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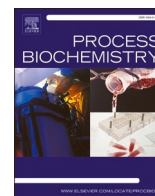
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Eco-efficient downstream processing of 1,3-propanediol applicable to various fermentation processes

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ABSTRACT

PDO (1,3-propanediol) is a platform chemical that is obtained by petrochemical routes and by fermentation. The latter needs relatively complex downstream processing after fermentation, due to the modest concentration of the high-boiling product, and the presence of microorganisms and many impurities in the fermentation medium. This novel research proposes an original large-scale (production capacity of 23 – 32 ktonne/y) process for the final purification of PDO and dominant by-products, from the fermentation of glucose or glycerol. Following the initial microfiltration, diafiltration, ultrafiltration and ion exchange steps, heat pump-assisted vacuum distillation was implemented to remove most of the water from the broth. Afterwards, an advanced highly-integrated dividing-wall column was designed to allow the final purification of PDO (product purity > 99.9 wt%) from light and heavy by-products. Fermentation by-products that are present in significant amounts can also be recovered and valorized. Overall, the developed final purification processes demonstrate cost-effectiveness (0.150 – 0.274 \$/kg) and energy-efficiency (1.258 – 3.175 kW_{th}/kg) which contributes to the competitiveness of the overall downstream processing (0.256 – 0.384 \$/kg and 1.487 – 3.496 kW_{th}/kg).

1. Introduction

Due to the depletion of fossil fuels, strict environmental regulations and concerns regarding energy security, conversion of renewable feedstocks to different bio-chemicals is rapidly attracting attention. In that respect, there is a global focus on the production of bulk chemicals such as ethanol, isopropanol, butanol, lactic acid, 1,3-propanediol, 1,4-butanediol, etc. by fermentation [1]. 1,3-Propanediol (PDO) is an attractive platform chemical that can be used as a monomer for the production of different polymers (e.g. polyesters and polyurethanes) which have good resistance to stains and wash fastness properties [2]. Furthermore, PDO has potential applications as a solvent, antifreeze or protective agent and in the synthesis of pharmaceuticals, cosmetics, detergents, laminates, resins and adhesives [3]. The global demand for PDO increased significantly after the start of the commercial polytrimethylene terephthalate (PTT) production by Shell in 1995 [3]. Due to its unique zigzag structure, PTT has many advantages compared to similar polymers (e.g. polyethylene terephthalate (PET) and polybutylene terephthalate (PBT)). It has excellent tensile and stretch recovery because applied forces do not only cause stretching but also trigger bending and twisting of molecular bonds. Thus, a PTT fiber has

superior stretch recovery abilities. Moreover, PTT-based fabrics are soft, easily dyeable with the possibility of multiple deep shades, resistant to many stains and exhibit superior wash fastness. Among others, PTT has great potential for applications in the carpet, textile, film and packaging industries [3]. According to openly available market data, the bulk price for high-purity PDO is about 3.8 – 4.2 \$/kg. In 2021, the PDO market was estimated at 433.4 million \$ with an expected growth rate of 11.5% [4], while the PTT market was valued at 896.8 million \$ with an expected growth rate of 5.4% [5].

Traditionally, PDO has been produced by petrochemical synthesis whereby production processes from acrolein by DuPont and from ethylene oxide by Shell are the most dominant [6]. In the first route, acrolein is converted to 3-hydroxypropanol by catalytic solution phase hydration, followed by hydrogenation to obtain PDO. In the second route, hydroformylation of ethylene oxide is used to produce 3-hydroxypropanol that is later extracted and hydrogenated to PDO. The most significant drawbacks of these conventional processes are the requirements for high operating pressure and temperature, usage of expensive catalysts, presence of toxic intermediates, very low yields (about 40 and 80% for the acrolein and ethylene oxide-based routes, respectively) and environmental concerns [3]. To avoid these

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drawbacks, industrial production of PDO by microorganisms has been developed [1,7]. Currently, the microbial production of PDO is mainly based on two different fermentation technologies. The first fermentation route uses a recombinant *Escherichia coli* to obtain PDO from glucose. The commercialization of this production method has been undertaken by DuPont and Genencor [8,9]. The second way to microbially produce PDO is fermentation of glycerol by different microorganisms (natural or genetically engineered strains) [10–14]. Being a major byproduct of the biodiesel production processes, glycerol is a useful feedstock for PDO production [2]. The fermentation of glycerol to PDO has been commercialized in China and France [15]. Significant research effort has been put into developing genetically engineered microorganisms, enhancing metabolic efficiency and increasing fermentation titers [2,7,9]. Nonetheless, there are still some bottlenecks in the fermentative production of PDO (e.g. low titer due to product inhibition, low yield, high formation of by-products, etc. [7]). Many of the mentioned drawbacks of the fermentation process will reflect on the downstream processing performance. However, the recovery of PDO from complex fermentation broth has not received nearly as much attention [7]. Low product concentrations, large amounts of water that has a lower boiling point than PDO, presence of microorganisms, biopolymers and inorganics in the fermentation medium, etc., are challenges for an efficient recovery process on an industrial scale. Accordingly, the downstream processing costs of bulk biochemicals can contribute 20 – 40% to the total production costs [16]. Considering the importance of the separations for the commercial viability of the biotechnological process [17, 18], the main goal of this original research is to enhance the fermentative PDO production by an intensified recovery process that can be applied to various fermentation pathways. In that respect, the focus of this work is on developing a highly advanced process for the final purification of PDO after the initial filtration and ion exchange steps, which will be shortly explained later. In the heart of the developed process is an integrated dividing-wall column (DWC) that can efficiently recover high-purity PDO product while removing all the light and heavy by-products that may be present. The developed process was also extended to purifying and valorizing by-products that are present in significant amounts.

2. Problem statement

The complexity of the downstream processing is mainly attributed to the relatively low product concentrations in the broth (about 5 – 15% depending on the fermentation method). Furthermore, PDO's high boiling point, low volatility, and high hydrophilicity complicate recovery from a highly dilute fermentation broth. Lastly, the potential

formation of by-products (e.g. 2,3-butanediol, ethanol, acetic acid, etc.) and the presence of residual substrates, biopolymers and inorganics introduce additional difficulties. Due to the complex fermentation broth, several steps are often required in the downstream processing (see Fig. 1) [19,20]. Since fermentation broth is usually very dilute and PDO has a higher boiling point compared to water, initial removal of biomass, biopolymers and inorganics from the medium is needed prior to the final purification. Conventionally, the initial step is the removal of cells from the fermentation broth by microfiltration. Nonetheless, some liquid containing valuable PDO product will also be removed with the cells and an additional cell washing by diafiltration is needed to maximize the PDO recovery. After the microfiltration step, some biopolymers that are present in the microfiltered broth will be removed by an additional ultrafiltration step. Furthermore, inorganics remaining from the fermentation (e.g. salts) are commonly removed from the filtered broth by ion exchange steps, resulting in a dilute desalted aqueous solution. Lastly, a preconcentration step to remove the majority of water and a final purification step to remove the remaining light and heavy by-products are needed to obtain a high-purity PDO product. Besides the previously mentioned common methods for the initial recovery steps, several other techniques have been investigated (e.g. chromatography [21,22], extraction [23], reactive extraction [24–26], salting-out extraction [27–29], sugaring-out extraction [30], etc.). Nonetheless, these methods are often studied on a small scale and are often not applicable for scale-up to an industrial capacity due to low achievable recoveries (extraction, reactive extraction), insufficient product purities (extraction, reactive extraction), high energy requirements (chromatography, salting-out extraction), large need for additional chemicals and problems related to their recovery and reuse (extraction, reactive extraction, salting-out extraction) [2,20].

The last two steps in the downstream processing (preconcentration and final purification) may significantly contribute to the total recovery costs due to the high energy use. To the best of our knowledge, only a simple sequence of distillation columns has been proposed to remove present water and purify PDO from light and heavy impurities [19, 31–34]. This original research substantially strengthens the development of sustainable microbial PDO production by advancing these two final steps in the recovery process. An enhanced process consisting of a heat pump-assisted vacuum distillation followed by an integrated dividing-wall column was developed to efficiently recover high-purity PDO from a dilute broth with simultaneous removal of light and heavy components. This configuration may bring significant energy savings compared to the conventional simple sequence of distillation columns. Furthermore, an integrated column design such as DWC brings additional benefits in terms of capital investment and required plant

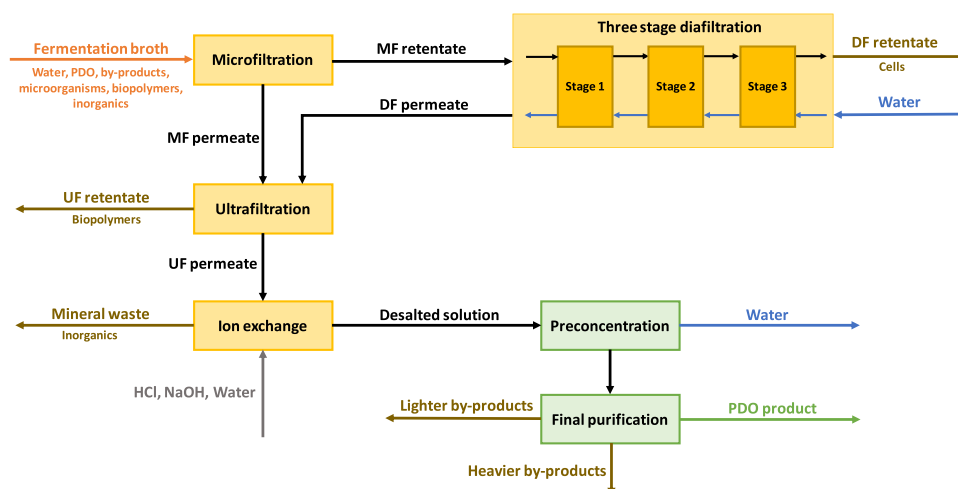


Fig. 1. General downstream processing steps for purification of PDO after fermentation.

space as it integrates multiple column shells into one unit while also decreasing the number of required heat exchangers. Furthermore, the proposed process is adaptable to the different compositions of the feed stream and can be used for purification after fermentation from glucose using *E. coli* or fermentation from glycerol using different microorganisms. Rigorous simulations for all operations in the developed process were designed in Aspen Plus. A detailed economic and environmental analysis was conducted to evaluate the performance of the designed recovery process. Approximate costs for the initial separation steps (microfiltration, cell washing, ultrafiltration and ion exchange) were also calculated and added to the costs for the designed preconcentration and final purification steps to obtain a complete picture of the downstream processing performance.

3. Methods

3.1. Process design and simulation

Since microbial production of PDO is mainly based on two routes (fermentation from glucose and fermentation from glycerol), two recovery processes were designed (further referred to as case 1 and case 2). The composition of the fermentation broth was taken from the published literature and presented in Table 1. In the case of fermentation from glucose using *E. coli* strain (case 1), the composition of the broth is the following: 12.90 wt% PDO, 5.35 wt% dry cells, 1.48 wt% glycerol, 0.20 wt% inorganics, 0.10 wt% biopolymers, 0.10 wt% glucose and remaining 79.96 wt% water [9]. Alternatively, in the case of fermentation from glycerol using *Klebsiella pneumoniae* (case 2), the composition of the broth is the following: 10.21 wt% PDO, 5.35 wt% dry cells, 3.17 wt% 2,3-butanediol (BDO), 1.33 wt% succinic acid, 0.41 wt% ethanol, 0.25 wt% lactic acid, 0.25 wt% acetic acid, 0.20 wt% inorganics, 0.10 wt% biopolymers and 78.72 wt% water [13]. Inorganics include mainly salts remaining from the fermentation medium, while biopolymers stand for the lysed microorganisms and other present organic molecules. Thus, the amount of formed byproducts is much higher in the case when glycerol is used as a substrate (case 2). Due to the highly complex mixtures, the NRTL-HOC property method was used to describe the interactions between different components. The validation of the chosen property model against the available literature data is presented in the Supplementary Information file.

The primary focus during the design of the preconcentration and final purification steps in the PDO recovery was on minimizing total energy requirements. Optimization of a chemical process is a non-convex mixed-integer nonlinear problem (MINLP), for which there is no theoretical assurance of a global optimum. However, reducing the

external energy requirements will significantly lower the total recovery costs. The reason for this is the particularly significant portion of energy supply costs (both thermal and electrical) in the total OPEX. Some of the decision variables that were considered in process development are the total number of trays in the columns, the placement of the feed tray, reflux ratio, distillate to feed ratio, boilup ratio, vapor fraction, compression ratio, etc. Furthermore, several constraints were accounted for, such as high recovery and high purity requirements for PDO product and all recovered by-products, maintaining a high purity of the water stream for recycling to fermentation, temperature limitations, etc.

The flowsheets of the developed recovery processes are presented in Fig. 2 and Fig. 3, while the compositions of the main process stream are presented in Table 2 and Table 3.

3.2. Economic analysis

The performance of the developed recovery process was evaluated following the published NREL methodology [35]. According to this methodology, the total capital costs (CAPEX) include costs of equipment purchase and installation, warehouse, site development, additional piping, proratable expenses, field expenses, home office and construction, working capital, etc. The costs of equipment purchase and installation in the preconcentration and the final purification parts of the recovery process were calculated using the published cost correlations [36], with a Marshall and Swift cost index of 1638.2 (end of 2018) [37]. The approximate costs of the initial downstream processing steps (i.e. microfiltration, diafiltration, ultrafiltration and ion exchange) were estimated by adjusting the market prices from the available literature [32] to the assumed process capacity using the *six-tenths factor rule* [38] and installation factors [35]. According to the same methodology [35], the operating expenses (OPEX) consist of the costs for utilities, operating labor [39,40], maintenance, property insurance, waste treatment [41], membrane and resin replacement [42,43], etc. Thereby, the following approximations of utility costs were taken into account: 60.48 \$/MWh for electricity, 28.01 \$/MWh for low-pressure steam, 29.59 \$/MWh for medium-pressure steam, 35.59 \$/MWh for high-pressure steam, 1.27 \$/MWh for cooling water and 15.95 \$/MWh for chilled water [36]. The total annual costs (TAC) account for both CAPEX and OPEX with a payback period (PBP) of 10 years and were calculated using the following equation: $TAC = CAPEX/PBP + OPEX$. To expand the performed economic evaluation, further analysis of the PBP influence on TAC was conducted. The specific costs were obtained considering the total flowrate of the products (PDO and the recovered by-products).

Table 1

composition of the fermentation broth and the feed stream to the preconcentration with boiling points of main components at 1 bar.

Component	Mass fraction in the fermentation broth	Mass fraction in the feed stream to preconcentration	Boiling point (C)
Case 1			
Water	0.7996	0.8893	100.00
1,3-Propanediol	0.1290	0.1002	214.22
Glycerol	0.0148	0.0105	287.85
Glucose	0.0001	0.0001	/
Dry cells	0.0535	0.0000	/
Inorganics	0.0020	0.0000	/
Biopolymers	0.0010	0.0000	/
Case 2			
Ethanol	0.0041	0.0029	78.29
Water	0.7872	0.8820	100.00
Acetic acid	0.0025	0.0018	117.90
2,3-Butanediol	0.0317	0.0225	180.70
1,3-Propanediol	0.1021	0.0795	214.22
Lactic acid	0.0025	0.0018	216.85
Succinic acid	0.0133	0.0094	317.85
Dry cells	0.0535	0.0000	/
Inorganics	0.0020	0.0000	/
Biopolymers	0.0010	0.0000	/

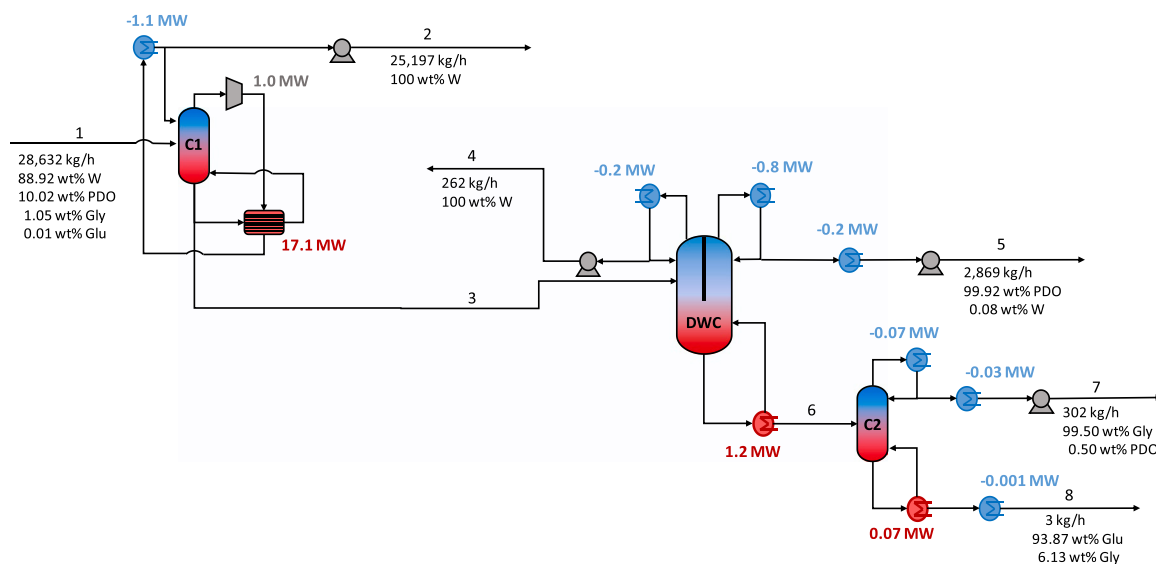


Fig. 2. Downstream process for the recovery of PDO after fermentation - Case 1a (excluding column C2) and Case 1b (including column C2), conditions and compositions of the numbered process streams are given in Table 2 (abbreviations: W – water, PDO – 1,3-propanediol, Gly – glycerol, Glu – glucose).

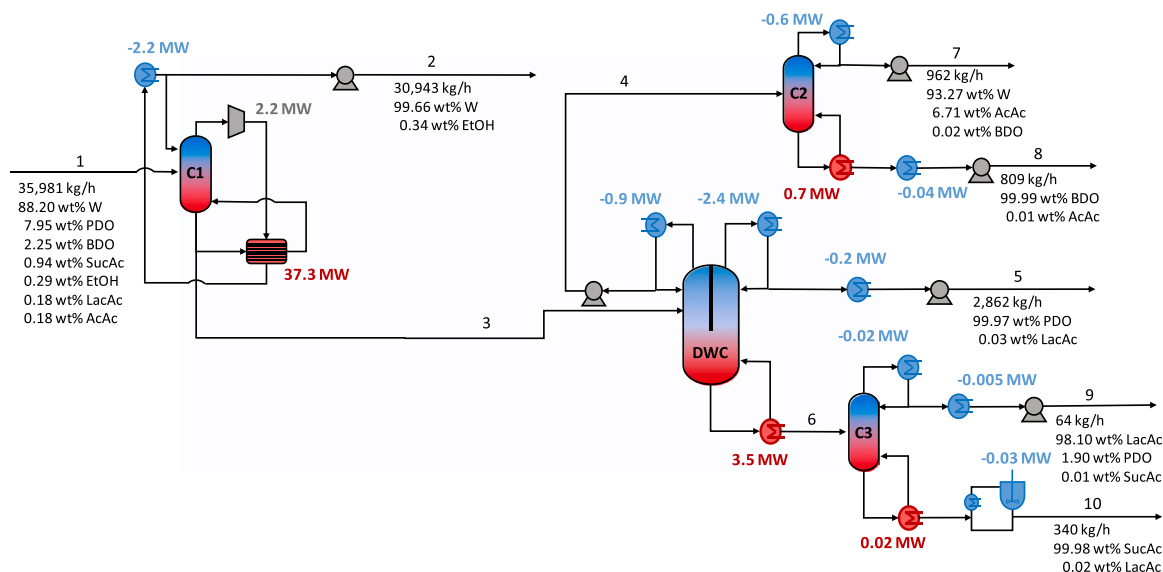


Fig. 3. Downstream process for the recovery of PDO after fermentation – Case 2a (excluding columns C2 and C3) and Case 2b (including columns C2 and C3), conditions and compositions of the numbered process streams are presented in Table 3 (abbreviations: W – water, PDO – 1,3-propanediol, BDO – 2,3-butanediol, SucAc – succinic acid, EtOH – ethanol, LacAc – lactic acid, AcAc – acetic acid).

Table 2

Conditions and compositions of the main streams from Fig. 2 (Cases 1a and 1b).

Stream	1	2	3	4	5	6	7	8
Temperature [C]	37.0	36.2	59.0	24.1	30.2	190.0	30.0	30.0
Pressure [bar]	1.000	1.000	0.069	1.000	1.000	0.041	1.000	0.034
Flowrate [kg/h]	28,632	25,197	3436	262	2869	305	302	3
Mass fractions								
Water	0.8892	1.0000	0.0768	1.0000	0.0008	0.0000	0.0000	0.0000
1,3-Propanediol	0.1002	0.0000	0.8349	0.0000	0.9992	0.0050	0.0050	0.0000
Glycerol	0.0105	0.0000	0.0875	0.0000	0.0000	0.9857	0.9950	0.0613
Glucose	0.0001	0.0000	0.0008	0.0000	0.0000	0.0094	0.0000	0.9387

3.3. Sustainability assessment

Several key sustainability metrics (energy intensity, water consumption, greenhouse gas emissions, material intensity, waste water

intensity, pollutant and toxic emissions) [44,45] were determined to evaluate the environmental impact of the new recovery processes.

Table 3

Conditions and compositions of the main streams from Fig. 3 (Cases 2a and 2b).

Stream	1	2	3	4	5	6	7	8	9	10
Temperature [C]	37.0	35.9	46.8	25.7	30.0	171.1	24.3	30.0	30.0	30.0
Pressure [bar]	1.000	0.060	0.069	0.030	1.000	0.041	1.000	1.000	0.020	1.000
Flowrate [kg/h]	35,981	30,943	5037	1771	2862	404	962	809	64	340
Mass fractions										
Water	0.8820	0.9966	0.1782	0.5067	0.0000	0.0000	0.9327	0.0000	0.0000	0.0000
1,3-Propanediol	0.0795	0.0000	0.5681	0.0000	0.9997	0.0030	0.0000	0.0000	0.0190	0.0000
2,3-Butanediol	0.0225	0.0000	0.1606	0.4568	0.0000	0.0000	0.0002	0.9999	0.0000	0.0000
Succinic acid	0.0094	0.0000	0.0675	0.0000	0.0000	0.8408	0.0000	0.0000	0.0001	0.9998
Ethanol	0.0029	0.0034	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Lactic acid	0.0018	0.0000	0.0129	0.0000	0.0003	0.1562	0.0000	0.0000	0.9810	0.0002
Acetic acid	0.0018	0.0000	0.0129	0.0365	0.0000	0.0000	0.0671	0.0001	0.0000	0.0000

- *Energy intensity* presents the amount of total energy that is required to recover a kilogram of product [44], whereby a distinction is made between the types of used energy. Thermal and electrical energy requirements present the specific amounts of used thermal and electrical energy, respectively. The primary energy requirements account for both thermal and electrical energy through an electrical-to-thermal conversion factor (a conservative value of 2.5 was used [46]). The total energy requirements for the initial recovery steps were calculated using the following data on the specific energy usage: 2, 5, 5 and 0.7 kWh/m³ for microfiltration, diafiltration, ultrafiltration and ion exchange, respectively [47,48].
- *Water consumption* is a measure of water needed per kilogram of recovered product. This metric accounts for 7% loss of cooling water [44] and 70% recovery of condensate in the steam cycle [49].
- *Greenhouse gas emissions* account for the amount of carbon-dioxide (CO₂) that is emitted per kilogram of product [44]. These emissions were determined using literature recommendations [37,50] that correlate electrical and thermal energy usage with the amount of emitted CO₂. Furthermore, since the source of electricity is very important, a distinction was made between green and grey electricity usage (electricity from renewable sources and fossil fuels, respectively).
- *Material intensity* presents the amount of waste (excluding waste water) that is formed per kilogram of recovered product [44].
- *Waste water intensity* is a measure of water that needs to be sent to waste water treatment per kilogram of product [45].
- *Pollutant and toxic materials* account for the formed pollutants and toxic materials per kilogram of the recovered products [44].

The specific values of all sustainability metrics were obtained considering the total products flowrate (PDO and the recovered by-products).

4. Results and discussion

4.1. Initial downstream processing

To ensure a fair comparison between the two cases, the total production capacity of about 23 ktonne/y of PDO was assumed, and the flowrates of the feed streams to the recovery process were back-calculated accordingly: 23,800 kg/h in case 1 and 30,000 kg/h in case 2. The chosen plant capacity is similar to the starting industrial plants for PDO fermentation from glycerol in Jiangsu, China (capacity of about 20 ktonne/y) [2]. Considering the complexity of the fermentation broths, several steps are required in the downstream processing (see Fig. 1) [19]. Thus, the composition of the feed stream to the preconcentration and final purification steps (see Fig. 1) will differ from the composition of the broth from the fermenter. A reasonable composition of the feed stream for these steps was obtained by performing mass balance calculations for the prior downstream processing steps. These calculations were fully automated in Excel as described in more detail below.

The initial step in the recovery process is the removal of cells by microfiltration. It was assumed that all cells were removed from the broth in this step, whereby microfiltration can reach about 120 g of dry cells per kilogram (equivalent to about 480 g of wet cells mass per kilogram). Therefore, some liquid containing PDO will be separated with the cells in the microfiltration retentate. Since about 41.5% of the PDO from the fermentation broth will be separated in the microfiltration retentate, a cell washing step is needed to minimize the loss of PDO to about 4%. Washing of the microfiltration retentate can be performed in a three-stage counter-current diafiltration, whereby water is used as the washing liquid. Higher amounts of washing water will decrease the loss of PDO but will result in more dilute streams that complicate further downstream processing. Thus, 90% recovery of PDO from the microfiltration retentate was assumed and the flowrate of washing water was varied to close the mass balances for the diafiltration part of the recovery process. Furthermore, the filtered fermentation broth (microfiltration permeate) and washing water enriched with fermentation products (diafiltration permeate) were jointly sent to the ultrafiltration. This step is necessary to remove biopolymers that were not removed in the previous microfiltration step. Ultrafiltration membranes can be used as a selective barrier for separation of the remaining larger organic molecules [51]. It was assumed that about 50 g/L of biopolymers could be obtained in the ultrafiltration retentate while being completely removed from the permeate. However, the degree of biopolymer removal will strongly depend on the applied ultrafiltration technology. Additional washing may be applied to recover PDO from the ultrafiltration retentate. Nonetheless, only about 1.4% of PDO from the fermentation broth will be lost with the biopolymers in this stream. Such an additional washing step would result in even higher dilution of the stream that is sent to further downstream processing. This would lead to larger equipment units and higher energy requirements. Therefore, recovering the PDO from the ultrafiltration retentate was not considered in this study. Furthermore, the removal of inorganics from the ultrafiltration permeate is necessary after the ultrafiltration step. This can be achieved in a series of cation and anion exchange units. Cation exchange units contain resin in H⁺ form that can be regenerated with an acid solution (e.g. HCl). Contrarily, anion exchange resin is in OH⁻ form and is recovered with a base solution (e.g. NaOH). To ensure a continuous operation, at least two cation exchange and two anion exchange trains need to operate alternately. The following approximations were assumed when calculating mass balances for the ion exchange step: 99% of inorganics were removed from the ultrafiltration retentate, 1% of PDO and 10% of other present organic compounds were lost in this step, which resulted in 2% dilution.

The obtained desalted solution is the feed stream for the following preconcentration and final purification steps which are the main focus of this paper (see Table 1). In case 1, this stream has a flowrate of 28,633 kg/h and contains about 10.02 wt% PDO, 1.05 wt% glycerol, 0.01 wt% glucose and 88.93 wt% water. Due to the washing water in the diafiltration step and the dilution in the ion exchange, the feed stream to the preconcentration step is more dilute compared to the broth from the

fermenter. Similarly, the desalted solution in case 2 has a flowrate of about 35,981 kg/h, with the following composition: 7.95 wt% PDO, 2.25 wt% BDO, 0.94 wt% succinic acid, 0.29 wt% ethanol, 0.18 wt% lactic acid, 0.18 wt% acetic acid and 88.20 wt% water. Block flow diagrams with mass balance calculations of these initial separation steps (microfiltration, diafiltration, ultrafiltration and ion exchange) in case 1 and case 2 are presented in the [Supplementary Information](#) file.

4.2. Preconcentration

The previously described initial purification steps are needed to remove cells, organic and inorganic impurities from the fermentation broth. Nonetheless, the desalted solution that is obtained after the ion exchange is still very dilute and a preconcentration step is required to remove large amounts of water. Being the only lighter component than PDO in the desalted solution, pure water can be obtained as the top product in case 1, while the bottom product consists of PDO, glycerol, glucose and some water. Contrarily, in case 2, ethanol will be separated with water as the top product while PDO, BDO, succinic acid, lactic acid, acetic acid and some water will be obtained at the bottom. Vacuum distillation in column C1 can be applied to facilitate the separation and reduce energy requirements for this step. The operating pressure of 0.060 bar (top pressure) was chosen to minimize reboiler duty while keeping the condensation temperature (about 36 °C) appropriate for the usage of inexpensive cooling utilities (e.g. cooling water). Due to the reduced pressure operation, structured packing type Mellapak 250 with a pressure drop of 0.225 mbar per theoretical stage was selected as internals [52]. Lower distillation temperatures also minimize the risk of degradation of trace impurities such as glucose that leads to yellowing of the purified PDO.

The distillate-to-feed mass ratio for column C1 was varied to minimize the total energy requirements for column C1 and the following removal of the remaining light impurities and water (the next step in the recovery process, further discussed in [Section 4.3](#)). More water separated in the distillate of column C1 would result in a higher reboiler duty of column C1, but a less intensive next separation. Nonetheless, the temperature difference at the top and the bottom of column C1 increases as the distillate-to-feed ratio increases because the bottom product becomes more concentrated with higher boiling components. Consequently, the implementation of heat pump systems might not be so effective. In case the temperature difference at the top and the bottom of the distillation column is not large, a mechanical vapor recompression (MVR) system can be applied to decrease the total energy requirements. This heat pump system implies compressing vapor from the top of the column and using it to evaporate the bottom liquid [53]. As a result, the electrical energy required to power the compressor can replace much larger amounts of thermal energy, while allowing complete electrification of this step. If the temperature difference between the top and the bottom of the distillation column is too large, the top vapor cannot be compressed enough to provide sufficient heat to the bottom liquid. Thus, the influence of the distillate-to-feed ratio of column C1 was varied to minimize the total energy requirements for the preconcentration step (in column C1) and the following removal of light impurities (as discussed in [Section 4.3](#)). Alternatively, multi-effect distillation may be implemented to reduce the thermal energy requirements for the preconcentration step in the recovery process. This energy-saving technique implies using multiple evaporators, each operating at successively lower pressure. The vapor from one evaporator is used as a heating medium in the next one, resulting in significant energy savings. Consequently, external heating is usually only needed to heat up the stream in the part of the process with the highest pressure. Even though the implementation of multi-effect evaporation can reduce significantly the overall energy requirements, an external thermal energy supply is still needed. Contrarily, the MVR system (which gives similar or better energy savings) can allow complete electrification of the preconcentration step which is an important step towards (green) electrification of industrial

bioprocesses.

In case 1, water is the only component lighter than PDO in the feed stream to the preconcentration step (see [Table 1](#)). Theoretically, all water can be removed in column C1 and subsequent removal of light components is not needed. Nonetheless, this results in a very large temperature difference at the top and the bottom of this column (about 36 and 141 °C at the top and the bottom, respectively), which makes it impossible to apply the MVR system. Thus, the total energy requirements in case all water is removed in only one distillation column are much higher (more than 5.8 times higher) than if two columns were used, whereby the MVR system is applied to the first column. Finally, a distillate-to-feed ratio of 0.88 on a mass basis was defined as the operating specification for column C1 as this value leads to the minimal energy requirements. The top product from column C1 is pure water, while the bottom product contains PDO, some water and heavy impurities (83.49, 7.68, 8.75 and 0.08 wt% of PDO, water, glycerol and glucose, respectively).

In case 2, most of the water and ethanol can be obtained as the top product from column C1, while the remaining water with light impurities (acetic acid and BDO) can be removed at the top of the next distillation column (further discussed in [Section 4.3](#)). The minimal energy requirements for these steps were obtained using a distillate-to-feed ratio of 0.86 and using MVR for column C1. The top product from column C1 is 99.66 wt% water with 0.34 wt% ethanol, which may be recycled back upstream. The bottom product from C1 contains mainly PDO (about 56.81 wt%), with some water (17.82 wt%), light impurities (1.29 wt% acetic acid and 16.06 wt% BDO) and heavy impurities (6.75 wt% succinic and 1.29 wt% lactic acid). Additionally, depending on the fermentation strategy, some residual substrate (glycerol) might be present in this stream.

Thus, in both cases, the MVR system was applied to the preconcentration column C1, allowing a complete electrification of this step. However, due to the presence of more by-products and the lower temperature differences between PDO and the first lighter and heavier component, the separations are more complex in case 2. Accordingly, a higher reflux ratio (0.80 compared to 0.01), reboiler duty (37.3 MW_{th} compared to 17.1 MW_{th}) and compressor duty (2.2 MW_e compared to 1.0 MW_e) are needed in case 2 than in case 1. The energy savings obtained with the implementation of this heat pump system can be expressed through the coefficient of performance (COP). This value is equal to the ratio of the exchanged heat (between the compressed vapor and bottom liquid) and the required compressor duty [53]. COP values greater than the electrical-to-thermal conversion factor (with a conservative value of 2.5 [46]) indicate that the heat pump system reduces the total energy requirements. COP values for the MVR systems applied to column C1 are 16.3 and 17.0 for case 1 and case 2, respectively. Thus, the implementation of these heat pumps reduced the total energy requirements for the preconcentration step by about 85%.

4.3. Final purification in an integrated dividing-wall column

Even though most of the water from the feed stream is removed in the preconcentration column C1, a much smaller amount of water (in case 1) and some light components (in case 2) need to be removed in the next distillation column. The top product from this column would be water and all components lighter than PDO (pure water in case 1, water with BDO and acetic acid in case 2), while the bottom product would be PDO with the remaining heavier components (glycerol and glucose in case 1, succinic and lactic acid in case 2). Lastly, to obtain pure PDO product, an additional distillation step is needed to remove heavy impurities. The top product from this column would be pure PDO, while the bottom product would consist of the remaining heavy components. Thus, a sequence of at least two conventional distillation columns would be needed to separate high-purity PDO product from all lighter and heavier components. Alternatively, a thermodynamically equivalent highly integrated dividing-wall column system (DWC) [54] can be used

to replace this sequence of two distillation columns (see Fig. 4).

A dividing-wall column with a common bottom section and a divided overhead section is the proper column design. This design implies the initial removal of light components, followed by the subsequent purification of PDO from heavy components. Thus, the DWC has two top products (lighter components and PDO) and two condensers, while having only one bottom product (heavier components) and one reboiler. Due to the large temperature difference between the top products (about 24 – 26 °C and 116 – 123 °C), thermal insulation will be needed for the internal wall to ensure the energy efficiency of DWC. As another option, a dividing-wall column with a common overhead section and a dividing bottom section is a possible DWC column design. It implies the initial removal of heavier components, followed by purification of PDO from lighter components. Thus, PDO is obtained as one of the two bottom products (PDO and heavier components), while lighter components are the only top product. In this design, the temperature difference between two products at the dividing side of the column (PDO and heavier components) would be smaller (< 50 °C). However, this DWC design

would result in more than 54% higher energy requirements because the PDO product has to be evaporated twice. Thus, DWC with the common bottom and the divided overhead section is the best configuration in terms of total energy requirements.

As the DWC process unit is not available off-the-shelf in Aspen Plus, a thermodynamically equivalent sequence of two distillation columns was used in simulations, as presented in Fig. 4. The left and right parts of DWC are presented with DWC_L and DWC_R , respectively, whereby DWC_L has only a condenser, while DWC_R has both a reboiler and condenser. The number of stages, position of the feed stage, operating pressure, distillate rate, reflux ratio and vapor split were varied to ensure recovery of high-purity PDO product while minimizing total energy requirements. The condenser pressure of 0.030 bar with a pressure drop of 0.225 mbar per theoretical stage was defined for both DWC_L and DWC_R to minimize the required heating duty for DWC while maintaining DWC_L condenser temperature sufficiently high (about 26 °C) for the usage of chilled water. Due to the operation under reduced pressure, the structured packing type Mellapak 250 was also selected for DWC internals

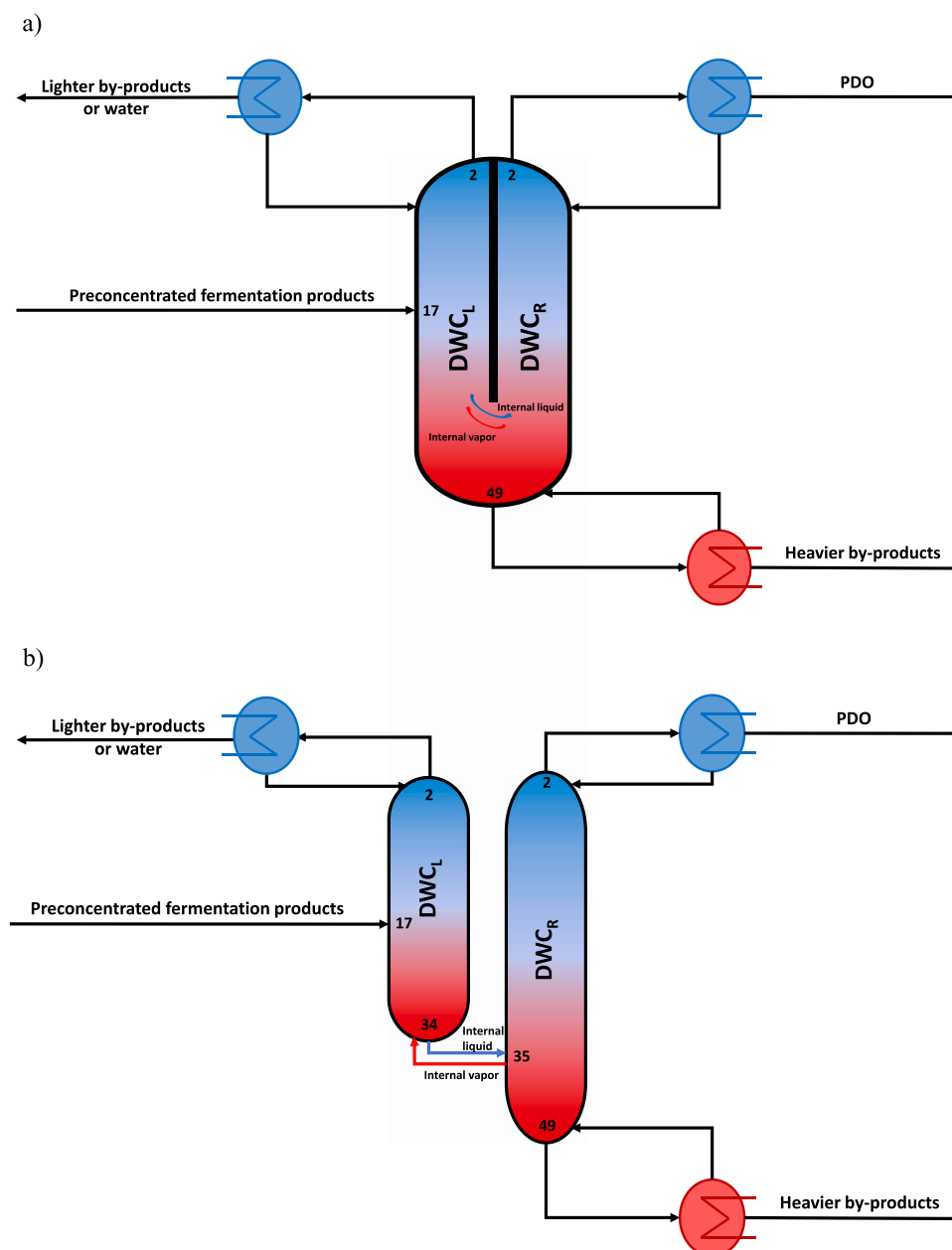


Fig. 4. DWC design (a) and the equivalent sequence of distillation columns (b) - the numbers in the column indicate the column tray number.

[52]. DWC has 50 stages in total, whereby the convention in Aspen Plus implies that the first stage is a condenser, while the last one is a reboiler. The wall is placed at the top 34 stages (33 excluding condensers). The feed stream to DWC, the pre-concentrated mixture from the bottom of column C1, is fed to the 17th stage of DWC_L (also the 17th stage of DWC). The top product from DWC_L contains water (in case 1) and all components lighter than PDO (BDO and acetic acid in case 2). As there is no reboiler, the bottom liquid from DWC_L goes to DWC_R , while a part of the vapor rising in DWC_R (29.7 and 32.8% in case 1 and case 2, respectively) is redirected to DWC_L to ensure sufficient vapor flow in the left side of DWC. The top product from DWC_R is a high-purity PDO product (> 99.9 wt%), while the bottom product contains all heavier components (glycerol and glucose in case 1, succinic and lactic acid in case 2).

The described DWC was designed to minimize the energy requirements for the considered compositions of the fermentation broth. Nonetheless, different compositions of the feed stream to DWC might require additional tuning of operating parameters to obtain efficient separation. Thus, the proposed DWC design can be adapted to effectively separate high-purity PDO product from lighter and heavier by-products

that may be formed in various fermentation processes.

4.3.1. Case study 1: PDO fermentation from glucose

In this case, the feed stream to DWC contains mainly PDO and water, with some glycerol and glucose. As water is the only component lighter than PDO, it will be obtained at the top of DWC_L with purity of 100 wt%. The top product from DWC_R is high-purity PDO (99.92 wt%), while the bottom product is mainly glycerol (98.57 wt%) with some glucose (0.94 wt%) and a small amount of remaining PDO (0.50 wt%). The temperature and liquid phase composition profiles of DWC are presented in Fig. 5. It can be seen that the temperature in DWC_L increases around the location of the feed stage and at the bottom due to the removal of light water. Furthermore, the temperature in DWC_R decreases at the top and increases at the bottom, due to the higher concentrations of PDO and heavier components, respectively. The concentration of water increases at the top of DWC_L , while it is almost insignificant at all stages of DWC_R . Furthermore, the mass fraction of PDO approaches 1 at the top of DWC_R , while the mass fractions of glycerol and glucose increase at the bottom of DWC_R . It can be seen from the profiles in Fig. 5 that fewer stages might be sufficient for this

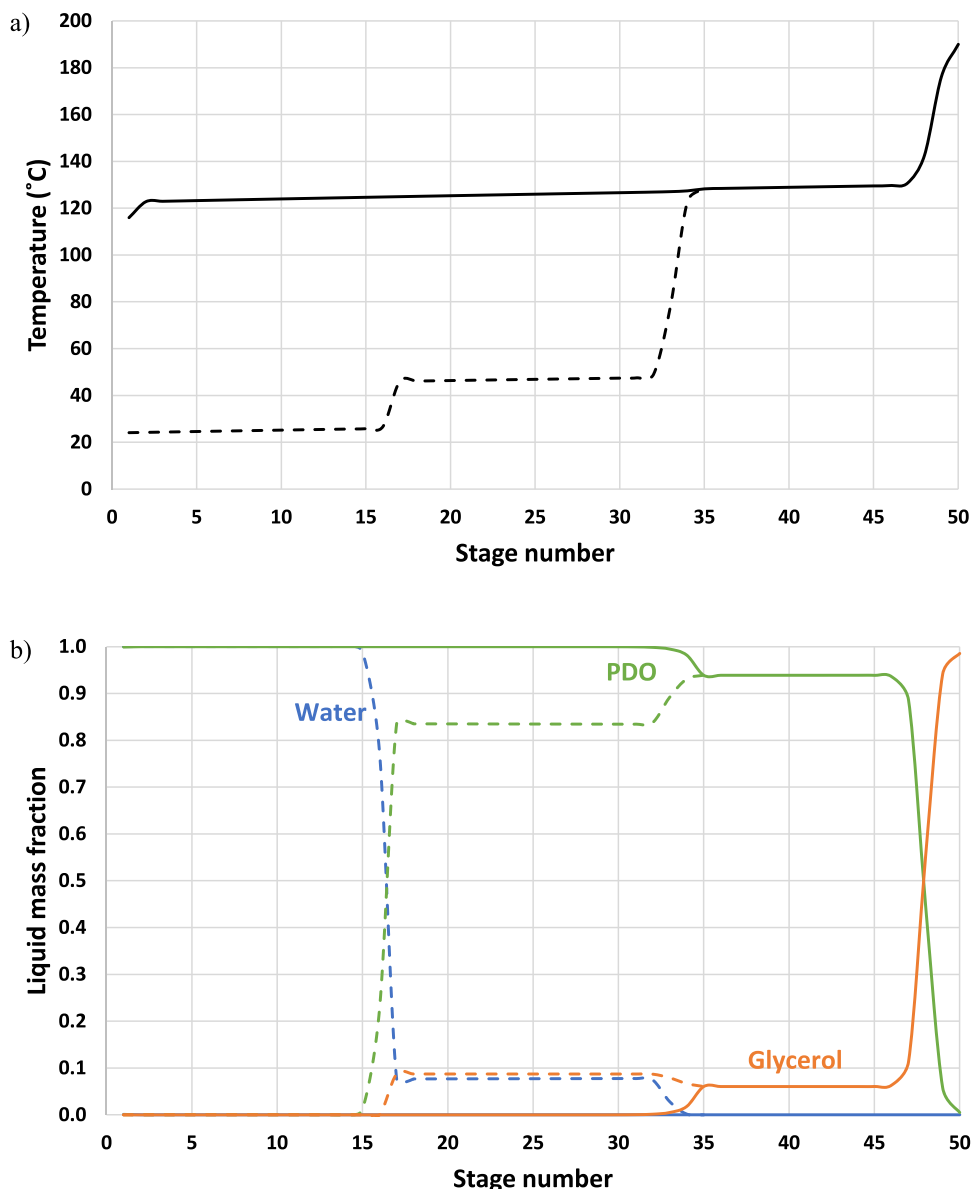


Fig. 5. Temperature (a) and composition (b) profiles of DWC designed for case 1 (right side – full line, left side – dashed line).

separation due to the large difference in boiling points of the components. However, the defined number of stages will allow separation in case more by-products are present (as in case 2) and reduce the total required reboiler duty for DWC.

The top water stream is very pure (100 wt%) and may be used somewhere (e.g. in the fermentation). Regarding the bottom product, two alternatives were considered: case 1a in which the whole glycerol-glucose mixture was considered as a waste stream which would be the worst-case scenario and case 1b in which glycerol was recovered by an additional vacuum distillation step in column C2. Reduced pressure (condenser pressure of 0.030 bar) and pH control need to be applied to avoid polymerization of glycerol to polyglycerol, dehydration to acrolein or oxidation to glyceroic acid [55]. The top product of column C2 is glycerol (99.50 wt%) which satisfies technical grade standards (min. 95.5 wt% [56]). The bottom product contains glucose (93.87 wt%) and some remaining glycerol (6.13 wt%). This stream was considered as the waste stream in further analysis of case 1b. Nonetheless, if there are potential uses of this stream, the performance of the overall process would be just slightly better as the flowrate of this stream is not significant.

4.3.2. Case study 2: PDO fermentation from glycerol

In this case, the desalted solution that is fed to column C1 contains by-products both lighter and heavier than PDO. Thus, the top product from DWC_L contains the remaining water, BDO and acetic acid (50.67, 45.68 and 3.65 wt%, respectively). As in case 1, the top product from DWC_R is a high-purity PDO product (99.98 wt%), while the bottom contains mainly succinic and lactic acids with a small amount of remaining PDO (84.08, 15.62 and 0.03 wt% of succinic acid, lactic acid and PDO respectively). The temperature and liquid phase composition profiles are presented in Fig. 6. The temperature at DWC_L reduces at the top due to the separation of lighter components while it increases around the feed stage and at the bottom. The temperature at DWC_R increases slightly from the top to the bottom, whereby the largest increase is at the lowest stages due to the concentration of heavy components. The concentrations of water, BDO and acetic acid increase at the top of DWC_L , while they are almost negligible at all stages of DWC_R . The mass fraction of PDO increases towards the top of DWC_R and approaches 1, while the mass fractions of succinic and acetic acids increase towards the bottom of DWC_R . The liquid composition profiles presented in Fig. 6 are not as flat as in case 1, which indicates that 50 stages are needed for

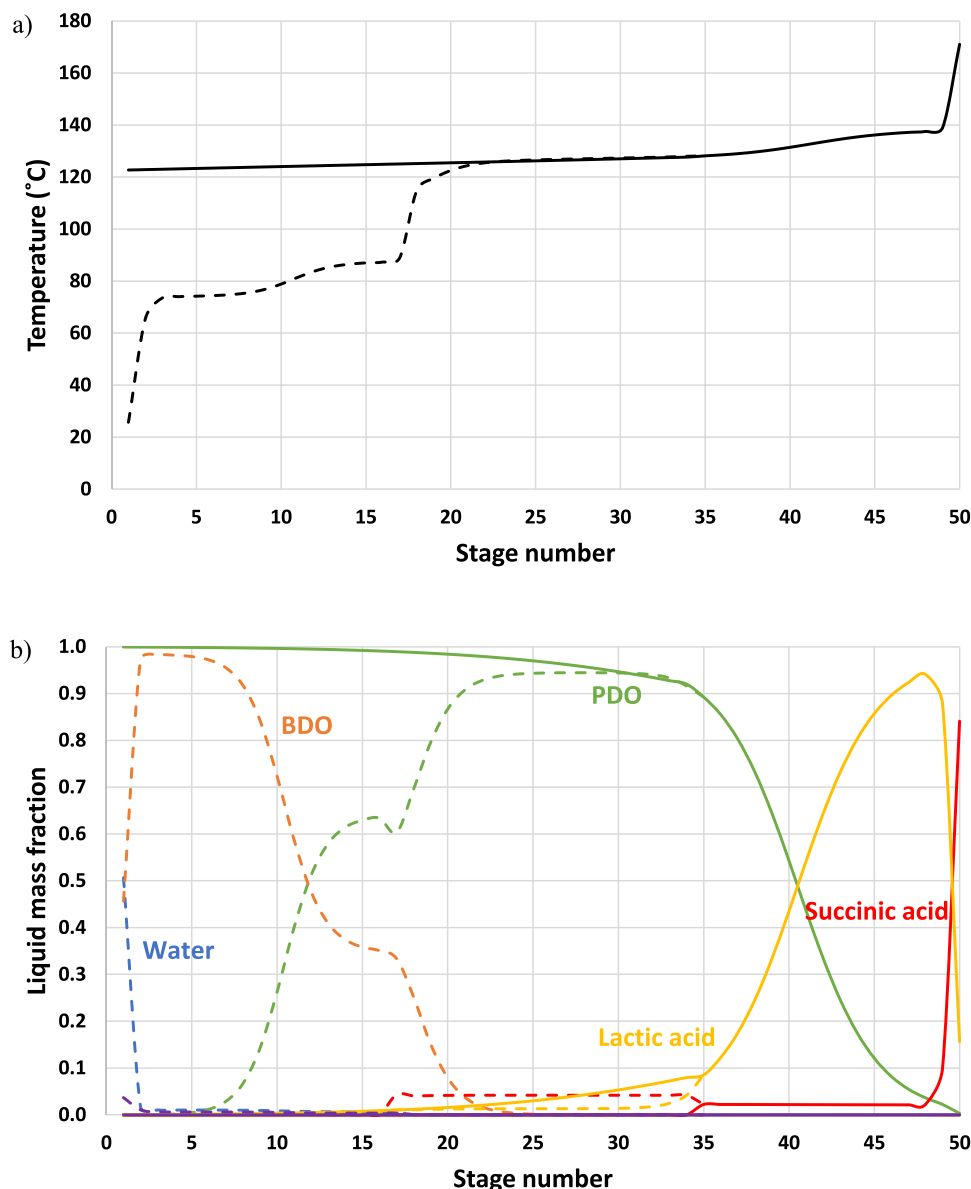


Fig. 6. Temperature (a) and composition (b) profiles of DWC designed for cases 2a and 2b (right side – full line, left side – dashed line).

these separations. This is due to the presence of more by-products and lower differences in boiling points between PDO and the first lighter and heavier components (BDO and lactic acid). As a result of more complex separation, the required reflux ratio in DWC_R and reboiler duty are higher in case 2 (2.5 and 3.5 MW_{th} , respectively) as compared to case 1 (0.2 and 1.2 MW_{th} , respectively).

As in case 1, two scenarios were analyzed: case 2a (the worst-case scenario) in which the bottom stream with heavier by-products (succinic and lactic acid) and the top stream with remaining water and lighter by-products (BDO and acetic acid) were considered as waste streams, and case 2b in which BDO and succinic acid were recovered as valuable by-products that are present in significant amounts (about 6 and 3 ktonne/y, respectively).

Due to the large boiling point difference between BDO and acetic acid, a simple vacuum distillation step is sufficient to obtain a high-purity BDO by-product (100 wt%) at the bottom of column C2. The top product from this column is a water – acetic acid mixture (about 93.27 wt% water and 6.71 wt% acetic acid) that needs to be sent to wastewater treatment. Due to a large temperature difference between the top and the bottom of this column (24 and 99 °C, respectively), MVR cannot be implemented to this column and low-pressure steam is needed for heating. Nonetheless, the required reboiler duty for this column is not large (less than 0.7 MW) due to the relatively easy separation. Furthermore, due to the large difference in boiling points (see Table 1), succinic acid may be separated from lactic acid in distillation column C3. Reduced pressure (condenser pressure of 0.020 bar) distillation is needed to maintain the temperatures lower than the succinic acid decomposition temperature (about 235 °C [57]) and to minimize lactic acid oligomerization. Moreover, it should be noted that further testing is required to check the exact extent of the oligomerization reactions. Nonetheless, the bottom product from this column is succinic acid (99.98 wt%) that will crystallize after cooling. The top product is a very small process stream that mainly consists of lactic acid (98.10 wt%) and small amounts of PDO (1.90 wt%). This stream was considered a waste stream in further analysis due to lactic acid oligomerization. In case the remaining substrate is present in the bottom stream from column C1, an additional distillation step will be needed to separate succinic acid from the remaining glycerol. Lastly, it should be noted that the esterification reactions may happen due to the presence of alcohol (PDO) and carboxylic acids (succinic and lactic acid). Nonetheless, the esterification reactions without an acid catalyst are very slow [58], while the structured packing in DWC offers the advantage of lower liquid holdup and shorter residence time compared to tray internals. Furthermore, PDO concentrations are very low at the bottom stages of DWC, where concentrations of acids are significant. Thus, the influence of the esterification reactions will likely be negligible but additional testing might be needed prior to implementation on real-life industrial processes.

4.4. Economic analysis

The determined economic indicators are summarized in Table 4 and Table 5, and presented in Fig. 7 and Fig. 8, while the PBP analysis is presented in Fig. 9. The total costs of installing all equipment units for the overall recovery process are 7613, 7938, 12,205 and 13,081 k\$ in cases 1a, 1b, 2a and 2b. Thereby, the costs of equipment in the preconcentration and final purification parts of the recovery processes are the major contributors to the total equipment costs (about 79 – 86%). Among the equipment costs of the preconcentration and final purification, the biggest contribution is the cost of distillation columns (about 38 – 39%), compressors in heat pump systems (about 28 – 32%) and heat exchangers (about 26 – 27%), while costs for pumps and flash vessels are much smaller (about 3 – 6 and <1%). Among the equipment costs of the initial recovery steps, the biggest contribution is due to the cation and anion exchange modules (40 – 41 and 30%, respectively) and pumps (about 22 – 23%), while the costs of filtration modules are much lower (about 1, 3 and 3% for microfiltration, diafiltration and ultrafiltration

Table 4

Key performance indicators in terms of economics and sustainability of the PDO recovery process in cases 1a and 1b: initial recovery steps (a), preconcentration and final purification steps (b) and total recovery process (c).

	Case 1a			Case 1b		
	(a)	(b)	(c)	(a)	(b)	(c)
Economic indicators						
CAPEX [k\$]	11,006	2908	13,914	11,592	2908	14,500
OPEX [k\$/y]	2725	2355	5080	2634	2398	5032
OPEX [\$/kg _{product}]	0.119	0.103	0.221	0.104	0.095	0.198
TAC [k\$/y]	3826	2646	6472	3793	2689	6482
TAC [\$/kg _{product}]	0.167	0.115	0.282	0.150	0.106	0.256
Sustainability metrics						
Thermal energy requirements [kW _{th} /kg _{product}]	0.403	0.000	0.403	0.386	0.000	0.386
Electrical energy requirements [kW _e /kg _{product}]	0.379	0.102	0.480	0.349	0.092	0.440
Primary energy requirements [kW _{th} /kg _{product}]	1.350	0.254	1.604	1.258	0.230	1.487
Water consumption [m ³ /kg _{product}]	0.138	0.000	0.138	0.129	0.000	0.129
Water loss [m ³ /kg _{product}]	0.010	0.000	0.010	0.009	0.000	0.009
CO ₂ emissions, grey electricity [kg _{CO2} /kg _{product}]	0.245	0.046	0.292	0.229	0.042	0.271
CO ₂ emissions, green electricity [kg _{CO2} /kg _{product}]	0.073	0.000	0.073	0.070	0.000	0.070
Material intensity [kg _{waste} /kg _{product}]	0.106	0.640	0.746	0.001	0.579	0.580
Waste water intensity [kg _{waste} /kg _{product}]	0.000	4.823	4.823	0.000	4.364	4.364
Pollutant emissions [kg _{pollutant} /kg _{product}]	0.000	0.000	0.000	0.000	0.000	0.000
Toxic emissions [kg _{toxic material} /kg _{product}]	0.000	0.000	0.000	0.000	0.000	0.000

modules). Overall, the reason for much lower equipment costs in case 1 is the lower feed flowrate due to the more concentrated feed stream. The calculated CAPEX for the total recovery process are 13,914 and 14,500 k\$ for cases 1a and 1b, 22,304 and 23,885 k\$ for cases 2a and 2b. Since the total equipment costs make up the largest part of the total CAPEX (about 54 – 55% in all cases whereby equipment costs of the designed preconcentration and final purification steps, and the initial recovery steps are about 43 – 47% and 11 – 8% of CAPEX, respectively), the higher CAPEX in cases 2a and 2b are mainly due to the higher equipment cost.

The determined OPEX for the total recovery process are 5080, 5032, 6567 and 6848 k\$/y in cases 1a, 1b, 2a and 2b, respectively. Expressed per kilogram of recovered product, the total OPEX are 0.221, 0.198, 0.287 and 0.213 \$/kg in cases 1a, 1b, 2a and 2b, respectively. Thereby, the contribution of the designed preconcentration and final purification parts is about 54, 52, 67 and 69% of the total OPEX. The largest contributor to OPEX in all cases is the cost of operating labor (59% of the total OPEX in cases 1a and 1b, 46 and 44% of the total OPEX in cases 2a and 2b). The higher contribution of labor costs in total OPEX in case 1 is mainly due to the lower value of OPEX, while the absolute value of labor costs is approximately the same in all cases. Similarly, the contribution of electricity and heating utilities costs in cases 1a and 1b (about 13 and 7% of the total OPEX, respectively) are lower compared to the contribution in cases 2a and 2b (about 19 and 12 – 14% of the total OPEX, respectively) due to the lower feed stream flowrate. Nonetheless, it

Table 5

Key performance indicators in terms of economics and sustainability of the PDO recovery process in cases 2a and 2b: initial recovery steps (a), preconcentration and final purification steps (b) and total recovery process (c).

	Case 2a			Case 2b		
	(a)	(b)	(c)	(a)	(b)	(c)
Economic indicators						
CAPEX [k\$]	18,917	3387	22,304	20,498	3387	23,885
OPEX [k\$/y]	4386	2181	6567	4743	2106	6848
OPEX [\$/kg _{product}]	0.192	0.095	0.287	0.148	0.066	0.213
TAC [k\$/y]	6278	2520	8797	6792	2444	9237
TAC [\$/kg _{product}]	0.274	0.110	0.384	0.212	0.076	0.288
Sustainability metrics						
Thermal energy requirements [kW _{th} /kg _{product}]	1.222	0.000	1.222	1.045	0.000	1.045
Electrical energy requirements [kW _{el} /kg _{product}]	0.782	0.128	0.910	0.567	0.092	0.659
Primary energy requirements [kW _{th} /kg _{product}]	3.175	0.321	3.496	2.462	0.229	2.691
Water consumption [m _w ³ /kg _{product}]	0.348	0.000	0.348	0.278	0.000	0.278
Water loss [m _w ³ /kg _{product}]	0.025	0.000	0.025	0.020	0.000	0.020
CO ₂ emissions, grey electricity [kg _{CO2} /kg _{product}]	0.542	0.058	0.600	0.417	0.042	0.459
CO ₂ emissions, green electricity [kg _{CO2} /kg _{product}]	0.185	0.000	0.185	0.159	0.000	0.159
Material intensity [kg _{waste} /kg _{product}]	0.446	0.852	1.299	0.032	0.608	0.640
Waste water intensity [kg _{waste} /kg _{product}]	0.314	6.089	6.403	0.224	4.345	4.569
Pollutant emissions [kg _{pollutant} /kg _{product}]	0.000	0.000	0.000	0.000	0.000	0.000
Toxic emissions [kg _{toxic material} /kg _{product}]	0.000	0.000	0.000	0.000	0.000	0.000

should be noted that the costs of utilities are mainly due to the preconcentration and final purification steps. Furthermore, waste treatment costs (including waste water treatment) are higher in cases 1a and 2a (about 5 and 4% of the total OPEX, respectively) than in cases 1b and 2b (about 3% of the total OPEX). The biggest contributor to the total waste treatment costs is the waste water from diafiltration, ultrafiltration and ion exchange steps. Moreover, the waste treatment costs are lower in downstream processing after fermentation from glucose (cases 1a, 1b) due to fewer by-products in the fermentation broth. Significant contributors to the total OPEX are costs of the additional chemicals required to regenerate cation and anion exchange resins (about 8 – 9% of the total OPEX) and costs of membrane and resin replacements (about 3 – 4% of the total OPEX).

Thus, TAC that includes both CAPEX and OPEX with PBP of 10 years are 6472, 6482, 8797 and 9237 k\$/y for the total recovery process in cases 1a, 1b, 2a and 2b, respectively. Expressed per kilogram of recovered product, TAC are 0.282 \$/kg for case 1a, 0.256 \$/kg for case 1b, 0.384 \$/kg for case 2a and 0.288 \$/kg for case 2b. Less expensive recovery in cases 1a and 1b as compared to cases 2a and 2b is due to the higher product concentration, smaller amounts of by-products in the feed stream and larger temperature differences between PDO and by-products. Furthermore, recovering the fermentation by-products from the broth (e.g. glycerol in case 1b, BDO and succinic acid in case 2b) can substantially reduce specific TAC (reduction of more than 9% in case 1b compared to case 1a, and reduction of about 25% in case 2b compared to

case 2b) despite somewhat higher CAPEX due to the additional equipment units. This arises because more product is recovered, while less waste is produced. Consequently, TAC is lower due to the lower costs of waste management, while specific TAC is distributed to a higher amount of recovered products. Lastly, the contribution of the designed preconcentration and final purification steps to the total TAC are 59, 59, 71 and 74% in cases 1a, 1b, 2a and 2b. The largest contribution of these steps in cases 2a and 2b is due to more complex separations (more dilute fermentation broth, higher concentrations of by-products, lower temperature differences between PDO and by-products). Considering the significant contribution of the preconcentration and final purification costs to the total recovery costs, the proposed advanced process design might significantly improve the overall process viability. Furthermore, since the costs of biobased PDO production were estimated to 1.37 – 2.40 \$/kg for the fermentation of biomass [59] and 0.96 – 1.09 \$/kg for the fermentation of raw glycerol [60], with prevailing recovery costs, the results of this study present a major step forward in the development of competitive fermentative PDO production.

Moreover, the analysis of the PBP influence on TAC for the total PDO recovery process (see Fig. 9) shows competitive process performance even for shorter PBP [59,61]. For example, for PBP of only one year, TAC are higher than 1.0 \$/kg solely in case 2a. Thus, in the case of multiple fermentation by-products present in the broth, recovering those present in substantial quantities may enhance the economic performance of the overall process.

4.5. Sustainability assessment

The calculated values of sustainability metrics are summarized in Table 4 and Table 5.

- **Energy intensity:** Due to the required external heating in the distillation steps, the thermal energy requirements of the total recovery process are 0.403, 0.386, 1.222 and 1.045 kW_{th}/kg in cases 1a, 1b, 2a and 2b, respectively. Significantly more thermal energy is required in cases 2a and 2b due to the lower product concentration and more complex separation in DWC as compared to cases 1a and 1b. The electrical energy requirements for the total recovery process are 0.480, 0.440, 0.910 and 0.659 kW_{el}/kg in cases 1a, 1b 2a and 2b, respectively. Thereby, the contribution of the designed preconcentration and final purification steps to the total electrical energy requirements is 79 – 86%. Due to the more complex separation in the preconcentration column C1, a higher reflux ratio is needed in cases 2a and 2b. Consequently, a larger compressor duty in the MVR system applied to this column is required. As electricity to power this compressor is the biggest contributor to electrical energy usage, the electrical energy requirements are higher in cases 2a and 2b compared to cases 1a and 1b. Furthermore, the total primary energy requirements for the overall recovery process are 1.604, 1.487, 3.496 and 2.691 kW_{th}/kg in case 1a, case 1b, case 2a and case 2b, respectively, whereby the preconcentration and final purification contribute to 84 – 91%. Thus, the more complex feed stream in cases 2a and 2b leads to more energy-intensive downstream processing. Nonetheless, the proposed recovery processes are highly energy-efficient compared to the reported literature data for biobased (nonrenewable energy use of 10.3 kWh/kg) and petroleum-based PDO production (nonrenewable energy use of 16.9 kWh/kg) [31].
- **Water consumption:** In the calculation of water consumption metrics, it was assumed that high-purity water streams separated in the preconcentration and final purification parts of the process may be reused in the initial recovery steps (e.g. water required for the diafiltration and ion exchange steps) to reduce the overall fresh water requirements. As a consequence of higher energy use in the distillation, more water is needed in cases 2a and 2b (0.348 and 0.278 m_w³/kg, respectively) compared to cases 1a and 1b (0.138 and 0.129 m_w³/kg). Accordingly, the amounts of lost water are 0.010,

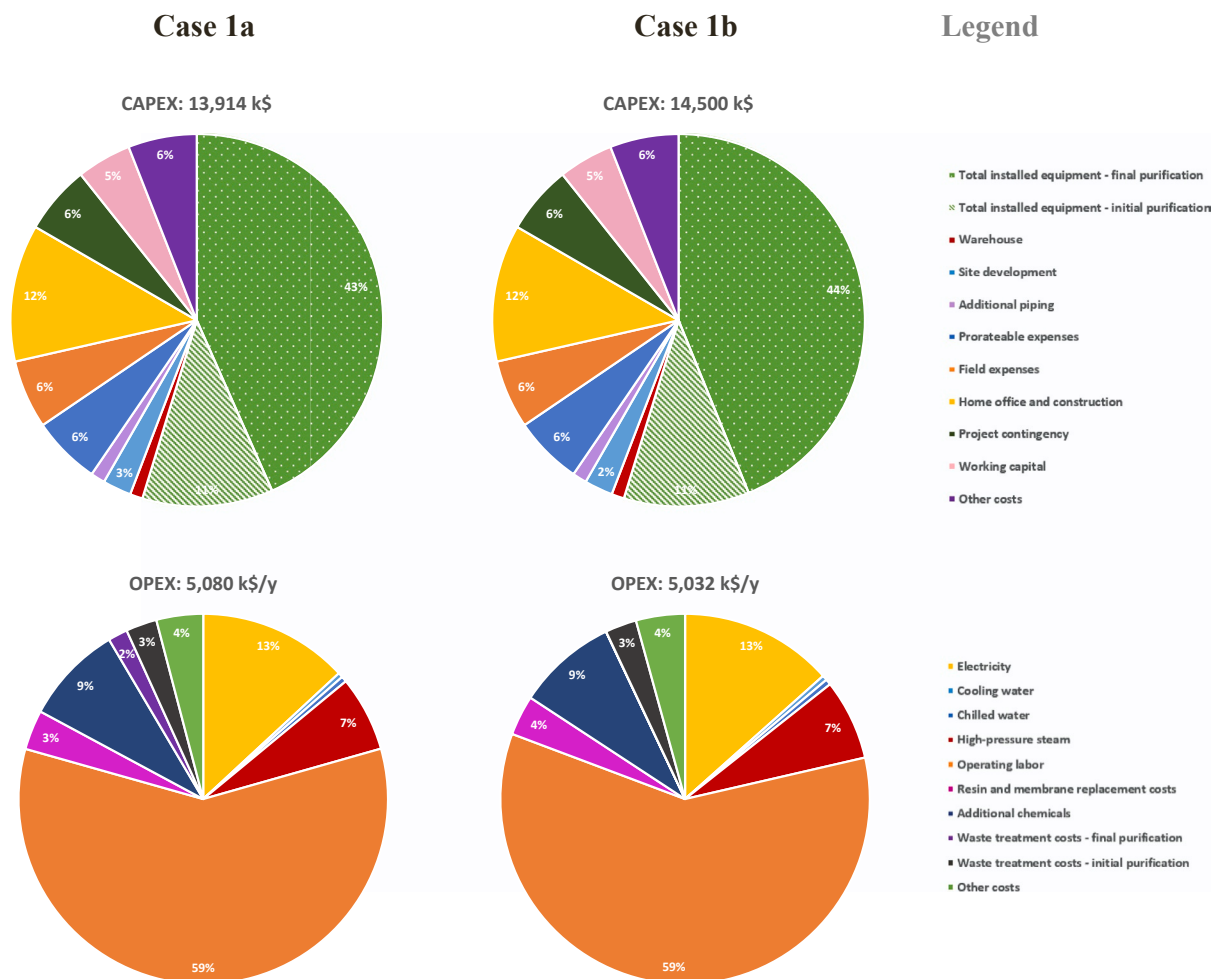


Fig. 7. Comparison of economic indicators of the total recovery process in cases 1a and 1b.

0.009, 0.025 and 0.020 m^3/kg for cases 1a, 1b, 2a and 2b, respectively.

- Greenhouse gas emissions: Due to higher energy requirements, CO_2 emissions are higher in cases 2a and 2b (0.600 and 0.459 $\text{kg}_{\text{CO}_2}/\text{kg}$ if grey electricity is used, 0.185 and 0.159 $\text{kg}_{\text{CO}_2}/\text{kg}$ if green electricity is used, respectively) compared to cases 1a and 1b (0.292 and 0.271 $\text{kg}_{\text{CO}_2}/\text{kg}$ if grey electricity is used, 0.073 and 0.070 $\text{kg}_{\text{CO}_2}/\text{kg}$ if green electricity is used). Given that CO_2 emissions of the total biobased and petroleum-based PDO production process were estimated to 2.5 – 5.9 $\text{kg}_{\text{CO}_2}/\text{kg}$ [59] and 7.0 $\text{kg}_{\text{CO}_2}/\text{kg}$ [31], the proposed recovery processes have much lower environmental impact.
- Material intensity: Considering only the designed preconcentration and final purification parts of the PDO recovery process, material intensity metric is the lowest in case 1b (0.001 $\text{kg}_{\text{waste}}/\text{kg}$) as the top product from DWC_L is high-purity water that is not a waste stream, while glycerol is recovered from the bottom of DWC_R . If the glycerol is not recovered, as in case 1a, the material intensity metric is significantly higher (0.106 $\text{kg}_{\text{waste}}/\text{kg}$). Contrarily, there is the largest amount of waste per kilogram product in case 2a (0.446 $\text{kg}_{\text{waste}}/\text{kg}$) as no fermentation by-products are recovered. If BDO and succinic acid are recovered as in case 2b, the material intensity metric is significantly lower (0.032 $\text{kg}_{\text{waste}}/\text{kg}$). However, the initial recovery steps (microfiltration, diafiltration, ultrafiltration and ion exchange) will result in much higher waste formation due to the removal of biomass, biopolymers, inorganics, etc. Thus, the estimated material intensity metrics for these steps are 0.640, 0.579, 0.852 and 0.608 $\text{kg}_{\text{waste}}/\text{kg}$ in cases 1a, 1b, 2a and 2b. Considering the material intensity of the initial steps in the downstream process,

recovery of by-products that are present in significant amounts can be suggested to minimize the impact of the overall process.

- Waste water intensity: Due to the need to remove valuable products from the microfiltration retentate and regenerate anion and cation resins, significant amounts of waste water are formed in the initial recovery steps. The values of waste water intensity metrics in cases 1a/b, 2a/b are 4.823, 4.364, 6.403 and 4.569 $\text{kg}_{\text{waste water}}/\text{kg}$.
- Pollutant and toxic materials: Since all waste streams are accounted for in the material and waste water intensity metrics, while no pollutants and toxic materials are formed, the values of these metrics are zero in all cases.

5. Conclusion

The new downstream process proposed in this study was proven effective for 1,3-propanediol recovery after various fermentation processes: from glucose using *E. coli* (cases 1a and 1b) or from glycerol using *K. pneumoniae* (cases 2a and 2b). Following the initial separation of cells, biopolymers and inorganics by conventional filtration and ion-exchange steps, a vacuum distillation step can be implemented to remove most of the present water. This step may be enhanced with a mechanical vapor recompression heat pump system to significantly decrease the overall energy usage. The final product purification can be performed in an integrated dividing-wall column that can efficiently separate high-purity 1,3-propanediol (>99.9 wt%) from lighter and heavier by-products. Recovering and valorizing by-products that are present in significant amounts in the fermentation broth is suggested to substantially reduce the total recovery costs (from 0.282 to 0.256 \$/kg in cases 1a and 1b, or

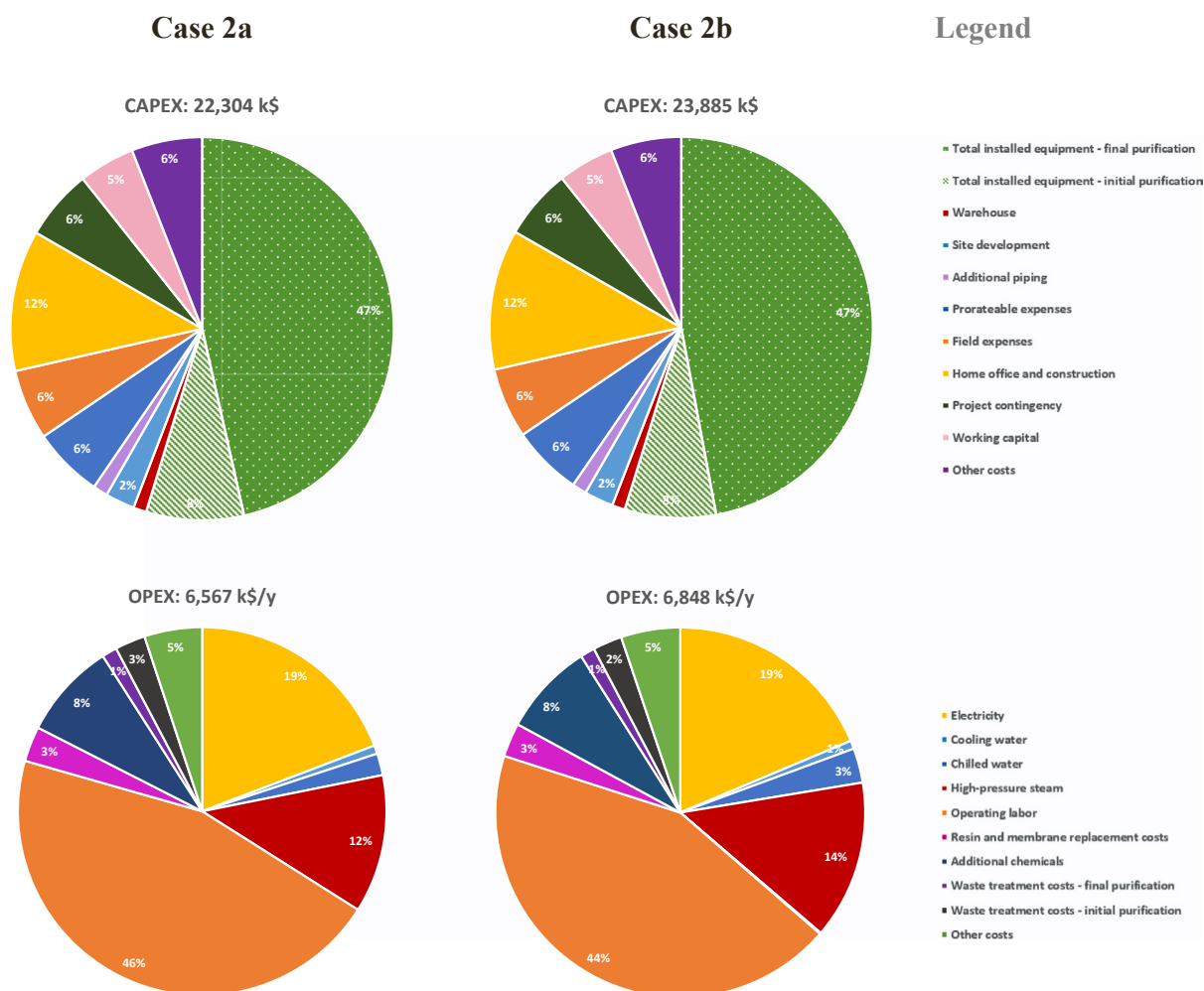


Fig. 8. Comparison of economic indicators of the total recovery process in cases 2a and 2b.

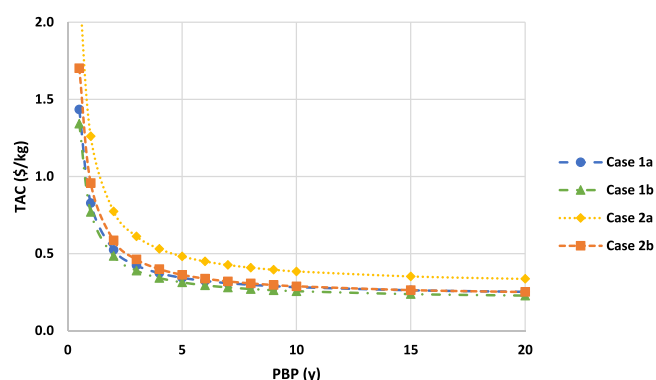


Fig. 9. Influence of the payback period on TAC for the overall recovery process.

from 0.384 to 0.288 \$/kg in cases 2a and 2b) and energy requirements (from 1.604 to 1.487 kW_{th}/kg in cases 1a and 1b, or from 3.496 to 2.691 kW_{th}/kg in cases 2a and 2b). Considering that water removal and final purification significantly contribute to the total downstream processing costs (59 – 74%), the results of this original research advance the large-scale 1,3-propanediol production (about 23 ktonne/y of 1,3-propanediol and 2 – 9 ktonne/y of by-products) by proposing a highly-integrated recovery process that can adapt to different compositions of fermentation broth. Depending on the specific concentrations

of light and heavy impurities after the ion exchange step, the proposed process design can be easily adjusted to efficiently recover high-purity PDO product.

Lastly, by comparing the recovery after two different fermentation processes this study emphasizes the importance of the broth composition on the downstream processing performance. Less diluted fermentation broth with fewer by-products in cases 1a and 1b results in more cost-effective and energy-efficient downstream processing. In that respect, the upstream fermentation and downstream recovery parts should be developed simultaneously to ensure the competitiveness and viability of the overall bioprocess.

CRedit authorship contribution statement

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

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.procbio.2024.04.040](https://doi.org/10.1016/j.procbio.2024.04.040).

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