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DOI
10.1016/j.seppur.2023.124320

Publication date
2023

Document Version
Final published version

Published in
Separation and Purification Technology

Citation (APA)
Janković, T., Straathof, A. J. J., & Kiss, A. A. (2023). Advanced downstream processing of bioethanol from syngas fermentation. *Separation and Purification Technology*, *322*, Article 124320. https://doi.org/10.1016/j.seppur.2023.124320

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Separation and Purification Technology 322 (2023) 124320

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Advanced downstream processing of bioethanol from syngas fermentation

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ARTICLE INFO

Keywords:
Syngas fermentation
Downstream processing
Bioethanol
Fluid separation
Heat pumps

ABSTRACT

Syngas fermentation is used industrially to produce diluted bioethanol (about 1–6 wt%). This research study proposes a novel downstream process that recovers bioethanol in an energy-efficient and cost-effective manner, improves fermentation yield by recycling all fermentation broth components (microbes, acetate and water), and is designed for full-scale industrial-level application. Therefore, vacuum distillation at fermentation temperature was conceptually studied as an initial ethanol recovery step, leading to a bottom stream that may be recycled. Advanced separation and purification techniques were designed to recover 99.5% of initially present ethanol as high-purity product (99.8 wt%). Mechanical vapor recompression and heat integration methods were used to maximize sustainability and eco-efficiency of the proposed recovery process. Implementation of these techniques on a process using 6 wt% ethanol feed stream decreased the total annual costs by 54.2% (from 0.175 to 0.080 $\$/kg_{EtOH}$), reduced the primary energy requirement by 66.1% (from 2.82 to 0.96 $kW_{th}h/kg_{EtOH}$), lowered the CO_2 emission by up to 82.6% (from 0.414 to 0.072 kg_{CO2}/kg_{EtOH}), and reduced the fresh water usage by 62.6% (from 0.242 to 0.091 m^3_W/kg_{EtOH}). Sensitivity analysis for ethanol concentrations ranging from 6 to 1 wt% showed that the recovery costs and energy use increased to 0.336 $\$/kg_{EtOH}$ and 1.78 $kW_{th}h/kg_{EtOH}$ respectively. Since ethanol recovery performs better but fermentation will perform worse at higher ethanol concentration in fermentation broth, there is a trade-off concentration for the overall process. The current analysis is an important step toward determining this trade-off.

1. Introduction

Rapidly increasing energy demands have resulted in the over-consumption of fossil fuels and diminishing availability of fossil carbon sources. Furthermore, increasing concerns over environmental pollution, climate changes and energy security unavoidably lead to the need for more sustainable energy resources [1]. Due to their environmental impact, biofuels are gaining significance as a potential renewable alternative to fossil fuels [2]. Technologies for the production of first-generation biofuels are already mature and well-established. However, the dominant feedstock is biomass that can be used for dietary purposes, such as corn or sugarcane. For this reason, the major drawback of first-generation biofuels is that their production directly threatens food availability [3].

Second-generation biofuels are derived from energy-dense lignocellulosic materials that are either waste material or are grown on non-arable land. Therefore, the production of second-generation biofuels overcomes the major limitation of first-generation biofuels [4]. One approach in second-generation bioethanol production is the implementation of lignocellulosic fermentation. Due to the complex structure of biomass, pretreatment and enzymatic hydrolysis steps are necessary prior to the fermentation [5]. During these steps, lignin is removed from cellulose and hemicellulose chains which are then further broken into fermentable sugars. A significant drawback of this method is that the pretreatment step is usually very economically demanding and can contribute up to 30–40% to the total cost in biorefineries [6]. Furthermore, lignin, which makes about 40% of the biomass, is not converted into biofuel [7]. However, in biomass gasification processes the energy and carbon from lignin can also be used. This process implies the gasification of biomass to produce syngas, a gas mixture rich in carbon monoxide (CO) and hydrogen (H_2) [7]. Generally, syngas is an important base material in chemical industry. It can be used as a hydrogen source for the production of commercially valuable chemicals [8]. One commonly produced chemical from syngas is methanol. Bimetallic catalysts, high temperatures (220–250 °C) and pressures (50–100 bar) are needed for the production process [9]. Another valuable chemical that can be obtained from syngas is ethanol. As a feedstock for biofuel production, syngas is traditionally further converted by

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https://doi.org/10.1016/j.seppur.2023.124320
Received 6 April 2023; Received in revised form 5 June 2023; Accepted 7 June 2023
Available online 10 June 2023
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the thermochemical Fischer-Tropsch process. However, this process requires high temperature (150–350 °C) and pressure (up to 30 bar) [10], as well as expensive catalysts. Furthermore, an additional water–gas shift reaction step is often required to obtain the exact H_2:CO ratio needed for certain catalysts [11].

An alternative to the Fischer-Tropsch process is the syngas fermentation, in which different acetogenic organisms are used to ferment syngas into biofuels and biochemicals [12]. The schematic representation of the bioethanol production process from syngas is presented in Fig. 1. The advantages of the gas fermentation process compared to the thermochemical process are moderate process conditions (temperatures below 40 °C and pressure below 10 bar [13]), adaptability of microorganisms to different H_2:CO ratios in syngas, and tolerance to many impurities which would lead to poisoning of chemical catalysts [4]. Due to the relatively high tolerance of microorganisms, a wide range of substrates can be used for the gas fermentation process. In addition to lignocellulosic biomass, organic industrial waste and municipal waste can be used as feedstock for the gasification process, while industrial off-gases can be used as a substrate for the gas fermentation process [7]. Furthermore, another renewable source of syngas is the electrochemical conversion of carbon dioxide (CO_2) and water (H_2O) [14]. However, there are several requirements for scaling-up syngas fermentation processes to a commercial scale. When it comes to the syngas conversion part of the biofuel production process, it is necessary to provide a high gas-to-liquid mass transfer rate, effective regulation of this rate is needed and proper foam control [15]. Additionally, a considerable drawback of the syngas fermentation process is the relatively low product concentration [13]. Therefore, improved separation and purification techniques are needed to recover fermentation products in a cost- and energy-efficient way.

Nowadays, gas fermentation for the production of bioethanol is scaled-up to industrial operation. The company LanzaTech opened the first commercial plant in China in 2018 [16], while expanding the manufacturing to other plants later on. This plant is using steel mill off-gases as a carbon source, while producing ethanol as the main product [17]. Exact data on the commercial process is not openly accessible, but the reactor for syngas fermentation process is a gas-lift reactor with an external loop [15,18]. The syngas fermentation broth is removed continuously from the bioreactor and sent to the ethanol purification section which is a distillation-based system. Other by-products are present only in traces and are not recovered. Formation of waste can be minimized by sending part of spent biomass to the anaerobic digestion or using it to make a fresh nutrient mixture that is continuously being fed to the bioreactor [19]. Many different methodologies and reactor types have been proposed for converting syngas to valuable biochemicals [20], but, to the best of our knowledge, the purification of syngas fermentation products is not that well studied. Since the downstream processing costs for bulk fermentation products, such as bioethanol, can add up to 20–40% of total production cost [21], optimization of this step can significantly improve the economic viability of the biofuel production process.

For this reason, this original research study focuses on enhancing the downstream processing of syngas fermentation products. The original contribution of this research is an eco-efficient process design for the effective bioethanol recovery from the syngas fermentation broth. The proposed novel downstream process consists of several distillation steps, whereby the first separation is performed under reduced pressure. Operating under vacuum and avoiding usage of additional chemicals ensures that the microorganisms remain unhurt and can be recycled back to the fermenter, together with most of the water and acetic acid. Advanced heat pumping and heat integration techniques are used to improve the process performance in terms of economic and environmental impacts. Therefore, the proposed enhanced downstream process recovers high-purity ethanol product while preventing loss of biomass and increasing the fermentation yield by enabling closed loop process operation. Additionally, the influence of the bioethanol concentration in the fermentation broth on the key performance indicators of the proposed recovery process is analyzed.

2. Methods

2.1. Process design and simulation

The commercial syngas fermentation processes are continuous, whereby fermentation broth is constantly removed from the bioreactor. In addition to ethanol, which is the main product of the fermentation process, the removed broth also contains different coproducts of microorganisms' metabolism, as well as some living microorganisms [19]. For the current study, the composition of this fermentation broth stream, which is the feed stream for the bioethanol recovery process, is taken from the literature [22] and presented in Table 1. The stream's flowrate is calculated based on the assumption that bioethanol production capacity of an industrial facility is about 150 ML/y (approximately 117 ktonne/y) [23].

The main requirements for the downstream process are high ethanol

Table 1
Condition and composition of the feed stream [22].

Parameter [unit]	Value
Temperature [°C]	37
Pressure [bar]	1
Mass flow [ktonne/y]	1905.3
Water mass fraction [-]	0.9215
Ethanol mass fraction [-]	0.0614
Acetic acid mass fraction [-]	0.0006
2,3-Butanediol mass fraction [-]	0.0085
Microorganisms mass fraction [-]	0.0081

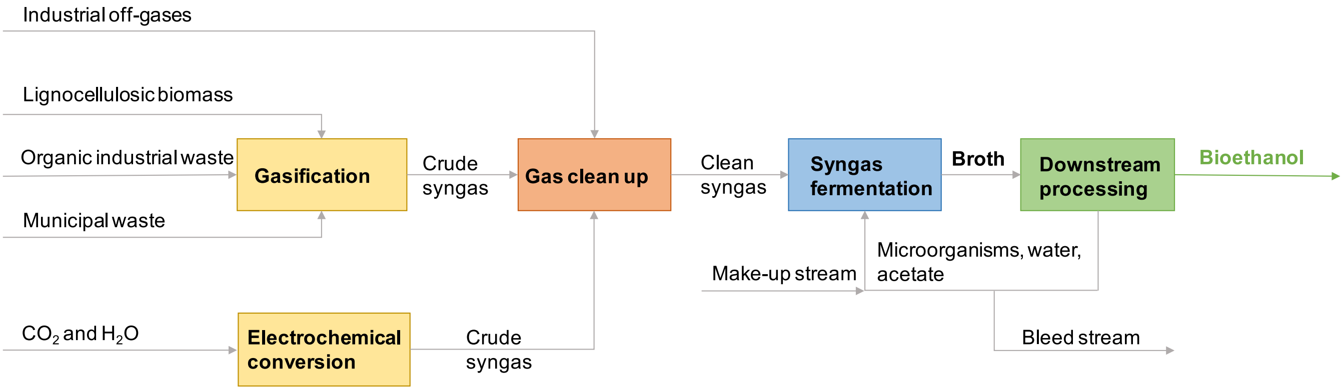

Fig. 1. Process scheme of the bioethanol production by syngas fermentation.

recovery in a form of high-purity product, operating conditions that enable viability of present microorganisms and possibility to reduce upstream fermentation cost by recycling microorganisms, water and acetate. The major challenges in designing an optimal ethanol recovery process are the presence of living microorganisms in broth removed from the bioreactor, very low ethanol concentration, and constrains due to the ethanol – water azeotrope formation [24].

In order to avoid loss of living biomass, separated microorganisms from the fermentation product stream should be recycled back to the bioreactor. This requires an initial separation step that does not use any additional chemicals that might harm living microorganisms, that is performed at temperatures that are not lethal for the microorganisms, and that has residence time short enough for microorganisms to survive during shortage of nutrients. Therefore, vacuum distillation is selected, in which the microorganisms will directly flow to the aqueous bottom stream. For glucose to alcohol fermentation with yeast, it has been shown that stable pilot-scale operation is possible if fermentation broth is sent through a packed distillation column [25]. For purifying the top stream of the vacuum distillation column, additional distillations steps are designed. Performing these distillations under vacuum could offer a slight advantage, as the separation process becomes easier due to increased difference in relative volatility. However, implementing reduced pressure to all the following steps would require larger equipment and higher capital costs (CAPEX), resulting in no actual benefits compared to operating at ambient pressure. Therefore, the distillation steps following the first vacuum separation are performed under atmospheric pressure.

Rigorous simulations for every part of the proposed ethanol recovery process were performed in Aspen Plus. Thermodynamic properties are determined using the NRTL property method together with the Hayden O'Connell model for vapor phase association, due to the presence of acetic acid in the initial mixture [26]. The boiling points of the involved components and azeotropes are summarized in Table 2. Ethanol, which is the main product from syngas fermentation, has the lowest boiling point. Therefore, it could be separated as the top product in the distillation. However, due to the formation of the azeotrope, some water is separated together with ethanol. The other components have higher boiling points. Consequently, acetic acid and 2,3-butanediol, together with most of the water and present microorganisms are obtained at the bottom of a column. Note that acetic acid will actually only to a small extent be in the form of the volatile undissociated species at the fermentation pH, and largely be present as non-volatile sodium acetate salt. In the distillation calculations both species are modelled as undissociated acetic acid, hence it is a worst-case analysis. Since other products of microorganisms' metabolism are present in extremely low concentrations, commercial syngas fermentation processes focus solely on bioethanol recovery [19]. The aqueous solution containing small amounts of coproducts can be recycled to the bioreactor together with the microorganisms. This allows the bioethanol production process to be run in a closed loop and is expected to improve the overall efficiency [4]. Apart from avoiding the loss of biomass, returning this stream to the fermenter will result in higher ethanol yield. Namely, recycling of acetic acid will increase the concentration of extracellular acetate in the fermentation broth to a level that enhances ethanol production [27,28].

The separated ethanol solution has to be further treated in order to obtain a final bioethanol purity that satisfies the required standards: 99.8 vol% in EU, 99.0 vol% in US and 99.6 vol% in Brazil [29]. Due to the azeotrope formation (Table 2), water – ethanol separation is complex and requires several steps. Firstly, the diluted mixture has to be preconcentrated. Although many different separation techniques have been proposed for this step [30,31], distillation remains the most commonly used for industrial application [32]. The maximal ethanol purity that can be obtained in the distillate from the preconcentration step is nearly azeotropic concentration. However, as ethanol concentration gets closer to the azeotropic one, the energy requirement for the preconcentration steps rises. Nevertheless, the energy requirement for further ethanol dehydration decreases as the feed stream to this part of process becomes richer in ethanol. The optimal ethanol concentration after the preconcentration step, in terms of energy requirements and total purification cost was reported to be 91 wt% [33]. Therefore, the preconcentration step in this work is designed to obtain distillate with 91 wt% ethanol.

Table 2
Boiling points of all components and azeotropes (at 1 bar).

Pure components		Azeotropes		
Component	Tb [°C]	Component	Mass fraction	T [°C]/type
Ethanol	78.31	Ethanol	0.9557	78.15/homogeneous
Water	100.00	Water	0.0443	
Acetic Acid	118.01			
2,3-butanediol	180.51			

Secondly, in order to obtain high-purity product, a dehydration step is needed. The most suitable techniques for large scale ethanol dehydration are extractive distillation, azeotropic distillation and usage of molecular sieves [32]. Since the flowrates considered for this process design are very large and the average experimental water adsorption capacity of zeolites is in range 0.011–0.387 $g_{water}/g_{zeolite}$ [34], a rather large amount of zeolites is needed for ethanol dehydration (e.g. for a plant capacity of 150 ML/y ethanol, the 91 wt% ethanol stream includes 1437.1 kg_{water}/h for which 1045.6–29.7 $tonne_{zeolite}$ is needed for 8 h operation). Azeotropic distillation is more energy intensive than extractive distillation, because the light solvent used has to be completely evaporated. Moreover, solvent flowrate is also larger in azeotropic distillation [35]. Therefore, extractive distillation is commonly considered as the best solution for the industrial scale bioethanol purification [29]. This separation technique implies addition of a high-boiling solvent to the ethanol – water mixture. Ethylene glycol is a frequently used solvent for large-scale application [32]. In contrast to solvents used in azeotropic distillation, this solvent does not form an azeotrope with any present component. Instead, it changes the relative volatility of the present components [36]. The ternary system ethanol – water – ethylene glycol forms a single azeotrope without any liquid phase splitting areas [24]. In addition to lower energy requirement and smaller needed solvent flowrate, extractive distillation is more flexible regarding process sequence and requires a less complex control system compared to azeotropic distillation [37]. Furthermore, results of a comparative study of these three purification methods (molecular sieves, azeotropic distillation and extractive distillation) show that extractive distillation is the optimal method in terms of both investment and operating costs [38]. Therefore, extractive distillation with ethylene glycol is chosen as the optimal technique for the ethanol dehydration step.

2.2. Economic evaluation

In order to properly evaluate the eco-efficiency of designed process, a complete economic analysis, including both total capital (CAPEX) and operating (OPEX) cost, is performed following the published NREL methodology [39]. The total CAPEX is calculated taking into account direct capital costs, related to the equipment purchase and installation costs, as well as other indirect capital costs. Cost estimation correlations are used to calculate the installation cost for process equipment [40]. Marshall and Swift cost index value from the end of 2018 (1,638.2) is used in the equipment cost calculation [41]. In addition to the process equipment installation cost, in calculation of CAPEX the following factors are taken into account: home office and construction, field expenses, prorateable expenses, project contingency, working capital, site development, additional piping, warehouse and solvent initial cost [39]. The total OPEX is determined considering both variable and fixed operating costs. The variable operating costs include costs for utilities and make-up solvent, while fixed operating costs imply costs for labor, maintenance and property insurance [39]. The cost for all used utilities is calculated following the recommendations from the published literature [40]. Even though utilities costs depend on the site location, the following costs are taken for approximate calculation: 16.8 $/GJ for electricity, 7.78 $/GJ for low-pressure steam, 8.22 $/GJ for medium-pressure steam, 9.88 $/GJ for high-pressure steam, 4.43 $/GJ for chilled water and 0.35 $/GJ for cooling water [40]. The total annual cost (TAC) is calculated using a payback period of 10 years (as well as 5 years as an alternative economic scenario). In addition to the estimation of the total annual cost, the minimum added price for bioethanol downstream processing is calculated using the NREL methodology [39].

2.3. Sustainability assessment

The growing concerns on environmental pollution undoubtedly emphasize the need for more sustainable development. Several key sustainability metrics were calculated to evaluate the environmental performance of proposed bioethanol recovery process: energy intensity, water consumption, material intensity, toxic emissions and pollutant emissions complemented with greenhouse gas emissions [42]. Better process performance, in terms of environmental impact, results in lower values of these sustainability metrics.

- ***Energy intensity*** is a measure of heat and electrical energy needed for the process. It is expressed per kilogram of product [42]. The primary energy requirement takes into account both the thermal and the electrical energy usage, whereby inefficiencies in power generation are considered through the thermal-electrical conversion. The thermal-electrical conversion factor quantifies the amount of heat needed to produce a unit of electrical output, and is typically expressed as the ratio of heat input to electrical output. This factor accounts for the overall energy efficiency of the electricity generation, including all losses in the conversion process and distribution systems. A conservative value of 2.5 is used for the calculation of the primary energy requirement [43]. Based on pertinent industry data from BP [44], the estimated efficiency factor for converting non-fossil electricity to primary energy is about 40%, with a positive trend of improvement. Thus, about 2.5 units of primary energy are required to produce 1 unit of electricity, so the used value for the thermal-electrical conversion is a realistic one.
- ***Water consumption*** is expressed as the amount of fresh water used per unit output [45].
- ***Material intensity*** presents the amount of formed waste per kilogram of product [42].
- ***Greenhouse gas emission*** is expressed as the amount of carbon dioxide (CO_2) emitted per kilogram of product [45]. This sustainability metric is calculated based on the recommendations from literature [41,46]. The source of the used electricity can potentially have a significant impact on GHG emissions. To accurately assess these emissions, a clear differentiation is made between electricity obtained from fossil fuels (grey electricity) and electricity obtained from renewable sources (green electricity).
- ***Pollutants and toxic materials*** present amount of emitted pollutants and toxic materials per kilogram of product [42].

3. Results and discussion

This section describes the results related to the process design for the preconcentration, dehydration, and the overall downstream processing section. Additionally, a techno-economic analysis is performed and the key sustainability metrics are provided.

3.1. Design of the preconcentration section

This part of the process focuses on obtaining a 91 wt% ethanol stream [33] from the syngas fermentation product stream. Different process configurations for this part of downstream process are considered. The graphic representation of these configurations is given in Fig. 2. The base case scenario consists of a sequence of two distillation columns (C1 and C2). The first step in the recovery process is to separate ethanol from microorganisms, acetic acid and 2,3-butanediol. Since ethanol is the lightest of all present components, it will be separated in the distillate from C1 distillation column. Due to the azeotrope formation (Table 2), some water will also be separated with ethanol, resulting in a stream that has about 58 wt% ethanol. An aqueous solution (>98 wt % water) containing small amounts of acetic acid, 2,3-butanediol and present microorganisms is obtained as the bottom product. In order to improve efficiency of the overall bioethanol production process [4], this

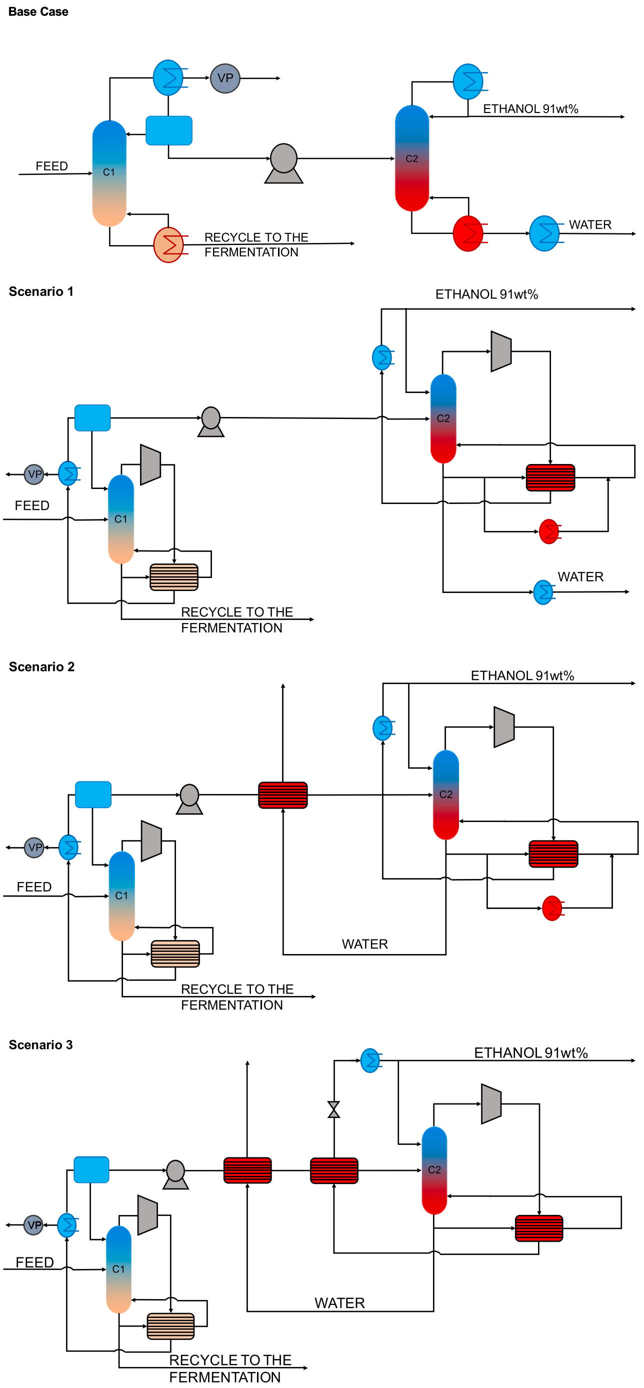

Fig. 2. Process configurations for the bioethanol preconcentration part of the process.

stream should be recycled to the bioreactor. The first distillation step is performed under reduced pressure to avoid operating at high temperatures that can harm the microorganisms. The conditions in column C1 can be designed to ensure the viability of the present microorganisms [47]. The operating pressure, pressure drop and internals are designed in such a way that the temperature of the bottom product does not exceed the temperature in the bioreactor [48]. Since this column operates under reduced pressure, structured packing type Sulzer Mellapak 250 is assumed for its internals [49]. The condenser pressure is set to 0.055 bar which, with a pressure drop of 0.225 mbar per theoretical stage, results in 0.064 bar pressure at the bottom of column. Relatable market data [50] are used when determining capital and energy costs for the vacuum pump that provides required pressures in column C1. With defined operating conditions, the temperature in the column varies from around 37 °C at the bottom to about 21 °C at the top. Therefore, chilled water can be used as a cooling utility in the condenser of column C1. Since there is no need for using expensive refrigeration utilities, the implementation of more complex separation techniques, such as pass-through distillation [51], can be avoided. Considering that the low-pressure distillate from column C1 is liquid, simple pumping is used to increase its pressure. This ethanol–water mixture is further preconcentrated by atmospheric distillation in column C2 to obtain 91 wt% ethanol in the distillate stream. Sieve trays internals are used for this column, with assumed pressure drop of 8 mbar per tray [52]. The bottom product from this column is a pure water stream that can be sent back to the fermentation. Additional cooling of this stream is necessary to keep operating conditions in the bioreactor optimal for the present microorganisms.

However, the heat content of the top vapor from column C2 is not sufficient to completely replace the external heating required for this column. It can provide about 89% heat needed to evaporate the bottom liquid. Therefore, two reboilers are used for column C2. Compressed top vapor is used instead of a heating medium in first reboiler, while external heating is used for the second reboiler. Even though there is still need for external heating, implementation of MVR to columns C1 and C2 drastically reduces energy requirement for the preconcentration part of the process.

The design parameters for distillation columns C1 and C2 are presented in Table 3. Due to the large flowrate of the feed stream, heating duties for columns C1 and C2 are very high. Therefore, improved heat integration methods (e.g. Pinch Analysis) must be considered to decrease energy requirements and several different scenarios are analyzed. Since temperatures in column C2 are much higher than in column C1, a first attempt of heat integration was to heat column C2 by using the product streams from column C1. Due to the significantly lower flowrates, heat content of these streams is not nearly enough to replace the external heating needed for column C1. Nonetheless, these columns are separating relatively close-boiling components (ethanol and water). Since the temperature difference between the top and bottom products from these columns is not large, heat pumps can be used to decrease the total energy requirements. By implementing mechanical vapor recompression (MVR), the vapor coming from the top of the distillation column is compressed and used to evaporate the liquid coming from the bottom of the column [53]. Scenario 1 implies implementation of MVR to both columns C1 and C2.

This process configuration (scenario 1) is further enhanced in order to obtain additional energy savings. Since the temperature of the distillate from the column C1 is at 21 °C, the feed stream for column C2 is subcooled liquid. Therefore, preheating this stream will decrease heating duty for column C2, and consequently the need for external heating. As the water stream from the bottom of the column C2 needs to be cooled in order to be recycled to the fermenter, it can be used to preheat the feed stream for this column. Scenario 2 implies implementation of MVR to both columns C1 and C2, with the described additional heat integration. Even though this heat exchange decreases reboiler duty for column C2, the compressed top vapor can provide about 95% of the required heat, and external heating is still needed. Since the bottom water stream from column C2 cannot heat up the feed stream to this column to the boiling state, additional heat integration is considered.

The top compressed stream from column C2 has to be additionally cooled after heat exchange in the MVR system. Consequently, the heat content of this stream can also be used to increase the temperature of the feed stream for column C2. Scenario 3 further improves scenario 2, by using both the bottom water product and the top stream from column C2 to heat the feed stream to this column to the boiling state. As a result of this heat integration, the reboiler duty for column C2 is decreased and heat of compressed top vapor can completely replace external heating. Consequently, only one reboiler is needed for column C2. Even though the equipment installation cost for this scenario is almost doubled as compared to the process configuration without using MVR and heat integration (base case), utility cost and total energy requirements are reduced by 87.9% and 77.9%, respectively. Since the process configuration in scenario 3 provides the highest energy and utility savings, it is selected for the preconcentration part of the process. The comparison of energy requirements, equipment and utility costs for all scenarios is summarized in Table 4.

3.2. *Design of the ethanol dehydration section*

The preconcentrated ethanol solution is further dehydrated by extractive distillation with ethylene glycol as solvent. For this ethanol dehydration part of process, an extractive distillation column C3 and a solvent recovery column C4 are needed. These columns are designed with sieve trays internals, which have a pressure drop of 8 mbar per tray [52]. The solvent-to-feed mass ratio for column C3 was varied to find the value with the lowest energy requirement for this part of the process (columns C3 and C4). A solvent-to-feed ratio of 1.2 was determined (see Fig. 3) and taken as the optimal value for process design. The design parameters of columns C3 and C4 are presented in Table 3. The top stream from column C3 is 99.8 wt% ethanol product. The bottom product, containing ethylene glycol and water, is sent to the solvent recovery column C4. Since water has a significantly lower boiling point than ethylene glycol, it is separated as high purity (>99.9 wt%) top product. To decrease the need for fresh water, this stream can also be cooled and recycled to the bioreactor. The bottom product from C4 is the

Table 3
Design parameters of the distillation columns.

Distillation column	C1	C2	C3	C4
Number of stages	40	30	32	16
Feed stage	20	15	4 (ethylene glycol)24 (91 wt% ethanol)	8
Top/bottom pressure [bar]	0.055/0.064	1/1.232	1/1.248	1/1.120
Top/bottom temperature [°C]	21/37	78/106	78/154	100/199
Reboiler duty [MW]	20.3	11.4	5.9	1.9
Condenser duty [MW]	−20.5	−11.2	−4.4	−1.2
Reflux ratio, mass	0.88	1.57	0.27	0.34
Column diameter [m]	4.2	2.4	1.5	1.0

Table 4
Comparison of various scenarios for the pre-concentration process.

	Primary energy requirements		Equipment cost		Utilities cost	
	Value* ($kW_{th}h/kg_{EtOH}$)	Difference (%)	Value (k$)	Difference (%)	Value (k$/y)	Difference (%)
Base case	2.09		4,490		13,752	
Scenario 1	0.55	−73.5	9,438	110.2	2,151	−84.4
Scenario 2	0.50	−76.0	9,533	112.3	1,873	−86.4
Scenario 3	**0.46**	**−77.9**	**9,569**	**113.1**	**1,667**	**−87.9**

* The value is per kg of 91 wt% ethanol.

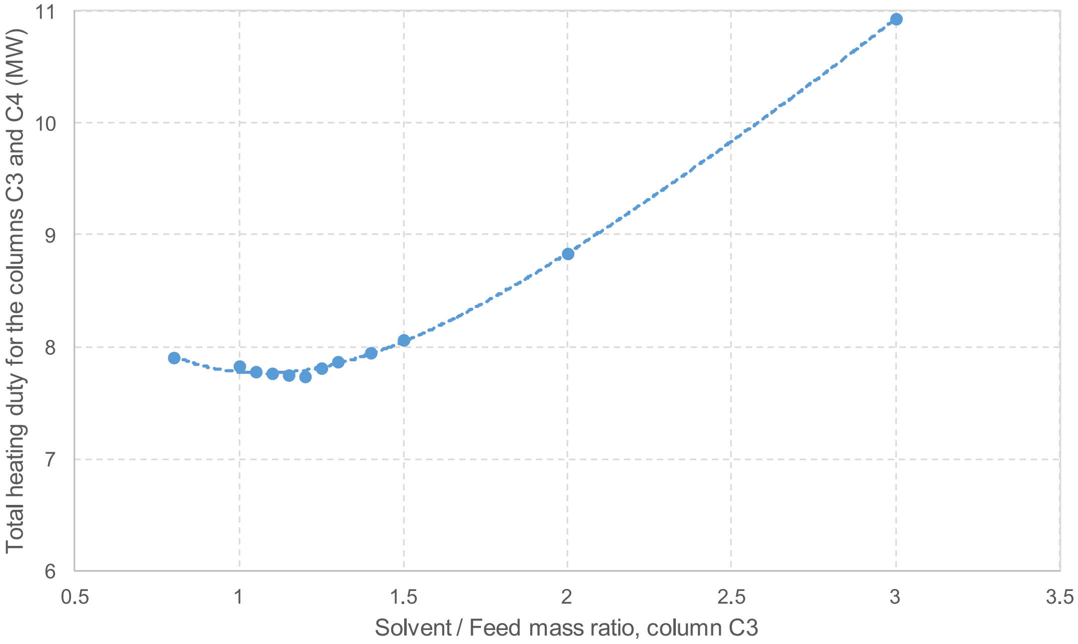

Fig. 3. Influence of the solvent-to-feed ratio in column C3 on the total duty for columns C3 and C4, in the base case design of the bioethanol dehydration by extractive distillation.

recovered solvent (>99.9 wt%) that is reused in the extractive distillation column C3.

The reboiler temperature for the column C3 is around 154 °C and medium-pressure steam can be used for heating. However, due to the high boiling point of ethylene glycol, the reboiler temperature for column C4 is approximately 199 °C. Therefore, more expensive high-pressure steam has to be used to heat this column. Since the recovered solvent from column C4 has to be cooled before being recycled to column C3 [33], it can be used to evaporate part of the liquid from column C3. Although the heat content of the recovered solvent is not sufficient to completely replace the need for external heating for column C3, this integration results in about 20.2% energy savings for heating this column.

Dividing-wall column (DWC) technology has been proposed as an alternative to the sequence of two distillation columns for bioethanol purification process [35,40,54]. Also in the present study a split shell column with a divided overhead section and a common bottoms section was simulated for this part of the recovery process. This type of DWC has two condensers and only one reboiler. High-purity ethanol and water are recovered as top products, while ethylene glycol is obtained at the bottom. Since DWC has only one reboiler, and the temperature in the reboiler is very high due to the presence of ethylene glycol, high-pressure steam has to be used as a heating utility for this column. In order to decrease high-pressure steam usage, a side reboiler is added to the DWC configuration. Ethylene glycol product stream is used instead of heating utility for this reboiler. Addition of a side reboiler decreases the need for high-pressure steam and lowers the total energy requirement below the amount needed for ethanol dehydration with a sequence of two distillation columns.

However, the sequence of two distillation columns with previously described inter-column heat integration still results in the lowest utility cost for the whole ethanol recovery process. This is mainly due to the high cost of high-pressure steam that is needed to heat the DWC. Additionally, applying heat integration to the sequence of two distillation columns reduces the energy requirements below those needed for DWC. The comparison of energy requirements and utility cost for the

Table 5
Comparison of energy requirements for the ethanol dehydration part of the process.

	Two distillation columns with heat integration	DWC with side reboiler
Heating duty covered with heat integration/side reboiler – ethanol dehydration part of process (MW_{th})	1.18	1.24
Need for medium-pressure steam – ethanol dehydration part of process (MW_{th})	4.68	n/a
Need for high-pressure steam – ethanol dehydration part of process (MW_{th})	1.87	6.71
Thermal energy requirements for full downstream process ($kW_{th}h/kg_{EtOH}$)	0.45	0.46
Electrical energy requirements for full downstream process ($kW_{e}h/kg_{EtOH}$)	0.20	0.20
Primary energy requirements for full downstream process ($kW_{th}h/kg_{EtOH}$)	0.96	0.97
Total utility cost for full downstream process (k$/y)	4,054	4,441

Table 6
Conditions and compositions of the main output streams.

Stream	Ethanol product stream (column C3)	Recycle to the fermenter (column C1)	Water (column C2)	Water (column C4)
Temperature [°C]	30.0	37.2	22.2	37.0
Pressure [bar]	1	0.064	1.2	1
Mass flow [ktonne/y]	116.4	1706.5	71.2	11.2
Water mass fraction	0.0016	0.9804	1	0.9996
Ethanol mass fraction	0.9980	0.0005	0	0.0004
Acetic acid mass fraction	0	0.0007	0	0
2,3-Butanediol mass fraction	0	0.0094	0	0
Microorganisms mass fraction	0	0.0090	0	0
Ethylene glycol mass fraction	0.0004	0	0	0

sequence of two distillation columns with heat integration and DWC with side reboiler is given in Table 5. The sequence of two distillation columns with heat integration provides the optimal process configuration in terms of total energy requirements and utility cost. Consequently, this process configuration is chosen for the design of the bioethanol recovery process.

3.3. Design of the full bioethanol recovery process

The compositions and conditions of the main output streams of bioethanol recovery process are presented in Table 6. Summarizing, the proposed distillation sequence recovers high-purity bioethanol product (99.8 wt%) from the syngas fermentation broth, with a recovery of 99.5%. The bottom product from the first distillation column, the aqueous solution with small amounts of acetic acid, 2,3-butanediol and microorganisms, can be recycled to the bioreactor. Additionally, two high-purity water streams can also be cooled and recycled to the fermentation step. Recycling these streams to the bioreactor prevents loss of biomass, decreases the need for fresh water and even improves ethanol yields in the bioreactor, resulting in more efficient overall process. Lastly, after the extractive distillation step, the used solvent is recovered and recycled. Therefore, since non-product streams can be recycled and reused, the formation of waste streams is avoided.

The process configuration for the whole bioethanol recovery process extends the base case for the preconcentration part, and consists of conventional distillation separations performed in columns C1, C2, C3 and C4. Therefore, the base process does not include any additional heat pumping or heat integration. The process flowsheet of this configuration is presented in Fig. 4. The enhanced process design, presented in Fig. 5, is obtained by implying several energy saving techniques to the base process. Firstly, the closeness of temperatures at the top and the bottom of columns C1 and C2 offers possibility to apply MVR to these columns. Secondly, additional heat integration is implemented in order to further decrease energy requirements. The top vapor stream and the bottom product from column C2 are used to heat up the feed stream to this column to the boiling state. This heat integration significantly reduces need for external heating for the whole process.

The coefficient of performance (COP) for the MVR system is equal to the ratio between the heat that is transferred from the heat source (top compressed vapor) to the heat sink (reboiler) and the required compressor duty. In the proposed optimal process design, COP for MVR applied to columns C1 and C2 equal 12.2 and 9.0 respectively. Since the very conservative value of electrical to thermal conversion factor of 2.5 [43,55] is still significantly lower than the COP values obtained for the designed MVR systems, it can be concluded that the proposed heat pumping and heat integration drastically improve the energy efficiency of the recovery process. Finally, the recovered solvent from the bottom of column C4 is used to partially heat column C3. This decreases the need for external heating for the column C3 by about 20.2%. All implemented enhancements result in significant reduction in total process costs and energy savings, which is analyzed in more detail in the following sections.

The proposed downstream process is designed for recovery of fuel-grade bioethanol from the syngas fermentation broth of specific composition (Table 1). However, due to specificity of operating conditions in the fermenter and microorganisms used to convert sugars into bioethanol, the composition of the fermentation broth might vary. Apart from the considered trace components, other impurities that can be detected mainly consisting of aldehydes, esters, alcohols and carboxylic acids [56]. This study focuses on production of fuel-grade ethanol, for which there are no strict upper limits for present impurities as long as minimal ethanol purity is obtained and the total acidity is below a

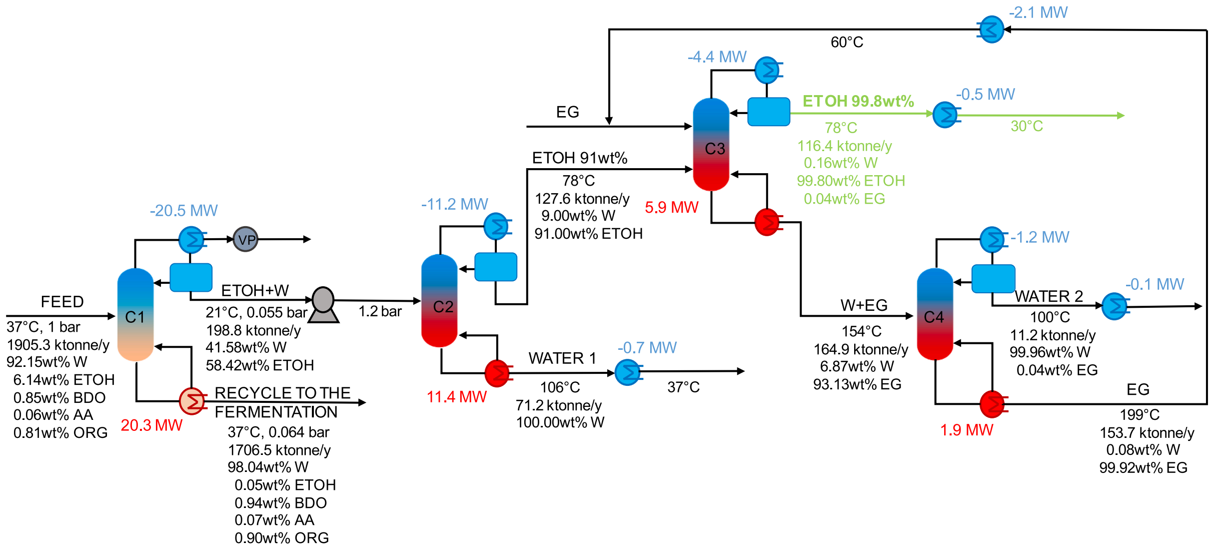

Fig. 4. Base case bioethanol recovery process flowsheet (W - water, ETOH - ethanol, BDO – 2,3-butanediol, AA - acetic acid, EG - ethylene glycol, ORG - microorganisms).

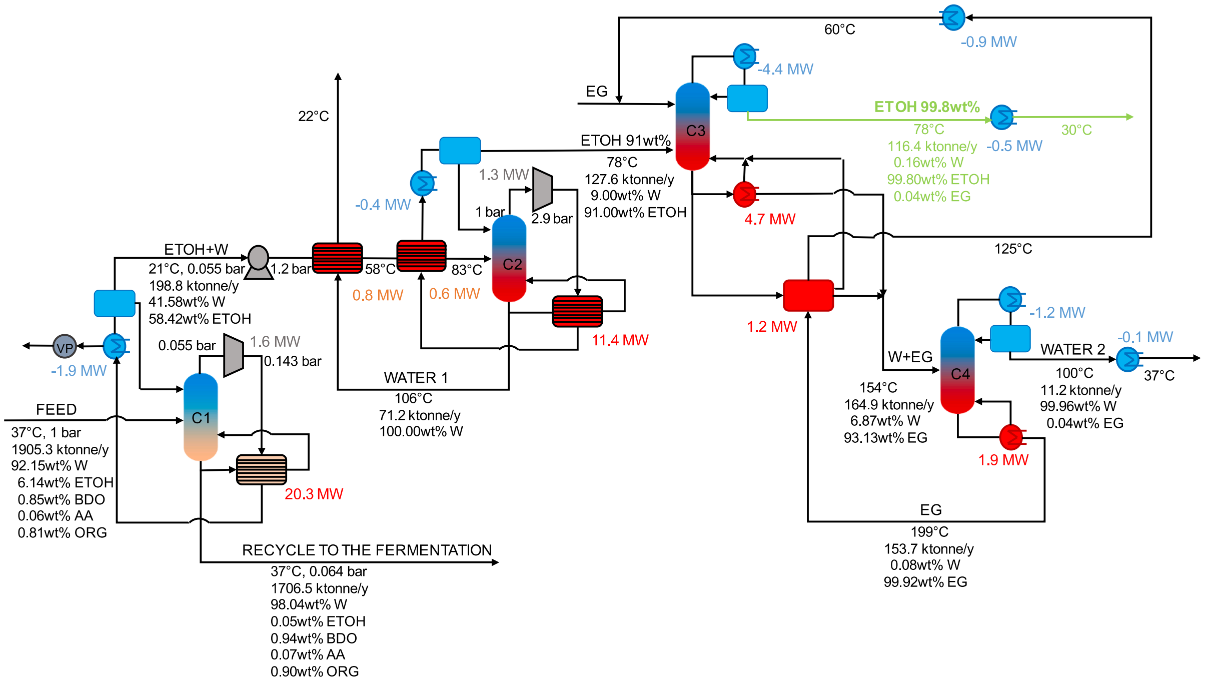

Fig. 5. Enhanced bioethanol recovery process flowsheet (W - water, EtOH - ethanol, BDO – 2,3-butanediol, AA - acetic acid, EG - ethylene glycol, ORG - microorganisms).

certain level [56]. However, the proposed recovery process can potentially be modified to produce also food- or solvent-grade ethanol for which purity specifications are more strict [57]. Therefore, the removal of present impurities might be required [56]. Additionally, acetaldehyde present in bioethanol can oxidize to acetic acid during storage period, which increases the fuel acidity and reduces its quality [58]. As a result, several modifications have been considered for the removal of various impurities in bioethanol production. An additional degassing column can be added to remove all the light components present, including acetaldehyde and ethyl acetate [58,59]. Alternatively, extractive distillation can be used to remove acetaldehyde and ethyl acetate, while removing methanol separately in demethylizer unit [60]. Apart from adding additional separation units, C1 column can be converted into a hybrid column that obtains bioethanol solution as a side-product, while separating heavier components at the bottom and volatile components on the top [61]. Furthermore, process intensification techniques, such as cyclic distillation are proven to be efficient in removing impurities in the industrial scale food-grade ethanol [62]. For smaller scale bioethanol purification, the heat integrated horizontal separation unit was developed to concentrate bioethanol solution, remove present volatile components and replace the first distillation column [63]. Besides from light and heavy impurities, medium-volatile impurities (such as 1-butanol, 2-methyl-1-propanol, 2-methyl-1-butanol, 3-methyl-1-butanol and benzaldehyde) can accumulate in a nearly azeotropic water–ethanol mixture. These components can be removed as side streams from the rectification column [56]. Summing up, depending on the specific syngas fermentation broth composition and bioethanol purity requirements, the proposed recovery process is sufficiently flexible to be modified as needed, in order to obtain a final product that satisfies the market demands.

3.4. Economic analysis

Several economic aspects for the base case and the enhanced process design are compared in Table 7. The total cost of process equipment

Table 7
Key performance indicators in terms of economics and sustainability.

	Base process	Enhanced process	Difference (%)
Economic indicators			
CAPEX (k$)	10,067	19,619	94.9
OPEX (k$/y)	19,402	7,384	−61.9
OPEX ($/$kg_{EtOH}$)	0.167	0.063	
TAC (k$/y)*	20,409/21,416	9,345/11,307	−54.2/−47.2
TAC ($/$kg_{EtOH}$)*	0.175/0.184	0.080/0.097	
Added selling price ($/$kg_{EtOH}$)*	0.179/0.188	0.086/0.102	−51.9/−45.8
Sustainability metrics			
Thermal energy requirements ($kW_{th}h/kg_{EtOH}$)	2.82	0.45	−84.0
Electrical energy requirements ($kW_{e}h/kg_{EtOH}$)	0	0.20	n/a
Primary energy requirements ($kW_{th}h/kg_{EtOH}$)	2.82	0.96	−66.1
Fresh water requiremets (m^3_W/kg_{EtOH})	0.242	0.091	−62.6
Fresh water loss (m^3_W/kg_{EtOH})	0.019	0.007	−64.7
CO_2 emissions (kg_{CO2}/kg_{EtOH})**	0.415/0.414	0.164/0.072	−60.4/−82.6
Material intensity (kg_{waste}/kg_{EtOH})	0	0	0
Pollutant emissions ($kg_{pollutant}/kg_{EtOH}$)	0	0	0
Toxic emissions ($kg_{toxic\ material}/kg_{EtOH}$)	0	0	0

[*] 10 years payback period/5 years payback period.
[**] Grey/green electricity.

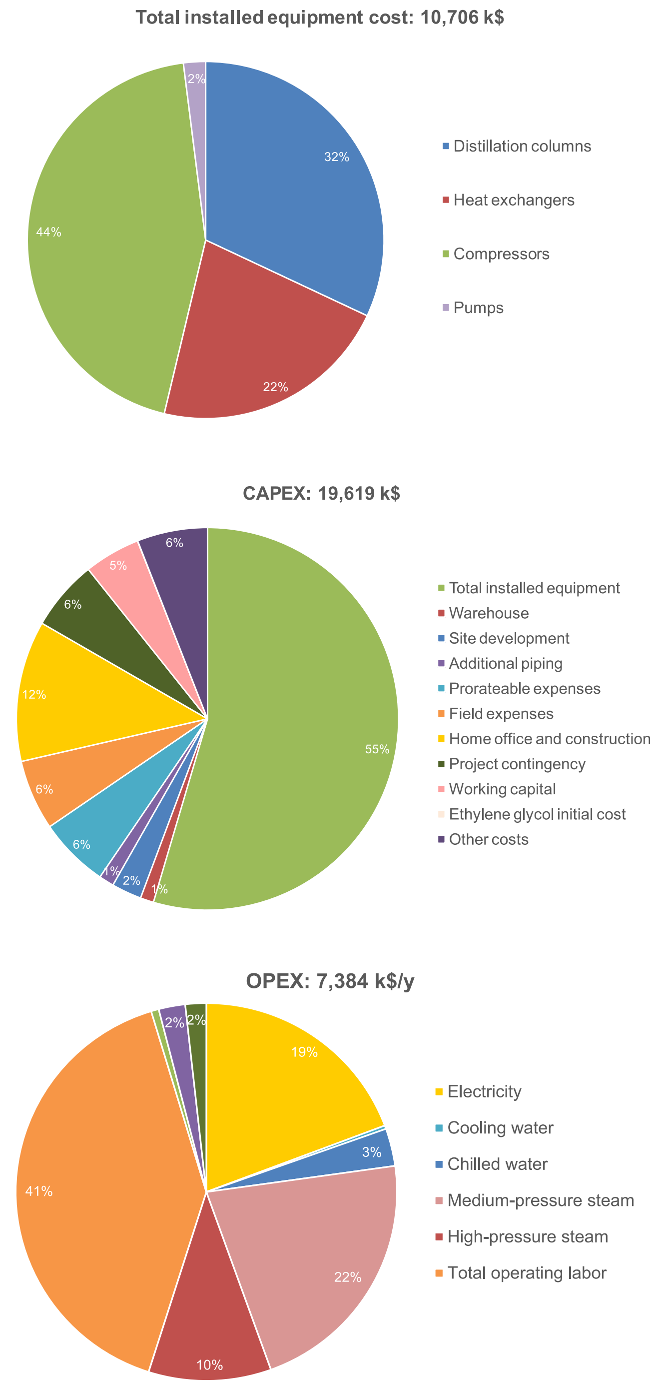

Fig. 6. Total installed equipment cost, CAPEX and OPEX for the enhanced process.

installation for the base case is about 5,570 k$, whereby the largest part is cost for the distillation columns (about 61.5%).

After the implementation of MVR and additional heat integration, the total process equipment installation cost increases by 92.2% and equals 10,706 k$. This significant increase is mainly due to the usage of compressors in the MVR systems, but also due to additional heat exchangers for the heat integration sequences. The cost distribution on different types of equipment for the enhanced case is presented in Fig. 6. The highest part of equipment installation cost (about 44.3%) is the installation cost of compressors for the MVR systems. The costs of the distillation columns and heat exchangers are 32.0% and 21.8% of the total equipment installation cost, respectively.

The total CAPEX for the base case process is about 10,067 k$, while for the enhanced process is 19,619 k$. This significant increase (about 94.9%) is mostly due to the more expensive process equipment which stands for as much as 54.6% of the total CAPEX for the enhanced process. The cost distribution between the different parts of the CAPEX for the enhanced process design is presented in Fig. 6.

The total OPEX for the base case process is about 19,402 k$/y, mostly due to the utilities cost (about 83.6% of the total OPEX) and labor cost (about 15.4% of the total OPEX). The highest contribution in utility cost is the cost for low-pressure steam (about 10,769 k$/y or 66.4% of total utility cost), chilled water needed in the condenser of column C1 (about 2,619 k$/y or 16.1% of total utility cost) and medium-pressure steam (about 2,007 k$/y or 12.4% of total utility cost). The total OPEX for the enhanced case process is about 7,384 k$/y. Therefore, the implementation of MVR and additional heat integration results in about 61.9% decrease of the OPEX (from 0.167 to 0.063 $/kg$_{\mathrm{EtOH}}$). Even though the use of compressors in the MVR systems increases electricity cost to about 1,423 k$/y, the cost for chilled water and medium-pressure steam are decreased to 238 and 1,603 k$/y, respectively, while the usage of low-pressure steam is completely avoided. The contribution of different parts of OPEX for the enhanced process is presented in Fig. 6. The reduced need for chilled water and medium-pressure steam, as well as the avoided need for low-pressure steam, decreases the total utility cost to about 54.9% of the total OPEX. Consequently, the contribution of the total labor cost is increased to about 40.4% of the total OPEX (in relative terms), without a significant change in its absolute value. The costs for maintenance, property insurance and ethylene glycol make-up are significantly lower, together about 4.7% of the total OPEX. Among utilities, the cost distribution is: 35.1% electricity cost, 39.5% medium-pressure steam cost, 19.0% high-pressure steam cost, 5.9% chilled water cost, and the remaining 0.5% is cooling water cost.

The enhanced process reduces TAC by about 54.2% (from 20,409 to 9,345 k$/y) with a typical payback period of 10 years, and by about 47.2%, (from 21,416 to 11,307 k$/y) when considering a shorter payback period of 5 years. Even though applying MVR and additional heat integration increases CAPEX, the significant reduction of the OPEX leads to a less expensive process overall. Expressed in relative terms (per kg of recovered bioethanol), the TAC for the base case and the enhanced process are 0.175 and 0.080 $/kg$_{\mathrm{EtOH}}$, respectively (for 10 year payback period), and 0.184 and 0.097 $/kg$_{\mathrm{EtOH}}$ (for 5 years payback period).

The minimum added price for the ethanol downstream processing in the base case scenario with payback periods of 10 and 5 years is 0.179 and 0.188 $/kg$_{\mathrm{EtOH}}$, respectively. When the enhanced process is used for downstream processing, these values are reduced by 51.9% and 45.8% to competitive values of only 0.086 and 0.102 $/kg$_{\mathrm{EtOH}}$, respectively.

3.5. Sustainability metrics

The main sustainability metrics for the designed enhanced process are summarized in Table 7.

- ***Energy intensity:*** The thermal energy requirement that takes into account the usage of low-, medium- and high-pressure steam for the base case process is 2.82 kW$_{\mathrm{th}}$h/kg$_{\mathrm{EtOH}}$. The implementation of MVR and heat integration significantly reduces need for heating utilities and results in 84.0% reduction in the thermal energy requirement, with final value of 0.45 kW$_{\mathrm{th}}$h/kg$_{\mathrm{EtOH}}$. Nonetheless, the electrical energy requirement for the base case process is negligible, while for the enhanced process it is equal to 0.20 kW$_{\mathrm{e}}$h/kg$_{\mathrm{EtOH}}$. This is due to the use of compressors for the MVR systems. The total energy requirement for the base case and the enhanced case is 2.82 and 0.96 kW$_{\mathrm{th}}$h/kg$_{\mathrm{EtOH}}$ respectively. Thus, the enhanced process design can provides 66.1% energy savings.
- ***Water consumption:*** The total need for cooling water is 0.240 m$^3_{\mathrm{W}}$/kg$_{\mathrm{EtOH}}$ for the base case and 0.090 m$^3_{\mathrm{W}}$/kg$_{\mathrm{EtOH}}$ for the enhanced process. The decrease of 62.4% in the required cooling water is

mostly due to the implementation of MVR heat pump systems. Commonly, it is estimated that about 7% of cooling water is lost [42]. Therefore, the loss of cooling water expressed per unit of recovered bioethanol is 0.017 and 0.006 m_W^3/kg_{EtOH} for the base case and the enhanced process, respectively. Additionally, a steam condensate recovery of 70% is assumed to account for potential steam leaks, condensate losses, steam trap failures, and other possible inefficiencies in the steam generation and usage process [64]. Taking this into account, the total water usage is reduced by 62.6%, from 0.242 m_W^3/kg_{EtOH} for the base case to 0.091 m_W^3/kg_{EtOH} for the enhanced process. The total specific loss of water is also decreased by about 64.7%, from 0.019 m_W^3/kg_{EtOH} for the base case to 0.007 m_W^3/kg_{EtOH} for the enhanced process.

- ***Material intensity:*** Besides high-purity ethanol product, output streams from both the base and the enhanced process are (Table 6): the aqueous solution containing living microorganisms and products of their metabolism other than ethanol and the two high-purity water streams. In order to prevent loss of biomass and decrease need for fresh water in the fermenter, these streams can be recycled to the syngas fermentation step. Since all output streams are either product streams or can be reused (e.g. recycled to the fermentation), there is no formation of additional waste. Therefore, the material intensity is zero.
- ***Greenhouse gas emission:*** The total CO_2 emission for the base case process is 0.415 kg_{CO2}/kg_{EtOH} (for grey electricity usage) and 0.414 kg_{CO2}/kg_{EtOH} (for green electricity usage). This minor difference is due to the low influence of electricity in this process configuration. The enhanced process (with MVR and heat integration) reduces the total CO_2 emission by 60.4% and 82.6% if grey or green electricity is used, respectively. More precisely, the enhanced process emits 0.164 kg_{CO2}/kg_{EtOH} (grey electricity case) and 0.072 kg_{CO2}/kg_{EtOH} (green electricity case). Due to the implementation of the MVR systems, the electricity cost becomes significant (about 19.3% of OPEX). The source of electricity substantially influences the total GHG emissions of the proposed bioethanol recovery process design.
- ***Pollutants and toxic materials:*** Both the base case and the enhanced case processes do not emit pollutants (other than CO_2) and toxic materials. Consequently, the sustainability metrics characterizing these indicators are equal to zero.

3.6. *Sensitivity analysis: Effect of the feed concentration*

Even though the nominal design considered 6 wt% ethanol in syngas fermentation broth, the ethanol concentration in industrial fermentation broth may be somewhat different for various plants. To determine the impact of the ethanol concentration in the feed stream (the broth stream continuously removed from the fermenter), this mass fraction is decreased while keeping the total feed flowrate constant. The concentrations of microbes and acetic acid are also kept constant. In reality, modest changes might occur in the concentration of these nonvolatile components, but such changes would have no significant on the performance of the proposed recovery process, as these are recovered as bottom stream of the first separations unit (vacuum distillation). Moreover, to determine if the proposed process can efficiently treat also more diluted feed streams, the size of process equipment is not varied in this analysis.

The changes of key performance indicators for different ethanol fractions in the fermentation broth are listed in Table 8 and illustrated in Fig. 7. Large differences are found if the ethanol concentration in the fermentation broth decreases from 6 to 1 wt%: The total annual cost per kg of recovered bioethanol exponentially increases from 0.080 to 0.336 $/$kg_{EtOH}$. Since the equipment installation cost (the highest part of CAPEX) does not change, the increase in TAC is mostly due to the increase in OPEX. Similarly, the total OPEX per kilogram of recovered bioethanol increases from 0.063 to 0.233 $/$kg_{EtOH}$ and the added price for bioethanol downstream processing follows the same increasing trend. This value rises from 0.086 to 0.371 $/$kg_{EtOH}$.

In addition to the economic analysis, the calculation of the process sustainability metrics is also performed. If the ethanol concentration in fermentation broth decreases from 6 to 1 wt%, changes of the thermal energy requirement per unit product are negligible. However, the electrical energy requirement significantly increases, from 0.20 to 0.53 kW_eh/kg_{EtOH}. This is due to a higher compression duty in the MVR systems. With decreasing initial ethanol concentration, a smaller fraction of the feed stream needs to be evaporated in columns C1 and C2. Thus, the top steam flowrate used to evaporate the bottom liquid in MVR heat pump system becomes smaller and a higher pressure ratio is needed in order to provide sufficient heat exchange. Consequently, the total primary energy requirement per unit of recovered bioethanol increases from 0.96 to 1.78 $kW_{th}h/kg_{EtOH}$. Still, this is much less than the value of 8.9 MJ/kg_{EtOH} (2.5 $kW_{th}h/kg_{EtOH}$) that has been reported by others for similar recovery of fuel grade ethanol from a 1 wt% ethanol feed stream [65].

Lastly, the CO_2 emission is significantly affected by the initial concentration of ethanol if grey electricity is used for power supply. This is due to the high impact of electricity used to power compressors in the MVR systems. If the ethanol concentration in fermentation broth decreases from 6 to 1 wt%, the total CO_2 emission per kilogram of recovered bioethanol with usage of grey electricity increases from 0.164 to 0.315 kg_{CO2}/kg_{EtOH}. On the contrary, the total CO_2 emission per kilogram of recovered bioethanol with usage of green electricity hardly changes, since changes in the thermal energy requirement are negligible.

Summing up, higher ethanol concentration in the fermentation broth results in a more profitable and a more sustainable downstream process. Considering the trends in Fig. 7, increasing ethanol concentration beyond 6 wt% would marginally improve overall performance of downstream process. However, lower ethanol concentrations (about

Table 8
Changes in key performance indicators for various feed compositions.

Ethanol mass fraction in the fermentation broth	0.06	0.05	0.04	0.03	0.02	0.01
Economic indicators						
OPEX ($/$kg_{EtOH}$)	0.063	0.071	0.083	0.100	0.134	0.233
TAC ($/$kg_{EtOH}$)	0.080	0.092	0.109	0.134	0.186	0.336
Added selling price ($/$kg_{EtOH}$)	0.086	0.099	0.118	0.146	0.204	0.371
Sustainability metrics						
Thermal energy requirements ($kW_{th}h/kg_{EtOH}$)	0.45	0.45	0.45	0.45	0.45	0.45
Electrical energy requirements (kW_eh/kg_{EtOH})	0.20	0.22	0.26	0.30	0.37	0.53
Primary energy requirements ($kW_{th}h/kg_{EtOH}$)	0.96	1.01	1.11	1.19	1.37	1.78
Fresh water requirements (m_W^3/kg_{EtOH})	0.09	0.09	0.09	0.09	0.09	0.09
Fresh water loss (m_W^3/kg_{EtOH})	0.007	0.007	0.007	0.007	0.007	0.007
CO_2 emissions (kg_{CO2}/kg_{EtOH})*	0.164 /0.072	0.174 /0.072	0.192 /0.072	0.207 /0.072	0.241 /0.072	0.315 /0.072

* Grey/green electricity.

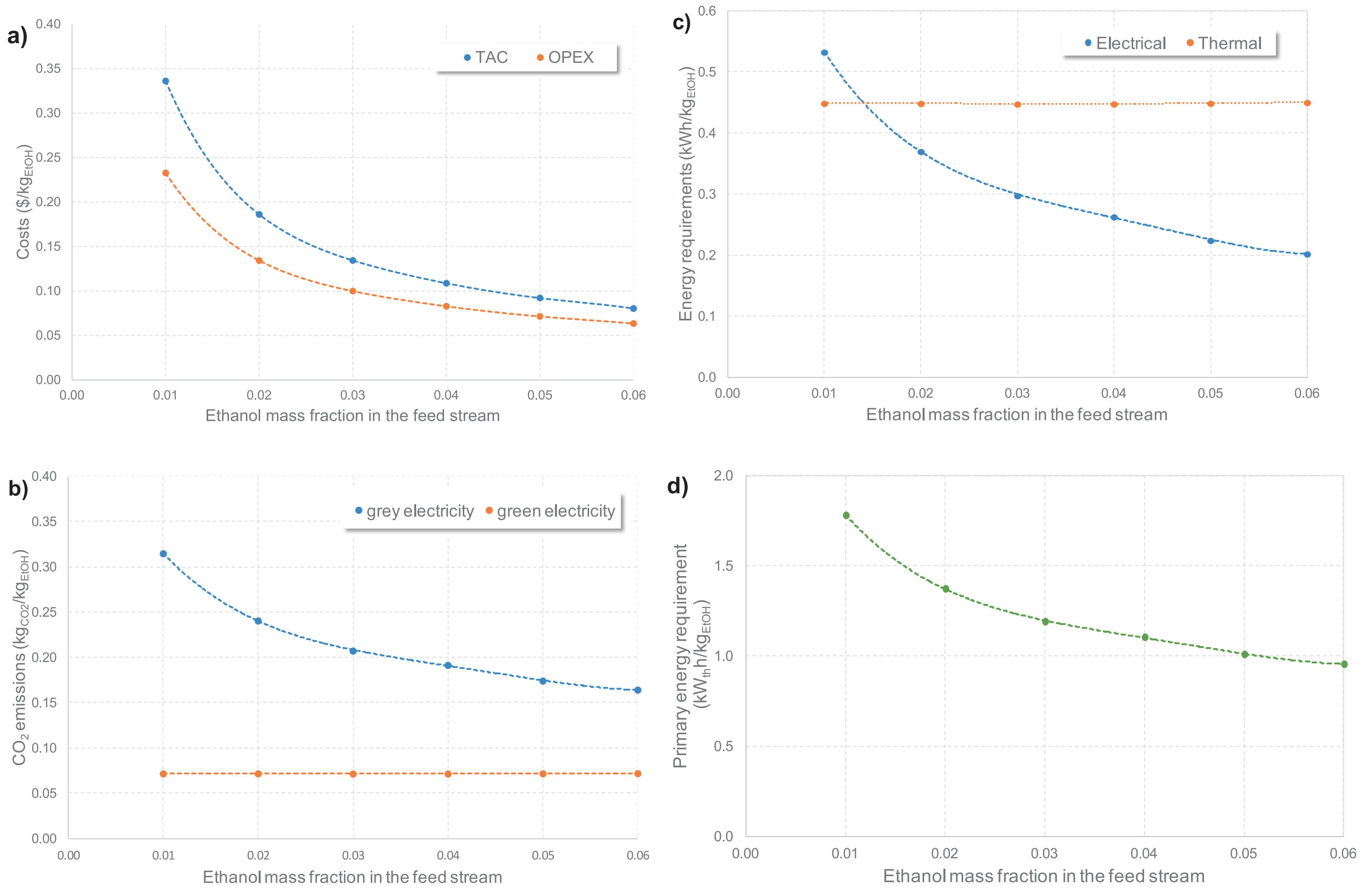

Fig. 7. Influence of the ethanol concentration in the feed stream (fermentation broth) on various parameters of the enhanced process: a) TAC and OPEX, b) CO_2 emissions, c) thermal and electrical energy requirements, d) primary energy requirement. The benchmark value of the ethanol mass fraction in the feed stream was 0.06.

2–3 wt%) during the fermentation do not lead to excessive downstream cost, and should remain in scope due to the effect of ethanol concentration on the upstream process. The bioethanol concentration obtained in the syngas fermentation broth determines energy requirements for the downstream processing, which further affects total production cost [66]. This concentration is limited by inhibitory effects that high ethanol concentration has on present microorganisms (reduced growth rate and CO consumption rate) [67]. Additionally, mass transfer limitations are common limiting factor for scaling-up of syngas fermentation processes. These can be overcame to certain extent by performing fermentation in a gas-lift reactor with an external loop [15,17]. Furthermore, a recent study proposed large-scale fermentation at higher biomass concentration to increase product yield [68]. However, there is undoubtedly an upper limit of ethanol concentration in the fermentation broth, which is highly dependent on the specific fermentation operating conditions and used microorganisms. Anyhow, it can be concluded that the cost of the upstream fermentation process will rise with increasing the ethanol concentration. On the contrary, lower ethanol concentration in the fermentation broth will result in a less profitable and sustainable downstream process. Moreover, the potential presence of other impurities, apart from considered ones, can have a significant effect on the downstream processing. Consequently, certain adjustments to the proposed recovery process might be needed before implementation in the specific case. The trade-off concentration of ethanol in the fermentation broth for the overall process including both upstream and downstream process parts is out-of-scope of this work, and still to be determined in future work that would perform a global optimization of the full process. However, the results from this research provide a valuable contribution to this goal and can be used in combination with relevant data from the upstream fermentation process.

Since it has been shown that use of vacuum in the first distillation leads to acceptable costs, there is an incentive to experimentally explore the feasibility of this vacuum distillation including the recycle of the bottom stream to fermentation. This is out of scope of the present work, but column fouling and foaming might be challenging. Nonetheless, previous reports showed that stable pilot-scale operation is possible when fermentation broth is sent through a packed distillation column, and that microorganisms can survive the vacuum conditions [25]. The used microorganisms are strictly anaerobic, such that oxygen needs to be excluded from the distillation column (which is common practice anyway). Due to the absence of fermentation conditions in the distillation column, the microbes' residence time in the column (typically a few minutes) has to be shorter than the time they can survive without syngas uptake. On the other hand, the risk of infection by other microorganisms seems negligible at these operation conditions. When recycling of the vacuum distillation bottom stream to fermentation is tested, the fraction to be purged and the growth rate required during fermentation will depend on the fraction of microorganisms that survive the distillation. A model-based optimization of the overall process will be useful not only to determine the optimal ethanol concentration during fermentation but also to determine the optimal operation conditions of the fermentation within the overall process.

4. Conclusions

The result of this research study is a highly advanced downstream process design for recovery of bioethanol in a large-scale syngas fermentation process (plant productivity of about 117 ktonne/y bioethanol), while avoiding negative effects on the living biomass present. Improved purification techniques were implemented to efficiently recover 99.5% of the ethanol from the very dilute fermentation broth (>92 wt% water) as high-purity product (99.8 wt% ethanol). Operating conditions for the first separation unit were designed to allow recycling the aqueous solution containing microorganisms and other products of their metabolism to the fermentation step. This prevents loss of biomass, allows the fermentation step to be performed in a closed loop, and should improve ethanol productivity. Moreover, the need for fresh water in the bioreactor was decreased by recycling two high-purity water streams.

By implementing MVR heat pumping systems and additional heat integration, the CAPEX increased by 94.9%, but OPEX decreased by 61.9% and TAC decreased by 54.2%, while the primary energy requirement reduced by 66.1%, CO_2 emission decreased by 60.4% or even 82.6% (for grey or green electricity), and fresh water requirement reduced by 62.6%. Thus, advanced energy saving techniques significantly improved the economic viability and sustainability of the proposed bioethanol recovery process.

Analysis of the influence of the ethanol concentration in the fermentation broth undoubtedly shows that higher ethanol concentration leads to a better performance of the downstream process. On the contrary, fermentation performance would decrease with increasing ethanol concentration due to the inhibitory effect on microorganisms. In that context, the proposed downstream process performance remains competitive even at lower feed concentrations of 2-3 wt% ethanol (which would allow better fermentation performance). While the exact trade-off concentration for the full process of bioethanol production by syngas fermentation is yet to be determined, the results of this research provide a valuable contribution to that goal and should to be coupled with relevant data from the upstream fermentation process.

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.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2023.124320.

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