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Acetone-butanol-ethanol fermentation products recovery: Challenges and opportunities

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ABSTRACT

Nowadays, global warming is one of the most significant concerns in modern societies, which entails considerable costs to the environment, health, economy, etc. Fossil fuels play an essential role in this phenomenon and finding an alternative for them has been the research topic for the past few decades. Among the array of options available, biofuel stands out as a highly effective and environmentally sustainable alternative. Biobutanol presents properties like high heating value, low volatility, high viscosity, and low corrosion. Additionally, it is a much safer option for use, and its ability to blend with gasoline and other fuels turns it into a suitable and promising renewable alternative. Biobutanol can be produced from the agricultural industry's residues by the acetone-butanol-ethanol (ABE) fermentation process. The separation and purification of biobutanol from the fermentation broth account for 40 % of the plant budget, which is notable. Various separation techniques like liquid-liquid extraction, membrane perstraction, gas stripping, vacuum flash, membrane pervaporation, thermopervaporation, reverse osmosis, adsorption, etc., are applied. A befitting separation method must produce sufficient butanol concentration in the output and reduce the final product's cost so biobutanol can compete economically with other fuels. This work reviewed the existing processes for the separation and purification of butanol from ABE fermentation, including advanced methods. All methods will be discussed in detail considering environmental and economic parameters and each technique's superiors and challenges.

1. Introduction

In light of the pressing global environmental challenges posed by climate change, the quest for viable alternatives to the widespread reliance on fossil fuels has gained paramount importance. As our planet confronts the ominous specter of climate change, driven in large part by the emissions from fossil fuel combustion, the imperative for sustainable, eco-friendly energy sources has become the defining challenge of our time (Segovia-Hernández et al., 2023). This scientific paper takes up the mantle of this crucial endeavor, seeking to explore the potential of biofuels derived from biomass, with an acute focus on the production of bio-butanol through the intricate process of Acetone-Butanol-Ethanol (ABE) fermentation. The backdrop for this exploration is firmly grounded in the broader objectives of sustainability and the circular economy, encapsulating the dual dimensions of ecological responsibility and economic pragmatism (Torre et al., 2023a).

The global scientific community has, for many years, been resolutely dedicated to the quest for alternative fuels that can strike the delicate balance between reducing environmental impacts through fewer byproduct emissions and remaining economically competitive. Governments across the world have also heeded the call, recognizing the critical need to enact novel regulatory frameworks that incentivize the transition towards greener fuel consumption within their communities (Liu et al., 2022a). The imperative to align economic viability with environmental responsibility has emerged as the driving force behind this transformative endeavor.

The journey towards sustainable energy solutions has led to the pivotal role of biofuels, derived from renewable biomass resources.

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Biomass, with its inherent abundance across the globe, presents a unique opportunity for the production of biofuels that are not only readily accessible but also cost-effective (Segovia-Hernández et al., 2022). However, in the evolving landscape of sustainability and ethics in energy discussions, the ethical use of edible resources for fuel production has cast a long shadow of concern. The ethical dilemma surrounding edible resources has spurred researchers to explore the untapped potential of agricultural waste and residual materials, such as lignocellulosic biomass. This shift towards biomass utilization effectively transforms waste streams into valuable biofuel feedstock, aligning with the principles of the circular economy (D. Kushwaha et al., 2019).

Biofuels, a diverse category of alternative fuels, are systematically classified into primary, secondary, and third-generation fuels. Within this classification framework, ABE fermentation assumes a significant role as a secondary biofuel. The scientific community has expended substantial efforts in researching the potential of bio-butanol, a product of ABE fermentation, as a promising alternative fuel source (Mukherjee et al., 2020). However, technical and economic challenges have led to a burgeoning interest in the utilization of ABE fermentation itself as a fuel blend. This paradigm shift represents a compelling development in the pursuit of sustainable energy alternatives.

Central to the advancement of sustainable bio-butanol production are the strategies aimed at reducing production costs. It underscores two primary strategies (Torre et al., 2023a):

a) Genetic Engineering: The intricate manipulation of microorganisms used in ABE production processes, designed to enhance product yield and concentration, thereby reducing overall production costs. Genetic engineering in ABE fermentation holds the promise of efficiency and sustainability, which are key elements in achieving economic viability.
b) Enhanced Separation and Purification: The optimization of downstream processes, encompassing the critical steps of separation and purification. This strategic focus aims at not only maintaining high product purity but also maximizing the recovery of bio-butanol from the complex ABE fermentation output. Effective separation and purification processes are vital to sustain both economic efficiency and ecological responsibility.

Bio-butanol, a four-carbon saturated alcohol, exhibits an intriguing array of physicochemical properties that set it apart from conventional fossil fuels. These exceptional properties encompass a high heating value, low volatility, high viscosity, and low corrosion, collectively endowing bio-butanol with inherent safety and promise as an alternative fuel. Its compatibility with gasoline and various other fuels, facilitated by efficient transportation through pipelines, heightened energy storage capacity, superior octane rating, and improved blend stability, positions it as an appealing option. Furthermore, its potential for reducing emissions and substituting for conventional fuels without engine modifications underscores its versatility (Torre et al., 2023a). When compared to ethanol, butanol boasts lower water solubility, hygroscopicity, vapor pressure, volatility, explosiveness, and corrosiveness. This multi-faceted nature allows bio-butanol to act as both a drop-in fuel and an additive to gasoline, without necessitating costly engine modifications. Moreover, the lower environmental footprint of bio-butanol makes it a greener, eco-friendly alternative (Iyyappan et al., 2021).

Bio-butanol is conventionally produced through ABE fermentation, featuring a typical ratio of 3:6:1 and a butanol concentration of approximately 3 %. In this section, we explore the intricacies of the bio-butanol production process, which involves the meticulous separation and purification of the products generated through ABE fermentation (Alam & Tanveer, 2020). This stage of the process is where the principles of sustainability and the circular economy come into play, calling for responsible resource utilization, waste reduction, and the optimization of energy and material flows.

Understanding the full spectrum of bio-butanol production requires a closer examination of the upstream processes in ABE fermentation. These processes encompass a broad range of methodologies, starting from the selection of raw materials and culminating in the fermentation techniques employed. A comprehensive understanding of these upstream processes is essential for the holistic optimization of the bio-butanol production pathway. It allows for the alignment of ecological and economic considerations, ensuring the sustainable and circular production of bio-butanol (Mailaram et al., 2021).

The downstream processes in bio-butanol production are equally pivotal. In this segment, we delve into the separation and purification methods developed to extract bio-butanol efficiently from the complex output of ABE fermentation. These methods not only serve the vital purpose of maintaining product purity but are also critical for enhancing the sustainability and economic viability of the entire process (Oksal & Kaymak, 2023). By optimizing these downstream processes, we can further advance the circular economy and responsible resource management in the production of sustainable biofuels.

Grounded in the principles of environmental responsibility and the circular economy, we have embarked on a journey to dissect the complexities of bio-butanol production through ABE fermentation. The unique properties of bio-butanol, coupled with its compatibility with existing engines and its reduced environmental impact, positions it as a promising contender in the quest for greener energy solutions. Strategies aimed at reducing production costs are charting a path towards economic viability (Torre et al., 2023b). By scrutinizing both the upstream and downstream processes, we have contributed to the broader objective of transitioning to more sustainable and circular economic practices within the realm of alternative fuel production. As the world grapples with the urgent need for sustainable energy solutions, the nexus of economic viability and environmental responsibility has never been more crucial (Gedam et al., 2023). In this era of ecological awakening and economic transformation, bio-butanol production stands as a symbol of our unwavering commitment to a greener, more sustainable future.

In this comprehensive paper, we initiate our exploration by delving into the upstream processes of ABE fermentation, elucidating the various methodologies employed for ABE production. Subsequently, we take a closer look at the upstream processes, which encompass the separation and purification of bio-butanol, thereby contributing to the broader objective of transitioning to more sustainable and circular economic practices within the realm of alternative fuel production. Ultimately, our work endeavors to bridge the gap between the urgent need for sustainable energy solutions and the economic viability of their production, firmly grounded in the principles of environmental responsibility and circular economy.

2. Stages for obtaining biobutanol from biomass

Obtaining biobutanol from biomass is a cutting-edge process at the forefront of research and development in the fields of biotechnology and renewable energy. In this section, we will delve into the various stages required to convert biological materials into biobutanol, a promising biofuel with a wide range of industrial and automotive applications (Eloka-Eboka & Maroa, 2023). As we progress through this journey, we will uncover the intricacies and challenges involved in each phase, from biomass collection and preparation to fermentation and distillation, elucidating how science and engineering converge to transform biomass into a sustainable and economically viable source of energy. The following will provide a detailed breakdown of the stages for obtaining biobutanol (Segovia-Hernandez et al., 2022):

a) Biomass Collection: In the initial stage of biobutanol production, biomass is sourced from various feedstock materials, which are rich in lignocellulosic components. These feedstocks can encompass a wide range of materials such as wood, agricultural residues (e.g., crop stalks and leaves), straw, rice husks, and other lignocellulosic

materials. The primary objective of this stage is to secure a sustainable and abundant supply of biomass resources. The collected biomass is subjected to meticulous preparation. This preparation process typically includes size reduction through shredding and tearing, which serves the dual purpose of reducing the feedstock into more manageable sizes and increasing its surface area. This enhanced surface area facilitates subsequent chemical and biological conversion processes, rendering the biomass more amenable to downstream processing (Hiloidhari et al., 2023; Qureshi et al., 2021).

b) Biomass Treatment: Biomass treatment encompasses a spectrum of physical, chemical, and biological processes designed to deconstruct the complex lignocellulosic matrix. Acidic or alkaline hydrolysis, for instance, involves exposing the biomass to carefully controlled pH levels and temperatures. This treatment not only solubilizes lignin and hemicellulose but also modifies the cellulose structure, making it more amenable to enzymatic or microbial degradation. Steam explosion, another pretreatment method, subjects the biomass to high-temperature and pressure conditions, leading to the breakdown of lignin and a reduced degree of polymerization in cellulose, further enhancing its accessibility to enzymes (Mankar et al., 2021; Rezania et al., 2020).

c) ABE Fermentation: It is a meticulously controlled bioprocess where the pretreated biomass hydrolysate, rich in fermentable sugars, is inoculated with solventogenic bacteria. These microorganisms belong to the Clostridium genus, and they exhibit a unique metabolic pathway capable of converting sugars into biobutanol, acetone, and ethanol. During fermentation, it is essential to maintain optimal conditions, such as pH, temperature, and nutrient availability, to maximize biobutanol production. The fermentation broth undergoes continuous monitoring to ensure the conversion of sugars into target biofuels, with biobutanol serving as the most valuable product due to its high energy density (Veza et al., 2021a).

d) Separation and Purification: Following ABE fermentation, the resulting fermentation broth contains a mixture of biobutanol, acetone, ethanol, and other components. To obtain high-purity biobutanol suitable for industrial applications, a separation and purification stage is initiated. This involves a series of separation techniques, such as distillation or solvent extraction, to isolate the individual components from the fermentation medium. Distillation is a common method used to separate and concentrate biobutanol, acetone, and ethanol. The separated biobutanol is further subjected to purification processes to remove any remaining impurities, ensuring the end product meets high-quality standards (Sánchez-Ramírez et al., 2023).

e) Product Recovery: After separation and purification, the isolated biobutanol is further subjected to product recovery techniques to obtain a concentrated and pure biobutanol stream. Techniques such as distillation, adsorption, or liquid-liquid extraction are utilized for this purpose. These processes are vital in ensuring that the final biobutanol product meets industry specifications and regulatory requirements. Distillation, for instance, allows for the recovery of biobutanol as a high-purity liquid, while other methods may involve adsorbents to selectively capture biobutanol (Segovia-Hernandez et al., n.d.).

f) Waste Recycling: The waste recycling phase is an integral part of sustainable biobutanol production. By-products like stillage, a liquid residue generated during fermentation, are not discarded but instead can be valorized. Anaerobic digestion is one environmentally friendly approach to treat stillage. This process converts organic matter in stillage into biogas, primarily composed of methane, which can be used as a renewable energy source. Additionally, the effluent from anaerobic digestion can be used as a nutrient-rich fertilizer or can be treated to meet discharge standards (J. Chen et al., 2021; Desta et al., 2021).

g) Storage and Distribution: The final, high-purity biobutanol product is stored in specialized tanks designed to maintain its chemical stability. These tanks may incorporate safety features to prevent ignition or contamination risks due to biobutanol's flammable nature. For distribution, biobutanol can be transported via dedicated pipelines, tankers, or railcars to end-users. It may be blended with gasoline or used as a standalone biofuel, contributing to the reduction of greenhouse gas emissions and enhancing energy security. Advanced techniques such as vapor phase inhibitors can be employed during transportation to maintain product quality and prevent degradation. The distribution phase aligns with environmental regulations and safety standards to ensure the safe and efficient use of biobutanol as a renewable fuel source (Momenitabar et al., 2022; Zhen et al., 2020).

Biobutanol production is a highly technical process that encounters challenges and opportunities at each of its stages. From biomass collection to biobutanol storage and distribution, a comprehensive approach is required to address challenges related to biomass availability, the efficiency of treatment and fermentation processes, product separation and purification, biobutanol recovery, and sustainable waste management. Simultaneously, exciting opportunities exist to enhance biobutanol production through technological advancements, process optimization, genetic engineering of microorganisms, and the implementation of more efficient separation methods (Pugazhendhi et al., 2019). Biobutanol production not only represents a potentially valuable source of sustainable biofuels but also fosters research and development in fields such as biotechnology, process engineering, and environmental management. Overcoming these challenges and leveraging these opportunities can lead to more efficient and environmentally friendly biobutanol production, contributing to climate change mitigation and promoting a more sustainable economy (Nilsson et al., 2020).

3. Biomass treatment

Lignocellulosic biomass, composed primarily of cellulose, hemicellulose, and lignin, represents a challenging substrate for ABE fermentation due to its recalcitrant nature. To unlock the potential of this abundant and sustainable feedstock, efficient pretreatment methods are crucial. These methods aim to break down the complex lignocellulosic structure, making the carbohydrates accessible to enzymes and microorganisms for subsequent fermentation (Das et al., 2021). Let's delve deeper into various lignocellulose pretreatment strategies:

3.1. Steam explosion

Steam explosion is a highly proven pretreatment method utilized in various industries, primarily relying on the application of high-temperature steam under elevated pressure. In the course of this process, lignocellulosic materials undergo rapid heating followed by a sudden depressurization, a phenomenon that leads to the physical disruption of the biomass. It's worth noting that the steam itself plays a crucial role by acting as a catalyst in this process, where it functions to break down hemicellulose and partially delignify the biomass. These actions significantly improve the accessibility of cellulose to enzymatic hydrolysis, making it more susceptible to this enzymatic action. One of the key merits of steam explosion lies in its effectiveness in breaking down lignin, a substantial factor in enhancing the accessibility of cellulose to enzymes. This, in turn, leads to a notable improvement in the yield of valuable products like acetone, butanol, and ethanol (ABE) that can be derived from the lignocellulosic materials subjected to this pretreatment method. This combination of physical disruption, hemicellulose, and lignin breakdown, and enhanced cellulose accessibility has firmly established steam explosion as a vital and efficient step in the conversion of biomass into valuable bio-based products (Bhuyar et al., 2022; Smichi et al., 2020).

3.2. Alkaline peroxide

Alkaline peroxide pretreatment is an advanced technique that entails the application of alkaline solutions and hydrogen peroxide to lignocellulosic biomass. The synergy of these two agents serves to significantly enhance the conversion of biomass into valuable products. The alkaline conditions in this process play a pivotal role by effectively breaking down lignin, the complex and often inhibitory polymer that encases cellulose and hemicellulose within the biomass matrix. Simultaneously, the alkaline environment also facilitates the selective removal of hemicellulose, which is beneficial in streamlining the subsequent conversion processes. Hydrogen peroxide, a powerful oxidizing agent, further complements the pretreatment by contributing to the delignification of the biomass. It acts on the lignin, breaking down its complex structure and thereby promoting its removal. Moreover, hydrogen peroxide aids in improving the accessibility of cellulose, making it more susceptible to enzymatic hydrolysis. As a result, this method is particularly effective in the removal of lignin, which is a crucial step in enhancing the production of valuable acetone, butanol, and ethanol (ABE) from lignocellulose feedstocks. In summary, alkaline peroxide pretreatment is a highly efficient and well-established approach for biomass conversion, effectively disrupting lignin and hemicellulose, and improving cellulose accessibility. This method's ability to target and remove lignin is of paramount importance in the context of ABE production and bioconversion processes, making it an indispensable technique in the field of biorefining (Huang et al., 2020; Mejica et al., 2022).

3.3. Alkaline-NaOH

Sodium hydroxide (NaOH) pretreatment is a widely adopted method for modifying the intricate structure of lignocellulosic biomass, making it more amenable to bioconversion processes. This approach, which involves the application of alkaline conditions using NaOH, offers several benefits in the context of lignocellulosic feedstock utilization. One of the primary advantages of alkaline-NaOH treatment is its ability to partially remove lignin, a complex and rigid polymer that encases cellulose and hemicellulose within the biomass matrix. By selectively breaking down lignin, this process enhances the accessibility of cellulose, which is a critical component for enzymatic hydrolysis. Furthermore, alkaline-NaOH treatment also effectively targets and breaks down hemicellulose, a polysaccharide that forms a complex network with cellulose and lignin. This breakdown of hemicellulose further contributes to the creation of a more digestible substrate for subsequent enzymatic hydrolysis and fermentation. By virtue of these actions, the NaOH pretreatment process can significantly improve the overall bioconversion efficiency of lignocellulosic materials. It not only renders cellulose more accessible for enzymatic degradation but also provides a platform for the release of fermentable sugars from the biomass. These sugars can then be readily utilized by microorganisms in the fermentation process to produce biofuels, biochemicals, or other value-added products. Sodium hydroxide (NaOH) pretreatment is a popular and effective choice for transforming lignocellulosic feedstocks into more easily digestible substrates, ultimately facilitating the production of biofuels and other bioproducts. Its lignin removal and hemicellulose breakdown properties make it a valuable tool in the quest for sustainable and renewable resource utilization (K.H. Lee et al., 2022; Niju et al., 2020).

3.4. Dilute acid

Dilute acid pretreatment is a versatile and well-established method for enhancing the enzymatic hydrolysis of lignocellulosic biomass. In this process, mild acids such as sulfuric acid or hydrochloric acid are applied to the biomass, resulting in a series of valuable transformations that make it highly amenable to subsequent bioconversion processes. A key feature of dilute acid pretreatment is its selective targeting of hemicellulose, one of the three major components of lignocellulosic materials. Hemicellulose is efficiently hydrolyzed by the acid under mild conditions, breaking down its complex structure into simpler sugar monomers. These monomers can then be readily converted into fermentable sugars, which are invaluable for various bioprocesses, including the production of biofuels and biochemicals. One of the significant advantages of this method is that it does not severely disrupt the cellulose structure, leaving it relatively intact. Cellulose is the primary carbohydrate of interest for bioconversion, as it can be enzymatically hydrolyzed into glucose, a key substrate for microbial fermentation. By leaving the cellulose structure mostly intact, dilute acid pretreatment ensures that a substantial portion of the cellulose remains available for enzymatic breakdown. Additionally, the removal of hemicellulose during pretreatment enhances the accessibility of cellulose. This is because hemicellulose, when present, can impede the enzymatic action on cellulose by creating a physical barrier. As a result, dilute acid pretreatment not only generates fermentable sugars directly from hemicellulose but also indirectly improves the potential yield of glucose from cellulose due to this increased accessibility. In summary, dilute acid pretreatment is a highly efficient method that selectively targets hemicellulose, leaving cellulose relatively intact and enhancing its accessibility for enzymatic hydrolysis. This process is a crucial step in the valorization of lignocellulosic feedstocks and the sustainable production of bio-based fuels and chemicals (López-Linares et al., 2021; Shangdiar et al., 2022).

3.5. Ethanol organosolv pretreatment

Organosolv pretreatment stands as a sophisticated method in the arsenal of lignocellulosic biomass conversion processes, offering distinctive advantages in terms of lignin removal and biomass disruption. This approach harnesses the power of organic solvents, with ethanol being a particularly popular choice, to effectively transform the recalcitrant lignocellulosic materials into more amenable feedstocks for bioconversion. A hallmark feature of organosolv pretreatment is its capacity to dissolve and remove lignin. Lignin, a complex and rigid polymeric compound, is a significant barrier to the accessibility of cellulose and hemicellulose, the carbohydrates of interest in bioconversion processes. By dissolving and removing lignin, organosolv pretreatment disrupts the lignocellulosic structure, exposing cellulose and hemicellulose to subsequent enzymatic actions. This deliberate disruption creates a more accessible and digestible substrate, thereby enhancing the efficiency of bioconversion processes. Ethanol, as a choice of organic solvent, is particularly effective in delignifying the biomass. It offers several advantages, including its ability to extract lignin while maintaining the structural integrity of cellulose and hemicellulose. This selective delignification not only yields higher-quality cellulose but also results in a lignin-rich stream that can potentially be valorized for various purposes, such as the production of value-added chemicals. Furthermore, organosolv pretreatment has been noted for its capacity to produce biomass fractions with lower levels of inhibitors, which can often interfere with downstream fermentation processes. This makes it a suitable method for generating lignocellulosic feedstocks that are conducive to efficient enzymatic hydrolysis and microbial conversion into biofuels and biochemicals. Organosolv pretreatment, particularly when employing ethanol as the organic solvent, is a powerful approach for lignin removal and biomass disruption. It significantly enhances the accessibility of cellulose and hemicellulose for enzymatic hydrolysis and offers opportunities for the valorization of lignin-rich byproducts, making it a key technique in the sustainable utilization of lignocellulosic biomass for biorefining applications (Riaz et al., 2022).

3.6. Acetone organosolv

Acetone organosolv pretreatment is a close relative of ethanol organosolv pretreatment, both being advanced techniques for the effective deconstruction of lignocellulosic biomass. In this method,

acetone, a powerful organic solvent, is employed to solubilize and remove lignin from the lignocellulosic feedstock. Much like ethanol organosolv, acetone organosolv pretreatment shares several key attributes and advantages that make it a compelling choice for biomass conversion. One of the primary objectives of acetone organosolv pretreatment is the efficient removal of lignin. Lignin, as a complex and resistant polymer, is a major impediment to the accessibility of cellulose and hemicellulose for enzymatic hydrolysis and subsequent conversion. By dissolving and removing lignin, acetone organosolv pretreatment effectively disrupts the lignocellulosic structure, unveiling cellulose and hemicellulose for enhanced accessibility. The ability of acetone to selectively dissolve lignin while preserving the integrity of cellulose and hemicellulose is a key feature of this method. This selective delignification process yields biomass fractions with higher-quality cellulose, which can be more readily converted into fermentable sugars through enzymatic hydrolysis. Additionally, acetone organosolv pretreatment has the potential to generate lignin-rich byproducts, which, like those produced in ethanol organosolv processes, can be explored for various applications. These byproducts may include valuable chemicals, materials, or even bioenergy sources, adding to the sustainability of the overall biomass utilization process. By partially disrupting the lignocellulosic structure, acetone organosolv pretreatment plays a crucial role in optimizing the feedstock for subsequent bioconversion. It creates a substrate that is more accessible for enzymatic hydrolysis, a critical step in the efficient conversion of lignocellulosic materials into biofuels, biochemicals, and other value-added products. In summary, acetone organosolv pretreatment is a powerful and promising method for lignin removal and biomass deconstruction, similar in principle to ethanol organosolv pretreatment. It holds great potential in the sustainable utilization of lignocellulosic biomass and in advancing the goals of biorefining and the bio-based economy (Segovia-Hernandez et al., n.d.).

Choosing the most suitable pretreatment method depends on various factors, including the feedstock composition, targeted ABE production, and the economics of the process. Pretreatment should balance the efficient removal of lignin and hemicellulose to improve carbohydrate accessibility while minimizing the production of inhibitory compounds like furfural and HMF (Sarker et al., 2024). Additionally, care should be taken to manage the environmental and economic aspects of the chosen pretreatment method. Selecting the right strategy ensures that lignocellulosic biomass can be efficiently converted into fermentable sugars and subsequently into valuable ABE products in a sustainable and cost-effective manner (W.H. Chen et al., 2022).

The inhibitors generated during the preliminary treatment phase exert a significant impact on ABE production, potentially leading to reduced yields. These process inhibitors, arising from pretreatment and neutralization procedures, encompass various chemical entities (A. Kushwaha et al., 2022)

- Weak acids resulting from hemicellulose degradation, including acetic, levulinic, and formic acids.
- Furan derivatives originating from pentose and hexose sources, namely furfural and hydroxymethylfurfural (HMF).
- Phenolic compounds arising from lignin degradation, such as p-coumaric acid, ferulic acid, hydroxybenzoic acid, vanillic acid, syringaldehyde, vanillin, p-hydroxybenzaldehyde, o-hydroxybenzaldehyde, and m-hydroxybenzaldehyde (Luo et al., 2020).
- Salts produced during acid-base neutralization, including sodium acetate, sodium chloride, and sodium sulfate.

ABE production, typically mediated by bacteria of the Clostridium genus, can be impeded by these various compounds resulting from the pretreatment method and the composition of the feedstock. Further elucidation of ABE fermentation processes will be provided in subsequent sections. The emergence of by-products during pretreatment has prompted exploration into their separation and purification, given the market viability of certain components. Noteworthy examples include the intensified purification of levulinic acid; and furfural purification endeavors (Contreras-Zarazúa et al., 2022).

Lignocellulose pretreatment plays a pivotal role in ABE (Acetone, Butanol, Ethanol) production from lignocellulosic biomass sources. Herein, we elucidate the advantages and challenges associated with this process (Segovia-Hernandez et al., 2022):

Advantages:

- Enhanced Carbohydrate Accessibility: The primary objective of pretreatment is to dismantle the intricate structure of lignocellulose, facilitating the release of carbohydrates such as cellulose and hemicellulose, which are essential for ABE production. By improving the accessibility of these substrates, fermentation yield is maximized.
- Increased Yield of Fermentable Sugars: Effective pretreatment results in the greater release of fermentable sugars, leading to higher ABE production. This enhances process efficiency and profitability.
- Inhibitor Reduction: Some lignocellulosic components, such as hydroxymethylfurfural (HMF) and furfural, can act as inhibitors during ABE fermentation. Adequate pretreatment can mitigate the formation of these compounds, reducing inhibition challenges during fermentation.
- Utilization of Sustainable Biomass: Lignocellulose is derived from renewable and sustainable materials like agricultural residues, wood, or municipal solid waste. The utilization of lignocellulosic biomass contributes to environmental sustainability by reducing reliance on non-renewable resources.
- Versatility: Various pretreatment methods are available, providing flexibility in selecting the most suitable strategy for specific biomass sources. This adaptability allows tailoring the process to different feedstock types.

Challenges:

- Process Complexity: Pretreatment is a sophisticated process that necessitates a profound understanding of lignocellulose chemistry and the selection of optimal conditions. Choosing the right method and pretreatment conditions can be a challenge in itself.
- Energy Costs: Certain pretreatment methods, such as high-pressure steam treatment, can demand significant energy consumption, potentially increasing operational costs and the carbon footprint of the process.
- Waste and Effluent Generation: Pretreatment can result in the generation of by-products and effluents that require proper management. The disposal of these waste products can pose environmental and economic challenges.
- Potential Sugar Losses: In some instances, pretreatment may lead to the degradation of sugars or the formation of undesirable compounds, which could reduce the overall yield in the fermentation process.
- Ongoing Research and Development Needs: The field of lignocellulose pretreatment is continuously evolving, with ongoing research aimed at developing more efficient and cost-effective methods. Staying abreast of the latest innovations and technologies is essential to maximize the benefits of pretreatment.
- Lignocellulose pretreatment offers significant advantages in ABE production from renewable biomass. Nevertheless, overcoming the technical and economic challenges associated with this process requires a meticulous approach and ongoing research and development efforts to enhance efficiency and sustainability in ABE production.

4. ABE fermentation process

The production of valuable chemicals such as acetone, n-butanol, and ethanol from carbohydrates through bacterial fermentation, specifically by strains of *Clostridium* bacteria, represents a significant area of

interest in the field of biotechnology (Nandhini et al., 2023). This process, known as ABE fermentation, has gained prominence due to its potential applications in both laboratory and industrial settings, with a particular focus on strains like *Clostridium acetobutylicum*, *Clostridium beijerinckii*, *Clostridium saccharobutylicum*, and *Clostridium saccharoperbutylacetonicum*.

Clostridium species, which are gram-positive, rod-shaped, spore-forming, and obligate anaerobes, exhibit versatility in utilizing a wide range of substrates, including pentoses (xylose and arabinose), hexoses (glucose, mannose, galactose, and fructose), disaccharides (sucrose, cellobiose, and lactose), and starch. The ABE fermentation process conducted by these microorganisms results in the production of three primary categories of products: (1) solvents, including acetone, butanol, and ethanol; (2) organic acids, such as acetic acid, lactic acid, and butyric acid; and (3) gases, including carbon dioxide and hydrogen (X. Chen et al., 2024).

ABE fermentation occurs in two distinct physiological phases, the acidogenic phase and the solventogenic phase. During the acidogenic phase, exponential bacterial growth is accompanied by the conversion of glucose into acetic or butyric acid, releasing energy vital for cell proliferation. The production of these acids leads to a significant drop in extracellular pH in batch cultivation, triggering the cells' transition into the stationary phase (M. Wang et al., 2023). As depicted in Fig. 1, one mole of glucose converted to either 2 moles of acetic acid or 1 mol of butyric acid accompanied by the release of energy (2 mol ATP), vital for cell growth. The production of acids causes a dramatic drop in extracellular pH in batch cultivation. In response to a significant pH decrease, the cells enter the stationary stage, and the organic acids are reassimilated to produce solvents - the solventogenic phase. Acetic acid is converted to ethanol or acetone, while butyric acid is converted to butanol. In the solventogenic phase, organic acids are re-assimilated to generate solvents. Acetic acid is converted into ethanol or acetone, while butyric acid is transformed into butanol. This phase is followed by the initiation of sporulation.

At its core, ABE fermentation involves the metabolic activity of certain microorganisms, typically strains from the Clostridium genus, to convert sugars into acetone, butanol, and ethanol. This metabolic pathway, known as the acetone-butanol-ethanol pathway, encompasses a series of biochemical reactions orchestrated by enzymes within the microbial cells. Initially, fermentable sugars derived from feedstock materials are transported into the microbial cells via specific transport systems. Within the intracellular environment, these sugars undergo glycolysis, yielding precursor metabolites such as pyruvate. Subsequently, pyruvate is converted into acetyl-CoA, a crucial precursor for the biosynthesis of acetone, butanol, and ethanol. Through a series of enzymatic reactions involving CoA transferases, acidogenic and solventogenic pathways are initiated, leading to the production of acetone, butanol, and ethanol. Notably, the balance between acidogenesis and solventogenesis is pivotal in determining the final product distribution. Acetone, butanol, and ethanol are then excreted from the microbial cells into the fermentation broth, where they accumulate as end products.

Simultaneous to the fermentation process, permeation mass transfer mechanisms govern the transport of molecules, including substrates, products, and by-products, across cell membranes and through the fermentation broth. This process involves the diffusion of molecules from regions of higher concentration to regions of lower concentration, driven by concentration gradients. In ABE fermentation, substrates such as sugars diffuse into microbial cells to sustain metabolic activity, while products such as acetone, butanol, and ethanol diffuse out of the cells into the fermentation broth, where they accumulate. Additionally, by-products and inhibitory compounds may diffuse both within the fermentation broth and across cell membranes, influencing microbial growth and metabolic activity. Importantly, the efficiency of permeation mass transfer is influenced by various factors, including cell membrane permeability, solubility of molecules in the fermentation broth, viscosity of the medium, and agitation intensity. Optimizing these factors is crucial for enhancing fermentation performance and maximizing product yields (Lin et al., 2023a).

Lignocellulose, as a feedstock for ABE fermentation, plays a crucial role in the economics of the process. Recent efforts have shifted towards using second-generation butanol extracted from lignocellulosic biomass sources, including municipal solid waste, agricultural residues, woodlot cuttings, crop residues, and waste Wood (Manna et al., 2023). Lignocellulosic materials are complex matrices consisting of cellulose,

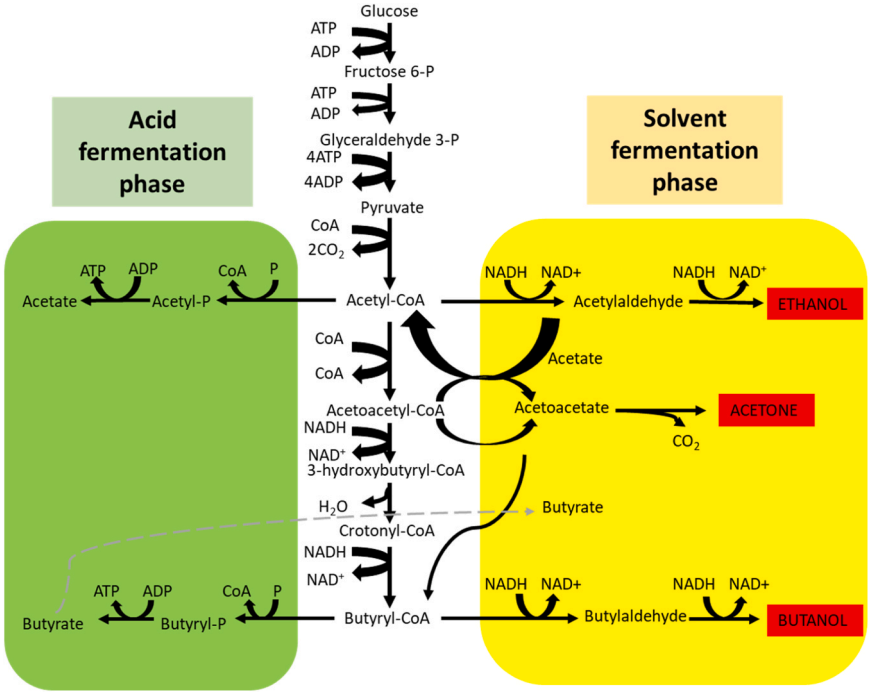

Fig. 1. Primary metabolism of *C. acetobutylicum*. The yellow square indicates acidogenic phase metabolism, and the green rectangle shows the solventogenic phase metabolism (Karimi et al., 2015).

hemicellulose, and lignin. These materials require pretreatment to disrupt the biomass matrix and make carbohydrates accessible to enzymes and microorganisms, followed by hydrolysis to obtain monomeric sugars. Various pretreatment methods, such as steam explosion, alkaline peroxide, alkaline-NaOH, dilute acid, ethanol organosolv pretreatment, and acetone organosolv, have been developed to enhance butanol production from lignocellulosic sources.

ABE fermenting microorganisms are susceptible to inhibitors present in lignocellulose hydrolysates, including hydroxymethylfurfural (HMF), furfural, and lignin derivatives. These inhibitors significantly affect both clostridium growth and ABE yield. Therefore, it is essential to choose pretreatment methods that minimize inhibitor generation, as high inhibitor concentrations require additional detoxification processes, leading to chemical consumption, sugar loss, and reduced product yield. Careful selection and optimization of pretreatment processes are imperative (Saeed et al., 2023).

The fermentation stage in ABE (Acetone-Butanol-Ethanol) fermentation represents the key nexus where various factors converge to influence the efficiency and success of butanol production. Within this intricate process, an array of condition factors intricately interplay to determine the overall yield, purity, and economic viability of butanol synthesis. Delving deeper into the complexities of fermentation, it becomes evident that several key elements warrant thorough examination and optimization to maximize production efficiency.

The microbial strains employed in ABE fermentation play a fundamental role in dictating process outcomes. Selecting robust and high-yielding strains from the Clostridium genus, capable of efficiently converting sugars into desired end products, is crucial. Factors such as strain specificity, metabolic pathways, and tolerance to fermentation conditions profoundly influence microbial performance and butanol productivity. Strain engineering and genetic modification techniques offer promising avenues for enhancing strain characteristics and optimizing fermentation outcomes (Veza et al., 2021b).

In the same way, the fermentation environment itself serves as a critical determinant of process efficiency. Parameters such as pH, temperature, oxygen availability, and nutrient concentrations exert significant influence on microbial growth kinetics, metabolic flux, and product selectivity. Achieving optimal conditions that promote high cell densities, metabolic activity, and butanol synthesis while minimizing undesirable by-products and metabolic inefficiencies is paramount. Advanced process monitoring and control strategies, coupled with computational modeling and optimization techniques, facilitate the precise manipulation and regulation of fermentation parameters to enhance butanol production (Azambuja & Goldbeck, 2020).

Furthermore, the composition and availability of substrates represent key considerations in ABE fermentation. The type and concentration of fermentable sugars present in the feedstock directly impact microbial growth and butanol synthesis rates. Balancing the carbon-to-nitrogen ratio, optimizing substrate utilization, and mitigating the inhibitory effects of certain substrates or by-products are essential for maximizing fermentation efficiency. Exploring diverse feedstock sources, including lignocellulosic biomass, agricultural residues, and industrial waste streams, offers opportunities to expand substrate options and enhance process sustainability.

Additionally, the management of fermentation by-products and by-product inhibition presents significant challenges in ABE fermentation. Acetone, ethanol, organic acids, and other metabolites generated during fermentation can accumulate and inhibit microbial activity, thereby reducing butanol yields and productivity. Implementing strategies such as in-situ product removal, metabolic engineering, and solvent-tolerant strains mitigate by-product inhibition and enhance overall process performance (Pinto et al., 2021).

Thus, optimizing fermentation conditions and parameters is essential for maximizing butanol production efficiency in ABE fermentation. By elucidating the intricate interactions between microbial physiology, environmental factors, substrate characteristics, and process dynamics, researchers can develop innovative strategies to enhance fermentation performance, advance process sustainability, and unlock the full potential of ABE fermentation as a viable route for butanol production (Shanmugam et al., 2021).

4.1. Inhibition in ABE fermentation

One of the primary difficulties of ABE fermentation is low butanol yield due to considerable production of many components as final products or by-products and intermediate components, which may have inhibitory effects on the microorganisms' performance. In this section, the main inhibitions during the ABE fermentation process are examined.

4.1.1. Product inhibition

4.1.1.1. Acid stress. As shown in Fig. 1, ABE fermentation process initiates with the acidogenic phase during the exponential growth period. In this stage, some acetic acid and butyric acid are generated from glucose. The production of these two acids leads to a decline in pH during batch cultivation. Consequently, poor pH control inhibits the metabolic pathway, commonly known as acidic stress. This stress arises from the rapid production of acids, surpassing their consumption by the cells (Karimi et al., 2015).

4.1.1.2. Solvent stress. Following the acidogenesis phase, fermentation directs the products to the solventogenic phase. In this phase, acetic acid can convert into either ethanol or acetone, while butanol is produced from butyric acid. Finally, *C. acetobutylicum* converts all of them into acetone, butanol, and ethanol in a ratio of 1:6:3, respectively. These generated solvents exhibit toxicity to the cells, with approximately 50 % inhibition of cell growth observed at 11, 51, and 84 g/l concentrations for butanol, ethanol, and acetone, respectively. Notably, butanol demonstrates significant toxicity to the cells. The inhibitory impacts of these solvents are recognized as solvent stress (Karimi et al., 2015).

4.1.2. Substrate inhibition

High substrate concentrations, which serve as the carbon source for fermentation, have an inhibitory effect on microbial activity because they can produce a high amount of butanol exceeding 10 g/L, which exerts significant inhibitory impacts on butanol production (Plaza et al., 2020; Chen et al., 2013). It has been reported in various works (Qureshi et al., 2001; Ounine et al., 1985; Sommer et al., 2013).

4.1.3. Toxic Compounds inhibition

Generally, in ABE process, bacteria are very sensitive to the fermentation conditions and compositions. Some by-products or impurities in the feedstock or fermentation broth can be toxic to the bacteria, affecting their growth and productivity.

It has been reported that minor amounts of oxygen have the potential to halt microorganisms' activity entirely, and certain chemicals in small amounts can influence the distribution of products (Choi et al., 2012; Han et al., 2013). For instance, a small quantity of zinc, such as 0.001 g/L ZnSO4.7H2O, can change product distribution by shifting to the solventogenic phase earlier (Wu et al., 2013).

4.2. Batch fermentation

Batch fermentation is a widely adopted mode in ABE (acetone-butanol-ethanol) fermentation processes, primarily owing to its straightforwardness and operational simplicity. In this operational mode, the complete fermentation process occurs within a sealed system with a predetermined initial culture medium volume. The typical duration of batch fermentation spans a range of 2–6 days, contingent on multiple factors encompassing specific environmental conditions and the nature of the substrate employed. A key constraint inherent to batch

fermentation is the progressive accumulation of butanol, which can reach toxic concentrations, culminating in the cessation of fermentation. Managing this butanol toxicity necessitates vigilant monitoring of its levels and often calls for the implementation of supplementary medium additions or other mitigation strategies (de Brito Bezerra et al., 2023).

Additionally, the periodic requirement for downtime during batch fermentation, primarily for equipment cleaning and sterilization, can have a direct impact on productivity and yield, introducing potential inefficiencies into the process (Lin et al., 2023b). As a result, there is an ongoing emphasis on improving batch fermentation methodologies to address the challenges related to butanol toxicity and process interruptions, aiming to enhance the overall efficiency and performance of ABE fermentation processes.

Advantages:

- Simplicity: Batch fermentation is straightforward to set up and operate, making it a preferred choice for small-scale and initial laboratory experiments.
- Reduced Risk of Contamination: Since batch fermentations are contained within a closed system with a fixed initial volume, there's less risk of external contamination.
- Lower Capital Costs: The equipment required for batch fermentation is often less complex and expensive than continuous systems.

Challenges:

- Lag Phase: Batch fermentation typically begins with a lag phase, a period of slow or no growth while the microorganisms adapt to their environment. This phase can delay the onset of solvent production.
- Product Inhibition: A major drawback of batch fermentation is the accumulation of the solvents, especially butanol, which can become toxic to the microorganisms. This inhibits further fermentation and necessitates additional strategies to mitigate toxicity.
- Downtime: Batch fermentation requires downtime for cleaning and sterilization between cycles, reducing the overall productivity.

4.3. Fed-batch fermentation

Fed-batch fermentation stands out as an exceptionally advantageous strategy in industrial biotechnology and fermentation processes, particularly when grappling with the toxicity associated with high substrate concentrations. This approach is pivotal in scenarios where the survival and performance of the microbial culture are paramount. The process commences in a conventional batch mode, utilizing an initial substrate concentration that has been carefully calibrated not to inhibit culture growth, ensuring a healthy outset. Moreover, the initial medium volume is maintained at reduced levels, optimizing resource utilization.

As the fermentation progresses, a key technique is implemented: the continuous and controlled addition of a concentrated substrate solution. This allows for the substrate concentration in the fermenter to be kept below toxic levels for the microbial culture. This control is especially vital in the case of toxic substrates like butanol, where keeping toxicity levels in check is crucial for extending the fermentation process, resulting in an extended production of the desired product and superior yields. However, it is imperative to recognize that fed-batch fermentation is not without its challenges. One of the most prominent challenges is that of product recovery. As the fermentation period is extended, efficient product recovery techniques need to be developed to enable the separation and purification of the desired product from the fermentation broth at the end of the process (Vamsi Krishna et al., 2022).This step is critical to ensuring product quality and purity. In an effort to further optimize this approach, fed-batch fermentation systems incorporating pH control have been explored. This ensures that the pH in the fermenter remains at optimal levels throughout, which is particularly relevant in the case of microbial cultures sensitive to acidity or alkalinity. Recent research, such as the study conducted by (Liu et al., 2022b), has demonstrated that this strategy can significantly accelerate lactic acid assimilation and boost productivity, underscoring how precise control of environmental factors can enhance the efficiency of fed-batch fermentation. In summary, fed-batch fermentation is a strategic technique that addresses substrate toxicity and allows for extended fermentation and increased yield. Despite its challenges, its capacity to produce substantial quantities of valuable products makes it an essential tool in biotechnology and the fermentation industry.

Advantages:

- Controlled Substrate Addition: Fed-batch fermentation overcomes the limitations of batch fermentation by introducing substrate (typically sugars) continuously or intermittently during the fermentation process. This controlled addition helps maintain optimal substrate levels without inhibiting the culture.
- Extended Fermentation Time: Fed-batch systems allow for longer fermentation periods, which can result in higher solvent yields and improved productivity compared to traditional batch fermentations.
- Reduced Product Inhibition: Since substrate is added incrementally, the accumulation of inhibitory products like butanol is minimized, allowing the fermentation to continue.

Challenges:

- Complexity: Fed-batch systems are more complex to set up and operate than batch systems. They require precise control and monitoring of substrate addition rates and conditions.
- Product Recovery: Continuous substrate addition requires efficient product recovery systems to prevent the loss of valuable solvents and maintain optimal conditions.
- Potential for Contamination: The longer fermentation times in fed-batch systems can increase the risk of contamination, necessitating stringent aseptic practices.

4.4. Continuous fermentation

Continuous fermentation is known for its potential to achieve high productivity and is characterized by maintaining the culture at its highest instantaneous value over an extended period. It offers the advantage of preventing non-productive downtime, a common characteristic of batch fermentation. The process begins in a batch mode, allowing the cells to reach exponential growth. In continuous fermentation, the culture never enters the stationary phase due to butanol toxicity. As the cells remain in the exponential phase, the reactor is supplied continuously with medium, and a product stream is simultaneously removed at a controlled flow rate. However, continuous ABE fermentation has a notable drawback – instability (Shariat Panahi et al., 2023). There are primarily two types of instability: metabolic oscillations and a long-term drift toward acid production, referred to as "degeneration." The first type is triggered by product inhibition, and the second results from high dilution rates. Continuous cultivations are typically conducted at low dilution rates to avoid these issues, which may not be economically favorable for product recovery. To address these challenges, multi-stage continuous fermentation systems have been developed, enabling separate bioreactors for growth, acid production, and solvent production (Raspolli Galletti et al., 2023). These systems help reduce fluctuations and increase solvent concentration, resulting in higher product yields.

Advantages:

- Steady-State Operation: Continuous fermentation allows for steady-state operation, where fresh medium is continuously added, and a product stream is simultaneously removed. This leads to consistent and stable conditions, minimizing downtime and maximizing productivity.

- High Productivity: Continuous fermentation systems can achieve higher productivities compared to batch and fed-batch modes due to the constant production of solvents.
- Optimized Metabolism: Continuous systems can maintain microorganisms in the exponential growth phase, optimizing metabolic activity and product formation.

Challenges:

- Instability: Continuous fermentation can face challenges related to stability, including metabolic oscillations and a shift toward acid production ("degeneration"). These issues can impact product quality and require careful control and monitoring.
- Product Recovery: Efficient product recovery systems are essential for continuous fermentation to avoid the loss of solvents and maintain the desired product concentrations.
- Complexity: Continuous systems are more complex to design and operate, requiring precise control of flow rates and environmental conditions.

The choice of fermentation mode in ABE production depends on various factors, including the scale of operation, the desired product yield, and the availability of resources. Batch fermentation is suitable for small-scale and research purposes, while fed-batch and continuous fermentation offer improved efficiency, productivity, and yield, albeit with increased complexity and the need for robust control and recovery systems (Segovia-Hernandez et al., 2022; Tekin et al., 2023). Selecting the appropriate fermentation mode is a crucial decision in optimizing ABE production for both laboratory and industrial applications.

5. ABE separation and purification

The separation of an ABE (Acetone-Butanol-Ethanol) effluent from fermentation poses several significant challenges from a thermodynamic perspective. Firstly, the mixture consists of multiple components with varying chemical properties, particularly in terms of boiling points and vapor pressures. Acetone, butanol, and ethanol each have distinct boiling points and vapor pressures, complicating the separation process.

Secondly, the presence of an azeotrope within the ABE mixture further complicates separation. Azeotropes are points at which the vapor phase composition matches that of the liquid phase, resulting in difficulties in achieving complete separation through conventional distillation methods. In the case of ABE fermentation, the formation of an azeotrope could lead to incomplete separation of the desired products.

Additionally, the relative volatilities of the components influence the separation efficiency. While acetone, butanol, and ethanol each have different volatilities, the presence of an azeotrope may alter the expected behavior during distillation. For instance, butanol's higher volatility compared to water is exploited in fermentation enhancement techniques such as gas stripping. However, the presence of an azeotrope complicates the separation process by limiting the achievable purity of the individual components.

Moreover, the thermodynamic behavior of the mixture, including factors such as temperature and pressure, also affects separation efficiency. The choice of operating conditions, such as temperature and pressure during distillation, must be carefully optimized to minimize energy consumption and maximize separation efficiency (Azambuja & Goldbeck, 2020).

Thus, the separation of an ABE effluent from fermentation presents significant challenges from a thermodynamic perspective due to the complex interplay of multiple components, the presence of an azeotrope, and the influence of operating conditions on separation efficiency. Addressing these challenges requires a thorough understanding of the thermodynamic properties of the mixture and careful optimization of separation processes.

The separation and purification of butanol from an ABE (Acetone-Butanol-Ethanol) fermentation effluent is a crucial step in the production of biofuels and biochemicals. Approximately, 14 % of the total production cost of biobutanol is related to separation and purification processes, and also, the equipment related to this part covers 80 % of the initial investment cost (Veza et al., 2021a). In some cases, separation can be performed within the same vessel where the ABE fermentation takes place. For example, the use of gas stripping within the fermenter can help remove butanol as it is produced. This method minimizes the need for additional equipment but can be challenging due to potential interference with the fermentation process and difficulty in achieving high purity in many situations, it is more common to perform separation in a dedicated unit separate from the fermentation vessel. This approach allows for better control of the separation process and the use of various separation techniques to achieve higher purity. The energy requirements of different methods of ABE separation reported by Goerlitz et al. are illustrated in Fig. 2 (Goerlitz et al., 2018). The second recovery mode, referred to herein as 'end-of-pipe,' recovers ABE after the fermentation has essentially reached completion. This works presents the review of this approach highlighting several alternatives, and its challenges and opportunities.

5.1. Distillation

One of the challenges that can occur during the distillation is water–organic azeotropic formation. A heterogeneous azeotrope between water and n-butanol occurs in 91.7–92.4 C and 38 %wt of water, and a homogeneous azeotrope between water and ethanol occurs in 78.1 C and 4.4 %wt of water (Kujawska et al., 2015). Due to the low concentration of butanol and its high boiling point, convectional distillation is required high energy demand and is not recommended due to economic considerations. The energy required for n-butanol recovery is 14.7–79.5 MJ/kg. Still, process optimization can reduce the energy required to about 20 MJ/kg, although the energy content of butanol is 36 MJ/kg (Hietaharju et al., 2020; Kujawska et al., 2015). Distillation is commonly used in conjunction with other methods.

Roffler et al. (Roffler et al., 1987) described the conventional butanol fermentation that produces 13.7 g/L butanol, 5.4 g/L acetone, and 1.5 g/L ethanol. In this process (Fig. 3), ABE is heated to 100 C, removed from the broth, and then goes to the beer stripper column. The vapor that is going out of the overhead of the beer stripper contains approximately 70 wt% water and 30 wt% ABE. It's going to the acetone column that works in a 0.7 atm and ethanol column that works in a 0.3 atm, and finally acetone and ethanol separate with 99.5 and 95 wt% purity, respectively. After that, the ethanol column's bottom product is mixed with the overheated stream of water stripper and is going to a decanter divided into two parts: water-rich and butanol-rich phases. Finally, in the last column, butanol stripper, butanol with a purity of 99.7 wt%, is obtained.

A slight increase in the concentration of butanol in the beer can cause positive changes in the distillation unit's energy requirement. Mariano et al. (2012a) reported that butanol recovery by flash fermentation and distillation requires 17 MJ/kg butanol and suggested a flash fermentation process that has reduced 39 % of energy consumption for butanol recovery with the conventional batch process. In this process (Fig. 4), the bioreactor worked at atmospheric pressure, and broth continuously circulated to a vacuum chamber and separated into acetone, n-butanol, and ethanol.

One of the alternatives of conventional recovery methods is using in-situ product recovery to decrease recovery costs. Grisales Díaz et al. (2020) represented an optimized process flow diagram with MATLAB® and Aspen Plus® for producing ABE, as shown in Fig. 5. In this study, to reduce energy requirement and increase productivity, they used tanks in-series for fermentation and vacuum evaporation for in situ product recovery. In this optimized process, the energy requirements for recovery and purification are just about 7MJ kg-1 butanol.

To produce ABE from corn stover. To have an optimal process, they

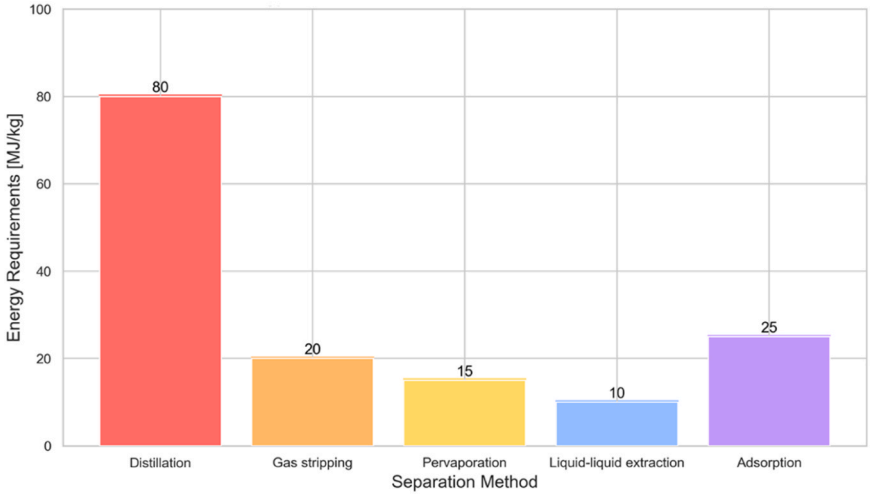

Fig. 2. The energy required in each ABE separation method. As represented, distillation requires the most energy and absorption the least.

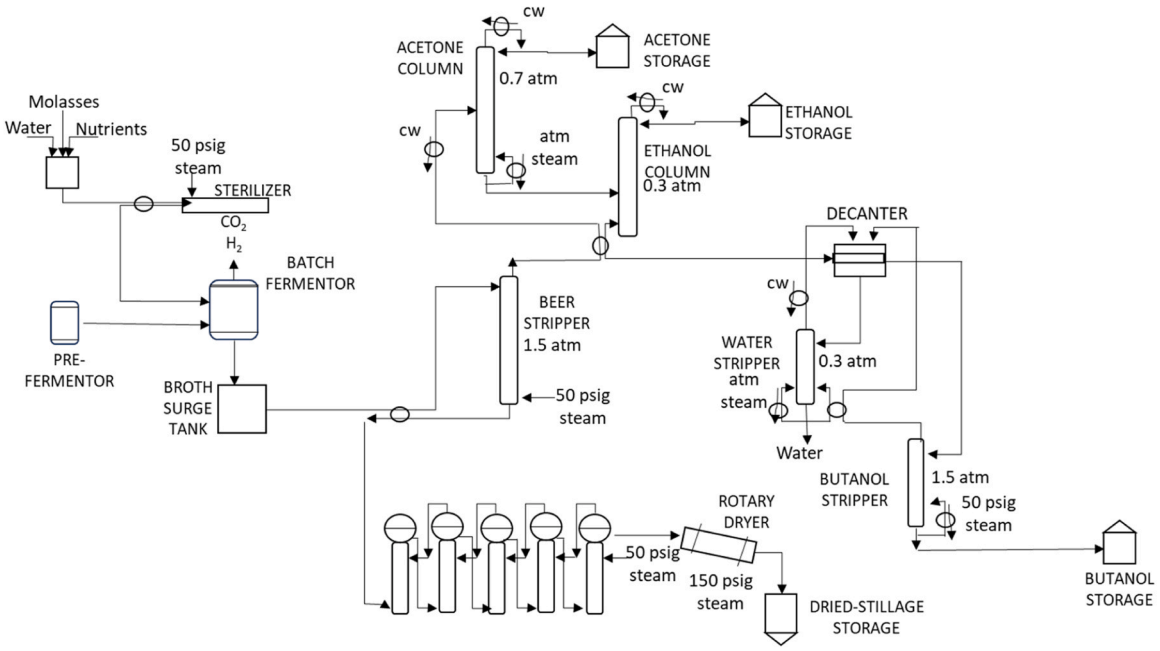

Fig. 3. schematic of the batch fermentation process suggested by Roffler et al. (Roffler et al., 1987).

used tanks-in-series with 5 or 6 reactors and used in-situ product recovery by vacuum evaporation. In this process, CS is a stripping column. C1s columns are used to recover ABE from the vinasses. C2 and C3 are used for purification, C2 for acetone and ethanol, and C3 for butanol.

One of the strategies to reduce the energy requirements of distillation is process integration for distillation. Still, integrated distillation systems need higher investment than conventional distillation systems, so we need some techno-economic analysis to decide using this way or not. However, there are some ways to achieve this: internal heat integrated distillation columns, vapor compression distillation, dividing wall columns, double-effect distillation, and cyclic distillation. For this purpose, Grisales Diaz et al. evaluated four heat integrated distillation systems and demonstrated that a process with three distillation columns with vapor compression (illustrated in Fig. 6) has the lowest energy requirement with fuel requirements of 7.3 MJ fuel/Kg-ABE (Grisales Diaz & Olivar Tost, 2018).

In summary:

Challenges:

- Azeotropes: One of the major challenges in using distillation for biobutanol separation is the formation of azeotropic mixtures with other components like water or ethanol. These azeotropes can make it difficult to achieve high-purity biobutanol through simple distillation.
- Energy Intensity: Distillation is known to be energy-intensive, especially when dealing with mixtures like ABE fermentation effluents. High heat requirements for vaporization and condensation can result in substantial energy costs.
- Thermal Sensitivity: Biobutanol is thermally sensitive and can degrade at high temperatures. Traditional distillation may risk product degradation, which can reduce yield and quality.
- Capital Costs: The installation and maintenance of distillation columns can be capital-intensive, making them less favorable in situations where cost-effectiveness is a primary concern.
- Environmental Impact: High energy consumption in distillation can result in a higher carbon footprint, which may not align with the sustainability goals of biofuel production.

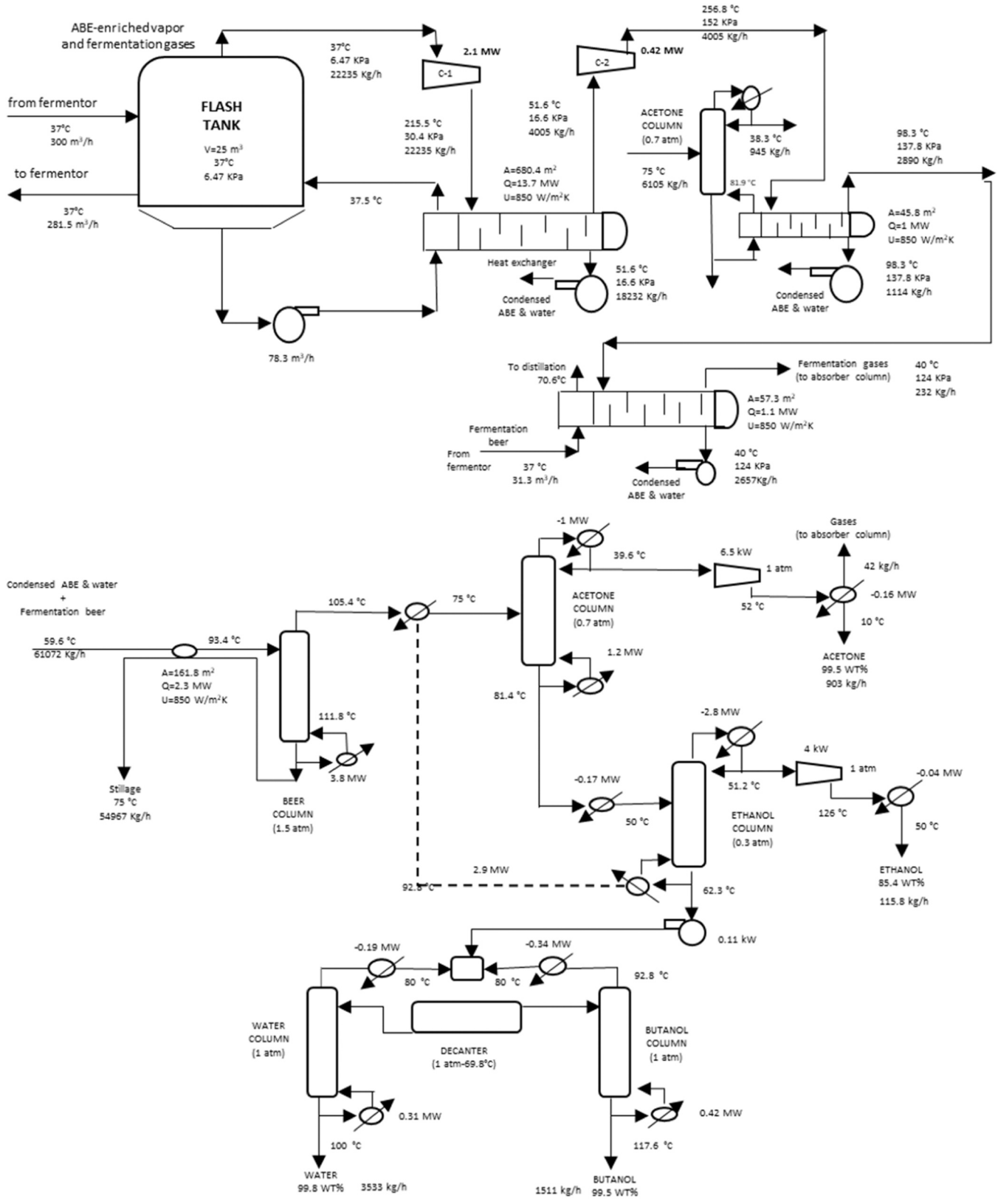

Fig. 4. A) heat integration scheme B) Downstream distillation unit suggested by Mariano et al. (2012b).

Opportunities:

- High Separation Efficiency: Distillation can offer high separation efficiency, especially when applied as a multistage process. This allows for the removal of impurities and the concentration of biobutanol.

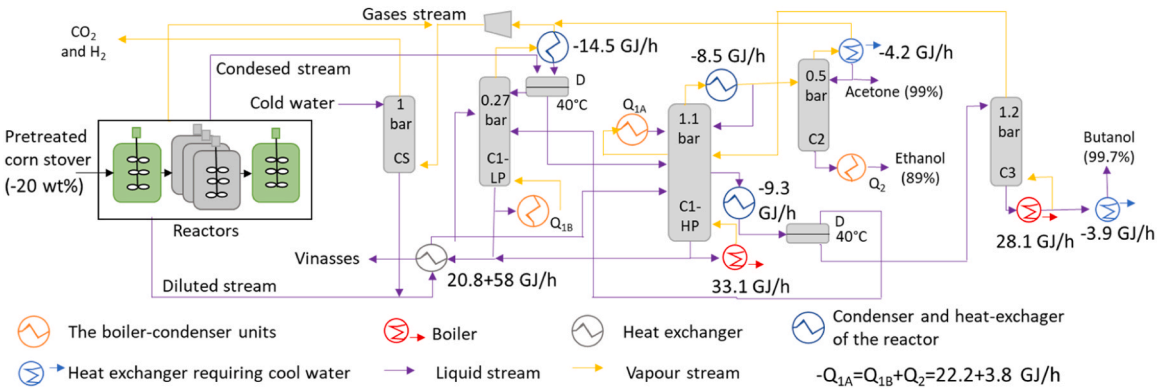

Fig. 5. ABE process suggested by Grisales Díaz et al. (Mariano et al., 2012b).

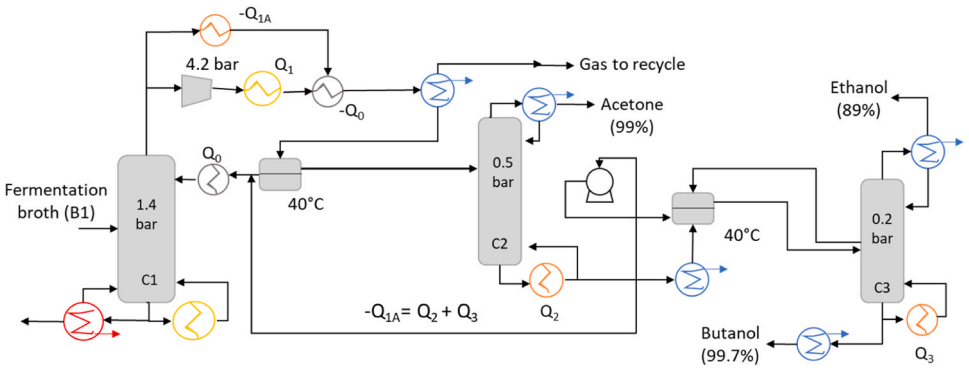

Fig. 6. In this process, acetone and ethanol were obtained in the top stage of the first column (C1). The vapor flow that exhausts the top of C1 is split into two streams. To reduce the compression work, one of them is compressed and another one is not. Acetone was obtained from the top of the C2 column. Ethanol and butanol were obtained from the top and bottom of the C3 column, respectively.

- Scalability: Distillation columns can be adapted to different production scales, from small-scale laboratory setups to industrial production facilities.
- Process Integration: Distillation can be integrated with other separation techniques, such as azeotrope breakers or additional columns, to improve separation efficiency and purity.
- Advanced Distillation Techniques: Advanced distillation techniques, such as extractive distillation or pressure swing distillation, are being developed to enhance separation efficiency and reduce energy consumption, addressing some of the challenges associated with traditional distillation.
- Waste Minimization: Distillation can help recover valuable by-products or recycle solvents in the biofuel production process, reducing waste and increasing sustainability.
- Operational Control: Modern distillation systems can be equipped with advanced process control and automation technology to optimize energy efficiency and maintain product quality.

So, while distillation columns are a well-established and effective separation method for biofuel production, they do come with challenges, particularly related to energy consumption and capital costs. However, with ongoing research and innovation, opportunities exist to mitigate these challenges, improve the energy efficiency of distillation, and enhance its environmental sustainability. Distillation remains a critical component in the biofuel industry, and its role continues to evolve as technology advances and sustainability requirements become more stringent.

5.2. *Liquid-liquid extraction (LLE)*

Initially, the focus of studies on recovering n-butanol through liquid-liquid extraction primarily involved batch fermentation (in situ extraction). Extracting agents were chosen based on their non-toxicity towards the fermentation bacteria. This led to the identification of two main categories of extracting agents: alkanes and alcohols. Alcohols generally exhibited high distribution ratios of butanol ($D > 5$) and moderate selectivities, while alkanes showed high selectivity but lower affinity for butanol ($D < 0.5$) (Kraemer et al., 2011; Matsumura et al., 1988).

Some authors consider oleyl alcohol as the benchmark solvent for butanol due to its favorable density (0.845–0.855 g/cm3), facilitating further separation of the extract from the raffinate. Reported distribution ratios for oleyl alcohol ranged from 3.0 to 4.1. However, one drawback of oleyl alcohol is its limited ability to separate acetone and ethanol, which can result in a high demand for solvent to prevent excessive accumulation of acetone in the fermentation broth (Kraemer et al., 2011).

Other solvents that have been tested for recovering biobutanol include glyceryl tributyrate, modified plant oils such as methylated crude palm oil, biodiesel, gasoline, decyl alcohol, mesitylene, n-hexyl acetate, surfactants, and ionic liquids (W. Chen et al., 2014; Evans & Wang, 1988; Ishii et al., 1985; Sánchez-Ramírez et al., 2015).

(A. Kurkijärvi et al., 2014) conducted a study on the extraction of ABE fermentation products using non-biocompatible solvents (1-heptanol, 1-octanol, and 1-decanol) in a dual extraction process with solvent regeneration. They found that the distribution coefficients for butanol recovery, determined at a temperature of 37 °C, were 11.26, 9.95, and 7.17 for 1-heptanol, 1-octanol, and 1-decanol, respectively. The authors suggested that this method could reduce the energy consumption of ABE

fermentation product recovery to less than 4 MJ kg-1. In another study by A.J. Kurkijärvi & Lehtonen (2014), a dual extraction method was described, which involved using petrol components as extraction solvents for ABE fermentation. This method utilized two extraction columns: the first column employed non-biocompatible solvents to effectively extract ABE products, while the second column was used to remove traces of the toxic solvent from the broth, making it biocompatible. After the extractions, the fermentation broth was recycled back to the reactor, allowing the reuse of unfermented nutrients, reaction intermediates, and remaining products. Immobilization and filtration steps were implemented in the process to prevent the migration of microbes to the extraction column. The authors claimed that the product mixture obtained from this process (ABE removed from the broth and extractants) could be used as a petrol additive without requiring additional purification steps. Simulation results indicated that ETBE and MTBE were the most effective solvents for butanol recovery, followed by TAME and TAEE. However, the concentration of ABE in the final product was low (7.6 kg of butanol in 477.4 kg total product, less than 16 g kg-1). Stoffers and Gorak (Stoffers et al., 2013) investigated the efficiency of butanol recovery using an ionic liquid, specifically 1-hexyl-3 methylimidazolium tetracyanoborate, in a continuous multi-stage extraction process using a mixer-settler unit. They achieved a selectivity of butanol recovery towards water ranging from 48 to 89, with a distribution coefficient for the tested system ranging from 5.2 to 6.5. They also proposed an extraction model based on NRTL parameters derived from experimental data on ternary mixtures. The results suggested that an equilibrium approach in the multi-stage extraction model could sufficiently capture the efficiency of individual stages without the need for separate modeling. Compared to other separation techniques, direct extraction offers high extractant capacity and selectivity for separating n-butanol from water. However, a drawback of this method in fermentation product recovery is the formation of emulsions and fouling of the extractant, which can lead to difficulties in phase separation and significant contamination of aqueous streams with chemicals (Groot et al., 1990).

Butanol purification by liquid-liquid extraction has been reported in multiple papers. It should be noted that most of the reported works refer to a posteriori separation, even extractions combined with some other unitary operation.

In 1988 Dadgar et al., considering economic issues, suggested a process flow diagram [Fig. 8] that combined distillation and solvent extraction for ABE purification. They also chose 2-ethyl-1-hexanol from the properties of 47 solvents (Dadgar & Foutch, 1988).

Sánchez-Ramírez et al. (2015) have analyzed and compared four different possible process designs for the purification of biobutanol production. Process modeling in Aspen Plus was performed, and the optimization was conducted using a differential evolution algorithm. The results indicated that the process consisted of a liquid−liquid equilibrium (LLE) column followed by steam stripping distillation proved to be a profitable design in current economic conditions, which was evaluated trough total annual cost (TAC) calculation (Fig. 7). This alternative process can be employed on an industrial scale to improve the process economics of biobutanol production. In a complementary paper it was shown that the use of a solar collector against steam in order to produce the required heat duty needed in every single distillation column to have a broader view about the environmental and economic impact of these devices (Sánchez-Ramírez et al., 2016).

New alternative hybrid configurations based on liquid–liquid extraction and distillation for biobutanol purification were presented by Errico et al. (2016). The alternatives are designed and optimized minimizing two objective functions: the total annual cost (TAC) as an economical index and the eco-indicator 99 as an environmental function. All the new configurations presented reduced the TAC compared to the traditional hybrid configuration; in particular, a thermally coupled alternative exhibited a 24.5 % reduction of the TAC together with an 11.8 % reduction of the environmental indicator. Also, intensified sequences represented a promising option in the reduction of the TAC, but with some penalty for the eco-indicator.

Sánchez-Ramírez et al. (2015) reported a separation technique based on LLE combined with dividing wall columns using multi-objective optimization. They proposed an optimized scheme considering three important parameters: economic index, environmental function, and control index. The final scheme suggested (Fig. 7) has the lowest total annual cost, the relatively low condition number, and eco-indicator99, among the other schemes (Sánchez-Ramírez et al., 2017).

The work developed by Patraşcu, et al. (2017) focuses on the development of eco-friendly and cost-effective methods for separating butanol in the acetone-butanol-ethanol (ABE) fermentation process. To achieve eco-efficient butanol separation, the authors propose a hybrid separation process that combines liquid-liquid extraction and adsorption. They describe a plant with a capacity of 40,000 tons per year (ktpy) of butanol was considered, with purities of 99.4 % weight for butanol, 99.4 % weight for acetone, and 91.4 % weight for ethanol. The simulation results demonstrated that the optimized process exhibited improved eco-efficiency, with a lower energy consumption of 1.24 kilowatt-hours per kilogram (kWh/kg) of butanol, reduced costs, and emissions.

The work presented by Contreras-Vargas et al. (2019) focuses on exploring different purification methods for separating a blend of butanol and ethanol from a fermentation effluent containing acetone, butanol, and ethanol (ABE). The paper explores various alternatives for purifying the blend of butanol and ethanol, including liquid-liquid extraction, pervaporation, and adsorption. The authors compare the performance of the different purification methods and identify the most promising techniques for obtaining high-purity products.

The control properties of four different intensified process designs for biobutanol purification are analyzed by Angelina-Martínez et al. (2015). The results, using the singular value decomposition technique, indicated that the scheme where only biobutanol flow is purified, and both ethanol and acetone leaving the purification process mixed with water and

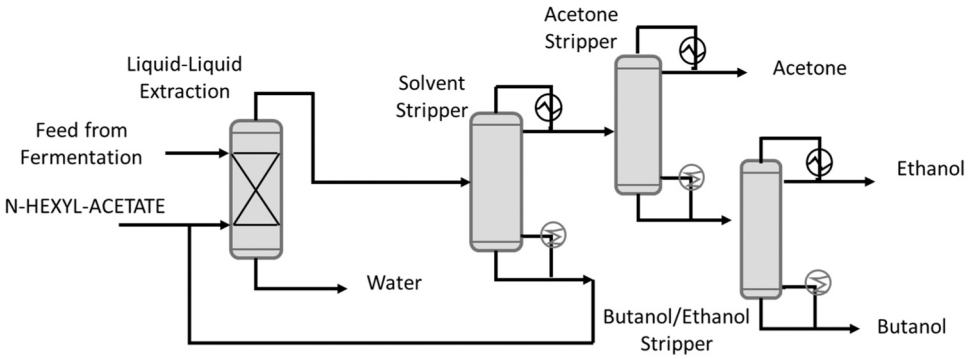

Fig. 7. Best scheme selected with the lowest total annual cost.

biobutanol traces, showed the best control properties

The separation process to produce biobutanol requires a lot of energy and yields lots of waste heat at low temperatures. Therefore, there is a need to propose options to reduce the required energy in the biobutanol separation process. González-Bravo et al. (2016) present an optimization approach for designing energy-integrated biobutanol separation processes. The optimization incorporates attractive separation options such as ABE fermentation using different solvents as well as incorporating several options for waste heat recovery involving integrated heat exchanger networks, stream Rankine cycles, organic Rankine cycles, and absorption refrigeration cycles. The results show significant economic and environmental benefits for the simultaneous consideration of the optimization of the separation process with the waste heat recovery for the biobutanol separation process.

Since biobutanol is produced from ABE fermentation, the process involves several substances that may cause explosion and fire and can lead to negative environmental and health impacts. Hence, it is desirable to incorporate environmental and safety issues in the design to determine the optimal separation structure. In the work by Martinez-Gomez et al. (2016) is presented an optimization strategy for the biobutanol separation process while accounting simultaneously for economic, environmental and safety objectives. The best economic solution involves elevated values of the Eco-Indicator 99, the best environmental solution incurs high costs, and the safest solution features less separation columns. The most compensated solutions include configurations that represent a balance among the economic, environmental and safety objectives.

A controllability analysis, in work by Sánchez-Ramírez et al. (2017) using the singular value decomposition technique and a closed-loop dynamic analysis was performed on several hybrid distillation processes including conventional, thermally coupled, thermodynamically equivalent, and intensified designs for the purification of biobutanol in ABE process (Fig. 8). The results indicated that under the closed-loop control policy, an intensified design which is integrated for only two distillation columns instead of three distillation columns, showed good dynamic behavior.

Using this method can significantly reduce energy consumption relative to distillation. For example, A. Kurkijärvi et al. (2014) proposed a process in which the amount of energy required to recover the product to less than 4 Mj Kg-1.

Flores-Cordero et al. (2022) have evaluated how the degree of intensification and the position of the intensification equipment affect the control behavior in the separation of butanol from ABE mixture. It has been considered due to the thermodynamic complexity of the mixture and the several intensification alternatives that the process can have. On the one hand, the results indicate that the most intensified equipment is not necessarily the best alternative from the operation and control point of view. On the other hand, a strong impact of the location

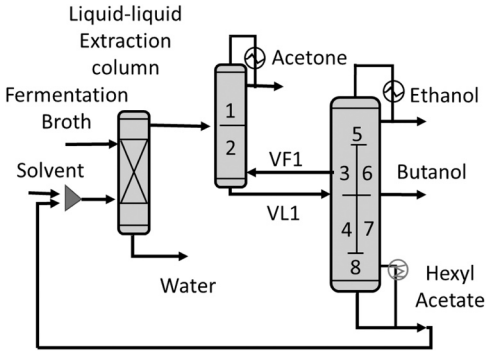

Fig. 8. The best scheme reported by Sánchez-Ramírez et al. was selected by multi-objective optimization with the lowest total annual cost, environmental impact, and condition number (Sánchez-Ramírez et al., 2017).

of the intensified equipment on controllability is observed. The configurations with the intensified equipment at the end of the separation were the alternatives with the best dynamic responses. In summary about using liquid-liquid extraction as a separation alternative:

Challenges:

- Complexity of the Mixture: ABE fermentation effluent, which contains acetone, butanol, and ethanol, can form intricate and highly interactive mixtures. Liquid-liquid extraction may face challenges in selectively separating butanol from this complex mixture due to the presence of azeotropes and other components.
- Solvent Selection: The choice of an appropriate solvent for liquid-liquid extraction is crucial. The solvent must have a high affinity for butanol, butanol selectivity, and the ability to form a two-phase system with the fermentation effluent. Identifying the right solvent can be a time-consuming and resource-intensive task.
- Solvent Recovery: Once butanol is extracted, the solvent needs to be efficiently recovered for reuse. Solvent recovery processes can add complexity and operational costs to the separation process.
- Maintenance and Fouling: Liquid-liquid extraction columns may be prone to fouling and require maintenance, particularly if the feedstock contains impurities or solid particles.
- Environmental Concerns: The choice of solvent for liquid-liquid extraction can impact the environmental sustainability of the process. Some solvents may be hazardous or ecologically harmful.

Opportunities:

- Selective Separation: Liquid-liquid extraction is well-suited for selective separation due to its ability to exploit differences in solubility between components. When properly designed, it can achieve high butanol purity.
- Azeotrope Breaking: Liquid-liquid extraction can effectively break azeotropes or deal with challenging separations, such as those encountered in ABE fermentation effluents.
- Integration with Fermentation: Liquid-liquid extraction can be integrated into the fermentation process, allowing for in-situ separation. This can lead to higher butanol yields and reduced energy consumption compared to standalone processes.
- Solvent Recycling: Efficient solvent recovery processes can help reduce the operational costs associated with liquid-liquid extraction, as recovered solvents can be reused.
- Process Optimization: Advances in process modeling and simulation tools allow for the optimization of liquid-liquid extraction systems to maximize separation efficiency and minimize energy consumption.
- Sustainability: Environmentally friendly solvents, such as ionic liquids or bio-based solvents, can be used in liquid-liquid extraction to enhance the sustainability of the separation process.
- Scalability: Liquid-liquid extraction systems can be scaled to accommodate different production volumes, making them suitable for various biobutanol production scales.

5.3. *Gas stripping*

Gas stripping is a separation process used in the purification of biobutanol, a valuable biofuel derived from ABE (Acetone-Butanol-Ethanol) fermentation. This technique relies on the principle that butanol and other volatile components can be selectively removed from a liquid mixture by passing a stripping gas, typically nitrogen or steam, through the solution. The volatile components are carried away with the stripping gas, leaving behind a more concentrated and purified biobutanol solution.

Challenges of Using Gas Stripping for Biobutanol Separation:

- Azeotropes: ABE fermentation effluents often form azeotropic mixtures with water or other components. Gas stripping may not be

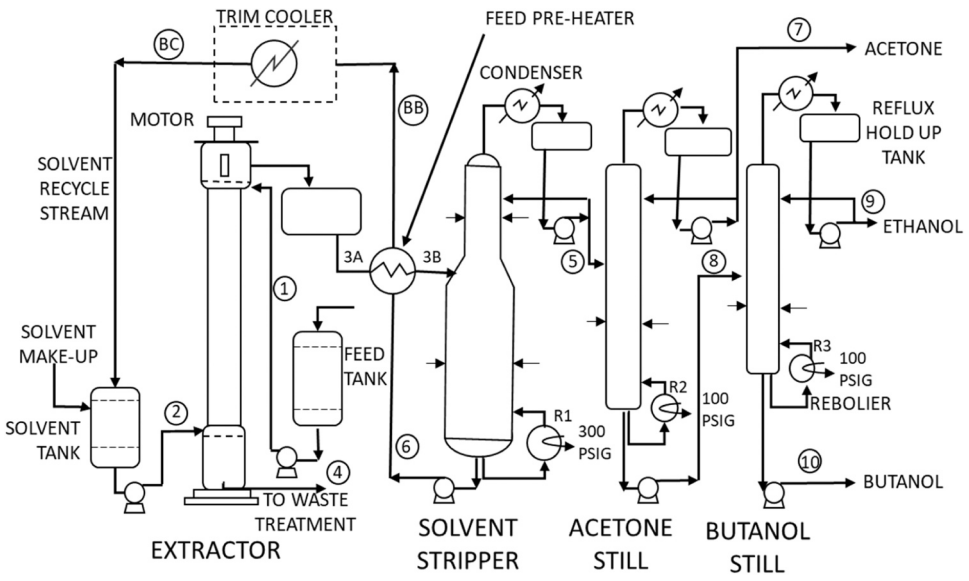

Fig. 9. In this process, the fermentation broth is sent into an extractor column, removing the existing water to reduce the energy required for distillation. The solvent stripper, and feeds entered a, and feeds are entered on plate 11. Finally, acetone separated in the acetone still column, ethanol and butanol in butanol still column (Dadgar & Foutch, 1988).

effective in breaking these azeotropes, and additional separation steps or techniques may be required.

- Energy Consumption: While gas stripping is generally considered more energy-efficient than distillation, it still requires energy to heat the solution and the stripping gas. Optimizing the process to reduce energy consumption is a challenge.
- Solvent Recovery: Gas stripping generates a vapor phase containing butanol and impurities. Recovering the butanol and returning the stripping gas for reuse can be technically challenging and may add to the operational complexity.
- High-Temperature Sensitivity: Biobutanol is sensitive to high temperatures, and excessive heat during gas stripping can lead to product degradation, affecting yield and quality.

Opportunities of Using Gas Stripping for Biobutanol Separation:

- Selective Separation: Gas stripping allows for selective separation of butanol, as it takes advantage of differences in volatility between butanol and other components in the ABE fermentation effluent.
- Lower Energy Consumption: Compared to traditional distillation, gas stripping generally requires less energy, making it a more energy-efficient option for biobutanol purification.
- Process Integration: Gas stripping can be integrated with other separation techniques, such as condensation or adsorption, to enhance separation efficiency and purity.
- Scalability: Gas stripping systems can be adapted to different production scales, from small laboratory setups to large industrial facilities.
- Environmental Sustainability: Gas stripping with the appropriate solvent choice can be environmentally friendly, especially when compared to energy-intensive separation methods.
- Process Optimization: Advances in process control and automation can optimize gas stripping, reducing energy consumption and improving product quality.

Thus, gas stripping is a valuable technique for purifying biobutanol by selectively removing volatile components. While it presents challenges such as azeotropes, energy consumption, and solvent recovery, it offers opportunities for selective separation, lower energy use, and integration with other separation methods. Proper process design and optimization are essential to maximize the efficiency and sustainability of gas stripping in biobutanol production. Regarding this separation, Taylor et al. represented a process flow diagram and concluded that recycling part of continuous fermentation content to a stripping column reduces production inhibition (Taylor et al., 1995).

5.4. Adsorption

Adsorption is a separation process that can be employed to separate biobutanol from complex mixtures, such as ABE (Acetone-Butanol-Ethanol) fermentation effluents. The principle of adsorption relies on the selective retention of specific components from a liquid mixture onto a solid adsorbent material.

Column Configurations for Biobutanol Adsorption:

Adsorption columns used for biobutanol separation typically consist of a packed bed of solid adsorbent material. There are two common column configurations for this purpose, Fixed-Bed Column and Simulated Moving Bed (SMB) Columns. In the Fixed-Bed Column, the solid adsorbent is packed into a cylindrical column, and the biobutanol-containing solution is passed through the column. The biobutanol is selectively adsorbed onto the solid adsorbent, while other components pass through. Once the adsorption capacity is reached, the column is typically regenerated by desorbing the biobutanol for recovery. On the other hand, Simulated Moving Bed (SMB) Column is a continuous chromatography technique that is increasingly used for biobutanol separation. It consists of multiple zones with adsorption and desorption sections. As the feed solution is continuously introduced into the column, different zones move in a coordinated manner, allowing for continuous separation and regeneration, resulting in higher productivity. The choice of adsorbent material is critical for the success of the adsorption process. Adsorbents used for biobutanol separation should exhibit high selectivity for butanol and good adsorption capacity. Currently, there are some adsorbents that have been used for bobutanol putification. For example, Activated carbon is a versatile adsorbent with a large surface area that can effectively adsorb butanol from aqueous solutions. It is readily available and cost-effective. Silica gel is another widely used adsorbent for biobutanol separation. It offers good selectivity and capacity for butanol. Ion exchange resins and various polymer-based resins can be tailored to specific separation tasks. They offer high selectivity and are particularly useful when a highly pure

butanol product is required. On the other hand Metal-Organic Frameworks (MOFs): MOFs are a class of porous materials with tunable properties. Specific MOFs have shown promise in selectively adsorbing butanol from fermentation effluents (Ezeji et al., 2007; S. Y. Lee et al., 2008; Zhang et al., 2010). Below, we highlight some challenges and opportunities in using adsorption for biobutanol purification:

Challenges:

- Adsorbent Selection: Choosing the right adsorbent material with high selectivity for butanol can be challenging. The adsorbent should ideally have a high adsorption capacity for butanol while excluding other components present in the fermentation effluent.
- Regeneration: Regenerating the adsorbent to recover the adsorbed butanol and allow for its reuse is a critical aspect of the adsorption process. Finding effective and environmentally friendly regeneration methods can be challenging.
- Competitive Adsorption: In ABE fermentation effluents, there are often multiple components, including acetone and ethanol, which can compete with butanol for adsorption sites on the adsorbent. Achieving high selectivity for butanol in the presence of these competitive adsorbates can be difficult.
- Scale-Up: Transitioning from laboratory-scale adsorption experiments to large-scale industrial applications can be challenging. Ensuring consistent and efficient adsorption under different scales requires careful engineering and process design.

Opportunities:

- Selective Separation: Adsorption allows for the selective separation of butanol from complex mixtures. By choosing or developing the right adsorbent, it is possible to achieve high selectivity and purity in the final biobutanol product.
- Process Optimization: Advances in process modeling and optimization tools enable the design of efficient adsorption processes. This includes optimizing operating conditions, flow rates, and regeneration cycles.
- Integration with Other Processes: Adsorption can be integrated with other separation techniques, such as distillation or membrane filtration, to create hybrid processes that enhance overall separation efficiency.
- Environmentally Friendly Adsorbents: Research is ongoing to develop environmentally friendly and sustainable adsorbents, including bio-based materials and metal-organic frameworks (MOFs), which may offer improved selectivity and capacity.
- Waste Reduction: Adsorption can help reduce waste and by-product generation by efficiently capturing butanol from fermentation effluents. This aligns with sustainability goals in biofuel production.
- Continuous Processes: Continuous chromatographic processes like the Simulated Moving Bed (SMB) offer opportunities for high productivity, making biobutanol separation more efficient.
- Resource Efficiency: Adsorption processes can often operate at milder conditions compared to distillation, resulting in lower energy consumption and reduced thermal degradation of the biobutanol product.

5.5. Pertraction

Pertraction can be described as a membrane-based liquid-liquid extraction that uses a porous membrane between two liquids' surfaces. In this process, the membrane is placed between extracting liquid (fermentation broth) and extractant. Some of the commonly used extractants are oleyl alcohol, polypropylene glycol, tributyrin, dibutylphthalate, 1-octanol, isopropyl-myristate,1-dodecanol, and 2-ethyl-1-hexanol. Thanks to a membrane's presence in this process and no direct contact between phases, there are no more liquid-liquid extraction problems. Still, there are other problems such as high-cost membrane production, clogging, and membrane fouling. Some of the widely used membranes are silicon, neoprene, latex, hydrophobic and hydrophilic membranes. The diffusion rate of butanol controls the total butanol transfer; thus, choosing the proper membrane is important. Membranes should also facilitate the transfer of butanol to the organic phase. Another important feature of this system is selective diffusion, which allows the system to extract the butanol alone from the fermentation broth (Bharathiraja et al., 2017; Kujawska et al., 2015). Below, are some challenges and opportunities of using pertraction for biobutanol purification.

Challenges:

- Solvent Selection: The choice of an appropriate solvent for pertraction is crucial. The solvent should have a high affinity for biobutanol, be immiscible with water, and exhibit good separation selectivity. Finding the ideal solvent can be a complex task.
- Azeotropes and Co-Solvents: ABE fermentation effluents often form azeotropic mixtures and may contain co-solvents. These complexities can interfere with the extraction process and require specialized solvent systems.
- Solvent Recovery: Efficient solvent recovery and recycle processes are needed to minimize the consumption of the extraction solvent and to ensure economic feasibility.
- Emulsion Formation: During pertraction, the formation of stable emulsions can be problematic. Emulsions can hinder the separation process and require additional demulsification steps.
- Energy Consumption: Pertraction may require energy for mixing, phase separation, and solvent recovery, which can affect the overall energy efficiency of the process.

Opportunities:

- Selective Separation: Pertraction offers the potential for highly selective extraction of biobutanol from fermentation effluents. Proper choice of solvent and process conditions can result in high purity of the extracted biobutanol.
- Process Integration: Pertraction can be integrated into the ABE fermentation process as an in-situ separation method. This can enhance biobutanol yields and reduce energy consumption compared to post-fermentation separation processes.
- Recyclability: The solvent used in pertraction can often be recycled, reducing the environmental impact and the operating costs associated with solvent consumption.
- Customization: Pertraction processes can be tailored to specific separation tasks, allowing for flexibility and adaptability to various feedstock compositions and process requirements.
- Environmental Sustainability: Depending on the choice of solvent, pertraction can be environmentally friendly, especially when compared to energy-intensive separation methods like distillation.
- Scalability: Pertraction processes can be scaled up or down to accommodate different production volumes, making them suitable for various biobutanol production scales.
- Continuous Operation: Pertraction can be designed for continuous operation, increasing process efficiency and productivity.

5.6. Pervaporation

Pervaporation is a membrane-based, simple, single-step separation, multipurpose unit operation, energy-efficient, clean end-product, and commercially competitive method used to remove components by partial vaporization through a membrane selectively (Arregoitia-Sarabia et al., 2022). In the fermentation process, organic components in the fermentation broth go into the vapor phase and remove based on the membrane's selectivity and diffusion rate. After that, it is recovered by condensation.

Integrating Batch fermentation and evaporation can reach 32.8 g/L

in ABE solvent, but coupling fed-batch fermentation to pervaporation can reach the concentration of 165.1 g/L (Bharathiraja et al., 2017).

For the first time, Cai et al. performed the two-stage pervaporation to decrease the ABE recovery cost. They used polydimethylsiloxane/ polyvinylidene fluoride (PDMS/PVDF) as the membrane. In this study, the final product cost using the two-stage hybrid in-situ product recovery decreased sharply. The final product containing 451.98 g/L of butanol, which was 41 times higher than butanol, exists in the fermentation broth (Cai et al., 2017). In the same manner than other separation alternatives, here are presented some challenges and opportunities:

Challenges:

- Membrane Selection: Choosing the right membrane material is a critical challenge. The membrane should be highly selective for biobutanol, and it should have the necessary permeability. Finding a membrane that can withstand the chemical and thermal conditions in ABE fermentation effluents is essential.
- Membrane Fouling: Membrane fouling can occur when the feed solution contains impurities that adhere to the membrane surface, reducing separation efficiency. This requires the development of anti-fouling membranes or effective fouling mitigation strategies.
- Azeotropes: ABE fermentation effluents often form azeotropic mixtures, making it challenging to achieve high purity separation of biobutanol through pervaporation. Selective removal of biobutanol from azeotropic mixtures is a challenge.
- Energy Consumption: Pervaporation may require energy to maintain the necessary temperature and vacuum conditions for effective separation, potentially impacting overall energy efficiency.

Opportunities:

- High Selectivity: Pervaporation offers the potential for highly selective separation of biobutanol from other components in the fermentation effluent. Proper membrane selection and process conditions can result in high-purity biobutanol.
- Energy Efficiency: Pervaporation can be more energy-efficient than traditional separation processes like distillation, especially for the removal of volatile components like butanol.
- Environmentally Friendly: Depending on the choice of membrane material, pervaporation can be an environmentally friendly separation method, particularly when compared to energy-intensive processes.
- Waste Reduction: Pervaporation can help reduce waste generation and streamline the biobutanol purification process by efficiently capturing and concentrating the target compound.
- Continuous Operation: Pervaporation can be designed for continuous operation, increasing process efficiency and productivity.
- Process Integration: Pervaporation can be integrated into the ABE fermentation process, allowing for in-situ separation. This can enhance biobutanol yields and reduce energy consumption compared to post-fermentation separation processes.
- Scalability: Pervaporation processes can be adapted to different production volumes, making them suitable for various biobutanol production scales.

5.7. Reverse osmosis

Reverse osmosis (RO) is a separation process that can be employed to separate biobutanol from complex mixtures, such as ABE (Acetone-Butanol-Ethanol) fermentation effluents. RO relies on a semi-permeable membrane that allows the passage of water while rejecting solutes and non-water components. RO for biobutanol separation typically involves the following configurations. For example, Spiral-Wound Membrane Modules are common in industrial applications. They consist of flat-sheet RO membranes wound around a perforated tube. This configuration allows for compact, efficient, and cost-effective operation. Other, Tubular Membrane Modules are used in specific cases, often for large-scale applications. In this setup, RO membranes are arranged in tubular form to facilitate high-flow rates and easy cleaning. Similarly, Plate and Frame Modules consist of RO membranes placed between plates and frames. While this configuration is less common in biobutanol separation, it may be suitable for specific applications. The choice of RO membrane material is critical for the success of the separation process. In the context of biobutanol separation, membranes should possess the following characteristics:

High Permeability to Water: The membrane should allow water to pass through while rejecting non-water components, including biobutanol.

High Selectivity for Biobutanol: The membrane should selectively reject biobutanol and other components in the fermentation effluent.

Chemical and Thermal Stability: The membrane should be stable in the chemical and thermal conditions encountered in ABE fermentation effluents.

Resistance to Fouling: Membrane fouling can occur due to impurities in the feed solution. Membranes should resist fouling or be easy to clean.

Membrane materials that can be considered for biobutanol separation include polymeric materials such as polyamide (PA), polyethersulfone (PES), and cellulose acetate, as well as ceramic materials in certain applications (Ezeji et al., 2007).

In the same way than other separation alternatives, here we present some challenges and opportunities about this separation alternative:

Challenges:

- Membrane Fouling: The fouling of RO membranes is a significant challenge, particularly when dealing with complex feed solutions like ABE fermentation effluents. Impurities, microorganisms, and solids in the feed can accumulate on the membrane surface, reducing permeate flux and requiring frequent cleaning.
- High Operating Pressure: RO typically requires high operating pressures to force water through the membrane. This can result in increased energy consumption, which may be a challenge, especially for large-scale industrial applications.
- Azeotropes and ABE Components: ABE fermentation effluents often contain azeotropic mixtures, which can complicate the separation process. Achieving selective separation of biobutanol from other ABE components and breaking azeotropes can be challenging.
- Membrane Material Compatibility: The choice of membrane material is crucial. The membrane should be compatible with the chemical and thermal conditions of the ABE fermentation effluents and should be resistant to degradation.

Opportunities:

- Selective Separation: RO offers the potential for selective separation of biobutanol, particularly when appropriately designed membranes are employed. This can lead to high-purity biobutanol products.
- Energy Efficiency: While RO does require energy to operate, it can be more energy-efficient than traditional separation methods, such as distillation. Advances in membrane technology and process optimization can further enhance energy efficiency.
- Waste Reduction: RO can help reduce waste generation by efficiently capturing biobutanol and other valuable components while allowing non-desired components to be concentrated and managed separately.
- Environmental Sustainability: Depending on the choice of membrane material and energy source, RO can be environmentally friendly and align with sustainability goals in biofuel production.
- Process Integration: RO can be integrated into the ABE fermentation process as an in-situ separation method. This integration can enhance biobutanol yields and reduce energy consumption compared to post-fermentation separation processes.

- Continuous Operation: RO can be designed for continuous operation, increasing process efficiency and productivity.
- Customization: RO processes can be tailored to specific separation tasks, allowing for flexibility and adaptability to various feedstock compositions and process requirements.

6. Hybrid butanol recovery processes

Because of the butanol's high inherent inhibiting effect during fermentation, one-stage separation techniques such as gas stripping, liquid-liquid extraction, adsorption, and pervaporation are not enough selectivity for butanol purification (Xue et al., 2017). Regarding water-butanol/ethanol azeotrope heterogeneity, sequence distillation towers or strippers are also essential for the successive purification of acetone, butanol, and ethanol. Consequently, hybrid technologies in rational design are required for *in situ* recovery of ABE fermentation products, with the object of energy savings and optimizing fermentation titers and productivity. Single technologies of separation have their limitations. The gas stripping method, for example, is known for its relatively low butanol selectivity and low butanol flux. Only low stripping gas flow rates can be used to prevent foaming. In situ extraction of 1-butanol is an effective technology. However, biocompatible solvents used in the extraction have equilibrium constants < 5 toward butanol (Lu & Li, 2014). Hydrophobic pervaporation has higher butanol selectivity (25–40). However, its butanol flux is low.

By coupling different single separation technologies, the overall system product recovery will be boosted. It is anticipated that the removal of butanol via *in situ* mode would dramatically boost the efficiency of the bioreactor and enable the use of more concentrated substrate solutions.

6.1. Gas stripping and pervaporation

The benefit of using in situ gas stripping before pervaporation is that salts, cell debris, and other fermentation media elements are not found in condensate stripping (Sarchami et al., 2016).

Gas stripping and pervaporation have been incorporated as a hybrid method for processing ABE fed-batch fermentation. Gas stripping is performed in situ for the recovery of butanol from the fermentation broth, and pervaporation is performed as an *ex-situ* process for the recovery of butanol from the gas stripping output source (Cai et al., 2015; Xue et al., 2016).

For the first time, Xue et al. evaluated a hybrid in-situ gas stripping-pervaporation to purify butanol from ABE fermentation. They used gas stripping (Fig. 10) to reduce butanol toxicity by continually removing it from the fermentation broth at butanol concentration above 8 g/L and performing pervaporation with the CNTs-PDMS MMM to increase the condensation of butanol. The final product mixture achieved 500 g/L butanol; also, it's an energy-efficient process. CNTs-PDMS MMM used in this process had a very efficient performance (Fig. 10) (Xue et al., 2016).

Nazemi Ashani et al. simulated a coupled gas stripping and pervaporation as a separate unit and reported a significant impact on the plant's energy requirements (Ashani et al., 2020).

6.2. Extraction-gas stripping

A promising integrated in-situ extraction-gas stripping has been reported. A biocompatible non-volatile solvent oleyl alcohol, with a high partition coefficient towards butanol was used as the *in situ* extractant t and nitrogen was used for gas stripping during ABE fermentation. Initially butanol was extracted with oleyl alcohol, and subsequently, after 48 hours of fermentation, gas stripping was initiated to remove butanol from the oleyl alcohol phase (Fig. 11) (Lu et al., 2016; Lu & Li, 2014). One advantage of the in-situ extraction-gas stripping process is that butanol is constantly extracted with nitrogen in the oleyl alcoholic step. Only a limited amount of oleyl alcohol is required without being saturated with butanol during ABE fermentation (Li et al., 2016).

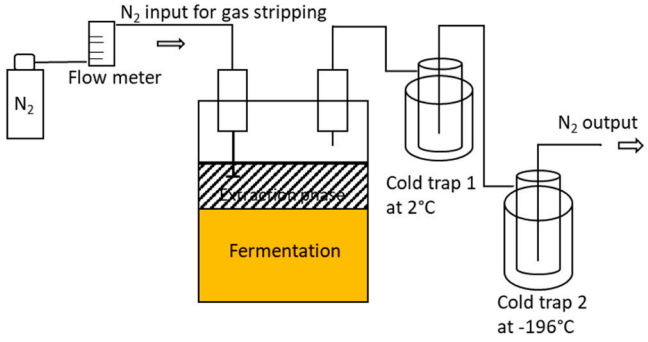

Fig. 11. Schematic of the ABE fermentation process coupled with the in situ integrated extraction-gas stripping technique.

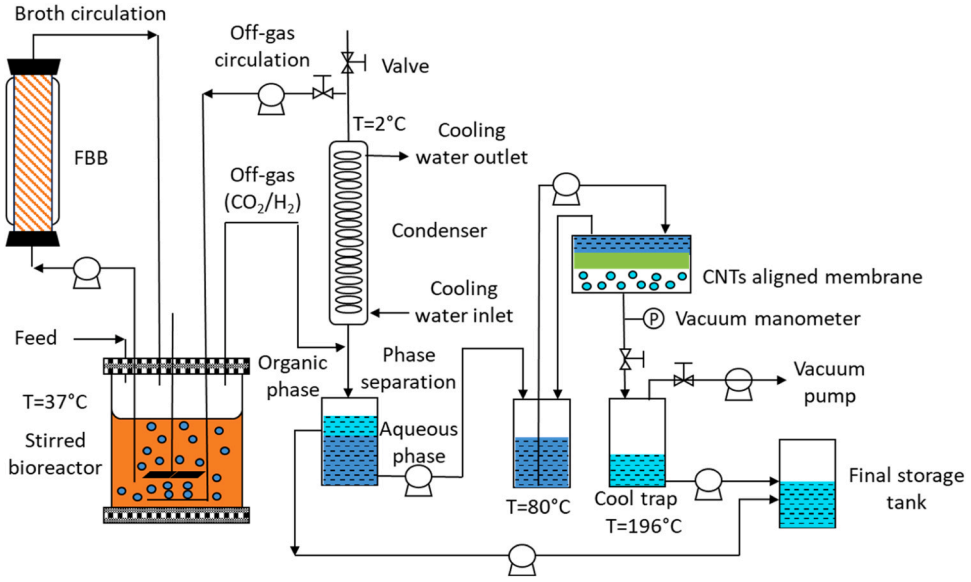

Fig. 10. The process suggested by Xue et al. in that they coupled gas stripping with the pervaporation process.

Meanwhile, as butanol is removed from the non-volatile oleyl alcohol process, butanol selectivity during gas stripping can be effective.

The appealing aspect of the integrated extracting gas removal process is its versatility with regard to the process design so that it is implemented during continuous ABE fermentation using immobilized cells (Li et al., 2016). As bacterial strains are immobilized on the packing bed, liquid-state oleyl alcohol stream extract produced butanol inside the packed bed. Oleyl alcohol-containing butanol can be subsequently regenerated by gas stripping so that it can be recycled back into the packed bed. As shown in Fig. 12, the designed procedure was carried out that a high glucose consumption of 52 g L^{-1} and a high yield of 0.21 g-butanol g-glucose^{-1} was obtained (W.R. Wang et al., 2016).

6.3. Gas stripping—gas permeation

Vane and Alvarez (Vane et al., 2013) proposed an experimental hybrid in-situ system including vapor stripping, vapor compression, and a vapor permeation membrane separation - termed 'membrane assisted vapor stripping' (MAVS). In the MAVS system, a liquid stream containing a solvent–water mixture is fed into the top of a vapor stripping column (Sarchami et al., 2016; Vane et al., 2013). The solvent was stripped from the water, and the overhead vapor leaving the column mainly contains solvent relative to the feed liquid because of favorable vapor-liquid equilibria (VLE). The overhead vapor is then compressed, and the higher-pressure vapor is fed to a vapor permeation module with a hydrophilic membrane (Vane et al., 2013). In this regard, water passes through the membrane while solvents are rejected. The water-rich permeate vapor is returned to the stripping column, which is a large portion of the stripping vapor. The solvent-enriched vapor, is at a sufficiently high pressure to condense against the column reboiler (Fig. 12).(Fig. 13)

6.4. Two-stage gas stripping

According to an assessment by Oudshoorn et al. (2009), the selectivity of gas stripping for butanol with the value of 4–22 is lower than distillation with an estimated selectivity of 72, so the recovered solvent is not concentrated enough. It has been proposed that using two-phase gas stripping could be advantageous to achieve substantial decreases in the energy used for downstream purification (Outram et al., 2017). In this context, Xue et al. (2013) proposed a two-stage gas stripping process coupled with ABE fed-batch fermentation. The first stage removed ABE

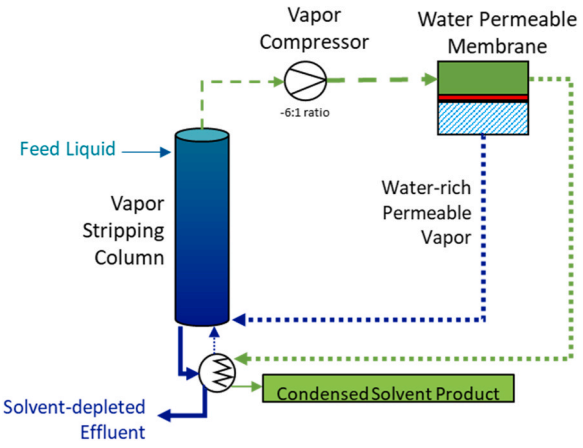

Fig. 13. Schematic diagram of the membrane-assisted vapor stripping (MAVS) hybrid process including steam stripping and vapor permeation. Adopted from [118].

in situ from the fermenter and the second stage concentrated the aqueous portion of the condensate from the first stage. The first-stage condensate contained 153 g ABE/L, while the second-stage condensate contained 447 g ABE/L (Xue et al., 2013). The first stage reduced inhibition in the fermenter, while the second stage increased condensate concentration. As the first stage is used to reduce the butanol inhibition in the fermenter, the second stage increases the condensate concentration.

Hybrid processes combine multiple separation techniques to enhance the efficiency and effectiveness of biobutanol separation from complex mixtures, such as ABE (Acetone-Butanol-Ethanol) fermentation effluents. These combinations can lead to unique challenges and opportunities. Here, we explore some of the key aspects of using hybrid processes for biobutanol separation:

Challenges:

- Process Integration: Coordinating the operation of multiple separation techniques within a hybrid process can be complex. Ensuring seamless integration and the efficient transfer of intermediate streams between units is a challenge.
- Energy Consumption: The energy requirements of hybrid processes can be significant, especially if the combined techniques involve

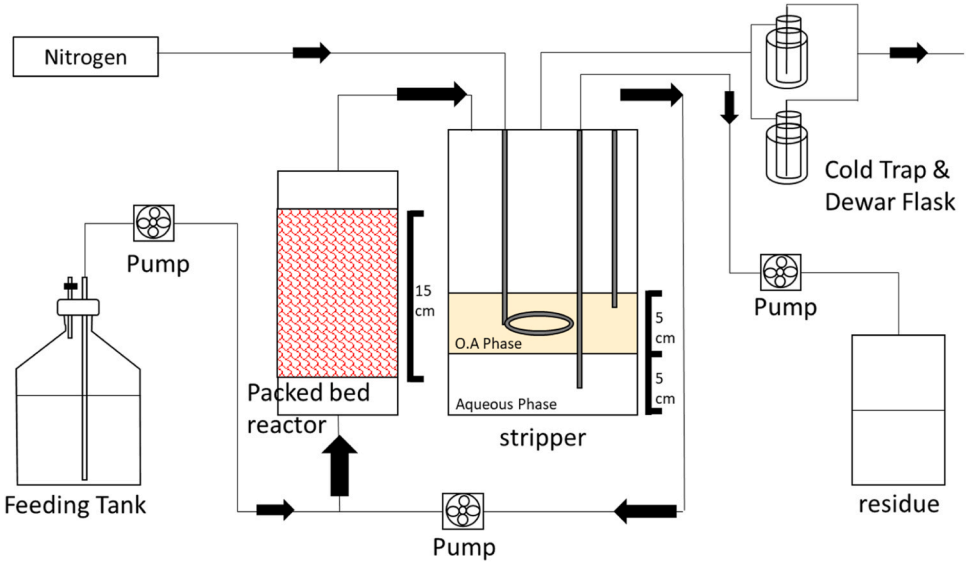

Fig. 12. Schematic of the integrated extraction-gas stripping process used in the immobilized cells-based continuous fermentation.

energy-intensive operations like distillation or evaporation. Managing energy costs while maintaining process efficiency is a key challenge.
- Waste Management: Hybrid processes may generate additional by-products or waste streams that need to be managed. Proper waste treatment and disposal can be a challenge, particularly for environmentally sustainable processes.
- Equipment Costs: The use of multiple separation units can lead to higher capital costs, making the implementation of hybrid processes financially demanding. Cost-effectiveness remains a critical challenge.

Opportunities:

- Enhanced Separation Efficiency: Hybrid processes offer the potential for more efficient separation of biobutanol from ABE fermentation effluents. Combining complementary techniques can lead to higher separation selectivity and purity.
- Energy Efficiency: While hybrid processes may have higher energy consumption, they can be designed to optimize energy usage and recover waste heat or energy from one unit to power another, improving overall energy efficiency.
- Waste Minimization: By judiciously selecting and integrating separation techniques, hybrid processes can help minimize waste generation and allow for the recovery of valuable by-products, aligning with sustainability goals.
- Selectivity and Azeotrope Breaking: Hybrid processes can address the challenges of azeotropes and competitive components in the ABE mixture. Combining techniques such as gas stripping and distillation can effectively break azeotropes.
- Process Flexibility: Hybrid processes can be tailored to specific feedstock compositions and separation goals, providing flexibility for different biobutanol production scales and scenarios.
- Continuous Operation: Some hybrid processes can be designed for continuous operation, which enhances process productivity and reduces downtime.
- Environmental Sustainability: The selection of environmentally friendly separation techniques and solvents can make hybrid processes more sustainable and align with green and clean biofuel production objectives.

7. Sustainable supply chains in the production of biobutanol

Sustainable supply chains play a crucial role in biobutanol production, as they ensure that this biofuel is sourced responsibly and environmentally friendly. The relevance and importance of these chains lie in several key aspects. Firstly, they promote the selection and use of renewable raw materials with low environmental impact for the production of biobutanol, such as residual biomass and sustainable energy crops. This helps reduce pressure on natural resources and prevent deforestation and ecosystem degradation. In addition, sustainable supply chains encourage responsible agricultural and forestry practices, including proper waste management and the adoption of more efficient and less polluting production techniques. These practices help mitigate greenhouse gas emissions and other negative impacts associated with biobutanol production. Furthermore, sustainable supply chains promote transparency, traceability and certification of products, allowing consumers and businesses to make informed decisions and support responsible production.

Quiroz-Ramírez et al. (2017) have simulated and optimized under a rigorous scheme an integrated process to produce acetone, butanol, and ethanol from lignocellulosic biomass. In this work a hybrid simultaneous system of saccharification-fermentation-separation to address the challenges faced in ABE fermentation is proposed, such as low concentration broths and inhibitory effects. The aim is to limit the production of inhibition products during both fermentation and enzymatic hydrolysis. To achieve this, a liquid-liquid extraction step is chosen as the recovery technique. The reactor was modeled and simulated using Matlab software, while Aspen Plus simulated the separation step. The optimization process considered various objective targets, including total annual cost and bioindexes related to fermentation, such as productivity, yield, and butanol concentration. The results identified a feasible operational zone where all objective targets were successfully met without compromising the goal of improving the biobutanol production process.

In the paper by Quiroz-Ramírez et al. (2017), a multiobjective optimization approach is presented to achieve the optimal planning of butanol production. This approach considers the selection of feedstock and the appropriate ratio of fermentable sugars as key factors. The multiobjective methodology is applied throughout both the fermentation and purification processes of butanol. The optimization problem aims to minimize the total annual cost and environmental impact as objective functions. The economic objective function takes into account factors such as bioresource availability, feedstock costs, fermentation conditions, and separation units. The environmental assessment considers the overall impact using the eco-indicator 99, which relies on a life cycle analysis methodology. These objective functions are applied to a case study for optimal planning in biobutanol production in Mexico. Through the optimization process, a set of solutions is generated, represented by a Pareto curve that identifies a range of optimal solutions for both objectives. Considering the best compromise between targets, the optimal solution involves initially using a raw material with a moderate sugar content, followed by a hybrid separation process consisting of a liquid-liquid extraction column and three thermally coupled distillation columns.

Arabi et al. (2019) introduced a mixed integer linear programming (MILP) model in their paper to plan and design a microalgae-based biobutanol supply chain network, with the aim of supporting the growth of the emerging microalgae industry in biofuel production. Microalgae is recognized as a promising feedstock due to its high sugar and oil content. The primary objective of their study was to minimize fixed costs associated with facility construction, transportation, and various operational activities such as harvesting, pretreatment, treatment, and energy conversion. The proposed model comprehensively considers supply, production, and distribution aspects and is designed as a multi-period model to account for temporal dynamics. To tackle uncertainties related to accurately estimating harvested and dried algae volumes, the authors utilized a fuzzy programming approach to handle such variability.

Santibañez-Aguilar et al. (2022) presented a mathematical model for planning a supply chain for the production of acetone, butanol, and ethanol through multiple biomass feedstocks. The proposed model took into account four objective functions related to sustainability dimensions in order to address some of the United Nations Sustainability Development Goals such as: 1.- End poverty in all its forms everywhere because is focused on selected marginalized sites to install the described supply chain and 2.-Ensure access to affordable. Reliable, sustainable, and modern energy for all since the considered supply chain might produce two promising biofuels in the world for the transportation field. The multi-objective approach was addressed by generating several Pareto curves to illustrate the tradeoff between the considered objectives. The maximum reached profit was around $US 13,572 Million per year, which can be obtained with two different pairwise analyses. Nevertheless, if the social benefit is maximized, the profit decreases to $US 6000 Million per year. Therefore, results indicate that the supply chain entity's location has a crucial effect on the social impact.

In summary, sustainable supply chains are essential to ensure the relevance and importance of biobutanol as a viable and environmentally friendly alternative in the current energy landscape.

8. Industrial ABE production plant – a case study

According to Survase et al. (2019) there are only 12 industrial

biobutanol fermentation plants globally, 11 in China and 1 in Brazil. These plants mostly use sugars (molasses) or starch (corn, corn, cassava, sweet potato) as carbon sources.

Herein, biobutanol production from a corn plant is investigated, adapted from the Process Economics Program Reports of SRI, with a conversion capacity of 3.16 million pounds of corn grain per day and an annual production capacity of 187 million pounds of n-butanol. Acetone, ethanol, corn germ, fiber, and gluten are also produced as the process by-products. The n-butanol conceptual plant design consists of three sections: corn milling, fermentation, and solvent recovery.

8.1. Corn milling

As illustrated in Fig. 14, corn grains are held in grain bins, S-102A & B before cleaning. The corn grains are then washed, and the existing impurities are removed by the S-103 equipment. Then the corn enters the T-101 AP steeping tank and is in contact with acidic water at 50 °C. during steeping, and water absorption in corn kernels increases the grain size twice due to the loosening of the gluten layer on the surface of the corn, the starch in the corn is released, and in Grind mill S-105 and S-108 the germs in the corn kernels are separated.

Water is contained in corn particles along with other soluble substances including significant amounts of protein and sugar. Some of these substances are also removed by saturation with lactic fermentation products and bacterial cells. The germ in the slurry produced is separated from the other components by grinding. Corn kernels contain a significant amount of oil. Due to the lower density of oils than water, these oils can be separated using hydro cyclones in S-106 A&B and S-109 A&B. In addition, hydro cyclones remove low-density germs that remain in the sludge. The germs are then pumped to the S-110AC sieve plates to remove gluten and starch so that all available starch returns to the mainstream.

Germs are dehydrated using screw press S-111. To reduce the moisture of microbes up to 2–4 %, they are dried using a rotary steam tube dryer S-112. To remove the fiber and form starch and gluten, the corn-water slurry of the lower outlet of the S-109 cyclones was crushed and sieved. Using S-115, all the components are crushed in the kernel, then in screens S-116A, with the selectivity of fiber to gluten and starch, the starch is separated, and the water is used to wash the fiber to recover more starch and gluten in the mainstream is used.

The obtained fiber is dewatered in two stages: screen centrifuge S-117 (reduction of humidity to 65–75 %) and screw press S-118 (reduction of humidity to 10 %). If steep corn liquor is added to the wet fiber, the mixture is dried in an S-119 dryer to obtain a corn gluten feed. Also, to separate starch and gluten from each other, S-122 and S-123 centrifuges are used to separate the gluten solution because gluten is less dense than starch.

In the final separation step in cyclones S-128A-I, the starch solution removed from the centrifuge is diluted and spun several times to achieve a purity of about 99.5 % starch, resulting in a crude starch slurry with 33–40 % solid content. To Fermentation unit is sent.

8.2. Fermentation

Steepwater and starch slurry are sterilized with E-201 and E-202, respectively, before fermentation. A part of each is sent to seed production. A total of 10 % of the slurry is cut off for seed processing. In fermentation, a hyper-butanol-producing mutation of *Clostridium beijerinckii* is used in the fermentation process. A series of four fermenters are used for cell growth. The seed train is performed in batch mode, with

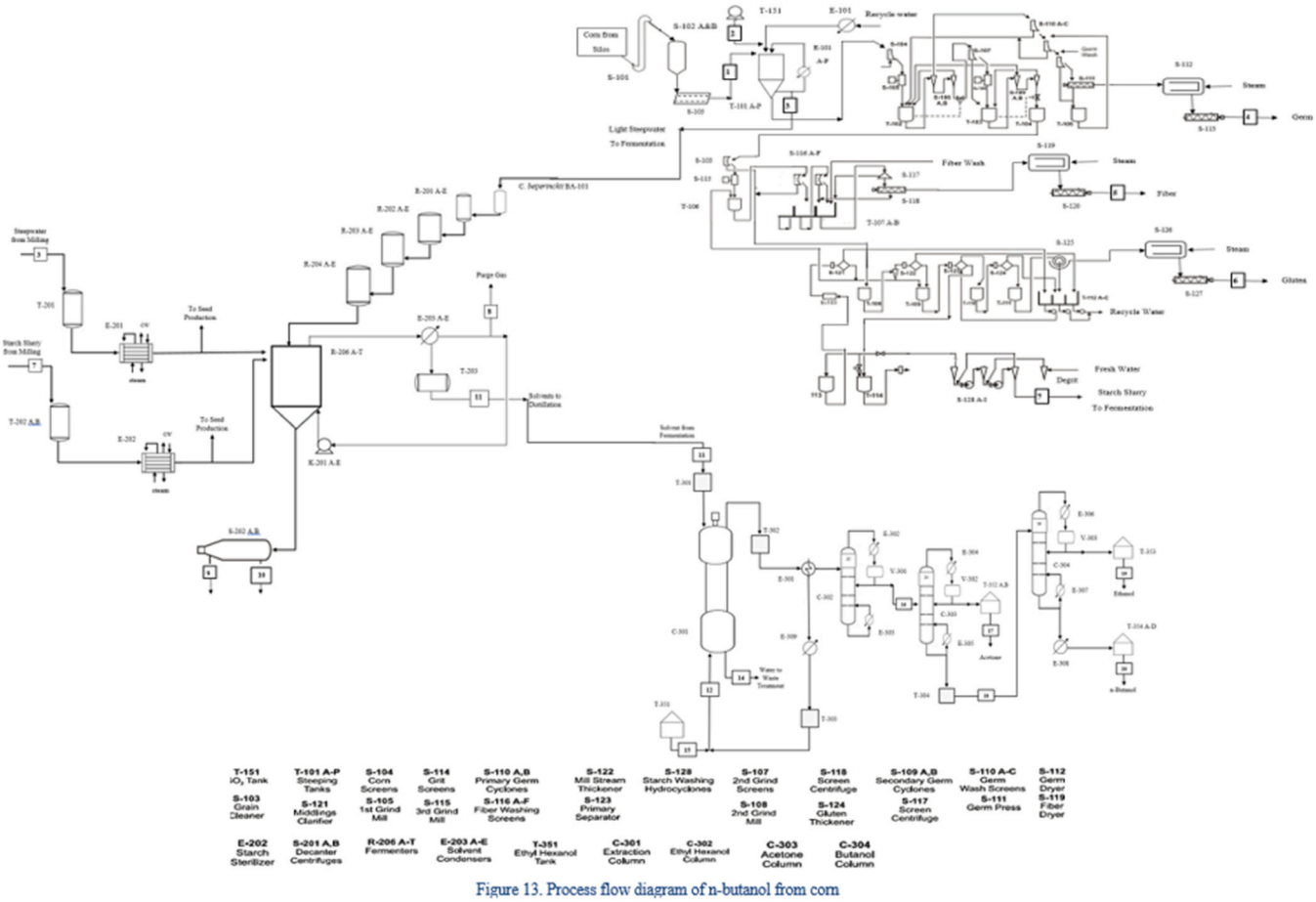

Figure 13. Process flow diagram of n-butanol from corn

Fig. 14. Process flow diagram of n-butanol from corn.

each stage having a batch time of 24 h.

The key fermenters, R206A-T, are used for fed-batch anaerobic fermentation to produce butanol, acetone, and some ethanol which are inoculated with R-204A-E seed broth. The fermentation is carried out anaerobically, with hydrogen/carbon dioxide gas flowing through the fermentors to remove the solvent from the broth. The exhaust gas from the fermentors is vented to condensers, which contain butanol, acetone, and ethanol. T-203 is used to collect diluted solvents.

After finishing the feed-batch process, the fermenter broth is centrifuged using decanter centrifuges S-201A&B. The water is recycled and the cells from the fermentation broth are discarded.

8.3. Solvent recovery

In the solvent recovery stage, individual solvents are recovered from the aqueous mixture of solvents in T-203 through extraction and distillation. The extraction column, C-301, receives the diluted solvent mixture from the fermentation portion and extracts solvents from the aqueous phase into the organic phase. In a sequence of combining and relaxing parts, ethyl hexanol enters C-301 from the bottom and passes up the column, coming into contact with the aqueous process. The raffinate phase containing 99.6 % water exits from the bottom of the column process that exits from the bottom of the column and enters the waste treatment plant. T-302 extracts the extract step, which contains 98.3 % solvent. Via extraction and distillation, individual solvents are extracted from the aqueous mixture of solvents in T-203. C-301 collects the dissolved solvent mixture from the fermentation section and removes solvents from the aqueous phase into the organic phase.

As the stream is fed to C-302, mixed solvents from T-302 are heated to 184°C using interchanger E-301. Ethylhexanol from the bottom of C-302 is recycled to T-303 for use in the extraction column after acting as a heat source for E-301. The acetone column, C-303, absorbs the overhead stream from C-302. Acetone is retrieved as an overhead source from C-303. Before shipment, the solvent is stored offsite in T-352 A&B. The bottom stream from C-303 containing primarily butanol and some ethanol and water is fed to the butanol column C-304. The overhead stream comprises ethanol primarily and is collected in T-353. Butanol with 99.5 % purity leaves the bottom of the column. Butanol is subsequently collected offside in T-354 before shipment.

9. Challenges and opportunities in the biobutanol production process in the context of sustainability

The production of biobutanol from biomass represents a significant opportunity to promote the circular economy, sustainability and the achievement of the objectives of the 2030 Agenda. However, this process is not without challenges that must be addressed to make the most of its potential (García-Franco et al., 2021). Below, we will explore both the challenges and opportunities that this process entails:

9.1. Opportunities

The production of biobutanol from biomass offers a significant opportunity for reducing carbon emissions. This alternative to fossil fuels plays a crucial role in addressing the global challenge of mitigating greenhouse gas emissions, aligning with the Sustainable Development Goals (SDGs) of the 2030 Agenda, particularly SDG 13 (Climate Action).

In addition, biobutanol production contributes to the promotion of a circular economy by using biomass as its feedstock. This approach encourages sustainable resource management, the reuse of organic waste, and responsible consumption and production, thus supporting SDG 12 (Responsible Consumption and Production).

Furthermore, it helps diversify energy sources, reducing dependence on fossil fuels. This diversification enhances energy security and accessibility, a key aspect of SDG 7 (Affordable and Clean Energy).

The production of biomass for biobutanol presents an opportunity for sustainable rural development. It can create economic opportunities in rural areas, addressing poverty and supporting decent work and economic growth, as outlined in SDG 1 (No Poverty) and SDG 8 (Decent Work and Economic Growth).

9.2. Challenges

On the other hand, there are several challenges to address in the production of biobutanol from biomass. Efficiency is a primary concern; improving the efficiency of the production process is crucial. The process can be costlier and less efficient compared to conventional biofuel production methods.

A potential ethical and social concern arises from the competition between biomass production for biobutanol and food production. Striking the right balance between biomass utilization and food security is paramount.

Sustainable management of the biomass used is another significant challenge. Protecting ecosystems, conserving biodiversity, and responsibly managing land and water resources are critical for ensuring minimal adverse environmental impacts.

The establishment of infrastructure for biobutanol production, distribution, and utilization often requires substantial investments. Logistics must also be optimized to ensure a consistent and efficient supply.

Lastly, developing clear and comprehensive regulatory frameworks and standards is crucial to ensure the sustainable and safe production and utilization of biobutanol while meeting societal and environmental requirements.

The production of biobutanol from biomass represents a promising pathway to address critical sustainability challenges in the context of the circular economy and the 2030 Agenda. Its potential to reduce carbon emissions, promote a circular economy, diversify energy sources, and support rural development aligns with various Sustainable Development Goals. However, the journey to fully harness these benefits is not without its hurdles. Enhancing the efficiency of biobutanol production, managing competition with food production, ensuring sustainable biomass practices, addressing infrastructure and logistical challenges, and establishing clear regulatory frameworks are vital areas that require attention (Solarte-Toro et al., 2022).

Effective collaboration among governments, industry stakeholders, and civil society is essential to overcome these challenges and unlock the full potential of biobutanol production from biomass. By doing so, we can move closer to a more sustainable and circular economy, while contributing to the achievement of the SDGs outlined in the 2030 Agenda (Ncube et al., 2023). This synergy between environmental and developmental goals is a testament to the potential of biobutanol in shaping a more sustainable and resilient future.

10. Conclusion

The production of biobutanol from lignocellulosic biomass not only stands as a technologically promising solution to reduce our carbon footprint and enhance sustainability but also poses a rich landscape of challenges and opportunities. At the heart of this endeavor lies the intricate conversion of lignocellulosic feedstocks into biobutanol, which entails a sequence of biochemical processes. While the ultimate goal is to harness this sustainable energy source efficiently, multiple hurdles must be addressed. One formidable challenge is optimizing enzymatic efficiency. Lignocellulosic biomass is composed of complex structures, and breaking down these intricate matrices into their constituent sugars, which can be subsequently fermented into biobutanol, requires the use of enzymes. Enhancing the efficiency of these enzymes to accelerate the hydrolysis of biomass while minimizing costs remains a critical area of research. Another vital aspect is substrate management. The lignocellulosic feedstock used for biobutanol production varies in composition, quality, and accessibility. Strategies for handling this variability and ensuring a consistent and reliable substrate supply are pivotal for the

economic viability of the process. Moreover, chemical inhibitions within the fermentation process can hinder biobutanol production. These inhibitory compounds, often by-products of the biomass pretreatment, can affect the performance of microorganisms used in the fermentation. Overcoming these inhibitions requires innovative bioprocess engineering and strain development. However, these challenges present unique opportunities for innovation. Continuous research in biotechnology, genetic engineering, and process optimization can lead to the development of microbial strains better suited for biobutanol production, as well as the design of more efficient and cost-effective enzyme cocktails. Additionally, a focus on waste management and the reduction of the overall carbon footprint of biobutanol production can lead to more sustainable practices. Utilizing waste streams and developing circular economy principles within the biobutanol production cycle can minimize environmental impact and resource waste. Finally, the production of biobutanol from lignocellulosic biomass holds tremendous potential to contribute to a more sustainable future. By addressing these challenges and capitalizing on the opportunities presented, we can not only harness the benefits of this renewable energy source but also pave the way for more efficient and environmentally responsible processes that align with the principles of sustainability. This endeavor represents a collaborative effort involving academia, industry, and policymakers to drive the transition to a greener and economically viable future.

Declaration of Competing Interest

The corresponding author, Juan-Gabriel Segovia-Hernandez, is an editor for the journal Chemical Engineering Research and Design, but has had no access to, or involvement in, the peer review process for this paper or its handling by the journal at any point.

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References

Alam, M.S., Tanveer, M.S., 2020. Conversion of biomass into biofuel: a cutting-edge technology. Bioreact.: Sustain. Des. Ind. Appl. Mitig. GHG Emiss. 55–74. https://doi.org/10.1016/B978-0-12-821264-6.00005-X.

Angelina-Martínez, A.Y., Sánchez-Ramírez, E., Quiroz-Ramírez, J.J., Segovia-Hernández, J.G., 2015. Controllability analysis of process alternatives for biobutanol purification. Chem. Eng. Technol. *38* (9), 1591–1598. ⟨https://doi.org/10.1002/ceat.201500103⟩.

Arabi, M., Yaghoubi, S., Tajik, J., 2019. A mathematical model for microalgae-based biobutanol supply chain network design under harvesting and drying uncertainties. Energy *179*, 1004–1016. https://doi.org/10.1016/J.ENERGY.2019.04.219.

Arregoitia-Sarabia, C., González-Revuelta, D., Fallanza, M., Ortiz, A., Gorri, D., 2022. PEBA/PDMS composite multilayer hollow fiber membranes for the selective separation of butanol by pervaporation. Membranes *12* (10), 1007. ⟨https://doi.org/10.3390/MEMBRANES12101007/S1⟩.

Ashani, P.N., Shafiei, M., Karimi, K., 2020. Biobutanol production from municipal solid waste: technical and economic analysis. Bioresour. Technol. *308*, 123267 https://doi.org/10.1016/J.BIORTECH.2020.123267.

Azambuja, S.P.H., Goldbeck, R., 2020. Butanol production by Saccharomyces cerevisiae: perspectives, strategies and challenges. World J. Microbiol. Biotechnol. *36* (3), 1–9. ⟨https://doi.org/10.1007/S11274-020-02828-Z/METRICS⟩.

Bharathiraja, B., Jayamuthunagai, J., Sudharsanaa, T., Bharghavi, A., Praveenkumar, R., Chakravarthy, M., Devarajan, Y., 2017. Biobutanol – an impending biofuel for future: a review on upstream and downstream processing tecniques. Renew. Sustain. Energy Rev. *68*, 788–807. https://doi.org/10.1016/J.RSER.2016.10.017.

Bhuyar, P., Trejo, M., Mishra, P., Unpaprom, Y., Velu, G., Ramaraj, R., 2022. Advancements of fermentable sugar yield by pretreatment and steam explosion during enzymatic saccharification of Amorphophallus sp. starchy tuber for bioethanol production. Fuel *323*, 124406. https://doi.org/10.1016/J.FUEL.2022.124406.

Cai, D., Chang, Z., Gao, L., Chen, C., Niu, Y., Qin, P., Wang, Z., Tan, T., 2015. Acetone–butanol–ethanol (ABE) fermentation integrated with simplified gas stripping using sweet sorghum bagasse as immobilized carrier. Chem. Eng. J. *277*, 176–185. https://doi.org/10.1016/J.CEJ.2015.04.101.

Cai, D., Hu, S., Miao, Q., Chen, C., Chen, H., Zhang, C., Li, P., Qin, P., Tan, T., 2017. Two-stage pervaporation process for effective in situ removal acetone-butanol-ethanol from fermentation broth. Bioresour. Technol. *224*, 380–388. https://doi.org/10.1016/J.BIORTECH.2016.11.010.

Chen, J., Zhang, B., Luo, L., Zhang, F., Yi, Y., Shan, Y., Liu, B., Zhou, Y., Wang, X., Lü, X., 2021. A review on recycling techniques for bioethanol production from lignocellulosic biomass. Renew. Sustain. Energy Rev. *149*, 111370 https://doi.org/10.1016/J.RSER.2021.111370.

Chen, W.H., Nižetić, S., Sirohi, R., Huang, Z., Luque, R., M.Papadopoulos, A., Sakthivel, R., Phuong Nguyen, X., Tuan Hoang, A., 2022. Liquid hot water as sustainable biomass pretreatment technique for bioenergy production: a review. Bioresour. Technol. *344*, 126207 https://doi.org/10.1016/J.BIORTECH.2021.126207.

Chen, W., Huang, K., Chen, H., Xia, C., Wu, G., Wang, K., 2014. Design and operation of dividing-wall distillation columns. 1. Diminishing the black-hole problem through over-design. Chem. Eng. Process.: Process.Intensif. *75*, 90–109. https://doi.org/10.1016/j.cep.2013.11.007.

Chen, X., Li, Y., Li, X., Shi, J., Liu, L., 2024. Exploring the potential of multiple lignocellulosic biomass as a feedstock for biobutanol production. Fuel *357*, 129697. https://doi.org/10.1016/J.FUEL.2023.129697.

Chen, Y., Zhou, T., Liu, D., Li, A., Xu, S., Liu, Q., Li, B., Ying, H., 2013. Production of butanol from glucose and xylose with immobilized cells of *Clostridium acetobutylicum*. Biotechnol. Bioprocess Eng. 18, 234–241.

Choi, S.J., Lee, J., Jang, Y.S., Park, J.H., Lee, S.Y., Kim, I.H., 2012. Effects of nutritional enrichment on the production of acetone-butanol-ethanol (ABE) by *Clostridium acetobutylicum*. J. Microbiol. 50, 1063–1066.

Contreras-Vargas, C.A., Gómez-Castro, F.I., Sánchez-Ramírez, E., Segovia-Hernández, J. G., Morales-Rodríguez, R., Gamiño-Arroyo, Z., 2019. Alternatives for the purification of the blend butanol/ethanol from an acetone/butanol/ethanol fermentation effluent. Chem. Eng. Technol. *42* (5), 1088–1100. https://doi.org/10.1002/ceat.201800641.

Contreras-Zarazúa, G., Martin-Martin, M., Sánchez-Ramirez, E., Segovia-Hernández, J. G., 2022. Furfural production from agricultural residues using different intensified separation and pretreatment alternatives. Economic and environmental assessment. Chem. Eng. Process. Process. Intensif. *171*, 108569 https://doi.org/10.1016/J.CEP.2021.108569.

Dadgar, A.M., Foutch, G.L., 1988. Improving the acetone-butanol fermentation process with liquid-liquid extraction. Biotechnol. Prog. *4* (1), 36–39. https://doi.org/10.1002/BTPR.5420040107.

Das, N., Jena, P.K., Padhi, D., Kumar Mohanty, M., Sahoo, G., 2021. A comprehensive review of characterization, pretreatment and its applications on different lignocellulosic biomass for bioethanol production. *2021 13:2* Biomass-.-. Convers. Biorefinery *13* (2), 1503–1527. https://doi.org/10.1007/S13399-021-01294-3.

de Brito Bezerra, P.K.S., de Azevedo, J.C.S., dos Santos, E.S., 2023. Biobutanol production by batch and fed-batch fermentations from the green coconut husk hydrolysate using C. beijerinckii ATCC 10132. Biomass Convers. Biorefinery 1–13. ⟨https://doi.org/10.1007/S13399-023-04537-7/METRICS⟩.

Desta, M., Lee, T., Wu, H., 2021. Well-to-wheel analysis of energy use and greenhouse gas emissions of acetone-butanol-ethanol from corn and corn stover. Renew. Energy *170*, 72–80. https://doi.org/10.1016/J.RENENE.2021.01.079.

Eloka-Eboka, A.C., Maroa, S., 2023. Biobutanol fermentation research and development: feedstock, process and biofuel production. Adv. Dev. Biobutanol. Prod. 79–103. https://doi.org/10.1016/B978-0-323-91178-8.00007-2.

Errico, M., Sanchez-Ramirez, E., Quiroz-Ramìrez, J.J., Segovia-Hernandez, J.G., Rong, B.-G., 2016. Synthesis and design of new hybrid configurations for biobutanol purification. Comput. Chem. Eng. *84*, 482–492. https://doi.org/10.1016/j.compchemeng.2015.10.009.

Evans, P.J., Wang, H.Y., 1988. Enhancement of butanol formation by *Clostridium acetobutylicum* in the presence of decanol-oleyl alcohol mixed extractants. Appl. Environ. Microbiol. *54* (7), 1662–1667. https://doi.org/10.1128/aem.54.7.1662-1667.1988.

Ezeji, T.C., Qureshi, N., Blaschek, H.P., 2007. Bioproduction of butanol from biomass: from genes to bioreactors. Curr. Opin. Biotechnol. *18* (3), 220–227. https://doi.org/10.1016/J.COPBIO.2007.04.002.

Flores-Cordero, E., Sánchez-Ramírez, E., Contreras-Zarazúa, G., Ramírez-Márquez, C., Segovia-Hernández, J.G., 2022. Purification of Butanol from the ABE Mixture: effect of intensification on the dynamic behavior. Ind. Eng. Chem. Res. *61* (49), 17963–17975. ⟨https://doi.org/10.1021/ACS.IECR.2C02417/ASSET/IMAGES/LARGE/IE2C02417_0006.JPEG⟩.

Gedam, P.S., Raut, A.N., Dhamole, P.B., Gole, V.L., 2023. Challenges in biobutanol fermentation and separation. Biorefinery: A Sustain. Approach Prod. Biomater., Biochem. Biofuels 87–110. ⟨https://doi.org/10.1007/978-981-19-7481-6_4/COVER⟩.

Goerlitz, R., Weisleder, L., Wuttig, S., Trippel, S., Karstens, K., Goetz, P., Niebelschuetz, H., 2018. Bio-butanol downstream processing: regeneration of adsorbents and selective exclusion of fermentation by-products. Adsorption *24* (1), 95–104. ⟨https://doi.org/10.1007/S10450-017-9918-X/FIGURES/8⟩.

González-Bravo, R., Sánchez-Ramírez, E., Quiroz-Ramírez, J.J., Segovia-Hernández, J.G., Lira-Barragán, L.F., Ponce-Ortega, J.M., 2016. Total Heat Integration in the Biobutanol Separation Process. Ind. Eng. Chem. Res. *55* (11), 3000–3012. ⟨https://doi.org/10.1021/ACS.IECR.5B03168/SUPPL_FILE/IE5B03168_SI_001.PDF⟩.

Grisales Diaz, V.H., Olivar Tost, G., 2018. Energy efficiency of acetone, butanol, and ethanol (ABE) recovery by heat-integrated distillation. Bioprocess Biosyst. Eng. *41* (3), 395–405. https://doi.org/10.1007/s00449-017-1874-z.

Grisales Díaz, V.H., Willis, M.J., von Stosch, M., Olivar Tost, G., Prado-Rubio, O., 2020. Assessing the energy requirements for butanol production using fermentation tanks-in-series operated under vacuum. Renew. Energy *160*, 1253–1264. https://doi.org/10.1016/J.RENENE.2020.07.039.

Groot, W.J., Soedjak, H.S., Donck, P.B., Lans, R.G.J.M., Van, Luyben, K.C.A.M., Timmer, J.M.K., 1990. Bioprocess Eng. Butan Recovery Ferment. Liq. -Liq. Extr. Membr. Solvent Extr. *5*, 203–216.

Han, B., Ujor, V., Lai, L.B., Gopalan, V., Ezeji, T.C., 2013. Use of proteomic analysis to elucidate the role of calcium in acetone-butanol-ethanol fermentation by *Clostridium beijerinckii NCIMB 8052*. Appl. Environ. Microbiol. 79 (1), 282–293.

Hietaharju, J., Kangas, J., Yang, M., Kuittinen, S., Pappinen, A., Tanskanen, J., 2020. Negative impact of butyric acid on butanol recovery by pervaporation with a silicalite-1 membrane from ABE fermentation. Sep. Purif. Technol. *245*, 116883 https://doi.org/10.1016/J.SEPPUR.2020.116883.

Hiloidhari, M., Sharno, M.A., Baruah, D.C., Bezbaruah, A.N., 2023. Green and sustainable biomass supply chain for environmental, social and economic benefits. Biomass-.-. Bioenergy *175*, 106893. https://doi.org/10.1016/J.BIOMBIOE.2023.106893.

Huang, C., Zhan, Y., Du, X., Zhou, Y., Yu, L., Meng, X., Jiao, J., Fang, G., Ragauskas, A.J., 2020. Modified alkaline peroxide pretreatment: An efficient path forward for bioethanol production from bamboo. Energy Convers. Manag. *224*, 113365 https://doi.org/10.1016/J.ENCONMAN.2020.113365.

Ishii, S., Taya, M., Kobayashi, T., 1985. Production of butanol by *clostridium acetobutylicum* in extractive fermentation system. J. Chem. Eng. Jpn. *18* (2), 125–130. https://doi.org/10.1252/jcej.18.125.

Iyyappan, J., Bharathiraja, B., Vaishnavi, A., Prathiba, S., 2021. Overview of Current Developments in Biobutanol Production Methods and Future Perspectives. Methods Mol. Biol. *2290*, 3–21. ⟨https://doi.org/10.1007/978-1-0716-1323-8_1/COVER⟩.

Karimi, K., Tabatabaei, M., Horváth, I.S., Kumar, R., 2015. Recent trends in acetone, butanol, and ethanol (ABE) production. Biofuel Res. J. *2* (4), 301–308. https://doi.org/10.18331/BRJ2015.2.4.4.

Kraemer, K., Harwardt, A., Bronneberg, R., Marquardt, W., 2011. Separation of butanol from acetone–butanol–ethanol fermentation by a hybrid extraction–distillation process. Comput. Chem. Eng. *35* (5), 949–963. https://doi.org/10.1016/j.compchemeng.2011.01.028.

Kujawska, A., Kujawski, J., Bryjak, M., Kujawski, W., 2015. ABE fermentation products recovery methods—a review. Renew. Sustain. Energy Rev. *48*, 648–661. https://doi.org/10.1016/J.RSER.2015.04.028.

Kurkijärvi, A.J., Lehtonen, J., 2014. Dual extraction process for the utilization of an acetone–butanol–ethanol mixture in gasoline. Ind. Eng. Chem. Res. *53* (31), 12379–12386. https://doi.org/10.1021/ie500131x.

Kurkijärvi, A., Lehtonen, J., Linnekoski, J., 2014. Novel dual extraction process for acetone–butanol–ethanol fermentation. Sep. Purif. Technol. *124*, 18–25. https://doi.org/10.1016/J.SEPPUR.2014.01.007.

Kushwaha, A., Goswami, S., Sultana, A., Katiyar, N.K., Athar, M., Dubey, L., Goswami, L., Hussain, C.M., Kareem, M.A., 2022. Waste biomass to biobutanol: recent trends and advancements. Waste -to-Energy Approaches Towards Zero Waste: Interdiscip. Methods Control. Waste 393–423. https://doi.org/10.1016/B978-0-323-85387-3.00004-5.

Kushwaha, D., Srivastava, N., Mishra, I., Upadhyay, S.N., Mishra, P.K., 2019. Recent trends in biobutanol production. Rev. Chem. Eng. *35* (4), 475–504. ⟨https://doi.org/10.1515/REVCE-2017-0041/ASSET/GRAPHIC/J_REVCE-2017-0041_CV_005.JPG⟩.

Lee, K.H., Lee, S.K., Lee, J., Kim, S., Kim, S.W., Park, C., Yoo, H.Y., 2022. Energy-efficient glucose recovery from chestnut shell by optimization of NaOH pretreatment at room temperature and application to bioethanol production. Environ. Res. *208*, 112710 https://doi.org/10.1016/J.ENVRES.2022.112710.

Lee, S.Y., Park, J.H., Jang, S.H., Nielsen, L.K., Kim, J., Jung, K.S., 2008. Fermentative butanol production by clostridia. Biotechnol. Bioeng. *101* (2), 209–228. https://doi.org/10.1002/BIT.22003.

Li, S.-Y., Chiang, C.-J., Tseng, I.-T., He, C.-R., Chao, Y.-P., 2016. Bioreactors and in situ product recovery techniques for acetone-butanol-ethanol fermentation. FEMS Microbiol. Lett. *363*, 107. https://doi.org/10.1093/femsle/fnw107.

Lin, Z., Cong, W., Zhang, J., 2023a. Biobutanol Production from Acetone–Butanol–Ethanol Fermentation: Developments and Prospects. Fermentation *9* (9), 847. https://doi.org/10.3390/FERMENTATION9090847. *2023, Vol. 9, Page 847*.

Lin, Z., Cong, W., Zhang, J., 2023b. Biobutanol production from acetone–butanol–ethanol fermentation: developments and prospects. Fermentation *9* (9), 847. https://doi.org/10.3390/FERMENTATION9090847.

Liu, Y., Yuan, Y., Ramya, G., Mohan Singh, S., Thuy Lan Chi, N., Pugazhendhi, A., Xia, C., Mathimani, T., 2022a. A review on the promising fuel of the future – Biobutanol; the hindrances and future perspectives. Fuel *327*, 125166. https://doi.org/10.1016/J.FUEL.2022.125166.

Liu, Y., Yuan, Y., Ramya, G., Mohan Singh, S., Thuy Lan Chi, N., Pugazhendhi, A., Xia, C., Mathimani, T., 2022b. A review on the promising fuel of the future – Biobutanol; the hindrances and future perspectives. Fuel *327*, 125166. https://doi.org/10.1016/J.FUEL.2022.125166.

López-Linares, J.C., García-Cubero, M.T., Coca, M., Lucas, S., 2021. Efficient biobutanol production by acetone-butanol-ethanol fermentation from spent coffee grounds with microwave assisted dilute sulfuric acid pretreatment. Bioresour. Technol. *320*, 124348 https://doi.org/10.1016/J.BIORTECH.2020.124348.

Lu, K.M., Chiang, Y.S., Wang, Y.R., Chein, R.Y., Li, S.Y., 2016. Performance of fed-batch acetone–butanol–ethanol (ABE) fermentation coupled with the integrated in situ extraction-gas stripping process and the fractional condensation. J. Taiwan Inst. Chem. Eng. *60*, 119–123. https://doi.org/10.1016/J.JTICE.2015.10.044.

Lu, K.M., Li, S.Y., 2014. An integrated in situ extraction-gas stripping process for Acetone–Butanol–Ethanol (ABE) fermentation. J. Taiwan Inst. Chem. Eng. *45* (5), 2106–2110. https://doi.org/10.1016/J.JTICE.2014.06.023.

Luo, H., Zheng, P., Bilal, M., Xie, F., Zeng, Q., Zhu, C., Yang, R., Wang, Z., 2020. Efficient bio-butanol production from lignocellulosic waste by elucidating the mechanisms of *Clostridium acetobutylicum* response to phenolic inhibitors. Sci. Total Environ. *710*, 136399 https://doi.org/10.1016/J.SCITOTENV.2019.136399.

Mailaram, S., Kumar, P., Kunamalla, A., Saklecha, P., Maity, S.K., 2021. Biomass, biorefinery, and biofuels. Sustain. Fuel Technol. Handb. 51–87. https://doi.org/10.1016/B978-0-12-822989-7.00003-2.

Mankar, A.R., Pandey, A., Modak, A., Pant, K.K., 2021. Pretreatment of lignocellulosic biomass: A review on recent advances. Bioresour. Technol. *334*, 125235 https://doi.org/10.1016/J.BIORTECH.2021.125235.

Manna, M.S., Mazumder, A., Bhowmick, T.K., Gayen, K., 2023. Economic analysis of biobutanol recovery from the acetone-butanol-ethanol fermentation using molasses. J. Indian Chem. Soc. *100* (1), 100809 https://doi.org/10.1016/J.JICS.2022.100809.

Mariano, A.P., Filho, R.M., Ezeji, T.C., 2012a. Energy requirements during butanol production and in situ recovery by cyclic vacuum. Renew. Energy *47*, 183–187. https://doi.org/10.1016/j.renene.2012.04.041.

Mariano, A.P., Filho, R.M., Ezeji, T.C., 2012b. Energy requirements during butanol production and in situ recovery by cyclic vacuum. Renew. Energy *47*, 183–187. https://doi.org/10.1016/j.renene.2012.04.041.

Martinez-Gomez, J., Sánchez-Ramírez, E., Quiroz-Ramírez, J.J., Segovia-Hernandez, J. G., Ponce-Ortega, J.M., El-Halwagi, M.M., 2016. Involving economic, environmental and safety issues in the optimal purification of biobutanol. Process Saf. Environ. Prot. *103* (Part B)), 365–376. https://doi.org/10.1016/j.psep.2016.04.018.

Matsumura, M., Kataoka, H., Sueki, M., Araki, K., 1988. Energy saving effect of pervaporation using oleyl alcohol liquid membrane in butanol purification. Bioprocess Eng. *3* (2), 93–100. https://doi.org/10.1007/BF00369334.

Mejica, G.F.C., Unpaprom, Y., Whangchai, K., Ramaraj, R., 2022. Cellulosic-derived bioethanol from Limnocharis flava utilizing alkaline pretreatment. Biomass Convers. Biorefinery *12* (5), 1737–1743. ⟨https://doi.org/10.1007/S13399-020-01218-7/METRICS⟩.

Momenitabar, M., Dehdari Ebrahimi, Z., Ghasemi, P., 2022. Designing a sustainable bioethanol supply chain network: a combination of machine learning and meta-heuristic algorithms. Ind. Crops Prod. *189*, 115848 https://doi.org/10.1016/J.INDCROP.2022.115848.

Mukherjee, M., Goswami, G., Mondal, P.K., Das, D., 2020. Biobutanol as a potential alternative to petroleum fuel: Sustainable bioprocess and cost analysis. Fuel *278*, 118403. https://doi.org/10.1016/J.FUEL.2020.118403.

Ncube, A., Mtetwa, S., Bukhari, M., Fiorentino, G., Passaro, R., 2023. Circular economy and green chemistry: the need for radical innovative approaches in the design for new products. *2023, Vol. 16, Page 1752* Energies *16* (4), 1752. https://doi.org/10.3390/EN16041752.

Niju, S., Nishanthini, T., Balajii, M., 2020. Alkaline hydrogen peroxide-pretreated sugarcane tops for bioethanol production—a process optimization study. Biomass Convers. Biorefinery *10* (1), 149–165. ⟨https://doi.org/10.1007/S13399-019-00524-Z/METRICS⟩.

Nilsson, A., Shabestary, K., Brandão, M., Hudson, E.P., 2020. Environmental impacts and limitations of third-generation biobutanol: life cycle assessment of n-butanol produced by genetically engineered cyanobacteria. J. Ind. Ecol. *24* (1), 205–216. https://doi.org/10.1111/JIEC.12843.

Oksal, I.N., Kaymak, D.B., 2023. Design and control of an energy-efficient intensified process for biobutanol purification from isopropanol-butanol-ethanol (IBE) fermentation broth. Chem. Eng. Process. - Process. Intensif. *193*, 109542 https://doi.org/10.1016/J.CEP.2023.109542.

Oudshoorn, A., Van Der Wielen, L.A.M., Straathof, A.J.J., 2009. Assessment of options for selective 1-butanol recovery from aqueous solution. Ind. Eng. Chem. Res. *48* (15), 7325–7336. ⟨https://doi.org/10.1021/IE900537W/ASSET/IMAGES/IE-2009-00537W_M007.GIF⟩.

Ounine, K., Petitdemange, H., Raval, G., Gay, R., 1985. Regulation and butanol inhibition of D-xylose and D-glucose uptake in *Clostridium acetobutylicum*. Appl. Environ. Microbiol. 49 (4), 874–878.

Outram, V., Lalander, C.A., Lee, J.G.M., Davies, E.T., Harvey, A.P., 2017. Applied in situ product recovery in ABE fermentation. Biotechnol. Prog. *33* (3), 563–579. https://doi.org/10.1002/BTPR.2446.

Pinto, T., Flores-Alsina, X., Gernaey, K.V., Junicke, H., 2021. Alone or together? A review on pure and mixed microbial cultures for butanol production. Renew. Sustain. Energy Rev. *147*, 111244 https://doi.org/10.1016/J.RSER.2021.111244.

Plaza, P.E., Coca, M., Lucas, S., Fernández-Delgado, M., López-Linares, J.C., García-Cubero, M.T., 2020. Efficient use of brewer's spent grain hydrolysates in ABE fermentation by *Clostridium beijerinkii*. Effect of high solid loads in the enzymatic hydrolysis. J. Chem. Technol. Biotechnol. 95 (9), 2393–2402.

Pugazhendhi, A., Mathimani, T., Varjani, S., Rene, E.R., Kumar, G., Kim, S.H., Ponnusamy, V.K., Yoon, J.J., 2019. Biobutanol as a promising liquid fuel for the future - recent updates and perspectives. Fuel *253*, 637–646. https://doi.org/10.1016/J.FUEL.2019.04.139.

Quiroz-Ramírez, J.J., Sánchez-Ramírez, E., Hernández, S., Ramírez-Prado, J.H., Segovia-Hernández, J.G., 2017. Multiobjective stochastic optimization approach applied to a hybrid process production-separation in the production of biobutanol. Ind. Eng. Chem. Res. *56* (7), 1823–1833. ⟨https://doi.org/10.1021/ACS.IECR.6B04230/ASSET/IMAGES/LARGE/IE-2016-04230P_0005.JPEG⟩.

Quiroz-Ramírez, J.J., Sánchez-Ramírez, E., Hernández-Castro, S., Segovia-Hernández, J. G., Ponce-Ortega, J.M., 2017. Optimal planning of feedstock for butanol production considering economic and environmental aspects. ACS Sustain. Chem. Eng. *5* (5), 4018–4030. https://doi.org/10.1021/acssuschemeng.7b00015.

Qureshi, N., Saha, B.C., Liu, S., Ezeji, T.C., Nichols, N.N., 2021. Cellulosic Butanol Biorefinery: Production of Biobutanol from High Solid Loadings of Sweet Sorghum Bagasse—Simultaneous Saccharification, Fermentation, and Product Recovery. *2021, Vol. 7, Page 310* Fermentation *7* (4), 310. https://doi.org/10.3390/FERMENTATION7040310.

Raspolli Galletti, A.M., Antonetti, C., Fulignati, S., Licursi, D., Dell'Omo, S., Benito, P., Wilbers, E., Heeres, H.J., 2023. Upgrading bio-butanol in the presence of copper-hydrotalcite derived mixed oxides: From batch to continuous flow catalytic process highly selective to butyl butyrate. Catal. Today *423*, 114288. https://doi.org/10.1016/J.CATTOD.2023.114288.

Rezania, S., Oryani, B., Cho, J., Talaiekhozani, A., Sabbagh, F., Hashemi, B., Rupani, P.F., Mohammadi, A.A., 2020. Different pretreatment technologies of lignocellulosic biomass for bioethanol production: an overview. Energy *199*, 117457. https://doi.org/10.1016/J.ENERGY.2020.117457.

Riaz, S., Mazhar, S., Abidi, S.H., Syed, Q., Abbas, N., Saleem, Y., Nadeem, A.A., Maryam, M., Essa, R., Ashfaq, S., 2022. Biobutanol production from sustainable biomass process of anaerobic ABE fermentation for industrial applications. Arch. Microbiol. *204* (11), 1–9. ⟨https://doi.org/10.1007/S00203-022-03284-Z/METRICS⟩.

Roffler, S., Blanch, H.W., Wilke, C.R., 1987. Extractive Fermentation of Acetone and Butanol: Process Design and Economic Evaluation. Biotechnol. Prog. *3* (3), 131–140. https://doi.org/10.1002/BTPR.5420030304.

Saeed, F., Govardhan, B., Kalyani, S., Shyamsunder, M., Sundergopal, S., 2023. Mixed-matrix ZIF-loaded membranes for effective separation of bio-butanol from fermentation broth. Biochem. Eng. J. *196*, 108940 https://doi.org/10.1016/J.BEJ.2023.108940.

Sánchez-Ramírez, E., Huerta-Rosas, B., Segovia-Hernandez, J.G., Quiroz-Ramírez, J.J., 2023. Developments in biobutanol industrial production. Adv. Dev. Biobutanol Prod. 47–78. https://doi.org/10.1016/B978-0-323-91178-8.00003-5.

Sánchez-Ramírez, E., Quiroz-Ramírez, J.J., Hernández, S., Segovia-Hernández, J.G., Kiss, A.A., 2017. Optimal hybrid separations for intensified downstream processing of biobutanol. Sep. Purif. Technol. *185*, 149–159. https://doi.org/10.1016/J.SEPPUR.2017.05.011.

Sánchez-Ramírez, E., Quiroz-Ramírez, J.J., Segovia-Hernández, J.G., Hernández, S., Bonilla-Petriciolet, A., 2015. Process alternatives for biobutanol purification: Design and optimization. Ind. Eng. Chem. Res. *54* (1), 351–358. ⟨https://doi.org/10.1021/IE503975G/ASSET/IMAGES/LARGE/IE-2014-03975G_0006.JPEG⟩.

Sánchez-Ramírez, E., Quiroz-Ramírez, J.J., Segovia-Hernández, J.G., Hernández, S., Ponce-Ortega, J.M., 2016. Economic and environmental optimization of the biobutanol purification process. Clean. Technol. Environ. Policy *18* (2), 395–411. ⟨https://doi.org/10.1007/S10098-015-1024-8/FIGURES/12⟩.

Santibañez-Aguilar, J.E., Quiroz-Ramírez, J.J., Sánchez-Ramírez, E., Segovia-Hernández, J.G., Flores-Tlacuahuac, A., Ponce-Ortega, J.M., 2022. Marginalization index as social measure for Acetone-Butanol-Ethanol supply chain planning. Renew. Sustain. Energy Rev. *154*, 111816 https://doi.org/10.1016/J.RSER.2021.111816.

Sarchami, T., Munch, G., Johnson, E., Kießlich, S., Rehmann, L., 2016. A Review of Process-Design Challenges for Industrial Fermentation of Butanol from Crude Glycerol by Non-Biphasic *Clostridium pasteurianum*. *2016, Vol. 2, Page 13* Fermentation *2* (2), 13. https://doi.org/10.3390/FERMENTATION2020013.

Segovia-Hernández, J.G., Hernández, S., Cossío-Vargas, E., Sánchez-Ramírez, E., 2023. Challenges and opportunities in process intensification to achieve the UN's 2030 agenda: Goals 6, 7, 9, 12 and 13. Chem. Eng. Process. - Process. Intensif. *192*, 109507 https://doi.org/10.1016/J.CEP.2023.109507.

Segovia-Hernández, J.G., Sanchez-Ramirez, E., Alcocer-Garcia, H., Romero-Garcia, A.G., Quiroz-Ramirez, J.J., 2022. Sustain. Prod. Biofuels Using Intensified Process. https://doi.org/10.1007/978-3-031-13216-2.

Segovia-Hernandez, J.Gabriel, Behera, Shuvashish, Sanchez-Ramirez, Eduardo, 2022. Advances and developments in biobutanol production, 1st ed., Vol. 1. Science Direct ⟨http://www.sciencedirect.com:5070/book/9780323911788/advances-and-developments-in-biobutanol-production⟩.

Shangdiar, S., Lin, Y.C., Ponnusamy, V.K., Wu, T.Y., 2022. Pretreatment of lignocellulosic biomass from sugar bagasse under microwave assisted dilute acid hydrolysis for biobutanol production. Bioresour. Technol. *361*, 127724 https://doi.org/10.1016/J.BIORTECH.2022.127724.

Shanmugam, S., Hari, A., Kumar, D., Rajendran, K., Mathimani, T., Atabani, A.E., Brindhadevi, K., Pugazhendhi, A., 2021. Recent developments and strategies in genome engineering and integrated fermentation approaches for biobutanol production from microalgae. Fuel *285*, 119052. https://doi.org/10.1016/J.FUEL.2020.119052.

Shariat Panahi, H.K., Dehhaghi, M., Guillemin, G.J., Chukwudi Okonkwo, C., Kinder, J. E., Ezeji, T.C., 2023. Bio-butanol production: scope, significance, and applications. Adv. Dev. Biobutanol Prod. 1–45. https://doi.org/10.1016/B978-0-323-91178-8.00008-4.

Smichi, N., Messaoudi, Y., Allaf, K., Gargouri, M., 2020. Steam explosion (SE) and instant controlled pressure drop (DIC) as thermo-hydro-mechanical pretreatment methods for bioethanol production. Bioprocess Biosyst. Eng. *43* (6), 945–957. ⟨https://doi.org/10.1007/S00449-020-02297-6/METRICS⟩.

Solarte-Toro, J.C., Laghezza, M., Fiore, S., Berruti, F., Moustakas, K., Cardona Alzate, C. A., 2022. Review of the impact of socio-economic conditions on the development and implementation of biorefineries. Fuel *328*, 125169. https://doi.org/10.1016/J.FUEL.2022.125169.

Sommer, B., Garbe, D., Schrepfer, P., Brück, T., 2013. Characterization of a highly thermostable ß-hydroxybutyryl CoA dehydrogenase from *Clostridium acetobutylicum ATCC 824*. J. Mol. Catal. B: Enzym. 98, 138–144.

Stoffers, M., Heitmann, S., Lutze, P., Górak, A., 2013. Integrated processing for the separation of biobutanol. Part A: experimental investigation and process modelling. Green. Process. Synth. *2* (2), 101–120. ⟨https://doi.org/10.1515/GPS-2013-0009/MACHINEREADABLECITATION/RIS⟩.

Survase, S.A., Zebroski, R., Bayuadri, C., Wang, Z., Adamos, G., Nagy, G., Pylkkanen, V., 2019. Membrane assisted continuous production of solvents with integrated solvent removal using liquid-liquid extraction. Bioresour. Technol. *280*, 378–386. https://doi.org/10.1016/J.BIORTECH.2019.02.024.

Taylor, F., Kurantz, M.J., Goldberg, N., Craig, J.C., 1995. Continuous fermentation and stripping of ethanol. Biotechnol. Prog. *11* (6), 693–698. https://doi.org/10.1021/BP00036A014.

Tekin, N., Karatay, S.E., Dönmez, G., 2023. Optimization studies about efficient biobutanol production from industrial tea waste by *Clostridium beijerinckii*. Fuel *331*, 125763. https://doi.org/10.1016/J.FUEL.2022.125763.

Torre, R.M., Álvaro, A.G., Palomar, C.R., de Godos Crespo, de G.C., de Almeida Guimarães, V., Hedo, E.B., 2023a. Developmental perspectives of the biofuel-based economy. Biofuels Circ. Econ. 133–156. ⟨https://doi.org/10.1007/978-981-19-5837-3_9/COVER⟩.

Torre, R.M., Álvaro, A.G., Palomar, C.R., de Godos Crespo, de G.C., de Almeida Guimarães, V., Hedo, E.B., 2023b. Developmental Perspectives of the Biofuel-Based Economy. Biofuels Circ. Econ. 133–156. ⟨https://doi.org/10.1007/978-981-19-5837-3_9/COVER⟩.

Vamsi Krishna, K., Bharathi, N., George Shiju, S., Alagesan Paari, K., Malaviya, A., 2022. An updated review on advancement in fermentative production strategies for biobutanol using Clostridium spp. *2022 29:32* Environ. Sci. Pollut. Res. *29* (32), 47988–48019. https://doi.org/10.1007/S11356-022-20637-9.

Vane, L.M., Alvarez, F.R., Rosenblum, L., Govindaswamy, S., 2013. Hybrid vapor stripping–vapor permeation process for recovery and dehydration of 1-butanol and acetone/butanol/ethanol from dilute aqueous solutions. Part 2. Experimental validation with simple mixtures and actual fermentation broth. J. Chem. Technol. Biotechnol. *88* (8), 1448–1458. https://doi.org/10.1002/JCTB.4086.

Veza, I., Muhamad Said, M.F., Latiff, Z.A., 2021a. Recent advances in butanol production by acetone-butanol-ethanol (ABE) fermentation. Biomass Bioenergy *144*, 105919. https://doi.org/10.1016/J.BIOMBIOE.2020.105919.

Veza, I., Muhamad Said, M.F., Latiff, Z.A., 2021b. Recent advances in butanol production by acetone-butanol-ethanol (ABE) fermentation. Biomass Bioenergy *144*, 105919. https://doi.org/10.1016/J.BIOMBIOE.2020.105919.

Wang, M., Zhang, Q., Gao, H.P., Cao, C.H., 2023. Simultaneous saccharification and fermentation for biobutanol production from corn starch via ABE fermentation. BioResources *18* (3), 4935–4942. https://doi.org/10.15376/BIORES.18.3.4935-4942.

Wang, Y.R., Chiang, Y.S., Chuang, P.J., Chao, Y.P., Li, S.Y., 2016. Direct in situ butanol recovery inside the packed bed during continuous acetone-butanol-ethanol (ABE) fermentation. Appl. Microbiol. Biotechnol. *100* (17), 7449–7456. ⟨https://doi.org/10.1007/S00253-016-7443-6/TABLES/3⟩.

Wu, Y.D., Xue, C., Chen, L.J., Bai, F.W., 2013. Effect of zinc supplementation on acetone–butanol–ethanol fermentation by *Clostridium acetobutylicum*. J. Biotechnol. 165 (1), 18–21.

Xue, C., Liu, F., Xu, M., Zhao, J., Chen, L., Ren, J., Bai, F., Yang, S.T., 2016. A novel in situ gas stripping-pervaporation process integrated with acetone-butanol-ethanol fermentation for hyper n-butanol production. Biotechnol. Bioeng. *113* (1), 120–129. https://doi.org/10.1002/BIT.25666.

Xue, C., Zhao, J., Chen, L., Yang, S.T., Bai, F., 2017. Recent advances and state-of-the-art strategies in strain and process engineering for biobutanol production by *Clostridium acetobutylicum*. Biotechnol. Adv. *35* (2), 310–322. https://doi.org/10.1016/J.BIOTECHADV.2017.01.007.

Xue, C., Zhao, J., Liu, F., Lu, C., Yang, S.T., Bai, F.W., 2013. Two-stage in situ gas stripping for enhanced butanol fermentation and energy-saving product recovery. Bioresour. Technol. *135*, 396–402. https://doi.org/10.1016/J.BIORTECH.2012.07.062.

Zhang, X., Shanmugam, K.T., Ingram, L.O., 2010. Fermentation of glycerol to succinate by metabolically engineered strains of Escherichia coli. Appl. Environ. Microbiol. *76* (8), 2397–2401. ⟨https://doi.org/10.1128/AEM.02902-09/SUPPL_FILE/AEM2902_09_SUPPL_TABLE.PDF⟩.

Zhen, X., Wang, Y., Liu, D., 2020. Bio-butanol as a new generation of clean alternative fuel for SI (spark ignition) and CI (compression ignition) engines. Renew. Energy *147*, 2494–2521. https://doi.org/10.1016/J.RENENE.2019.10.119.