https://doi.org/10.3311/PPch.18574

Periodica Polytechnica Chemical Engineering, 66(2), pp. 279–296, 2022

Lignocellulosic Biomass – A Sustainable Feedstock for Acetone-Butanol-Ethanol Fermentation

Lorianna Mahalingam[1], Rahmath Abdulla[1*], Suraya Abdul Sani[1], Mohd Khalizan Sabullah[1], Ainol Azifa Mohd Faik[1], Mailin Misson[2]

[1] Department of Biotechnology, Faculty of Science and Natural Resources, University Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia
[2] Biotechnology Research Institute, University Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia
* Corresponding author, e-mail: rahmath@ums.edu.my

Received: 17 May 2021, Accepted: 17 September 2021, Published online: 18 January 2022

Abstract

Biobutanol has been identified as a promising future biofuel. However, generally the extraction and separation of biobutanol from the fermentation mixture is a costly process. Therefore, the idea of using acetone-butanol-ethanol (ABE) mixture directly as biofuel were proposed to eliminate the recovery process. ABE has been identified as a promising future biofuel. The feedstocks play an important role in the feasibility of ABE as a fuel. Lignocellulosic biomass is seen as a promising feedstock for the production of biofuels. Thus, in this review, ABE biofuel is been summarized from three aspects namely (i) selection of feedstocks, (ii) microbial selection and (iii) hydrolysis, fermentation, and purification techniques. Anaerobic fermentation together with commonly employed recovery processes are discussed in the second part of this review. This review concludes with different challenges and future research in ABE fermentation that can pave the way for future commercialization of this promising biofuel.

Keywords

fermentation, anaerobic, ABE, lignocellulosic biomass, mixed microbe

1 Introduction

Biomass, one of the well-known renewable resources, are utilized to produce various types of biofuels which in turn can support up to 14% of the world's energy demands [1]. The production of biofuels are mostly based on living organisms that contain over 80% of renewable materials, which are mostly derived from photosynthesis and therefore referred to as solar energy sources (Table 1) [2]. It is difficult to explain the term biofuel itself as it is a fossil fuel. However, biofuel has a unique similarity to other energy sources since it is carbon dioxide neutral [2].

Biofuels have emerged as a promising option to alleviate the energy crisis to a greater degree as there has been a major decline in the availability of fossil fuels for the last few decades. In the first half of the 20th century, the second-largest industrial fermentation process was the acetone-butanol-ethanol (ABE) fermentation. The key attraction that gives biofuels greater advantages as compared to fossil fuels is the continuous availability of feedstocks throughout the year, which leads to improving engine performance and helps in minimizing greenhouse gas emissions [3, 4]. Comparative analysis done by Fu et al. [5] shows that the soot emissions of ABE are lower as compared to diesel. The reasons for the different levels of soot emissions between ABE and diesel are due to the difference in fuel compositions, molecular structures, and fuel physico-chemical characteristics [5].

As the need for energy constantly increased worldwide, the search for renewable energy sources has increased considerably. Biofuels have caught much attention worldwide mainly because of environmental friendly and biodegradable nature. Biofuels Research Advisory Council of European Union has proposed an increase of 25% biofuels in transportation sector by the end of 2030. Besides, the US Energy Independence and Security Act proposed an increment of 36 billion gallons of biofuels in transportation by 2022. Other than that, the National Energy Administration of China has announced that the production of ethanol and biodiesel is expected to hit 4.0 and 2.0 million tons by the year 2020 [6].

Currently, some of the biofuels commonly produced are primary alcohols such as methanol, ethanol, and butanol.

Cite this article as: Mahalingam, L., Abdulla, R., Sani, S. A., Sabullah, M. K., Faik, A. A. M., Misson, M. "Lignocellulosic Biomass – A Sustainable Feedstock for Acetone-Butanol-Ethanol Fermentation", Periodica Polytechnica Chemical Engineering, 66(2), pp. 279–296, 2022. https://doi.org/10.3311/PPch.18574

Table 1 Comparison between fossil fuel and biofuel

Main issues	Fossil fuel	Renewable energy (biofuels)
Resources scarcity	Very significant	Not significant
Important of location	High	Moderate
Amount of energy per unit	Low amount of energy per unit biomass	High amount of energy per unit mass
Pollution	Less pollution	High pollution
Gas emission	Emits low amounts of unfavorable gases	Emits high amounts of unfavorable gases
Impact on health	Toxic biproduct	Non-toxic
Geopolitical power	Asymmetric	Less asymmetric
International competition	High	Low
International interdependence	High	Low in domestic, high if imported
Security of supply	High	Moderate
Critical materials	Not important	Important
Cybersecurity	Not important	Important
Key market aspects	Demand and supply, export and import	Storage, intermittency, infrastructure management

Methanol is currently produced from fossil fuels such as natural gas and coal [7]. However, due to its renewability, less toxicity, higher energy density and lower carbon footprint ethanol gained more attention [8, 9]. Butanol, on the other hand, has a higher calorific value, higher cetane number, and lower latent heat of evaporation. The main butanol characteristics such as lower volatility and hydrophobicity shows advantages over ethanol as it is less corrosive to the fuel system and is more desirable for transportation and storage [8, 10]. However, total annual cost (TAC) for extraction of butanol from ABE mixture is expensive and not economically feasible [6, 11]. Moreover, the downstream process to obtain acetone, butanol, and ethanol requires 20% to 50% of the total operating cost [12]. Thus, researchers have blended ABE with diesel and used in transportation [13]. In future ABE has the potential to be an alternative transportation biofuel with the advancement in fermentation engineering [11]. To make this feasible, it is very important to understand the entire process of ABE production. Most of the existing literature on ABE focus only on upstream or downstream production process. However, this review paper presents a study on comparison of existing research on ABE production with different substrates, microbes and purification processes.

2 ABE as a potential biofuel

Many countries have started search for a more stable energy source that can put the oil crisis to an end. This includes the use of biofuels as an attractive option from economic, social and environmental perspective. Since 2003, there was a remarkable increase in the production of biofuels from 6.4 to 23.4 billion gallons in 2013 [14]. One of the most striking biofuel, which is biobutanol, is produced in many countries including USA, UK, Slovakia, and France [15]. Biobutanol is produced through ABE fermentation. However, the recovery of butanol from ABE solvent is yet relatively expensive and challenging. Thus, ABE solvent is directly used in order to cut down the cost of purification.

Blends of ABE and gasoline in diesel engines have shown promising results such as increase in gasoline engine torque. This is mainly attributed by ABE since it has higher latent heat of vaporization, higher octane number, and have extra oxygen, which contributes to reducing the mixture temperature, and increased charge density, which results in greater engine torque [16]. Based on research by Li et al. [17], it was reported that the ABE-gasoline mixture increased engine torque by 10.9% [17]. Nithyanandan et al. [18], have studied the performance and emission of ABE-gasoline blends and found that the addition of a small amount of ABE can increase the efficiency and reduce the emissions [18]. Another study by Wu et al. [19], reported that ABE-diesel blends provided substantial reduction in NO_x and soot emissions. Additionally a ratio of 6:3:1 ABE gave the highest combustion efficiency together with reduction in soot emissions [19].

In short, biofuels such as ABE have the potential to reduce particulate matter (PM), hydrocarbon, NO_x, and carbon monoxide (CO) emissions, which eventually contributes to lesser environmental pollution. Therefore, to make ABE fermentation engineering practical and economically feasible, the research should be directed to focus primarily on the selection of feedstocks, the selection of microbial strains, and the optimization of fermentation techniques.

Anaerobic bacteria mainly from *Clostridial genera* are normally employed for the ABE fermentation [20]. The clostridial microorganisms are important in the process as these microbes can convert sugar, starch, whey, cellulose, and lignin into biofuels as compared to single-cell microorganisms (yeast) that can only convert sugar into alcohols and carbon dioxide [12].

Renewable and sustainable feedstocks of lignocellulosic biomass have great potential to be utilized for ABE fermentation [20]. As *Clostridia* bacteria can convert carbohydrates, cellulose, and lignin, the lignocellulosic biomasses are considered as one of the inexpensive and attractive feedstocks in the ABE fermentation process. With ease in availability, eco-friendly and carbon-rich, lignocellulosic biomasses are considered as the most favourable feedstock for the ABE biofuel [21, 22].

2.1 Feedstock selections

One of the important aspects to take into consideration in producing biofuel is the type of feedstocks. Currently, the feedstocks used for industrial production of biofuels are mainly food crops such as corn and cassava. However, due to the food vs fuel feud, lignocellulosic biomass namely corn straw, rice straw, apple pomace, cassava bagasse, wheat straw, and oil palm empty fruit bunches are gaining immense potential as a sustainable and renewable feedstock for ABE production [23]. Use of microalgae such as *Chlorella sp*., *Schizochytrium sp*., and *Botryococcus braunii* as feedstocks are also gaining importance these days [24]. Based on the type of feedstocks used, biofuels are divided into mainly three generations.

The first-generation biofuels utilized food crops such as maize (corn), sugarcane, molasses, or sorghum [25, 26]. Global biofuel production is on the rise and the three major producers are USA, Brazil, and Europe. The USA and Brazil contributes to 85% of the world's biofuel production. However, the usage of corn and sugar cane in their production seems to have a negative impact on food security and biodiversity [25]. The cause of these issues is the primary reason why first-generation biofuels have fallen into disfavour [27].

The second-generation biofuels are produced from feedstocks that does not compete with the production of human food and this is a significant alternative as it solves the problems of food versus fuel feud [28]. Lignocellulose biomass is complex structure composed of cellulose, hemicellulose, and lignin. This complex contains glucose, various monosaccharides, and crosslinked phenolic polymers which can be utilized to produce biofuels. Chemical and biological processes must be done on small scale to verify the degree of success in producing biofuels. Pre-treatment and hydrolysis are the two crucial steps in processing lignocellulosic before the production of biofuels. However, these steps have made second-generation biofuel more expensive and become an obstacle to the commercialization of biofuels [29, 30]. Third-generation biofuels are fuels that come from algal biomass. The use of algal biomass cause a few issues such as geographical and technical problems as algal has high water content and the removal of water will cost and consume more energy [31].

Many researchers have done experimental designs to determine the best substrate and best conditions to obtained high production of ABE. Zhang et al. [32], has utilized the steam-explosion method on corn straw to produce ABE via fermentation by using *Clostridium acetobutylicum zzu-02* and *Clostridium beijerinckii zzu-01*. Research done by Olivia-Rodriguez et al. [33], demonstrated that agave hydrolysate has the potential for ABE production using co-culture of *Bacillus subtilis* CDBB 555 and *Clostridium acetobutylicum* ATCC 824 without anaerobic pretreatment. Nimbalkar et al. [34], investigated the production of ABE by using pea pod waste as feed material. The investigation leads to a result where the ABE fermentation of detoxified pea pod waste reveals a low production of total solvent with approximately 50% utilization of sugars. Overall, pea pod waste serves as the basis for the recovery of vegetable waste biomass for the development of ABE. Another cost-effective of ABE production was achieved by using rice straw as feedstock. The batch fermentation coupled with *in situ* product recovery with gas stripping of feedstock using *Clostridium sporogenes* NCIM 2918 result in high titer of alcohol production [35]. Another research aimed at the systematic use of both apple pomace soluble sugar and acidic or alkali hydrolyzed sugar for the development of ABE by anaerobic fermentation (*Clostridium beijerinckii* P260). The result showed the superiority of the combination of water-soluble sugar and hydrolyzed sugar in apple pomace to produce ABE. The process developed for this study can be adapted and extended to other food processing by-products or waste products, such as white grape pomace, citrus, and pineapple peels [23]. In 2015, a study of microalgae (*Chlorella sorokiniana* CY1) as feedstock in the production of biofuel via ABE fermentation has been done using the most common bacterial strain *Clostridium acetobutylicum* ATCC 824 [36]. Direct conversion of wastewater algal biomass to produce biofuel has been done using *Clostridium phytofermentans* DSM1183.

High levels of glucose, galactose, xylose, and rhamnose found in wastewater algae contributed to the source of biofuel conversion [37]. Lipid extracted algae (LEA) is an ideal feedstock in the production of biofuels since it is a non-food crop that is mainly composed of readily fermented carbohydrates such as starch. This study technique demonstrated the compatibility of single-feed biofuel processing, such as *Chlorella vulgaris UTEX 2714* and *Clostridium saccharobutylicum*, as fermenting bacteria and may help to reduce feedstock costs [38].

2.1.1 Lignocellulosic biomass as suitable feedstocks

One of the major obstacles in the production of ABE is to find a sustainable and renewable feedstock. The feedstock used for biofuel production is expensive as for example the market price for gasoline is in the range of 2.03–3.83 USD per gallon, while the price of biofuels exceeded this price [20]. Hence, to up-scale ABE production to industrial scale, it is important to reduce the production cost below 2.18 USD per kg to obtain a positive economic result and compete with the traditional fossil fuel production (1.5 to 2 USD per kg) [39]. Therefore, renewable, and inexpensive feedstock such as lignocellulosic biomass open a new opportunity in biofuels production industries [20]. Table 2 [23, 32–38, 40-56] shows various potential feedstock that been utilized in ABE fermentation.

Lignocellulosic biomasses are non-food feedstocks [57] that are available in large amounts globally and their utilization for the generation of biochemicals is currently drawing considerable attention. The availability and low cost of these materials make them especially attractive feedstocks to replace scarce fossil resources and reduce their negative effect on the environment [58]. Besides, most of the biomasses cause waste disposal problems, therefore, turning these into useable biofuels is a great environmental approach [21]. In Malaysia, the total biomass fractions are 72,962 kt/yr and 5,863 GWh of potential annual generation. These fractions are classified into four different groups according to their resources, such as oil palm, rice, sugarcane bagasse, and municipal solid wastes [59].

Lignocellulosic biomasses have high proportions of complex carbohydrates such as cellulose, hemicellulose, and lignin [60]. Lignocellulose is a complex matrix that includes several different polysaccharides, phenolic polymers, and proteins. Cellulose is a major component of land plant cell walls containing large energy that has real potential for conversion into biofuel. Cellulose is insoluble glucose components or polymers that exist as crystalline microfibrils. Hemicellulose comprises various pentose and hexose, which are attached to the cellulose microfibrils. Meanwhile, lignin composed of phenyl propane polymer which forms a complex cross-linking between the cellulose and hemicellulose [21].

2.2 Microbe selections

The selection of bacterial strains for the ABE fermentation is crucial since it determines fermentation performance and influences methods for feedstock pre-treatment, hydrolysis, and solvent recovery. Clostridium is the most employed microbe in ABE fermentation. The most commonly used Clostridium strains in ABE fuel production are *Clostridium acetobutylicum, Clostridium beijerinckii, Clostridium saccharoacetobutylicum, Clostridium aurantibutyricum,* and *Clostridium sporogenes*. Few non-*Clostridium* strains have also been reported for ABE fuel production such as *Escherichia coli, Bacillus sp., Pseudomonas sp., Lactobacillus sp.,* and *Saccharomyces sp.* [6, 57]. The different strains of microorganisms that utilized in ABE fermentation are shown in Table 3 [23, 32, 35, 40, 44–45, 48–50, 53, 61–65].

It is known that *Clostridium* strains can utilize various types of simple and complex carbohydrates. The productivity of wild-type *Clostridium* strains is limited by solvent tolerance and low cell density during the solventogenic phase of Clostridium growth. To solve this problem, mutations have been introduced where hydrogen peroxide is used to activate the mutation of the *Clostridium* genus strain. The N-methyl-N-nitro-N-nitrosoguanidine (MNNG) tends to function best of all mutations [66]. The mutation of the *Clostridium* strains through molecular engineering was expected to increase the bacterial tolerance towards the solvent produced during the fermentation process and helps to maintain the bacteria cell density during the solventogenic phase. Qurenshi and Blaschek [67] identified the ability of *Clostridium beijerinckii* BA101 strains to produce solvents in a concentration range of 27–29 g/L. The properties of the bacteria have been studied in terms of the influence of fermentation substrate and inhibition of solvent production.

Yan et al., has reported that some of the *Clostridium cellulyticum* strains, including metabolically engineered and wild-type strains can produce value-added products directly from cellulose. However, there is still lack of wild-type strains that can produce butanol directly from cellulose or xylan [68]. Jiang et al. [69], has achieved significant success in engineering acetone production out of solventogenic *Clostridium* by disrupting the acetoacetate

Table 2 Various feedstocks utilized in ABE fermentation

Type	Substrate	Bacterial strain	Production of ABE (g/L)	References
Sucrose/Starch	*Agave Lechuguilla*	*Bacillus subtilis* CDBB 555, *Clostridium acetobutylicum* ATCC 824	12.62	[33]
	Sago starch	*Clostridium saccharobutylicum* DSM13864	9.1	[40]
	Degermed corn	*Clostridium beijerinckii* BA101	14.28	[41]
	Starch and glucose	*Clostridium beijerinckii* BA101	9.9	[42]
	Corn straw	*Clostridium acetobutylicum zzu-02, Clostridium beijerinckii zzu-01*	15.82	[32]
	Peapod waste	*Clostridium acetobutylicum* B527	5.94	[34]
	Rice straw	*Clostridium sporogenes* NCIM 2918	23.5	[35]
	Apple pomace	*Clostridium beijerinckii* P260	10.80	[23]
	Cassava bagasse	*Clostridium acetobutylicum* JB200	108.5	[43]
	Corn stover	*Clostridium saccharobutylicum* DSM 13864	11.43	[44]
	Wheat straw	*Clostridium beijerinckii* P260	21.42	[45]
Lignocellulosic biomass	*Pinacum virgatum*	*Clostridium saccharoperbutylacetonicum* N1-4	13.9	[46]
		Clostridium beijerinckii CECT 508	6.26	[47]
	Oil palm empty fruit bunch	*Clostridium acetobutylicum* ATCC 824	2.51	[48]
	Sago pith residue	*Clostridium acetobutylicum* ATCC 824	4.22	[49]
	Beechwood	*Clostridium acetobutyicum* DSM 792	4.12	[50]
	Barley straw	*Clostridium beijerinckii* P260	26.64	[51]
	Corn fibers	*Clostridium beijerinckii* BA101	9.3	[52]
	Corn stover and switchgrass (1:1)	*Clostridium beijerinckii* P260	26.27	[53]
	Switchgrass	*Clostridium beijerinckii* P260	1.48	[53]
	Wheat straw	*Clostridium beijerinckii* P260	16.59	[54]
Microalgae	*Chlorella sorokiniana* CY1	*Clostridium acetobutylicum* ATCC 824	6.32	[36]
	Wastewater algal	*Clostridium phytofermentans* DSM1183	11.92	[37]
	Chlorella vulgaris UTEX 271	*Clostridium saccharobutylicum*	11.50	[38]
Glycerol	Glycerol	*Clostridium pasteurianum* ATCC 6013	18.30	[55]
Syngas	Syngas	*Clostridium carboxidivorans* $P7^T$	0.009	[56]

decarboxylase gene (*adc)* in *C. acetobutylicum*. The presence of exogenous electron acceptor methyl viologen in engineered strain increases the carbon flow towards butanol instead of acetone in ABE fermentation, so results in higher amount production of butanol [69]. However, butanol production through such strategies is expensive. Therefore, to obtain an economical yet simple process, the use of bacterial strains (non-clostridial bacteria) that can directly ferment lignocellulosic materials is desirable [68].

Other than that, the current molecular engineering techniques also help to improve the result of ABE fermentation. Zhang et al. [70] have developed an effective genome editing method for *Clostridium tyrobutylicum* based on an endogenous type I-B CRISPR-Cas system. The PAM sequences for DNA targeting purposes have been established. Multiplex genome engineering purposes have been achieved with an efficiency of 100% by using lactose inducible promoters to guide the transcription of CRISPR array. High butanol production (26.2 g/L) by batch fermentation has been recorded by using the engineered strain [70].

2.2.1 Mixed microbe culture

The creation of genetically modified microorganisms with the combined ability to utilize lignocellulose and produce solvent are difficult due to the limited existing tools in genetic engineering. A more convenient and feasible approach to produce ABE in fermentation is by mixed culture of both cellulolytic and solventogenic bacteria.

Table 3 Strains utilized in ABE fermentation

Strains	Main solvent product	Production titer (g/L)	Ref.
Clostridium acetobutylicum ATCC 824	ABE	25.0	[61]
		2.51	[48]
		4.22	[49]
		6.1	[62]
Clostridium beijerinckii P260	ABE	10.80	[23]
		14.6	[53]
		21.42	[45]
Clostridium saccharoperbutylecetonicum N1-4	ABE	16.0	[63]
Clostridium Saccharobutylicum DSM 13864	ABE	9.29	[44]
		9.1	[40]
Clostridium beijerinckii BA101	ABE	8.8	[64]
Clostridium acetobutylicum T64	ABE	15.3	[65]
Clostridium acetobutylicum zzu-02, Clostridium beijerinckii zzu-01	ABE	15.82	[32]
Clostridium sporogenes NCIM 2918	ABE	26.40	[35]
Clostridium acetobutyicum DSM 792	ABE	4.12	[50]

This technique is preferable due to the potential for synergistic use of two organisms' metabolic pathways [71]. Consolidated bioprocessing (CBP) is a technology in which pre-treatment (hydrolysis) and fermentation of biomass is carried out in a single unit, requiring minimum equipment and energy consumption and in theory, achieving a high concentration of the substrate. A crucial element in the growth of CBP is the mixed culture of microorganisms [72]. The first culture that involves is known as a hydrolytic microorganism which converts the hemicellulose fraction into cellulose fraction. The second culture involves is the *Clostridium sp.*, where it converts the fraction of cellulose into solvents [73]. In the mixed culture, microorganisms may develop potential synergistic utilization of metabolic pathways from interspecies.

However, the co-culture between a cellulolytic bacterium and solventogenic bacteria might develop a new problem to verify the optimal growth of the co-culture. Pinto et al. [74] have done an investigation, using *Clostridium thermocellum* and *Clostridium saccharoperbutylacetonicum* as cellulolytic and a butanol-producing bacterium respectively. Both of the bacteria has different optimal temperature, but they successfully cultured both bacteria at 30 °C. Other than that, another research of co-culture between *Bacillus subtilis* and *Clostridium butylicum* resulted in a 6.5-fold in ABE production compared to single culture (*Clostridium butylicum*) [74].

3 Pre-treatment, fermentation, and purification

A typical conversion process of lignocellulosic biomass to ABE involves three major steps, which are pre-treatment, fermentation together with purification and recovery. The schematic diagram showing the flow of ABE production are shown in Fig. 1. The pre-treatment method is important to break down lignocellulosic components into fermentable sugars. The fermentation process only occurs after the pre-treatment process where the ABE producing bacteria are added to enhance the conversion of sugar into biofuel. Purification and recovery are the last crucial steps in producing ABE where this process involves the separation of biofuel from fermentation broth [75].

3.1 Pre-treatment

An ideal pe-treatment should include a few important aspects:

1. pre-treatment should be able to separate lignin and hemicellulose from the cellulose microfibrils complex,
2. it should be able to improve the sugar yield,
3. able to reduce excessive loss of carbohydrates due to degradation and
4. cost-effective.

There are a few different methods of pre-treatment available for biomass conversion which include dilute acid, alkali, hot water, ammonia fiber explosion, carbon dioxide explosion, and organic solvent [21].

Lignocellulose consists primarily of cellulose, hemicellulose, and lignin, which are bound together by covalent bonding, various intermolecular bridges, and Van der Waals forces, creating a complex structure, and making it resistant to a few hydrolysis methods and insoluble in water. Dilute acid pretreatment can solubilize the hemicellulose and thereby disrupt the lignocellulosic. Cellulose (40–50% of total dry matter) is a glucose polymer-bound by β-1,4 glycosidic bonds and the basic building block is cellobiose, a glucose dimer [76]. Cellulose bonds can be hydrolyzed by special enzymes known as cellulase. Hemicellulose is a highly branched heteropolysaccharide (20–40% of total dry matter) composed of several sugars (C5 and C6). The individual sugars of

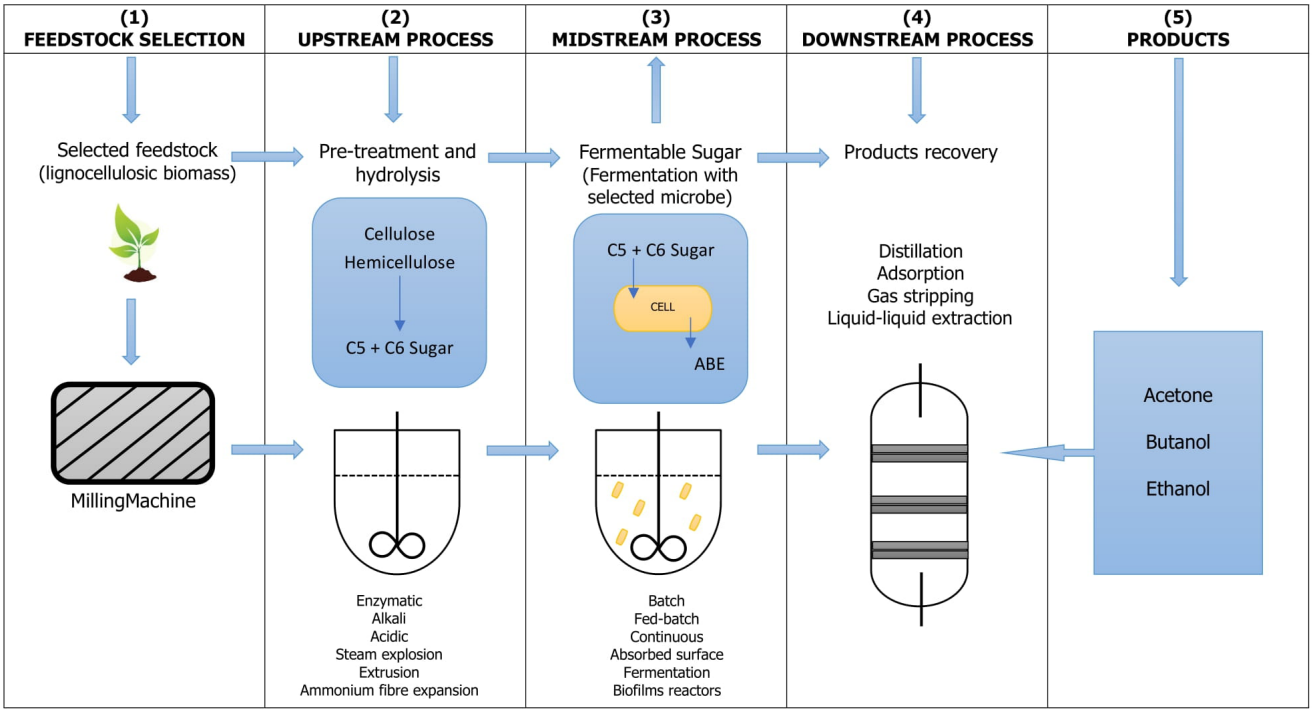

Fig. 1 A schematic diagram of fermentative ABE production from lignocellulosic biomass

hemicellulose can be different depending on the species of the plant. However, hemicellulose hydrolysis can produce a mixture of glucose, galactose, mannose, arabinose, xylose, and rhamnose. A total of 20-25% of the total dry matter of feedstock are lignin. The conversion of the biomass-to-bioenergy process is mostly hindered by lignin as it provides mechanical supports and water impermeability to the secondary cell walls of plants and acts as a physical and biochemical barrier [77].

3.1.1 Acid hydrolysis

Acid hydrolysis can be done by using concentrated sulfuric acid and hydrochloric acid (H_2SO_4 and HCl). A high yield of sugar can be obtained from cellulose by using concentrated acid with low temperature. However, due to high concentrations of acid in the hydrolysis process, it will cause corrosion of the equipment, environmental toxicity, and the high cost needed for acid recovery. Compared to a concentrated acid, dilute acid requires lower acid concentration but to produce a high yield of glucose higher temperatures and strong conditions is needed. Dilute acid hydrolysis is also known to have a negative influence on the enzymatic hydrolysis of biomass [78]. In addition, the downstream fermentation process will be inhibited when acid is associated with products such as furfural, hydroxymethylfurfural (HFM), and acetic acids used for biomass pretreatment [79].

3.1.2 Enzymatic hydrolysis

Enzymatic hydrolysis is an alternative and environmentally safe process as compared to acid hydrolysis. It is also cost-efficient if the enzyme is generated locally by microbes [80]. Enzymatic hydrolysis is performed by cellulase, which is highly specific. The utility cost of enzymatic hydrolysis is low since it is typically done under mild conditions and does not cause corrosion problems. Microorganisms which produce the cellulase can be both aerobic or anaerobic such as *Bacillus, Clostridium,* and *Pseudomonas*. However, anaerobic microbes such as *Clostridium* only produces cellulase with high specific activity and does not produce high enzyme titers. Cellulase is usually the mixture of several enzymes [81].

The three major enzymes are endoglucanase, exoglucanase, and β-glucosidase. During the enzyme hydrolysis, cellulose will be degraded by cellulases to reducing sugars which then will be fermented by yeast or bacteria to alcohol (acetone, butanol, ethanol) [82]. The action of endoglucanase will strike with low crystallinity in the cellulose fiber region that produces free chain-ends. Exoglucanase then can further degrade the molecule by removing cellobiose units from the free chain-ends [83]. The cellobiose is then hydrolyzed by another type of enzyme known as *β*-glucosidase to produce glucose. In addition to the three main classes of enzymes, there are also a variety of ancillary enzymes that target hemicelluloses, such as

glucoronidase, acetylesterase, xylanase, *β*-xylosidase, galactomannanase, and glucomannanase [81].

3.2 Anaerobic fermentation of ABE

The fermentation of sugar glycerol or lignocellulose feed in the presence of various microorganisms of the Clostriaceae family are the most desirable routes for the production of ABE. Fermentation of ABE using *Clostridia* species has a complex intracellular pathway. Solvents (acetone, butanol, ethanol), organic acids (lactic acid, acetic acid, butyric acid), and gasses (carbon dioxide and hydrogen) are essential products formed in the intracellular pathway [57]. A simplified biochemical process of ABE are shown in Fig. 2.

The fermentation of the ABE process can be divided into two parts which are acidogenesis and solventogenesis. Acidogenesis is the process of sugar conversion into organic acids while solventogenesis is the process of solvent production. Acidogenesis occurs during the first phase of fermentation where the microbes grow exponentially. These microbes produce mainly acetate and butyrate which cause the pH to decrease to around 4.5. In response to pH, microbe cells shift the metabolic activity from acidogenesis to solventogenesis which causes the production rate to fall. The high production of acid in the first phase induces the solventogenic enzyme for the second phase of fermentation. The acetate and butyrate are consumed as a substrate for the biosynthesis of acetone and butanol. During this phase, microbial growth remains constant [84].

3.2.1 Acidogenesis

The metabolic pathways of the ABE fermentation start by utilization of glucose from hydrolysis of carbohydrates that are broken down by amylase enzyme to form volatile fatty acids (VFAs) (acetate and butyrate), alcohol (ethanol and butanol), H_2, ad CO_2 by *C. acetobutylicum* via the anaerobic fermentation. The carbon from carbohydrates which is in the form of pentose and hexose sugars will be metabolized via pyruvate. Formations of 2 moles of pyruvate with a net formation of 2 moles of adenosine triphosphate (ATP) and 2 moles of nicotinamide adenine dinucleotide (NADH) when 1 mole of sugar are degraded. Then it will form acetyl-CoA and carbon dioxide (CO_2) when the pyruvate is converted. Other intermediates will be formed when Acetyl-CoA is further converted. This conversion ultimately leads to oxidized products (acetone, acetate) and reduce products such as butanol and ethanol. The first occurrence of intermediate and acid formation is acidogenesis and occurs under particular conditions such as pH greater than 5 and iron limitation. The ATP is generated continuously in the process [15, 85].

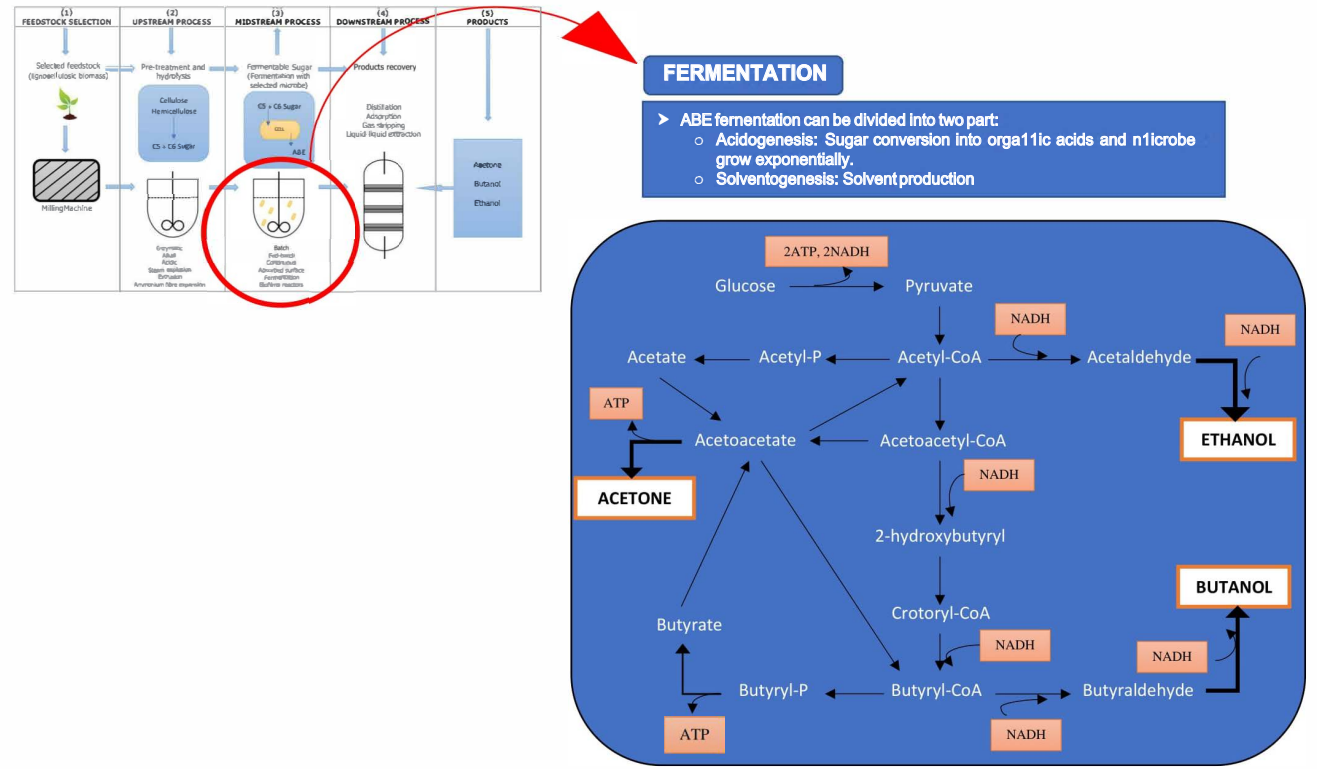

Fig. 2 A schematic diagram of the biochemical process of ABE

With 1 ATP generated, acetate is produced directly from Acetyl-CoA via phosphotransacetylase and acetate kinase. The formation of Acetyl-CoA from pyruvate can flow into two different pathways. The first pathway usually occurs in facultative anaerobe (*Eschericia coli*) which is known as the pyruvate formate-lyase (PFL) pathway where it produces Acetyl-CoA and formate. The second pathway is where Acetyl-CoA is generated and reduces ferredoxin which is known as the pyruvate ferredoxin oxidoreductase (PFOR) pathway [86].

$$C_2H_3O_3 + H_2O + F_{dox} \rightarrow C_2H_3O_2 + CO_2 + 2H^+ + F_{dred} + ATP$$

The production of butyrate is controlled by phosphotransbutyrylase (PTB) and butyrate kinase which together form a pathway that enables clostridia to convert butyryl-CoA to butyrate. The conversion of butyryl-CoA to butyrate produce 1 ATP. This pathway is for *C. acetobutylicum* because under certain fermentation conditions the PTB and butyrate kinase is inactive, producing little or no butyrate, and the available butyryl-CoA is channelled towards the formation of butanol [87].

3.2.2 Solventogenesis

To produce acetone, butanol, ethanol, acetic acid, butyric acid, hydrogen, and carbon dioxide as the main product, the process of re-assimilation of acid need to occur where this process is known as the solventogenesis. This phase in fermentation usually takes place in different types of Clostridia strains. The formation of CoA derivatives is produced by the assimilation of acetate and butyrate with the aid of acetyl-CoA transferase with acetoacetyl-CoA as CoA donors. The formation of acetate occurs through the CoAT pathway where acetate and butyrate are utilized in the process. Butyryl-CoA is converted to butyraldehydes and eventually to ethanol and butanol. Meanwhile, acetoacetyl-CoA transforms to acetone and acetaldehydes into ethanol [51, 88–90].

During the acidogenesis phase, acetate was produced rapidly involving the reaction of phosphotransacetylase and acetate kinase. However, during the solventogenesis phase, the activity of acetate kinase decreased rapidly to a low level. Meanwhile, ethanol is formed by acetaldehyde [88]. Butanol can be produced by Clostridium from the reduction of butyryl-CoA with NADH in the standard fermentation process of ABE. The synthesis of ethanol is reduced by NADH by acetyl-CoA from pyruvate, with acetaldehyde as an intermediate [86].

3.3 Products separation and recovery

The purification and recovery process is an important downstream step in ABE fermentation. There are various types of the recovery process that can be selectively recovered acetone, *n*-butanol, and ethanol from fermentation broth. The commonly used ABE recovery processes are distillation, adsorption, gas tripping, and liquid-liquid extraction, perstraction and pervaporation. The advantages and disadvantages of different purification method of ABE are shown in Table 4, while the comparison between the purification method are shown in Table 5 [91–102].

3.3.1 Distillation

Distillation is a well-known method in ABE separation where the separation occurs due to the difference in volatilities of separated components. The distillation is based on different boiling points of ABE solvents. When the mixture of solvents is boiling, the vapours released will be a different compound than the solvent in the boiling liquids. There are a few different modes of distillation such as continuous distillation, batch distillation, fractional distillation, and steam distillation [103, 104]. Roffler et al. [105], described a more conventional distillation process where acetone, *n*-butanol, and ethanol were heated at 100 °C by heat exchange and removed from the broth by a stream of vapours. The obtained vapours contain 70% of water and 30% of solvent mixtures. Further separation was done by using 4 distillation columns and in the first column 99.5 wt% of acetone is removed. The residual is then removed to another column known as the ethanol column and 95 wt% of ethanol is extracted and the bottom products are redirected to separate water and *n*-butanol. The *n*-butanol is redirected to an *n*-butanol stripper and finally extracted a 99.7 wt% of *n*-butanol [105]. van Wyck et al. [106], described continuous fermentation with integrated ABE recovery. In this process, the bioreactor worked at atmospheric pressure and the broth was continuously circulated in a vacuum chamber which the solvents (acetone, *n*-butanol, and ethanol) were boiled and condensed. This modified process allows the production and extraction of up to 30-37 g/L of *n*-butanol. Distillation is the conventional method, but is also an energy intensive process which required 18-79.5 MJ/kg butanol depend on the types of pre-treatment applied and separation techniques. The lowest rage number reported is 50 MJ/kg which is 50% less and now more separation method has been investigated to reduce butanol toxicity and reduce

Table 4 Advantages and disadvantages of solvent purification method

Types of ABE recovery method	Advantages	Disadvantages
Distillation	Simple operation	Requires high energy Low selectivity Time consuming
Adsorption	Low energy requirement No emulsion form	Adsorbent regeneration
Gas stripping	Simple operation No harm to culture Only strips volatile solvents Can operate under fermentation set temperature	Low selectivity Low efficiency Requires high gas flow rate
Liquid-liquid extraction	High selectivity High efficiency	Forming emulsion Toxic to culture High cost for extractant recovery
Perstraction	High selectivity Low toxic to culture (compared to LLE)	Form emulsion Membrane fouling
Pervaporation	High selectivity Low temperature needed Low operating cost No harm to culture No loss of substrate or nutrient from fermentation broth	Membrane fouling High liquid flow rates needed

Table 5 Comparison of different purification methods used in ABE recovery

Types of ABE recovery method	Types of substrates	Microorganisms	ABE yield (g/g)	Ref.
Distillation	Glucose	*Clostridium beijerinckii* BA101	0.39	[92]
	Glucose	*Clostridium acetobutylicum* JB200	0.37	[92]
	Glucose	*Clostridium acetobutylicum* SolRH	0.37	[92]
Adsorption	Glucose	*Clostridium acetobutylicum* ATCC 824	0.28	[93]
	Glucose	*Clostridium acetobutylicum*	0.32	[94]
	Glucose	*Clostridium acetobutylicum*	0.32	[94]
Gas stripping	Whey permeate	*Clostridium acetobutylicum* P262	0.40	[95]
	Glucose	*Clostridium beijerinckii* BA101	0.41	[91]
	Glucose	*Clostridium* sp. DSM 2152	0.34	[96]
Liquid-liquid extraction	Sugar mixture	*Clostridium acetobutylicum* DSM 792	0.38	[97]
	Glucose	*Clostridium acetobutylicum* B5313	0.35	[98]
Perstraction	Whey permeate	*Clostridium acetobutylicum* P262	0.35	[99]
	Whey permeate	*Clostridium acetobutylicum* P262	0.37	[99]
Pervaporation	Glucose	*Clostridium acetobutylicum* (CICC 8012)	0.24	[100]
	Glucose	*Clostridium acetobutylicum* DP 217	0.37	[101]
	Glucose	*Clostridium acetobutylicum* ATCC 824	0.28	[102]

energy usage [106]. Distillation is the most popular technique used in the ABE industry, but these techniques consume high energy and low selectivity. Due to this factors, other product recovery technique is being investigated.

3.3.2 Adsorption

Adsorption is a technique where solvents are adsorbed onto the surface of a suitable adsorbent. The adsorbed solvents are then released by increasing temperature or by using a displacer to produce a concentrated solvent. The adsorption technique is an energy-efficient process and can be used to selectively separate solvents from fermentation broth [107, 108]. In selecting a suitable absorbent, many factors need to be considered such as adsorption rate, adsorption capacity, ease of adsorption, selectivity to the desired product, and cost of the absorbent [109]. It

was found that *n*-butanol was adsorbed more efficiently compared to ethanol when tested with adsorption on mesoporous carbon (MPCs) with surface area ranging from 500 to 1300 m^2/g. It also concludes that the capacity of solvents adsorption increased with the increase of adsorbents surface area. In addition, MPCs are thermally and chemically stable throughout the measurement process [110]. Lin et al. [111], reported that the usage of microporous adsorption resin (KA-I) with cross-linked polystyrene framework as adsorbent for *n*-butanol removal from ABE mixture at ratio 3:6:1 showed that the KA-I resin selectively absorbed *n*-butanol and only a small amount of ethanol and acetone were absorbed. The study also concludes that the adsorption capacity and rate of *n*-butanol removal are directly proportional to the increased temperature. Although absorption techniques possess high selectivity toward butanol, there are still several problems in the product recovery which is the difficulty in desorption of organic compound and bacteria can adhere to the adsorbent and deceased the adsorption efficiency especially when the adsorbent is recycled [107, 112, 113].

3.3.3 Gas stripping

Gas stripping is a simple and efficient way to recover solvent from fermentation broth. The recovery process starts with gas is bubbled through the fermentation broth then pass through a condenser to recover the solvents. The stripped gas is then recycled back to the fermenter and the process continues until all the sugar is utilized [114]. Given the strong inhibition of butanol during fermentation, using gas stripping should lead to higher productivity and yield. A large amount of gas circulation will not cause any cell damaged but in fact, it will cause foaming. The performance of the gas stripping depends on the gas flow rate, antifoam, and presence of other components in the fermentation broth [115–117]. Ezeji et al. [91], tested various parameters on the performance of ABE recovery from fermentation broth which include the presence of acetone, ethanol, gas recycle rate, and bubble size. The usage of sparger gas striping mode causes more foam as compared to an impeller and therefore it increased the need for antifoam. The addition of more antifoam to the fermentation broth causes toxic effects to the microbe. It is found that when the gas recycles rates and constant gas stripping rates are at 80 cm^3/s and 0.054 per hour respectively are already sufficient to maintain the *n*-butanol concentration below the toxic level during the fermentation process. The performance of gas stripping towards different fermentation system (batch, fed-batch, continuous) are also observed. The yield and productivity of fed-batch and continuous fermentation are both higher than batch fermentation. However, the fed-batch fermentation failed after 201 hours due to the accumulation of unknown inhibitors such as salts and dead cells. Therefore, it is reported that the effectiveness of gas striping is only effective in continuous fermentation only [118, 119].

3.3.4 Liquid-liquid extraction (LLE)

Liquid-liquid extraction is another technique to remove solvents from the fermentation broth and this process involves the addition of water-insoluble organic extractant into the fermentation broth to extract solvents selectively. This technique requires an organic solvent that can separate desirable solvents without removing the substrate, water, and nutrients from the actual fermentation broth [117, 120]. Until now, extractants with high butanol distribution coefficients were found to be toxic to butanol-producing bacteria. Oleyl alcohol is one the most used extractant to separate *n*-butanol because of its ability to extract *n*-butanol in high yield and is relatively low toxic to butanol producing bacteria. A good extractant such as *n*- decanol is avoided in the removal of *n*-butanol from fermentation broth. This is because *n*-decanol can cause bacteria to strain destruction. Therefore, to overcome the negative impact on bacteria, researchers such as Evan and Wang have tried the combination of toxic decanol and non-toxic oleyl alcohol for *n*-butanol recovery. At a constant pH value equal to 4.5 an increase in *n*-butanol production with the addition of decanol was observed. Approximately 90 mM of *n*-butanol as products without the addition of decanol, 150 mM *n*-butanol with 0.3% vol of decanol, and 40 mM of *n*-butanol with 0.4% vol of decanol [121]. Some researchers also study the non-ionic surfactant as an extractant to save on the downstream process cost. The study of extractant using a non-ionic surfactant to remove *n*-butanol from fermentation broth are tested based on its biocompatibility. They found out that the L62 could be considered an extractant as it did not interrupt the yield and productivity of fermentation. Butanol partition coefficient in L62-water ranged from 3 to 4 and the yield of butanol is 6-times higher. At the end of the fermentation, 95% of the butanol present in the surfactant-rich phase was removed by evaporation and its concentration reached 106.8 g/L. The same surfactant was used for another three-extraction cycles and the same butanol recovery was obtained in each cycle [122]. However, there are some problems using

extractants in solvents recovery such as loss of extractant, toxicity to culture, emulsion formation, and sometimes an accumulation of biomass.

3.3.5 Perstraction

Perstraction or also known as membrane extraction is a method that was developed to overcome the problems encountered with LLE. This method works on the same principle as LLE, however the organic solvent and fermentation broth are separated by a membrane. However, there are very limited reports in the literature on the perstraction of ABE fermentation. Qureshi et al. [99], conducted a study using the perstraction method using silicone membrane and oleyl alcohol as extractant solvent and resulted in 0.24 g/L of ABE production [99].

3.3.6 Pervaporation

The Pervaporation process involves a membrane between the fermentation broth and the gaseous phase. Pervaporation shows to increases the substance utilization, productivity, and yield of ABE fermentation. The important procedure in this method is to choose the right membrane which selectively allows the transfer of ABE. The choice of the membrane is important to avoid blockage from cells adhering to it. One of the most tested membranes is silicone as it is widely available commercially, inexpensive, and easy to manipulate in a laboratory scale [123, 124]. However, there has been a new approach towards using composite membranes by utilizing combination material to improve the membrane selectivity and flux performance. The new improved membrane includes silicate-silicone composite membrane, silicate-polydimethylsiloxane (PDMS), ceramic composite, zeolite mixed PDMS, and carbon nanotube-filled PDMS. Selectivity and flux increase with the decrease of membrane thickness. Polymers have high flux, cheaper, and are easy to fabricate into the membrane. Inorganic materials are often selective to butanol but are expensive. Therefore, by combining two materials the membrane should be more selective with sufficient flux and not having a problem with the cost for scale-up. Li et al. [126], used silicate-PDMS membrane and were able to extract 201 g/L ABE while Xue et al. [128], used zeolite-PDMS resulting in 253 g/L ABE [125–128].

4 Challenges

While ABE fermentation has several advantages, the ABE process has several challenges that impede its commercial production. ABE is not economically viable since the biggest issue is the challenge in processing fermentable sugars since the feedstock used has a rigid structure and the hydrolytic enzyme is costly for hydrolysis purposes [129]. The implementation of pretreatment, which is also a costly process, is also required [130]. In pretreatment processes, HMF induces inhibitory effects on the growth of clostridium and thus decreases the production of ABE [131]. In addition, the hydrolysate formed by pretreatment is a mixture of different ingredients, including sugars, which cannot be stimulated just like pure glucose [132]. In comparison, hemicellulose and cellulose hydrolysate produce mostly xylose in the case of biomass agriculture. Therefore, if the optimization is done on pure glucose, it will not achieve the same effect as hydrolysate. In fact, the co-consumption of different sugars takes place in the case of fermentation of hydrolysate to ABE, which is much more complicated than the fermentation of pure glucose [133]. In industrial-scale operations, the production of ethanol is usually between 5–9% and can go up to 16%, whereas the production of ABE is 2–4%. The cost of isolation and purification of ABE is also far greater. This is partly due to the toxicity of the solvent to the bacteria producing ABE [134–135].

5 Conclusion

Energy is an important source of needs for the growth of economics and social progress. Therefore, to ensure energy stability, the measurement and design strategies to support the production of biofuels such as ABE need to be taken. This review, presents an overview of ABE production which focuses on the feedstock, microbe, fermentation and recovery processess. Using agricultural wastes as feedstock becomes a great option due to its abundance and its nature-friendly characteristics. However, the major limitation for the commercialization of ABE is the high production cost especially in the hydrolysis and recovery process. But to some extent, the prospect of using lignocellulosic biomass as feedstocks is still difficult to be interpreted as more time and efforts are required to explore its ability as a sustainable feedstock. However, the main expectation and contribution of ABE production are to help to solve the fossil fuel crisis and to produce a more suitable and cleaner energy for the earth.

Acknowledgement

UMS grants SBK0421-2018 and GUG0401-2/2019.

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