



# Environmental evaluation and comparison of hybrid separation methods based on distillation and pervaporation for dehydration of binary alcohol mixtures with life cycle, PESTLE, and multi-criteria decision analyses

Huyen Trang Do Thi, Andras Jozsef Toth \*

Environmental and Process Engineering Research Group, Department of Chemical and Environmental Process Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3, H-1111 Budapest, Hungary

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## ABSTRACT

To achieve net-zero CO<sub>2</sub> emissions by 2050, improving energy efficiency in the chemical industry is crucial. The study focuses on an environmentally friendly hybrid distillation (D)-pervaporation (PV) process to enhance energy efficiency and purity in ethanol–water and isobutanol–water mixtures, these are typical wastes in the chemical industry. Three configurations—D + PV, D + PV + D, and D + PV + D with partial Heat Integration (HI)—are evaluated for separation of ethanol–water and isobutanol–water mixtures employing the Life Cycle Assessment with Environmental Footprint (EF) V3.1 (adapted) and ReCiPe 2016 Endpoint (H) V1.08 methods, using SimaPro V9.5 software and EcoInvent V3.9.1 database. The study also incorporates a PESTLE analysis and Multi-Criteria Decision Analysis to identify the most advantageous process for ethanol and isobutanol scenarios. The research evaluates these systems in a comprehensive manner, including technology, CO<sub>2</sub> emissions, impacts on human health, ecosystems, resources, and Total Annual Cost (TAC). The exploration of hybrid process enhancements includes alternative renewable energy sources (i.e., solar, wind, hydro, and biofuel) and comprehensive heat integration based on Pinch Analysis using Hint V2.2 software. Results indicate that D + PV + D is the most suitable for isobutanol–water scenarios based on MCDA and Pinch analysis. In isobutanol scenarios, D + PV + D + HI reduces CO<sub>2</sub> emissions, and human health, ecosystems, and resources impact by 15.5 %, 11.2 %, 12.6 %, and 14.6 %, respectively, with a significant 40.0 % decrease in TAC compared to D + PV. Integrating renewable energy sources further enhances its sustainability, achieving a single score of approximately one-third lower than fossil fuel consumption. Promoting renewable energy and Integrating energy flows align seamlessly with Green Chemistry and Engineering principles, representing a crucial stride towards sustainable and eco-friendly industrial practices.

## 1. Introduction

Engineers face the perpetual challenge of designing and developing

production processes that meet production requirements while being economically viable and environmentally conscious. In pursuit of these goals, engineers must utilize natural resources efficiently, which can be

*Abbreviations:*  $\bar{D}_i$ , Component *i* transport coefficient [kmol/(m<sup>2</sup>.h)];  $\bar{\gamma}_i$ , Component *i* medium activity coefficient [-];  $E_i$ , Component *i* activation energy [kJ/mol];  $J_i$ , Partial flux [kmol/(m<sup>2</sup>.h)];  $p_{i0}$ , Pressure of pure *i* component vapor [bar];  $p_{i1}$ , Pressure of component *i* on the feed side [bar];  $p_{i3}$ , Pressure of component *i* on the permeate side [bar];  $x_{i1}$ , Component *i* in the feed concentration [wt%];  $Q^*$ , Heat stream [kg/h];  $c_{p,water}$ , Heat capacity of water [kJ/kg.K];  $m_{(cooling)}^*$ , Stream of cooling water [kg/h];  $\Delta T$ , Temperature difference [K];  $B$ , Constant in Equation (1) [-]; CTUe, Comparative Toxic Unit for ecosystem; CTUh, Comparative Toxic Unit for human; CV, Coefficient of Variation; D, Distillation; DALYs, Disability Adjusted Life Years; EDPV, Hybrid Extraction Distillation Pervaporation; EF, Environmental Footprint; FU, Function Unit; GHGs, Greenhouse Gases; HEN, Heat Exchanger Network; HI, Heat Integration; IC, Investment Cost [€]; IPPC, Integrated Pollution Prevention and Control Directive; LCA, Life Cycle Analysis; LCI, Life Cycle Inventory; LCIA, Life Cycle Inventory Assessment; MCS, Monte Carlo Simulations; OC, Operating Cost [€]; PAF, Potentially Affected Fraction; PV, Pervaporation;  $Q_0$ , Porous support layer of the membrane permeability coefficient [kmol/(m<sup>2</sup>.h.bar)]; SD, Standard Deviation; SEM, Standard Error of the Mean; TAC, Total Annual Cost [€/year]; TCED, Three-Column Extraction Distillation; TCPSD, Three-Column Pressure Swing Distillation; TIC, Total investment cost [€/year]; TOC, Total operation cost [€/year]; VOC, Volatile Organic Compounds.

\* Corresponding author.

E-mail address: [andrasjozseftoth@edu.bme.hu](mailto:andrasjozseftoth@edu.bme.hu) (A.J. Toth).

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achieved through on-site or off-site practices such as material and energy recycling [1]. Increasingly, advanced technologies contribute to sustainable resource management and align with the growing adoption of clean technologies to meet environmental requirements and promote sustainable development and consumption. Among the numerous techniques involved, distillation and pervaporation stand out as crucial tools that play a key role in the optimization of resources in various industries.

Distillation is a typical chemical process that accounts for 90–95 % of industrial separations [2], achieving high-purity products up to 95–99 wt% [3]. However, the application of distillation is limited to separating solvents with similar boiling points – azeotropic, low-concentration mixtures, thermosensitive organic compounds, and high energy consumption [4,5]. Pervaporation, a membrane-based method, offers 50–70 % energy savings and eco-friendly operation [6,7]. It can dehydrate organic compounds, eliminate minor amounts of objectionable organic compounds from water-organic mixtures, especially azeotropic mixtures [8]. The hybrid process of distillation with pervaporation is widely regarded to be a green technology due to its ability to reduce thermal and pressure requirements, resulting in energy savings while producing a higher-purity product [9]. Several previous studies have investigated aqueous alcohol mixtures by several hybrid processes such as triple-column azeotropic distillation system – D + D [10], triple-column distillation combined heat integration – D + HI [11], organophilic-hydrophilic pervaporation system – PV + PV [12], distillation-assisted hydrophilic pervaporation – D + PV [13], pervaporation-assisted distillation of permeate stream – PV + D [14], distillation-assisted hydrophilic pervaporation combined heat integration – D + PV + HI [15], organophilic pervaporation-distillation-hydrophilic pervaporation – PV + D + PV [12], etc. Rom et al. [16] simulated the hybrid D + PV process to separate aqueous butanol solutions using Aspen Plus software. They showed that the hybrid D + PV process requires 50 % less energy than the distillation process for obtaining 99 wt% of butanol products. Another research shows the D + PV + D approach presents a more cost-effective and energy-saving biofuel manufacturing option than traditional azeotropic distillation (saving more than 20 % of Total Annual Cost); this separation method can generate high-purity products (more than 2.5 % alcohol purification) without requiring extensive recycling streams [1]. The hybrid distillation-pervaporation process stands out as a greener separation method, boasting a reduction in CO<sub>2</sub> emissions by 46.5 %, 65.1 %, and 84.8 % compared to triple-column extractive distillation and triple-column pressure-swing distillation with and without partial heat integration, respectively [17].

The azeotropic aqueous mixtures of alcohol are the main focus of this work, such as ethanol and isobutanol. The azeotropic point classification of both alcohols corresponds to the minimal boiling point azeotropes, defined by the singular characteristic of boiling at lower temperatures than the pure state of either component. The azeotropic points at 1 bar for ethanol and isobutanol with water are approximately 95.5 wt% at 78.1 °C and 67.6 wt% at 89.5 °C, respectively [18]. A hybrid pervaporation-distillation process can efficiently separate ethanol, butanol from water with lower energy requirements and high-purity outcomes [16,19–21].

This study examines the separation of alcohol-water mixtures using a hybrid distillation-hydrophilic pervaporation-distillation system, D + PV + D. While there's a growing focus on greener technology solutions, environmental considerations often receive less attention compared to economic and energy aspects in separation technologies [4,14,22]. Therefore, this research evaluates the D + PV + D system comprehensively, including technology, energy, economics, its impact on climate change, human health, ecosystems, and resource utilization through Life Cycle Assessment (LCA). Notably, it explores partial thermal integration, a novel aspect often overlooked in prior studies, and assesses hybrid process improvements to reduce negative impacts and energy consumption, such as incorporating renewable energy sources and

comprehensive heat integration. These findings hold promise for various industries dealing with liquid waste streams, offering more sustainable waste management practices.

The study evaluates three configurations: (i) distillation-hydrophilic pervaporation (D + PV), (ii) distillation-hydrophilic pervaporation-distillation (D + PV + D), and (iii) distillation-hydrophilic pervaporation-distillation with partial heat integration (D + PV + D + HI), focusing on achieving 99.9 wt% purity ethanol-water and isobutanol-water mixtures. In addition to LCA, the study employs PESTLE analysis (Political, Economic, Social, Technological, and Environmental factors) to identify key focus points. Multi-Criteria Decision Analysis (MCDA) is then used to assess these factors' relative importance for a holistic perspective on the viability and sustainability of the hybrid processes. Utilizing methods like LCA, PESTLE, MCDA, and Pinch analysis, this research provides a comprehensive evaluation of D + PV + D and D + PV + D + HI hybrid processes, particularly scrutinizing D + PV + D coupled with heat integration for the first time. The use of multiple analytical tools and the assessment of novel configurations contribute to the uniqueness and depth of the research compared to other studies in the field, which may focus on specific aspects or rely solely on one methodology for decision-making. These applied analysis methods are briefly described in Section 2, which provides a general overview. The detailed simulations are presented to ensure the reproducibility of future research. The assessment includes simulations, LCA, and economic considerations, emphasizing the integration of renewable energy sources and comprehensive heat integration to increase efficiency and decrease environmental impacts in Section 3. This section also carefully outlines the study's limitations and future research opportunities. Finally, Section 4 highlights the significance of the critical findings in the conclusion.

## 2. Materials and methods

### 2.1. Simulation of separation of processes

The composition of feed mixtures was carefully chosen to address a practical separation challenge encountered in our work environment: the regeneration of waste solvents. The task is to separate an assumed 10 wt% alcohol-water mixture with a 1000 kg/h feed rate at 20 °C and 1 bar, specifically the ethanol-water and isobutanol-water. The goal is to obtain 99.9 wt% purity of alcohol and water products. This particular composition represents the water-rich phase of the alcohol-water mixture is heterogeneous azeotropic. The professional flowchart simulator ChemCAD V6.5 is designed to simulate the hybrid separation.

#### 2.1.1. Hybrid distillation- hydrophilic- pervaporation system (D + PV)

The hybrid process is built up of a distillation step and a hydrophilic pervaporation step, see Fig. 1.a. The configuration and parameters for the D + PV system are derived from the research conducted by Toth et al. [23].

In the first step, for both ethanol and isobutanol scenarios, the distillation column is optimized at 40 stages, and the charging is in the middle of the distillation column, the 20th stage. Water is the bottom product (W) of the column. The high alcohol matter phase (Distillate) is passed into the pervaporation membrane. The high-purity alcohol is obtained from the bottom product of the process as retentate (R) of pervaporation. The distillation procedure was performed using the UNIQUAC thermodynamic model for SCDS column. It is assumed that the columns operate at 1 bar under no pressure drop. The heat exchangers induced are responsible for the 20 °C control of the final products.

The pervaporation membrane module is implemented as a user subroutine in ChemCAD, and the pervaporation model employed was developed by Valentinyi et al. [24], who demonstrated its accuracy for various mixtures. The selected approach is derived from one of Raubenbach's pervaporation models [25], as represented by Equation (1).

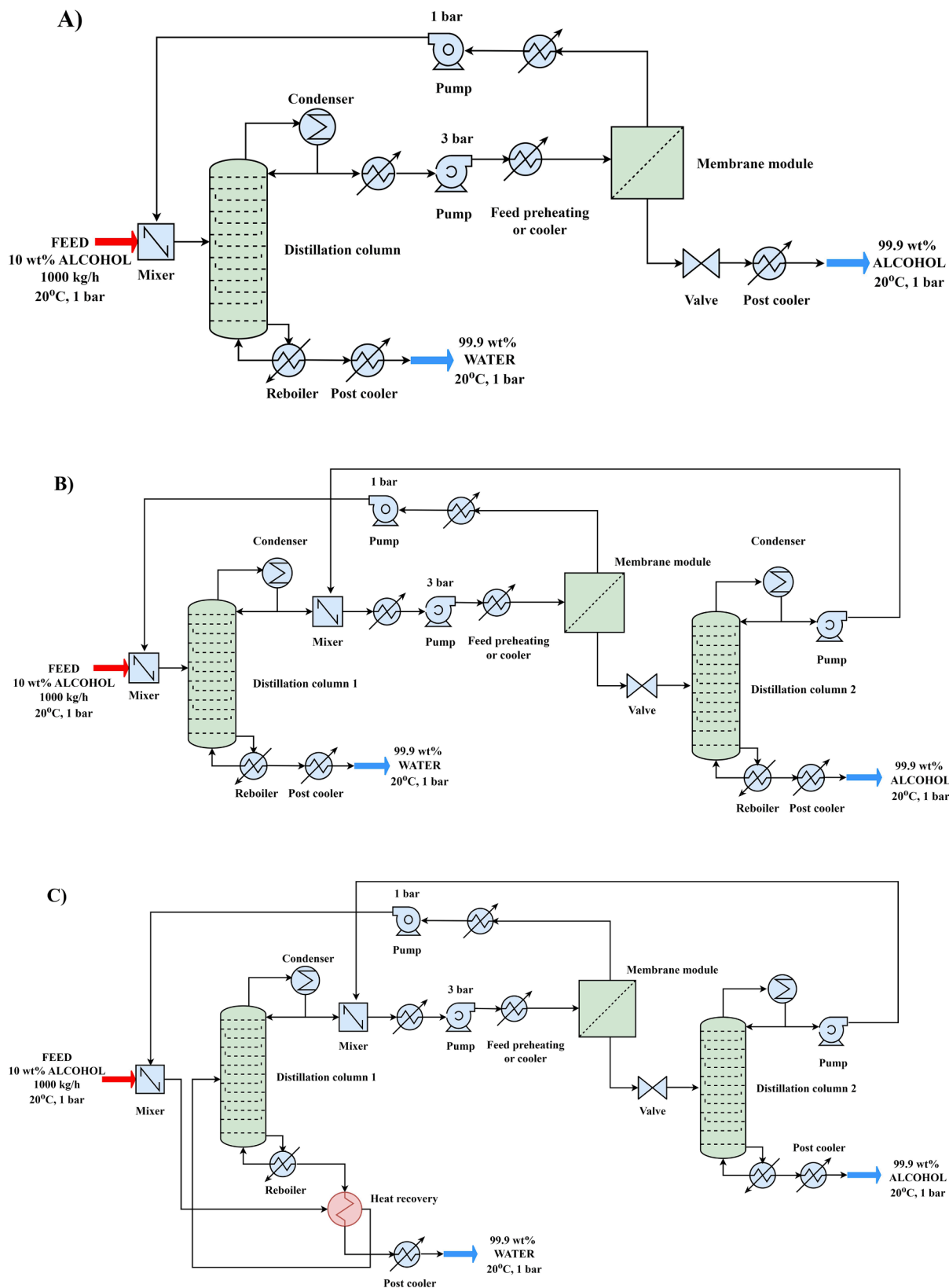


Fig. 1. Flowsheets of (a) D + PV system, (b) D + PV + D system, (c) D + PV + D + HI system.

This model has been rigorously tested in many case studies and demonstrated to be efficient in the description of pervaporation for applications in engineering [26]. It is a reliable tool for process design to meet organophilic and hydrophilic pervaporation control requirements.

The empirical parameter B signifies the concentration dependence of the transport coefficient. It is necessary to obtain experimental results from laboratory tests and perform additional calculations to estimate the pervaporation parameters. For a detailed overview of the model as can

be seen in Fig. S1 in Supporting information section, refer to the publications by Toth et al. [23] and Andre et al. [15]. Table 1 displays the key transport parameters utilized in the model.

$$J_i = \frac{1}{1 + \left\{ \frac{[\bar{D}_i \cdot \exp(B \cdot x_{i1})]}{(Q_0 \cdot P_{i0} \cdot \bar{T}_i)} \right\}} \cdot \frac{[\bar{D}_i \cdot \exp(B \cdot x_{i1})]}{\bar{T}_i} \cdot \left( \frac{P_{i1} - P_{i3}}{P_{i0}} \right) \quad i = (1, \dots, k) \quad (1)$$

In the pervaporation process, the liquid feed undergoes selective permeation through a membrane driven by partial pressure differentials. The resultant vapor is subsequently condensed through a cold trap. Following membrane contact, the feed is separated into two streams: the permeate (P)- which successfully traverses the membrane, and the retentate (R)- which cannot pass through. The feed side is maintained at either atmospheric or a pressure level necessary to keep the feed in liquid form. A vacuum is placed on the permeate side to facilitate the separation process. The utilization of the feed as a source for the heat of vaporization in the PV process induces a decline in temperature within the retentate stream. This temperature decline subsequently induces a reduction in mass transfer flux [27]. To optimize the mass transfer flux, a strategic arrangement employs multiple pervaporation modules configured in a cross-flow, in-series layout, as seen in Fig. S2 in the Supporting Information section. This configuration is designed to augment the flux, necessitating the incorporation of pre-heating mechanisms at the inlet of each module to elevate its temperature [28]. The heat exchanger allows temperature adjustment, and the pump raises the pressure upstream of the first PV unit. The retentate flow is heated by additional heat exchangers after each PV unit, excluding the last module. The membrane surface area per unit is limited to a location that provides an allowable temperature drop, with the PV stopping when the temperature drops below 50 °C [26]. In addition to temperature control, there is a gradual reduction in the pressure of the retentate flow. As the number of processing units (PV) significantly increases, likely 20–30 units, the membrane pressure drops below the standard operating conditions for the PV membrane. In such instances, it becomes imperative to install supplementary pumps to restore the optimal operating parameters of the PV membrane system. This intervention ensures the efficient and compliant functionality of the membrane system even under high unit demands. The permeate flows exiting the pervaporation units are combined, mixed, refrigerated, re-pressurized by a pump, and mixed into the distillation column feed flow. The feed temperature and pressure applied in the PV units are 90 °C-3 bar in the ethanol–water case, and 70 °C-3 bar in the isobutanol-water mixture, where the permeate pressure is 0.008 bar, which was taken from the experimental setup for the stabilisation of PV operation [23,24,26]. The surface area of the PV used in the membrane modules was kept as small as possible because the more significant the surface area, the higher the cost from an economic point of view [29]. Thus, the membrane surface area was taken to be less than 10 m<sup>2</sup>.

Permeate products from the membrane units are collected, cooled to the initial 20 °C by a heat exchanger, recirculated, and mixed with the

**Table 1**

Estimated hydrophilic pervaporation membrane parameters for ethanol–water and isobutanol-water mixtures.

Mixtures		Ethanol-Water	Isobutanol-Water
PV Membrane		PERVAP™ 4510	PERVAP™ 1510
Permeability [kmol/m <sup>2</sup> hbar]		1.00E+08	1.00E+08
Transport coefficient [kmol/m <sup>2</sup> .h]	Water	2.02E–04	5.35E–04
	Alcohol	1.93E–05	2.63E–03
Activity energy [kJ/kmol]	Water	77,877	58,247
	Alcohol	128,572	52,252
Parameter “B” [-]	Water	2.63	8.12
	Alcohol	–8.68	–8.06
Reference		[23]	[26]

feed stream using a pump. This recirculation ensures that no residue is generated during the process.

### 2.1.2. Hybrid distillation- hydrophilic pervaporation-distillation system (D + PV + D)

In D + PV + D, the pervaporation step moves the compound through the azeotropic point. An additional distillation step after the membrane modules to obtain an azeotropic composition as top product and a bottom product with the desired high-purity composition, as seen in Fig. 1.b. The retentate flow leaving the last membrane unit of the hydrophilic pervaporation system is fed to a Distillation column 2. If the retentate pressure exceeds the working pressure of the second distillation column, a valve is employed to reduce the pressure of the stream before its entry into the column. The inlet pressure is introduced into both two distillation columns at 1 bar. The membrane area of the PV system, its operating conditions, and the second distillation column have all undergone meticulous optimization to ensure the production of the most efficient and top-quality product. These refined systems are engineered to operate with utmost stability, enhancing the overall performance of the recycled processes. The distillate product is recycled and mixed with the product from first distillation column.

### 2.1.3. Hybrid distillation- hydrophilic pervaporation-distillation with partial heat integration system (D + PV + D + HI)

Applying hybrid distillation in conjunction with the pervaporation process necessitates a substantial amount of heat. Consequently, our analysis incorporates a comprehensive set encompassing heat integration as an essential component. To optimize the net energy input, a strategic approach involves transferring heat from surplus points to demand points.

In Fig. 1.c, the partial heat integration process is illustrated, wherein the thermal energy derived from the bottom product of the first distillation column is employed to preheat the incoming feed stream through a dedicated heat recovery unit. An alternate configuration of the heat integration strategy involves harnessing the thermal energy from the product stream of the second column. Notably, the temperature differential between the bottom product flow from the second distillation column and the incoming feed flow is quite low. So, the heat integration in the second column has been deemed non-significant and is not considered in this study.

## 2.2. Life cycle assessment

Life cycle assessment (LCA) effectively analyzes the impact on the environment of separation systems by evaluating the potential impacts of activities within the system boundaries [30]. LCA provides a comprehensive understanding of resource consumption and environmental impact, enabling measures to reduce human impact and address environmental problems throughout the system’s life cycle. However, LCA has limitations [31]: it does not cover the impact of post-product use, and data gathering can be costly and uncertain. Subjective choices in impact categories and weighting methods may narrow sustainability perspectives and lead to varied stakeholder interpretations.

This research followed the guidelines of LCA as specified in ISO 14040:2006 [32] and ISO 14044:2006 [33] standards. The LCA process consists of four main stages: (1) defining the goal and scope, (2) life cycle inventory analysis, (3) life cycle impact assessment, and (4) interpreting the obtained results [34].

### 2.2.1. Goal and scope

The LCA was conducted to assess the environmental impacts of three hybrid technologies for alcohol removal: D + PV, D + PV + D, and D + PV + D + HI. The modelling was performed using SimaPro V9.5 software and the Ecoinvent V3.9.1 database. This version features enhanced documentation and updated emission factors for improved accessibility and accuracy. The assessment employed two impact evaluation

methods: Environmental Footprint (EF) V3.1 (adapted) method, and ReCiPe 2016 Endpoint (H) V1.08. The study focused on the operational phase of the processes, encompassing chemical inputs and energy requirements, known as a “gate-to-gate” analysis.

The functional unit (FU) is specified as 1 kg of output stream containing 99.9 % by weight of alcohol for one operating hour.

2.2.2. Inventory data

In the initial phase of conducting an LCA analysis, it is crucial to carefully define the process boundary, as it significantly influences the final results. In specific case, the sole focus is on the operation of the separation process. Therefore, a gate-to-gate life cycle assessment for two alcohol-water mixture separations using hybrid technologies like D + PV, D + PV + D, and D + PV + D + HI is undertaken. The study extensively examines the reclamation of pure components, which is why the system boundaries encompass the entire separation system, including its operational requirements, such as materials and energy. The global geographical location scope has been assumed in this study. The inventory data for each process for one operating hour to obtain 1 kg of products with a 99.9 wt% purity is shown in Table 2. The inventory data is derived from a combination of simulation results and calculated values. Specifically, Equation (2) is utilized in the calculation of cooling water requirements [35].

$$m_{cooling}^* = \frac{Q^*}{C_{p,water} \cdot \Delta T} \tag{2}$$

2.2.3. Life cycle impact assessment

The purpose of Life Cycle Impact Assessment- LCIA is to offer further information better to understand the environmental significance of Inventory Analysis results [36]. LCIA assesses human health, natural environment, natural resources, and sometimes man-made environment. It’s mostly automated in LCA software, but understanding underlying principles and indicator meanings is crucial for informed method selection and result interpretation [37].

In this study, the following evaluation methods were applied: Environmental Footprint (EF) V3.1 (adapted), and ReCiPe 2016 Endpoint (H) V1.08.

EF V3.1 (Adapted) method

The Environmental Footprint (EF) method, used in the European Commission’s transition phase, now employs EF V3.1 (adapted), which

Table 2

Inventory data for one operating hour to obtain 1 kg of products with a 99.9 wt% purity.

		Ethanol-Water			Isobutanol-Water		
		D + PV	D + PV + D	D + PV + D + HI	D + PV	D + PV + D	D + PV + D + HI
Input	Alcohol [kg]	0.10	0.10	0.10	0.10	0.10	0.10
	Water [kg]	0.91	0.90	0.91	0.91	0.91	0.91
	Heating energy [MJ]	5.99	18.34	15.41	8.06	8.72	5.21
	Cooling water [kg]	10.96	10.18	1.13	17.78	17.86	8.78
	Vacuum energy [kJ]	0.30	1.21	1.21	0.71	0.40	0.40
	Alcohol [kg]	1.00	1.00	1.00	1.00	1.00	1.00
	Water [kg]	9.07	9.06	9.11	9.08	9.08	9.08
Output	Cooling water [kg]	10.96	10.18	1.13	17.78	17.86	8.78

includes updated impact categories such as climate change, acidification, ozone formation, human toxicity, and ecotoxicity. This method covers 28 impact categories, focusing this analysis on climate change, human carcinogenic toxicity, and ecotoxic effects in freshwater. The Comparative Toxic Unit for human (CTUh) measures human toxicity impact in cases per kilogram of chemical emitted per unit mass, indicating increased morbidity in the global human population. The CTUe, expressed as PAF.m<sup>3</sup>.year/kg, quantifies how toxic chemicals affect ecosystems over time by considering the Potentially Affected Fraction (PAF). Climate change impact is assessed using Global Warming Potential, representing greenhouse gas emissions in kilograms of CO<sub>2</sub> equivalent over a 100-year horizon.

ReCiPe 2016 Endpoint (H) V1.08

ReCiPe 2016 V1.08 assesses eighteen midpoint and three categories of endpoint effects from global perspectives (H-hierarchical, E-egalitarianism, and I-individualism) with accurate characterization factors. It focuses on human health (measured in disability-adjusted life years-DALYs), ecosystem quality (expressed as species.year), and resource scarcity (in USD) [38]. DALYs quantify years lost due to disease or accidents, while ecosystem quality considers species loss across various ecosystems over time. Resource scarcity reflects additional costs linked to the extraction of fossil and mineral resources in the future. This study adopts the ReCiPe 2016 Endpoint (H) V1.08 methodology, incorporating policy principles and relevant factors such as timeframe.

2.2.4. Uncertainty analysis

Uncertainties in LCA studies are often overlooked despite their potential significance [36]. Uncertainty can be defined as the difference between measured/calculated values and the true value. There are various types of uncertainty, including parameter, variability, model, scenario, relevance and epistemic uncertainty [37,39]. ISO 14040 mentions uncertainty in LCI, LCIA, and Interpretation phases but lacks concrete guidance. Ongoing initiatives are addressing this gap. Uncertainty can be managed by improving data, and models, reaching a consensus, etc. While current LCA studies increasingly consider uncertainties, the focus remains on parameter uncertainty. Some tools offer pedigree matrix, numerical, or analytical approaches for handling uncertainty [37]. The predominant method for propagating uncertainty is through a numerical technique known as Monte Carlo simulation, accessible in prominent LCA software such as GaBi, SimaPro, openLCA, and others [40]. This method fundamentally involves iteratively performing model calculations, with input parameters sampled from their specified probability distributions [41].

This study employs SimaPro V9.5 to perform an uncertainty analysis by conducting Monte Carlo Simulations (MCS) with 10,000 iterations at a 95 % confidence level to assess and quantify uncertainty.

2.3. PESTLE factors combined with multi-criteria decision analysis (MCDA)

PESTLE is an acronym for Political, Economic, Social, Technological, Legal, and Environmental factors. It offers a broad view of the tech landscape, helping assess and compare competing processes. This tool considers macro and micro-environmental factors for decision-making, relying on extensive data. However, predicting trends is challenging due to rapid technological changes, necessitating regular updates. Despite demanding significant data, PESTLE identifies opportunities and risks that should not be ignored, varying across regions and countries or even within a single country due to socio-cultural differences. To maintain effectiveness, the process should be repeated regularly from different perspectives. The scope of PESTLE analysis with sub-factors for investigated hybrid processes is described in Fig. 2.

2.3.1. Political and legal

Political and legal factors are defined by government influence on the economy or a specific industry. This influence can be exerted

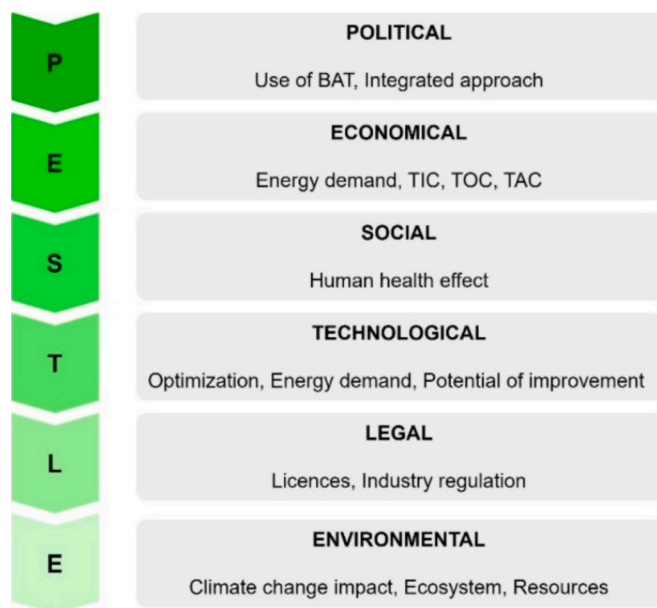


Fig. 2. The scope of PESTLE analysis.

through tax policies, fiscal measures, trade regulations, quotas, resource allocation, and import–export laws, encouraging or constraining industry growth [42].

The European Parliament and Commission actively support integrated pollution prevention and control through the Integrated Pollution Prevention and Control Directive (IPPC) established in 1996 (96/61/EC) [43]. Subsequent directives were implemented, such as the one targeting Volatile Organic Compounds (VOC) in 1999 (1999/13/EC) [44]. In 2010, the Industrial Emission Directive (IED) (2010/75/EU) [45] replaced several existing directives, consolidating and broadening considerations, including energy efficiency. In December 2019, the European Commission introduced the European Green Deal [46], aiming for climate neutrality by 2050, enshrined in the European Climate Law. The EU is committed to becoming the first continent to balance CO<sub>2</sub> emissions by 2050, as ratified in the 2021 Climate Law. The EU also seeks a minimum 55 % reduction in net greenhouse gas emissions by 2030 and promotes technological research for sustainable goals, including pollution prevention, ecosystem preservation, emission reduction, and renewable energy sources [47–49].

### 2.3.2. Economical

Typically, the total Annual Cost (TAC) is computed by factoring in both the investment cost (IC) and the operating cost (OC). The IC pertains to all units, while the OC pertains to utilities. For this study, it is assumed that the distillation column and pervaporation membrane have a plant life of ten and two years, respectively, and they each operate for 8,000 h per year. The cooling and heating utility expenses for this study are delineated as follows: 4.43 €/GJ for chilled water at 278 K and 14.05 €/GJ for low-pressure steam at 433 K [50]. Notably, the cost data for PV is presented in 2007 price levels. The currency conversion from USD to Euro is based on an identical exchange rate. The PV membrane is valued at 1,063 €/m<sup>2</sup>, while the replacement cost is 200 €/m<sup>2</sup> [51]. The detailed cost calculation equations derived from Douglas [52] and González et al. [51] are listed in Table S1 in the Supporting Information.

### 2.3.3. Social and environmental

MCDA software incorporates Social and Environmental factors through numerical outputs from LCIA. In Fig. 2, the environmental factor encompasses damage to ecosystems, resources, and climate change, while the social factor is represented by its impact on human health.

### 2.3.4. Technological

The primary technological sub-factors are evaluated through a literature review, and these assigned sub-factors encompass optimizing the separation process for achieving 99.9 wt% purity products, assessing energy requirements, and evaluating the potential for technological enhancements.

### 2.3.5. MCDA

MCDA methods systematically address decision-making limitations by evaluating alternatives and identifying the best options. While valuable, MCDA has limitations, including subjective determination of factor weights, reliance on the decision maker's opinion, data requirements, complexity, and oversimplification of real-world situations. When appropriately applied, MCDA can enhance decision-making, but the decision-maker(s) should ultimately make the final decision rather than solely dictated by the MCDA results [53]. Various MCDA methods (e.g., TOPSIS, FMAVT, FMAA, MAVT, MAUT, AHP, etc.) help determine optimal selections. In this study, TOPSIS was applied, which is a multi-aspect method, choosing the option closest from the positive ideal and furthest away from the negative ideal [54].

Decerns MCDA V1.5 software assesses hybrid distillation–pervaporation of alcohol–water mixture separation processes. Decerns aids in policy analysis, considering land use, environmental protection, and risk management [55].

## 2.4. Pinch analysis

Pinch Analysis provides a simple approach to minimizing the energy requirement of the process by deriving a specific set of thermodynamically feasible energy targets [56]. The key aspects of this methodology involve calculating energy and cost targets for the process and clarifying the minimum energy consumption and the associated minimum cost of the heat exchanger network (HEN) required to achieve this minimum. HEN plays a pivotal role in recovering heat from hot process streams and transferring it to cold process streams, thereby reducing the cooling and heating duties of external utilities like steam and cooling water [57]. The efficiency of the recovery system relies on the operating assumptions and design of the separating system and the reactor. This method does not guarantee an optimal solution; however, as a robust approximation of the optimal network, it allows the development of a HEN with minimum energy consumption [58]. Furthermore, the pinch method gives engineers full control over the design process, helping to identify parameters limiting energy savings. Due to its advantages, this method has become a widely accepted and well-established tool in HEN design.

In this research, the Hint (Heat Integration) V2.2 software is applied for the pinch design of heat exchanger networks in hybrid processes. The ChemCAD simulation, as can be seen in Section 3.1, supplies data on heat exchangers and enters stream parameters, which are systematically gathered and integrated into a unified heat exchange system. This system is designed to optimize energy efficiency by effectively repurposing excess energy.

## 3. Results and discussion

### 3.1. Optimization of hybrid processes for separation of alcohol–water mixtures

Detailed simulation results are described in Table S2 in the Supporting Information.

The object is to enhance the efficiency of D + PV and D + PV + D processes, achieving a 99.9 wt% extraction of purified water and alcohol using a flowchart simulator powered by ChemCAD software. The variable under investigation is the effective size of the PV membrane area, which serves as a controllable parameter. Each module in the pervaporation setup has a membrane surface area of less than 10 m<sup>2</sup>. To attain a 99.9 wt% alcohol concentration, expanding the PV membrane area by

increasing the number of individual membrane units is necessary.

First, the D + PV system operates as depicted in Fig. 1a. The feed for the distillation process is sourced from the recycled stream. The distillation's bottom product is water with a purity of 99.9 wt%. On the other hand, Distillation is constrained in its ability to purify the mixture beyond the azeotropic point, resulting in the distillate product consisting of ethanol and isobutanol, with concentrations of 87.2 wt% and 66.3 wt %, respectively. Fig. 3 presents the results of simulations involving the D + PV process. Fig. 3a illustrates the evolution of alcohol concentrations in the retentate within the PV membrane area. As the PV membrane area expands, there is a corresponding change in the alcohol concentration within the retentate. Fig. 3b provides insights into the heat duties associated with this process. It is worth noting that the distillation column's reboiler exhibits the highest energy consumption, with the condenser and post cooler following suit, in line with the characteristics of the material streams. Examining the graphical representations, both alcohol mixtures exhibit a distinctive curved pattern. The trend is characterized by a rapid ascent until the membrane area reaches 100 m<sup>2</sup>, followed by a more gradual and steady increase.

In the D + PV system, achieving a 99.9 % purity in water and ethanol is most easily accomplished with ethanol, and it requires the least amount of heat duty compared to the isobutanol. Specifically, to attain the desired outcome with the ethanol–water mixture, resulting in a total PV membrane area of 200 m<sup>2</sup> are needed. In contrast, isobutanol necessitates the total membrane area of 300 m<sup>2</sup> to achieve a 99.9 %

isobutanol concentration in the final stream. The heat requirement for this process is about 595 MJ/h for ethanol and 800 MJ/h for isobutanol, respectively.

The suitability of the method can be attributed to the distinction between the azeotropic and boiling points of individual substances. There are both the minimal boiling point azeotropes. In the case of the ethanol–water mixture, where an azeotropic point coincides closely with the boiling temperature of ethanol at 78.1 °C and 78.2 °C at 1 bar, the compound obtained at the azeotropic point exhibits a commendable quality of 95.5 wt%. In contrast, the isobutanol–water mixture presents an azeotropic point with more disparate boiling temperatures for isobutanol, recorded at 89.5 °C and 107.5 °C at 1 bar. Consequently, the compound derived at the isobutanol–water azeotropic point demonstrates a quality of 67.6 wt%. This distinction underscores that to attain the target 99.9 wt% product purity, the ethanol system requires fewer PV membranes to go through the azeotropic point, resulting in a product with higher purity than isobutanol.

When employing the D + PV + D system to separate the mixture containing ethanol–water and isobutanol–water mixtures, it requires a total of 130 m<sup>2</sup> of PV membrane in optimal performance for both two alcohols, ultimately achieving a 99.9 wt% purity for both water and alcohol fractions. To reach the specified target, the D + PV + D system necessitates 70 m<sup>2</sup> and 170 m<sup>2</sup> less PV membrane area than the D + PV system for separation of ethanol and isobutanol mixtures, respectively. The optimized configuration of the second distillation column, tailored

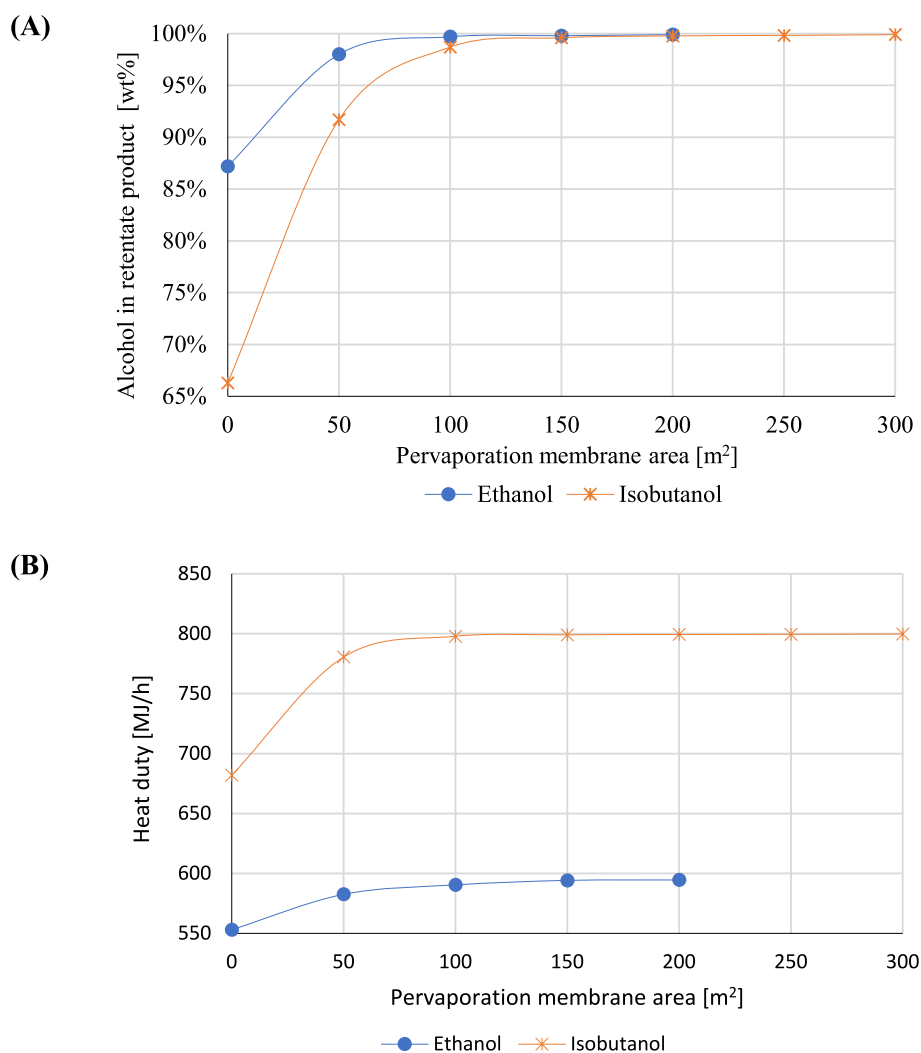


Fig. 3. The alcohol concentration in retentate product (a) and the heat duty (b) of the D + PV process while increasing the PV membrane area.

for ethanol–water separation, boasts 80 theoretical plates. The feed is strategically introduced at the midpoint, precisely at the 40th stage. For isobutanol–water scenario in the same column, 20 theoretical plates are employed, with the feed entering at the 10th stage. The composition of the flow before entering the second distillation column achieved a purity level of 99.6 wt% in both the ethanol–water and isobutanol–water mixture scenarios. Table 3 shows the computed heat duties for the D + PV + D method in the case of 99.9 wt% product purity in the separation of the ethanol–water and isobutanol–water mixtures. Notably, ethanol’s total heat duties are 2.23 times higher than isobutanol. It is important to highlight that the heat demand for the PV membrane system and associated heat exchangers is comparatively modest when juxtaposed with the overall heat duty of the D + PV + D system. Specifically, this component constitutes only 13.9 % of the total heat duty for isobutanol, while it represents a mere 1.7 % for ethanol.

Table 4 details the total heat duties for the D + PV + D + HI systems. Implementing heat integration in the first distillation column within the D + PV + D system yields significant reductions of 16.5 % and 36.7 % in the total heat requirements for ethanol–water and isobutanol–water scenarios, respectively, compared to the D + PV + D system without HI.

### 3.2. Life cycle assessment of hybrid processes for separation of alcohol–water mixtures in case obtain 1 kg of products with a 99.9 wt% purity

The summary of the life cycle impact assessment findings can be found in Table S3, which utilizes the Environmental Footprint (EF) V3.1 (adapted) method, and Table S4 for ReCiPe 2016 Endpoint (H) V1.08 in the Supporting Information section.

The categories of human health, ecosystems, resources, and climate change impacts for the six investigated separation processes are illustrated in Fig. 4. The summary of the Monte Carlo analysis, based on the EF V3.1 (adapted) method for climate change impact and the ReCiPe 2016 Endpoint (H) method for human health, ecosystems, and resource impacts, is presented in Table S5 in the Supporting Information. The uncertainty simulations follow a 95 % confidence level normal distribution, where CV measures dispersion, SD is the Standard Deviation, and SEM is the Standard Error of the Mean.

The effects of the filtration system on human health, ecosystems, and resources following the ReCiPe 2016 Endpoint (H) method (as shown in Fig. 4.a, 4.b, and 4.c), and climate change, using the EF V3.1 (adapted) method (as depicted in Fig. 4.d), vary across the two alcohol types. The impact of all four effects of the D + PV system for isobutanol–water is greater than that of ethanol–water. Conversely, when considering the agents of the D + PV + D system along with these factors, the impact change is completely opposite.

Of the three methods studied, D + PV has the most negligible negative impact on all four impacts for separating ethanol–water mixtures, followed by the D + PV + D + HI and D + PV + D systems. The partial heat integration process had the slightest impact on isobutanol–water separation, followed by D + PV, and finally, D + PV + D

systems. According to the ReCiPe 2016 Endpoint (H) method, the separation of the ethanol–water mixture using the D + PV + D method resulted in a negative impact 1.84–2.09 times greater compared to the D + PV system. In the case of the isobutanol–water mixture, the impact ranged from 1.02 to 1.03 times greater. In broad terms, conducting the Life Cycle Assessment (LCA) utilizing the ReCiPe 2016 Endpoint (H) and EF 3.1 (adapted) methodologies for both ethanol–water and isobutanol–water mixtures to achieve 99.9 wt% purity of ethanol and isobutanol separately, the D + PV system demonstrates distinct advantages over the D + PV + D system. However, when applying partial heat integration, the D + PV + D + HI system has improved the difference, especially being the most dominant among the three technologies for isobutanol.

Evaluating the climate change impact of the investigated technology, following the EF 3.0 methodology, the D + PV process for 1 kg 99.9 wt% ethanol separation emits  $4.31 \times 10^{-1}$  kg CO<sub>2</sub>-eq with an SD of  $1.47 \times 10^{-1}$ , SEM of  $1.47 \times 10^{-3}$ , CV of 34.4 %, and a value ranging from  $1.37 \times 10^{-1}$  to  $7.15 \times 10^{-1}$  kg CO<sub>2</sub>-eq. The amount of CO<sub>2</sub>-eq emissions from D + PV + D + HI for gained purity of isobutanol increases to  $6.33 \times 10^{-1}$  kg CO<sub>2</sub>-eq, with an SD of  $2.30 \times 10^{-1}$ , SEM of  $2.30 \times 10^{-3}$ , CV of 36.3 %, and a value ranging from  $1.87 \times 10^{-1}$  to  $1.09 \times 10^0$  kg CO<sub>2</sub>-eq.

Based on the ReCiPe 2016 Endpoint (H) method, when producing 1 kg of isobutanol with a purity of 99.9 wt%, employing the D + PV + D + HI process incurs a minuscule impact on human health, precisely measuring at  $1.24 \times 10^{-6}$  DALY, with an SD value of  $5.01 \times 10^{-7}$ . This translates to an estimated  $4.53 \times 10^{-4}$  days of disease per Functional Unit (FU) when employing the D + PV + D + HI process. Monte Carlo Simulation (MCS) results within the Human Health Impact category reveal that human health consequences span from  $2.66 \times 10^{-7}$  to  $2.24 \times 10^{-6}$  DALY, as outlined in Table S5. Regarding the impact on ecosystems, the D + PV + D + HI process is associated with a diminutive effect of  $2.66 \times 10^{-9}$  species-years, accompanied by an SD value of  $1.07 \times 10^{-9}$ . Moreover, an additional financial cost is attributed to resource scarcity, amounting to  $8.86 \times 10^{-2}$  dollars and an SD of  $3.33 \times 10^{-2}$ . The MCS results for the Ecosystems and Resources Impact categories span a range of  $5.83 \times 10^{-10}$  to  $4.78 \times 10^{-9}$  species-years and  $2.36 \times 10^{-2}$  to  $1.55 \times 10^{-1}$  USD, respectively.

Upon collectively examining Fig. 4 and the data presented in Table 2, it becomes evident that the trend in the impacts of these processes aligns with the variation in heat energy values. This implies that an increase in a process’s heat energy directly correlates with a heightened negative environmental impact. Specifically, the significance of heating energy as a pivotal input material is particularly pronounced, with its potential impact highlighted in the ReCiPe 2016 Endpoint (H) method. Within the D + PV process designed for ethanol and isobutanol scenarios, it exerts influence at 41.1 % and 27.7 %, respectively. Notably, in the D + PV + D system, heat energy assumes an even more substantial role, contributing 68.3 % and 29.2 % to the efficient removal of these alcohols. The distillation column emerges as a notable energy consumer in hybrid processes, concurrently emitting significant CO<sub>2</sub>. Implementing strategic measures becomes imperative to mitigate these environmental and

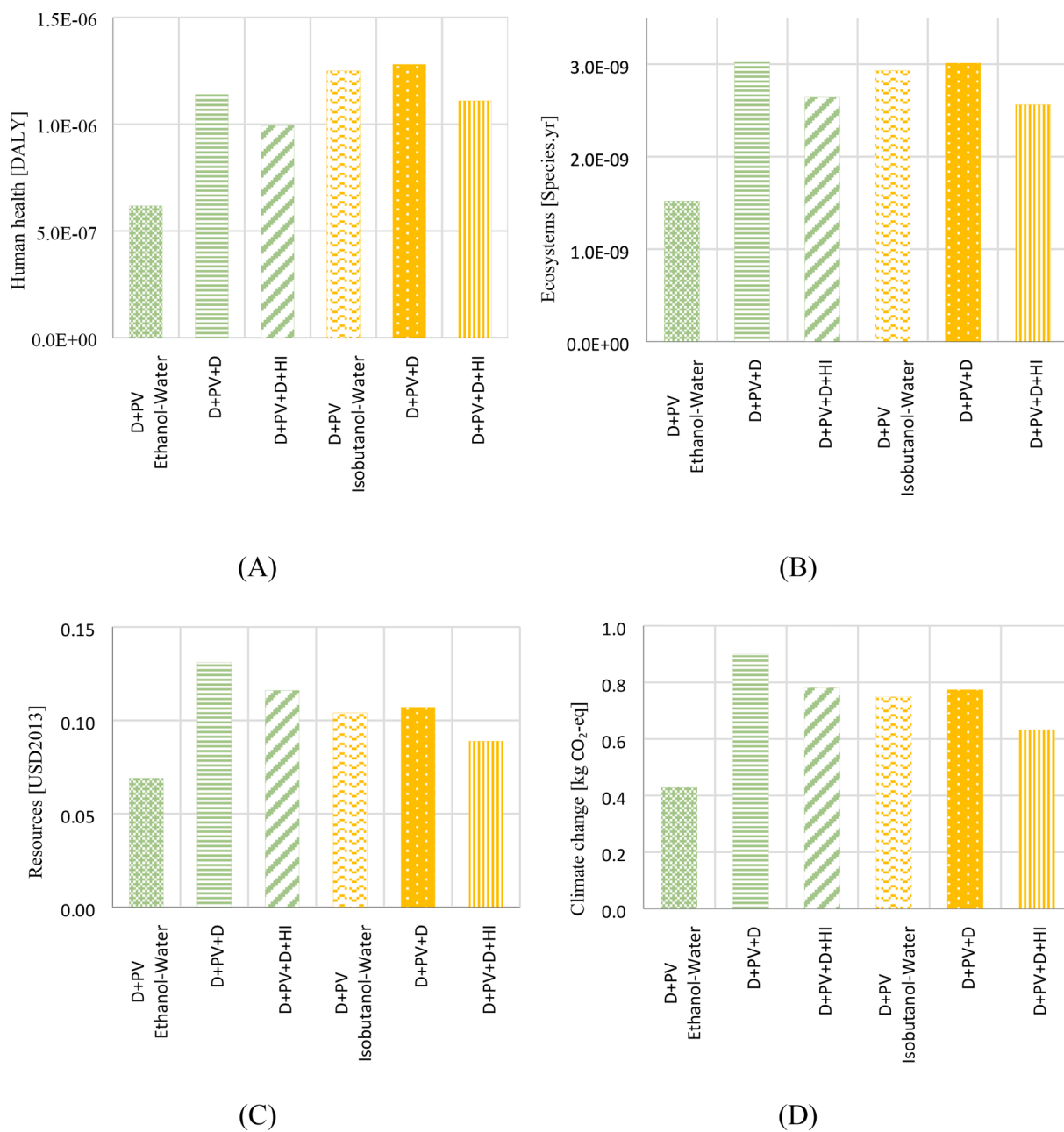
**Table 3**  
Calculated heat duties of D + PV + D for separation of 99.9 wt% water and alcohol.

Calculated heat duties		Ethanol		Isobutanol	
		Q <sub>heating</sub> [MJ/h]	Q <sub>cooling</sub> [MJ/h]	Q <sub>heating</sub> [MJ/h]	Q <sub>cooling</sub> [MJ/h]
1st Distillation	Reboiler	713.56		685.44	
	Condenser		−396.13		−348.23
	Post cooler		−299.81		−299.85
PV	Feed preheating/cooler	15.91			−10.23
	Feed pump	0.12		0.04	
	Retentate heating	14.86		113.87	
	Permeate cooler		−17.86		−128.02
2nd Distillation	Reboiler	1,080.19		17.44	
	Condenser		−1,095.41		−5.40
	Post cooler		−15.42		−25.07
Total	1,824.63	1,824.63	816.79	−816.79	



**Table 4**  
Calculated heat duties of D + PV + D + HI for separation of 99.9 wt% water and alcohol.

Calculated heat duties		Ethanol		Isobutanol	
		Q <sub>heating</sub> [MJ/h]	Q <sub>cooling</sub> [MJ/h]	Q <sub>heating</sub> [MJ/h]	Q <sub>cooling</sub> [MJ/h]
1st Distillation	Reboiler	414.49		385.59	
	Condenser		-396.87		-348.22
	Post cooler		0.00		0.00
PV	Feed preheating/cooler	15.88			-10.23
	Feed pump	0.12		0.04	
	Retentate heating	15.02		113.87	
	Permeate cooler		-18.09		-128.04
2nd Distillation	Reboiler	1,078.65		17.45	
	Condenser		-1,093.86		-5.39
	Post cooler		-15.34		-25.07
<b>Total</b>		<b>1,524.16</b>	<b>-1,524.16</b>	<b>516.95</b>	<b>-516.95</b>



**Fig. 4.** (a) Human health, (b) Ecosystems, (c) Resources damage category based on ReCiPe 2016 Endpoint (H) method, and (d) Climate change damage category based on EF 3.1 (adapted) method of the investigated processes.

resource challenges. Techniques such as harnessing waste heat, adopting heat-integrated systems, employing high-efficiency generation methods, and incorporating renewable energy sources can significantly reduce overall energy consumption. Integrating alternative energy systems into distillation processes helps cut costs and lessen reliance on fossil fuels, mitigating adverse impacts on human health, ecosystems, and finite resources. A prime example of such improvements is evident in the D + PV + D + HI system, where the contribution of internal heating is curtailed to 65.6 % and 20.1 % for ethanol and isobutanol removal, respectively. While, in the case of ethanol–water, this remains 24.5 % higher than in the D + PV system, the reduction for isobutanol is noteworthy at 7.6 %. The other significant contributing factors encompass electrical energy and cooling water.

### 3.3. Economic side of hybrid processes

Fig. 5a provides a comprehensive overview of the total cost for the studied hybrid separation systems. The percentage of TOC and TIC in the TAC of each hybrid process is depicted in Fig. 5b. Detailed data on TOC, TIC, and TAC of distillation columns, heat exchangers and PV membranes can be found in Tables S6–S8 in Supporting Information.

The breakdown of investment costs (IC) across external columns, internal columns, condensers, heat exchangers, and PV components unveils distinctive variations among the evaluated processes. In the ethanol–water scenario, the D + PV process consistently emerges with

the lowest IC at about 97,000 €/year, while the D + PV + D system incurs the highest at about 163,000 €/year. Although the TIC value of D + PV is the smallest, it accounts for the highest percentage of TAC, making up 56.7 %, while the remaining two methods, D + PV + D and D + PV + D + HI, account for 35.9 % and 46.0 % of TAC, respectively. Conversely, for isobutanol–water separation, the IC of the D + PV system is 1.78 times larger than that of the D + PV + D, a difference that increases to 1.81 times for the D + PV + D + HI system. The ranking of TIC percentage in TAC for these three hybrid processes compared to ethanol and isobutanol scenarios is identical. This discrepancy is attributed to variations in PV membrane area and boiler size, wherein systems requiring more PV, larger heat exchangers, and distillation columns necessitate higher initial investments. The D + PV system exhibits a predominant investment cost allocation in both ethanol and isobutanol scenarios, with the highest percentage attributed to PV (41.6 % for ethanol, 40.2 % for isobutanol). Following this, the distribution descends in the order of external column, reboiler, internal column, and condenser. However, in the D + PV + D and D + PV + D + HI systems, there is a notable shift in the investment cost distribution. The percentage allocated to the boiler, reboiler, and condenser experiences an increase. At the same time, the investment cost for PV decreases significantly, representing only 10.2 %–13.2 % for the ethanol scenario and 26.4 % – 29.1 % for the isobutanol scenario.

Operating costs (OC), encompassing cooling, heating, and PV-related expenses, exhibit a parallel trend. A noteworthy observation is that the

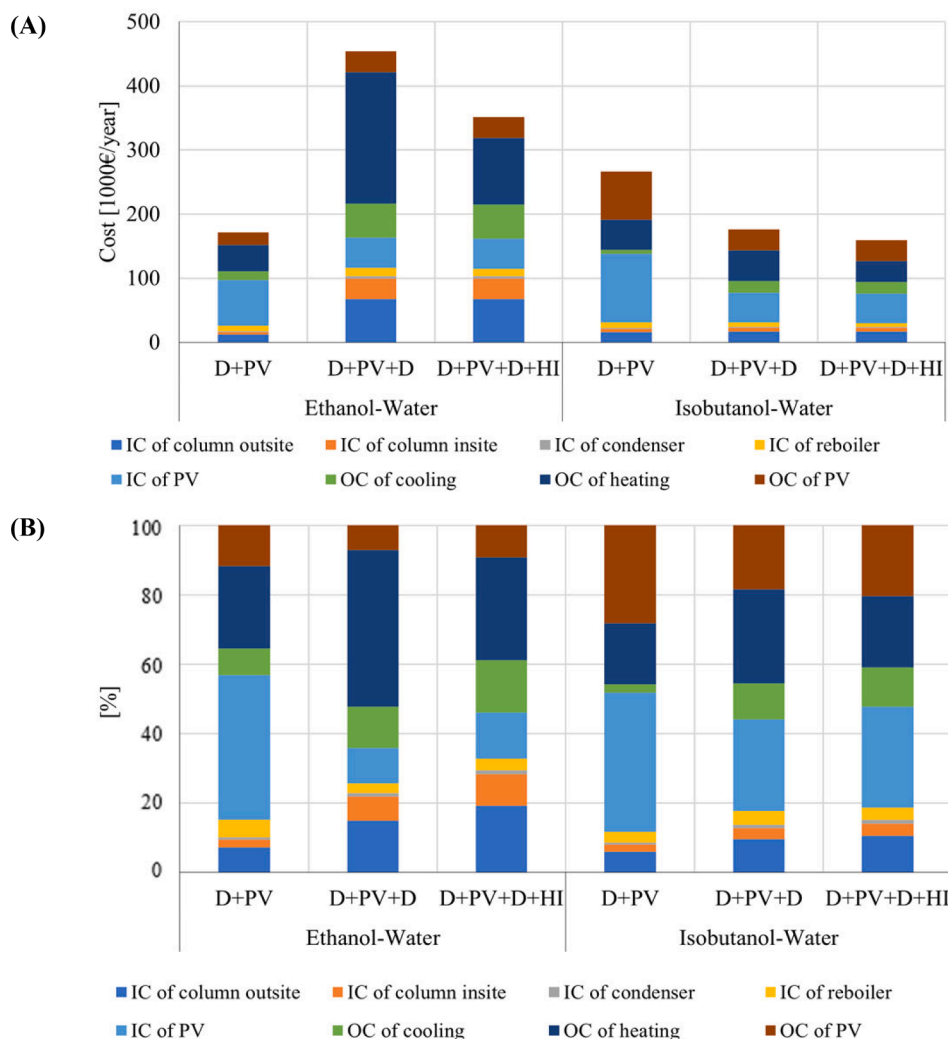


Fig. 5. (a) The value, and (b) percentage of the total investment cost and total operation cost of the investigated processes.

D + PV system records an IC larger than the OC for both ethanol and isobutanol, whereas the D + PV + D and D + PV + D + HI systems feature an OC exceeding the IC. With the exception of the D + PV scenario for isobutanol, all other five cases consistently show that the highest percentage of OC is attributed to heating, followed by PV and cooling.

Combining IC and OC yields the total annual cost (TAC), offering a holistic perspective on the economic viability of each process. The results highlight the D + PV process as the most economically favorable choice across ethanol–water separation scenarios, with a TAC of about 172,000 €/year. In contrast, the D + PV + D system registers the highest TAC at 454,000 €/year, followed by the D + PV + D + HI system at 351,000 €/year. Notably, for isobutanol–water mixture scenario, the TAC of all systems decreases, with values of about 266,000 €/year, 176,000 €/year, and 160,000 €/year for D + PV, D + PV + D, and D + PV + D + HI, respectively.

Dian Ning Chia et al. (2023) [14] calculated the TAC of D + PV and D + PV + D hybrid processes to separate azeotropic ethyl acetate/ethanol mixture with a minimum boiling point. The feed composition was 0.2/0.8 mol/mol at a flow rate of 200 kmol/h, with the aim of obtaining at least 99 mol% purity of ethyl acetate and ethanol in the corresponding product streams. The PV membrane was operated at a maximum allowable temperature of 70 °C, a feed pressure of 5 bar, and a permeate side pressure of 400 Pa. Assumptions were made regarding the operational parameters, including 8,400 h per year of distillation operation, an eight-year plant lifespan, and a two-year membrane lifetime. The results indicated that the D + PV + D and D + PV configurations required membrane areas of 522 m<sup>2</sup> and 1,224 m<sup>2</sup>, respectively. Notably, the TAC of the D + PV + D system was found to be 10.3 % lower compared to the D + PV process. These findings align with our study's results, suggesting that the D + PV + D system offers advantages in minimizing membrane area and investment costs for PV membrane units. Consequently, beyond its applicability in separating isobutanol–water mixtures, the D + PV + D configuration proves to be well-suited for separating ethyl acetate/ethanol mixtures based on cost factors.

In the hybrid processes, the investment cost of pervaporation membranes contributes a significant fraction of the TAC. Depending on the number of pervaporation units, the TIC of pervaporation may exceed that of the distillation column. However, despite the potentially higher up-front investment in membranes, the operational cost benefits of membrane operation outweigh the high energy requirements of standard distillation processes, especially in the face of increasingly scarce energy resources and rising global energy prices. For example, hybrid extraction distillation pervaporation (EDPV) was compared with three-column extraction distillation (TCED) and three-column pressure swing distillation (TCPSD) for the separation of ethyl acetate/ethanol/water mixture in a recent study, the TAC of EDPV was found to be 22.2 % higher than TCED but significantly lower, 61.1 % and 28.6 %, compared to TCPSD without partial heat integration and with partial heat integration (HI), respectively [17].

This comprehensive economic evaluation underscores the pivotal role of process configuration in determining the economic feasibility of ethanol–water and isobutanol–water separation, providing critical insights for decision-making in industrial applications. Further refinements and optimizations may be identified through detailed assessments and sensitivity analyses.

### 3.4. Results of PESTLE and MCDA analysis

The analyzed PESTLE factors are employed as numerical input parameters in the MCDA framework. Specifically, environmental and social factors are derived from the impact assessment findings in Section 3.2, economic factors are drawn from the economic analysis in Section 3.3, while political and legal, as well as technological factors, undergo assessment based on their TOPSIS Scores, with higher scores signifying superior performance, as evident in Table 5. Classical TOPSIS method

**Table 5**

Classical TOPSIS method for qualitative criterion assessments (the higher value is better).

	Ethanol–Water			Isobutanol–Water		
	D + PV	D + PV + D	D + PV + D + HI	D + PV	D + PV + D	D + PV + D + HI
Political & Legal	5	8	9	4	8	9
Social	8	5	6	4	3	5
Technological	5	7	8	3	7	8
Economic	8	2	4	5	8	9
Environmental	8	3	5	6	4	7

assesses qualitative criteria on a scale from 1 to 10, where a higher value indicates better performance.

The assignment of weights to factors is a subjective process, often influenced by the decision-maker's personal judgment. In this study, social and environmental factors carry the most significant weight, at 0.325, followed by economic factors at 0.175, and technological factors at 0.113. Conversely, political and legal factors are assigned relatively lower importance, with a weight of 0.062. It's important to note that the cumulative weight of all factors equals 1, ensuring a comprehensive assessment.

Fig. 6 presents the Multi-Criteria Decision Analysis (MCDA) results, underscoring the optimal alternative for ethanol–water mixture separation as the D + PV process, attaining a notable TOPSIS score of 0.869. Conversely, for separating isobutanol–water mixtures, the D + PV + D + HI technology outperforms the D + PV system, showcasing a superior TOPSIS score of 0.637 instead of 0.395. The results indicate that the D + PV process stands out as the most effective method for removing ethanol from water mixtures, as evidenced by its high TOPSIS score. Conversely, in scenarios involving the separation of isobutanol from water, the D + PV + D + HI system emerges as the preferred choice, boasting a significantly elevated TOPSIS score.

In summary, the MCDA outcomes underscore the efficiency of different technologies in distinct separation scenarios. D + PV excels in ethanol–water mixtures, while the D + PV + D + HI system demonstrates superior performance in isobutanol–water mixtures, emphasizing the importance of tailoring the approach to the specific components being processed.

### 3.5. Results of using renewable energy sources in hybrid processes

The global imperative to promote renewable energy has become paramount as nations strive to confront climate change, bolster energy security, and transition towards sustainable, cleaner energy sources. In alignment to achieve climate neutrality by 2050, the European Union (EU) has fervently championed the widespread application of renewable energy across various economic sectors. This study also evaluates using renewable energy to replace traditional energy to reduce the negative impacts of hybrid processes on humans and the environment. Five energy sources are investigated for the requirement of electricity and heat in hybrid processes: hard coal, solar, wind offshore, hydro run of river, and biofuel.

Adopting renewable energy in hybrid processes offers multifaceted advantages, encompassing environmental and economic dimensions. Fig. 7 illustrates the substantial change observed when incorporating various energy sources into the hybrid system, presented as percentages for ethanol (Fig. 7a) and isobutanol (Fig. 7b) based on ReCiPe method's single score. A comprehensive breakdown of the single score for ethanol and isobutanol, considering alternative energy sources, is provided in Tables S9 and S10 in the Supporting Information.

Notably, renewable energy sources exhibit a significantly lower environmental impact—ranging from 70.43 % to 94.36 %—compared to fossil fuels. Integrating renewable energy in hybrid processes

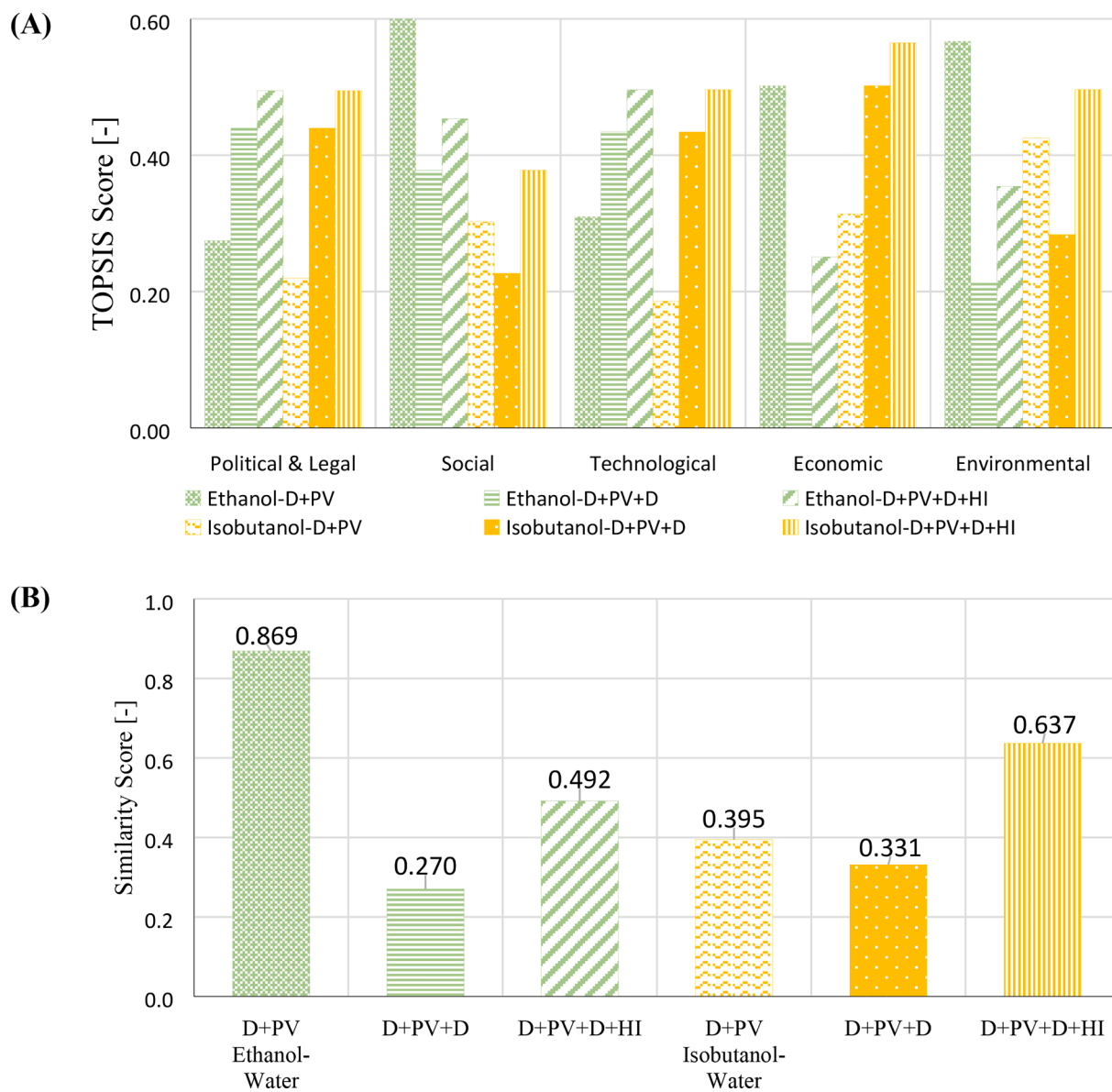


Fig. 6. (a) The Topsis Score diagram, (b) Final result of the MCDA.

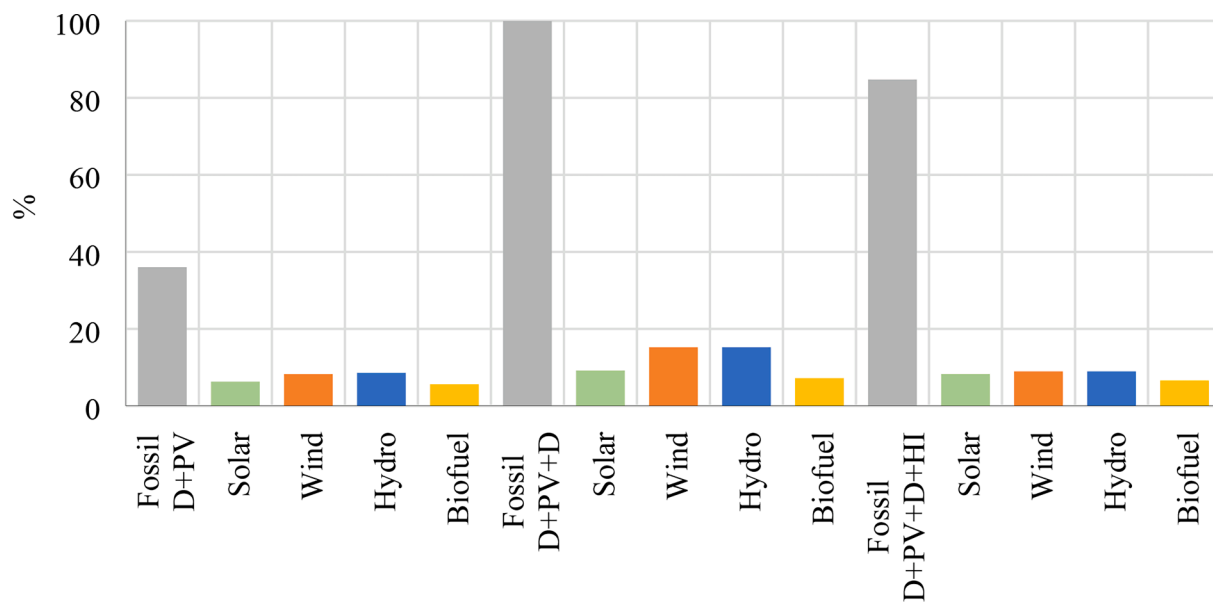
contributes substantially to an overall reduction in the carbon footprint associated with production. Substitution efficiency of renewable energy is particularly pronounced in energy-intensive processes like separating the ethanol–water mixture. Further analysis reveals that biofuel emerges as the most advantageous energy source for both ethanol and isobutanol hybrid processes, resulting in the lowest single score compared to hard coal, solar, wind, and hydro—with solar ranking second, followed by wind, and hydro showing comparable impacts. The adverse effects associated with the D + PV + D and D + PV + D + HI systems, as discussed in section 3.2, can be substantially mitigated through the utilization of heat and electricity derived from renewable energy sources. In the scenario of D + PV + D + HI for ethanol, the proportions of biofuel, solar, wind, and hydro energy stand at 7.79 %, 9.77 %, 10.57 %, and 10.57 %, respectively, as opposed to their counterpart, hard coal. Similarly, in the context of D + PV + D + HI for isobutanol, the corresponding percentages for biofuel, solar, wind, and hydro energy are 31.95 %, 33.48 %, 37.87 %, and 37.87 %, presenting a notable contrast with the utilization of fossil fuel.

Beyond the immediate environmental benefits, adopting renewable energy alternatives offers a strategic advantage by reducing dependence

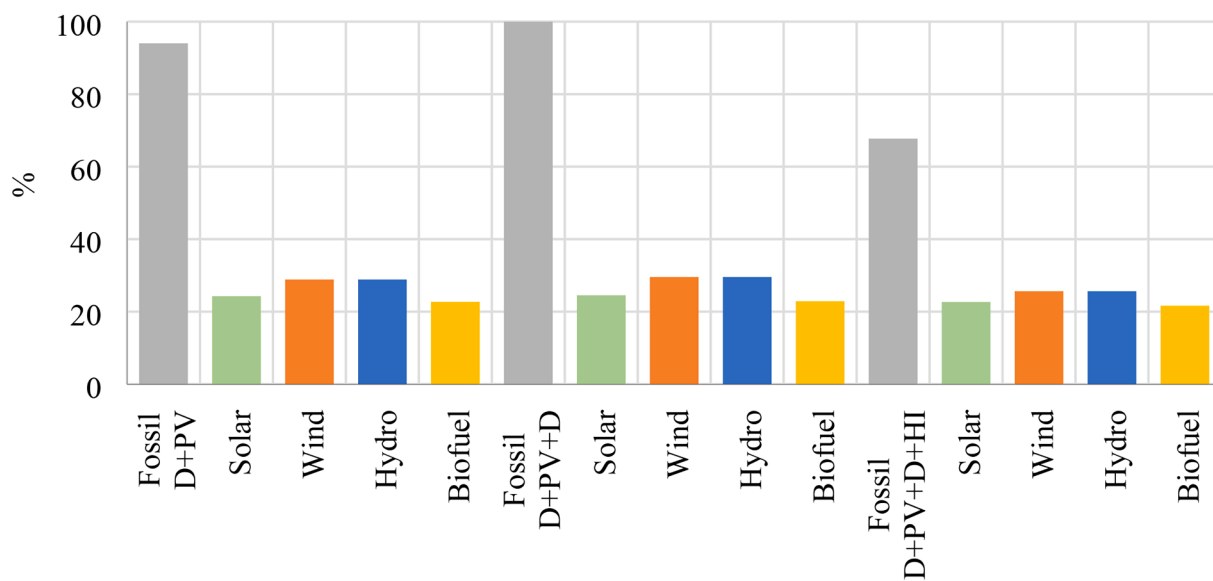
on external energy sources, notably, fossil fuels susceptible to price volatility and geopolitical uncertainties. This transition enhances energy security, benefiting both businesses and nations alike. Moreover, incorporating renewable energy in hybrid processes promotes innovation and technological advancements. Ongoing efforts by researchers and engineers to optimize renewable energy systems for industrial applications promise more efficient and sustainable processes, contributing to a transformative shift towards a cleaner, resilient energy future.

### 3.6. Results of comprehensive heat integration with Pinch analysis of hybrid processes

An alternative strategy to mitigate the adverse effects (discussed in Section 3.2) of hybrid processes involves optimizing energy consumption by implementing comprehensive heat integration based on Pinch Analysis. The identified minimum temperature difference ranges from 10 to 50 K. Optimal comprehensive heat integration is achieved with minimum utility requirements. This signifies a lower energy target and a smaller Pinch temperature, resulting in highly efficient heat exchange and integration within the system. Detailed consideration of minimum



(A) Ethanol-Water mixture



(B) Isobutanol-Water mixture

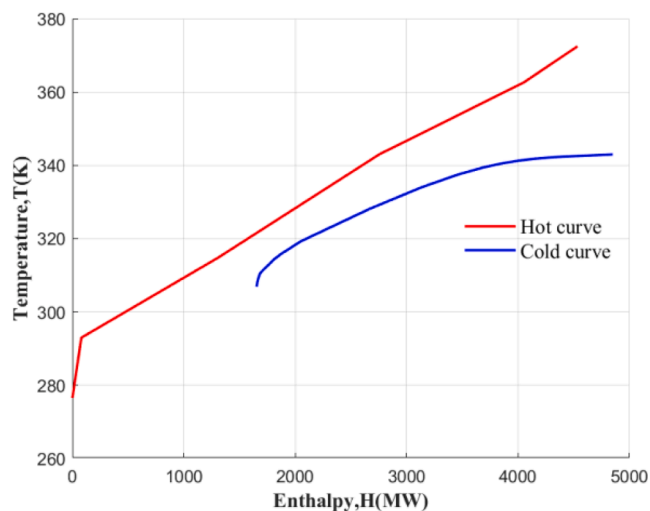
**Fig. 7.** The change in percentages of the investigated hybrid processes combination with energy alternatives for (a) ethanol–water mixture and (b) isobutanol–water mixture based on the single score of ReCiPe 2016 Endpoint (H) method.

utility requirements is crucial to achieving optimal heat integration because it reduces costs, saves resources, refines processes and minimizes environmental impact, as well as increases efficiency.

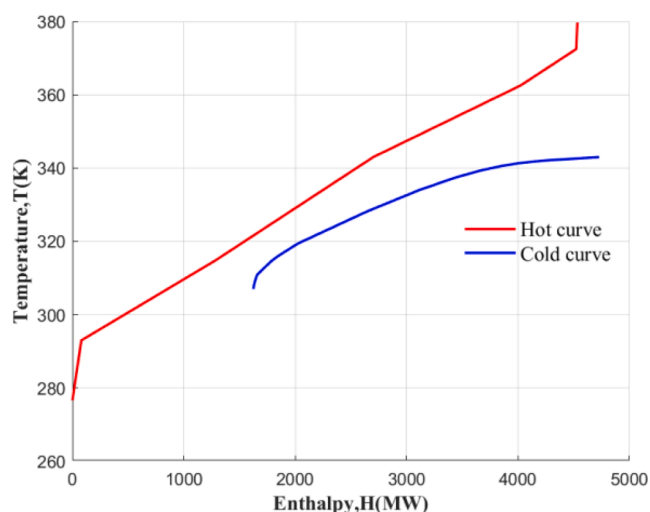
Composite Curve figures offer a visually insightful representation of potential energy recovery opportunities. These prospects become particularly promising when a substantial overlap exists between the Cold and Hot Composite Curves. In the case of separating ethanol–water mixtures, D + PV, D + PV + D, and D + PV + D + HI exhibit limited heat integration ability due to a relatively small overlap between the cold and hot streams. However, for isobutanol–water mixture scenario, combining heat integration across all three systems, especially in D + PV and D + PV + D systems, proves highly effective, as illustrated in Fig. 8.

The summarized Composite Curve of the investigated hybrid processes for both ethanol–water and isobutanol–water separation is presented in Fig. S3 of the Supporting Information section. Notably, these graphs illustrate the correlation between temperature and enthalpy for 1 kg of output stream containing 99.9 wt% of alcohol.

In Fig. 8, the visual comparison of the two composite curve graphs, namely D + PV and D + PV + D, for isobutanol scenarios reveals minimal disparity in terms of slope and distance. Specifically, in the instance of D + PV for isobutanol, the hot stream (depicted by the red line) enters the heat exchanger at 372.49 K from the right and leaves at the left side at 276.56 K. Employing a counter-current heat transfer approach, the cold stream (illustrated by the blue line) flows into the exchanger at



(A) D+PV



(B) D+PV+D

Fig. 8. Composite Curve of (a) D + PV and (b) D + PV + D hybrid process for separation of isobutanol-water mixture.

306.9 K on the left side and out at 343.00 K on the right side. The horizontal separation between the red and blue lines denotes the heat transfer rate from the hot to cold streams. Furthermore, the slope of the hot or cold streamline is inversely proportional to the stream's capacity to release or absorb heat. In the D + PV + D + HI scenario for isobutanol, the graph exhibits a larger slope and distance between the cold and hot streams, indicating diminished effectiveness compared to the D + PV and D + PV + D systems. This observation suggests that heat integration in the presence of D + PV + D + HI process is less efficient, as evidenced

Table 6  
Results of heat integration based on Hint software.

Parameters	Ethanol-Water			Isobutanol-Water			Unit
	D + PV	D + PV + D	D + PV + D + HI	D + PV	D + PV + D	D + PV + D + HI	
Pinch temperature	356	356	298	324	321	297	K
Heating target	1,485	7,877	8,282	317	196	3,477	kW
Cooling target	3,146	3,516	1,152	1,653	1,624	587	kW

by the expanded slope and distance metrics. The heat transfer of each stream within the D + PV + D system for isobutanol is illustrated in the heat exchanger network diagram showcased in Fig. S4 of the Supporting Information.

The results of comprehensive heat integration based on Pinch analysis are summarized in Table 6. In isobutanol scenarios, a comparison between the D + PV and D + PV + D systems reveals that the D + PV + D system is more effective and has a lower energy target (total heating and cooling target) and Pinch temperature. In Table 6, the Pinch temperature of the D + PV + D process for separating the isobutanol-water mixture is 321 K, with minimum cooling and heating duties requirements of 1,624 kW and 196 kW, respectively.

### 3.7. Limitations and suggestions for future research

Some notable limitations in this study should be mentioned. While the operation of the separation processes is considered, the manufacturing and waste discharge phases are neglected because of limited data availability. Overlooking these stages may have significant environmental impacts, potentially affecting the overall results. Stainless steel is commonly used to construct distillation columns due to its exceptional corrosion resistance and mechanical properties. Conversely, some pervaporation membranes are made of polymer materials that may not be in accordance with environmentally friendly practices. Consequently, there are concerns about the waste management and sustainability of the disposal of these materials.

Hybrid distillation and pervaporation processes offer significant advantages, such as improved separation efficiency and reduced energy consumption compared to conventional distillation, but they also have limitations. These hybrid processes may not apply to all separation tasks or feed compositions. While the D + PV + D + HI system is optimal for isobutanol-water mixture separation, the D + PV configuration is better for ethanol-water separation. Specificity highlights the need to consider feed mixtures' selectivity and compatibility with available membranes, limiting the processes' applicability in specific industries or applications. Hybrid processes are challenging to maintain due to their complexity and multiple interacting components. Pervaporation membranes are susceptible to fouling, leading to a degradation in separation performance with increasing time. Therefore, the regular maintenance of equipment (such as membranes, pumps, valves, etc.) is essential for optimal performance and durability.

Several opportunities for future research could be explored to address these limitations and further improve the performance and applicability of hybrid distillation and pervaporation processes:

- Investigating environmentally friendly alternative materials with low investment costs for pervaporation membranes and distillation.
- Conducting comprehensive scale-up studies to bridge the gap between laboratory-scale experiments and industrial-scale applications of hybrid distillation and pervaporation processes while addressing challenges related to mass transfer, heat transfer, and system dynamics.
- Development of advanced optimization algorithms and control strategies for optimizing hybrid distillation and pervaporation processes. The performance of these algorithms should consider factors such as feed composition variability, membrane clogging dynamics,

and energy consumption to achieve optimal performance under variable operating conditions.

- Reducing energy consumption by increasing heat integration and exploring the application of renewable energy sources, especially biofuel and hydrogen energy sources. Identifying opportunities to integrate these processes into biofuel production paths can further improve efficiency and sustainability.

#### 4. Conclusion

This study systematically evaluates and compares three hybrid process configurations—D + PV, D + PV + D, and D + PV + D + HI—targeting the separation of ethanol–water and isobutanol–water mixtures using LCA, PESTLE, and MCDA methods to identify energy-efficient and environmentally friendly solutions. This study represents a significant advancement as it thoroughly examines the D + PV + D and D + PV + D + HI hybrid systems for the first time based on technology, environmental impacts, and economic aspects through various methods.

D + PV process achieves outstanding separation results, yielding a 99.9 wt% purity for ethanol and water. However, for isobutanol–water separation, maintaining the same purity requires numerous membranes. Specifically, for ethanol and isobutanol scenarios, a total PV membrane area of 200 m<sup>2</sup> and 300 m<sup>2</sup> is required, respectively. A more efficient alternative arises with the introduction of a second distillation column (D + PV + D), requiring only 130 m<sup>2</sup> of PV membrane for optimal performance in separating both alcohols. Given the relatively high investment cost of PV membranes, the reduction in the total membrane area required results in savings of 35 % and 57 % in TIC for ethanol and isobutanol, respectively.

While D + PV + D proves effective, it imposes significant energy and heat requirements, potentially impacting human health and the environment. Heat integration mitigates these concerns, saving excess heat, reducing energy input, and promoting sustainability. Enhancement of the D + PV + D + HI system reflects a commitment to efficient and sustainable separation processes. The EF method reveals CO<sub>2</sub>-eq emissions for D + PV + D + HI in isobutanol scenarios is 6.33 × 10<sup>-1</sup> kg CO<sub>2</sub>-eq, with an SD of 2.30 × 10<sup>-1</sup>, SEM of 2.30 × 10<sup>-3</sup>, CV of 36.3 %, and a value ranging from 1.87 × 10<sup>-1</sup> to 1.09 × 10<sup>0</sup> kg CO<sub>2</sub>-eq, which are 0.85 and 0.82 times that of D + PV + D and D + PV, respectively. D + PV + D + HI also demonstrates 11.2 %, 12.6 %, and 14.6 % smaller impacts on human health, ecosystems, and resources and a 40.0 % reduction in TAC than D + PV system.

The investigation illustrates a clear correspondence between the environmental impacts, TAC value, and the heat energy requirements of these hybrid processes. A discernible correlation emerges: lower heating energy corresponds to reduced environmental impact and TAC.

Exploring hybrid process improvements extends to alternative renewable energy sources and comprehensive heat integration based on Pinch Analysis. In the D + PV + D + HI for isobutanol scenario, biofuel, solar, wind, and hydro energy comprise 32.0 %, 33.5 %, 37.9 %, and 37.9 %, respectively, contrasting fossil fuel usage. Based on Pinch analysis, heat integration is limited for ethanol–water mixtures; isobutanol–water separation benefits from combined heat integration across D + PV, D + PV + D systems. Notably, the D + PV + D system is the most effective, requiring fewer heat exchangers, a smaller heat exchanger area, and a lower energy target than other processes.

Finally, this research significantly improves separation technologies and emphasizes integrating sustainability into industrial processes. By evaluating hybrid process configurations, it identifies efficient separation methods while promoting greener industrial practices. This is consistent with worldwide efforts to address climate change and achieve net-zero CO<sub>2</sub> emissions. Overall, this study provides a framework for sustainable decision-making in industry and contributes to a more sustainable future.

#### CRedit authorship contribution statement

**Huyen Trang Do Thi:** Writing – original draft, Visualization, Methodology, Investigation. **Andras Jozsef Toth:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2024.127684>.

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