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ABSTRACT

It is a popular fact that the world's dependency on fossil fuel has caused unfavourable effects, including lessening crude oil reserve, decreasing air quality, rising global temperature, unpredictable weather change, and so on. As the effort to promote sustainability and independency from fossil fuel, bioethanol is now favoured as the blend or fossil petrol substitute. However, the feedstock functionality of first generation bioethanol production is restricted due to its edibleness since it would clash the feeding purpose. Second generation bioethanol production fulfils the impractical gap of first generation since it employs non-edible feedstock sourced from agriculture and forestry wastes. Lignocellulosic and starchy materials in them are convertible to fermentable sugars that are able to be further processed, resulting anhydrous bioethanol as the end product. This paper critically reviews the existing variance of second generation bioethanol production methodologies, namely pre-treatment, hydrolysis, fermentation and distillation, as well as the worth of second generation production for future reference. The discussions in this paper are also fit as the fundamental for feasible planning of second generation bioethanol production plant.

Contents

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1. Introduction

Transportation sector, inevitably, contributes the rise of petroleum consumption the most, which closely linked to harmful environment impacts. The world's consumption of fossil fuels by transportation sector accounts for 60%, which consequently contributes to the massive pollution generation to the environment [1]. Moreover, global transportation sector contributes 19% of carbon dioxide (CO_2) which about 8 kg CO_2/gallon petrol, and more than 70% of carbon monoxide (CO) [2,3]. Malaysia, as one of rapidly developing countries in the South East Asia, appears to grow a similar pattern in pollution generation in its transportation sector. As reported in Compendium of Environment Statistics 2013 by Department of Statistics (DoS) Malaysia [4], in year 2012 transportation sector in Malaysia contributed the most of the atmosphere pollutions by 68.5%. In the same year, transportation sector degraded the air quality by emitting 1.78 million-tonnes of CO, 226.2 ktonnes of NO_2, 14.4 ktonnes of SO_2 and 4.6 ktonnes of particulate matters. Moreover, 6.5% and 5.1% of CO and SO_2 emissions increased respectively from 2011 to 2012, while 4.5% increment occurred on both NO_2 and particulate matters emissions. One of the solutions in reducing environmental impact is by using biofuel to replace fossil fuel. Simply, biodiesel is used to replace diesel whereas bioethanol used to replace petrol. Study on biodiesel production and performance have widely been conducted as can be found in refs [5–13]. However, study on second generation bioethanol production is still limited.

Bioethanol is a renewable and sustainable liquid fuel that is expected to have a promising future in tackling today's global energy crisis and the worsening environment quality. In 2011, the world's bioethanol production was stated to be above 100 billion litres and was expected to increase up to 3–7% p.a in the year 2012–2015, which shows that bioethanol is already being seen as one preferable alternative energy source to substitute the fossil fuel [14]. Bioethanol is not a new energy source since it has been used extensively in Europe and the United States early 1900s, but it was ignored due to its high production cost compare to petrol. The bioethanol production was then continued due to the oil crisis in 1970s [15]. With its high octane number of 108, bioethanol becomes a favourable fuel internal combustion engine to prevent engine knocking and early ignition, thus leads to high antiknock value [16]. Although it has 68% lower energy content compared to petrol, bioethanol's high oxygen content makes the combustion cleaner and results lower emission of toxic substances [17]. Bioethanol also helps to reduce CO_2 emission up to 80% compared to using petrol, thus promotes a cleaner environment for the future [18]. The criteria of the bioethanol to substitute, or to be blended with, petrol is prescribed under ASTM D4806 standard, which sets the quality requirements of bioethanol for spark-ignited engine [19].

The development of second generation bioethanol production may not be as advanced as the first generation production. However, looking at the feedstock's availability, second generation holds a gigantic potential if implemented nationally. For instance, as the world's second largest oil palm producer, Malaysia generates excessive oil palm wastes of which are usually unprocessed and thrown. It is recorded that 85.5% of the total nation's agricultural industry waste comes from oil palm industry [20]. From the amount of waste generated, Malaysia could sustain the national ethanol supply to support the fossil fuel demand and reduce the environmental harmful impact. Although replacing tropical forests with oil palm plantations is responsible for the large amounts of carbon released into the atmosphere, utilising oil palm waste might contribute to reducing the carbon emission. But the sustainability issue is still there since the net CO_2 emission lifecycle, from both direct and indirect land use, tends to exceed the safe limit. Capital investment in second generation production indeed seems highly risky. However, it has been strongly suggested that every little investment in the first generation production should be gradually allocated to the second generation production development for the future readiness. Also, experts have forecasted that second generation production will replace first generation in the near future [21]. Similarly in biodiesel, Malaysia has shown the interest in second generation of biodiesel production from various non-edible feedstock as contribution in the renewable energy demand for the compression engine vehicles [9–11,22,23].

The quality of bioethanol produced is majorly dependent on the production routes. As bioethanol production in general consists of several sequential procedures, namely pre-treatment, hydrolysis, fermentation and distillation, each of the stage is branched and each branch will give different results in ethanol quality as well as overall production cost. Moreover, the current available technologies enrich the possibilities in bioethanol production routes. For instance, a study showed that acid hydrolysis by sulphuric acid gives sugar conversion efficiency of 76% for cellulose to glucose, and 90% from hemicellulose to xylose [24]. The type of source of sugar also determines the quality of ethanol produced from fermentation, as the same author claimed that glucose can be fermented into ethanol with efficiency about 75%, while 50% with xylose [24]. Another example is comparison between mechanical and acid pre-treatment. Mechanical pre-treatment is indeed convenient and conventional, but it consumes high energy to run. Meanwhile, acid pre-treatment, another common pre-treatment method to increase the feedstock surface area, tends to corrode production equipment [25]. The selected method from the available technologies will give different outcome, advantage and disadvantage from the overall production process. This leads to the importance of bioethanol production method selection, especially for a country to initiate or implement national second generation bioethanol prospect as its renewable energy industry sector. In addition, to regulate second generation bioethanol policies government requires a thorough study of the available production technologies to determine the viable route for the country.

This paper provides a critical and complete review on second generation bioethanol production through the accessible existing methods. Generally ethanol production comprises pre-treatment, hydrolysis, fermentation and distillation to achieve anhydrous ethanol as the end product, and this paper describes the available technologies for each production stage. This paper also discusses production methods from lignocellulosic and starchy biomass, results, advantages and disadvantages of the technologies from compilation of reported works.

2. Second generation bioethanol production

2.1. Pre-treatment

The principle objectives of pre-treatment process to begin the biofuel production are (i) as the physical material's size reduction method [26], (ii) provision of the components exposure (hemicellulose, cellulose, starch) as prior to hydrolysis to yield improved reducing sugars [27], (iii) provision of better hydrolysis access for the enzymes to hydrolyse the carbohydrate into fermentable sugars in the subsequent enzymatic hydrolysis method [28] and (iv) reduction of crystallinity degree of the cellulose matrix [29]. It is frequently emphasised that pre-treatment process is highly recommended as it gives subsequent or direct yield of the fermentable sugars; prevents premature degradation of the yielded sugars; prevents inhibitors formation prior hydrolysis and fermentation; lowers the processing cost; and lowers the demand of conventional energy in general [30,31].

In the typical starchy agricultural waste, physical size reduction as the result of the pre-treatment is sufficient. This approach is usually done by any simple mechanical pre-treatment since starchy material distinctively provides easier direct access to hydrolysis (enzymatically through amylases). With reduced size of starch (e.g. starch milling with fine powder as the end pre-treatment product) an easy hydrolysis method (e.g. heating the starch with water) can be opted as the method to hydrolyse the starch, although the ethanol yield may be varied according to the other stages' method and procedure in the overall production. This phenomenon is possible due to the nature of the starch that comprises direct long chains of glucose forming polysaccharide as the complex form of sugar. Starch is also soluble in water. As the starch is mixed with water and presence of heat, the hydrogen bonds of the starch react with water molecules and dissolved. As the result, the gelatinization of starch occurred. However, this occurrence is undesirable in the bioethanol production since gel is an undesirable medium for the whole procedures.

In lignocellulosic materials, pre-treatment is commonly functioned as deformation of the rigid components, which structured of lignin, cellulose and hemicellulose; and resulting in the degradation of the crystallinity degree, which is required as the adequate condition prior hydrolysis. Physical reduction pre-treatment (mechanically) alone is also suitable for the lignocellulosic material. However, with an additional method, by chemical pre-treatment for instance, would deliver a smoother condition for hydrolysis as the following stage. The combination would also bring out a better yield of reducing sugars at the end of hydrolysis. Refaat [32] explored various types of the pre-treatments in bioethanol production from the typical lignocellulosic material (Table 1). The wide choices of pre-treatment method for lignocellulosic material are to bring up the amorphous form of the celluloses, so that enzymes in hydrolysis stage can efficiently consume them and resulting more sugar monomers at the end of the process [29]. It requires more effort to attain complex sugars (carbohydrate) in the lignocellulosic materials to be converted into the sugar monomers. Table 1 sums the available pre-treatment methods can be used in the production [32]. These pre-treatment methods are categorically specified under biological pre-treatment, chemical pre-treatment, physical pre-treatment and physicochemical pre-treatment.

2.1.1. Biological pre-treatment

Biological pre-treatment employs microorganisms to perform the pre-treatment task. The employed microorganisms in this method specifically possess the capability to degrade the lignocellulosic

Table 1
Different pre-treatment methods for lignocellulosic materials in bioethanol production [32].

Pre-treatment method	Main effects	Advantages	Disadvantage/limitations
Ammonia fibre explosion (AFEX)	• Increases accessible surface area • Removes lignin and hemicelluloses to an extent	• Low formation of inhibitors	• Not efficient for biomass with high lignin content • High cost of large amount of ammonia
Ammonia recycled percolation (ARP)	• Removes lignin	• Highly selective delignification	• High energy consumption
Alkali	• Removes lignin and hemicelluloses • Increases accessible surface area	• High digestibility • High lignin removal	• Long residence times • Irrecoverable salts formation
Biological pre-treatment	• Degrades lignin and hemicellulose	• Low energy consumption	• Low rate of hydrolysis
Concentrated acid	• Hydrolyses both hemicelluloses and cellulose	• High glucose yield • Reduction in the operational costs due to moderate operation temperature • Low formation of degradation products • No enzymes are required	• Acid recovery is mandatory • Equipment corrosion • Generation of inhibitory compounds
Diluted acid	• Hydrolyses hemicelluloses • Renders cellulose more amenable for a further enzymatic treatment • Alters lignin structure	• Less corrosion problems than concentrated acid • Low formation of inhibitors	• Generation of degradation products due to high temperature • Low sugar concentration exit stream
Ionic liquids	• Reduces cellulose crystallinity • Removes lignin	• High digestibility • Green solvents	• Large-scale application still under investigation
Mechanical	• Reduces cellulose crystallinity	• No formation of inhibitors	• High power and energy consumption
Organisolv	• Hydrolyses lignin and hemicelluloses	• Pure lignin recovery • High digestibility	• High cost • Solvents need to be drained and recycled
Ozonolysis	• Reduces lignin content	• No formation of inhibitors • Mild operational conditions	• High cost of large amount of ozone needed
Steam explosion	• Causes lignin transformation • Causes hemicelluloses solubilisation	• Cost effective • Higher yield of glucose and hemicelluloses	• Generation of inhibitory compounds • Partial hemicellulose degradation • Incomplete disruption of the lignin-carbohydrate matrix
Supercritical fluid technology	• Increases accessible surface area	• Cost effective • No formation of inhibitors	• Does not affect lignin and hemicelluloses • Very high pressure requirements
Wet oxidation	• Removes lignin	• Low formation of inhibitors	• High cost of oxygen and alkaline catalyst

components of the feedstock to amorphous form [33,34]. The typical microorganisms used as the liberator of the complex lignocellulosic structure are brown rot, soft rot and white rot fungi [35]. Brown rot type is able to degrade cellulose, while both soft and white rot are able to degrade both cellulose and lignin [34]. From all these fungi types, white rot fungi type is known as the most favourable biological pre-treatment agent. The ability of the fungi to degrade the lignocellulosic structure lies on the hydrolytic system and ligninolytic system, which are responsible in producing hydrolases for polysaccharide liberation and in breaking the lignin structure, respectively [36].

Biological pre-treatment is favourable due to its sustainability to the environment. During the process, biological pre-treatment only requires mild condition, which means no excessive energy addition is needed. The built-in ability of the fungi to degrade lignocellulosic wall makes this process requires no additional chemical substance. Therefore this approach is safe from any harmful effects. However, pre-treating the lignocellulosic feedstock by this method results in a slower production rate. Hence this approach is unfavourable for the big-scale industry. To lessen the unfavourableness, this pre-treatment method is useful in delivering more potential of the feedstock if another pre-treatment method is paired with biological pre-treatment [33].

As a study of fungal pre-treatment for saccharification of sugarcane bagasse into sugars, Deswal et al. [37] employed white rot type fungi, which are *Pleurotus florida, Coriolopsis caperata* RCK 2011 and *Ganoderma* sp. rckk-02. The saccharification was further proceeded by hydrolysis from crude celullase produced from brown rot fungus *Fomitopsis* sp. RCK2010. Resulted from this study, the lignin component from sugarcane bagasse was degraded 7.91%, 5.48% and 5.58% by *Pleurotus florida, Coriolopsis caperata* RCK 2011 and *Ganoderma* sp. rckk-02 respectively. After the enzymatic hydrolysis from the crude cellulose, the reducing sugars concentrations released were 303.33, 192.52 and 220.86 mg/g of substrate from *Pleurotus florida, Coriolopsis caperata* RCK 2011 and *Ganoderma* sp. rckk-02 respectively, showing 1.5–2.4 fold higher than the non-pre-treated sugarcane bagasse. Although the authors did not analyse the ethanol content through fermentation process, the presence of reducing sugars as the product of fungal pre-treatment indicates the potential for second generation bioethanol production. Another contribution in biological pre-treatment in bioethanol production research is by Millati et al. [38]. In their research, biological pre-treatment was commenced by employing *Pleurotus florida* within period of 28 days on oil palm empty fruit bunch (OPEFB) and oat straw. The ethanol concentrations produced were 14.25% and 49.88% from OPEFB and oat straw respectively.

Table 2 shows the reported studies of biological pre-treatments from different biomass sources with the employed fungi [39–50]. Table 3 shows the results of biological pre-treatment on different lignocellulosic materials from the view of the yielded reducing sugars content [37,41,45,48,51–53]. These reported studies indicate the interest of many researchers in utilising biological approach for pre-treatment process, hence widen the potential range of bioethanol production. It is noticed that there is utterly rare report on biological pre-treatment of starchy materials. Utilising the reported fungi as the pre-treatment agent to the starchy materials is then strongly advisable as the additional research contribution in second generation bioethanol production.

2.1.2. Chemical pre-treatment

Specific supporting chemical substances are expected to be added in chemical pre-treatment. The purpose is the same: to guide the lignocellulosic or the starchy materials into the better form for hydrolysis process as the next sequence of the production series. Although there is no the absolute best method for pre-treatment stage, chemical pre-treatment (dilute acid pre-treatment) is believed to be the most suitable for the commercial scale application [54]. Chemical pre-treatment is approachable due to its likability: chemical substances are easier to be obtained, cheaper and does not get affected by the technological development (unlike enzymes, the engineered enzymes cost more than the traditional enzymes), less hassle in storage and chemical substances are mostly durable with the proper storage. The chemical substances degrade the walls of lignocellulosic and the complex carbohydrate chain of starch through direct chemical reaction that only requires less energy (in heat form), although it takes more time and produces comparatively lesser sugar yield (for alkali pre-treatment) [27].

There are several common acids used in acid pre-treatment, for instance, hydrochloric acid, phosphoric acid, nitric acid, and sulphuric acid as the most popular to be used in lignocellulosic material; also several organic acids such as peracetic acid, maleic acid, lactic acid and acetic acid [32,55]. In general, acid pre-treatment can be performed by two methods: concentrated acid pre-treatment and dilute acid pre-treatment. In concentrated acid pre-treatment, only shorter time and mild temperature are required to yield the sugar monomers [56]. This method is also able to produce monosaccharides by degrading the polysaccharide's glycosidic linkages. In the practice, concentrated acid has drawbacks as it forms inhibitors, easily corrodes the production equipment and inclines the sugar monomer degradations tendency [32,57]. In

Table 2
Reported biological pre-treatment research on different lignocelullosic materials.

Fungus employed	Material	Ref.
Aspergillus awamori	Sugarcane trash	[39]
Aspergillus terreus	Sugarcane trash	[39]
Ceriporiopsis subvermispora	Corn stover	[40,41]
Echinodontium taxodii	Corn stover	[43]
Echinodontium taxodii	Softwood	[45]
Echinodontium taxodii	Hardwood	[45]
Fusarium concolor	Wheat straw	[44]
Irpex lacteus	Corn stover	[42,43]
Phanerochaete chrysosporium	Wheat straw	[47]
Phanerochaete chrysosporium	Rice straw	[46]
Phanerochaete chrysosporium	Cotton stalks	[48]
Pleurotus ostreatus	Corn stover	[43]
Pleurotus ostreatus	Rice hull	[50]
Pycnoporus cinnabarinus	Wheat straw	[47]
Pycnoporus sanguineus	Cereal straw	[49]
Trichoderma reesei	Sugarcane trash	[39]
Trichoderma viride	Sugarcane trash	[39]

Table 3
Reducing sugar yielded from biological pre-treatment of different lignocellulosic feedstock.

Fungus employed	Material	Reducing sugars yield (mg/g)	Ref.
Ceriporiopsis subvermispora	Corn stover	233	[41]
Coriolopsis caperata RCK2011	Sugarcane bagasse	192.52	[37]
Echinodontium taxodii	Bamboo culms	100	[53]
Echinodontium taxodii 2538	China fir	60	[45]
Echinodontium taxodii 2538	Chinese willow	175	[45]
Ganoderma sp.rckk-02	Sugarcane bagasse	194.86	[37]
Iprex lacteus	Wheat straw	120	[51]
Phanerochaete chrysosporium	Cotton stalks	55.6	[48]
Pleurotus florida	Sugarcane bagasse	303.33	[37]
Pleurotus ostreatus	Rice hull	80	[45]
Pleurotus ostreatus	Rice straw	118.5	[52]
Trametes versicolor	Bamboo culms	98	[53]

regard to this matter, dilute acid pre-treatment is used for the better conduct. Dilute acid pre-treatment leads to the same outcome as the concentrated acid pre-treatment which to yield the sugar monomers, although it behaves differently than concentrated acid pre-treatment. Typically, dilute acid pre-treatment can be performed through different paths: batch process with low temperature (less than 433 K or 160 °C) and high substrates loading (ranges 10–40 w/w%); and continuous process with high temperature (more than 433 K or 160 °C) and low substrates loading (ranges 5–10 w/w%) [31]. Pre-treatment with dilute acid does not require acid recovery with negligible acid loss [32].

Dilute acid pre-treatment is popular in bioethanol production from lignocellulosic biomass. From a research of Bermuda grass pre-treatment, 204.1 mg/g of reducing sugars was produced per biomass weight basis by employing 1.2 wt% dilute sulphuric acid at 121 °C and 60 min [58]. Another bioethanol production attempt from inedible sources was conducted by taking silver grass as the feedstock through dilute acid pre-treatment [59]. After 30 min of dilute acid pre-treatment at 121 °C, the silver grass produced 70–75% xylan sugars and 64.3% theoretical ethanol was able to be extracted after 48 h of fermentation. Rice straw was also pre-treated by dilute acid in a study by ref [60]. The acid pre-treated rice straw drew 9.71 g/L of glucose, which was uplifted to 11.45 g/L of glucose after it underwent enzymatic hydrolysis by cellulase from *Trichoderma reesei*. This study yielded 52.75% of theoretical ethanol from the combination of acid pre-treatment with enzymatic hydrolysis, compared to acid pre-treatment alone of which yielded 11.26%. Study on acid pre-treatment of durian seed was performed also in the conduct of second generation bioethanol production from starchy material [61]. The study utilised 0.6% dilute sulphuric acid and 5 w/v% substrate loading beforehand the enzymatic hydrolysis, and it yielded 23.66 g/L of reducing sugars. At the end of this study, the ethanol quality was recorded as 51.2% of theoretical value.

While acid pre-treatment is good in degrading mostly hemicellulose component in the lignocellulosic biomass, alkali pre-treatment breaks more lignin component into a better accessible form for hydrolysis afterward [32]. In alkali pre-treatment, NaOH and lime ($Ca(OH)_2$) are found as the most frequent alkaline solution to be used in alkali pre-treatment, as performed in several researches [62–67]. NH_4OH (ammonia) is also commonly employed as the pre-treatment agent in the attempt to produce second generation bioethanol [62,63,68]. According to the mentioned references, these alkali substance are chosen for their specialty in degrading mostly lignin compound. In lignocellulosic material, NaOH gives better internal surface by swelling it and brings to lignin degradation. NaOH pre-treated lignocellulosic biomass results higher porosity that leads to better glucose yield after enzymatic hydrolysis by attacking the ester bonds [69]. Employing dilute NaOH is wiser than employing concentrated NaOH for the environmental and economic benefits. Lime gives a better access for the enzyme in the next hydrolysis stage to strike the cellulose, by removing uronic acid substitutions and acetyl compounds [55]. A study of lignocellulosic biomass pre-treatment reported lime pre-treatment was performed on poplar wood at temperature of 423 K for 6 h, corn stover at 373 K for 13 h, switchgrass for 2 h at 373 K, and wheat straw for 3 h at 385 K [27]. In order to improve the digestibility exposure on the heavy-lignin feedstock, an oxidising agent is necessary to be mixed with the alkali [32]. Addition of hydrogen peroxide (H_2O_2) as the oxidising agent in the alkaline pre-treatment of tobacco waste resulted 347.2% of sugar improvement than the untreated waste [70]. The improvement is due to the ability of hydrogen peroxide to oxidise the degrading-resistant reducing ends of ligocellulosic's carbohydrate in alkaline environment [71]. An organic acid, peracetic acid ($C_2H_4O_3$), is known for its effectiveness as an oxidising agent by cutting the aromatic structure in lignin. From a study of alkaline pre-treatment of sugarcane bagasse, $C_2H_4O_3$ gives better digestibility enhancement for the enzyme to hydrolyse the sugarcane bagasse than H_2O_2 as the oxidising agent [72]. In a recent research, Toquero and Bolado [62] compared the results of four different pre-treatments of wheat straw: dilute NaOH with autoclave, dilute HCl with autoclave, thermal autoclaving, and alkaline peroxide (NaOH with H_2O_2). After 72 h of hydrolysis, it was found that alkaline peroxide pre-treatment yielded the most glucose and xylose of 31.83 g/L and 13.75 g/L respectively. Ethanol with concentration of 17.37 g/L was observed after fermentation by *Pichia stipitis* in 24 h. The effectiveness of using ozone in enhancing sugar yield has also been reported, as it produced sugar of 88.6% from wheat straw than 29% from the non-ozonised, although this method is infeasible from the economic perspective [32,73].

Organosolv is also seen as one chemical pre-treatment that dissolves lignin in the lignocellulosic biomass. This method is performed by mixing organic solvent with inorganic acid as the catalyst, such as HCl or H_2SO_4. Since the typical organic solvents, for instance ethanol, methanol, phenol, acetone, triethylene glycol and ethylene glycol, are combustible, this pre-treatment method must be performed under extreme safety care [74]. A study by Li et al. [75] revealed bioethanol production with quality of 93% by organosolv pre-treatment using acetone and phosphoric acid from lignocellulosic biomasses. Although its effectiveness in producing high quality bioethanol, this method is considered to be industrially impractical due to high solvents cost [74].

Pre-treatment method using ionic liquid fractures the non-covalent structure between hemicellulose, lignin and cellulose, as caused by the strong hydrogen bond acceptors of the ionic liquid contained in chloride [76]. It is reported that the most effective ionic liquids are 1-allyl-3-methylimidazolium chloride and 1-butyl3-methylimidazolium chloride [77]. In comparison with dilute acid pre-treatment, ionic liquid pre-treatment showed 16.7-fold of enzymatic hydrolysis enhancement from switchgrass, as ionic liquid gave more exposed surface area, lesser crystallinity of cellulose and lesser lignin obtained [78]. Although the effect of the suitability with enzymes and fermentation microorganism is still under investigation, Ionic liquid pre-treatment is considered as a green, sustainable method [32].

2.1.3. Mechanical pre-treatment

Another path to pre-treating the biomass is by mechanical pre-treatment, where the size of biomass is physically reduced through cutting, chopping or material breaking method. Likewise any other pre-treatment method, mechanical pre-treatment is purposed to degrade the biomass crystallinity, thus enhancing the rest of the bioethanol production processes [33]. Conventionally, physical size reduction can be done by wet disk milling, ball milling [79], vibratory ball milling, compression milling [35], hammer milling [80] and roll milling [81]. A comparison study was performed and it showed that smaller size of corn stover (about 53–75 μm) produced greater outcome by 1.5-fold than the larger size substrate [82]. This proves mechanical comminution can afford 5–25% improvement of hydrolysis product and boosts 23–59% rate of hydrolysis, depending on the milling techniques [83]. The most well-known challenge for mechanical pre-treatment is its vast power consumption. It has been reported that physical reduction approach by mechanical pre-treatment uses one-third of the total energy consumption of entire bioethanol production [84]. A study revealed energy consumption of hammer milling pre-treatment of wheat straw, which consumes 51.6 and 11.4 kWh/tonne of feedstock to produce sizes of 0.8 and 3.2 mm respectively [80]. Power consumption for mechanical comminution can be controlled by adjusting the sizes of the initial input and desired final substrate. In addition, the material's woody characteristics and moisture

content also influence the power input for this pre-treatment [33,80]. It is desirable to have fine form of biomass from mechanical pre-treatment, but when the subsequent process involves liquid, using extremely fine size of biomass may form lump [35].

Extrusion is a more advanced method of mechanical comminution. Biomass pre-treatment by extrusion widens the access for enzyme to strike the better exposed carbohydrates. It involves shearing and mixing of the feedstock to go through the extruder at certain high temperature, causing deformation of biomass physically, and even chemically [85]. Factors, such as speed of the screw, temperature and compression ratio, should be controlled to achieve the efficiency of extrusion pre-treatment [86]. In a study by Lee et al. [87], Douglas fir was extruded prior to hydrolysis, and it resulted 62.4% conversion of the feedstock into glucose. Also reported by the same researchers, due to its ability to run continuously with zero effluent waste, extrusion method is recognised as one feasible pre-treatment method for industry-scale application without causing any environmental problem.

Microwave irradiation practices electromagnetic field application to cause internal heating of an object. In bioethanol production, this approach is executable in the purpose of structural disruption of the pre-treated biomass. In lignocellulosic material, microwave attacks the polar bonds by vibrating the structure until the material is internally heated. As the result, complex lignocellulosic structure is fractured, widening the practicable area for the subsequent enzymatic attack [88]. Microwave treatment is reckoned as an improvement effort through assisting other treatment methods. In one of the recent studies, microwave was assigned to assist hydrothermal hydrolysis of sago pith waste [89]. This study claimed that the microwave assisted hydrothermal hydrolysis consumed only 33 kJ and 69 kJ per every gram production of glucose and ethanol respectively, which graded as energy efficient.

2.1.4. Physicochemical pre-treatment

Steam explosion pre-treatment applies combination of hydrothermal and sudden pressure change in treating the biomass. Initially the biomass is exposed to a high temperature and pressure for few seconds to minutes, then the process ends after depressurisation takes place on the biomass which when the steam explodes the biomass's fibres. This method is categorized under physicochemical pre-treatment for its fused mechanical- and chemical-driven characteristics. Mechanical-wise, the steam strikes the biomass causing fibres separation, physically shortens the fibres. While chemical-wise, auto-hydrolysis of acetyl groups that exists in hemicellulose takes place under high temperature, forming acetic acid; and acidic environment can be initiated when the water is treated at high temperature [90]. For this nature, steam explosion would be more beneficial on hemicellulose-rich biomass. Having benefits of high xylose recovery production (around 45–65%), lesser energy usage and environmentally friendly, steam explosion is favourable economically for bioethanol production [91–93]. On the other hand, inhibitors formation as the by-product of steam explosion method is one major challenge that may disturb the microbial activity on the subsequent production stage (fermentation) [94].

Ammonia fibre explosion (AFEX) has quite similar principle with steam explosion, only with ammonia as the explosion agent. AFEX process depends on the immediate high pressure launch on the biomass, forcing the recoverable and recyclable ammonia to burst the biomass's structure and leaves some ammonia traces on the biomass that is advantageous as the microbe's nitrogen source [57,90]. Likewise steam explosion, AFEX brings both mechanical and chemical pre-treatment characteristics, which are bulk density lessening, widens accessible area (mechanical-wise); and crystallisation reduction, lignin breakage, hemicellulose degradation (chemical-wise) [90]. This method is strong on fibrous biomass, for instance sugarcane bagasse, than on the lignin-rich substrates, such as forestry residues [31]. Inhibitors formation is negligible in AFEX pre-treatment, as reported that AFEX pre-treatment produces 100–1000-fold of lesser carboxylic acids than NaOH alkaline pre-treatment and 36-fold of lesser furans than dilute acid pre-treatment [95].

Also utilising ammonia as the same pre-treatment agent, ammonia recycled percolation (ARP) flows recoverable aqueous ammonia through the biomass reactor. ARP is strong in lignin removal with high quality, without any containment of sodium and sulphur unlike any other conventional pre-treatment methods, and hence it leads to high quality pre-treatment product [96]. In contrary to AFEX pre-treatment, ARP is more suitable for hardwood and lignin-rich biomass, including oak wood waste and paper pulp sludge [97,98]. One primary challenge of this pre-treatment method is the unfavourableness in the total energy consumption cost.

In wet oxidation pre-treatment, the biomass is subjected to high pressure and temperature (about 500–2000 kPa and 170–200 °C respectively) for around 10–15 min. This approach degrades lignocellulosic material with less inhibitors, removes lignin, and lowers cellulose crystalline, hence it provides better condition for the subsequent processes (enzymatic hydrolysis and fermentation) to work on the pre-treated product. However, this method has the common challenge in energy efficiency and capital cost since this pre-treatment method involves high temperature and pressure [99,100].

The practice of supercritical fluid technology contributes to the variance of possible pre-treatment methods for bioethanol production. Carbon dioxide (CO_2) as the supercritical fluid is commonly employed for coffee decaffeination process. However, the benefits of both gas (in mass transfer) and liquid (in solvating) properties existed in supercritical fluid, low inhibitory products, efficient in lignin removal at mild environment (low temperature, non-acidic and non-corrosive), make this method as a favourable pre-treatment method in bioethanol production compared to ammonia and steam explosion methods. Additionally, CO_2 as the supercritical fluid pierces the crystalline easier without degrading the desired sugar monomers because of its mild environment [101].

2.2. Hydrolysis

Hydrolysis process separates long chain of carbohydrate (from cellulose or starch) with addition of water molecule and is usually catalysed by enzyme or acid. This stage is critical in bioethanol production since the quality of hydrolysate will affect the subsequent fermentation process, which interconnected to the ethanol's quality as the end product. Hydrolysis process is needed since microorganisms (that are employed in the later process of fermentation) are only able to digest simpler sugar form derived from the complex carbohydrate of biomass. Enzymatic hydrolysis is known for its economical challenge from high cost of enzymes and considered impractical for commercial purposes. However, in comparison with acid hydrolysis, enzymes works at a mild environment, hence less equipment maintenance cost will be needed. Moreover, disposal system for acid hydrolysis is essential to consider and it requires additional cost to take into account. Another major problem is acid's ability to gradually degrade the sugar monomers once they are formed in a hostile acidic environment with high temperature [102,103].

2.2.1. Enzymatic hydrolysis of lignocellulosic biomass

Lignocellulosic, which majorly composed of cellulose, hemicellulose and lignin, is degradable enzymatically with respect to the major constituents. Cellulose is set by glucose chains that are connected by β-1,4 linkages. In nature, cellulose has certain degree of crystallinity that is formed by the hydrogen bonding along the

chains. The presence of cellulose crystallinity is believed to affect hydrolysis process, as such slower hydrolysis rate and lower enzyme adsorption are taking place when crystallinity is high [104]. Rather than the rigid crystalline area, amorphous zone in cellulose is easier to be degraded. However, in order to reduce the crystallinity of the biomass, mechanical pre-treatment method suits the purpose. Cellulase is the specific enzyme to degrade cellulose compound. According to cellulases enzymatic activity, the classification is branched according to the specific task: endoglucanase (EC 3.2.1.4), *exo*glucanase (EC 3.2.1.91) and β-glucosidase (EC 3.2.1.21).

The formation of 1,4-β-D-glucanohydrolase in endoglucanase targets the region with low crystallinity (amorphous zones) in the cellulose. Endoglucanase initiates the hydrolysis by linking β-1,4 bond of the cellulose with water molecule. Shorter, free-chain ends (reducing and non-reducing ends) are formed afterwards (Fig. 1) [105]. 1,4-β-D glucan cellobiohydrolase in *exo*glucanase works in degrading the (shorter) cellulose structure, by altering both ends (reducing and non-reducing) chains to form two-unit glucoses (cellobioses, Fig. 2) [106]. Since the simplest monomer is expected for the subsequent fermentation process, cellobioses are further treated by β-glucosidase. β-glucosidase strikes the cellobioses and produce glucoses as the sugar monomers (Fig. 3) [107–110].

Enzymes for hemicellulose structure are complex yet more specified in their purposes. Unlike cellulose, hemicellulose is typically easier to hydrolyse due to its more amorphous property. Xylan, as one of the components in hemicellulose, is a polysaccharide with xylose as the singular unit. In softwoods, xylan accounts for 10–15% of the hemicelluloses, and 10–35% in hardwoods [111]. Xylanase is specially served for xylan by aiming at both main and outer chains. To degrade xylan's main chain, endo-β-1,4-xylanase (EC 3.2.1.8) and β-xylosidase (EC 3.2.1.37) are employed. Endo-β-1,4-xylanase degrades xylan long chains into shorter chains (xylan oligosaccharide, Fig. 4) [112]. The sequential process to reduce the oligosaccharide is by employing β-xylosidase to yield xyropyranose, a pyranose form of xylose (Fig. 5) [113]. On the other hand, enzymes specifically to degrade the outer chains are so-called accessory xylanolytic enzymes, including feruloyl esterase (EC 3.1.1.73), α-L-arabinofuranosidase (EC 3.2.1.55), α-glucuronidase (EC 3.2.1.139), and acetylxylan esterase (EC 3.1.1.72) [114].

Although lignin establishes strong bonds of the cellulosic fibres, it is recognised as to lessen the approachability of cellulose to the cellulases [115]. It was reported that in aqueous solution lignin adsorbs protein and tends to bond and precipitate with protein [116,117]. In fact, lignin is believed to resist cellulases enzymatic activities, causing lower hydrolysis quality [118]. The presence of lignin in hydrolysis is unfavourable, hence lignin removal process should be performed to maximise the effectiveness of hydrolysis by cellulase. In lignin removal fibrils of microcellulose are openly exposed and neatly separated, as such that providing better access for the cellulases [116,119]. There are many studies performed in the effort of delignification of the materials to yield better fermentable sugars. A study on effect of milling pre-treatment in cotton stalks reported that pre-treated cotton stalks produces lower lignin (0.6%) and higher cellulose (92%) compared to the one without milling pre-treatment (26.4% of lignin and 44% of cellulose) [120].

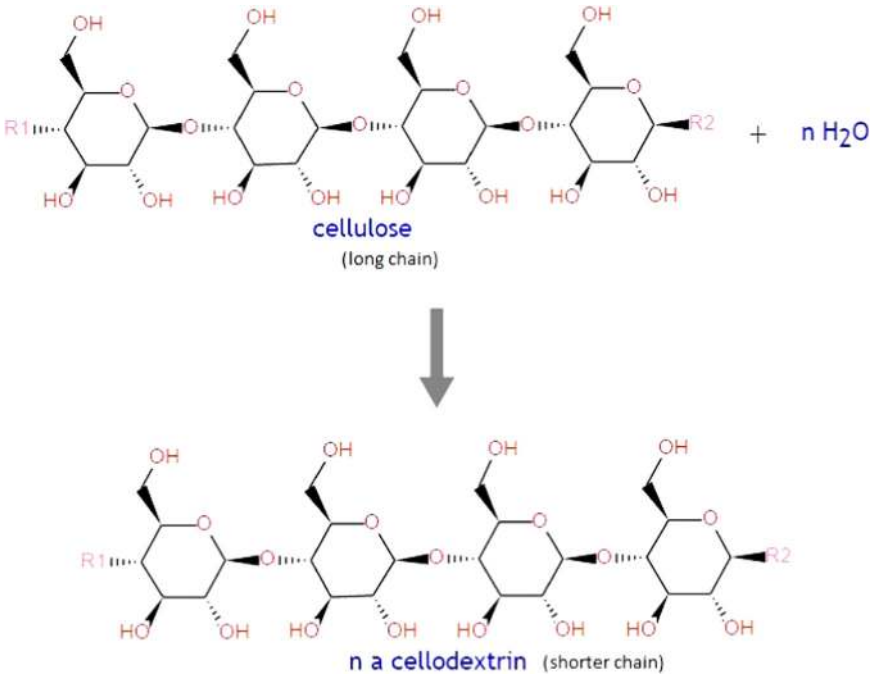

Fig. 1. Reaction in cellulose hydrolysis catalysed by *endo*glucanase (1,4-β-D-glucanohydrolase), resulting shorter chain of cellulose (cellodextrin) [105].

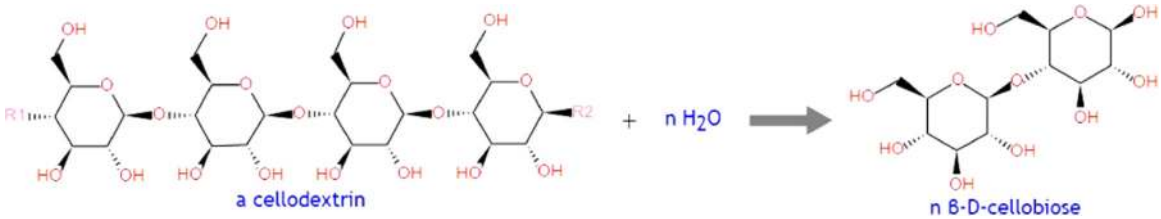

Fig. 2. Reaction of cellodextrin catalysed by *exo*glucanase (1,4-β-D glucan cellobiohydrolase), producing cellobiose [106].

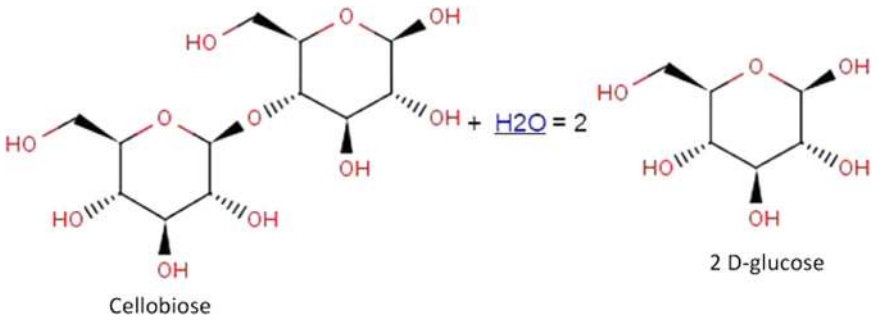

Fig. 3. Reaction of cellobiose with water molecule resulting 2 glucose units, as the reaction catalysed by β-glucosidase [110].

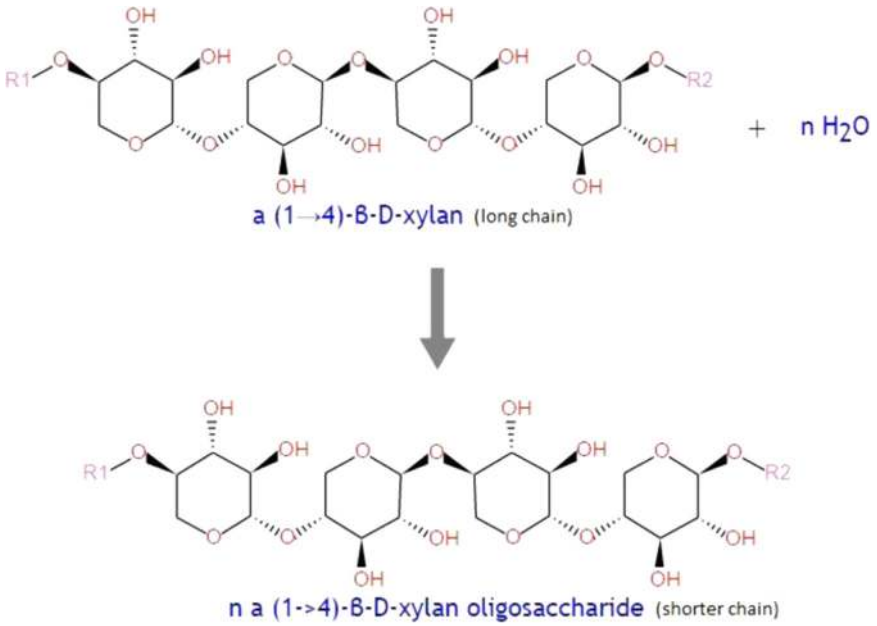

Fig. 4. Reaction of xylan hydrolysis catalysed by endo-β-1,4-xylanase, resulting shorter chain of xylan (xylan oligosaccharide) [112].

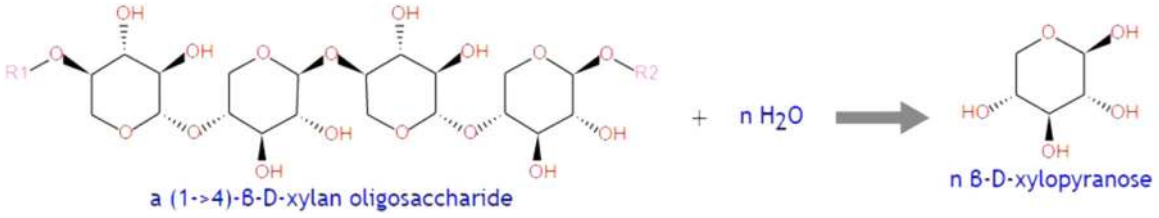

Fig. 5. Reaction of xylan oligosaccharide hydrolysis catalysed by β-xylosidase, producing xylopyranose [113].

The ability of hemicellulases to degrade hemicellulose structure into sugar monomers, apparently, is not so favourable for cellulose hydrolysis. Products of hemicellulose hydrolysis, including xylose, xylooligosaccharides, galactose, mannose, act as strong inhibitors to cellulase and β -glucosidase [121,122]. This indicates the focus on cellulases employability should be aimed only for the cellulose-rich materials, so that it would be economically wise to emphasise only on cellulose degrading type of enzymes. Similarly, the usage of hemicellulolytic enzymes is advised only for the hemicellulose-rich material, since the mentioned literatures indicate that sugars from hemicellulose could slower the cellulase activity. With this principle the overall production cost needed can be estimated according to the nature of the materials. Additionally, focusing on the material's nature helps in the selection of the suitable microorganism to act as fermentation agent in the subsequent fermentation process, for the reason that specific microorganism is needed to digest the specific sugar accordingly.

2.2.2. Enzymatic hydrolysis of starchy biomass

Likewise lignocellulosic material, starch is also one source of carbohydrate, only with different chemical structures and characteristics. Glucose molecular structure in starch is linked with α-glucosidic bonds, in contrast with the glucose structure in cellulose that is linked by β –glucosidic bonds. Therefore starch is composed by linear α-1,4-linked glucans—amylose; and the same linear linkage branching with α-1,6 linkages—amylopectin (Fig. 6) [123]. Physically, amylose is a linear glucose polymer with glucose unit up to 6000 units, while amylopectin is much shorter of 10–60 glucose units where the α-1,6 linkage branch contains 15–45 glucose units [124]. Amylolytic enzymes, or called amylases, are the groups of enzymes specifically to degrade glucose linkages in starch. The groups are divided into four according to the functionality: endoamylases, exoamylases, debranching enzymes and tranferases [125].

The inner zone in amylose and amylopectin, which where α-1,4 glycosidic bonds are existed, is hydrolysed by endoamylase. The

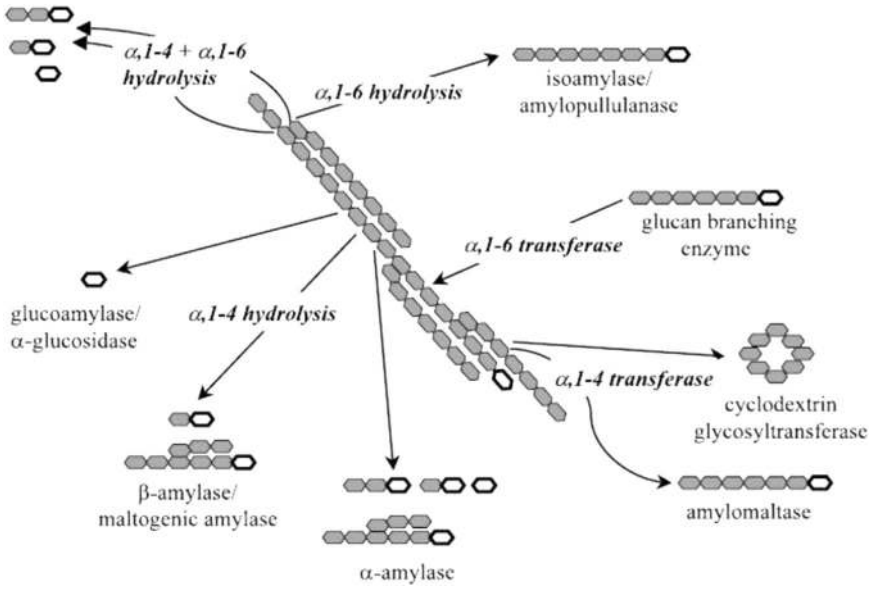

Fig. 6. Types of amylases according to the working zones (hollow ring depicts reducing ends) [123].

most favoured endoamylase that is able to cut down the α-1,4 glycosidic bonds is α-amylase (EC 3.2.1.1). This enzyme reduces the long chain of the sugar polymer and leaves shorter, varied lengths products (α-configured oligosaccharides and α-limit dextrins) [124,126]. Besides, α-amylase works in random manner and releases few glucose and maltose as well (Fig. 7) [127].

The second group of amylases, exoamylases, aim the external zone (exo-) of both amylose and amylopectin. Glucoamylase (or also called amyloglucosidase; EC 3.2.1.3) and α-glucosidase (EC 3.2.1.20) are exoamylases that are capable to degrade α-1,4 as well as α-1,6 bonds (Figs. 8 and 9) [128–131]. Another example of exoamylases, β-amylases (EC 3.2.1.2), is limited to only degrade α-1,4 glucosidic bonds. In catalysing the hydrolysis process, glucoamylase gives better performance on long polysaccharides, while α-glucosidase prefers to work on maltooligosaccharides. The hydrolysis products by exoamylases are maltose and glucose, as low molecular structure residues [125,132].

Debranching enzymes work on α-1,6 glycosidic bonds on different parts of polysaccharide depending on employed debranching enzymes. Isoamylase (EC 3.2.1.68), as one example of debranching enzymes, degrades only α-1,6 linkages in amylopectin. Another type of debranching enzymes, pullulanase type I (EC 3.2.1.41), is able to degrade α-1,6 linkages in both amylopectin and pullulan. Pullulanase type II is another group of the debranching enzymes that is able to degrade α-1,4 as well as α-1,6 glycosidic bonds, leaving maltotriose and maltose as the products [124].

As the last group of amylases, transferases form a new glycosidic bond by transferring molecules from the donor to the acceptor. The formation of new α-1,4 glycosidic bonds are catalysed by amylomaltase (EC 2.4.1.25) and cyclodextrin glycosyltransferase (EC 2.4.1.19), where the later enzyme also forms cyclodextrin rings consisted 6–8 glucose units that are linked by the α-1,4 bonds [124].

A careful and well-analysed hydrolysis method is essential in bioethanol production since the hydrolysate compositions determine which fermentation agent fits the best to fulfil the ethanol production objective. The wild type of *Saccharomyces cerevisiae*, for instance, is only be able to convert glucose as one of the simplest sugar forms [32]. This indicates that this specific type of fermentation agent is only prime to the glucose-producing materials, which cellulose and amylose are dominant. Whereas for xylose-producing materials, which is hemicellulose-dominant materials, the employment of wild *Saccharomyces cerevisiae* is not suitable. Thus, it is wise to be highly selective in employing the type of enzymes, especially from the standpoint of suitability as well as economical. It is acknowledged that enzymatic hydrolysis requires more cost, but with the proper planning analysis (e.g. employing combinations of hydrolysis methods, decision on plant scale, raw material selection and collection methods, etc.) can be resulted to the most viable approach. Also, coupled with thorough techno-economic studies, it will contribute to the routes formation of the most effective second generation ethanol production plant.

2.3. Fermentation

Fermentation is one critical process in bioethanol production, where the ethanol is directly produced from the metabolic activity of the fermentation agent. Hydrolysate, in this process, is introduced to a specific fermentation agent (yeast or bacteria) best according to the suitability to digest the respective sugar compounds. A type of glucose-fermenting bacteria, for instance, *Zymomonas mobilis* prefers glucose-rich hydrolysate as their 'food' and leaving ethanol compound as the product. It is rather hard to expect the hydrolysate to be entirely uniform in terms of the sugar monomer, it would be fractions of different monomers and several other oligosaccharides with probable inhibitors or indigestible substances. Theoretically, each kg of glucose and xylose can produce 0.49 kg carbon dioxide with 0.51 kg of ethanol [92].

Fermentation in particular requires the supporting conditions for the microbes to sustain, namely temperature and pH range [133]. As *meso*philic organisms, most of fermentation agents are comfortable within 303–311 K temperature [134]. For bacteria type of fermentation microbes, pH of 6.5–7.5 are typically essential to sustain the bacteria's growth [135]. Meanwhile, fungi are capable to resist more acidic environment of pH 3.5–5.0 [55]. Moreover, additional factors that play important role in the fermentation process are the microbes' growth rate and genetic stability; tolerance of inhibitors, osmosis and alcohol; productivity and the yield of ethanol [133].

There are numbers of discovered bacteria suitable as fermentation microorganisms. The most well-known fermentation bacteria, *Zymomonas mobilis* converts glucose, sucrose and fructose to ethanol. A study was performed in bioethanol production using *Zymomonas mobilis* as the fermentation agent, and it yielded theoretical ethanol of 97% with experimental ethanol concentration of 12%

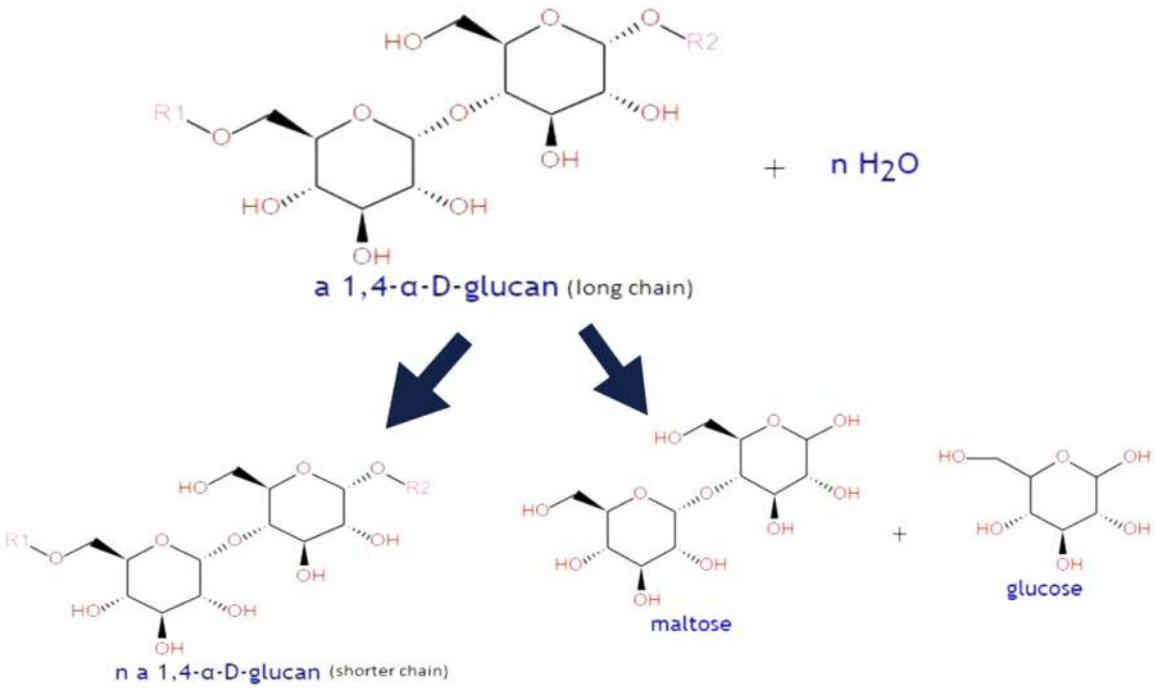

Fig. 7. Reaction of long chained amylose hydrolysis catalysed by α-amylase (EC 3.2.1.1) in random manner, producing shorter polysaccharide, maltose and glucose [127].

(w/v) [136]. Likewise *Zymomonas mobilis*, *Saccharomyces cerevisiae* is one microbe (yeast type) that naturally consumes hexose sugars (e.g. glucose, fructose). Although known as the most commonly employed microorganisms, both *Z. mobilis* and *S. cerevisiae* are incapable to ferment pentose sugars. *Candida shehatae*, *Pichia stipitis*, and *Pachysolen tannophilus* are recognised in their ability to convert pentose sugars (xylose). However, these bacteria only result low efficiency with high-caring handling; they are vulnerable to acid environment, inhibitors and ethanol with high concentration [137].

The limitations of the natural type bacteria and yeasts drive many researches to modify the behaviour and function genetically. Through microorganisms engineering, besides improvement of the end product's quality, additional fermenting capability that is other than the native function can be achieved, i.e. ability to ferment more than one type of sugars. From their research, Buaban et al. [138] reported that by using engineered *Pichia stipitis* BCC15191 as the fermentation agent it resulted 8.4 g/L of ethanol concentration after 24 h of fermentation of hydrolysed sugarcane bagasse. The study was also reported that the employed engineered *Pichia stipitis* BCC15191 was able to ferment both xylose and glucose, whereas the wild type of *Pichia stipitis* is only capable in fermenting xylose sugar. The more of engineered microorganisms employed in the effort to enhance ethanol yield is listed in Table 4 [138–151].

From the fundamental of the production conduct, there are alternatives in ethanol production including separate hydrolysis and fermentation (SHF); and simultaneous saccharification and fermentation (SSF). In a review paper written by Balat et al. [55], SHF method separates hydrolysis and fermentation process with the focus in taking full advantage of each of the process. The hydrolysate is entered into the first reactor to get the glucose component fermented. The ethanol is distilled afterwards, then the remaining of the hydrolysate is flowed into the second reactor to get the xylose components fermented. Similarly, the ethanol is removed through distillation process afterwards. The main drawback from this process is the inhibition formation after hydrolysis, which reduces the hydrolysis rate and hence gives a lower and slower ethanol production.

In contrary with SHF, SSF method allows the enzymes to perform hydrolysis to release the sugars and immediately ferment those sugars into ethanol without any separation process in between. This way also prevents the reduction of the monomers formed after hydrolysis process. Additionally, SSF is claimed to result higher ethanol yield since the hydrolysis inhibitions are solved by fermentation process, which makes this approach is desirable [30,152,153]. A study by Sun and Cheng [33] revealed other benefits from SSF method, including lesser employment of enzymes; faster production period; and less number and volume of reactors needed, hence lower cost required since both sugars releasing and sugars fermenting processes are commenced simultaneously. Srimachai et al. [154] extracted ethanol from oil palm frond by SSF method, and the experiment resulted 0.32 g-ethanol/g-glucose, or about 62.75% of the theoretical ethanol yield. The researchers also analysed the total energy required to run the overall production, which was calculated as 745 kWh/tonne of oil palm frond. However, it is a challenge to control the solution environment since enzymes and microorganisms are employable only within the preference temperature and pH. Most enzymes can still be comfortable with mild acid environment ($pH < 5$) and resistant to more than 313 K of temperature, although those conditions threaten the microorganisms' sustainability [155].

Mixing different fermenting microorganisms is seen to be one additional contribution to the alternative methods in ethanol production, which also comes with the term simultaneous saccharification and co-fermentation (SSCF). This approach allows the mixed-culture microbes to commence the continuous process without sugars separation, to use various materials as the substrate, and no involvement of sterilisation [156]. SSCF has been proven effective in ethanol production from corn stover [157], municipal solid wastes [158] and sugarcane bagasse [159].

Another alternative is by consolidated bioprocessing (CBP). In ethanol production from cellulosic materials, this approach performs self-cellulase production, hydrolysis of the substrates and fermentation of hexose as well as pentose sugars within the same reactor by utilising the ability of certain microorganisms to perform these tasks [160]. In comparison to SHF method, CBP method offers better benefits including lower production cost due to lesser steps required and no additional purchase of enzymes; better efficiency of conversion; and lesser energy required to run the

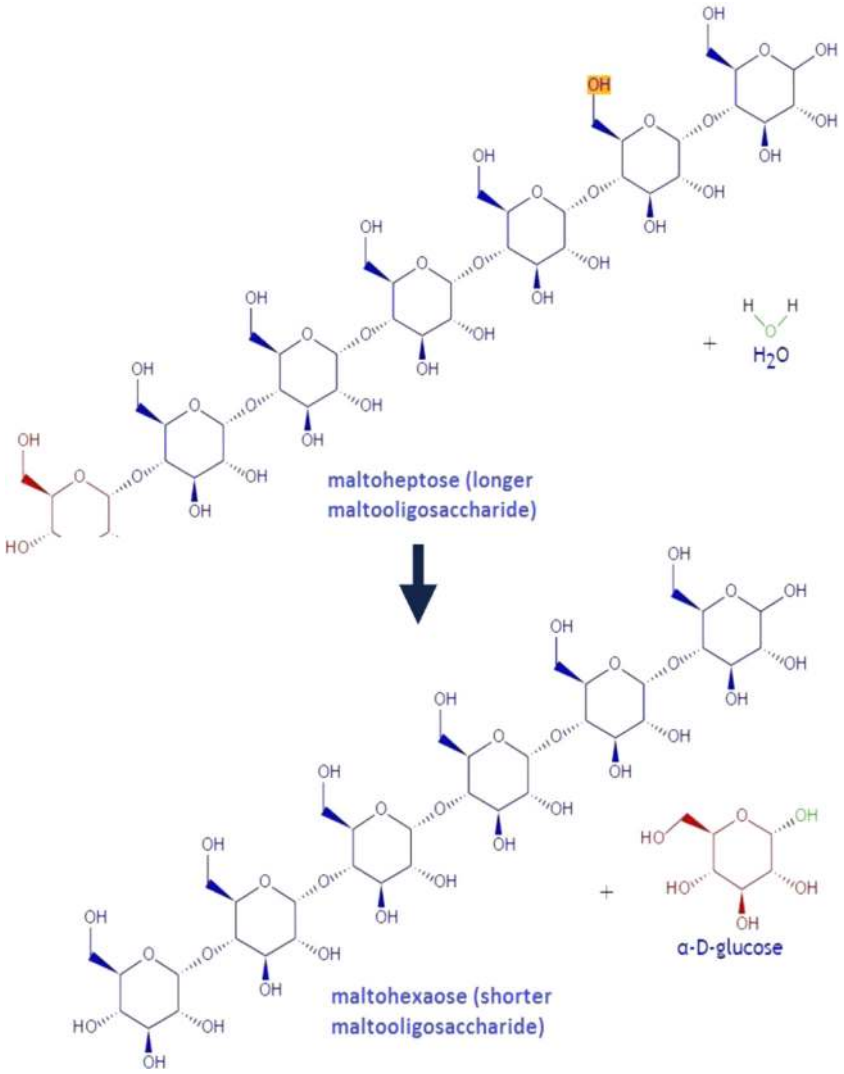

Fig. 8. Reaction of maltooligosaccharide hydrolysis catalysed by α-glucosidase (EC 3.2.1.20) producing shorter maltooligosaccharide and glucose [128–131].

production [161]. The differences between fermentation methods are also schematically displayed in Fig. 10 by ref [162].

It is uncommon for wild type of microorganisms to work on CBP method, but several studies have reported the employment of specific microorganism in CBP method. *Trichoderma reesei* is known as a cellulotyic type of fungi that is native in secreting enzymes to degrade lignocellulosic material [163]. In addition, several fungi, namely *Fusarium oxysporum*, *Neurospora crassa* and *Paecilomyces sp* are said to be practicable for CBP, as well as bacterium *Clostridium thermocellum* [35]. However, the development of CBP method is encouraged due to the weaknesses it brings, including low rate of ethanol conversion process and considerably low ethanol yield [163].

For the auspicious advantage of low total cost production, there have been many efforts in the attempt to improve the feasibility of CBP method in ethanol production, which mainly focused on the modification of employed microorganisms genetically. The paths of modification are exclusively classified into two terms: CBP category I and CBP category II. In CBP strains modification category I centres at the effort to modify the cellulolytic (cellulase producer) microbes so that are able to produce ethanol as well (ethanologen). Although category I is classified to be at the preliminary development stage, a study by Amore and Faraco [164] described the potential of several fungi towards the strains modification, which ascribed to category I. They include *Trichoderma reesei, Aspergillus* spp. (mostly *Aspergillus sojae, Aspergillus niger, Aspergillus oryzae* and *Aspergillus terreus*), *Fusarium oxysporum*, and *Rhizopus* spp. (*Rhizopus koji, Rhizopus oryzae* and *Rhizopus stolonifera*). In contrary to category I, CBP strains modification of category II emphasises on the genes modification of naturally ethanologen microbes to equip cellulolytic property. Category II modification path aims at the ability of the engineered microbes to produce different essential exo- and endo-glucanases, to ferment all saccharides degraded from the substrates, and to be able grow sustainably by depending only from the substrates as the carbon resource. Various bacteria, namely *Escherichia coli*, *Klebsiella oxytoca*, and *Zymomonas mobilis* are reported to have been modified through modification CBP category II; as well as various yeasts, including *Candida shehatae*, *Pachysolen tannophilus*, *Saccharomyces cerevisiae*, and *Pichia stipitis* [165,166].

2.4. Distillation

The ethanol solution resulted from fermentation process needs to be further processed to remove the water content, giving dry with high quality ethanol product, or also called anhydrous ethanol. In general, removal of water content can be done by the principle of distillation, which is done by utilising the difference of boiling points of the mixtures in a solution. When the mixture is heated to the ethanol boiling point (78.2 °C), ethanol in the mixture will be vaporised and separated from the other component

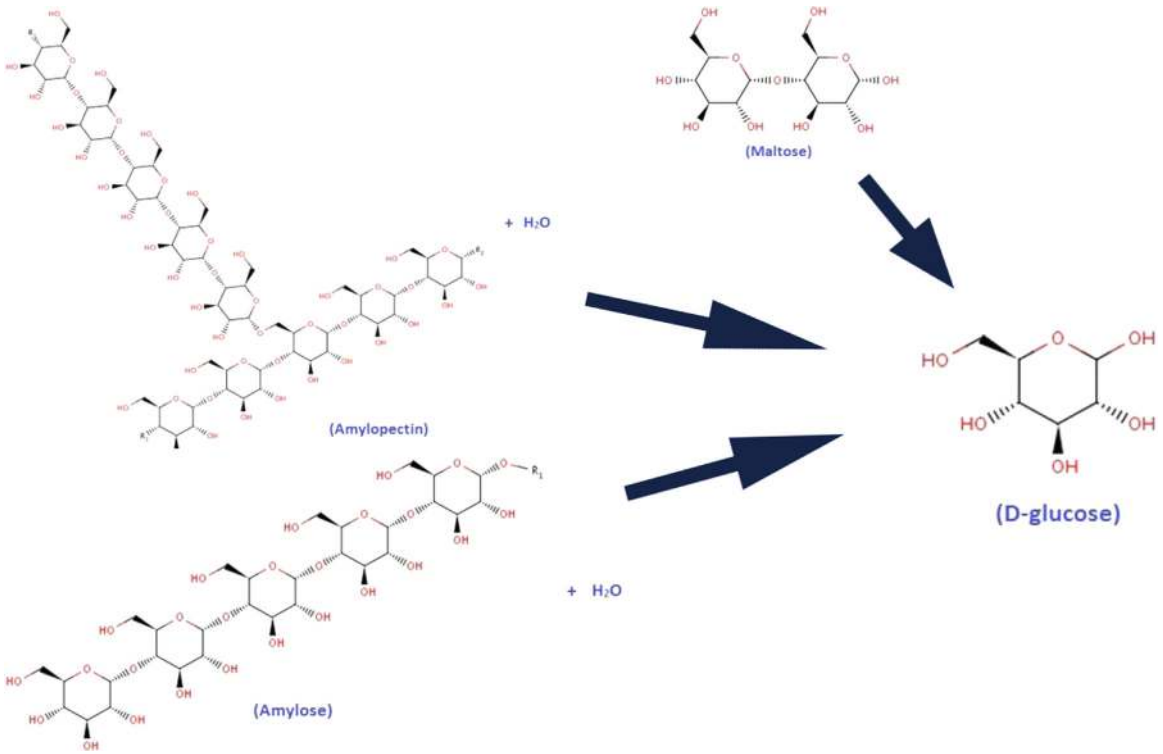

Fig. 9. Reaction of maltose, amylopectin and amylose hydrolysis catalysed by glucoamylase (EC 3.2.1.3), producing glucose [128–131].

(water). Anhydrous ethanol holds minimum of 99.5% of ethanol by volume, with the water content is strictly cannot be more than 0.5% by volume [167]. Besides anhydrous ethanol is widely exploited for industries of pharmaceutical, cosmetics, etc., it also has been exploited its potential for fossil petrol substitution. This leads to many researches in developing techniques in producing anhydrous ethanol. A study done by Kumar et al. [167] reviewed the existing several distillation techniques to produce anhydrous ethanol. The anhydrous ethanol can be produced from any of the following techniques: (i) adsorption process, (ii) azeotropic distillation, (iii) chemical dehydration, (iv) diffusion distillation, (v) extractive distillation, (vi) membrane process, and (vii) vacuum distillation.

2.4.1. *Adsorption distillation*

In their review, Kumar et al. [167] stated that distillation through adsorption method utilises the difference in molecular sizes of the ethanol-water mixture to entrap the excess water content. Adsorption distillation uses molecular sieve that is able to separate the ethanol from the mixture according to the size of the sieve's apertures. Ethanol's molecules of 4 Å in diameter are separated from water molecules by the sieve with 3 Å in diameter, since water molecules are typically size 2.5 Å in diameter.

In typical adsorption distillation process, minimum two beds of molecular sieve in bulk are required. In the column where ethanol-water vapour is fed and introduced to the first bed, water vapour molecules fill the voids of the molecular sieve and are adsorbed. As the mixture vapour stream keeps flowing, the water molecules absorption occurs uninterruptedly until the maximum amount of the water molecules can be absorbed by the bed, separating the ethanol dehydrated and anhydrous. Once the bed is full with water molecules, swap of the fresh bed replacing the hydrated bed is then performed with the help from automation system or control valve. The bed is regenerative, making it able to be reused for numerous multiple times of absorption process. Zeolite is one instance of absorbent material that makes the reusable property possible. Although low cost and environmental friendly, organic (derived from plants, such as cornmeal, sawdust, straw, cellulose) absorbents are incapable to be regenerative [167]. However, the involvement of organic materials as absorbent is still favourable. Benson and George [168] conducted a research of the usage of different lignocellulosic materials as the absorbent to produce anhydrous ethanol. The research resulted 90, 97 and 95 wt% of ethanol after absorption distillation using bleached wood pulp, kenaf core and oak sawdust respectively.

Regenerating the sieves is one focus in adsorption distillation method. To remove or desorb the adsorbed water molecules conventionally is by exposing the sieves to high temperature and allowing stream of gas to expel the adsorbate (trapped water molecules). Since it is important to maintain the high temperature (around 288 °C) over long time (2–4 h) only for the sieves regenerating process, high energy requirement from this process is also projected into the overall energy input in the bioethanol production. Organic absorbents are also inefficient when the adsorption process is higher than the ambient temperature [167].

2.4.2. *Azeotropic distillation*

The conduct of azeotropic distillation is can only be done by (i) adding third chemical substance in the binary azeotropic mixture; (ii) and where the binary mixture disobeys Raoult's law [167]. Addition of entrainer (the third additional chemical substance) amends the azeotropes relative volatilities and is recovered through decantation, distillation or other recovery methods suitable to have it reusable in continuous manner [169]. The same author also illustrated the distillation scheme for azeotropic distillation to remove the water content from ethanol-water mixture in Fig. 11 [169]. The mixture is flowed into the azeotropic distillation column and the entrainer is introduced from the above feed inlet, while the bottom of the column is where anhydrous ethanol is gathered and collected. The feeding of the mixture with entrainer results ternary azeotrope, which is then streamed to a decanter to get it recycled before it gets back to feed the mixture in the azeotropic distillation column.

Table 4
List of engineered microorganisms employed in the improvement of ethanol production.

Employed microorganism	Microorganism type	Features	Substrate used	Ethanol yield	Ref.
Candida shehatae NCL-3501	Yeast	Co-ferment xylose and glucose	Rice straw	• 0.45 g/g of sugar by autohydrolysis • 0.5 g/g of sugar by immobilized cells	[139]
Clostridium thermocellum DSM1313	Bacterium	Improved ethanol yield	Not specified	• 0.8 g/L at 0.5 g/L cellobiose	[151]
Clostridium thermocellum YD01	Bacterium	Improved ethanol yield	Not specified (cellobiose)	• 1.33 mol-ethanol/mole-glucose equivalent (three times than resulted from the wild type)	[141]
Clostridium thermocellum YD02	Bacterium	Improved ethanol yield	Not specified (cellobiose)	• 1.28 mol-ethanol/mole-glucose equivalent (three times than resulted from the wild type)	[141]
Escherichia coli KO11	Bacterium	Ferment both xylose and glucose	Sugarcane bagasse	• 31.5 g/L or theoretically 91.5% after 48 h fermentation	[149]
Escherichia coli FBR5	Bacterium	Ferment xylose	Xylose	• 0.5 g/g of xylose	[147]
Escherichia coli FBR5	Bacterium	Ferment xylose and arabinose, the process was bioabated by *Coniochaeta ligniaria* NRRL30616	Rice hull	• 2.25% (w/v)	[145]
Pichia stipitis A	Bacterium	Adapted at hydrolysate increased concentration	Wheat straw	• 0.41 g_p/g_s	[146]
Pichia stipitis NRRL Y-7124	Bacterium	Adapted at hydrolysate increased concentration	Wheat straw	• 0.35 g_p/g_s	[146]
Pichia stipitis BCC15191	Bacterium	Ferment both xylose and glucose	Sugarcane bagasse	• 8.4 g/L after 24 h fermentation	[138]
Saccharomyces cerevisiae D5a	Yeast	Improved ethanol yield	Rice hull	• 0.58% (w/v) or 100% theoretical yield	[145]
Saccharomyces cerevisiae 590. E1	Yeast	Ferment glucose and cellobiose	Whatman paper	• 1.09% from 2% glucose • 1.16% from 2% cellobiose	[150]
Saccharomyces cerevisiae 590. E1	Yeast	Ferment cellulose without additional enzymatic hydrolysis process	Corn stover	• 63% theoretical ethanol after 96 h fermentation	[150]
Saccharomyces cerevisiae RWB 217	Yeast	Ferment glucose and xylose	2% glucose +2% xylose	• 0.43 g/g of sugars	[143]
Saccharomyces cerevisiae RWB 218	Yeast	Ferment glucose and xylose	2% glucose +2% xylose	• 0.4 g/g of sugars	[143]
Zymomonas mobilis ZM4(pZB5)	Bacterium	Ferment both xylose and glucose	Stillage (residue from starch fermentation)	• 11 g/L with supplementation with 10 g/L of glucose • 28 g/L with supplementation with 5 g/L yeast extract and 40 g/L glucose	[140]
Zymomonas mobilis AX101	Bacterium	Ferment glucose, xylose and arabinose	Various agricultural wastes (dominated with wheat straw and corn stover)	• 3.54 g/L.h (no presence of acetic acid) • 1.17 g/L.h (with presence of acetic acid)	[144]
Thermoanaerobacterium saccharolyticum ALK2	Bacterium	Improved ethanol yield, able to ferment glucose, xylose, mannose and arabinose	Not specified	• 37 g/L	[148]
Thermoanaerobacter mathranii BG1L1	Bacterium	Improved ethanol yield	Wheat straw	• 0.39–0.42 g/g sugars	[142]

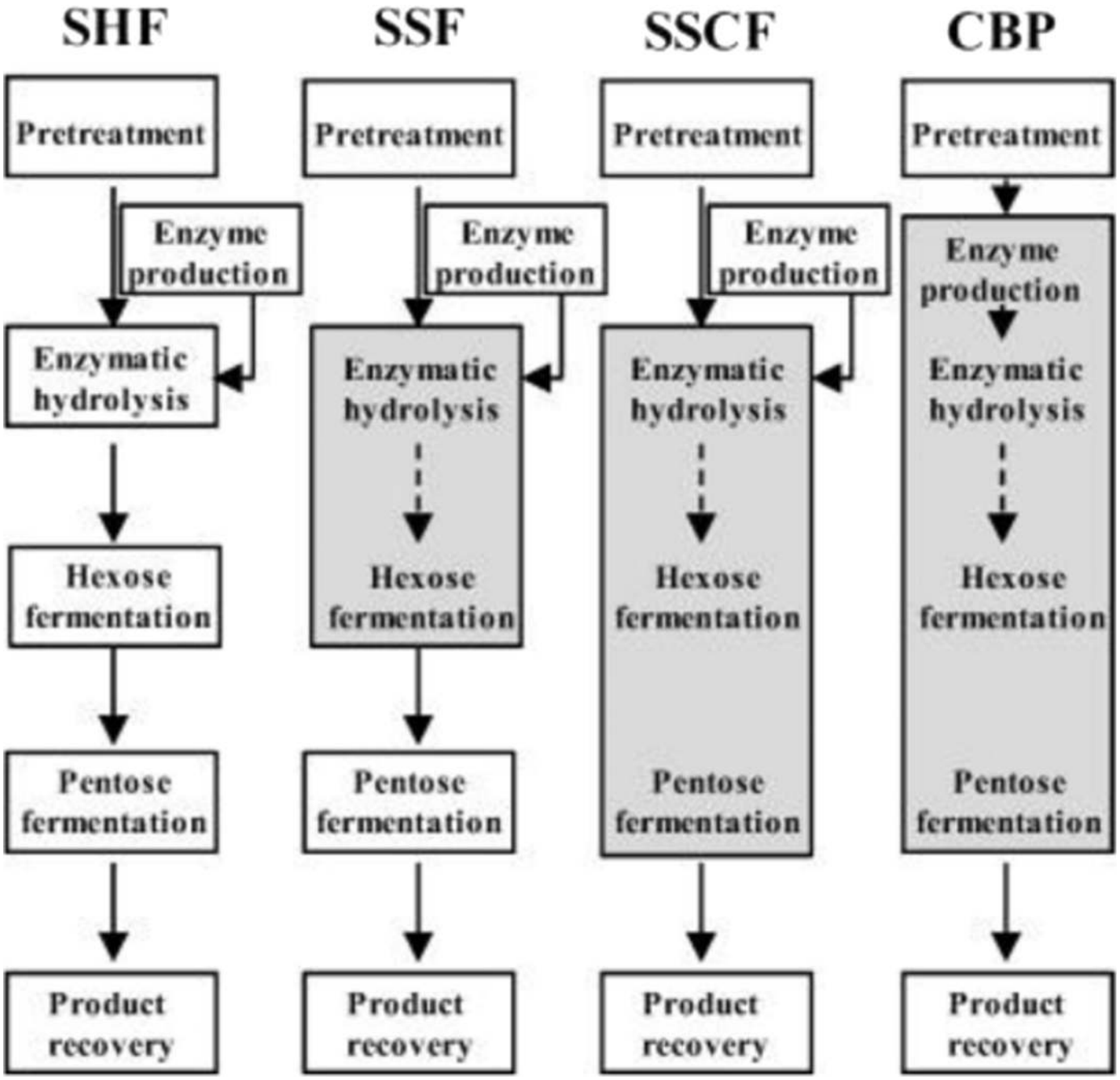

Fig. 10. Schematic diagrams of different available methods of ethanol production [162].

The most frequently used entrainers are cyclohexane and benzene, despite the nature of benzene possesses carcinogenic property [167,169]. Other researches also have utilised other different chemical substances as entrainers in azeotropic distillation to produce anhydrous ethanol, namely acetone [170], diethyl ether [171], hexane [172], isooctane [170], n-heptane [173], n-pentane [169,171] and polymers [174]. However, azeotropic distillation still draws concerns, especially in economy-wise. This distillation method involves high principal cost and energy input. The necessity of maintaining large stream of entrainer flow to have it keep continuously circulated draws more of distillation cost. The usage of harmful entrainer, e.g. benzene, is also undesirable to the overall anhydrous ethanol production as it could damage the human operator as well as the environment [167].

2.4.3. Chemical dehydration

Dehydration through hygroscopic chemical substances is one of the most conventional methods in producing anhydrous ethanol. The hygroscopic substances are introduced to the ethanol-water mixture (in liquid or vapour phase), forcing the substances to hydrate with the water molecules. For laboratory scale dehydration, calcium oxide or quicklime is the most frequently used to force the chemical reaction with water, forming the obvious insoluble calcium hydroxide as the result and leaving the ethanol at the top. Dehydration by quicklime is typically done with the ratio water to quicklime 1:4.2, means for every 1 kg of removable water content must be at least reacted with 4.2 kg of quicklime. Distillation or thorough filtration is required to completely remove the calcium dioxide in the mixture, and it can be recycled for the next batch use by reversing the calcium hydroxide reaction with

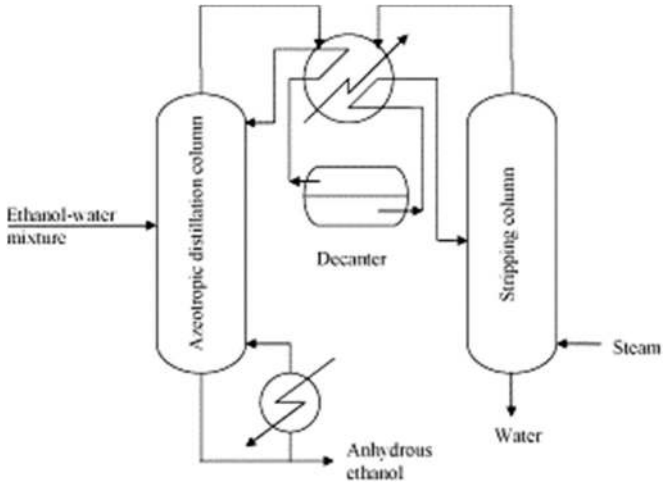

Fig. 11. Azeotropic distillation scheme [169].

water to produce calcium oxide. Quicklime dehydration method apparently consumes a quite large energy amount due to the need of high temperature during the process, although this method produces high quality of anhydrous ethanol for above 97%. Furthermore, this method seems impractical for continuous, large scale ethanol dehydration process since the removal of the insoluble calcium hydroxide is performed per batch, unless continuous distillation plant is installed which practically adds up the total production cost of the ethanol production [167].

2.4.4. *Diffusion distillation*

This distillation method was initially studied by Fullarton and Schlunder [175], who proposed separation by diffusion through the voids of intern gas then condensed. The mixture is vaporised at before the boiling temperature and the diffusion affects the volatility of the mixture and inert gas's diffusivity. In their research, different several pre-distillation mixtures of alcohol and water were tested, namely isopropanol-methanol-water and binary isopropanol-water, and the tests were run with variance of condensation, evaporation temperatures, inert gasses and wetted-wall column's annular widths. The authors claimed that their research was in alignment with Stefan-Maxwell and vapour-liquid equilibrium equations through experimental modelling analysis from perspective of a single point behaviour. Other researchers also have reported their studies of diffusion distillation process (Table 5) [175–180].

2.4.5. *Extractive distillation*

In the chemical and pharmaceutical industries extractive distillation is a popular method to produce higher purity of a liquid component by separating the component from the mixture by addition of a non-volatile solvent. In fact in the Second World War this technique was used for production of butadiene and toluene with fine purity [181]. The solvent addition is purposed to separate the components. The component with higher volatility (light component) presents at the column's top while the added solvent presents at the column's bottom along with the component with lower volatility (heavy component). As the result from this separation based on the volatility, the light component is extracted out from the first column, while the heavy component is run into the second distillation column along with the added solvent which to be separated here (Fig. 12) [182,183]. The process in the second column, in addition, recycles the used solvent, which is able to be utilised again in the first column as continuous extractive distillation technique [184].

The extracted component out of the columns, which by other words the decision which component comes out as the light component to be extracted at the first column while the other is taken out at the second column, is dependent on the selection of the added solvent. In general, the used solvent must possess several important properties, including ability to easily recovered, non-toxic substance, holds boiling point higher than the mixture, and thermally stable [185]. In a research by Yuan et al. [181], additional selection criteria of solvent in extractive distillation was planned and performed in their study to distillate various binary azeotropic mixtures, which by comparing the dielectric constant and boiling point of the mixture's components with the potential solvents. Here, dielectric constant acts as the polarity property in which the solvent's polarity should be close to the heavy component to let the interaction occurs. Consequently, heavy component should have close dielectric constant with the solvent; both are then as the bottom product in the first column beforehand flowed to the second column. In a binary azeotropic mixture, assignation of heavy and light component is determined by the boiling point. Light component that is taken out in the first column is due to its lower boiling point, or higher volatility. On the other hand, heavy component is drawn with the solvent to the second column due to its higher resistance to vaporise compared to the other component in the binary mixture. The desired product to be extracted from the binary mixture can be from either light or heavy component. For example in ethyl acetate-ethanol binary mixture, the desired fine ethanol extraction is drawn from the second column. In this combination, ethyl acetate and ethanol have insignificant difference in their boiling points, which are 77 and 78.3 °C respectively. However, by adding solvent with higher dielectric constant than ethanol in the mixture, for instance N,N-dimethylformamide, N-methyl-2-pyrrolidone, dimethyl sulfoxide with dielectric constant of 36.71, 32 and 48.9 respectively, makes ethanol acts as the heavy component due to the closer dielectric constant value with ethanol (dielectric constant: 25.7) than that of ethyl acetate (dielectric constant: 6.02). Table 6 lists typical substances used as the mixtures and solvents in extractive distillation [186,187].

The energy requirement for extractive distillation with liquid solvent apparently does not support the overall cost efficiency despite the fine outcome it produces. To run the distillation, average ratio of mixture feed to solvent is 1:5, which also makes the solvent recovery process drains a large sum of energy [188]. The hazard of the solvent is also one of the shortcomings in the technique. Ethylene glycol, as the typical solvent in anhydrous ethanol production, is extremely toxic to human's health that may cause kidney failure, cardio-pulmonary failure and central nervous depression [189].

Extractive distillation using soluble salt to replace liquid solvent is an alternative to achieve the same objective with lesser drawbacks. The soluble salt serves as the separating agent and intervenes the azeotropic system in the mixture. It uplifts the volatility of the component with the higher volatility than the other, and therefore eases the components separation. Salt effect, the name of the phenomenon, occurs due to the salt's ions tendency of solvation with the less volatile component in the mixture. The extracted component, which changes its phase from liquid to vapour, due to its higher volatility is salted out [167]. The amiabilities of using salt as the separating agent include low toxicity, much lesser energy consumption since evaporation-condensation system cycle is trivial (comparison of energy consumption is listed in Table 7 by refs [171,190,191]), salts recyclability, lesser dimension needed in the column design, corrosion resistive and better in material handling (transporting) [190,192]. The usage procedure of salt in extractive distillation is likewise as that of liquid solvent. The soluble salt is added through the top feed and streamed down to the bottom of the column. The removal of the salt is concurrent with the heavy product at the column's bottom.

Researchers have shown interest in utilising salt as the separating agent in extractive distillation of ethanol-water mixture.

Table 5
Researches on diffusion distillation for anhydrous ethanol production.

Researcher(s)	Description of the study	Ref.
Fullarton and Schlunder	• Diffusion distillation study by varying alcohol-water mixtures, inert gasses, condensation and evaporative temperatures, wetted-wall column's annular widths. • Alcohol-water mixtures including: isopropanol-methanol-water and isopropanol-water. • Illustrated by Stefan-Maxwell and vapour-liquid equilibrium equations modelling. • Does not further explain the essence behind the diffusion distillation process. • Results obtained are not further process to show possible potential separation extension.	[175]
McDowell and Davis	• Improvement of Fullarton and Schlunder modelling study by computerised simulation. • Reveals the important parameters and gives wider exposure of the nature of diffusion distillation through the integral column which created by the simulation.	[178]
Taylor and Krishna	• Suggests the improved method by McDowell and Davis to be practiced in anhydrous ethanol production.	[180]
Chung et al.	• Performed diffusion distillation with observation on the effect of the distillation parameters, including temperature in evaporation and condensation process, annular widths and the selection of the inert gas.	[176]
Kim et al.	• Modelling development of previous researches by including heat transfer of sensible heat • Algorithm development to compute interfacial temperature to have better accuracy.	[177]
Singh and Prasad	• Proposed a way to obtain the optimum temperature of vaporisation by a introducing new variable $S_{az}(N_2/N_1)$, which quantified as 46 °C. • The experimental results were aligned with the theory of Stefan-Maxwell equations.	[179]

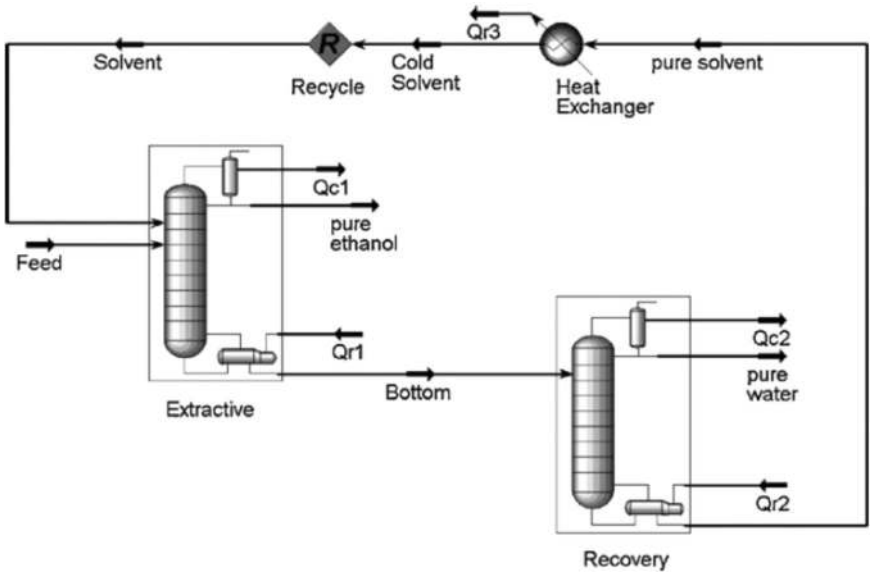

Fig. 12. Extractive distillation schematic diagram (water-ethanol binary azeotropic mixture). Extractive column is where the light component extracted, while heavy component is extracted at the recovery column [182,183].

Soares et al. [193] conducted a study in using different salts to dehydrate ethanol from ethanol-water azeotrop, including calcium chloride, potassium acetate, sodium chloride, sodium-potassium acetate mixture and calcium nitrate. The study observed the ethanol concentration on the top and the bottom feed of the column, which showed enhancement by the salt addition than the one without. Ligero and Ravagnani [190] performed salt extractive distillation by varying the salt recovery processes. The first proposed process was by introducing the salt to the ethanol-water feed in the first column. The bottom products, water and salt, were drawn to the multiple recovery columns where they were evaporated and dried (by spray dryer). Anhydrous ethanol produced from this process was drawn out from the first column as the top product. In contrary, the second proposed process by the same authors was by pre-treating the feed prior introducing it to the separating salt. In the first column, the feed was distilled to have better ethanol concentration and was flowed to the second column afterwards. The salt was initiated in the second column with the more concentrated ethanol in the feed. The difference lies on the salt recovery step, where evaporation columns were unnecessary and only spray dryer was installed to recycle the salt. From the energy consumption analysis, 82% of the total energy consumption, or 22.1 MW accounted for the first proposed process was spent only on the salt recovery process. The opposite was found on the second proposed process, which salt recovery process only accounted 9.7% of the total energy consumption, or 0.555 MW. The authors also claimed that the second proposed process requires lesser dimension of the equipment, absence of multiples recovery columns, lesser cool water and hot air for condensation and drying process, and is easy to be installed. Usage of salt as the separating agent has also reported to be suitable in salt-solvent combination for extractive distillation. In a study by Lei et al. [194], calcium chloride was mixed with ethylene glycol in ethanol-water mixture, and it was compared with distillation process of plain ethanol-water and ethanol-water with only ethylene glycol as the separating solvent. The presence of calcium chloride salt with solvent was observed enhancing than the other processes tested. This however limited to the concentration of the salt mixed with solvent, which was best at 5–10%. Mixing salt with solvent benefits in the ways of lowering required salt to be recovered, lesser theoretical plates, and lesser equipment cost and energy consumption.

Table 6
List of substances with boiling points and dielectric constant [186,187].

Substance	Boiling point (°C)	Dielectric constant
1-butanol	117.7	17.8
1-propanol	97	20.1
1,2-dichloroethane	83.5	10.42
1,3,5-Trimethylbenzene	164.716	2.279
1,4-dioxane	101.1	2.21
2-butanol	99.5	17.26
2-butanone	79.6	18.6
2-propanol	82.4	18.3(25)
2-methylpyridine	129.4	9.46
3-methylpyridine	143.8	10.71
Acetic acid	118	6.2
Acetone	56.3	20.7
Acetonitrile	81.65	36.64
Butyl ether	142	3.06
Carbon tetrachloride	76.8	2.24
Chlorobenzene	131.7	5.69
Chloroform	61.2	4.81
Cyclohexane	80.7	2.02
Diethylbenzene	181.102	2.369
Diglyme (diethylene glycol dimethyl ether)	162	7.23
DME, glyme (1,2-dimethoxy-ethane)	84.5	7.3
DMF (N,N-dimethylformamide)	153	36.71
DMSO (dimethyl sulfoxide)	189	48.9
Ethanol	78.3	25.7
Ethyl acetate	77	6.02
Ethylene glycol	195	37.7
Glycerine	290	42.5
Heptane	98	1.92
Hexamethylphosphoramide (HMPA)	232.5	31.3
Methanol	64.6	32.6
Methylene chloride	39.8	9.08
n-Hexane	68.7	1.89
NMP (N-methyl-2-pyrrolidone)	204	32
Nitromethane	101.2	35.9
Pentane	36.1	1.84
Pyrrole	130	8
Tetrahydrofuran (THF)	65.4	7.58
Toluene	110.6	2.38
Triethyl amine	88.9	2.4
Water	100	78.54
Xylene	144.4	2.266

*Note: values of dielectric constants are taken at averagely 20–25 °C

Table 7
Energy consumption in extractive distillation by various separation agent [171,190,191].

Type of agent	Separation agent	Consumption of energy (MJ/kg ethanol)
Liquid solvent	Benzene	13.59
Liquid solvent	Ethylene glycol	34.06
Liquid solvent	Diethyl ether	13.59
Liquid solvent	Pentene	10.87
Salt	Calcium chloride	5.02
Salt	Potassium acetate	9.27
Vacuum	Vacuum	11.72

2.4.6. Membrane distillation

Distillation through membrane stimulates mass transfer of specific component from the mixture through a semipermeable membrane by permeability principle (Fig. 13) [195]. Surface tension of the membrane blocks the feed, while the volatile component crosses the membrane. Typically, organic polymers are chosen as the membrane, though some gas, liquid, metal and ceramic materials are also applicable. For the real application, membrane distillation is useful in wastewater treatment, desalination of seawater, dairy processing and separating volatile components [167,195].

In their study of membrane distillation, Lewandowicz et al. [196] ran an experiment for ethanol recovery attempt. In their

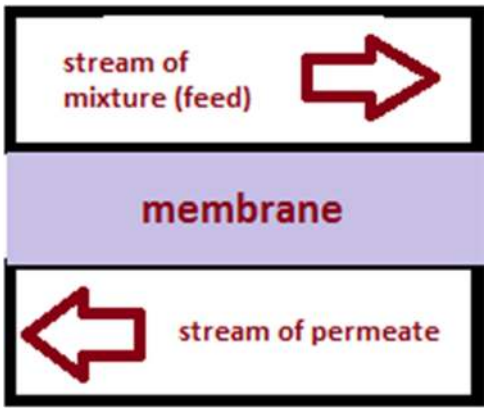

Fig. 13. Simplified version of membrane distillation process [195].

experiment, the ethanol mixture used was produced independently from molasses wort undergone fermentation process (Lyophilised *S. cerevisiae* was employed in the fermentation). The selected membrane material was polypropylene microporous hydrophobic capillary, with dimensions of 0.2 μm pore diameter, capillaries diameter 1.8 and 2.6 mm for inside and outside respectively (Fig. 14) [182,197]. Temperature difference of 20 °C was set between the distillate and fermentation bioreactor: 15 °C at the distillate side while 35 °C at the fermentation bioreactor. Compared to batch fermentation (without membrane distillation), ethanol recovery with membrane distillation was observed to be 15.6% higher. In continuous fermentation (with membrane distillation) ethanol produced was 0.45 g ethanol/g glucose, which visibly higher than the one produced in batch fermentation (0.38 g ethanol/g glucose). Membrane distillation also increased the ethanol productivity of the process from 1.4 g/L.h ethanol by batch fermentation to 2.15 g/L.h.

Although frequently mistaken with membrane distillation, pervaporation is another type of membrane process that also can be exploited in producing anhydrous ethanol. To distinguish the two, some essential characteristic must be examined. Based on the material selection, pervaporation technique uses thick polymer membranes, while microporous, non-wetting membranes are employed in membrane distillation [198]. The permeability force in pervaporation is from the low vapour pressure established by condensation of the permeate vapour. On the other hand, membrane distillation forces permeability from the difference of partial pressure between the membrane pores' sides. Membrane material selection in pervaporation is dependent upon the affinity of the feed to the membrane, while membrane distillation selects its membrane materials according to the membrane properties and the application of the distillation process [198,199]. Regarding the membrane selection for membrane distillation, a recent study by Wang and Chung [195] reported the development of membrane fabrication, including mixed matrix membranes and other membranes modifications.

Traditionally, anhydrous ethanol can be achieved by vacuum distillation, which is by lowering the pressure below 11.5 kPa to disrupt the azeotrope system of the ethanol-water. Once the azeotrope is disrupted, the separation can be run conventionally, which usually takes two columns: first column is at moderate pressure, where the second column is at the low pressure [167]. Nevertheless, modification of conventional vacuum distillation to vacuum membrane distillation has been performed by Izquierdo-Gil and Jonsson [200] to gain both vacuum and membrane distillation favourable properties. In their research, factors affecting the ethanol distillation were observed, including pore sizes and materials of the membrane, temperature of the feed, native characters of the mixtures and flow

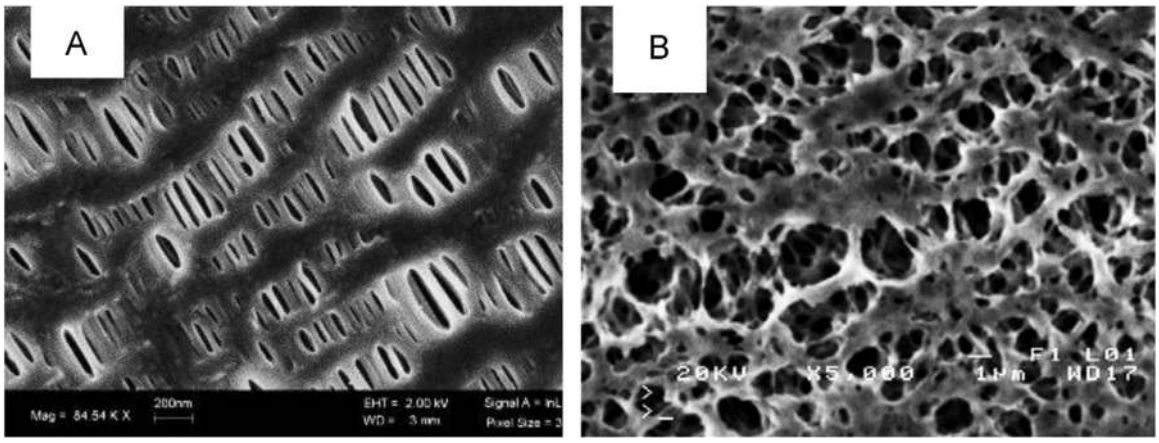

Fig. 14. Polypropylene membrane under scanning electron microscope. (A) Undergone melt-extrusion-mono-axially-stretching fabrication. (B) Undergone thermally induces phase separation (TIPS) fabrication [182,197].

rate of the cycle. Additionally, the membranes used were polytetrafluoroethylene, polypropylene and polyvinylidene fluoride with variance of pore sizes. This study displayed highly reliable experimental results as they were agreed with the theoretical estimations by Knudsen model.

Membrane distillation holds several practical benefits, for instance, works at rather lower temperature and pressure, perfect theoretical separation and less mechanical properties requirement [195]. In contrast to those, Lewandowicz et al. [196] claimed that membrane distillation technique is impractical once it is installed in a commercial scale, which namely due to the heat loss and module design problems that further expand the cost inefficiency. Suitability of the selected material for membrane is another challenge since the membrane fabrication spends high technological, energy and production costs [195].

3. The future of second generation bioethanol production

When second generation bioethanol is implemented wholly in industry, it becomes an industrial strategy to fulfil both industries demands in energy sector (especially renewable energy sector) for its biofuel product; and agricultural sector for its role in utilising the biomass as value added product. Also, unsurprisingly bioethanol has gained many popularity in both developed and developing countries since the reliance of fossil petrol has always been harmfully striking the global environment, air quality, as well as the oil reserves. At the current state, first generation production is well-developed in several countries to supply the bioethanol demand for transportation sector. However, the dependence of first generation production in its edible feedstock has started to raise many sceptical opinions questioning the sustainability issue of this approach. The edible feedstock is concerned to contribute negative impacts in the world's societies since it looks inhumane and irony to 'feed' the vehicle than millions of malnourished world's population. The prospect of second generation bioethanol production eliminates the bad image of bioethanol production since it simply utilises the non-edible feedstock (from agricultural and forestry biomass).

Second generation bioethanol production is forecasted to be excelled than the first generation production in approximately the next ten years due to the unfavourable characteristic of the first generation feedstock. In fact, it is expected that second generation bioethanol production will overlap the dominance of the first generation production in the biofuel global market [201]. The International Energy Agency (IEA) [202] has forecasted the cost of production of bioethanol from lignocellulosic biomass. IEA reported that by 2030 the cost of bioethanol production can reach as low as US$ 0.55–0.65/lge (litre gasoline equivalent). The forecasting also predicted the production cost by 2050 would reach a slightly smaller range of US$ 0.55–0.60/lge. The forecast is noted with the scenarios of 50% reduction of annual carbon dioxide emission by 2050, high priority in the second generation production global development, and the expectation to drastically fulfil the 26% of biofuel demand for transportation sector from year 2030–2050. In a techno-economic study in Colombia by Quintero et al. [203], production cost of bioethanol from empty fruit bunch as the lignocellulosic feedstock is as low as US$ 0.58/litre for the stand-alone production plant, and US$ 0.49/litre by the co-generation plant system. The authors also reported the analysis of bioethanol production from other lignocellulosic materials, which is listed in Table 8 [203]. In Malaysia, Tye et al. [204] described the production cost of bioethanol is estimated as around US$ 5.62/GJ, which is comparable with the petrol fuel production cost of US$ 5.12/GJ (US$1 ≈ RM4.23, as per December 2015 rate). Even though at the moment it seems that bioethanol production cost is higher than petrol, the feedstock cost accounts majorly in the total production cost. This means it is possible to have a feasible, in fact cheaper, bioethanol production cost than fossil fuel in the future.

The sustainable future for second generation production is strongly related with the development of the current technology. The advance in technology is what makes the current production of 270 l/tonne biomass to as high as 400 l/tonne biomass in the future year 2030 as forecasted by the National Renewable Energy Laboratory (NREL) [205]. The success of second generation production is also impeccably reliant to the government policies. The capital investment in this route is undeniably high and risky. But with the support from the government by its policies will not only help uplift the possibility of second generation production, but also will allow the further actions of many research applications to suppress the environmental harms caused by the emissions of the non-renewable energy products. Sims et al. [54] stated that in the establishment of policies regarding the route of second generation production there are several points and objectives needed to be covered, including (i) improvement of crop productivity along with the balance ecosystems, (ii) evaluation on greenhouse gas emission and soil carbon content, (iii) analysis of the total production cost from collection to distribution and (iv) opportunities to allow production from different technologies to produce the better production efficiency. The same authors also suggested the government to imply the policies through tax credits or fuel-blending targets. The visible outcomes may be directly obtained by setting the national fuel-blending targets, although tax credits

Table 8
Production cost from different lignocellulosic materials [203].

Biomass	Production cost from stand-alone plant (US$/litre)	Production cost from co-generation plant (US$/litre)
Coffee cut stems	0.68	0.59
Empty fruit bunch	0.58	0.49
Rice husk	0.64	0.53
Sugarcane bagasse	0.77	0.68

bring the potential in the improvement of the production cost. Government policies should also charm the private industrial players to contribute to the actualisation of the new route, thus shorter development period and more positive impacts are reachable. Consequently, this interesting industry of bioethanol production can also open many employment opportunities and develop rural areas of where the biomass is mostly collected from. This because to develop a new branch of industry it requires human resources with high educational level, of which the industry will subsequently elevate the society's educational level to fill the vacancies. In other words, the new industry will not only beneficial to satisfy the energy demand renewably but also to develop the society to the better economy state [21]. With a solid commitment from all industrial players and supporting policies set by the government, the benefits of second generation production are feasibly extractable.

It is well-known that second generation bioethanol production is still at its embryonic phase. However, experts have started to develop the suitable approach by conducting numerous studies to carry out the concept into real-life scale. Limayem and Ricke [206] suggested to use Life Cycle Analysis (LCA) to compare the favourability from multiple possible routes resulted from the growing technologies development. Moreover, the authors also suggested to optimise each of the production stage, to yield the ideal amount of ethanol. The optimisation can be done by setting up the preferable constrains as the parameters, for instance amount of water used, total energy used, total production cost, amount of waste produced, etc. Moreover, pre-treatment, as the beginning stage of bioethanol production, can be taken into the focus in optimisation to result better fermentable sugar. Haghighi Mood et al. [25] reported various pre-treatment methods in second generation bioethanol production as well as their limitations. The authors stated that the most suitable pre-treatment method can be applied through the basic comprehension of the available pre-treatment technologies, feedstock characteristics, and the connection between these two.

As one of South East Asia countries with enormous tropical biodiversity, Malaysia has the appealing tremendous potential seen from the availability of raw feedstock, yet Malaysia still has not implemented the second generation bioethanol policy to its national primary sectors, especially the transportation sector which can benefit directly from the production of bioethanol. LCA and optimisation of bioethanol production in Malaysia, therefore, are essential as the fundamental to start the prospect. Goh et al. [207] studied the possibility of lignocellulosic bioethanol in Malaysia. They claimed that to validate the establishment of bioethanol refineries must include availability of the feedstock, domestic demand, feedstock collection scheme, proper feedstock storage and transportation. In fact, these factors can be considered in LCA study for Malaysia case according to the real condition in Malaysia. Optimisation study is equally essential in order to design the suitable bioethanol refinery sites in Malaysia, which can be done commonly by response surface methodology (RSM), and various optimisation analysis techniques including Box-Behnken, central composite rotatable designs (CCRD), partial factorial and full factorial [208]. As one scenario example, oil palm biomass can be focused as the primary Malaysia's tropical feedstock for bioethanol production, since it is the home of 5.1 million hectares of oil palm and occupies 77% of Malaysia's agricultural land [209]. Because of this massive oil palm production in Malaysia, the potential of second generation bioethanol that could be produced from oil palm biomass has been reported as about 13.5 million-tonnes in 2014 alone, which makes oil palm biomass is the wisest choice to be considered here [210]. Oil palm biomass is high in cellulose and low in lignin, especially in frond, empty fruit bunch (EFB) and trunk [207], hence ammonia fibre explosion (AFEX) is one suitable pre-treatment method for this biomass type [211]. Besides the advantage of having ammonia traces during the process and further utilised as microbes food (as nitrogen source) [57,90], oil palm biomass pre-treatment via AFEX also requires no effort in inhibitors removal process, hence lesser refinery cost is required. Hydrolysis can be done enzymatically by cellulase. Balat [211] stated that enzymatic hydrolysis requires lesser utility cost, and Saini et al. [208] found that commercial enzyme technology is developing very well which leads to the cost reduction of the commercial enzyme. To simplify the production, enzymatic hydrolysis of oil palm biomass in Malaysia can be co-conducted with fermentation, or is called as simultaneous saccharification and fermentation (SSF) method. The obvious value to select this method is the simultaneous process reduces the direct production cost, than having separate conventional hydrolysis and fermentation processes that automatically needs higher processing cost to fulfil. To refine the fermentation product, extractive distillation method by Ligero and Ravagnani [190] can be performed afterwards, since the method is claimed to require lesser energy input with the good quality of distillation product. Although, it must be noted that this benefit can only be gained with soluble salt as the separating agent, along with other benefits of low toxicity, less space required in the column, easier to be logistically transported, tough against corrosion and its recyclability characteristic [190,192].

As one of rapidly developing countries in the Southeast Asia and one nation with massive potential in green technology, Malaysia is one good model to be set a new standard on second generation bioethanol scheme, and it seen capable to afford the technologies mentioned in the given scenario example. However, a thorough study (e.g. LCA study) is still compulsory for Malaysia in order to establish the second generation bioethanol production nationally. The existence of national car manufacturers, Proton and Perodua, may actually help Malaysia to promote the actualisation of bioethanol fuel as the product of the national renewable energy sector, such as by manufacturing flexible-fuel vehicles (FFV) in the future, as long as it is paired with the adequate government policies to initiate and attract the investors into the programme [207]. Malaysia can look up to Brazil, which as one of the leading bioethanol implementers, in terms of practicing the national bioethanol policies. Brazil includes several important key points in energy policy making, which are comprised of: involving private sector in the entire national bioethanol production development, enforcing fuel tax policy that based on carbon-footprint, granting research funds for bioethanol production further development and FFV endorsement [207,212]. A more local perspective is delivered by Poh and Kong [213] in a study of renewable energy policy analysis in Malaysia. The authors suggested that in order to initiate the second generation bioethanol policy, it should be started with a consistent awareness spreading programme on second generation bioethanol to all layers of society and industries. Also, Malaysia's government must involve external (private) sectors in running this new renewable energy scheme and should ease and secure any loan relevant to second generation bioethanol scheme to attract more investors. Further, as an additional supporting study, Tye et al. [204] revealed that 10% ethanol blend in petrol

(E10) is economically feasible for Malaysia; second generation bioethanol production in Malaysia could help to increase Malaysia's Gross Domestic Product (GDP) as well as elevate the overall national economy; and EFB is a viable feedstock for bioethanol production in Malaysia since it is estimated to have the potential of 2324 ktoe/year in the future.

4. Conclusion

Second generation bioethanol production is an encouraging solution indeed to solve the energy and environmental crisis. The flexibility it offers, which is seen from the various possible routes of the production and various existing production technologies, endorses more development to obtain the better efficient production, feasible cost production and lesser national emission. Described in this paper, different technology possesses unique abilities and drawbacks right from the beginning of pre-treatment to the refining process by distillation. In fact, this paper is valuable as the reference when it comes to the actual ethanol production industry since those facts are critical in influencing the absolute decision in planning second generation bioethanol plant. Moreover, second generation bioethanol is beneficial from the perspective of industry since agricultural and forestry wastes are practically have zero value for the industry as well as for the food, which helps to decrease the feedstock cost in the total production cost.

The actualisation in second generation ethanol production in a nation is also determined by the involvement of the government by issuing supporting energy policies. From the various existing technologies, there is no evidence to show the best route in producing second generation bioethanol, but the initiation is definitely essential to overcome the horrifying issue of energy and environmental crisis. Here, government must display the strong level of support, willingness and consistency for the programme. The policies should aid the R&D of second generation bioethanol, as well as to invite the shareholders to put their shares into the programme. For example, Malaysia, with its massive sources of second generation bioethanol, holds the potential to initiate the national implementation of bioethanol fuel, especially for its growing transportation sector. Malaysia's tropical geographical location provides the vast amount of tropical agricultural and forestry wastes, and its economic stability will sustain to initiate the programme. Again, Malaysia's government plays critical role to actualise the second generation bioethanol industry. Moreover, it is recommended for the government to invite private sectors along, locally and internationally, to assist the development of second generation bioethanol industry in the country.

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References

[1] IEA. Key world energy statistics 2008. Paris, 2008.
[2] Goldemberg J. Environmental and ecological dimensions of biofuels. In: Proceedings of the conference on the ecological dimensions of biofuels. Washington DC, 2008.
[3] Balat M, Balat H. Recent trends in global production and utilization of bioethanol fuel. Appl Energy 2009;86:2273–82.
[4] Statistics Do. Compendium of Environment Statistics. In: Statistics Do, editor. Malaysia, 2013. p. 20–21.
[5] Silitonga AS, Masjuki HH, Mahlia TMI, Ong HC, Chong WT, Boosroh MH. Overview properties of biodiesel diesel blends from edible and non-edible feedstock. Renew Sustain Energy Rev 2013;22:346–60.
[6] Silitonga AS, Masjuki HH, Mahlia TMI, Ong HC, Atabani AE, Chong WT. A global comparative review of biodiesel production from Jatropha curcas using different homogeneous acid and alkaline catalysts: Study of physical and chemical properties. Renew Sustain Energy Rev 2013;24:514–33.
[7] Silitonga AS, Atabani AE, Mahlia TMI, Masjuki HH, Badruddin IA, Mekhilef S. A review on prospect of Jatropha curcas for biodiesel in Indonesia. Renew Sustain Energy Rev 2011;15:3733–56.
[8] Ong HC, Silitonga AS, Masjuki HH, Mahlia TMI, Chong WT, Boosroh MH. Production and comparative fuel properties of biodiesel from non-edible oils: Jatropha curcas, Sterculia foetida and Ceiba pentandra. Energy Convers Manag 2013;73:245–55.
[9] Ong HC, Masjuki HH, Mahlia TMI, Silitonga AS, Chong WT, Yusaf T. Engine performance and emissions using *Jatropha curcas*, *Ceiba pentandra* and *Calophyllum inophyllum* biodiesel in a CI diesel engine. Energy 2014;69:427–45.
[10] Silitonga AS, Ong HC, Mahlia TMI, Masjuki HH, Chong WT. Biodiesel conversion from high FFA crude *Jatropha curcas*, *Calophyllum inophyllum* and *Ceiba pentandra* Oil. Energy Procedia 2014;61:480–3.
[11] Ong HC, Masjuki HH, Mahlia TMI, Silitonga AS, Chong WT, Leong KY. Optimization of biodiesel production and engine performance from high free fatty acid Calophyllum inophyllum oil in CI diesel engine. Energy Convers Manag 2014;81:30–40.
[12] de Almeida VF, García-Moreno PJ, Guadix A, Guadix EM. Biodiesel production from mixtures of waste fish oil, palm oil and waste frying oil: Optimization of fuel properties. Fuel Process Technol 2015;133:152–60.
[13] Adewale P, Dumont M-J, Ngadi M. Recent trends of biodiesel production from animal fat wastes and associated production techniques. Renew Sustain Energy Rev 2015;45:574–88.
[14] OECD-FAO. Agricultural outlook 2011–2020. Organisation For Economic Co-Operation And Development; 2012.
[15] Balat M. New biofuel production technologies. Energy Educ Sci Technol 2009:147–61.
[16] Balat M. Global biofuel processing and production trends. Energu Explor Exploit 2007;25:195–218.
[17] Krylova AY, Kozyukov EA, Lapidus AL. Ethanol and diesel fuel from plant raw materials: a review. Solid Fuel Chem 2008:358–64.
[18] Lashinky A, Schwartz ND. How to beat the high cost of gasoline. Fortune, 2006.
[19] Sebayang AH, Masjuki HH, Ong HC, Dharma S, Silitonga AS, Mahlia TMI, et al. A perspective on bioethanol production from biomass as alternative fuel for spark ignition engine. RSC Adv 2016;6:14964–92.
[20] MA Hassan, Y. Shirai Palm oil biomass utilization in Malaysia for the production of bioplastic. 2003.
[21] Goh CS, Lee KT. Second-generation biofuel (SGB) in Southeast Asia via lignocellulosic biorefinery: Penny-foolish but pound-wise. Renew Sust Energy Rev 2011;15:2714–8.
[22] Silitonga AS, Ong HC, Mahlia TMI, Masjuki HH, Chong WT. Characterization and production of *Ceiba pentandra* biodiesel and its blends. Fuel. 2013;108:855–8.
[23] Ong HC, Silitonga AS, Mahlia TMI, Masjuki HH, Chong WT. Investigation of biodiesel production from *Cerbera manghas* biofuel sources. Energy Procedia 2014;61:436–9.
[24] Demirbas A. Bioethanol from cellulosic materials: a renewable motor fuel from biomass. Energy Sources Part A 2005;27:327–37.
[25] Haghighi Mood S, Hossein Golfeshan A, Tabatabaei M, Salehi Jouzani G, Najafi GH, Gholami M, et al. Lignocellulosic biomass to bioethanol, a comprehensive review with a focus on pretreatment. Renew Sustain Energy Rev 2013;27:77–93.
[26] Graf A, Koehler T. Oregon cellulose-ethanol study: an evaluation of the potential for ethanol production in Oregon using cellulosebased feedstocks. Salem, Oregon, USA: Oregon Dept Of Energy; 2000.
[27] Mosier N, Wyman C, Dale B, Elander R, Holtzapple Y, Ladisch M. Features of promising technologies for pretreatment of lignocellulosic biomass. Bioresour Technol 2005:96.
[28] Patel S, Onkarappa R, Ks S. Funkal pretreatment studies on rice husk and bagasse for ethanol production. Electron J Environ Agric Food Chem 2007;6:1921–6.
[29] Sanchez Ó, Cardona C. Trends in biotechnological production of fuel ethanol from different feedstocks. Bioresour Technol 2008;99:5270–95.
[30] Gupta A, Verma JP. Sustainable bio-ethanol production from agro-residues: areview. Renew Sust Energ Rev 2014;2015:550–67.
[31] Silverstein R. A Comparison of chemical pretreatment methods for converting cotton stalks to ethanol. North Carolina State University; 2004.
[32] Refaat AA. 5.13 – Biofuels from waste materials. In: Sayigh A, editor. Comprehensive renewable energy. Oxford: Elsevier; 2012. p. 217–61.
[33] Sun Y, Cheng J. Hydrolysis of lignocellulosic material for ethanol production: a review. Bioresour. Technol 2002;98:673–86.
[34] Prasad S, Singh A, Joshi H. Ethanol as an alternative fuel from agricultural, industrial and urban residues. Resour Conserv Recycl 2007:50.
[35] Sarkar N, Ghosh S, Bannerjee S, Aikat K. Bioethanol production from agricultural wastes: an overview. Renew Energy 2012;37:19–27.
[36] Sanchez C. Lignocellulosic residues: biodegradation and bioconversion by fungi. Biotechnol Adv. 2009;27:185–94.
[37] Deswal D, Gupta R, Nandal P, Kuhad RC. Fungal pretreatment improves amenability of lignocellulosic material for its saccharification to sugars.

Carbohyd Polym 2013;99:264–9.
[38] Millati R, Mustikaningrum G, Yuliana A, Cahyanto MN, Niklasson C, Taherzadeh MJ. 2nd Generation ethanol by zygomycetes fungi at elevated temperature. In: Proceedings of the International Conference on alternative energy in developing countries and emerging economies (2013 AEDCEE). Bangkok, Thailand, 2013. p. 104–109.
[39] Singh P, Suman A, Tiwari P. Biological pretreatment of sugarcane trash for its conversion to fermentable sugars. World J Microb Biot. 2008;24:667–73.
[40] Wan C, Li Y. Microbial pretreatment of corn stover with *Ceriporiopsis subvermispora* for enzymatic hydrolysis and ethanol production. Bioresource Technol 2010;101:6398–403.
[41] Wan C, Li Y. Microbial delignification of corn stover by *Ceriporiopsis subvermispora* for improving cellulose digestibility. Enzyme Microb Tech 2010;47:31–6.
[42] Yang X, Ma F, Zeng Y. Structure alteration of lignin in corn stover degraded by white-rot fungus Irpex lacteus CD2. Int Biodeter Biodegr 2010;64:119–23.
[43] Yang X, Zeng Y, Ma F. Effect of biopretreatment on thermogravimetric and chemical characteristics of corn stover by different white-rot fungi. Bioresour Technol 2010;101:5475–9.
[44] Li L, Li X-Z, Tang W-Z. Screening of a fungus capable of powerful and selective delignification on wheat straw. Lett Appl Microbiol 2008;47:415–20.
[45] Yu H, Guo G, Zhang X, Yan K, Xu C. The effect of biological pretreatment with the selective white-rot fungus Echinodontium taxodii on enzymatic hydrolysis of softwoods and hardwoods. Bioresource Technol 2009;100:5170–5.
[46] Bak J, Ko J, Choi I-G. Fungal pretreatment of lignocellulose by Phanerochaete chrysosporium to produce ethanol from rice straw. Biotechnol Bioeng 2009;104:471–82.
[47] Kuhar S, Nair L, Kuhad R. Pretreatment of lignocellulosic material with fungi capable of higher lignin degradation and lower carbohydrate degradation improves substrate acid hydrolysis and eventual conversion to ethanol. Can J Microbiol 2008;54:305–13.
[48] Shi J, Chinn M, Sharma-Shivappa R. Microbial pretreatment of cotton stalks by solid state cultivation of Phanerochaete chrysosporium. Bioresource Technol 2009;99:6556–64.
[49] Lu C, Wang H, Luo Y, Guo L. An efficient system for pre-delignification of gramineous biofuel feedstock in vitro: application of a laccase from Pycnoporus sanguineus H275. Process Biochem 2010;45:1141–7.
[50] Yu J, Zhang J, He J. Combination of mild physical or chemical pretreatment with biological pretreatment for enzymatic hydrolysis of rice hull. Bioresour Technol 2008;100:903–8.
[51] Dias AA, Freitas GS, Marques GSM, Sampaio A, Fraga IS, Rodrigues MAM. Enzymatic saccharification of biologically pre treated wheat straw with white rot fungi. Bioresour Technol 2010:101.
[52] Taniguchi M, Suzuki H, Watanable D, Sakai K, Hoshino K, Tanaka T. Evaluation of pretreatment with *Pleurotus ostreatus* for enzymatic hydrolysis of rice straw. J Biosci Bioeng 2005;100:637–43.
[53] Zhang X, Yu H, Huang H, Liu Y. Evaluation of biological pretreatment with white rot fungi for the enzymatic hydrolysis of bamboo culms. Int Biodeter Biodegr 2007;60:159–64.
[54] Sims REH, Mabee W, Saddler JN, Taylor M. An overview of second generation biofuel technologies. Bioresource Technol 2009;101:1570–80.
[55] Balat M, Balat H, Oz C. Progress in bioethanol processing. Prog Energy Combust. 2008;34:551–73.
[56] Iranmahboob J, Nadim F, Monemi S. Optimizing acid-hydrolysis: A critical step for production of ethanol from mixed wood chips. Biomass Bioenerg 2002;22:401–4.
[57] Laureano-Perez L, Teymouri F, Alizadeh H, Dale B. Understanding factors that limit enzymatic hydrolysis of biomass: Characterization of pretreated corn stover. Appl Biochem Biotech 2005;124:1081–99.
[58] Sun Y, Cheng J. Dilute acid pretreatment of rye straw and bermudagrass for ethanol production. Bioresour Technol 2005;96:1599–606.
[59] Guo G, Chen W, Chen W, Men L, Hwang W. Characterization of dilute acid pretreatment of silvergrass for ethanol production. Bioresour Technol 2008:99.
[60] HB Aditiya, KP Sing, M Hanif, TMI. Mahlia effect of acid pretreatment on enzymatic hydrolysis in bioethanol production from rice straw, 2015.
[61] Aditiya HB, Chong WT, Ghazali KA, Mahlia TMI. Acid pre treatment of durian seed to improve glucose yield as second generation bioethanol. REEGETECH Proceeding. Bandung, Indonesia, 2014. p. 100–105.
[62] Toquero C, Bolado S. Effect of four pretreatments on enzymatic hydrolysis and ethanol fermentation of wheat straw. Influence of inhibitors and washing. Bioresour Technol 2014;157:68–76.
[63] Eliana C, Jorge R, Juan P, Luis R. Effects of the pretreatment method on enzymatic hydrolysis and ethanol fermentability of the cellulosic fraction from elephant grass. Fuel 2014;118:41–7.
[64] Cheng Y-S, Zheng Y, Yu C. Evaluation of high solids alkaline pretreatment of rice straw. Appl Biochem Biotechnol 2010;162:1768–84.
[65] Xu J, Cheng J, Shama-Shivappa R, Burns J. Lime pretreatment of switchgrass at mild temperatures for ethanol production. Bioresour Technol 2010;101:2900–3.
[66] Saha BC, Cotta MA. Lime pretreatment, enzymatic saccharification and fermentation of rice hulls to ethanol. Biomass Bioenergy 2008;32:971–7.
[67] Sierra R, Granda C, Holtzapple M. Short term lime pretreatment of poplar wood. Biotechnol Prog 2009;25:323–32.
[68] Kim T, Taylor F, Hicks K. Bioethanol production from barley hull using SAA (soaking in aqueous ammonia) pretreatment. Bioresour Technol 2008;99:5694–702.
[69] Kang KE, Jeong GT, Park DH. Pretreatment of rapeseed straw by sodium hydroxide. Bioprocess Biosyst Eng 2012;35:705–13.
[70] Shen G, Tao H, Zhao M. Effect of hydrogen peroxide pretreatment on the enzymatic hydrolysis of cellulose. J Food Process Eng 2011:34.
[71] Gupta R, Lee Y. Pretreatment of corn stover and hybrid poplar by sodium hydroxide and hydrogen peroxide. Biotechnol Prog 2010;26:1180–6.
[72] Zhao XB, Wang L, Liu DH. Effect of several factors on peracetic acid pretreatment of sugarcane bagasse for enzymatic hydrolysis. J Chem Technol Biot 2007;82:1115–21.
[73] García-Cubero M, González-Benito G, Indacoechea I. Effect of ozonolysis pretreatment on enzymatic digestibility of wheat and rye st. Bioresour Technol 2009;100:1608–13.
[74] Zhao X, Cheng K, Liu D. Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis. Appl Microbiol Biot 2009;82:815–27.
[75] Li H, Kim N-J, Jiang M. Simultaneous saccharification and fermentation of lignocellulosic residues pretreated with phosphoric acid–acetone for bioethanol production. Bioresour Technol 2009;100:3245–51.
[76] Swatloski R, Spear S, Holbrey J, Rogers R. Dissolution of cellulose with ionic liquids. J Am Chem Soc 2002;124:4974–5.
[77] Vitz J, Erdmenger T, Haensch C, Schubert U. Extended dissolution studies of cellulose in imidazolium based ionic liquids. Green Chem 2009;11:417–24.
[78] Li C, Knierim B, Manisseri C. Comparison of dilute acid and ionic liquid pretreatment of switchgrass: biomass recalcitrance, delignification and enzymatic saccharification. Bioresource Technol 2010;101:4900–6.
[79] da Silva A, Inoue H, Endo T, Yano S, Bon E. Milling pretreatment of sugarcane bagasse and straw for enzymatic hydrolysis and ethanol fermentation. Bioresour Technol 2010;101:7402–9.
[80] Talebnia F, Karakashev D, Angelidaki I. Production of bioethanol from wheat straw: an overview on pretreatment, hydrolysis and fermentation. Bioresour Technol 2010;101:4744–53.
[81] Qi B, Aldrich C, Lorenzen L, Wolfaardt G. Acidogenic fermentation of lignocellulosic substrate with activated sludge. Chem Eng Commun 2005;192:1221–42.
[82] Zeng M, Mosier N, Huang C-P, et al. Microscopic examination of changes of plant cell structure in corn stover due to hot water pretreatment and enzymatic hydrolysis. Biotechnol Bioeng 2007;97:265–78.
[83] Hendriks A, Zeeman G. Pretreatments to enhance the digestibility of lignocellulosic biomass. Bioresour Technol 2009;100:10–8.
[84] Aden A, Ruth M, Ibsen K. Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover.USA: National Renewable Energy Laboratory; 2002.
[85] Zhan X, Wang D, Bean S, et al. Ethanol production from supercritical fluid extrusion cooked sorghum. Ind Crop Prod 2006;23:304–10.
[86] Karunanithy C, Muthukumarappan K. Influence of extruder temperature and screw speed on pretreatment of corn stover while varying enzymes and their ratios. Appl Biochem Biotech 2010;162:264–79.
[87] Lee SH, Teramoto Y, Endo T. Enzymatic saccharification of woody biomass micro/nanofibrillated by continuous extrusion process I – effect of additives with cellulose affinity. Bioresour Technol 2009;100:275–9.
[88] Ma H, Liu W-W, Chen X, et al. Enhanced enzymatic saccharification of rice straw by microwave pretreatment. Bioresour Technol 2009;100:1279–84.
[89] Thangavelu SK, Ahmed AS, Ani FN. Bioethanol production from sago pith waste using microwave hydrothermal hydrolysis accelerated by carbon dioxide. Appl Energ 2014;128:277–83.
[90] Alvira P, Tomas Pejo E, Ballesteros M, Negro M. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: a review. Bioresource Technol 2010;101:4851–61.
[91] Neves M, Kimura T, Shimizu N, Nakajima M. State of the art and future trends of bioethanol production, dynamic biochemistry, process biotechnology and molecular biology. Global Science Books; 2007. p. 1–13.
[92] Hamelinck C, Hooijdonk G, Faaij A. Ethanol from lignocellulosic biomass: techno economic performance in short, middle and long term. Biomass Bioenerg 2005;28:384–410.
[93] Avellar B, Glasser W. Steam-assisted biomass fractionation. I. Process considerations and economic evaluation. Biomass Bioenerg 1998;14:205–18.
[94] Garcia-Aparicio M, Ballesteros I, Gónzalez A. Effect of inhibitors released during steam-explosion pretreatment of barley straw on enzymatic hydrolysis. Appl Biochem Biotech 2006;129:278–88.
[95] Chundawat S, Vismeh R, Sharma L. Multifaceted characterization of cell wall decomposition products formed during ammonia fiber expansion (AFEX) and dilute acid based pretreatments. Bioresource Technol 2010;101:8429–38.
[96] Yoon H, Wu Z, Lee Y. Ammonia-recycled percolation process for pretreatment of biomass feedstock. Appl Biochem Biotech 1995;51–52:5–19.
[97] Kim JS, Kim H, Lee JS. Pretreatment characteristics of waste oak wood by ammonia percolation. Appl Biochem Biotech 2008;148:15–22.
[98] Kim JS, Lee YY, Park SC. Pretreatment of wastepaper and pulp mill sludge by aqueous ammonia and hydrogen peroxide. Appl Biochem Biotech 2000;84–86:129–39.
[99] Banerjee S, Sen R, Pandey R. Evaluation of wet air oxidation as a pretreatment strategy for bioethanol production from rice husk and process optimization. Biomass Bioenerg 2009;33:1680–6.
[100] Martín C, Thomsen M, Hauggaard H, Thomsem A. Wet oxidation pretreatment, enzymatic hydrolysis and simultaneous saccharification and fermentation of clover–ryegrass mixtures. Bioresour Technol 2008;99:8777–82.
[101] Zheng Y, Lin H-M, Tsao G. Pretreatment for cellulose hydrolysis by carbon

dioxide explosion. Biotechnol Prog 1998;14:890–6.
[102] Mosier N, Ladisch C, Ladisch M. Characterization of acid catalytic domains for cellulose hydrolysis and glucose degradation. Biotechnol Bioeng 2002;79:610–8.
[103] Ferreira S, Durate A, Ribeiro M, Queiroz J, Domingues F. Response surface optimization of enzymatic hydrolysis of *Cistus ladanifer* and *Cytisus striatus* for bioethanol production. Biochem Eng J 2009;45:192–200.
[104] Yang B, Dai Z, Ding S-Y, Wyman CE. Enzymatic hydrolysis of cellulosic biomass. Biofuels 2011;2:421–50.
[105] MetaCyc. MetaCyc Reaction: 3.2.1.4. 2014.
[106] MetaCyc. MetaCyc Reaction: 3.2.1.91. 2014.
[107] Kaiser B, Janeen R, Johnson T. Biofuels as a sustainable energy source: an update of the applications of proteomics in bioenergy crops and algae. J Proteomics 2013;93:234–44.
[108] Herrera S. Bonkers about biofuels. Nat Biotechnol 2006;24:755–60.
[109] RE Quiroz Castañeda, JL. Folch Mallol Hydrolysis of biomass mediated by cellulases for the production of sugars. 2013.
[110] Brenda. Reaction catalyzed by beta-glucosidase (3.2.1.21), Sulfolobus solfataricus beta-glycosidase (3.2.1.B26), Pyrococcus furiosus beta-glycosidase (3.2.1.B28), glucan 1,4-beta-glucosidase (3.2.1.74), lactase (3.2.1.108). 2015.
[111] Sixta H. Handbook of pulp.Weinheim, Germany: Wiley-VCH Verlag Gmbh & Co. Kgaa,; 2006.
[112] MetaCyc. MetaCyc Reaction: 3.2.1.8. 2014.
[113] MetaCyc. MetaCyc Reaction: 3.2.1.37. 2014.
[114] Biely P. Xylanolytic enzymes. In: Whitaker JR, Voragen A, Wong D, editors. Handbook of Food enzymology. NY: Marcel Dekker Inc.; 2003. p. 879–916.
[115] Wyman C, Dale B, Elander R, Holtzapple M, Ladisch M, Lee Y. Coordinated development of leading biomass pretreatment technologies. Bioresour Technol 2005;96:1959–66.
[116] Yang B, Wyman C. BSA treatment to enhance enzymatic hydrolysis of cellulose in lignin containing substrates. Biotechnol Bioeng 2006;94:611–7.
[117] Kawamoto H, Nakatsubo F, Murakami K. Protein-adsorbing capacities of lignin samples. Mokuzai Gakkaishi 1992;38:81–4.
[118] Lu Y, Yang B, Gregg D, Saddler J, Mansfield S. Cellulase adsorption and an evaluation of enzyme recycle during hydrolysis of steam-exploded softwood residues. Appl Biochem Biotech 2002;98:641–54.
[119] Jeoh T, Ishizawa C, Davis M, Himmel M, Adney W, Johnson D. Cellulase digestibility of pretreated biomass is limited by cellulose accessibility. Biotechnol Bioeng. 2007;98:112–22.
[120] Yuldashev B, Rabinovich M, Rakhimov M. Comparative study of cellulase behavior on the cellulose and lignocellulose surface during enzymic hydrolysis. Prikl Biokhim Mikrobiol 1993:29.
[121] Ximenes E, Kim Y, Mosier N, Dien B, Ladisch M. Deactivation of cellulases by phenols. Enzyme Microb Tech 2011;48:54–60.
[122] Xiao Z, Zhang X, Gregg David J, Saddler John N. Effects of sugar inhibition on cellulases and b-glucosidase during enzymatic hydrolysis of softwood substrates. Appl Biochem Biotech 2004;113–116:1115–26.
[123] Horváthová V, Janeèek S, Sturdík E. Amylolytic enzymes: their specicities, origins and properties. Biologia 2000;6:605–15.
[124] Maarel MJECvd, Veen Bvd, Uitdehaag JCM, Leemhuis H, Dijkhuizen L. Properties and applications of starch converting enzymes of the α-amylase family. J Biotechnol 2001;94:137–55.
[125] LHS. Guimarães Carbohydrates from biomass: sources and transformation by microbial enzymes. Carbohydrates comprehensive studies on glycobiology and glycotechnology, 2012.
[126] MetaCyc. MetaCyc Reaction: 3.2.1.1. 2014.
[127] Kennedy J, Cabral J, Sá-Correira I, White C. Starch biomass: a chemical feedstock for enzyme and fermentation processes. In: Galliard T, editor. Starch: properties and potential. New York: John Wiley & Sons; 1987.
[128] MetaCyc. MetaCyc Reaction: 3.2.1.20. 2015.
[129] Brenda. Reaction catalyzed by glucan 1,4-alpha-glucosidase (3.2.1.3). 2015.
[130] Brenda. Reaction catalyzed by glucan 1,4-alpha-glucosidase (3.2.1.3), cyclomaltodextrinase (3.2.1.54). 2015.
[131] Brenda. Reaction catalyzed by glucan 1,4-alpha-glucosidase (3.2.1.3), sucrose alpha-glucosidase (3.2.1.48). 2015.
[132] Pandey A, Nigam P, Soccol CR, Soccol VY, Singh D, Mohan R. Advances in microbial amylases. Biotechnol Appl Biochem 2000;31:135–52.
[133] Demirbas A. Ethanol from cellulosic biomass resources. J Green Ener 2004;1:79–87.
[134] Hettenhaus J. Ethanol fermentation strains: present and future requirements for biomass to ethanol commercialization. United States Department Of Energy And National Renewable Energy Laboratory; 1998.
[135] Aminifarshidmehr N. The management of chronic suppurative otitis media with acid media solution. Am J Otol 1996;17:24–5.
[136] Mohagheghi A, Evans K, Chou Y, Zhang M. Cofermentation of glucose, xylose, and arabinose by genomic DNA–integrated xylose/arabinose fermenting strain of zymomonas mobilis AX101. Appl Biochem Biotech 2002;98–100:885–98.
[137] Hahn-hägerdal B, Karhumaa K, Fonseca C, Spencer-martins I, Gorwa-grauslund MF. Towards industrial pentose-fermenting yeast strains. Appl Microbiol Biot 2007;74:937–53.
[138] Buaban B, Inoue H, Yano S, Tanapongpipat S, Ruanglek V, Champreda V, et al. Bioethanol production from ball milled bagasse using an on-site produced fungal enzyme cocktail and xylose-fermenting Pichia stipitis. J Biosci Bioeng 2010;110:18–25.
[139] Abbi M, Kuhad R, Singh A. Fermentation of xylose and rice straw hydrolysate to ethanol by *Candida shehatae* NCL-3501. J Ind Microbiol Biotechnol 1996;17:20–3.
[140] Davis L, Jeon Y-J, Svenson C, Rogers P, Pearce J, Peiris P. Evaluation of wheat stillage for ethanol production by recombinant Zymomonas mobilis. Biomass Bioenerg 2005;29:49–59.
[141] Deng Y, Olson DG, Zhou J, Herring CD, Joe Shaw A, Lynd LR. Redirecting carbon flux through exogenous pyruvate kinase to achieve high ethanol yields in Clostridium thermocellum. Metab Eng 2013;15:151–8.
[142] Georgieva TI, Mikkelsen MJ, Ahring BK. Ethanol production from wet-exploded wheat straw hydrolysate by thermophilic anaerobic bacterium Thermoanaerobacter BG1L1 in a continuous immobilized reactor. Appl Biochem Biotechnol 2008;145:99–110.
[143] Kuyper M, Toirkens MJ, Diderich JA, Winkler AA, van Dijken JP, Pronk JT. Evolutionary engineering of mixed-sugar utilization by a xylose-fermenting Saccharomyces cerevisiae strain. FEMS Yeast Res 2005;5:925–34.
[144] Lawford H, Rousseau J. Performance testing of zymomonas mobilis metabolically engineered for cofermentation of glucose, xylose, and arabinose. In: Finkelstein M, McMillan J, Davison B, editors. Biotechnology for fuels and chemicals. Humana Press; 2002. p. 429–48.
[145] Nichols NN, Hector RE, Saha BC, Frazer SE, Kennedy GJ. Biological abatement of inhibitors in rice hull hydrolyzate and fermentation to ethanol using conventional and engineered microbes. Biomass Bioenerg 2014;67:79–88.
[146] Nigam JN. Ethanol production from wheat straw hemicellulose hydrolysate by Pichia stipitis. J Biotechnol 2001;2001:17–27.
[147] Qureshi N, Dien BS, Nichols NN, Saha BC, Cotta MA. Genetically engineered Escherichia coli for ethanol production from xylose: substrate and product inhibition and kinetic parameters. Food Bioprod Process 2006;84:114–22.
[148] Shaw AJ, Podkaminer KK, Desai SG, Bardsley JS, Rogers SR, Thorne PG et al. Metabolic engineering of a thermophilic bacterium to produce ethanol at high yield. 2008. p. 13769–13774.
[149] Takahashi C, Lima K, Takahashi D, Alterthum F. Fermentation of sugar cane bagasse hemicellulosic hydrolysate and sugar mixtures to ethanol by recombinant Escherichia coli KO11. World J Microb Biot 2000:16.
[150] Xin Qing Z, Qian L, Lei Yu H, Fan L, Wen Wen Q, Feng Wu B. Exploration of a natural reservoir of flocculating genes from various Saccharomyces cerevisiae strains and improved ethanol fermentation using stable genetically engineered flocculating yeast strains. Process Biochem 2011:1612–9.
[151] Tripathi SA, Olson DG, Argyros DA, Miller BB, Barrett TF, Murphy DM. Development of pyrF-based genetic system for targeted gene deletion in Clostridium thermocellum and creation of a pta mutant. Appl Environ Microbiol 2010;76:6591–9.
[152] Dien B, Cotta M, Jeffries T. Bacteria engineered for fuel ethanol production: current status. Appl Microbiol Biotechnol 2003;63:258–66.
[153] Chandel A, Es C, Rudravaram R, Narasu M, Rao L, Ravindra P. Economics and environmental impact of bioethanol production technologies: an appraisal. Biotechnol Molec Biol Rev 2007;2:14–32.
[154] Srimachai T, Thonglimp V, O-Thong S. Ethanol and methane production from oil palm frond by two stage SSF. In: Proceedings of the international conference on alternative energy in developing countries and emerging economies, 2014.
[155] Huang L, Jin B, Lant P, Zhou J. Simultaneous saccharification and fermentation of potato starch wastewater to lactic acid by *Rhizopus oryzae* and *Rhizopus arrhizus*. Biochem Eng J 2005;23:265–76.
[156] Kleerebezem R, van Loosdrecht MCM. Mixed culture biotechnology for bioenergy production. Curr Opin Biotech 2007;18:207–12.
[157] Thanakoses P, Black A, Holtzapple M. Fermentation of corn stover to carboxylic acids. Biotechnol Bioeng 2003;83:191–200.
[158] Chan W, Holtzapple M. Conversion of municipal solid wastes to carboxylic acids by thermophilic fermentation. Appl Biochem Biotech 2003;111:93–112.
[159] Fu Z, Holtzapple M. Anaerobic mixed culture fermentation of aqueous ammonia-treated sugarcane bagasse in consolidated bioprocessing. Biotechnol Bioeng 2010;106:216–27.
[160] van Zyl W, Lynd L, Den Haan R, McBride J. Consolidated bioprocessing for bioethanol production using Saccharomyces cerevisiae. Adv Biochem Eng Biot 2007;108:205–35.
[161] Carere C, Sparling R, Cicek N, Levin D. Third generation biofuels via direct cellulose fermentation. Int J Mol Sci 2008;9:1342–60.
[162] Parisutham V D, Kim TH, Lee SK. Feasibilities of consolidated bioprocessing microbes: from pretreatment to biofuel production. Bioresour Technol 2014;161:431–40.
[163] Xu Q, Singh A, Himmel M. Perspectives and new directions for the production of bioethanol using consolidated bioprocessing of lignocellulose. Curr Opin Biotech 2009;20:364–71.
[164] Amore A, Faraco V. Potential of fungi as category I consolidated bioprocessing organisms for cellulosic ethanol production. Renew Sust Energ Rev 2012;16:3286–301.
[165] la Grange D, den Haan R, van Zyl W. Engineering cellulolytic ability into bioprocessing organisms. Appl Microbiol Biot 2010;87:1195–208.
[166] Elkins JG, Raman B, Keller M. Engineered microbial systems for enhanced conversion of lignocellulosic biomass. Curr Opin Biotech 2010;21:657–62.
[167] Kumar S, Singh N, Prasad R. Anhydrous ethanol: a renewable source of energy. Renew Sust Energ Rev 2010;14:1830–44.
[168] Benson T, George C. Cellulose based adsorbent materials for the dehydration of ethanol using thermal swing adsorption. Adsorption 2005;11:697–701.
[169] Treybal R. Mass-transfer operations. 3rd ed. Singapore: Mcgraw-Hill Book Co.; 1980.

[170] Gomis V, Pedraza R, Frances O, Font A, Asensi J. Dehydration of ethanol using azeotropic distillation with isooctane. Ind Eng Chem Res 2007;46:4572–6.
[171] Black C. Distillation modeling of ethanol recovery and dehydration processes for ethanol and gasohol. Chem Eng Prog 1980;76:78–85.
[172] Gomis V, Font A, Pedraza R, Saquete M. Isobaric vapour liquid and vapour liquid liquid equilibrium data for the system water+ethanol+cyclohexane. Fluid Phase Equilib 2005;235:7–10.
[173] Gomis V, Font A, Saquete M. Isobaric vapour liquid and vapour liquid liquid equilibrium data for the system water+ethanol+n-heptane at 101.3 kPa. Fluid Phase Equilib 2006;248:206–10.
[174] Al Amer AM. Investigating polymeric entrainers for azeotropic distillation of the ethanol/water and MTBE/methanol systems. Ind Eng Chem Res 2000;39:3901–6.
[175] Fullarton D, Schlunder E. Diffusion distillation a new separation process for azeotropic mixtures Part I selectivity and transfer efficiency. Chem Eng Process 1986;20:255–63.
[176] Chung I, Song K, Hong W, Chang H. Ethanol dehydration by evaporation and diffusion in an inert gas layer. Hwahak Konghak 1994;32:734–41.
[177] Kim S, Lee D, Hong W. Modeling of ethanol dehydration by diffusion distillation in consideration of the sensible heat transfer. Korean J Chem Eng 1996;13:275–81.
[178] McDowell J, Davis J. A characterization of diffusion distillation for azeotropic separation. Ind Eng Chem Res 1988;27:2139–48.
[179] Singh N, Prasad R. Fuel grade ethanol by diffusion distillation: an experimental study. J Chem Technol Biot 2011;86:724–30.
[180] Taylor R, Krishna R. Multicomponent mass transfer.New York: Johnwiley & Sons, Inc.; 1993.
[181] Shenfeng Y, Cancan Z, Hong Y, Zhirong C, Wendong Y. Study on the separation of binary azeotropicmixtures by continuous extractive distillation. Chem Eng Res Des 2014;93:113–9.
[182] Gryta M. Effectiveness of water desalination by membrane distillation process. Membranes 2012;2:415–29.
[183] Ravagnani MASS, Reis MHM, Filho RM, Wolf-Maciel MR. Anhydrous ethanol production by extractive distillation: a solvent case study. Process Saf Environ 2009;88:67–73.
[184] Gil ID, Botia DC, Ortiz P, Sanchez OF. Extractive distillation of acetone/methanol mixture using water as entrainer. Ind Eng Chem Res 2009;48:4858–65.
[185] Lladosa E, Monton JB, Burguet MC, Munoz R. Phaseequilibria involved in extractive distillation of dipropylether+1-propyl alcohol using 2-ethoxyethanol as entrainer. Fluid Phase Equilibr 2007;255:62–9.
[186] Cheng NL. Solvent handbook.Beijing: Chem Ind Press; 2008.
[187] Vogel AI, Tatchell AR, Furnis BS, Hannaford AJ, Smith PWG. Vogel's textbook of practical organic chemistry. 5th ed.Longman Group UK Limited; 1989.
[188] Wolf Maciel M, Brito R. Evaluation of the dynamic behaviour of an extractive column for dehydration of aqueous ethanol mixtures. Comput Chem Eng 1995;19:405–8.
[189] Letha PM, Gregersen M. Ethylene-glycol poisoning. Forensic Sci Int 2005;155:179–84.
[190] Ligero EL, Ravagnani TMK. Dehydration of ethanol with salt extractive distillation a comparative analysis between processes with salt recovery. Chem Eng Process 2003;42:543–52.
[191] Barba D, Brandani V, Di Giacomo G. Hyperazeotropic ethanol salted out by extractive distillation: theoretical evaluation and experimental check. Chem Eng Sci 1985;40:2287–92.
[192] Gil ID, Uyazán AM, Aguilar JL, Rodriguez G, Caicedo LA. Separation of ethanol and water by extractive distillation with salt and solvent as entrainer: process simulation. Braz J Chem Eng 2008;25:207–15.
[193] Soares RB, Pessoa FLP, Mendes MF. Dehydration of ethanol with different salts in apacked distillation column. Process Saf Environ 2014;2015:147–53.
[194] Lei Z, Wang H, Zhoub R, Duan Z. Influence of salt added to solvent on extractive distillation. Chem Eng J 2002;87:149.
[195] Wang P, Chung T-S. Recent advances in membrane distillation processes: Membrane development, configuration design and application exploring. J Membr Sci 2015;474:39–56.
[196] Lewandowicz G, Białas W, Marczewski B, Szymanowska D. Application of membrane distillation for ethanol recovery during fuel ethanol production. J Membr Sci 2011;375:212–9.
[197] Korikov AP, Kosaraju PB, Sirkar KK. Interfacially polymerized hydrophilic microporous thin film composite membranes on porous polypropylene hollow fibers and flat films. J Membr Sci 2006;279:588–600.
[198] Hatti-Kaul R. Downstream processing in industrial biotechnology. In: Soetaert W, Vandamme EJ, editors. Industrial biotechnology, sustainable growth and economic success. WILEY-VCH Verlag; 2010. p. 279–323.
[199] Khayet M. Membrane distillation. In: Li NN, Fane AG, Ho WSW, Matsuura T, editors. Advanced membrane technology and applications. John Wiley & Sons; 2008. p. 297–371.
[200] Izquierdo-Gil MA, Jonsson G. Factors affecting flux and ethanol separation performance in vacuum membrane distillation (VMD). J Membrane Sci 2003;214:113–30.
[201] de Wit M, Junginger M, Lensink S, Londo M, Faaij A. Competition between biofuels: modelling technological learning and cost reductions over time. Biomass Bioenerg 2010;34:218–26.
[202] IEA. Energy technology perspectives. Paris2008.
[203] Quintero JA, Moncada J, Cardona CA. Techno economic analysis of bioethanol production from lignocellulosic residues in Colombia: a process simulation approach. Bioresource Technol 2013;139:300–7.
[204] Tye YY, Lee KT, Wan Abdullah WN, Leh CP. Second-generation bioethanol as a sustainable energy source in Malaysia transportation sector: Status, potential and future prospects. Renew Sustain Energy Rev 2011;15:4521–36.
[205] Larson E. Biofuel production technologies: status, prospects and implications for trade and development.New York and Geneva: United States Department of Energy; 2008.
[206] Limayem A, Ricke SC. Lignocellulosic biomass for bioethanol production: current perspectives, potential issues and future prospects. Prog Energy Combus Sci 2012;38:449–67.
[207] Goh CS, Tan KT, Lee KT, Bhatia S. Bio-ethanol from lignocellulose: status, perspectives and challenges in Malaysia. Bioresour Technol 2010;101:4834–41.
[208] Saini J, Saini R, Tewari L. Lignocellulosic agriculture wastes as biomass feedstocks for second-generation bioethanol production: concepts and recent developments. 3 Biotech. 2014:1–17.
[209] Plantation SD. Palm oil facts & figures. Malaysia2014.
[210] Aditiya HB, Chong WT, Mahlia TMI, Sebayang AH, Berawi MA, Nur H. Second generation bioethanol potential from selected Malaysia's biodiversity biomasses: a review. Waste Manag 2016;47(Part A):46–61.
[211] Balat M. Production of bioethanol from lignocellulosic materials via the biochemical pathway: a review. Energy Convers Manag 2011;52:858–75.
[212] Tan KT, Lee KT, Mohamed AR. Role of energy policy in renewable energy accomplishment: The case of second-generation bioethanol. Energy Policy 2008;36:3360–5.
[213] Poh KM, Kong HW. Renewable energy in Malaysia: a policy analysis. Energy Sustain Dev 2002;6:31–9.