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A perspective on downstream processing performance for recovery of bioalcohols

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Abstract

Even though industrial biotechnology is successfully used for the production of some chemicals, for many other chemicals it is not yet competitive with conventional petrochemical production. Usually, fermentation as well as downstream processing requires improvement. Downstream processing has to deal with low product concentrations, microorganisms, impurities and thermodynamic constraints (e.g., azeotropes), which often makes it very challenging and expensive, especially on a large scale. However, downstream processing of biochemicals has not attracted as much attention as upstream fermentation processes. In that context, this perspective paper offers a lightly referenced scholarly opinion about the downstream processing performance of different bioalcohols after fermentation. Due to the stronger toxicity effects on microbes, the achievable concentrations of monohydric aliphatic alcohols in the fermentation broth decrease with the increasing chain length. Specifically, the concentrations used here are 6.14, 5.00, 1.61 and 0.24 wt% of ethanol, isopropanol, isobutanol and hexanol, respectively. More dilute fermentation broths lead to more complex recovery processes. According to our previous work, the total purification costs increase from 0.080 USD kg^{-1} for ethanol, 0.109 USD kg^{-1} for isopropanol and 0.161 USD kg^{-1} for isobutanol to 0.529 USD kg^{-1} for hexanol. A similar trend is noticeable for the energy usage (0.960, 1.348, 2.018 and 3.069 kW$_{th}$h kg^{-1}, respectively) and the related CO_2 emissions (0.164, 0.221, 0.449 and 0.555 kg$_{CO2}$ kg^{-1}, respectively). This work shows that advanced separation and purification based on process intensification principles are crucial for overall efficient production processes. The achievable product concentration in the fermentation broth – and not so much the alcohol chain length – has the biggest influence on the performance of downstream processing. Therefore, simultaneous development of both upstream and downstream processing is necessary to ensure the competitiveness and viability of industrial fermentation processes.

Supporting information may be found in the online version of this article.

Keywords: bioalcohols; fermentation; downstream processing; industrial biotechnology; sustainability

INTRODUCTION

Rapidly growing energy needs have resulted in extensive consumption and reduction of fossil carbon sources. Consequently, concerns about energy security, environmental pollution and climate change drive the necessary transition from the petrochemical industry to more sustainable production processes.[1] In that respect, biochemicals and biofuels potentially present renewable alternatives for conventional fossil carbon-based chemicals.[2] Significant research efforts have been put into developing methods for the production of numerous platform chemicals from renewable sources. The advantages of these technologies over traditional petrochemical production processes are potentially lower environmental impact due to mild operating conditions and the use of renewable sources.[3] Depending on the nature of the microorganisms used, different substrates can be used in the fermentation. For example, energy-dense lignocellulosic biomass can be converted to bioethanol instead of being wasted. The second-generation biofuel production method by lignocellulosic fermentation can strengthen energy security without competing with food production.[4] Besides ethanol, higher alcohols (e.g., isobutanol, butanol, hexanol) can also be obtained by fermentation from carbohydrate-based substrates.[5] An alternative option is to use syngas as a substrate for microorganisms. Due to the relatively high tolerance of microorganisms, different sources of gas (e.g., gasified biomass, industrial off-gases) can be used. Producing valuable biochemicals by syngas fermentation avoids difficulties related to the biomass pretreatment (a necessary step in lignocellulosic fermentation), increases the amount of carbon that is converted to products and may significantly reduce carbon dioxide emissions if industrial off-gases are used.[6] Nonetheless, both lignocellulosic and syngas fermentation have great potential for the production of bioalcohols on an industrial scale. LanzaTech opened the first commercial plant for ethanol production by syngas fermentation in China in 2018, subsequently expanding manufacturing to other plants.[7] The same

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company has recently tested isopropanol and acetone production by syngas fermentation on a pilot plant scale but this technology has not reached an industrial scale yet.[8,9] Furthermore, isobutanol was first commercially produced by the company Gevo, followed by a joint venture of BP and DuPoint (Butamax).[10,11] To the best of our knowledge, industrial production of longer-chain alcohols has not been established yet.

As discussed in more detail below, the end-product toxicity of bioalcohols to microbes limits the achievable product concentrations in the broth and remains the main challenge for the production of bioalcohols by fermentation.[12] Consequently, advanced purification processes are needed to separate valuable products from the highly dilute fermentation broth. Furthermore, a large processing throughput is required for an industrially relevant production capacity.[12] Accordingly, the costs related to the downstream processing can considerably contribute to the total production costs (20–40%).[13] For example, the purification costs of ethanol and butanol were estimated to be about 21–29%[14-17] (recovery by azeotropic distillation,[14] distillation coupled with molecular sieves,[15,16] pressure-swing distillation[17]) and 40%[18] (recovery by distillation) of the total production costs. Therefore, significant improvements in downstream processing are needed to increase the competitiveness and viability of industrial fermentation technologies.[19] So far, substantial research effort has been put into genetic engineering to obtain more resistant microorganisms and increase fermentation titer.[3] Yet, the recovery of fermentation products has not attracted nearly as much attention. An efficient purification process may lead to a more sustainable bioprocess by reducing total production costs, energy requirements, CO_2 emissions and water requirements. Considering the significant impact of the downstream process on the overall competitiveness of industrial fermentation, this perspective paper focuses on the effects of different bioalcohols on downstream processing performance. The results of this study offer a valuable indication of the cost associated with the purification process that must not be overlooked when developing an industrial fermentation process.[20]

MAJOR CHALLENGES FOR RECOVERY OF BIOALCOHOLS FROM FERMENTATION

The relatively low achievable concentration of bioalcohol in the broth is one of the main challenges in downstream processing. The end-product toxicity phenomenon refers to the inhibitory effects bioalcohols have on microbial growth, substrate consumption or product formation.[12] The critical concentration of bioalcohols for product formation is strongly related to the hydrophilicity of the product. Typically, a larger amount of more hydrophobic products can accumulate in the cell membrane.[21] In general, this activity leads to the disruption of membrane integrity and fluidity, which can result in inhibition of carbon-substrate uptake, nutrient transport, membrane potential dependent ATP production and energy generation, intracellular acidification, leakage from protoplasm, etc. More hydrophobic alcohols (e.g., butanol) can cause greater disruption of the lipid bilayers of cell membranes and more inhibition compared to less hydrophobic alcohols (e.g., ethanol) at the same concentrations.[22] Thus, longer-chain alcohols are more toxic to microorganisms compared to shorter-chain alcohols due to stronger inhibition effects.[21] Accordingly, concentrations of ethanol in the fermentation broth that microorganisms can tolerate (5–6 wt%[23] from syngas fermentation or 5–12 wt % from glucose fermentation)[24] are higher than non-harmful concentrations of isopropanol (4–5 wt% from syngas fermentation),[25] isobutanol (~1.6 wt% from glucose fermentation)[26] and 1-hexanol (~0.2 wt% from glucose fermentation).[27] Besides the nature of the fermentation product, pH, substrate type, microbe type, temperature, aeration, nutrients and additives also influence the extent of inhibition.[21] The concurrent alcohol fermentation and recovery (CARAF) may mitigate the end-product inhibition problem by allowing continuous product removal during fermentation.[12]

Due to the low achievable product concentrations, large bioreactors are needed to ensure industrial production capacity. Consequently, large throughputs have to be processed after the fermentation which is closely associated with high capital and operating costs. Water dominates the composition of the stream that is sent to downstream processing. Removing all the water in a cost-effective and energy-efficient way is very challenging.[12]

Furthermore, the microorganisms in the fermentation broth need to be removed from the product in an initial purification step. These microorganisms, with most of the separated water, may be returned to the fermentation to avoid loss of biomass, increase product-to-substrate yield and reduce water requirements.[28] Therefore, an interesting strategy is to separate valuable fermentation products from most of the broth without harming microbial viability. To achieve this, the use of high temperatures and the addition of chemicals that might be toxic to microbes must be avoided in the initial separation steps. Consequently, for removing bioalcohols from the fermentation broth, we advocate the use of an initial separation step performed under reduced pressure at temperatures that do not harm the used microbes.

Moreover, the boiling points of alcohols commonly produced by fermentation (ethanol, isopropanol, isobutanol, butanol, etc.) and water are relatively close (see Table 1). All these alcohols form azeotropes with water (see Table 1), which complicates their purification. Thus, advanced fluid separation techniques are required to break the formed azeotropes and allow the recovery of high-purity products.

Considering all the mentioned challenges, eco-efficient downstream processes are needed to make industrial fermentation economically viable and more competitive compared to conventional petrochemical-based production processes.

DOWNSTREAM PROCESSING APPROACH

Due to the highly complex feed stream (broth taken from the fermenter), several steps are required in the downstream processing.[29] A generic block flow diagram for the purification of alcohols from the dilute fermentation broth is presented in Fig. 1 and discussed hereafter. Ethanol, isopropanol, isobutanol and 1-hexanol (further referred to as hexanol) were chosen as typical C2, C3, C4 and C6 alcohols that can be obtained by fermentation. Given that differences regarding toxicity to microorganisms, achievable fermentation titers, physical and thermodynamic properties, market price, etc., are much larger among alcohols with different number of carbon atoms than among different isomers of alcohols with the same number of carbon atoms, similar trends in downstream processing performance may be expected if different isomers were chosen. Furthermore, the fermentative production of methanol and C5 alcohols has not attracted that much attention and was therefore not analyzed in this study.[5] Similarly, there have been only a few studies on the production of C8 alcohols by microbial fermentation.[30] Due to the very low achievable titers (maximum about 0.1 g L^{-1} of 1-octanol),[31]

Table 1. Boiling points (T_b) of pure components and azeotrope formation at 1 bar

Pure components		Azeotrope		
Component	T_b (°C)	Component	Mass fraction	T (°C)
Ethanol	78.3	Ethanol	0.9562	78.2
Isopropanol	82.1	Water	0.0438	
Water	100.0	Isopropanol	0.8717	80.1
Isobutanol	107.7	Water	0.1283	
1-Butanol	117.8	Isobutanol	0.6527	90.3
Hexanol	156.8	Water	0.3473	
		1-Butanol	0.5798	92.5
		Water	0.4202	
		Hexanol	0.3185	97.8
		Water	0.6815	

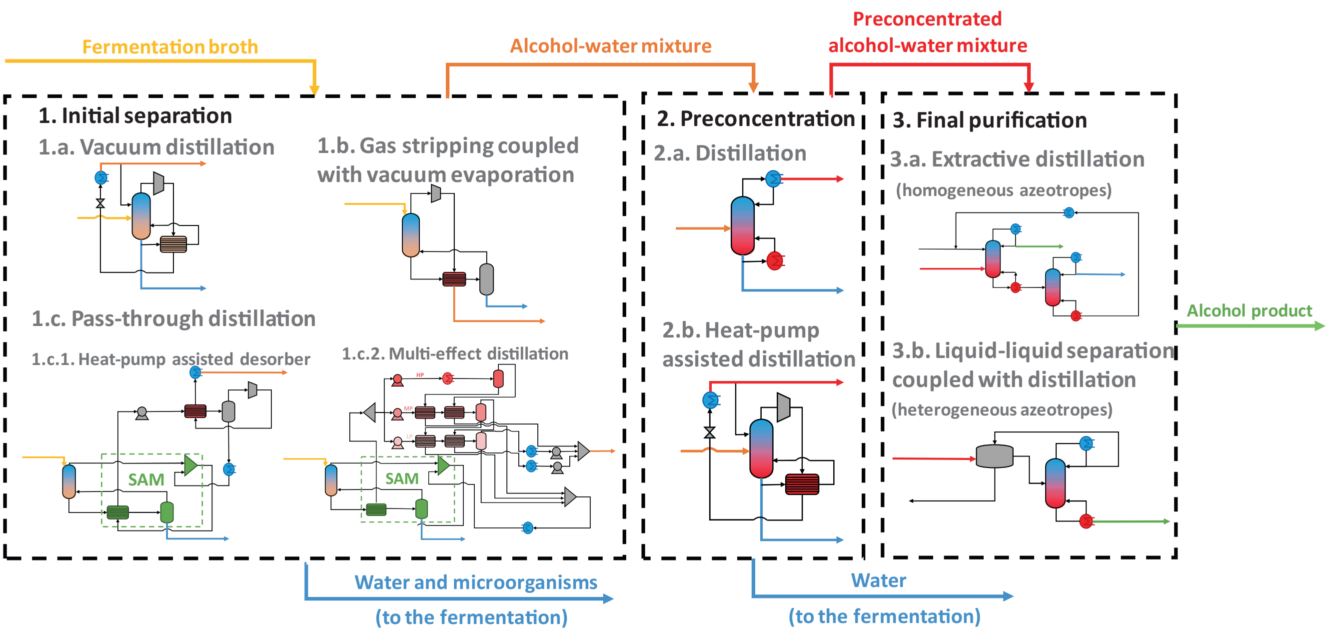

Figure 1. Generic flowsheets of downstream processing of alcohols from dilute fermentation broth. The final purification can be performed by extractive distillation (to deal with the formation of homogeneous alcohol–water azeotropes) or by liquid–liquid separation and distillation (to break the heterogeneous alcohol–water azeotropes).

additional research is needed to make the 1-octanol fermentation competitive to those of shorter-chain alcohols.[32]

The first step in the recovery process is the removal of the dissolved CO_2 by simple flashing under reduced pressure. In the case that some amount of bioalcohol is taken up by the CO_2-rich vapor, the alcohol can be absorbed by water and returned to the recovery process. Furthermore, the formation of minimum boiling azeotropes (see Table 1) allows the separation of volatile products from most of the broth. This can be performed in several ways. In-situ vacuum distillation,[33] heat pump-assisted vacuum distillation[34] or a novel hybrid combination of gas stripping and heat pump-assisted vacuum evaporation[35,36] can be implemented if operating under reduced pressure does not result in the need for expensive refrigeration. Alternatively, pass-through distillation can be employed to avoid high operating costs related to condensation at extremely low temperatures. This state-of-the-art separation method allows evaporation and condensation to be performed under different pressures (and temperatures) by separating them with an absorption–desorption loop with electrolyte absorption fluid.[12,37] Enhancing this technology with a vapor recompression heat pump system or multi-effect distillation results in highly competitive recovery processes.[38] Nonetheless, all these techniques (e.g. heat pump-assisted vacuum distillation, gas stripping coupled with heat pump-assisted vacuum evaporation and pass-through distillation enhanced with vapor recompression or multi-effect distillation) allow the separation of bioalcohols under conditions that are appropriate for the microorganisms. Then, most of the fermentation broth with microorganisms might be recycled to enhance the fermentation process.

Even though large amounts of water are commonly removed after this initial separation step, further downstream processing is required to obtain high-purity final bioproducts. A preconcentration step is often needed before the final purification (see Fig. 1) to minimize energy requirements. The exact method or the final step in the downstream processing strongly depends on the nature of the azeotrope bioalcohol product forms with water. For example, extractive distillation with ethylene glycol is the optimal technique for large-scale ethanol purification, both in terms of investment and operating costs.[39,40] This method has also been suggested for isopropanol recovery from an aqueous stream.[41] Contrarily, isobutanol, 1-butanol and hexanol form heterogeneous azeotropes with water, and simple liquid–liquid phase separation can be used. Moreover, different methods of process intensification should be considered. For instance, distillation using a highly integrated azeotropic dividing-wall column has been proven to efficiently purify ABE (acetone–butanol–ethanol)[42] and IBE (isopropanol–butanol–ethanol)[36] fermentation products. As a key step in the recovery process, a pinch analysis should be performed to ensure maximal recovery of energy within the process. Due to the high water concentrations and close-boiling components, heat pump systems often have to be implemented to maximize energy savings.[43] In addition to minimizing external energy requirements, the implementation of heat pumps is an important step toward the electrification of industrial biotechnology. For example, advanced heat pump systems have been proven to enable complete electrification of the downstream process after IBE fermentation, allowing operation powered by only green electricity.[36]

To ensure a fair comparison, a complete economic analysis of the downstream processes for the purification of various alcohols was performed following the known NREL procedure.[44] Total annual costs (TAC) include both capital (CAPEX) and operating (OPEX) expenses with a payback period of 1 year. The total capital expenditures (CAPEX) cover the equipment purchase and installation costs, home office and construction, field expenses, proratable expenses, project contingency, working capital, site development, additional piping and warehouse. The total operating expenses (OPEX) include the cost of utilities, operating labor, maintenance and property insurance. Also, the environmental performance of the recovery process was analyzed by comparing several sustainability metrics: energy requirements, CO_2 emissions, water consumption, material intensity, pollutants and toxic emissions.[45]

EFFECTS OF FERMENTATION PRODUCTS ON DOWNSTREAM PROCESSING

Even though all alcohols commonly produced by fermentation and considered here (e.g., ethanol, isopropanol, isobutanol, hexanol) behave somewhat similarly in aqueous systems (e.g., all form minimum boiling azeotropes with water), the performance of the overall bioalcohol production process strongly depends on the type of the alcohol that is produced. Lower concentrations are achievable in fermenters for longer alcohols; thus larger bioreactors are required to obtain a relevant production capacity. Consequently, the capital and operating costs of the upstream fermentation part will increase. However, market demands for these alcohols are different, which strongly affects the magnitude of the required production capacity. The global ethanol market was estimated to be about 102 Mt in 2022, with a growth rate of 4.80% until 2032.[46] Being significantly smaller compared to ethanol, the global isopropanol market in 2022 was about 3.1 Mt with a growth rate of about 3.22% until 2035.[47] Even smaller, the global isobutanol market was estimated to be 0.65 Mt in 2022, with an expected growth of 5.05% until 2032.[48]

In addition to influencing the upstream fermentation process, the type of bioalcohol produced significantly affects the performance of the downstream process. More precisely, the purification of fermentation products from more dilute broth in a cost-effective and energy-efficient way is more challenging. Thus, downstream processing costs can also be expected to be higher with the increase in the chain length of the bioalcohol product due to the more diluted fermentation broth. Figure 2 shows the main key performance indicators for the highly advanced downstream processes based on process intensification principles for the purification of different alcohols after fermentation. Note that this figure is a summary of the determined economic and sustainability metrics that are presented in the Supplementary Information file (see Table S4).

Realistically achievable concentrations of alcohols in the fermentation broth were assumed, as follows: 6.14 wt% ethanol,[23] 5.01 wt% isopropanol including small amounts of acetone,[25] 1.61 wt% isobutanol[26] and 0.24 wt% hexanol.[27] Nonetheless, it should be noted that the achievable concentrations of alcohols may vary depending on the type of fermentation process, which would significantly affect the performance of the downstream process. For example, higher concentrations of ethanol (about 5–12 wt%)[24] are achievable in fermentation from glucose compared to fermentation from syngas (about 5–6 wt%).[23] Thus, the downstream process would be less expensive after ethanol fermentation from glucose due to the higher product concentrations in the broth. Furthermore, due to the specific market demands for these alcohols, different plant production capacities were assumed for each of them: 100,[34] 100,[49] 50[35] and 10 kt per year of ethanol, isopropanol and acetone, isobutanol and hexanol production, respectively. A recently published methodology for the purification of volatile biochemicals was used to ensure comparable scenarios for all considered alcohols.[29] All of the mentioned downstream processes were obtained after maximal energy recovery within the system, which resulted in a significant reduction of the total recovery costs. The total recovery costs increase with the chain length of alcohols, whereby the most significant increase happens from C4 to higher alcohols. Calculated following the NREL methodology[44] with 10 years payback period, the total recovery costs are 0.080 USD kg^{-1} for ethanol,[34] 0.109 USD kg^{-1} for isopropanol and acetone,[49] 0.161 USD kg^{-1} for isobutanol[35] and 0.529 USD kg^{-1} for hexanol. For comparison, the reported production cost of lignocellulosic bioethanol is about 0.83 USD kg^{-1},[50] while the production costs of biobased and fossil fuel-based butanol were estimated to be 1.24 and 1.01 USD kg^{-1}, respectively.[51] Thus, it can be concluded that the downstream processes analyzed in this study are highly competitive. However, it should be noted that there is a large increase in the downstream processing cost if the obtained alcohol concentration in the fermentation broth is lower than 1 wt% (about 1 g L^{-1}). There are multiple reasons for this trend. Firstly, the total capital costs do not decrease directly proportionally with the production capacity if product concentration in the broth also decreases. More dilute feed streams still require relatively large equipment units for the initial separation and preconcentration steps (e.g., if vacuum distillation is used for the initial separation step, column diameter for the first column is in the range 4.0–4.3 m), whereby only the equipment units for the final purification are smaller due to the lower amounts of final products. Moreover, the total operating costs increase with the decrease in alcohol concentration in the feed stream: 0.063 USD kg^{-1} for ethanol,[34] 0.081 USD kg^{-1} for isopropanol,[49] 0.117 USD kg^{-1} for isobutanol[35]

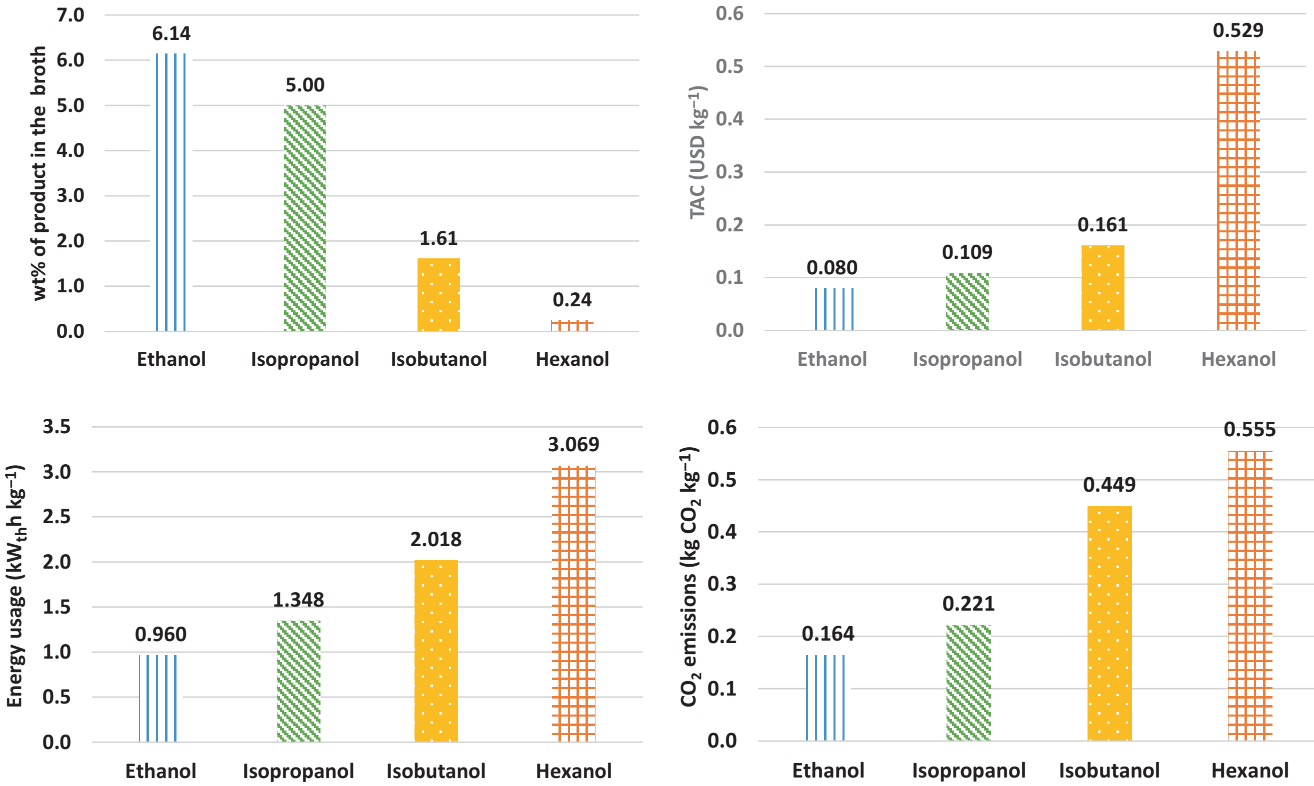

Figure 2. Comparison of downstream processing performance for different alcohols. TAC, total annual costs.

and 0.529 USD kg^{-1} for hexanol. This is mainly due to the higher energy needed per kilogram of recovered product. For example, the initial separation of bioalcohols from most of the fermentation broth is usually very energy intensive, and mechanical vapor recompression (MVR) or other heat pump needs to be applied to decrease the energy usage for this step.[43] In this system, vapor containing valuable fermentation products can be compressed and used to evaporate these products from a dilute aqueous solution. Thus, the electrical energy required to power the compressor can replace a significantly higher amounts of thermal energy. If the concentration of alcohol in the feed stream is lower, less vapor needs to be formed. However, a higher compression ratio is needed to ensure that the smaller amount of compressed vapor can provide sufficient heat to the dilute aqueous solution. If this initial separation is performed by vacuum distillation, a higher reflux ratio is needed to provide sufficient liquid flow down the column. Consequently, the required heating duty for this column would be larger and the necessary compressor duty in the MVR system would also increase (e.g., compressor duties in the MVR systems implemented to the initial vacuum distillation columns are about 1.6,[34] 2.5[49] and 3.5[35] MW for ethanol, isopropanol and isobutanol recovery). The electrical energy requirements in the recovery processes originate mainly from the compressors in the heat pump systems (as the energy required for the pumps represents only a minor part of the total electrical energy usage), so higher compressor duties (in the case of more dilute feed streams) lead to an increase in the energy usage expressed per kilogram of recovered alcohol (e.g., 0.200,[34] 0.338,[49] 0.807[35] and 1.169 kW_eh kg^{-1} for ethanol, isopropanol, isobutanol and for hexanol, respectively). Additionally, heat pump systems might not be able to completely replace the use of steam for heating. For instance, ethanol and isopropanol form homogeneous azeotropes with water that need to be treated to obtain high-purity bioalcohol final products. Extractive distillation with ethylene glycol has been proven to be the best option for large-scale purification in terms of initial investment and operating costs.[39-41] However, ethylene glycol, which makes the most of the bottom product, has a much higher boiling point as compared to ethanol or isopropanol (about 197.2 °C compared to 78.3 and 82.1 °C, respectively), which are obtained as top products. Due to the large temperature difference between the top and bottom of the distillation column, heat pump systems cannot be implemented, and external heating is required. Somewhat more thermal energy is needed for isopropanol purification compared to ethanol purification (0.502 $kW_{th}h$ kg^{-1} for isopropanol[49] compared to 0.450 $kW_{th}h$ kg^{-1} for ethanol[34]). However, isobutanol and hexanol form heterogeneous azeotropes with water, and simple liquid–liquid phase separation combined with conventional distillation is sufficient to provide high-purity products. In the case of isobutanol recovery, pure isobutanol is obtained as the bottom product from the distillation column, while nearly azeotropic isobutanol–water mixture is obtained as the top product. Since the temperature difference is not large (about 107.7 °C at the bottom and 90.3 °C at the top), MVR can be applied to decrease the total energy requirements for that separation part by about 40%.[35] Thus, the complete electrification of the isobutanol recovery after the fermentation is possible and there is no need for use of external thermal energy.[35] On the contrary, even though hexanol forms a minimum boiling azeotrope with water (97.8 °C), it has a much higher boiling point (156.8 °C). Therefore, MVR cannot be applied to the final purification step and steam must be used for heating, resulting in higher thermal energy requirements as compared to isobutanol recovery (0.145 $kW_{th}h$ kg^{-1}), but still lower than those for ethanol and

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isopropanol recovery due to the absence of a high-boiling solvent. Nonetheless, the total primary energy requirements – which take into account both electrical and thermal energy through the electrical-to-thermal conversion factor (conservative value of 2.5)[52] – increase with increase in the alcohol chain length: 0.960, 1.348, 2.018 and 3.069 $kW_{th}h\ kg^{-1}$ for ethanol, isopropanol, isobutanol and hexanol, respectively. Another important key performance indicator is the amount of carbon dioxide (CO_2) that is emitted per kilogram of recovered product. Since these emissions are related to the total energy requirements, an increase in alcohol chain length also results in higher CO_2 emissions in the downstream processing: 0.164,[34] 0.221,[49] 0.449,[35] and 0.555 $kg_{CO2}\ kg^{-1}$ for ethanol, isopropanol, isobutanol and hexanol. In comparison, the carbon footprints of ethanol[53] and petrochemically produced isopropanol[9] were estimated to be 0.81 and 1.85 $kg_{CO2}\ kg^{-1}$, respectively.

It should be noted that more expensive downstream processing in the case of longer-chain alcohols is mostly due to lower product concentrations in the feed stream and not the nature of the alcohol. The nature of the alcohol (e.g. hydrophobicity) substantially affects the fermentation process and determines the product concentration in the feed stream to the downstream processing. Moreover, the recovery of isobutanol and hexanol from aqueous mixtures is somewhat easier compared to the purification of ethanol and isopropanol due to the heterogeneity of the formed azeotropes (see Table 1). In these cases, a simple liquid–liquid phase separation followed by conventional distillation can be used to recover high-purity products. Contrarily, ethanol and isopropanol form homogeneous azeotropes and more complex extractive distillation (using a high-boiling solvent) is needed. A comparison of the total recovery costs of ethanol and higher alcohols starting from various concentrations in the fermentation broth is presented in Fig. 3. Due to similar physical properties, isopropanol and ethanol recovery costs are comparable. Furthermore, it can be seen that the low concentrations of longer-chain alcohols in the fermentation broth are the main reason for the more expensive downstream processing. For example, the total isobutanol recovery costs starting from 1.61 wt% in the feed stream are lower than the expected ethanol recovery costs starting from the same initial concentration. The reason for this has already been mentioned, namely the easier separation that results from the heterogeneity of the isobutanol–water azeotrope. Thus, the concentration of the alcohol product in the fermentation broth has the most significant influence on the downstream processing performance. Nonetheless, in the case of higher alcohols with lower achievable fermentation titers, the overall production process might still be viable because of less complex separations. Lastly, even though expressed per kilogram of recovered bioalcohols, the results presented in Fig. 3 were obtained assuming different production capacities (100 kt per year of ethanol and isopropanol separately, 50 kt per year of isobutanol and 10 kt per year of hexanol). Thus, TAC for recovering hexanol and isobutanol might benefit from the economy of scale, assuming that there is sufficient market demand to increase the production capacity. However, since OPEX is roughly proportional to the production capacity, it is only the contribution of CAPEX that may decrease. Yet, considering that CAPEX makes only a minor part of TAC, whereas the contribution of OPEX is much larger,[34,35,49] changes in the production capacity should not significantly affect the trend presented in Fig. 3.

Thus, even though recovering higher alcohols after fermentation is more expensive due to the more dilute feed stream, the market prices of these alcohols are higher. According to the available data, the prices of these alcohols at the end of 2023 in North America were the following: 0.591 USD kg^{-1} for ethanol,[54] 1.310 USD kg^{-1} for isopropanol,[55] 2.043 USD kg^{-1} for isobutanol[56] and 2.500 USD kg^{-1} for hexanol.[57] Consequently, the total purification costs correspond to about 13.5%, 8.3%, 7.9% and 21.2% of the current market prices for ethanol, isopropanol, isobutanol and hexanol, respectively. Thus, producing longer-chain alcohols might be more profitable, despite the more costly downstream processing due to the higher market prices of these chemicals. Additionally, a margin between market price and total recovery costs is 0.511, 1.201, 1.882 and 1.971 USD kg^{-1} for ethanol, isopropanol, isobutanol and hexanol, respectively. However, this margin does not include fermentation costs and would further reduce once these costs are also included. To the best of our knowledge, a complete comparison of the fermentation costs for different alcohols has not been reported, and literature data focused on the production of only one alcohol cannot be compared due to the differences in the applied methodologies for evaluating the process performance.[58-61] Even though the margin

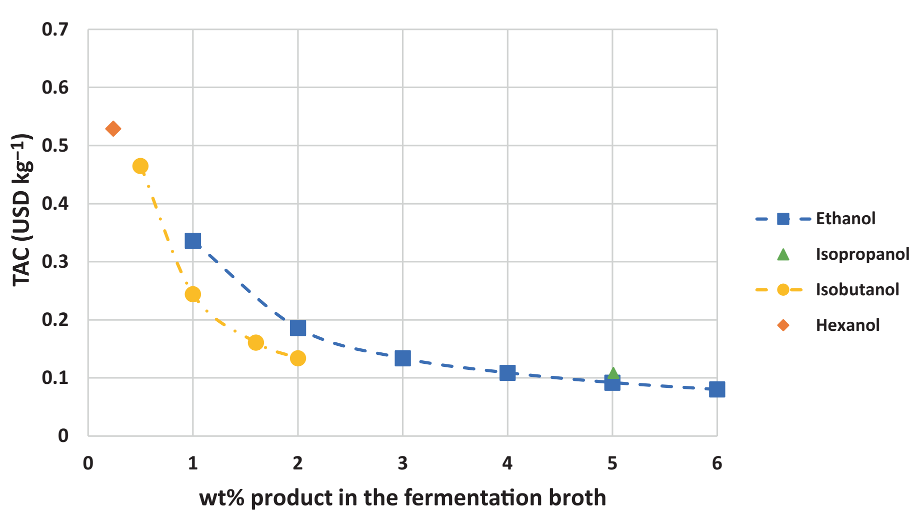

Figure 3. Influence of product concentration in the fermentation broth on the total recovery costs. TAC, total annual costs.

between market price and total production costs increases with the increasing chain length of alcohols, it can be expected that fermentation costs increase as well. This is mainly due to the lower achievable concentrations, which leads to the larger required bioreactors, and higher capital and operating costs. However, additional research and a fair comparison (on the same basis) of the fermentation processes for different alcohols are needed to obtain a full picture. Notably, the cost of both upstream fermentation and downstream processes should be taken into account to ensure a sustainable and competitive design of an industrial-scale plant. In that respect, this perspective paper expresses the importance of downstream processing in the overall bioalcohol production process. Furthermore, the overall comparison offers valuable insight into the performance of downstream processing that can be expected industrially. This information is of substantial significance for the development of large-scale fermentative production of bioalcohols.

CONCLUSIONS

This perspective paper offers a key critical insight into the eco-efficiency and performance of downstream processing for the purification of different alcohols (ethanol, isopropanol, isobutanol, hexanol) from fermentation broth. Achievable concentrations of longer-chained alcohols are lower due to stronger toxic effects. Consequently, the purification of valuable fermentation products from more dilute streams is more economically and environmentally intensive. Accordingly, the total purification costs for ethanol, isopropanol, isobutanol and hexanol are 0.080, 0.109, 0.161 and 0.529 USD kg^{-1}, respectively. Similarly, the energy requirements (0.960, 1.348, 2.018 and 3.069 $kW_{th}h\ kg^{-1}$, respectively) and CO_2 emissions (0.164, 0.221, 0.449 and 0.555 $kg_{CO2}\ kg^{-1}$, respectively) follow analogous trends. However, the more expensive downstream processing in the case of longer-chain alcohols is mainly due to the lower concentrations in the fermentation broth and not the nature of the alcohol product. In the case of very low product concentrations in the feed stream, alternative recovery techniques (e.g., liquid–liquid extraction) may be explored to ensure that the total production costs are minimized. In that respect, all accompanying costs in the downstream processing should be taken into account (e.g., recovery of used solvents or other additional chemicals) to obtain a complete picture of the overall process performance.

Despite more expensive recovery processes, longer-chain alcohols are higher-value products with smaller markets. Thus, the choice of the most profitable alcohol to produce should be made after coupling and analyzing the performance of both upstream and downstream processes. This perspective paper emphasizes the influence of downstream processing on the competitiveness of industrial fermentation process, while also offering insights into the performance that can be expected for large-scale purification processes. In that respect, the results presented here should be combined with relevant data from fermentation to obtain a complete picture of the performance of the entire bioalcohol production processes.

DATA AVAILABILITY STATEMENT

Data are available upon reasonable request from the corresponding author.

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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