating conditions of the chemical process routes under study.

2.2. *Second stage: Assessment of alternatives*

During this stage, the performance of each chemical process route is assessed in the economic, environmental and social dimensions through sustainability indicators. In this study, the social dimension is represented by two indicator groups: safety and occupational health, as presented in Fig. 2.

2.2.1. *Selection of indicators*

This study proposes a set of indicators to calculate the performance of chemical process routes. Most of these were previously used by Srinivasan and Nhan (2008), Young et al. (2000) and Carvalho et al. (2008), while some others were modified or proposed within the present study. The equations used for calculation of the sustainability indicators are summarized in Table 2. It is important to note that it is not always necessary to use all the listed indicators in order to calculate the sustainability of a chemical process route. Some of these can be disregarded or additional ones can be included. Decision-makers have to select the most appropriate indicators according to process characteristics, the specific context of the selection problem, and the availability and quality of the information.

2.2.2. *Calculation of indicators*

2.2.2.1. *Economic indicator group.* The present approach uses added value as economic indicator. It is calculated from the difference between product prices and raw material costs

Table 2 – Sustainability indicators for the calculation of the Sustainable Cumulative Index (*SCI*) of the chemical process route.

Indicator	Meaning	Equation		Nomenclature		Comments
Economic indicators						
Total normalized added Value ($\overline{VAT_r}$)	The added value corresponds to the difference between product prices and raw material costs. It can be normalized by dividing it by the sale price of products. The normalized added value ($\overline{VA_r}$) is dimensionless. The total normalized added value ($\overline{VAT_r}$) corresponds to one minus the normalized added value ($\overline{VA_r}$) as shown in Eq. (5). A lower value of $\overline{VAT_r}$ means better economic performance. If $\overline{VAT_r}$ is greater than one, the chemical process route is not economically attractive.	$VA_r = \sum_{1}^{NP} VA_p$	(1)	CF_p	Conversion factor product *p*	Eqs. (1)–(4) were taken from Carvalho et al. (2008) and modified to suit the approach proposed in this study
		$VA_p = m_p \left[PP_p - CF_p \left(\sum_{1}^{RM} \frac{\lvert\nu rm\rvert M rm Pc rm}{\lvert\nu p\rvert M p} \right) \right]$	(2)	M	Molecular weight of product *p* or raw material *rm*	
		$CF_p = \frac{\lvert\nu p\rvert M p}{\sum_{1}^{NP} \lvert\nu p\rvert M p}$	(3)	m_p	Mass of product *p*	
		$\overline{VA_r} = \frac{VA r}{\sum_{p=1}^{NP} M p PP p}$	(4)	NP	Total number of products	
				Pc_{rm}	Purchase price of raw material *rm*	
		$\overline{VAT_r} = 1 - \overline{VA_r}$	(5)	PP_p	Sale price of product *p*	Eq. (5) was proposed in this study
				RM	Total number of raw materials	
				VA	Added value of chemical process route *r* or product *p*	
				$\overline{VA_r}$	Normalized added value of chemical process route *r*	
				$\overline{VAT_r}$	Total normalized added value of chemical process route *r*	
				ν	Stoichiometric coefficient of product *p* or raw material *rm*	

Table 2 – (*Continued*)

Indicator	Meaning	Equation	Nomenclature		Comments
Environmental indicators					
Global warming potential (GWP)	"This impact category is determined by comparing the extent to which a unit mass of a chemical absorbs infrared radiation over its atmospheric lifetime to the extent that CO_2 absorbs infrared radiation over its respective lifetimes." (Young and Cabezas, 1999)	$\overline{\psi^{s}_{r,I}} = \frac{\sum_{c=1}^{C} Potencial_{c,I}}{(\langle(\text{Potencial})_r\rangle_I + 2\sigma_I) * C}$ (6)	C	Total number of compounds of chemical process route *r*	(Young and Cabezas, 1999). The normalization method was originally presented by Srinivasan and Nhan (2008), using only the component with the most critical potential value. Their normalized equations are based on 1710 chemical compounds and the Chebyshec theorem. The potential impact *I* of chemical process route *r*, $\overline{\psi^{s}_{r,I}}$ takes as reference the average of the impacts $\langle(Potenical)_r\rangle_I$ and twice the standard deviation for all the compounds involved in the reaction.
Ozone depletion potential (ODP)	"This impact category is determined by comparing the rate at which a unit mass of chemical reacts with ozone to form molecular oxygen to the rate at which a unit mass of CFC-11 (trichlorofluoromethane) reacts with ozone to form molecular oxygen. For a chemical to have ODP it must exist in the atmosphere long enough to reach the stratosphere, it, also, must contain a chlorine or bromine atom." (Young and Cabezas, 1999)		$\langle(Potenical)_r\rangle_I$	Average of impacts of components c in chemical process route *r* associated with the impact category *I*	
Photochemical oxidation potential (PCOP)	"This impact category is determined by comparing the rate at which a unit mass of chemical reacts with a hydroxyl radical ($OH^{\bullet}$) to the rate at which a unit mass of ethylene reacts with $OH^{\bullet}$." (Young and Cabezas, 1999)		$\langle(Potenical)_r\rangle_I$	Potential environmental impact of component c associated with the impact category *I*	
Acidification potential (AP)	"This impact category is determined by comparing the rate of release of H^+ in the atmosphere as promoted by a chemical to the rate of release of H^+ in the atmosphere as promoted by SO_2." (Young and Cabezas, 1999)		σ_I	Standard deviation of potential environmental impact of compounds associated with impact category *I*	

Table 2 – (Continued)

Indicator	Meaning	Equation		Nomenclature		Comments
Bio-concentration factor (*BCF*)	"Bio-concentration means net result of uptake, transformation and elimination of a substance in an organism due to waterborne exposure… The potential for bioaccumulation would normally be determined by using the octanol/water partition coefficient, usually reported as a $\log Kow$ determined by OECD Test Guideline 107 or 117." (United Nations, 2011)			$\overline{\psi_{r,I}^{s}}$	Normalized potential environmental impact of chemical process route *r* associated with impact category *I*	
Aquatic acute toxicity (*AATP*), L/mg	"Acute aquatic toxicity means the intrinsic property of a substance to be injurious to an organism in a short-term aquatic exposure to that substance… Acute aquatic toxicity would normally be determined using a fish 96 h LC_{50} (OECD Test Guideline 203 or equivalent), a crustacea species 48 h EC_{50} (OECD Test Guideline 202 or equivalent) and/or an algal species 72 or 96 hour EC_{50} (OECD Test Guideline 201 or equivalent)." (United Nations, 2011)	$AATP_c = \frac{1}{LC_{50c}}$	(7)	*AATP*	Aquatic acute toxicity	These indicators are part of the Globally Harmonized System of Classification and Labeling of Chemicals (GHS). The normalization method was originally presented by Srinivasan and Nhan (2008). The normalization is modified to consider all compounds.
				LC_{50}	Lethal concentration 50	
		$\overline{\psi_{r,I}^{s}} = 1 - \frac{\sum_{c=1}^{C} Potencial_{c,I}}{(\langle(\mathrm{Potencial})_r\rangle_I + 2\sigma_I) * C}$	(8)	Parameters of Eq. (8) are the same explained for Eq. (6).		
Potential degradability (*PD*)	"Degradation means the decomposition of organic molecules to smaller molecules and eventually to carbon dioxide, water and salts… Ready biodegradation can most easily be defined using the biodegradability tests (A-F) of OECD Test Guideline 301." (United Nations, 2011)	$PD_c = \frac{1}{D_c}$ and Eq. (8)	(9)	*D*	Ready biodegradation	
				PD	Potential degradability	

Table 2 – (*Continued*)

Indicator	Meaning	Equation		Nomenclature		Comments
Chronic aquatic toxicity (*CATP*), L/mg o ppm^{-1}	“Chronic aquatic toxicity means the intrinsic property of a substance to cause adverse effects to aquatic organisms during aquatic exposures which are determined in relation to the life-cycle of the organism... Chronic aquatic toxicity are determined according to the OECD Test Guidelines 210 (Fish Early Life Stage), or 211 (Daphnia Reproduction) and 201 (Algal Growth Inhibition)... NOECs or other equivalent ECx should be used.” (United Nations, 2011)	$CATP_c = \frac{1}{NOEC_c}$ and Eq. (8)	(10)	$CATP$	Chronic aquatic toxicity	
				$NOEC$	No observed effect concentration	
Renewable sources (R)	This indicator shows whether raw materials used in a chemical process routes are from renewable origin or not. It is zero for a renewable raw material and one in the case of a nonrenewable raw material. In the case of a partially renewable raw material, R_{rm} could be calculated apportioning the value according to the fraction of the molecular weight of renewable source.	$\overline{R_r} = \sum_{rm=1}^{RM} x_{rm} R_{rm}$	(11)	$\overline{R_r}$	Normalized renewable source of the chemical process route *r*	Eq. (11) was proposed in this study.
				R_{rm}	Value of renewable source of the raw material *rm*	
				RM	Total number of raw materials	
				x_{rm}	Fraction of the raw material *rm* in reactor feed	
Safety indicators						
Explosiveness (*Ex*)	“This is the tendency of chemicals to form an explosive mixture in the air”. It is calculated from the difference between the upper explosive limit (*UEL*) and the lower explosive limit (*LEL*) of each compound (Srinivasan and Nhan, 2008).	$\overline{Ex_r} = \sum_{c=1}^{C} \frac{Ex_C}{100C}$	(12)	C	Total number of compounds of chemical process route *r*	(Srinivasan and Nhan, 2008). The normalization is modified to consider all compounds involved in the chemical process route.
				Ex	Explosiveness	
				$\overline{Ex_r}$	Normalized explosiveness of the chemical process route *r*	

Table 2 – (*Continued*)

Indicator	Meaning	Equation		Nomenclature		Comments
				UEL	Upper explosive limit	
				LEL	Lower explosive limits	
Reactivity (Rx)	"This is the ability to react chemically in the presence of other chemicals" (Srinivasan and Nhan, 2008) and it is quantified by the classification given by the NFPA 704 (NFPA, 2012). This classification gives a value ranging from 0 (no hazard) to 4 (several impact).	$\overline{Rx_r} = \sum_{c=1}^{v} \frac{Rx_C}{4C}$	(13)	C	Total number of compounds of chemical process route r	
				$\overline{R_r}$	Normalized renewable source of the chemical process route r	
				R_{rm}	Value of renewable source of the raw material rm	
Flammability (Fx)	"This is the ease with which a material burns in the air" (King, 1990; Srinivasan and Nhan, 2008). This is quantified by the classification given by the NFPA 704 (NFPA, 2012).	$\overline{Fx_r} = \sum_{c=1}^{C} \frac{Fx_C}{4C}$	(14)	C	Total number of compounds of chemical process route r	
				Fx	Flammability	
				$\overline{Fx_r}$	Normalized flammability of the chemical process route r	
Temperature (Tr)	Reaction temperature scaled to a range of 0–1, using a frequency distribution of temperature for common reactions (Srinivasan and Nhan, 2008). When the chemical process route contents more than one chemical reaction, select the reaction temperature that leads to the highest normalized value of the indicator.	$\overline{T_r} = \begin{cases} 1 - e^{-(0.005T_r - 0.125)} & \text{for} \quad T_r > 25\,^{\circ}\mathrm{C} \\ 1 - e^{(0.020T_r - 0.500)} & \text{for} \quad T_r \leq 25\,^{\circ}\mathrm{C} \end{cases}$	(15)	T_r	Reaction temperature of the chemical process route r	(Srinivasan and Nhan, 2008; Young and Cabezas, 1999). The normalization is modified to consider all compounds.
				$\overline{T_r}$	Normalized reaction temperature of the chemical process route r	

Table 2 – (*Continued*)

Indicator	Meaning	Equation		Nomenclature		Comments
Pressure (*Pr*)	Reaction pressure scaled to a range of 0–1, using a frequency distribution of pressure for common reactions (Srinivasan and Nhan, 2008). When the chemical process route contents more than one chemical reaction, select the reaction pressure that leads to the highest normalized value of the indicator.	$\overline{P_r} = \begin{cases} 1 - e^{-0.03(P_r - 1)} & \text{for} \quad P_r > 1\,\text{atm} \\ 1 - e^{5.00(P_r - 1)} & \text{for} \quad P_r \le 1\,\text{atm} \end{cases}$	(16)	P_r	Pressure of the chemical process route *r*	
				$\overline{P_r}$	Normalized pressure of the chemical process route *r*	
Heat of reaction (ΔH_r)	Heat of reaction scaled to a range of 0–1, using a frequency distribution of heat of reaction for common reactions (Srinivasan and Nhan, 2008). When the chemical process route contents more than one chemical reaction, select the heat of reaction that leads to the highest normalized value of the indicator.	$\overline{\Delta H_r} = 1 - \frac{1}{1+4.45\times10^{-5}\,\Delta H_r^2}$	(17)	ΔH_r	Enthalpy of chemical process route *r*	
				$\overline{\Delta H_r}$	Normalized enthalpy of chemical process route *r*	
Yield (*Y*)	X and Y measure the quantity of raw material needed to achieve the desired production. Low values of *X* and Y indicate high recirculation rates and complex separation operations.	$\overline{Y_r} = \frac{100-Y_r}{100}$	(18)	Y_r	Yield of chemical process route *r*	(Srinivasan and Nhan, 2008)
				$\overline{Y_r}$	Normalized yield of reaction *r*	
Conversion (*X*)		$\overline{X_r} = \frac{100-X_r}{100}$	(19)	X_r	Conversion of chemical process route *r*	Its implementation is proposed in this study.
				$\overline{X_r}$	Normalized conversion of reaction *r*	

Table 2 – (*Continued*)

Indicator	Meaning	Equation		Nomenclature		Comments
Occupational health indicators						
Human toxicity potential by ingestion (*HTPI*), kg/mg	Human toxicity potential by ingestion (*HTPI*) is one of the four local toxicological categories from WAR algorithm (Young and Cabezas, 1999). For the calculation of *HTPI* of each compound the lethal dose value (LD_{50}) of each compound is used according to Eq. (20). "LD_{50} means the amount of a chemical, given all at once, which causes the death of 50% (one half) of a group of test animals" (United Nations, 2011). For the calculation of the *HTPI* impact of the chemical process route, Eq. (8) is applied.	$HTPI_c = \frac{1}{LD_{50c}}$ and Eq. (8)	(20)	*HTPE*	Human toxicity potential by ingestion	(Srinivasan and Nhan, 2008; Young and Cabezas, 1999)
				LD_{50}	Lethal dose 50	
Human toxicity potential by inhalation or dermal exposure (*HTPE*), m^3/mg	Human toxicity potential by inhalation or dermal exposure (*HTPE*) is one of the four local toxicological categories from WAR algorithm (Young and Cabezas, 1999). For the calculation of *HTPI* of each compound equation the threshold limit value – time weighted average (*TLVTWA*) of each compound is used as shown in Eq. (21). For the calculation of the *HTPE* impact of the chemical process route, Eq. (8) is applied.	$HTPE_c = \frac{1}{TLVTWA_c}$ and Eq. (8)	(21)	*HTPE*	Human toxicity potential by inhalation or dermal exposure	
				TLVTWA	Threshold limit value – time weighted average	
Toxicity	"This is a property of the substance that destroys life or injures health when introduced into or absorbed by a living organism" (Wells, 1980; Srinivasan and Nhan, 2008). This is quantified by the classification given by the NFPA 704 (NFPA, 2012).	$\overline{Tx_r} = \sum_{c=1}^{C} \frac{Tx_c}{4C}$	(22)	*Tx*	Toxicity	(Srinivasan and Nhan, 2008). The normalization is modified to consider all compounds.
				$\overline{Tx_r}$	Normalized toxicity of reaction *r*	

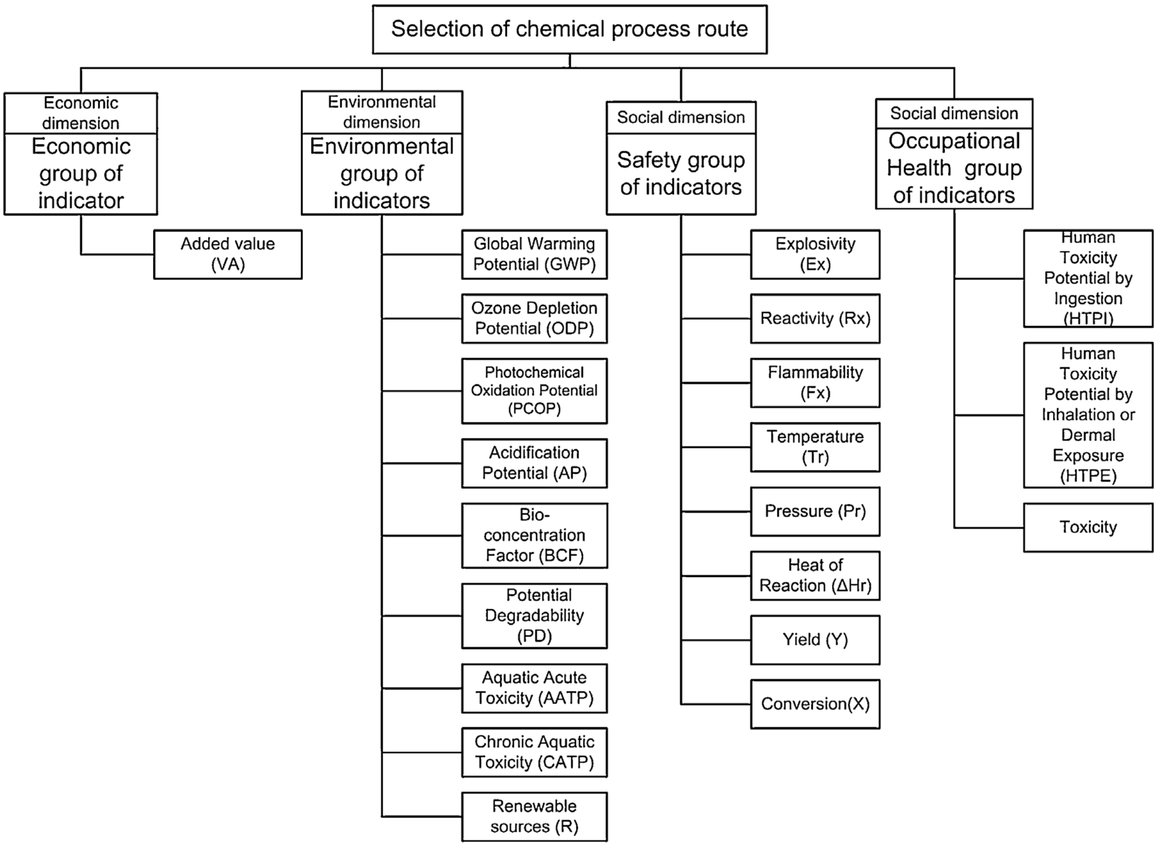

Fig. 2 – Sustainability indicators involved in the selection of a chemical process route.

considering the stoichiometry of each reaction, as shown in Eqs. (1)–(4). For its normalization, Eq. (5) is applied.

Energy costs are not considered in this analysis because when the chemical process route is being selected there is not enough information for the calculation of the energy requirements of the process. Chemical process route defines products and sub-products of the process and in this way it also constrains later decisions, specially upstream and downstream operations. Moreover, most of the energy is consumed by the latter, whose design is defined after the selection of the chemical process route. Methods to determine how the selection of a chemical process route affects the total energy consumption can be considered in a future research.

2.2.2.2. *Environmental indicator group*. Nine indicators are included to assess the environmental dimension of the different chemical process routes. The environmental indicators proposed are sub-classified into three groups:

- The first sub-group corresponds to four indicators that have been used in the calculation of the Potential Environmental Impact (PEI) by Young and Cabezas (1999) in the WAR algorithm and also by Srinivasan and Nhan (2008): global warming potential (*GWP*), ozone depletion potential (*ODP*), photochemical oxidation potential (*PCOP*), and acidification potential (*AP*).
- The second sub-group of indicators is calculated from properties established in the Globally Harmonized System of Classification and Labeling of Chemicals (GHS, United Nations, 2011). These four indicators evaluate the environmental hazards, particularly the impact of chemical substances in water: bio-concentration factor (*BCF*), primary degradation (*PD*), aquatic acute toxicity (*ATP*) and the chronic aquatic toxicity (*CAT*).
- The last sub-group is the renewable raw materials indicator (*RS*), which is a binary indicator proposed in this study. It measures the renewability of the raw materials employed in the reaction, which is a very important factor in the current chemical industry considering the trend to produce bio-based products. This indicator is zero in the case of a renewable raw material and one if it comes from fossil resources. In the case of raw material produced from renewable and non-renewable sources, the value will be the mass fraction from non-renewable origin.

Equations to calculate the normalized environmental indicators are listed in Table 2. For their normalization this study takes into account the individual indicators evaluated for all the components involved in the reactions as shown in Eqs. (6)–(11). Other approaches calculate indicators based on the component with the most critical value (Srinivasan and Nhan, 2008). In this work, they are calculated based on the average of all components. It means that all the components involved in a chemical process route have the same relative importance. This is done because it was considered that just using the most critical component for assessing a chemical process route can lead to an overestimation of its impact, for example when this component is used in small quantities or when the critical component is quickly consumed. Additionally, quantities of components change during the entire process as they are transformed from raw materials to products, making the weighted average inapplicable.

2.2.2.3. *Safety indicator group*. Safety indicators are related to the social dimension. In this case, the indicators proposed by

Srinivasan and Nhan (2008) were used. They are classified into two sub-groups: those related to the chemical nature of the compounds and those related to the operating conditions of the chemical process route.

- Related to the chemical nature of the compounds: explosiveness (*Ex*), reactivity (*Rx*), flammability (*Fx*)
- Related to the operating conditions: temperature (*T*), pressure (*P*), heat of reaction (ΔH_r), yield (*Y*) and conversion (*X*).

Eqs. (12)–(19) listed in Table 2 are used to calculate the normalized safety indicators. As previously indicated, the normalization procedure considers all components involved in each chemical process route.

2.2.2.4. Occupational health indicator group. As safety indicators, the occupational health indicators are also part of the social dimension. The indicators used in this study are: human toxicity potential by ingestion (*HTPI*), human toxicity potential by inhalation or dermal exposure (*HTPE*), and toxicity. Their calculation and normalization is described in Eqs. (20)–(22). The normalization procedure considers all components involved in each chemical process route.

2.3. *Third stage: Integration of assessments*

During this stage, indicators are combined to achieve an integrated sustainability assessment. This stage comprises the selection and application of an MCDA method to obtain weights and influences of the indicator groups previously described (Fig. 2), and the calculation of the Sustainable Cumulative Index (*SCI*) for each route under study.

In general, all MCDA methods organize a problem logically and provide tools for its visualization. The difference between them is the form in which each method evaluates alternatives relative to the criteria. To select one of them, decision-makers have to know the structure of the problem, the required input information, the modeling effort, and the outcomes that can be obtained. There are many MCDA methods that can be used to analyze a specific problem. Decision-makers need to know which of them better meets their preferences and they must correctly read the results to make a good decision. Description of different MCDA can be found elsewhere (Ishizaka and Nemery, 2013; Jato-Espino et al., 2014; Statnikov et al., 2005).

In this case, a combination of two MCDA methods was selected: Analytic Hierarchy Process (AHP) and Decision Making Trial and Evaluation Laboratory (DEMATEL). AHP is a method developed by Saaty (1980), whose principal advantage is its adaptability to different types of problems. It can be applied to complex problems, because it breaks them down into sub-problems and organizes them according to a hierarchical structure. Additionally, it does not require a prior definition of a preference function, but uses pairwise comparison between criteria and alternatives (Ishizaka and Nemery, 2013). Another advantage of this method is that additional and/or different indicators can be easily included in its structure.

DEMATEL is a method developed in 1972 by Gabus and Fontela, used to model the relation between variables. It is based on diagrams which separate the variables into two groups: causes and effects (Awhasti and Grzybowska, 2014). In this work the use of DEMATEL is proposed because it can identify the influences among the indicator groups. This approach combines the adaptability of AHP and the analysis of interdependences provided by DEMATEL to select the most sustainable chemical process route. For the application of both methods, the opinion of experts is required, because sustainability assessment is part of the specialized knowledge of different production sectors. Therefore, the relative importance and influences of dimensions as well as the type of indicators can change according to the type of industry.

2.3.1. *Calculation of weights of indicator groups using Analytic Hierarchy Process (AHP)*

AHP comprises four main steps: hierarchical structuring of the problem, assignment of weights, consistency test, and sensibility analysis (Ishizaka and Nemery, 2013).

- Hierarchical structuring of the problem: The method breaks down the problem and organizes its parts hierarchically. The top level is the goal of the decision, the second level comprises the criteria, and the lowest level contains the alternatives. In the chemical process route selection problem, the goal is to select the most sustainable one. The criteria are the four sustainability indicator groups shown in Fig. 2 (economic, environmental, safety and occupational health), and the alternatives are the different routes under consideration.
- Assignment of weights: Weights are calculated for each indicator group using the pairwise comparison given by experts and the eigenvalue method. The pairwise comparison is generally made on a ratio scale from 1 to 9, where 1 means equal importance among two indicator groups, and 9 means that one indicator group is much more important than the other.
- Consistency test: To know if the weights are meaningful, that is, that there are not contradictions between the answers given by each expert during pairwise comparison, a consistency test related to eigenvalue method is performed. In this study, the answers with a consistent index less than 20% are considered as consistent.
- Sensibility analysis: Weights are varied in order to observe the robustness of the solution.

2.3.2. *Calculation of influences between indicator groups using Decision Making Trial and Evaluation Laboratory (DEMATEL)*

DEMATEL comprises the following steps (Tan et al., 2012):

- Construction of the original impact matrix (**A**): This matrix is created from pairwise comparisons made by experts, who evaluate how a criterion *i* affects a criterion *j* using an integer scale from 0 to 4. Zero means no influence and four means a very strong influence of one criterion over another. Matrix **A**, composed of elements $a_{i,j}$, is an $n \times n$ matrix, where *n* corresponds to the criteria number. In this study, the criteria are the four indicator groups: economic, environmental, occupational health, and safety.
- Calculation of direct impact matrix (**M**): This matrix **M** is called also the normalized matrix of influences. The normalization seeks to establish the values of the whole influences for all criteria in a range between 0 and 1. In order to normalize these influences a *k* value is used. It is defined as the maximum absolute influences of the criterion *i* to the other criteria ($\sum_{1\leq i\leq n}^{n}\sum_{i=n}^{n} a_{ij}$; sum of the rows) and the sum of the influences of the criterion *j* ($\sum_{1\leq j\leq n}^{n}\sum_{j=n}^{n} a_{ij}$; sum of

the columns) as stated by Eq. (23). Then, the computed value of k is used to obtain $\mathbf{M}$ using Eq. (24).

$$k = \max\left[\max_{1\le i\le n}\sum_{j=1}^{n} a_{ij}, \max_{1\le i\le n}\sum_{i=1}^{n} a_{ij}\right] \tag{23}$$

$$\mathbf{M} = \frac{1}{k}\mathbf{A} \tag{24}$$

- Calculation of the total impact matrix ($\mathbf{T}$): $\mathbf{M}$ is divided by the subtraction between the identity matrix $\mathbf{I}$ and $\mathbf{M}$ to obtain $\mathbf{T}$.

$$\mathbf{T} = \frac{\mathbf{M}}{\mathbf{I}-\mathbf{M}} \tag{25}$$

- Calculation of influences: The rows and columns of T are added to get Ri and Cj respectively. Ri is the total influence of criterion i over all other criteria of the system, while Cj corresponds to the total influence of other criteria over criterion j.

$$Ri = \left[\sum_{j=1}^{n} t_{ij}\right]_{(n\times 1)} \tag{26}$$

$$Cj = \left[\sum_{i=1}^{n} t_{ij}\right]'_{(1\times n)} \tag{27}$$

- The value $Ri + Cj$ shows the magnitude of the influence of a criterion over others, and the value $Ri - Cj$ shows the difference between the influence given and received. If $Ri - Cj$ is larger than zero, the criterion is classified as causal, i.e., the criterion has an impact on others. On the other hand, if $Ri - Cj$ is smaller than zero, the criterion is classified as affected, that is, the criterion is impacted by others.
- Construction of influences map, where the horizontal axis corresponds to $Ri + Cj$ and the vertical axis to $Ri - Cj$.

More details about the application of the method can be found in the open literature (Tan et al., 2012; Awhasti and Grzybowska, 2014).

2.3.3. Calculation of Sustainable Cumulative Index (SCI) for each chemical process route

For the calculation of the Sustainable Cumulative Index (SCI) for each chemical process route, initially, a group index representing the effect of each of the four indicator group is calculated; subsequently, each group index is multiplied by its respective integrated weighting factor (IWF) calculated with Eqs. (28) and (29), and finally, they are added to obtain the SCI of the chemical process route, as shown in Eq. (30).

For the four indicator groups (economic, environmental, safety and occupational health), the group index is calculated with the average of the indicators forming each group (Fig. 2). It means each indicator within a group has the same relative importance. However, it would be possible to give them different weights in a similar way to that employed for the four indicator groups (by the implementation of AHP). Despite this, and considering that the objective of this work is to illustrate a decision-making methodology, the calculation of different weights for indicators will increase the complexity. Moreover, it could be a very complex task because the relative importance of the indicators can be function of the specific context (chemical industry, chemical products, regions, etc.).

Integrated weighting factor (IWF) combines the weights calculated with AHP and the effect of influences calculated with DEMATEL. It is calculated considering the logic of DEMATEL, according to which a causal criterion should have in some percent a greater weight than the one initially calculated by AHP (Eq. (28)). Similarly, affected criteria should have in some percent a lower weight than the one given by AHP (Eq. (29)). A sensitivity factor (P) is defined as a parameter representing the degree of impact of the influences obtained by DEMATEL on the weights obtained by AHP. This form of calculation keeps the sum of the integrated weighting factors at 100%, as required by the AHP method. The value of P has to be decided by the decision-maker. For example, if the decision-maker considers that influences between indicator groups are mild, P will be small. On the other hand, if he or she believes that the indicator groups are closely related, P will be high. In this study, P was varied in a sensitivity analysis to check how the selection of the chemical process route could be affected, when interrelations between sustainability dimensions are considered.

If, according to the results given by DEMATEL, the indicator group is causal,

$$IWF_{ig} = W_{AHP,ig} + P \cdot \frac{(Ri + Cj)_{DEMATEL,ig}}{\Sigma_{\text{all causal } ig}(Ri + Cj)_{DEMATEL,ig}} \tag{28}$$

If, according to the results given by DEMATEL, the indicator group is affected,

$$IWF_{ig} = W_{AHP,ig} - P \cdot \frac{(Ri + Cj)_{DEMATEL,ig}}{\Sigma_{\text{all causal } ig}(Ri + Cj)_{DEMATEL,ig}}$$
$$ig = \{ec, e, s, oh\} \tag{29}$$

Here IWF_{ig} represents the integrated weighting factor of each of the four indicator groups (ig), which are economic (ec), environmental (e), safety (s) and occupational health (oh). $W_{AHP,ig}$ corresponds to the weights of each indicator group given by AHP and $(Ri + Cj)_{DEMATEL,ig}$ is the influence of each indicator group given by DEMATEL. P is the percent in which weights are modified because of the effect of the influences. With these values it is possible to calculate the Sustainable Cumulative Index of each chemical process route (SCI_r) as shown in Eq. (30).

$$SCI_r = IWF_{ec}\cdot I_{ec} + IWF_e \cdot I_e + IWF_s \cdot I_s + IWF_{oh}\cdot I_{oh} \tag{30}$$

Here I_{ig} is the group index of each indicator group calculated with the average of indicators within each group (Fig. 2).

The larger the SCI value, the lower the sustainability of the chemical process route. With the result of SCI for each alternative, the decision-maker can rank them, compare them and finally select the most sustainable option.

3. Case study: selection of the chemical process route for the production of ethyl acetate

The methodology previously presented is illustrated with the selection of a chemical process route to produce ethyl acetate.

Table 3 – Standard specification for ethyl acetate (ASTM International, 2011).[a]

Property	Grade			
	85–88	99	99.5	99.5 urethane
Minimum purity (%p/p)	85.0–88.0	99	99.5	99.5
Max. alcohol (%p/p)	–	0.5	0.2	0.2
Highest possible color value (Pt-Co)	10	10	10	10
Distillation range (°C)	71.0–79.0	71.0–78.0	71.0–78.0	71.0–78.0
Max. non-volatile material (mg/100 ml)	5	5	5	5
Odor	Non-residual	Non-residual	Non-residual	Non-residual
Max. water (%p/p)	0.02	0.1	0.1	0.05
Max. acidity (%p/p)	0.01	0.01	0.01	0.01
Specific gravity 20/20 °C	0.882–0.887	0.900–0.903	0.900–0.903	0.900–0.903
Specific gravity 25/25 °C	0.877–0.882	0.895–0.898	0.895–0.898	0.895–0.898

[a] Reprinted, with permission, from ASTM D4614-11 Standard Specification for Ethyl Acetate (All Grades), copyright ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428. A copy of the complete standard may be obtained from ASTM, www.astm.org.

3.1. *Identification of alternatives*

3.1.1. *Knowledge of the product*

Ethyl acetate is a commodity widely used as a solvent in many chemical products and formulations, including epoxy and urethane coatings, inks, pharmaceuticals, herbicides, and foods. Table 3 contains some functional properties of ethyl acetate according to its grade (ASTM International, 2011). Physicochemical properties as well as safety data can be found in supplementary bibliography (NIST, 2011a; NTP, 2015; NIOSH USA, 2011), among others.

3.1.2. *Identification of chemical process routes*

This study evaluates the following chemical process routes for the production of ethyl acetate.

Reaction 1 corresponds to the reaction between acetic acid and ethanol in the presence of an acid catalyst. It is also known as Fischer esterification. This reaction is reversible and strategies to shift the reaction toward the products are implemented. The conditions under which this reaction occurs are shown in Table 5.

Reaction 2 corresponds to the dehydrogenation of ethanol to ethyl acetate. The catalyzed reaction occurs at a relatively high temperature and at a moderate pressure, as shown in Table 5.

Reaction 3 corresponds to the condensation or dimerization of acetaldehyde in the presence of a catalyst to produce ethyl acetate. The conditions for this reaction are shown in Table 5.

Reaction 4 corresponds to the direct addition of ethylene and acetic acid. In this reaction, acetic acid and ethylene react under conditions of relatively high temperature and at a moderate pressure to produce ethyl acetate. The conditions for this reaction are shown in Table 5.

The four reactions are shown in Fig. 3.

3.1.3. *Information gathering*

Table 4 summarizes most of the properties for the different compounds involved in the chemical process routes described in Fig. 3, excluding water. Table 5 presents some operating conditions used in each chemical process route. These values were obtained from technical reports of industrial processes and from the thermodynamic analysis of each reaction.

3.2. *Assessment of chemical process routes through sustainability indicators*

To illustrate the use of the methodology, most of the indicators described in Table 2 were included. Only ozone depletion potential (ODP) and acidification potential (AP) were excluded, because they are not relevant for the compounds involved in the chemical process routes assessed. Table 6 summarizes the results.

According to results in Table 6 there is not an entirely good chemical process route for the production of ethyl acetate. For example, reaction 4 has the best economic potential but the worst environmental and occupational health performance. On the other hand, reaction 2 has the best environmental and occupational health characteristics, but a relatively poor performance in safety and economic terms. To make a selection, a compromise between indicator groups has to be reached. MCDA methods are used to identify the most sustainable route by including the knowledge of experts about sustainability in the specific selection problem.

3.3. *Integration of assessments*

As described in Section 2.3, the Analytic Hierarchy Process (AHP) method was selected for the calculation of weights and Decision Making Trial and Evaluation Laboratory (DEMATEL) for the analysis of interactions. The calculation of weights and influences was made from data collected in two groups of analysts. The first group comprised 23 experts from different fields of the chemical sector (industrial experts in the market of plasticizers, oil and gas, chemical sales, academics and researchers). The second group comprises 22 senior students of chemical engineering. They were interviewed with an online survey that is presented in the supplementary material.[1]

The survey had three parts. The first was a general explanation about the objectives of the study, the chemical process under analysis, and the assessment scales. The second part asked the interviewee to perform the pairwise comparison between the four indicator groups, using the scaling ratio from 1 to 9 of AHP. The third part asked about the influences between pairs, with a scaling from 0 to 4 used for the calculation of DEMATEL.

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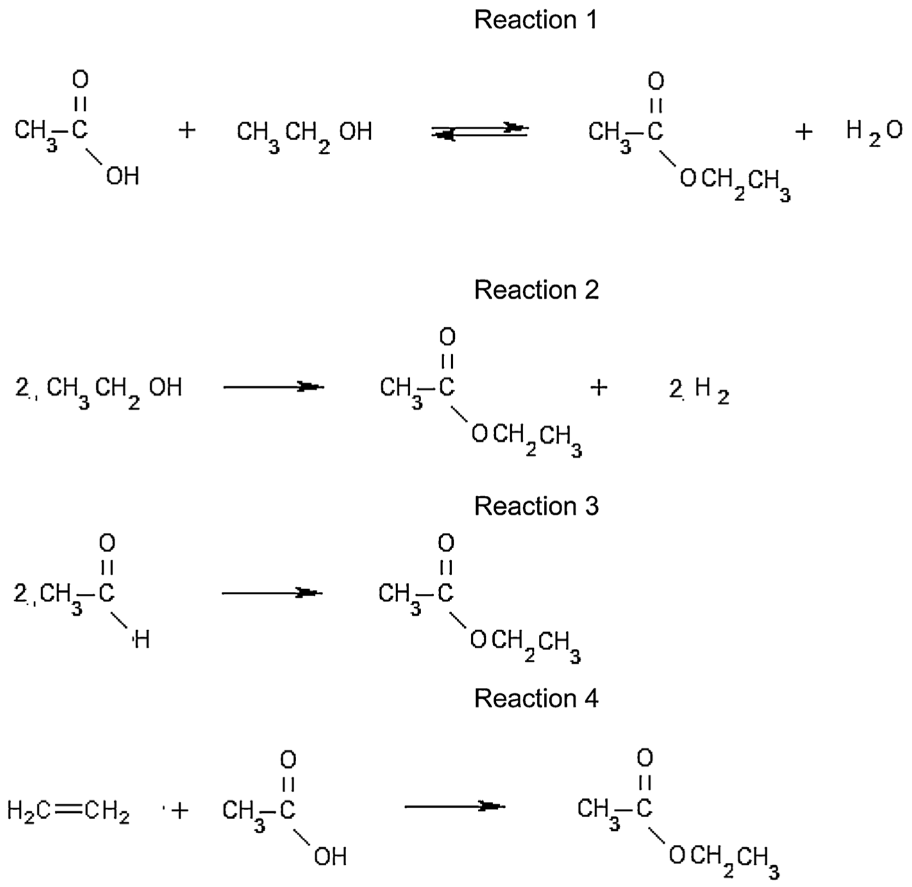
[1] https://docs.google.com/forms/d/1MQrgQnPf_F5me6ZbF4PYXaanmnohlw7ltn7gF4KHIbM/viewform?c=0&w=1.


Reaction 1

Reaction 2

Reaction 3

Reaction 4

Fig. 3 – Chemical process routes under analysis for ethyl acetate production. (Reaction 1) Fischer esterification between acetic acid and ethanol. (Reaction 2) Dehydrogenation of ethanol. (Reaction 3) Condensation of acetaldehyde. (Reaction 4) Direct addition of ethylene and acetic acid.

Table 4 – Properties used for the calculation of the sustainability indicators for the selection of the chemical process routes to produce ethyl acetate.

Properties	Acetic acid	Ethanol	Acetaldehyde	Ethylene	Ethyl acetate	Hydrogen
Price (U$/t)	655	1011	1002	1141	1852	2024[a]
UEL (%vol)	19.9	19	60	36	11.5	76
LEL (%vol)	4	3.3	4	2.7	2	4
Ex	0.159	0.157	0.56	0.333	0.095	0.72
Rx	2	0	2	2	0	0
Fx	2	3	4	4	3	4
RS	1	0	1	1	–	–
GWP	1.47	0	1.995	3.14	2	5.8
ODP	0	0	0	0	0	0
PCOP	0.187	0.407	1.8	2.5	0.167	–
AP	0	0	0	0	0	0
LC_{50} (mg/L)	410	11,200	37.2	50	256	–
AATP	2.4×10^{-3}	8.9×10^{-5}	2.7×10^{-2}	2.0×10^{-2}	3.9×10^{-3}	0
log *Kow*	−0.17	−0.32	−0.22	1.13	0.73	–
BCF	0.292	0.222	0.267	4	1.502	–
Degradability (%)	58	60	93	0	36	–
PD	1.724	1.667	1.075	–	2.778	0
NOEC (mg/L)	1.26	380	–	13	–	–
CATP	7.9×10^{-1}	2.6×10^{-3}	2.1×10^{-2}	7.7×10^{-2}	3.8×10^{-3}	0
EC_{50} (mg/L)	–	–	48	260	260	–
LD_{50} (mg/kg)	3530	3750	500	950,000	5620	–
HTPI	2.8×10^{-4}	2.7×10^{-4}	2.0×10^{-3}	1.1×10^{-6}	1.8×10^{-4}	0
TLV (ppm)	10	1000	200	400	400	–
HTPE	0.1	0.001	0.005	0.0025	0.0025	0
Toxicity	2	0	2	1	1	0

Sources: EPA (2012), ICIS (2008), IPCS and CCOHS (2014), IPPC (2007), Kegley et al. (2014), NIOSH USA (2011), NMSU (2015).

[a] The price of hydrogen (US Department of Energy, 2012) was not used for the calculation of the added value because it was considered that hydrogen produced in this reaction would probably be consumed within the process.

Table 5 – Operating conditions of the chemical process routes for the production of ethyl acetate.

Operating condition	Reaction 1	Reaction 2	Reaction 3	Reaction 4
Temperature	70[a]	245[b]	5[c]	195[d]
Pressure	1[a]	15[b]	1[c]	16[d]
Conversion	69.9[e]	94[b]	98[c]	8[d]
Yield	98.2[e]	45[b]	95[c]	97[d]
Time	1[a]	1[b]	1[c]	1[d]
Heat of reaction	−3.64[e]	30.0[e]	−86.7[e]	230.9[e]

[a] Conditions defined from Mazzotti et al. (1997) and Gui et al. (2004).

[b] Data reported for the dehydrogenation reaction in Colley et al. (2004). Reported space velocities for the reaction are between 0.2 h^{-1} and 1.5 h^{-1} depending on the catalyst. A value of approximately 0.5 h^{-1} is considered appropriate for preliminary calculations.

[c] Data reported for the dehydrogenation reaction in Törmäkangas and Koskinen (2001) and Riemenschneider and Bolt (2005). Reported reaction times for the reaction are between 0.2 h and 5 days. A value of 1 h is considered as appropriate for preliminary calculations.

[d] Data taken and calculated from Fullerton and Miller (2005). Although the authors reported a space velocity from 300 to 2000 h^{-1}, another source indicated a time of 3 h for a batch reaction (Kirk and Othmer, 1995) and a third source reported a time between 2 and 5 h (Gregory et al., 1983). A value of 1 h is considered appropriate for preliminary calculations.

[e] Values calculated from the thermodynamic properties reported in NIST (2011b) and Smith et al. (2001).

Table 6 – Normalized sustainability indicators of the chemical process routes for the production of ethyl acetate.

Indicator group	Normalized indicators	Reaction 1	Reaction 2	Reaction 3	Reaction 4
Economic indicator group	$\overline{VA_r}$	0.474	0.429	0.459	0.563
	Economic index	**0.526**	**0.571**	**0.541**	**0.437**
Environmental indicator group	$\overline{GWP^s_{r.I}}$	0.297	0.000	0.996	0.564
	$\overline{PCOP^s_{r.I}}$	0.363	0.305	0.299	0.262
	$\overline{BCF^s_{r.I}}$	0.271	0.262	0.330	0.338
	$\overline{PD^s_{r.I}}$	0.549	0.346	0.444	0.349
	$\overline{AATP^s_{r.I}}$	0.703	0.770	0.679	0.689
	$\overline{CATP^s_{r.I}}$	0.798	0.564	0.661	0.750
	$\overline{R^s_{r.I}}$	0.566	0.000	1.000	1.000
	Environmental index	**0.507**	**0.345**	**0.630**	**0.564**
Safety indicator group	$\overline{Ex_r}$	0.103	0.324	0.328	0.196
	$\overline{Rx_r}$	0.125	0.000	0.250	0.333
	$\overline{Fx_r}$	0.500	0.833	0.875	0.750
	$\overline{T_r}$	0.201	0.667	0.330	0.573
	$\overline{P_r}$	0.000	0.335	0.000	0.359
	$\overline{\Delta H_r}$	4.37×10^{-4}	0.039	0.251	0.703
	$\overline{Y_r}$	0.018	0.550	0.050	0.030
	$\overline{X_r}$	0.301	0.060	0.020	0.920
	Safety index	**0.156**	**0.351**	**0.263**	**0.483**
Occupational health indicator group	$\overline{HTPE^s_{r.I}}$	0.582	0.647	0.703	0.649
	$\overline{HTPE^s_{r.I}}$	0.793	0.683	0.485	0.756
	$\overline{Tx_r}$	0.188	0.083	0.375	0.333
	Occupational health index	**0.521**	**0.471**	**0.521**	**0.579**

3.3.1. *Calculation of weights of indicator groups using Analytic Hierarchy Process (AHP)*

With the answers of experts and students, AHP was applied in order to calculate the weights. The consistency of data was checked and, due the complexity of the problem and the responses obtained, only data with a consistency index of less than 20% were implemented in further analysis. After data filtration, consistent responses corresponded to 20 out of the 23 experts, and 13 out of the 22 senior students. The results for experts and students are presented in Fig. 4.

Weights are very similar for students and experts, safety being the most important indicator group. Surprisingly, the economic group has the lowest percentage for both surveyed populations. This result is interesting, because it means that even considering that commodities such as ethyl acetate have a low marginal utility, experts and students prioritize safety and environmental performance over the economic aspect, in accordance with one of the green engineering principles (Mendez, 2007). This can be explained by taking into account two factors. First, as mentioned before, there is more awareness of the importance of the social and environmental dimensions in process design. Unsafe and polluting processes are simply unacceptable. Second, for experts and students the dimensions are interrelated. For example, a

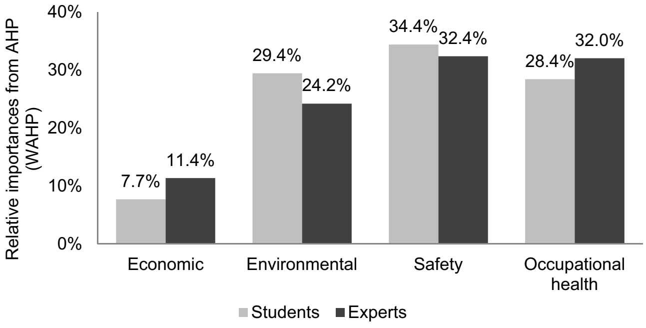


Fig. 4 – Relative importance of indicator groups calculated with Analytic Hierarchy Process (AHP) according to experts and students.

Table 7 – Results of the influences between indicators calculated with Decision Making Trial and Evaluation Laboratory (DEMATEL) according to experts and students.

Indicator groups	Influences					
	Results of DEMATEL for experts			Results of DEMATEL for students		
	R + C (intensity)	R − C (direction)		R + C (intensity)	R − C (direction)	
Economic	7.29	−0.23	Affected	8.23	−0.21	Affected
Environmental	7.85	−0.07	Affected	8.05	0.26	Causal
Safety	8.25	0.31	Causal	8.29	0.05	Causal
Occupational health	7.87	−0.00	Affected	7.87	−0.10	Affected

process that is inherently less safe than others requires additional investment to control potential risks. Similarly, an inherently safe process means lower operating cost and more reliability, which in the end has a positive effect on the economic dimension.

3.3.2. *Calculation of influences between indicator groups using Decision Making Trial and Evaluation Laboratory (DEMATEL)*

DEMATEL carefully explores the interrelations between indicator groups. The results of the method are summarized in Table 7 and Fig. 5. Fig. 5a shows that the expert panel considers that safety has a strong influence over all other indicator groups, and that the economic group is affected by the other three. For the expert panel, DEMATEL classifies safety as causal and the other three indicator groups as affected. On the other hand, Fig. 5b shows that students have a different perspective. For them the environmental indicator group takes precedence over the others, including safety, although the latter has a larger influence over occupational health and economics. For the student panel, DEMATEL classifies safety and environmental groups as causal and the other two as affected.

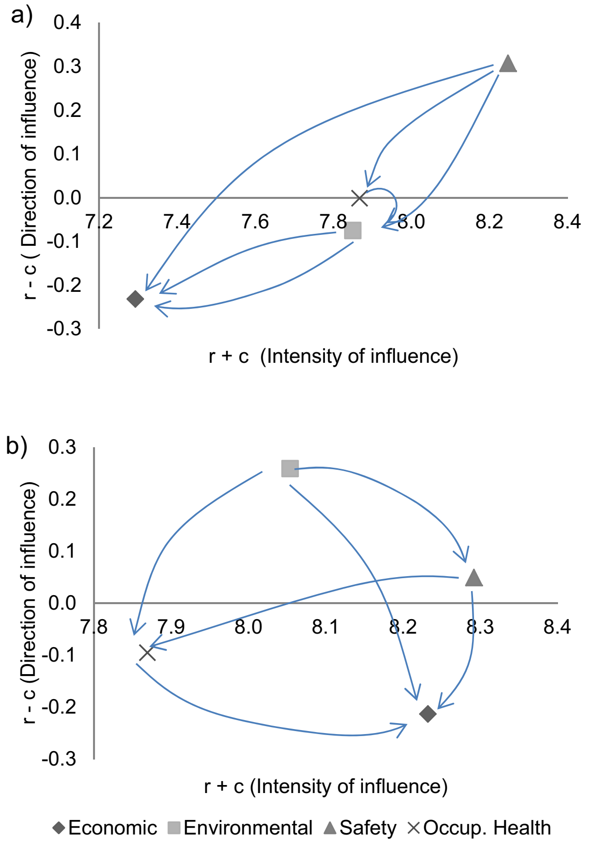


Fig. 5 – Impact diagram of indicator groups calculated with Decision Making Trial and Evaluation Laboratory (DEMATEL) according to (a) experts' survey and (b) students' survey.

3.3.3. *Calculation of the Sustainable Cumulative Index (SCI)*

This section presents the results of the integration of the different assessments. The first step is to calculate the integrated weighting factors, considering weights and influences among indicator groups using Eqs. (28) and (29). A variation of the sensitivity factor (P) allows the decision-maker to see how the integrated weighting factors are affected by the influences. To represent this effect, P is varied 5% each time, as shown in Fig. 6.

Fig. 6a shows the variation of integrated weighting factors for the expert panel. When P is equal to 0%, the original weights from AHP are obtained. As P increases, the integrated weighting factors of the economic, environmental and occupational health groups decrease, because they were classified as affected by DEMATEL. Correspondingly, the integrated weighting factor for safety increases, because it was classified as causal. Fig. 6b shows the analysis of the integrated weighting factors for the student panel, where two indicator groups, economic and occupational health, are considered as affected and their integrated weighting factors decrease with the increment of P, while the other two indicator groups, environmental and safety, are classified as causal and their weighting factors increase with the increment of P.

To select between the chemical process routes, the *SCI* for each route is calculated by Eq. (30) to obtain the alternative that represents the best compromise considering the importance and influences of the four indicator groups. The results (Fig. 7) show that the reaction between acetic acid and ethanol (Reaction 1) and the dehydrogenation of ethanol (Reaction 2) are the most sustainable of the alternatives. This can be explained in part because these chemical process routes have the best performance in safety and environmental criteria, respectively. However, in the case of the experts, as interrelations between criteria are considered and the value of P increases, the importance of safety also increases, and reaction 1 begins to be more favorable, as shown in Fig. 7a.

In the case of the students, even when influences are considered, the scores of both reactions are very similar, which means that either of them performs well in terms of sustainability according to their opinion. Although a further decision has to be taken, the methodology enabled screening-out of the worst options. To finally select one chemical process route, new information and new decision criteria must be searched for and agreed on. Concerning the case of experts, when influences are considered it is possible to observe that the choice of the first route is favored because, according to them, safety

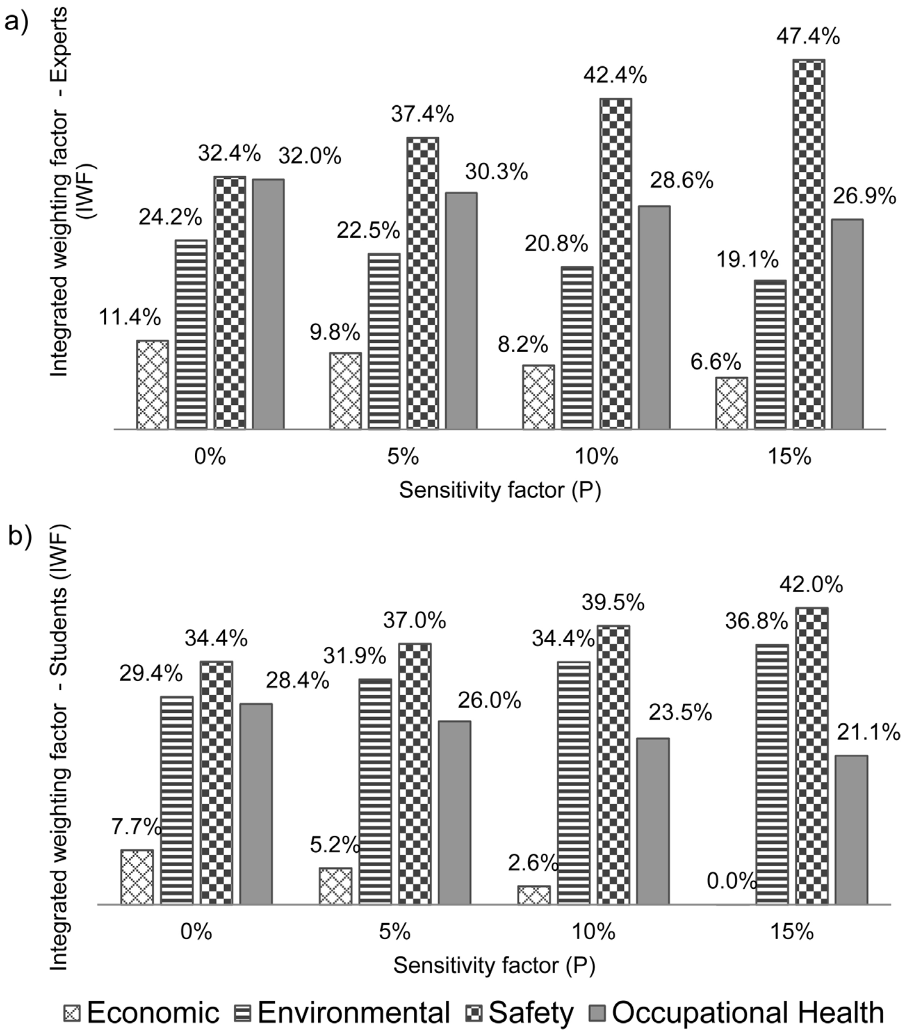


Fig. 6 – Sensitivity analysis of the integrated weighting factors (IWF) by changing the sensitivity factor (P) (a) according to experts; (b) according to students.

has a causal influence over other criteria and the first route is the safest of the alternatives.

4. Discussion

As the previous example has shown, the selection of a specific chemical process route based upon sustainability indicators must consider both the specific product characteristics and the preferences of the decision-maker. The obtained set of weights and influences is specific for ethyl acetate, which means that for another product the integrated weighting factors could be different, even if the values of the product indicators are similar. As a matter of example, we can consider the particular case of a radioactive product for nuclear applications. In this case, safety will greatly affect the other indicator groups and its weight will be dominant. This means that, for a given design case, this type of influences must be formalized and understood at the very early stages of the process synthesis. The proposed Sustainable Cumulative Index (SCI) seeks to provide this information to the decision-maker by means of the integration of AHP and DEMATEL.

Another interesting aspect to be considered is that there is not merely a sole decision-maker in this type of project, but a group of stakeholders that contributes to the decision. This aspect was illustrated in our example, where the preferences of two groups, experts and students, were evaluated. Although the profile of weights seems similar, there are interesting differences, for example, when comparing environmental and occupational health indicator groups (Fig. 4). More significant differences are observed when influences are considered (Fig. 5). Impact diagrams (Fig. 5) show that safety is the most influential dimension for experts, whereas for students it is environment.

Regarding the sensitivity factor (P), the objective is to provide further comprehension, not only on a particular value of influence, but in a dynamic way. This entails identifying how the intensity of the influences could determine a particular behavior of the weighting factors (Fig. 6) and of the SCI (Fig. 7). In this particular case, influence variation does not change the ranking of the chemical process routes under study, as Reaction 1 is still the best alternative. In this case, this analysis enables a better discrimination between alternatives (see trajectory of reactions 1 and 2 in Fig. 7a) or the original ranking is confirmed (as shown in Fig. 7b).

A potential improvement for the integration of methods to define a value of P could be based on a descriptive analysis of interrelations like component analysis (PCA) or correlation analysis. Another improvement could be made by the application of the AHP-DEMATEL method to both levels of aggregation of the problem (indicators and indicator groups).

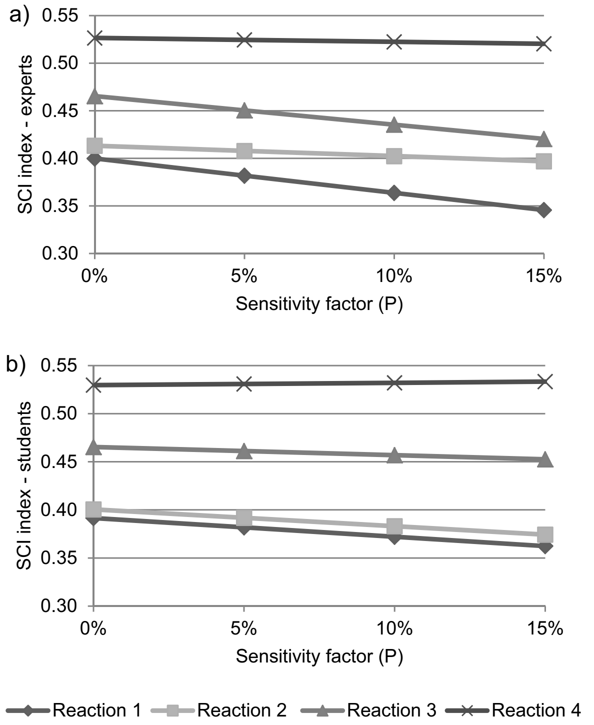


Fig. 7 – Sensitivity analysis of the Sustainable Cumulative Index (SCI) by changing the percentage P (a) according to experts; (b) according to students.

As observed, the methodology proposed here is easy to apply, and becomes a rapid conceptual design tool for the systematic decision-making at the early stages of the process synthesis. As it was shown, the methodology is based upon indicators that can be calculated from a basic knowledge of the properties of raw materials and products involved in the reaction, and a small quantity of data on the operating conditions of each process. A list of indicators was suggested in Table 2, although decision makers can add new indicators to the list or just consider those that better fit their specific problem and information.

The methodology also employs MCDA methods for the integration of assessments. These methods use the knowledge of experts to find the most sustainable alternative according to the specific context of the decision problem. The role of experts in a decision problem is fundamental because only they have the particular knowledge required to define the importance of some design aspects in comparison to others (Goodfellow et al., 2013). For the case study, two MCDA methods were employed: Analytic Hierarchy Process (AHP) and Decision Making Trial and Evaluation Laboratory (DEMATEL). Their integration enabled the consideration of weights and influences between sustainability criteria, which fits the selection problem of the most sustainable chemical process route, due to the high interrelation between them. The use of different methods is possible, provided that the method meets the decision problem characteristics and the decision-maker can interpret the results correctly. This methodology can be extended to other products and processes.

5. Conclusions

A methodology that assesses chemical process routes with sustainability indicators integrating MCDA methods was proposed in this study. The proposed methodology calculates a single sustainability index called Sustainable Cumulative Index (*SCI*), which provides a metric to discern different chemical process routes, taking into account weights (AHP) and influences (DEMATEL) between economic, environmental, safety, and occupational health indicator groups. The integration of AHP and DEMATEL is done with the help of a sensitivity factor (*P*), which seeks to represent the degree of relationship among the indicator groups. The proposed methodology was illustrated through the assessment and selection of a chemical process route to produce ethyl acetate. A survey was designed to obtain the information necessary to calculate weights and influences. It was answered by two groups of people related to the chemical industry, namely experts and senior students of chemical engineering. It was found that weighting factors for both groups are similar, the safety indicator group being the one with the largest weighting factor. However, experts and students showed a different understanding of the influence between indicator groups. For students, the reaction between acetic acid and ethanol and the dehydrogenation of ethanol are almost equal in terms of sustainability. For experts the former is preferable because safety indicators are considered more influential than the other sustainability indicator groups.

Nomenclature

A	original impact matrix – DEMATEL
$a_{i,j}$	element in position *i,j* of matrix **A** – DEMATEL
AATP	aquatic acute toxicity
AP	acidification potential
BCF	bio-concentration factor
C	total number of compounds of chemical process route *r*
CATP	chronic aquatic toxicity
CF_p	conversion factor of product *p*
Cj	total influence of other criteria over criterion *j*
D	ready biodegradation
ΔH_r	enthalpy of chemical process route *r*
$\overline{\Delta H_r}$	normalized enthalpy of chemical process route *r*
Ex	explosiveness
$\overline{Ex_r}$	normalized explosiveness of chemical process route *r*
Fx	flammability
$\overline{Fx_r}$	normalized flammability of the chemical process route *r*
GWP	global warming potential
HTPE	human toxicity potential by inhalation or dermal exposure
HTPI	human toxicity potential by ingestion
I	identity matrix
I_{ig}	group index of indicator group *ig*
IWF_{ig}	integrated weighting factor of indicator group *ig*
k	maximum value of rows and columns of **A** – DEMATEL
LC_{50}	lethal concentration 50
LD_{50}	lethal dose 50
M	direct impact matrix – DEMATEL
M	molecular weight of product *p* or raw material *rm*
m_p	mass of product *p*
NOEC	no observed effect concentration
NP	total number of products
ODP	ozone depletion potential

P	percent in which weights are modified because of the effect of the influences
P_r	pressure of the chemical process route *r*
$\overline{P_r}$	normalized pressure of the chemical process route *r*
Pc_{rm}	purchase price of raw material *rm*
PCOP	photochemical oxidation potential
PD	potential degradability
$\langle(\mathit{Potenical})_r\rangle_I$	average of impacts of components *c* in chemical process route *r* associated with the impact category *I*
$(\mathit{Potenical})_{c,I}$	potential environmental impact of component *c* associated with the impact category *I*
PP_p	sale price of product *p*
$\overline{R_r}$	normalized renewable source of the chemical process route *r*
R_{rm}	value of renewable source of the raw material *rm*
Ri	total influence of criterion *i* over all other criteria – DEMATEL
$Ri + Cj$	magnitude of the influence of a criterion over others – DEMATEL
$Ri - Cj$	difference between the influence given and received – DEMATEL
RM	total number of raw materials involved in the chemical process route *r*
Rx	reactivity
$\overline{Rx_r}$	normalized reactivity of the chemical process route *r*
SCI_r	Sustainable Cumulative Index of chemical process route *r*
T	total impact matrix – DEMATEL
t_{ij}	element in position *i,j* of matrix **T** – DEMATEL
T_r	reaction temperature of the chemical process route *r*
$\overline{T_r}$	normalized reaction temperature of the chemical process route *r*
TLVTWA	threshold limit value – time weighted average
Tx	toxicity
$\overline{Tx_r}$	normalized toxicity of chemical process route *r*
VA	added value of product *p* or chemical process route *r*
$\overline{VA_r}$	normalized added value of chemical process route *r*
$\overline{VAT_r}$	total normalized added value of chemical process route *r*
$W_{AHP,ig}$	weight of indicator group *ig* calculated with *AHP*
X_r	conversion of chemical process route *r*
$\overline{X_r}$	normalized conversion of chemical process route *r*
x_{rm}	fraction of the raw material *rm* in reactor feed
Y_r	yield of chemical process route *r*
$\overline{Y_r}$	normalized yield chemical process route *r*

Greek symbols

σ_I	standard deviation of potential environmental impact of compounds associated with impact category *I*
ν	stoichiometric coefficient of product *p* or raw material *rm*
$\overline{\psi^{s}_{r,I}}$	normalized potential environmental impact of chemical process route *r* associated with impact category *I*

Subscripts

c	compound involved in the chemical process route *r*
e	environmental indicator group
ec	economic indicator group
oh	occupational health
i	criteria *i* in DEMATEL
I	impact category: *GWP*, *ODP*, *PCOP*, *AP*, *BCF*, *PD*, *AATP*, *CATP*, *HTPI*, *HTPE*
ig	indicator groups: *ec*, *e*, *s*, *oh*
j	criteria *j* in DEMATEL
p	product
r	chemical process route *r*
rm	raw material
s	safety indicator group

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