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DOI

[10.1016/j.cep.2024.109689](https://doi.org/10.1016/j.cep.2024.109689)

Publication date

2024

Document Version

Final published version

Published in

Chemical Engineering and Processing - Process Intensification

Citation (APA)

Janković, T., Straathof, A. J. J., & Kiss, A. A. (2024). Thermally self-sufficient heat pump-assisted azeotropic dividing-wall column for biofuels recovery from isopropanol-butanol-ethanol fermentation. *Chemical Engineering and Processing - Process Intensification*, 197, Article 109689. <https://doi.org/10.1016/j.cep.2024.109689>

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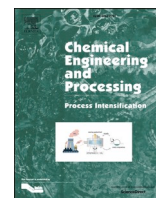
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Thermally self-sufficient heat pump-assisted azeotropic dividing-wall column for biofuels recovery from isopropanol-butanol-ethanol fermentation

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ARTICLE INFO

Keywords:

Process intensification
Downstream processing
Azeotropic dividing-wall column
Heat pumps
Process electrification

ABSTRACT

Isopropanol-butanol-ethanol (IBE) fermentation is a superior biofuel production technology as compared to acetone-butanol-ethanol (ABE) fermentation due to the better fuel properties of the obtained products. However, low product concentrations, thermodynamic constraints and the presence of microorganisms lead to complex downstream processing that limits the competitiveness of this biofuel production method. Thus, this original research proposes a novel thermally self-sufficient and eco-efficient downstream process for industrial-scale recovery after IBE fermentation (74 ktonne/y capacity), from a highly dilute broth (>97 wt% water). Gas stripping and heat pump-assisted vacuum evaporation were implemented to separate valuable products from most of the broth. Furthermore, an advanced highly integrated heat pump-assisted azeotropic dividing-wall column was designed to recover high-purity (99 wt%) butanol biofuel and isopropanol – ethanol fuel supplement (89 wt%). The proposed purification process recovers over 99 % of biofuel products in a cost-effective (0.130 \$/kg_{IBE}) and energy-efficient way (0.673 kW_{ch}/kg_{IBE}) while allowing full recycle of biomass and most of the separated water. Besides improving yield by continuously recovering the inhibitory products, fermentation can be further enhanced by avoiding biomass loss and reducing water requirements. Lastly, the implemented energy-saving techniques ensure complete electrification of the proposed IBE recovery process. Therefore, the original results of this research study significantly contribute to the development of sustainable biofuel production processes.

1. Introduction

The production of different biochemicals by fermentation potentially presents a great opportunity for sustainable development due to lower environmental impact, relatively mild process conditions and the possibility to use a wide range of substrates (e.g. lignocellulosic biomass, waste organic biomass, industrial off-gases) [1]. Nonetheless, inhibitory effects on microorganisms lead to low product concentrations that often limit industrial-scale fermentation. The end-product inhibition phenomenon may be mitigated by developing advanced concurrent alcohol recovery and fermentation (CARAF) methods that allow continuous removal of products while fermentation is ongoing [2]. However, purifying valuable bioproducts from very dilute fermentation broth in a cost-effective and energy-efficient way is especially challenging.

While technologies for the production of higher alcohols may not be as mature and well-developed as those for bioethanol, their higher

energy content potentially makes them superior renewable fuel alternatives. Compared to ethanol, 1-butanol (abbreviated to butanol) has a higher energy density (about 27–29.2 MJ/kg_{butanol} vs 19.6 MJ/kg_{ethanol}), a higher compatibility and mixing ratio with gasoline that eliminates the need to modify automobile engines, and lower corrosivity that facilitates storage and transport using existing infrastructure [3]. The common biobutanol production by fermentation is performed via the acetone – butanol – ethanol (ABE) pathway. However, limited variety and incomplete utilization of substrates, high by-product formation, and low productivity are limiting the industrial wide-spreading of ABE fermentation [4]. Furthermore, the extensive formation of acetone, which is a non-fuel and corrosive chemical, might jeopardize the economic viability of the ABE fermentation processes [5]. Significant effort has been put into genetic engineering to develop acetone-free butanol production. Nonetheless, the risk of unexpected behavior of modified microorganisms in industrial-scale semi-sterile processes is not

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<https://doi.org/10.1016/j.cep.2024.109689>

Received 10 December 2023; Received in revised form 9 January 2024; Accepted 24 January 2024

Available online 25 January 2024

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negligible [5]. Furthermore, inhibition of key genes for the synthesis of acetone resulted in higher acid concentrations but lower butanol production [6]. Therefore, converting acetone into another valuable chemical might be more beneficial than inhibiting its formation [4]. In that respect, isopropanol can be produced instead of acetone in isopropanol – butanol – ethanol (IBE) fermentation [7]. Isopropanol is an important commodity chemical that can also be used as a fuel supplement [8]. Furthermore, a mixture of solvents produced by IBE fermentation might be directly used as renewable automotive fuel [4,5,7]. Nonetheless, microorganisms commonly employed in the IBE fermentation are more easily inhibited by product formation, resulting in lower concentrations compared to the ABE fermentation [5]. Thus, advanced recovery processes are needed to support the development of industrial-scale biofuel production by the IBE fermentation.

To our knowledge, extensive work has been performed on product recovery from the ABE fermentation [9–18], but only a few studies have been published on downstream processing after the IBE fermentation. An efficient recovery process is needed to separate valuable products after the fermentation and purify them to meet market requirements. The feed stream for the recovery process is broth taken directly from the fermenter. Due to the end-product toxicity phenomenon, this stream is commonly a very dilute aqueous solution containing valuable fermentation products (butanol, isopropanol and ethanol), microorganisms, non-volatile inert components and potentially some CO₂ as a product of microorganisms metabolism. Thus, advanced separation techniques are needed to ensure adequate product recovery and purification from complex dilute mixture. In-situ recovery by gas-stripping and adsorption was combined with a sequence of seven distillation columns to purify fermentation products. However, the designed downstream processes resulted in high energy consumption even after heat integration [19]. A combination of extractive and azeotropic distillation, whereby butanol is used as an entrainer, was implemented for dehydration of IBE mixture starting from 4 to 6 wt% IBE in feed, with total energy requirements of about 6.5–8.2 MJ/kg_{IBE} [20]. Furthermore, a sequence of six distillation columns was designed to recover high-purity butanol and dehydrate isopropanol and ethanol mixture [21], using a feed stream (31,282 kg/h with 4.46 wt% butanol, 2.37 wt% isopropanol, 0.29 wt% ethanol and 92.88 wt% water) after the gas stripping in-situ product removal [19]. In this design, extractive distillation was used to remove water from the isopropanol and ethanol mixture [21], instead of previously proposed pressure swing distillation [19], resulting in lower energy consumption (about 1.2–2.2 kW_{th}/kg_{IBE}). Moreover, liquid-liquid extraction in combination with extractive distillation was developed to dehydrate the IBE mixture from 22,592 kg/h feed containing 5.47 mol% butanol, 3.57 mol% isopropanol and 0.02 mol% ethanol [22]. This design was extended with an organic Rankine cycle to reduce the total purification costs [23]. Further developing downstream processing after gas stripping in-situ product removal [19], a sequence of distillation columns, including extractive distillation with dimethyl sulfoxide, was suggested to reduce energy requirements (to about 2.8 kW_{th}/kg_{IBE}) [24]. Lastly, reactive distillation with ethylene oxide was proposed to recover butanol and dehydrate isopropanol – ethanol mixture [25] using the same feed [19]. Even though energy usage is reduced to about 1.7 kW_{th}/kg_{IBE}, and ethylene glycol is produced as a side product, using ethylene oxide to remove excess water may bring additional risks due to the extremely hazardous nature of this substance [26].

However, none of the suggested downstream processing methods was developed for a large-scale industrial IBE fermentation, with the largest butanol production capacity reported being cca. 11 ktonne/y [19,21,24,25]). Furthermore, several downstream processing studies [21,24,25] used the stream after gas stripping and adsorption as a feed, but the costs associated with these operations were excluded in the final evaluation of the purification process. Alternatively, even higher fermentation product concentrations were assumed [22,23] in the feed stream. Thus, the primary objective of this original research is to develop an enhanced recovery process for industrial-scale IBE

fermentation (74 ktonne/y IBE = 50, 20 and 4 ktonne/y of butanol, isopropanol and ethanol, respectively), directly from the dilute stream after the fermentation. The major novelty in this study is the design of an advanced heat pump-assisted azeotropic dividing-wall column, resulting in a less energy- and economically-intensive purification process. Enhancing dividing-wall columns with advanced heat pumping systems has already been researched and proven highly efficient for different systems [27–30]. Still, it has never been considered for recovery of the IBE fermentation products. Additionally, implementing a combination of gas stripping and heat pump-assisted vacuum evaporation removes products from a highly dilute fermentation broth (>97 wt% water) without harming microbial viability, thus allowing recycle of microorganisms with most of the water. Continuously removing inhibitory products from broth can significantly improve the upstream process by increasing fermentation productivity, avoiding loss of biomass and reducing water requirements [31]. Furthermore, the implementation of advanced heat pumping techniques ensures complete electrification, allowing the IBE recovery process to be powered only by renewable electricity. Therefore, the proposed downstream process recovers high-purity biofuels with the opportunity to enhance the upstream process, thus making a significant step toward more sustainable industrial biotechnology.

2. Problem approach

This section outlines the main challenges in designing recovery process and discusses the applied design method. Furthermore, it introduces the foundations of the economic evaluation and sustainability assessment used to evaluate the developed process.

2.1. Process design and simulation

The recovery process was designed for a large-scale industrial IBE fermentation, with a total production capacity of about 74 ktonne/y IBE (50, 20 and 4 ktonne/y of butanol, isopropanol and ethanol, respectively). Being taken from the fermentation step, the feed stream for this process is at atmospheric pressure (1 bar) and fermentation temperature (30 °C) [3]. Due to the inhibitory effects, fermentation broth contains relatively low product concentrations (approximately 1.73, 0.69 and 0.02 wt% of butanol, isopropanol and ethanol, respectively) [4]. Consequently, recovering valuable biochemicals from the highly dilute fermentation broth (>97 wt% water) cost-effectively and energy-efficiently is challenging. Besides the low product concentrations, thermodynamic constraints significantly complicate the recovery process (Table 1). In addition to two azeotropes that are present in the ABE fermentation (butanol – water and ethanol – water), the IBE fermentation products also form a third azeotrope (isopropanol – water), making the purification process even more complex. Due to a strongly non-ideal system, NRTL-HOC property method was chosen to describe the complex thermodynamic interactions between different components in the feed stream. HOC extension (Hayden-O'Connell) was included to reliably describe interactions of polar components in the vapor phase [32]. To ensure the validity of the chosen property model, the predicted thermodynamic properties, presented in Table 1, were tested against

Table 1
Boiling points of pure components and formation of azeotropes at 1 bar.

Pure components		Azeotropes		
Component	Boiling point (°C)	Component	Mass fraction	Temperature (°C) / type
Acetone	56.13	Ethanol	0.9562	78.15 /
Ethanol	78.31	Water	0.0438	homogeneous
Isopropanol	82.05	Isopropanol	0.8729	80.13 /
Water	100.02	Water	0.1271	homogeneous
Butanol	117.75	Butanol	0.5798	92.53 /
		Water	0.4202	heterogeneous

relevant literature [33]. The binary interaction parameters of this system are summarized in Table 2, while the ternary diagram and residue curve map are presented in Fig. 1. Additionally, some living microorganisms and non-volatile inert components are present in the feed stream. They can be realistically assumed to be nonvolatile. Therefore, they are completely removed in the first distillation step, and their separation does not need simulation. However, this is a limiting factor that determines operating conditions for the initial separation of valuable biochemicals from most of the fermentation broth. A combination of gas stripping and heat pump-assisted vacuum evaporation was chosen for this initial step to avoid the usage of additional chemicals that might harm microbial viability and maintain moderate temperatures. Exposing the microorganisms to a reduced pressure should be tested prior to implementation on a large-scale, but it has already been shown that vacuum does not compromise survival of the microorganisms [34–36]. Moreover, a degassing step under reduced pressure can be added to deal with any CO₂ present in the fermentation broth. Valuable products that are removed with CO₂ in the gas stream should be recaptured (absorbed) with water and returned to the (liquid) recovery process to minimize product losses. After the complete removal of the volatile organic products (recovery of over 99.9 %), the remaining aqueous stream may be recycled to the fermentation. Following the initial separation step, a less dilute product mixture can be sent to the novel heat pump-assisted azeotropic dividing-wall column (A-DWC). The bottom products from this highly integrated system are high-purity water (100 wt%) and butanol biofuel (99.0 wt%), while the top product is isopropanol – ethanol mixture (~89 wt% in total – 72 wt% isopropanol, 15 wt% ethanol, 11 wt% water and 2 wt% acetone) that can be used as fuel supplement [8,37–39]. Small amounts of acetone have been proven not to negatively affect fuel performance [40]. Furthermore, advanced heat pumping and heat integration methods were implemented to reduce overall recovery costs, energy requirements and CO₂ emissions. Rigorous simulations for every part of the recovery process are developed using Aspen Plus as an industrial computer-aided process engineering (CAPE) tool. The primary focus during the development of the IBE recovery process was on minimizing the total energy requirements. While there is no theoretical assurance of a global optimum for non-convex mixed-integer nonlinear problems (MINLP), as encountered in the optimization of chemical processes, reducing external energy needs contributes significantly to lowering the total recovery costs. This is particularly significant because a substantial portion of OPEX is linked to the energy supply costs (both thermal and electrical). Several decision variables were taken into consideration during the design process including the total number of trays in columns, placement of the feed tray, reflux ratio, distillate to feed ratio, boilup ratio, vapor fraction, compression ratio, etc. Additionally, several constraints were considered such as temperature limitations in the initial separation step (attributed to the presence of microorganisms), achieving high recoveries for products, ensuring high purities of the recovered products, maintaining a high purity of the water stream for recycling to the fermentation step, etc.

Table 2

Values of the NRTL-HOC binary interaction parameters (values of d_{ij} , e_{ij} , e_{ji} , f_{ij} and f_{ji} are zero).

Components $i - j$	a_{ij}	a_{ji}	b_{ij}	b_{ji}	c_{ij}
Water – Acetone	8.5012	−3.5004	−2280.09	1347.96	0.3
Water – Ethanol	3.7555	−0.9852	−676.031	302.237	0.3
Water – Isopropanol	6.6784	−1.3477	−1444.3	438.615	0.3
Water – Butanol	7.5558	−1.1934	−1390.56	455.482	0.3
Acetone – Ethanol	−1.1757	−0.0764	462.206	174.538	0.3
Acetone – Isopropanol	−2.6868	2.8235	909.193	−694.328	0.3
Acetone – Butanol	−10.984	10.8195	4065.8	−3764.79	0.3
Ethanol – Isopropanol	0.1288	0.657	−215.981	−42.6169	0.3
Ethanol – Butanol	0	0	−127.819	199.039	0.3
Isopropanol – Butanol	0	0	203.73	−208.906	0.3

2.2. Economic evaluation

The economic competitiveness of the proposed IBE recovery process was estimated following the published NREL methodology [41], which accounts for both the total capital (CAPEX) and operating (OPEX) costs. The calculation of CAPEX considers direct capital costs (equipment purchase and installation costs) and indirect capital costs (home office and construction expenses, field expenses, proratable expenses, project contingency, working capital, site development costs, additional piping expenses and warehouse). The calculation of OPEX accounts for fixed operating costs (operating labor, maintenance, and property insurance costs) and variable operating costs (utilities costs). The total annual costs (TAC) and minimum added selling price (MASP) were calculated using the same methodology [41]. More details about the methodology of economic evaluation are presented in the *Supplementary Information* file.

2.3. Sustainability assessment

The performance of the designed recovery process in terms of environmental impact, was assessed using key sustainability metrics, such as energy intensity, water consumption, material intensity, greenhouse gas emissions, pollutants and toxic materials [42]; whereby lower values of these metrics indicate better process performance results from a sustainability viewpoint.

- **Energy intensity** is a measure of the required thermal and electrical energy per kilogram of recovered product [42]. The total energy requirements take into account the electrical to thermal conversion factor (a conservative value of 2.5 is considered [43]).
- **Water consumption** presents the amount of water used per kilogram of recovered product [42]. Cooling water loss of 7 % [42] and a typical steam condensate recovery of 70 % [44] are assumed in the calculation of this indicator.
- **Material intensity** is equal to the amount of waste [42] or non-product [45,46] formed per kilogram of product.
- **Greenhouse gas emissions** present the amount of carbon dioxide (CO₂) that is emitted per kilogram of recovered product [42]. To express the difference in the source of used electricity, a clear distinction is made between grey electricity (sourced from conventional fossil fuels) and green electricity (sourced from renewable sources).
- **Pollutants and toxic materials** account for the amount of pollutants and toxic materials that are formed per kilogram of recovered product [42].

More details about the methodology used for the sustainability assessment are presented in the *Supplementary Information* file.

3. Results and discussion

This section contains the main results related to the process design of the IBE fermentation products recovery. The design and simulation method of the azeotropic dividing-wall column is presented in Fig. 2, while the temperature and liquid composition profiles along this column are shown in Fig. 3. The flowsheet of the designed process is illustrated in Fig. 4, whereby details about the main process streams are summarized in Table 3. Furthermore, the results of the economic and sustainability assessment are presented in Figs. 5, 6 and Table 4.

3.1. Gas stripping and vacuum evaporation

Initially, butanol, isopropanol and ethanol, with some water, need to be separated from the rest of the fermentation broth. Due to the present living microorganisms, operating conditions must not harm microbial viability. The combination of gas stripping and heat pump-assisted vacuum evaporation was designed for this initial separation step. Firstly, the feed stream (broth taken from the fermenter) is sent to the

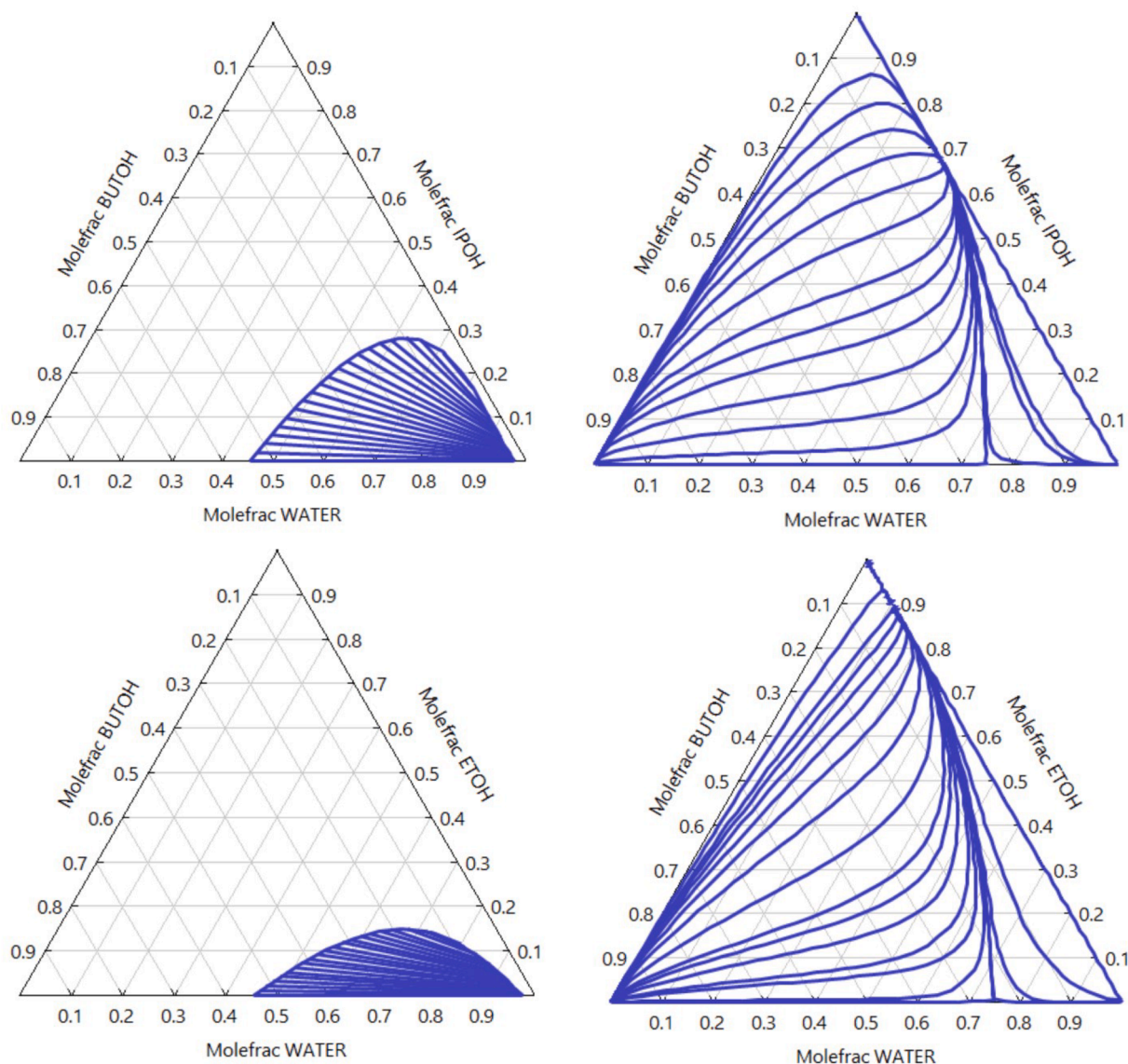


Fig. 1. Ternary diagrams (left) and residue curve maps (right) for the water-alcohols systems. Notation: butanol – BUTOH, isopropanol – IPOH, ethanol - ETOH.

stripping column C1 in which gas (bottom vapor) is used to strip volatile organic products from most of the fermentation broth. The operating pressure for this column was chosen to be 0.038 bar to maintain moderate temperatures. Due to the reduced pressure, structured packing type Sulzer Mellapak 250 (with a pressure drop of 0.225 mbar per theoretical stage) was chosen for column's internals [47]. The bottom aqueous stream, depleted of valuable fermentation products, is further partially evaporated under reduced pressure (0.042 bar). The remaining liquid, containing most of the present water with microorganisms and non-volatile inert components, may be recycled to the fermentation. The formed vapor is used in the stripping column C1 to remove butanol, isopropanol, and ethanol from the initial fermentation broth. However, since vacuum evaporation is very energy intensive (about 48 MW), an advanced heat pumping system is applied to reduce the need for external heating. Vapor recompression is implemented by compressing the product-rich top vapor from column C1 and using it to evaporate part of the depleted aqueous stream. A measure of obtained energy savings can be expressed through the coefficient of performance (COP), which is equal to the ratio of exchanged heat (between the compressed vapor and the liquid stream) and required compressor duty [48]. COP values higher than 2.5, which is the conservative value of electrical to thermal conversion factor [43], indicate energy efficiency of the implemented

heat pump systems. COP values for the described vapor recompression-assisted vacuum distillation is about 15.7, proving significant energy savings. Furthermore, complete electrification of this part of the process is achieved with the described vapor recompression design. Being separated in the vapor phase after gas stripping, valuable products need to be condensed for further treatment. After this initial separation, the obtained product mixture contains 8.1, 3.2, and 0.7 wt% of butanol, isopropanol, and ethanol, respectively. Despite the increased concentrations, further purification is needed to obtain high-purity biofuels.

3.2. Azeotropic Dividing-Wall Column (A-DWC)

Due to the formation of three azeotropes, several steps are required to obtain high-purity biofuel products. Firstly, the liquid mixture of fermentation products, recovered by the first separation step, is pumped to the atmospheric pressure (1 bar) for further purification. Even though a very large amount of water is removed in the first step (about 284,935 kg/h), additional preconcentration is needed. Butanol, isopropanol, and ethanol form azeotropes with water that have lower boiling points compared to pure water (Table 1). Thus, most of the present water can be removed as a bottom product from a distillation column, while all

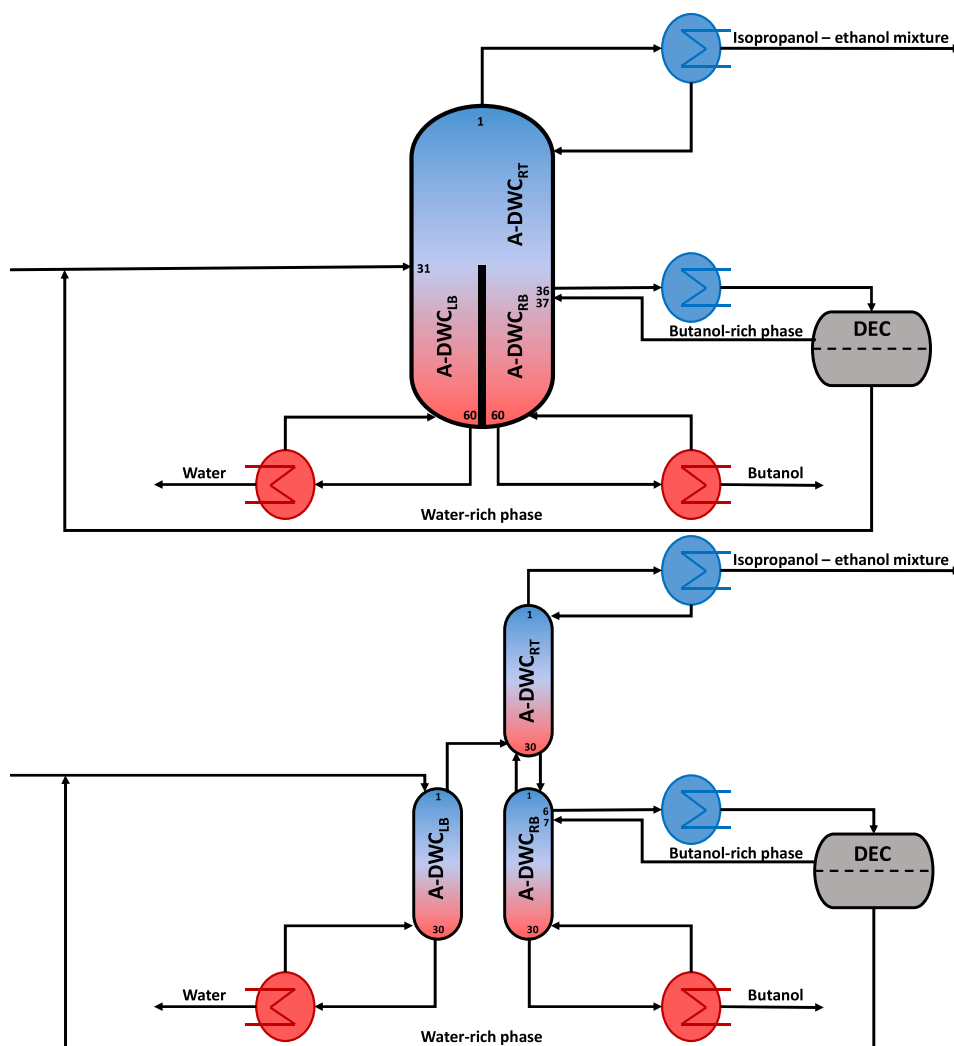


Fig. 2. A-DWC and equivalent configuration of distillation units (simulated in Aspen Plus).

valuable products are obtained as a top product. Furthermore, the mixture of valuable fermentation products, with some water, can be treated in another distillation column whereby isopropanol and ethanol are separated as a top product, while butanol is obtained as a bottom product. Since butanol – water azeotrope is heterogeneous (Table 1), an additional phase splitting in a decanter is needed to obtain a high-purity butanol product. Therefore, a sequence of at least two distillation columns with a decanter is needed to separate pure water, pure butanol and a mixture of isopropanol and ethanol. However, these columns can be merged into one azeotropic dividing-wall column (A-DWC) with a common overhead section and a divided bottom section (Fig. 2) [49]. In this highly integrated system, only one column shell with two reboilers and one condenser is needed. Water and butanol are obtained as the bottom products, while isopropanol – ethanol mixture is obtained as the top product. Additionally, a side stream to liquid-liquid phase splitting unit is needed due to the heterogeneity of the butanol – water azeotrope. Since this dividing-wall column unit is not available in Aspen Plus, an equivalent combination of three distillation columns is simulated (Fig. 2). The left part of A-DWC is presented with A-DWC_{LB}, while the right part of A-DWC is separated into top rectifying (A-DWC_{RT}) and bottom stripping (A-DWC_{RB}) sections.

In total, A-DWC has 60 stages, whereby the rectifying and stripping sections have 30 stages both. A pressure drop of 8 mbar per stage was assumed [50]. The aqueous product mixture, obtained after the initial separation step, is fed to the 31st stage of A-DWC on the left side, which

is the 1st stage of the left stripping section. Pure water (100 wt%) is obtained as the bottom product from the left side. A side stream is taken from the 6th stage of the right stripping section (36th stage of A-DWC) and sent to the decanter for liquid-liquid phase splitting. The butanol-rich phase is returned to the 7th stage of the right stripping section (37th stage of A-DWC), while the aqueous phase is recycled to the 1st stage of the left stripping section (31st stage of A-DWC). High-purity butanol product (99.0 wt%) is obtained as the bottom product from the right side. The mixture of isopropanol and ethanol, with some water, is obtained as the distillate (about 71.9, 14.8, 2.2, and 11.1 wt% of isopropanol, ethanol, acetone, and water, respectively). Liquid flowing down in the rectifying section of A-DWC is directed (using a liquid splitter or liquid redistributor) to the right stripping section, while the feed stream ensures sufficient liquid in the left stripping section.

The described integrated A-DWC design is further enhanced with heat pumping and heat integration. Firstly, the aqueous mixture of valuable fermentation products obtained after the initial separation is subcooled liquid and can be heated to the boiling state to reduce overall reboiler duty for A-DWC. Since pure water product from A-DWC can be recycled to the fermentation with prior cooling, this stream can be used for heating the feed stream to A-DWC. With this heat integration, the total reboiler duty for A-DWC is lowered by about 5.4 MW. Furthermore, as the top and bottom temperatures of the column are relatively close, mechanical vapor recompression (MVR) can be applied to reduce the

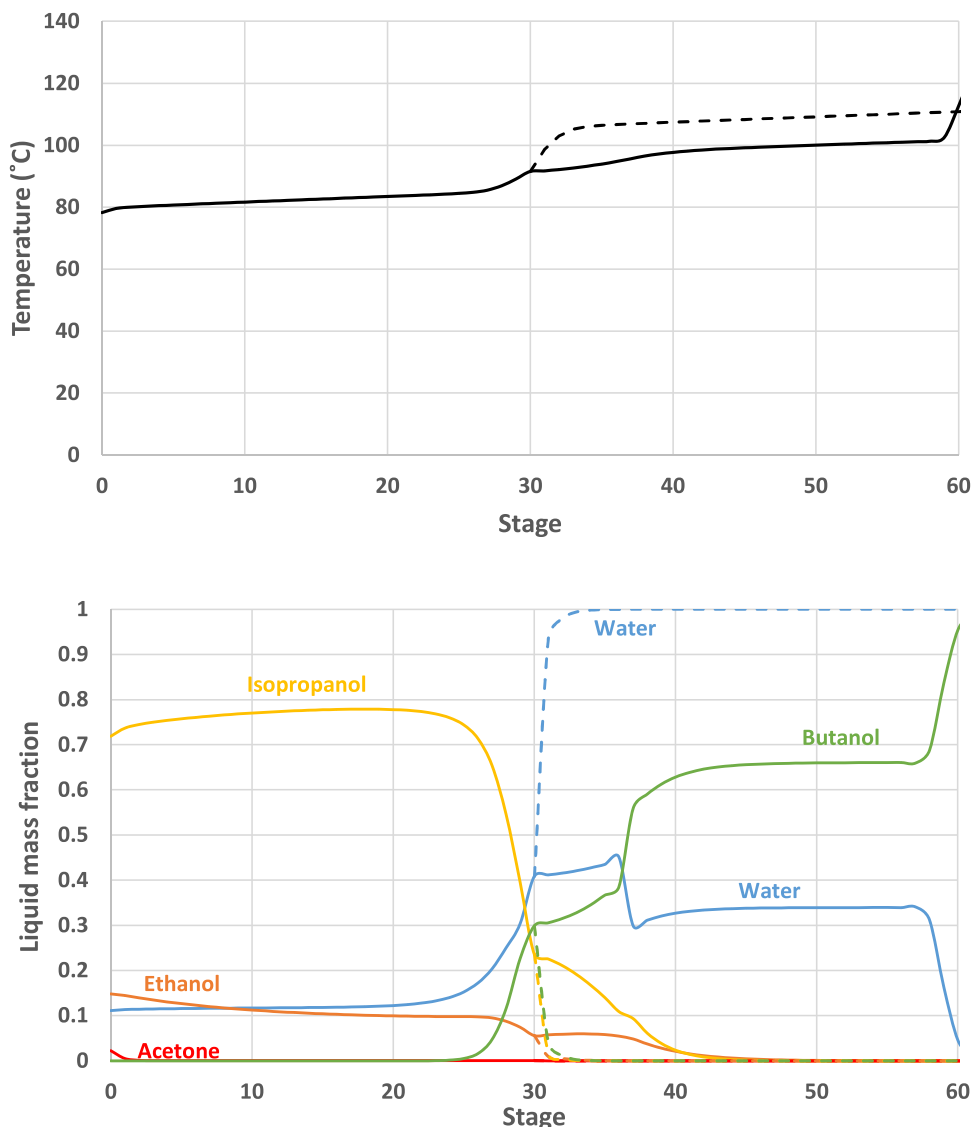


Fig. 3. Temperature and liquid composition profiles along A-DWC (full line – right side, dashed line – left side).

need for both external heating and external cooling [48]. In this heat pumping system, vapor from the top of the column is compressed and used to evaporate the bottom liquids from the left and right sides. COP of the MVR system applied to A-DWC is about 4.9. Thus, significant energy savings are obtained and complete electrification of this part of the process is provided with implementation of the advanced heat pumping systems. The implementation of the described heat integration and heat pumping results in a highly integrated system that might be challenging to control. Nevertheless, it has already been demonstrated that a comparable heat pump-assisted extractive distillation process can be properly controlled [51,52].

Temperature and liquid composition profiles in A-DWC are presented in Fig. 3. The bottom of A-DWC has two temperature and liquid composition profiles due to the splitted bottom and usage of two reboilers. The temperature difference between both sides of A-DWC is about 10 °C, which can be managed without using special insulation. Regarding liquid composition, Fig. 3 illustrates that the bottom products are high-purity water (100 wt%) and butanol (~99 wt%), while the top product is isopropanol – ethanol mixture with some water (about 72, 15, 2 and 11 and wt% of isopropanol, ethanol, water and acetone, respectively). Also, due to the withdrawal of the side stream from the 36th stage and the return of the organic phase on the 37th stage on the right

side, a sudden increase in butanol concentration and a decrease in water concentration can be observed between these stages.

3.3. Economic evaluation

The results of the performed economic evaluation are summarized in Table 4 and Fig. 5. The total cost for installing all equipment units is 18,474 k\$, whereby the largest contribution is the cost of compressors used in the applied heat pump systems (about 50 % of the total equipment cost). The costs of the installed heat exchangers, distillation columns, pumps, and flash vessels make remaining 50 % of the total equipment costs (about 27, 21, 1, and 1 %, respectively). The total CAPEX is equal to 33,922 k\$, whereby the biggest part is equipment installation cost (about 54 % of CAPEX). The total OPEX is 6,761 k\$/y or, expressed per kilogram of recovered biofuel, 0.086 \$/kg_{IBE}. The largest contribution to OPEX is the cost of electricity (about 47 % of OPEX), mainly due to the applied heat pump systems, and the cost of operating labor (about 44 % of OPEX). The contribution of the cost of cooling water and other operating costs is significantly lower (1 and about 8 % of OPEX, respectively). The total annual cost (TAC), accounting for both CAPEX and OPEX with a payback period of 10 years, is 10,153 k\$/y or, expressed per kilogram of recovered biofuels, 0.130

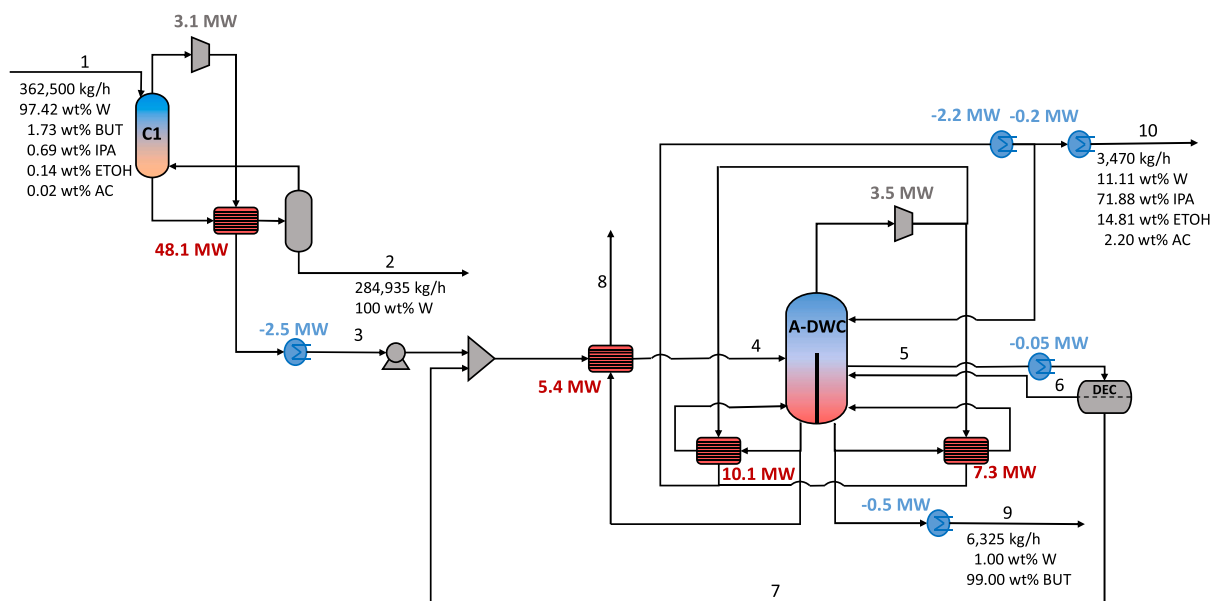


Fig. 4. Flowsheet of the recovery process after IBE fermentation (the compositions and conditions of main process streams are presented in Table 3).

Table 3

Condition and composition of main process streams, see Fig. 4.

Stream	1	2	3	4	5	6	7	8	9	10
Temperature (°C)	30.0	29.9	37.3	98.3	94.7	92.2	92.2	111.0	30.0	30.0
Pressure (bar)	1.000	0.042	0.080	1.450	1.280	1.280	1.280	1.480	1.480	1.000
Flowrate (kg/h)	362,500	284,935	77,561	90,214	32,300	19,646	12,654	67,768	6,325	3,470
Mass fractions										
Water	0.9742	1.0000	0.8795	0.8698	0.4509	0.2196	0.8101	1.0000	0.0100	0.1111
Butanol	0.0173	0.0000	0.0807	0.0832	0.3853	0.5702	0.0981	0.0000	0.9900	0.0000
Isopropanol	0.0069	0.0000	0.0322	0.0349	0.1091	0.1460	0.0519	0.0000	0.0000	0.7188
Ethanol	0.0014	0.0000	0.0066	0.0113	0.0547	0.0643	0.0399	0.0000	0.0000	0.1481
Acetone	0.0002	0.0000	0.0010	0.0008	0.0000	0.0000	0.0000	0.0000	0.0000	0.0220

\$/kg_{IBE}, which is in the same range as the cost of bioethanol. Additionally, the minimum added selling price for the biofuels recovery is 0.144 \$/kg_{IBE}. As the estimated market prices for butanol, isopropanol and ethanol are about 1.20, 1.12 and 0.89 \$/kg_{IBE} [53], the newly designed IBE recovery process is highly competitive. A detailed analysis of the effects of the implemented heat pump and heat integration systems on the economic performance is presented in the *Supplementary Information* file. Even though initial investment costs are higher due to additional equipment units that are needed, OPEX and consequently, TAC are drastically reduced (by 65.3 % and 51.7 %, respectively).

Furthermore, the flexibility of the performed economic evaluation is extended by analyzing the influence of the payback period on the TAC, which is presented in Fig. 6. Shorter payback periods lead to an increase in TAC. However, even with a payback period of 4 years or only 1 year, the TAC for biofuels recovery is lower than 0.20 \$/kg_{IBE} or 0.52 \$/kg_{IBE}, respectively, indicating the economic competitiveness of the designed recovery process.

3.4. Sustainability assessment

The calculated values of the main sustainability metrics are presented in Table 4.

- **Energy intensity:** Due to the implemented heat pump systems, both the initial separation step (gas stripping combined with vacuum evaporation) and the purification in A-DWC are independent of external heating (being thermally self-sufficient) and can be powered only by

electricity. The electrical energy requirements for the designed recovery process are 0.673 kW_h/kg_{IBE}, while the thermal energy requirements are equal to zero, making this process thermally self-sufficient. The primary energy requirements that account for all types of energy used are equivalent to 1.683 kW_{th}/kg_{IBE} in thermal energy units (to allow a fair comparison with other studies). Thus, besides improving energy efficiency, the implementation of heat pump systems is a significant step towards electrification of bio-refineries. Using renewable electricity instead of fossil-based thermal energy can drastically improve the sustainability and competitiveness of biofuel production processes.

- **Water consumption:** The total water need for the designed recovery process is 0.096 m³_W/kg_{IBE}, due to condensation of the vapor mixture of fermentation products and cooling condenser of A-DWC. Accordingly, the total loss of water is 0.007 m³_W/kg_{IBE}.
- **Material intensity:** Besides the recovered high-purity butanol and isopropanol – ethanol mixture, output streams from the designed purification process are the aqueous solution containing microorganisms and non-volatile inert components, and the high-purity water stream (bottom product from A-DWC). Since both streams may be recycled to the fermentation, the value of material intensity sustainability metrics is equal to zero.
- **Greenhouse gas emissions:** The total CO₂ emissions in the case of using grey electricity are 0.307 kg_{CO2}/kg_{IBE}. Nevertheless, if the designed recovery process can be powered by renewable electricity, the total CO₂ emissions are reduced to zero due to the complete electrification of the recovery process.

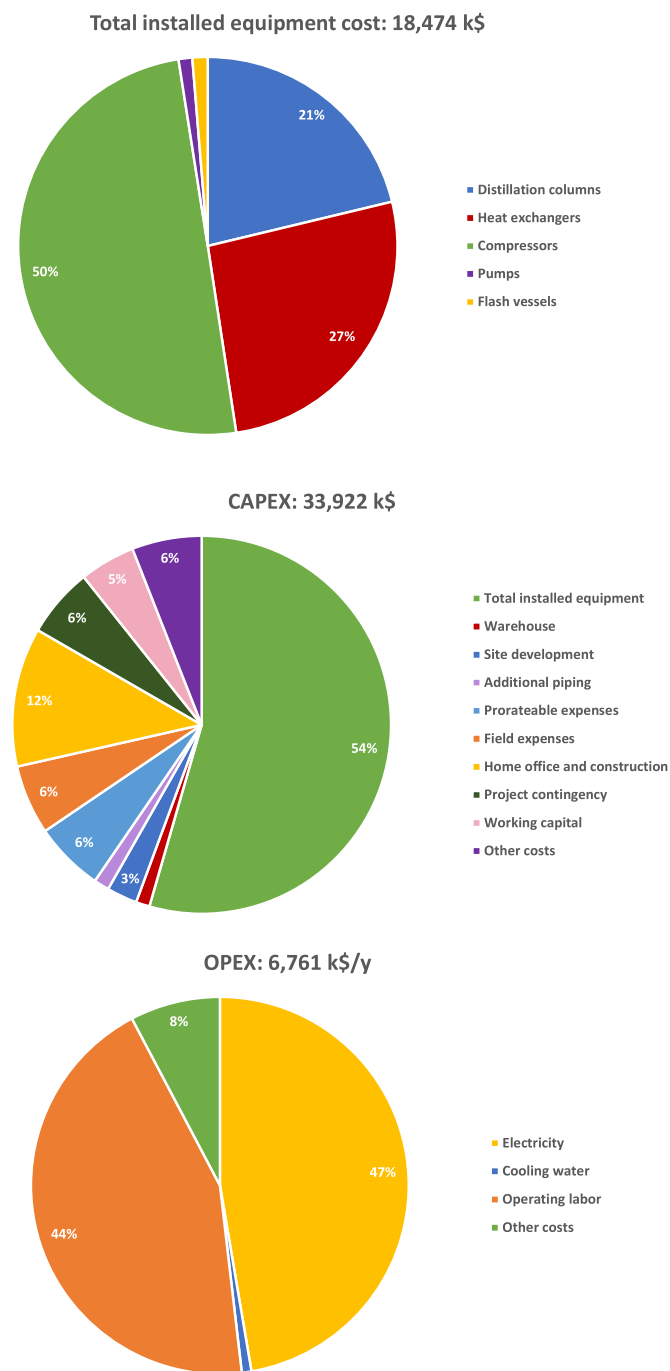


Fig. 5. Cost contribution to the CAPEX and OPEX.

- **Pollution and toxic materials:** Values of these metrics are zero as the designed recovery process does not emit any pollutants and toxic materials, apart from CO₂ that was already included in the greenhouse gas emissions metrics.

A detailed analysis of the effects of the implemented heat pump and heat integration systems on the sustainability metrics is presented in the *Supplementary Information* file. The implementation of these systems increased electrical energy requirements due to the usage of compressors in heat pump systems. Nonetheless, the thermal energy requirements are significantly reduced. Consequently, the primary energy requirements and CO₂ emissions, that are related to energy usage, are drastically decreased (by about 76.9 % and 62.0 %, respectively).

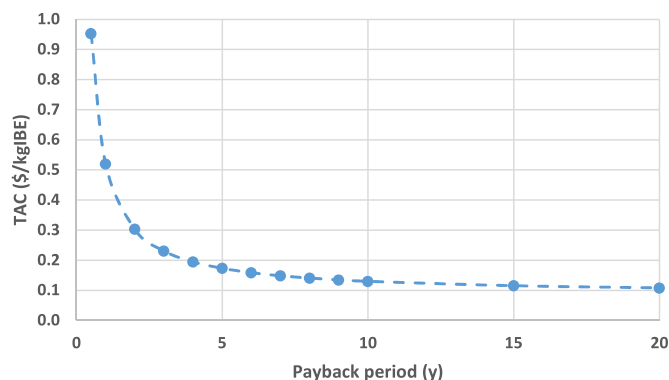


Fig. 6. Effect of the payback period on the IBE recovery costs.

Table 4

Economic indicators and sustainability metrics.

Economic indicators	Value
CAPEX (k\$)	33,922
OPEX (k\$/y)	6,761
OPEX (\$/kg _{IBE})	0.086
TAC (k\$/y)	10,153
TAC (\$/kg _{IBE})	0.130
MASP (\$/kg _{IBE})	0.144
Sustainability indicators	
Thermal energy requirements (kW _{th} h/kg _{IBE})	0.000
Electrical energy requirements (kW _e h/kg _{IBE})	0.673
Primary energy requirements (kW _e h/kg _{IBE}) / (kW _{th} h/kg _{IBE})	0.673 / 1.683
CO ₂ emissions (kg _{CO2} /kg _{IBE})*	0.307 / 0.000
Water consumption (m ³ _w /kg _{IBE})	0.096
Water loss (m ³ _w /kg _{IBE})	0.007
Pollutant emission (kg _{pollutant} /kg _{IBE})	0.000
Toxic materials emission (kg _{toxic material} /kg _{IBE})	0.000

* Grey / green electricity.

4. Conclusion

The original downstream processing design proposed here allows the eco-efficient large-scale (production capacity of 74 ktonne/y IBE) recovery of high-purity (99 wt%) butanol biofuel and isopropanol – ethanol fuel supplement (~89 wt%) from a very dilute fermentation broth (>97 wt% water). A novel combination of gas stripping and heat pump-assisted vacuum evaporation can be implemented to efficiently recover valuable products from most of the fermentation broth while allowing full recycle of biomass and most of the water back to the fermentation. Furthermore, a highly integrated heat pump-assisted azeotropic dividing-wall column allows the separation of pure butanol biofuel and water from an isopropanol – ethanol mixture that may be used as a fuel supplement. Lastly, the implementation of advanced heat pump and heat integration systems avoids any dependence on fossil-based thermal energy, thus presenting an important step toward the green electrification of industrial biotechnology. Therefore, the major significance of this original research study is the design of a cost-effective (0.130 \$/kg_{IBE}) and energy-efficient (0.673 kW_eh/kg_{IBE}) IBE recovery process that may significantly contribute to the application of sustainable biofuel production technology. It is worth noting that a good downstream processing cannot compensate for a poor fermentation (and the other way around), so both process steps have to be very good.

Author statement

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the

concept, design, analysis, writing, or revision of the manuscript. Furthermore, each author certifies that this material or similar material has not been and will not be submitted to or published in any other publication.

CRediT authorship contribution statement

Tamara Janković: Conceptualization, Methodology, Software, Data curation, Validation, Visualization, Writing – original draft, Writing – review & editing. **Adrie J.J. Straathof:** Conceptualization, Methodology, Formal analysis, Validation, Supervision, Writing – review & editing. **Anton A. Kiss:** Conceptualization, Methodology, Formal analysis, Investigation, Resources, Visualization, Validation, Supervision, Project administration, Writing – original draft, Writing – review & editing.

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.

Acknowledgments

All persons who have made substantial contributions to the work reported in the manuscript (e.g., technical help, writing and editing assistance, general support), but who do not meet the criteria for authorship, are named in the Acknowledgements and have given us their written permission to be named. If we have not included an Acknowledgements, then that indicates that we have not received substantial contributions from non-authors.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.cep.2024.109689](https://doi.org/10.1016/j.cep.2024.109689).

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