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Technological perspectives for utilisation of waste glycerol for the production of biofuels: A review

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ABSTRACT

The depletion of fossil fuel reserves and the ever-increasing demand for energy due to growing industries, rapid population growth, and increasing concerns about environmental pollution have led to the exploration of green and alternative fuels. Bioethanol is one of the most promising biofuels and a key factor in shifting the transportation sector's dependence from petroleum-based sources to renewable and sustainable energy sources. This review highlights the development of bioethanol from first to third-generation. First-generation sources include food crops, second-generation sources include feedstocks from agricultural residues, municipal waste or forestry waste, and third-generation sources include algal biomass to produce bioethanol for commercial scale in world are emphasised. Various methods such as pre-treatment, hydrolysis by acid and enzymes, fermentation to produce bioethanol, and distillation a separation processes to obtain anhydrous ethanol are described. Current advances in using biodiesel industrial by-product crude glycerol waste as the best alternative, renewable and sustainable source for ethanol production in the circular economy are also presented. The significant role of crude glycerol in various applications and the conversion of glycerol to ethanol are focused. In addition, the challenges and opportunities for future work are highlighted. The potential application of bioethanol as a biofuel to reduce environmental impact for a clean and sustainable future is described.

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1. Introduction

Global warming is one of the most significant issues worldwide, leading to massive climate change with the rise of sea level due to the unprecedented level of melting glaciers. The increase of the average global temperature from 1 °C–1.5 °C is forecasted through the Intergovernmental Panel on Climate Change (IPCC) (Albert, 2020). The increase in the global temperature is due to the rapid accumulation of greenhouse gases (GHGs), such as carbon dioxide (CO_2) produced by humans, and the transportation sector contributes to about 14% GHG emissions. The rise in environmental pollution and energy scarcity is a significant problem worldwide. Hence the development of renewable energy sources is required (Razmjoo et al., 2021). Renewable forms of energy include bioenergy, geothermal, solar, water, and wind. Fossil fuels like coal, oil, and natural gas are non-renewable energy sources that cannot regenerate at sustainable rates. About 50% of fossil fuels are consumed by vehicles. Fossil fuels will become scarce and are expected to be obsolete (Zeppini and van den Bergh, 2020). GHGs are responsible for climate change because of the emissions from fossil fuel combustion. Thus, many alternative fuels have been considered for fossil fuel replacement because energy demands continue to grow day by day. A comprehensive plan must reduce the emission of GHGs in transportation. Biofuels are promising substitutes for fossil fuels, which are utilised to supply energy for transportation systems. Biofuels are sustainable and environmentally friendly energy sources (Bórawski et al., 2019; Ćetković et al., 2021).

Biofuel is one of the alternative fuels produced from organic matter or wastes. Biofuel, particularly bioethanol and biodiesel, have unique properties. The liquid fuel is directly utilised in vehicle engines and distributed through fossil fuel systems, thus encouraging the local economy. Several methods have been developed for biomass conversion into solid, liquid, and gaseous fuels. Liquid fuels from biomass have received wide attention due to easy transportation, storage, and high energy density. Besides, these fuels are used in engines, turbines, and existing boilers (Oumer et al., 2018).

The biofuel industry utilises sources like food crops, biomass, and microorganisms to produce biodiesel and bioethanol (Rajendran et al., 2021). However, there are still challenges to utilise biofuels fully. Therefore, there is a need to identify the immediate and subsequent obstacles to the sustainable development of biofuels. Due to ongoing industrial and economic issues, there is an urgent need to find an efficient and environmentally friendly energy source (Kothari et al., 2020). The availability of natural resources like palm oil, rice husk, and others in various countries (Indonesia, USA, Brazil, Malaysia, Thailand, and China) is used to continuously produce biofuel to meet the world energy demand (Yusoff et al., 2021). The Biodiesel production per day in various countries is shown in Fig. 1. During biodiesel manufacturing, the glycerol waste is formed as the primary product, and the production process of biodiesel from vegetable oil or animal fat is shown in Fig. 2. The crude glycerol is utilised and converted to bioethanol (Chilakamarry et al., 2021b). Bioethanol is an attractive option for a renewable energy source. The advantages of bioethanol include a higher-octane number (i.e., 108), broader flammability limits, higher heat of vaporisation, and higher flame speed. Bioethanol has a more excellent compression

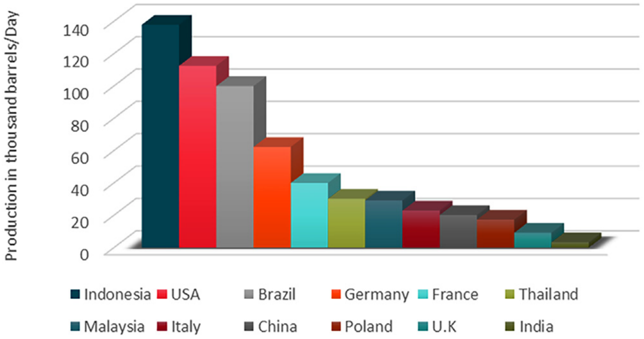

Fig. 1. Production of biodiesel worldwide in 2020 (Per day) (Sönnichsen, 2020).

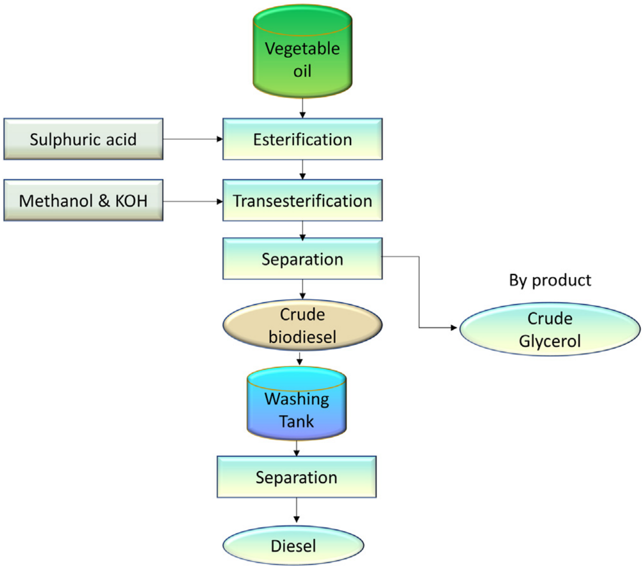

Fig. 2. Flow chart of biodiesel production from vegetable oil.

ratio, a lower burning period, and improved theoretical efficiency than gasoline in an internal combustion engine (ICE) (Barbosa et al., 2021).

Bioethanol utilisation reduces the dependency on crude petroleum, enhances energy security, and diversifies energy sources (Wu et al., 2021). The first-generation bioethanol is derived from the substrate containing sugar and starch, and their sources include sugarcane, sugar beet, corn, wheat, potato, and sorghum. Sugar-based ethanol is produced dominantly in Brazil from sugarcane. Starch-based ethanol is produced from corn significantly in the US, China, Canada, France, Germany and Sweden. Second-generation bioethanol is derived from plant biomass that is abundant and readily available in agricultural residues and forest wastes comprising lignocellulosic materials. The major feedstocks cane bagasse, corn stover, corn cobs, maize stover and wheat straw, are used to produce bioethanol. Third-generation bioethanol is explicitly derived from the algae. The present review focuses on bioethanol advancement by transforming from first-generation sources to third-generation sources. The biodiesel industry waste formed during biodiesel production as the major byproduct is considered feedstock for bioconversion to bioethanol for the circular economy. The significance of glycerol waste in numerous applications is described considering the waste to wealth concept. Various methods like pre-treatment, hydrolysis, strategies of fermentation process with distillation process have been discussed. The review encompasses the bioethanol properties and its potential application as a biofuel to reduce environmental pollution.

2. Bioethanol production from various sources

Various sources for ethanol production are categorised into three generation sources and is depicted in Fig. 3. The bioethanol produced from food crops, non-edible crops and algae biomass is called first, second, and third-generation sources (Chong et al., 2021).

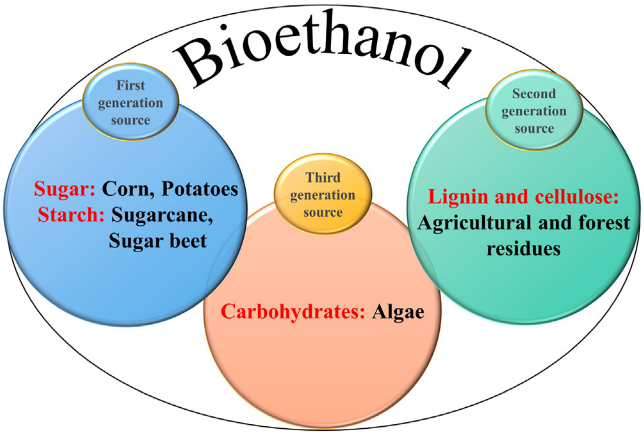

Fig. 3. Sources for bioethanol production.

2.1. First-generation sources

The first-generation sources from food crops contain more significant starch and sugar to produce bioethanol. The feedstocks for bioethanol production include starchy materials, such as barley, cassava, corn, maise, potato, wheat, and sucrose-containing crops like sugar cane, sugar beet, and sweet sorghum (Mohanty and Swain, 2019). Cereals contain high carbohydrates and low protein. The nitrogen content in cereals facilitates the aggregation of starch through protein synthesis. Two common kinds of cereal are barley and wheat. Barley is the most suitable winter crop with high adaptability and can withstand drought conditions.

Meanwhile, wheat grows in temperate regions. Cassava is available in tropical countries that produce bioethanol (Jiao et al., 2019). Sugar cane consists of 12%–17% sugar, with its glucose content of 10% and saccharose content of 90%. About 95% of sugar is extracted from a milling process, allowing bioethanol fermentation to be conducted (Ccopa Rivera et al., 2017). Sugar cane is cultivated in humid and semitropical regions, especially in Brazil and India. Sugar beet is also be utilised to produce bioethanol, which mainly grows in cooler regions, particularly Asia, Europe, and North America. Sweet sorghum has high starch and saccharose content in the stem, and the crop is grown in tropical countries.

First-generation sources convert the sugar/starchy material to ethanol by fermentation using microorganisms. The fermentation of sugars is called the first-generation ethanol process, in which yeast is cultured at 30 °C to convert the sugars to ethanol. The bioethanol production from starch/sugar-containing materials occurs in four steps; pre-treatment (hydrolysis, liquification-saccharification), fermentation, distillation and dehydration. Pre-treatment and dehydration are the two significant steps for the efficiency of ethanol production and total process cost. The main aim is to put the carbohydrate source in the fermentation medium. The sugar/starch materials are easily broken down to form ethanol by yeast. However, using food crops results in water shortage and over-fertilisation, leading to infertile lands and the high cost of crops. The main disadvantage of these crops is staple foods in developing and developed countries, leading to a global increase in food crisis and hunger. Corn and sugarcane cultivation requires costly pesticides and fertilisers that result in soil and water contamination cause environmental hazards. Corn and sugarcane cannot be considered a practical answer to the world's energy needs since both are staple foods in many parts of the world. This led to identify and utilise the feedstock that does not present the food versus fuel conflict for future renewable bioethanol production.

2.2. Second-generation sources

Second-generation biofuels use non-food sources as feedstock. Typically, the second-generation bioethanol is produced from lignocellulosic biomass and industrial wastes. Lignocellulose is a sustainable carbon source available in various plants, and these biomass materials are relatively inexpensive and readily available. The quantity of available lignocellulosic biomass depends on the climate, and it is tough to convert lignocellulose into reducing sugars compared to starch. Various plant biomass is obtained from agriculture wastes, woody wastes, green area wastes from parks and gardens, and forest wastes. Herbaceous harvests and perennial grasses (*Miscanthus sinensis* and *Miscanthus giganteus*) that grow in low fertility lands can be applied as energy crops. Examples of agricultural wastes include cereal straw (stover, rice husk, wheat straw, and corn cob) and bagasse from sugar cane processing (Boboescu et al., 2019). Examples of woody wastes and biomass from forests are the bark, sawdust, softwood trimmings, and hardwood chips, whereas branches, grass, and leaves are wastes from gardens and parks. Industrial wastes consist of spent grains from brewers and distilleries, and municipal solid wastes include food waste, paper kraft, and paper sludge contain lignocellulosic biomass. However, lignocellulosic bioethanol production requires feedstock preparation before fermentation, and cellulose and hemicellulose degradation are required for bioethanol production via sugar fermentation.

2.2.1. Agricultural residues

Agricultural residues consist of lignocellulosic materials: plant biomass containing cellulose, hemicellulose, lignin, and carbohydrate polymers bound to lignin. The residues from agricultural activities are mainly barley straw, corn stover, hazel nutshell, horticulture waste, miscanthus grass, rice straw, rice hull, rape straw, sugar cane tops, sugar cane bagasse, sweet sorghum bagasse, and wheat straw produce bioethanol. Miscanthus grass by NaOH pre-treatment in a bench-scale screw reactor produce bioethanol (Cha et al., 2015). Bioethanol is also produced from corn stover using acetic acid catalysed hydrothermal method (Katsimpouras et al., 2016) and sugar cane tops by alkaline treatment (Raghavi et al., 2016). Sugar cane bagasse was used for bioethanol production by ultrasonic pre-treatment (Methrath Liyakathali et al., 2016). Bioethanol was produced from rape straw using microwave-assisted sulphuric acid pre-treatment (Lu et al., 2011). Soybean straw and hull hydroxylate by subcritical water hydrolysis produce bioethanol (Vedovatto et al., 2021).

2.2.2. Woody biomass

Wood biomass from construction and demolition wastes, industrial hemp, and yellow poplar has been used for bioethanol production. Construction and demolition of wood wastes for bioethanol production include lumber, plywood, particleboard, and medium-density fibreboard. These materials are made into small pieces by cutting, chopping, and air drying, followed by hydrolysis with concentrated acid to form sugar. Bioethanol was obtained from industrial hemp with acid and alkali pre-treatment (Zhao et al., 2020b). Bioethanol produced from yellow poplar using acid hydrolysis and fermentation with *P. stipitis* (Cho et al., 2011), also produced from yellow poplar dust in mild alkali condition under ammonium solution (Kim et al., 2018).

2.2.3. Industrial, herbaceous, and municipal solid wastes

The wastes from the brewery, soft drink, and starch processing industries, wastes from fruit peel, food, and herbaceous crops are used to produce bioethanol. These wastes avoid the need for waste management by conversion into renewable fuels. Potato peel waste as feed stock produces bioethanol using *Wickerhamomyces anomalus* through saccharification and fermentation process by enzymatic hydrolysis. The saccharification is performed through thermal and chemical pre-treatment (Ben Atitallah et al., 2019). Bioethanol production from sweet sorghum waste by *Trichoderma citrinoviride* C1 (Kancelista et al., 2020). Simultaneous saccharification and fermentation (SSF) of pomegranate peel using cellulase and *S. cerevisiae* were optimised to produce bioethanol (Mazaheri et al., 2021). A thermochemical process converted coffee residue waste into bioethanol (Mendoza Martinez et al., 2021). Citrus peel waste by solvent-free microwave extraction has been identified as an effective process to produce bioethanol (Teigiserova et al., 2021). Oil palm trunk sap was used as feedstock with palm oil mill effluent as a nutrient by *S. cerevisiae* for bioethanol conversion (Samsudin and Mat Don, 2015). In the presence of microwave irradiation, soft drink waste water by photolytic and photocatalytic treatment produce ethanol (Remya and Swain, 2019). Bioethanol is produced from sago hampas using *S. cerevisiae*, amylolytic enzymes and cellulolytic enzymes by simultaneous saccharification and fermentation (SSF) (Hung et al., 2018).

Second-generation bioethanol is produced from lignocellulosic biomass. Lignocellulosic materials would minimise the potential conflict between the land use for food and animal feed production and energy feedstock production. Lignocellulosic materials are the most abundant renewable sources cheaper than traditional bioethanol raw materials and are grown in lower input fertilisers, pesticides, and energy. The chemical composition of lignocellulosic components of agriculture residues, weeds and other sources is described in Table 1 (Pandiyan et al., 2019). In the second-generation bioethanol process, pre-treatment is the significant step to obtain carbohydrates from lignocellulosic materials. By the effective pre-treatment method, chemical bonds of lignin, cellulose and hemicellulose structures are broken down to release the polysaccharides by preventing the inhibitor formation. However, second-generation bioethanol sources are best than the first generation. The second-generation bioethanol process has limitations, like forming inhibitors depending on the lignocellulosic structure, while the pre-treatment step causes problems during fermentation. The other limitation includes the use of enzymes to break the cellulose structure to obtain carbohydrates. The enzymes are expensive, and that increases the production cost. Alternative to enzymes, some microorganisms produce extracellular or intracellular cellulolytic secretion to hydrolyse cellulose and use the carbohydrate source to produce ethanol. The microorganism needs special conditions for inoculation, activation, and fermentation.

2.3. Third-generation source

Bioethanol is produced from the third-generation source by cultivating microalgae or single-celled organisms, mainly eukaryotes and prokaryotes. Microalgae use nutrients (carbon, nitrogen, phosphate, and sulphur) from the industrial waste stream as a medium to achieve higher biomass concentration. Effluent gases are produced from industrial power plants, wastewater, and organic waste products from hydrolysis and biogas production. Microalgae biologically segregate CO_2 after the combustion of fossil fuel sources and the gas converted into biofuels, thus decreasing GHGs (Ali et al., 2021). *Chlamydomonas reinhardtii*, *Eucheuma cottonii*, and red seaweed *Gracilaria sp*. were used to produce bioethanol. The production of bioethanol and biodiesel from Artic psychrophilic microalgae *Chlamydomonas* sp. KNMOO29C at low temperature (Kim et al., 2020). The oils from microalgae are a substitute for vegetable oils in producing biodiesel via alkaline transesterification with methanol. By simultaneous saccharification and fermentation (SSF), the red microalgae *Porphyridium cruentum* also produced bioethanol (Kim et al., 2017). Macroalgae cellulosic residue by simultaneous

Table 1
The percentage composition of lignocellulosic biomass.

Lignocellulosic biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)
Wheat straw	33.7	29.9	23.4	4.2
Rice straw	38	25	25	12
Corn cob	39.71	32.85	12.31	–
Sugarcane bagasse	36–39	28.5–31	12.5–13.9	0.8–1.1
Siam weed	41.0	22.3	20.7	2.8
Water hyacinth	18.4	49.2	3.5	–
Crofton weed	37.1	22.4	16.4	4.5
Silver grass	33.3	23.7	24.5	–
Carrot grass/famine weed	30.8	16.4	18.1	8.7
Switch grass	31.9	25.2	18.13	5.95

saccharification and fermentation (SSF) produced 81.5% of bioethanol yield (Chong et al., 2020; Tan and Lee, 2015). Seaweed *Ulva prolifera* by hydrogen peroxide pre-treatment and enzymatic hydrolysis produced bioethanol (Li et al., 2016). First to third-generation sources used for bioethanol production are described in Table 2.

Many researchers argue that algae biofuels could serve as the best alternative to first and second-generation biofuels. Algae can be grown quickly in saline water, fresh water and wastewater from the industries. They have higher photosynthetic efficiency and biomass productivity, a faster growth rate, and the highest carbon dioxide fixation and oxygen production efficiencies. Carbohydrate content is 25%–50% in green algae, 30%–50% in brown algae and 30%–60% in red algae. The macroalgae species like *Ascophyllum*, *Porphyra*, and *Palmaria* have a 70%–76% polysaccharide content. The bioethanol production using macroalgae is based on the fermentation of algal carbohydrates such as starch, sugar and cellulose. Hence algae are the feedstock for bioethanol production. Third-generation bioethanol production is involved in the exploration of microalgae. Alganol Biofuels Inc. developed technology to utilise sunlight trapping microalgal cells as a tiny biorefinery for ethanol production using a photobioreactor and produced 6000 gallon of ethanol per acre per year which is higher than corn-based crops. Algae cell walls consist of polysaccharides with no lignin and low hemicellulose levels that result in greater hydrolysis efficiency and fermentation yields. The algal polysaccharides are easily broken down than woody biomass. Bioethanol can be obtained from algae by saccharification and fermentation and intracellular fermentation of algae. Algae with a high starch are harvested and saccharified using suitable enzymes to convert the complex molecules into fermentable sugars. These sugars undergo fermentation in the fermentator under pH, temperature etc. Algal starch is metabolised into bioethanol, hydrogen, and acetate under dark and anaerobic conditions.

3. Glycerol waste from the biodiesel industry as the primary source for bioethanol production

Various wastes are converted to value-added products by researchers (Chaitanya Reddy et al., 2021; Chilakamarry et al., 2021a). The concept of waste to wealth also focussed on biodiesel industry waste. Crude glycerol is one of the significant sources of biodiesel production as a primary byproduct (Chilakamarry et al., 2021b). The worldwide biodiesel production with the crude glycerol formation is depicted in Fig. 4 (Nomanbhay et al., 2018). Animal fats and vegetable oils produce biodiesel via the transesterification process with glycerol as a byproduct. Glycerol can be converted via fermentation to pyruvate or phosphoenolpyruvate (PEP) with greater bioethanol yield than biomass glucose and xylose fermentation. The chemical composition of crude glycerol varies with catalysts used, recovery efficiency, transesterification reaction, and methanol and catalyst recovery. The composition of 11 types of chemicals in crude glycerol collected from several biodiesel producers in Australia showed 38%–96% glycerol content with over 29% ash and 14% methanol (Sarchami et al., 2016). Methanol and catalysts like sodium methoxide and potassium hydroxide are commonly used for biodiesel production. Catalysts, methanol, organic non-glycerol, salts, soaps, and water impurities are present in crude glycerol. For instance, crude glycerol obtained from biodiesel production using sunflower oil possessed 30%, 50%, 13%, 2%, and 2%–3% of glycerol, methanol, soaps, moisture, and salts, respectively (Yang et al., 2012).

About 10% of crude glycerol is generated from the biodiesel industry during the production, and the surplus of crude glycerol increases the environmental problem by disposal to land in waste form due to inorganic salts and other impurities. Glycerol in its pure form is used as feedstock (chemical, food, drugs, and pharmaceuticals) and in the production of fuel or fuel additives. Glycerol purification boosts its economic and applicable value, making biodiesel production more sustainable. The purification of crude glycerol by ion exchange, vacuum distillation, membrane separation and activated carbon adsorption. Glycerol utilisation is one of the capable options during biodiesel production for conversion into valuable products (Chol et al., 2018). Glycerol is an excellent carbon source for microorganisms that undergoes fermentation in aerobic or anaerobic conditions to convert ethanol (Kumar and Park, 2018). The glycerol as a substrate converts to dihydroxyacetone phosphate (DHP) followed by pyruvate, later to acetyl CoA, then acetaldehyde, and finally to ethanol. The ethanol produced from crude glycerol using microorganisms under aerobic or anaerobic conditions by the fermentation process, like *Escherichia coli* EH05 produced 20.7 g/L of ethanol with a productivity of 0.22 g/L/h (Oh et al., 2012), *Klebsiella pneumoniae* GEM167 resulted in 21.5 g/L ethanol production with the 0.93 g/L/h ethanol productivity (Oh et al., 2011). *Kluyvera cryocrescens* S26 generated 27 g/L ethanol with 0.61 g/L/h productivity (Pradima et al., 2017). By metabolic engineering of *Saccharomyces cerevisiae* is responsible for the efficient conversion of glycerol to ethanol (Khattab and Watanabe, 2021). Bioethanol production from crude glycerol by various microorganisms is described in Table 3.

Table 2
Various sources and fermentation process used to produce ethanol.

Substrate	Microorganism	Process	Ethanol produced in g/L	References
Corn	*S. cerevisiae*	Simultaneous saccharification and fermentation (SSF)	35.6	Gumienna et al. (2016)
Wheat & rye stillage	*S. cerevisiae*	Microwave acid treatment	20	Mikulski and Kłosowski (2020)
Potato tuber	*S. cerevisiae*	Acid hydrolysis	31	Tasić et al. (2009)
Sorghum	*S. cerevisiae*	Enzymatic hydrolysis & fermentation	81.5	Sebayang et al. (2017)
Corn & corn stover	*S. cerevisiae* & *Zymomonas mobilis*	Enzymatic hydrolysis	2.19 g/L/h	Chen et al. (2018b)
Rice straw	*Candida tropicalis*	Pre-treatment and sequential fermentation Ionic liquid (aqueous ammonia) at 121 °C for 1 h (10% solid loading)	26	Swain and Krishnan (2015)
Sugarcane bagasse	*S.cerevisiae* Y2034	NaOH pre-treatment with enzymatic hydrolysis (1:12 solid liquid ratio)	22.37	Wang et al. (2019)
Sugarcane bagasse	*S. cerevisiae PE-2*	Simultaneous saccharification and fermentation (SSF)	31.5	de Araujo Guilherme et al. (2019)
Rice hulls	*Scheffersomyces stipites* ATCC 58785	Enzymatic treatment by reducing sugar	25	Sim et al. (2020)
Wheat straw	*Issatchenkia orientalis* KJ27–7	Wheat straw hydrolysate by steam explosion	10.3	Zwirzitz et al. (2021)
Banana leaf waste	*S. cerevisiae*	Simultaneous saccharification and fermentation (SSF)	15.43	Suhag et al. (2020)
Miscanthus	*S. cerevisiae*	Semi-simultaneous saccharification and fermentation (SSSF)	8.77	Guo et al. (2019)
Sugarcane tops	*S. cerevisiae*	Alkaline hydrogen peroxide pre-treatment with acid hydrolysis and fermentation	9.9 vol%	Niju et al. (2019)
Sweet sorghum bagasse	*Kluyveromyces marxianus* CCT7735	Acid–base pre-treatment with saccharification	17.83	Tinôco et al. (2021)
Construction and demolition wood waste with softwood chip	*S. cerevisiae*	Steam treatment with hydrolysis	82.12	Boboescu et al. (2018)
Industrial hemp	*S. cerevisiae*	Simultaneous saccharification and fermentation (SSF) (Pre-treatment NaOH with enzymatic hydrolysis)	18.2–20.3	Zhao et al. (2020a)
Yellow poplar sawdust	*Pichia stipitis* CBS 722	Mild alkali treatment with ammonia solution followed by hydrolysis & fermentation	4.83	Kim et al. (2018)
Banana peel	*Kluyveromyces marxianus*	Pre-treatment with H_2SO_4& enzymatic hydrolysis	21	Palacios et al. (2017)
Apple pomace	*Pichia stipitis*	Separate hydrolysis and fermentation (SHF)	14.36	Kut et al. (2020)
Citrus peel waste	*Pichia kudriavzevil* KVMP10	Acid and enzyme hydrolysis	30.71	Patsalou et al. (2019)

(*continued on next page*)

3.1. Applications of crude glycerol

There is an increasing trend in converting crude glycerol from biodiesel production into bioethanol and other value-added products due to more carbon reduction in glycerol used as the sole organic carbon source. Besides bioethanol

Table 2 (*continued*).

Substrate	Microorganism	Process	Ethanol produced in g/L	References
Spent coffee grounds	*S. cerevisiae*	Dil acid hydrolysis & fermentation	3.9 (vol%)	Burniol-Figols et al. (2016)
Sorghum distillery residue	*S. cerevisiae*	Acid hydrolysis by wet torrefaction and saccharification	19.21	Chen et al. (2021)
Chlorella sp. biomass	*S. cerevisiae* TISTR 5339	Acid-hydrothermal pre-treatment & enzymatic hydrolysis	10.57	Ngamsirisomsakul et al. (2019)
Industrial algae waste	*S. cerevisiae*	Acid hydrolysis with H_2SO_4	11.66	Alfonsín et al. (2019)
Corn starch & *Spirulina* sp. LED 18	*S. cerevisiae* CAT-1	Simultaneous saccharification and fermentation (SSF)	73.83	Luiza Astolfi et al. (2020)

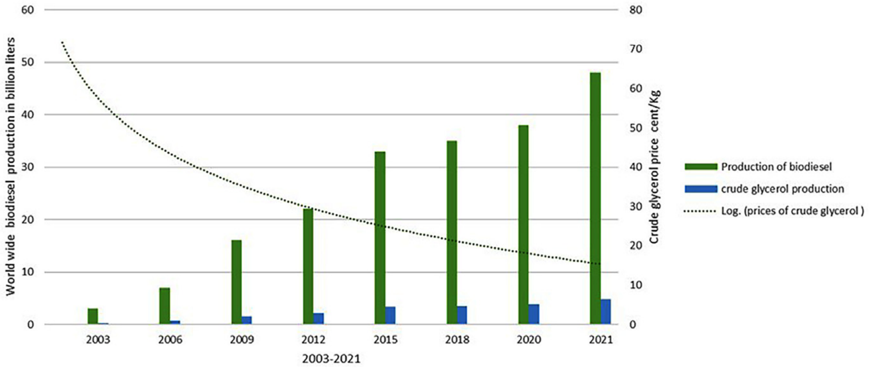

Fig. 4. Production of biodiesel and crude glycerol worldwide.

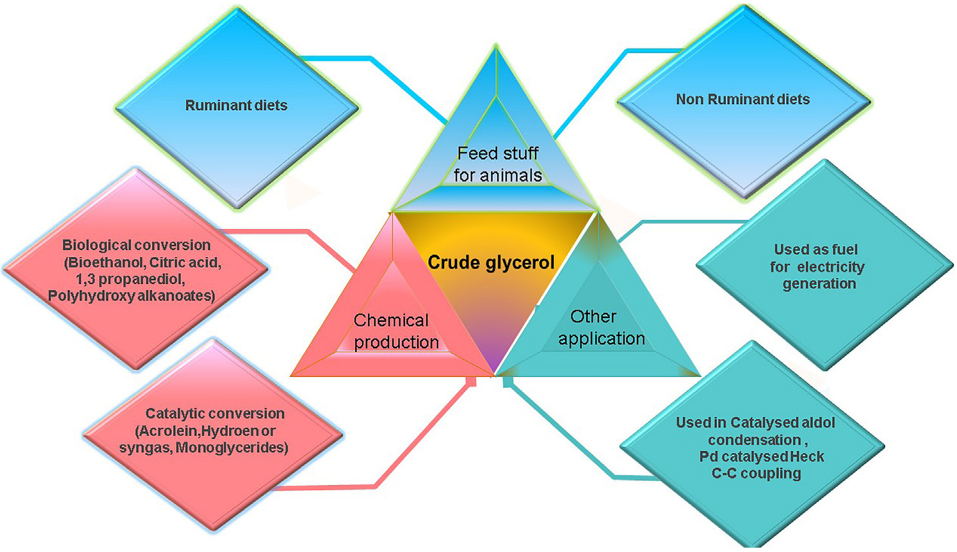

Fig. 5. Application of crude glycerol.

production, crude glycerol is used in many applications for chemical production through biological transformation and conventional catalytic conversion, as presented in Fig. 5.

Table 3
Microorganisms used for ethanol production by fermentation process from glycerol waste.

Sno	Microorganisms	Process condition and method	Ethanol yield or productivity	Substrate	References
1	*Enterobacter aerogenes* TISTR1468	−350 mV and −400 mV ORP in Fedbatch fermentation. Microaerobic condition with batch fermentation	30 g/L & 0.47 g/L/h 18.78 g/L & 0.26 g/L/h	Crude glycerol (CG)	Sunarno et al. (2020)
2	*Enterobacter* sp., *Klebsiella* sp.	Up-flow anaerobic sludge blanket (UASB) reactor under thermophilic conditions	50.77 mmol/L 51.09 mmol/L	Glycerol CG	Sittijunda and Reungsang (2020)
3	*K. pneumoniae* Kp17	Fed-batch reactor	17.3 g/L & 0.59 g/L/h	CG	da Silva et al. (2020)
4	*P. tannophilus* Y −475	Continuous flow reactor, 25 °C	0.63 ± 0.02 g/L/h	CG	Stepanov and Efremenko (2017)
5	*Enterobacter aeroegenes* TISTR 1468	pH 7, 37 °C at 150 rpm, Fed-batch fermentation	12.33 g/L	CG & tuna condensate	Sunarno et al. (2019)
6	*Enterobacter aeroegenes* G2WG	35 °C, 250 rpm Biostat fermenter with Fed batch fermentation. Batch fermentation	13.07 g/L & 0.36 g/L/h 14.77 g/L & 0.307 g/L/h	Waste glycerol (20 g/L) Waste glycerol (30 g/L)	Yuwa-amornpitak and Chookietwatana (2016)
7	*Klebsiella variicola* TB-83D	pH 9, 25 °C, Fed batch culture with methane fermentation digested slurry (MFDS)	14.6 g/L	CG	Seta et al. (2018)
8	Recombinant strains *Ogataea polymorpha*	37 °C, Overexpression of genes of glycerol catabolism	10.7 g/L 3.55 g/L	Pure glycerol CG	Semkiv et al. (2019)
9	*Klebsiella aeroegenes* ATCC 29007	pH 6, 37 °C, 180 rpm Batch fermentation	15.89 g/L	CG	Lee et al. (2020)
10	*K. cryocrescens* S26	37 °C, 180 rpm, Batch culture	27 g/L & 0.61 g/L/h	CG	Choi et al. (2011)
11	*K.pneumoniae* GEM167 *K.pneumoniae* pBR-pdc-adh	37 °C with 200 rpm Fed-batch fermentation	21.5 g/L & 0.93 g/L/h 25.0 g/L & 0.78 g/L/h	CG	Oh et al. (2011)
12	*Enterobacter aeroegenes* KKU-S1	pH 6.5, 37 °C, Anaerobic condition with fed-batch fermentation	116.2 mmol/L	Glycerol waste	Reungsang et al. (2013)
13	*E. aerogenes* ATCC 13048	37 °C with 120 rpm in Anaerobic condition by batch fermentation	12 g/L 12.8 g/L	Pure glycerol Crude glycerol	Nwachukwu et al. (2012)
14	Mixed cultures of *E. coli* CECT432, *E. coli* CECT434, *Enterobacter* cloacae MCM2/1	pH 6.34, 37 °C in jacketed bioreactor, Batch fermentation	1.21 mol/mol	CG	Maru et al. (2016)
15	*Saccharomyces cerevisiae*	Metabolically engineered strain YPH499 with palsmids (pGcyaDak, pGupCas) 30 °C, Batch	2.4 g/L	CG	Yu et al. (2010)
16	*Klebsiella variicola TB-83*	pH 9, 25 °C Batch fermentation	9.8 g/L	CG	Suzuki et al. (2014)

(*continued on next page*)

3.1.1. Chemicals developed by the bioconversion of raw glycerol

The anaerobic fermentation of glycerol produces propane-1,3-diol. *Klebsiella pneumoniae* utilised to convert simple glycerol to propane-1,3-diol in fed-batch culture. Crude glycerol was obtained in biodiesel production from jatropha using *K. pneumoniae* ATCC 15380 (Hiremath et al., 2011). Various microorganisms like *Clostridium butyricum, Clostridium diolis, Citrobacter freundii, Lactobacillus reuteri* and *L. brevis* produced 1,3-propanediol from crude glycerol (Vivek et al., 2017).

Table 3 (*continued*).

Sno	Microorganisms	Process condition and method	Ethanol yield or productivity	Substrate	References
17	*E. coli* SS1 *E. coli* BL21 E. coli SS1 *E. aerogenes* HU101	pH 7, 37 °C, Batch fermentation	1 mol/mol 0.991 mol/mol 0.592 mol/mol 0.594 mol/mol	Glycerol	Suhaimi et al. (2012)
18	*Escherichia coli K12*	37 °C and 200 rpm, Batch fermentation	3.6 g/L	CG	Chaudhary et al. (2012)
19	*Escherichia coli* MG1655	37 °C, 150 rpm, pH 6.30-6.35, Anaerobic condition Fed batch fermentation	7.58 g/L & 0.05 g/L/h	CG	Cofré et al. (2016)
20	*Pachysolen tannophilus* CBS404	pH 5, Staged batch fermentation	28.1 g/L & 0.11 g/L/h	CG	Jönsson and Martín (2016)

Citric acid is also formed from crude glycerine using *Y. lipolytica* ACA-DC 50109. *The Y. lipolytica strain ACA-YC 5029 ACA-YC 5029* is deemed an excellent choice for producing citric acid cultivated at high levels of crude glycerol (Sarris et al., 2019). *Rhodopseudomonas palustris* converted crude glycerol and pure glycerol into hydrogen through photo-fermentation (Chozhavendhan et al., 2019). *Enterobacter aerogenes* HU-101 was used to obtain higher bioethanol and hydrogen from glycerol (Nwachukwu et al., 2013). *Cupriavidus necator* valorised waste glycerol to poly (3-hydroxybutyrate) and poly (3-hydroxybutyrate-co-3-hydroxyvalerate). *Zobellella denitrificans* MW1 is used to produce polyhydroxy butyrate (PHB) from crude glycerol (Gahlawat and Soni, 2017). Microalgae fermentation produces omega-3 polyunsaturated fatty acids from biodiesel glycerol waste (Ethier, 2010). DHA-containing algae have been recognised as an alternative to fish oil that contains omega-3 fatty acids. Eicosapentaenoic acid is an omega-3 fatty acid produced from crude glycerine by culturing *Pythium irregular* (Fernandes et al., 2019).

Lipids produced from crude glycerol due to a sole-carbon source. For instance, crude glycerine was used to culture *Cryptococcus curvatus*, *S. limacinum*, and algae growth and lipid formation affected by the glycerol concentration, where a higher concentration led to negative growth. Oleaginous red yeast *Rhodotorula glutinis* TISTR 5159, *S. pararoseus* KM281507 is used to produce lipids and carotenoids from glycerol waste (Kot et al., 2016; Manowattana et al., 2018). *Chlorella protothecoides, Yarrowia lipolytica, and Cryptococcus curvatus* converted crude glycerol to lipids (Vivek et al., 2017). Eukaryotic microalgae *Chlorella protothecoides* with malic enzyme used for biodiesel production (Yan et al., 2019). *Escherichia coli* was utilised to produce succinic acid from crude glycerol (Aziati and Sakinah, 2018). *Clostridium pasteurianum* strain CT7 converted crude glycerol to butanol (Xin et al., 2017). *Gluconobacter* sp. NBRC3259 produced glyceric acid and dihydroxyacetone from crude glycerol (Kalia et al., 2016). *Ustilago maydis* acted as a biocatalyst to convert crude glycerol into glycolipid as a biosurfactant (Chowdhary et al., 2018). Crude glycerol produces biohydrogen, mannitol, and pigments.

3.1.2. Chemical production using conventional catalytic conversion

Chemical compounds like propanol are produced by hydrogenolysis of crude glycerol using Ni catalyst (Gatti et al., 2020). Crude glycerol, through dehydration using zeolite catalyst, produce acrolein (Widayat et al., 2020). Hydrogen is produced by steam reforming crude glycerol over Ni–La–Ti mixed oxide catalysts (Veiga et al., 2017). Hydrogen gas is produced by steam and oxidative steam reforming crude glycerol using mixed oxide catalysts (Veiga et al., 2020). Monoglycerides are obtained from a heterogeneous catalyst from a glycerolysis of triglycerides from crude glycerol (Buchori et al., 2020). Using ZSM-5/bentonite extrudates, ex-situ catalytic pyrolysis of crude glycerol in a tandem micro-reactor (TMR), a batch gramme scale reactor, and a continuous integrated bench-scale unit used for the synthesis of bio-based benzene, toluene, and xylenes (bio-BTX) (He et al., 2018). Catalytic conversion of biodiesel derived glycerol to solketal, a fuel additive (Zahid et al., 2020).

3.1.3. Glycerol as a feedstuff for animals

Glycerol is a feedstuff for animals. Recently, the utilisation of crude glycerol from biodiesel has been examined due to the increase in corn price and the availability of crude glycerol. Glycerol is a non-ruminant diet due to its excellent energy source and has high absorption rates. Once absorbed, glycerol can be converted to glucose for energy production by the enzyme glycerol kinase in animal livers. Crude glycerol samples as an energy source have been analysed from various biodiesel producers.

The digestible energy (DE) and metabolisable energy (ME) values for 85% crude glycerol were 14.9–15.3 MJ/kg and 13.9–14.8 MJ/kg. Crude glycerol is an outstanding source of calories for non-ruminants, and the ME values were 15.2 MJ ME/kg, 15.9 MJ ME/kg, and 13.4 MJ ME/kg for broilers, laying hens, and swine, respectively. Using crude glycerol recorded

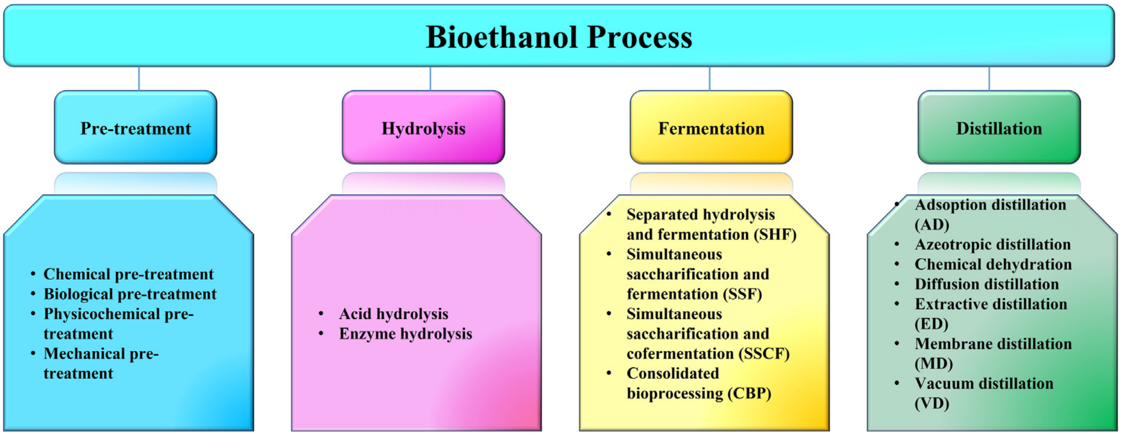

Fig. 6. Bioethanol process.

14.1 MJ/kg apparent DE and 16 MJ/kg nitrogen-corrected apparent ME (AMEn) for growing pigs and laying hens. For broiler chickens, the AMEn of crude glycerol is metabolised to 14.4 MJ/kg, almost 15.2 MJ/kg of the general energy (GE). The GE concentration of crude glycerine depends on glycerine, methanol, and fatty acids, with the ME around 85.4%. Crude glycerol (6%) to pigs' diets improved feed performance (Hernández et al., 2016). Meanwhile, for broiler diets, the higher intake level of crude glycerol increased the feed conversion ratio. The higher intake level did not disturb the growth performance and digestion of nutrients. Using 2.5% or 5% of crude glycerol is adequate, whereas 10% of crude glycerol resulted in poor feed flow. Thus, more studies need to be conducted on the influences of levels and crude glycerol quality (Kholif, 2019).

Crude glycerol used as ruminant diets because up to 15% of dry matter in lambs' diets improves feedlot performance. In the initial 14 days, there was no consequence on carcass features (Brant et al., 2021). Crude glycerol also used as a feed supplement for lactating goats (Novais-Eiras et al., 2018). Including crude glycerol improves the lactating dairy cows. As a pet food ingredient, crude glycerol can suppress corn in diets. However, there are adverse contaminants present in unprocessed glycerol from biodiesel. For instance, in a broiler's diet, the potassium amount could disrupt the electrolyte balance. The methanol content should be reduced due to its toxic nature (Nazato et al., 2019).

4. Bioethanol production processes from biomass

Bioethanol quality depends on pre-treatment, fermentation, hydrolysis, and distillation methods described in Fig. 6. Pre-treatment is the primary step in bioethanol production that involves the physical treatment for reducing the size of biomass and thermochemical treatment for biomass disruption to enhance porosity. The second phase involves hydrolysis that converts polymers like starch, cellulose, and hemicellulose to monomers. The third phase consists of the fermentation process that converts fermentable sugars to bioethanol using microorganisms or biocatalysts. The last phase is the distillation process. Researchers have developed different techniques to produce bioethanol from various substances.

4.1. Pre-treatment

Pre-treatment for biofuel production mainly involves physical size reduction of materials to expose components (cellulose, hemicellulose, and starch) to improve yield. Better access to enzymes enables the hydrolysis of carbohydrates to produce sugars through enzymatic hydrolysis. For starchy agriculture waste, the physical reduction was sufficient for the pre-treatment step, which was done using a simple mechanical process for starch materials to provide direct access to hydrolysis. The pre-treatment step involves the deformation of structured components of cellulose, lignin, and hemicellulose for lignocellulosic materials, thus reducing crystallinity degree. The physical reduction is also suitable for lignocellulosic materials. Chemical pre-treatment eases the subsequent hydrolysis process. Meanwhile, the combination of physical and chemical treatment produces a greater yield of reducing sugars (Hassan et al., 2018).

Biological pre-treatment uses microorganisms, especially white-rot, brown-rot, and soft-rot fungi, potentially degrade lignocellulosic components into an amorphous form. Brown-rot fungi can only degrade cellulose, whereas soft-rot and white-rot fungi can degrade cellulose and lignin. White-rot fungi are considered an effective biological treatment agent compared to brown- and soft-rot fungi. Biological treatment requires mild conditions only with low energy consumption. Additional chemical substances are unnecessary to degrade the lignocellulosic wall, hence making this method safer. However, biological pre-treatment is unfavourable for large-scale industries due to the slow production rate. Therefore, biological pre-treatment paired with another pre-treatment method to make the process feasible (Sharma et al., 2017).

Chemical pre-treatment uses chemical substances for the hydrolysis of lignocellulosic or starchy materials. Chemical pre-treatment is feasible due to easy availability, cheaper, less hassle in storage, durable with proper storage, and unaffected by scientific development. Chemical substances degrade lignocellulosic walls and starch by a direct chemical reaction involving low energy. However, more time is required, and a low yield is produced with alkaline treatment. Acid pre-treatment, strong acids like hydrochloric acid, nitric acid, phosphoric acid, and H_2SO_4 are commonly applied in lignocellulosic materials. Organic acids like ethanoic acid, 2-hydroxy-propanoic acid, cis-butenedioic acid, and peroxyacetic acid are also used for chemical pre-treatment (Zhao et al., 2017a). Two acid pre-treatment methods are concentrated and dilute. In concentrated acid pre-treatment, the process produces monosaccharides by degrading polysaccharides' glycosidic bonds in a shorter time and at a mild temperature. The disadvantages of concentrated acid pre-treatment are the formation of inhibitors, equipment corrosion, and a higher tendency of monomer degradation. Dilute acid pre-treatment is preferable as the approach produces the same outcome as concentrated acid pre-treatment (Solarte-Toro et al., 2019).

The most used alkali solutions are sodium hydroxide and lime for alkali pre-treatment, as reported by many researchers. NH_4OH is also utilised in the pre-treatment step to produce bioethanol. In lignocellulosic biomass, NaOH pre-treatment provides a better internal surface by swelling for lignin degradation. The pre-treatment step results in higher porosity to obtain more glucose yield through enzymatic hydrolysis. The dilute sodium hydroxide provides better substantial and commercial benefits than concentrated sodium hydroxide (Mankar et al., 2021). The pre-treatment of lignocellulosic material with $Ca(OH)_2$ was performed on poplar wood, corn stover, switchgrass, wheat straw and rice straw (Gu et al., 2015). Heavy lignin degradation improved by mixing the oxidising agent with alkali. Alkaline pre-treatment of sugar cane bagasse, peracetic acid demonstrated improved digestibility for the enzyme to hydrolyse sugar cane bagasse (Zhao et al., 2009). Bioethanol is produced from lignocellulosic materials using organic solvents, particularly acetone and phosphoric acid. Ionic liquids 1-allyl-3-methylimidazolium chloride (AMIM-Cl) and 1-butyl-3-methyl imidazolium chloride (BMIM-Cl) are the most effective ionic liquids for biomass pre-treatment. Ionic liquids produce biomass with higher surface area, less cellulose crystallinity, and lower lignin content. Therefore, ionic liquid pre-treatment is considered a green method (Aditiya et al., 2016).

Mechanical pre-treatment reduces the material size by breaking, cutting, or chopping materials. Therefore, biomass degradation is improved for bioethanol production. Milling techniques like ball-milling, compression-milling, hammer-milling, roll-milling, and vibratory ball-milling are examples of mechanical pre-treatment for physical size reduction. Extrusion is a progressive mechanical process. Biomass pre-treatment by extrusion improves the approach for an enzyme to upgrade exposure of carbohydrates. Extrusion involves shearing and mixing biomass at high temperatures for physical and chemical deformation (Mankar et al., 2021).

Applying an electromagnetic field for heating objects through microwave irradiation disrupts biomass structure. Bioethanol is produced using lignocellulosic materials by microwave irradiation. The polar bonds of biomass structure vibrate until the organic materials are heated thoroughly. As an outcome, the lignocellulosic material is fragmented, spreading the enzymatic attack area (Mankar et al., 2021).

Physicochemical pre-treatment by steam explosion involves hydrothermal process and sudden pressure change. The biomaterial is primarily subjected to excessive temperature and pressure for a limited minute, accompanied by depressurisation where the steam blasts the biomass. Steam explosion is advantageous for hemicellulose-rich materials. Bioethanol production is economically feasible due to the higher recovery of xylose between 45 to 65%, less energy utilisation, and the environmentally favourable nature of the steam explosion. Ammonia fibre explosion (AFEX) depends on the high pressure with recovery and recycles the NH_3 to burst the biomass by leaving few NH_3 traces on biomass, providing the microbe's nitrogen source. AFEX possesses mechanical pre-treatment features, which reduce the bulk quantity and wide area and chemical pre-treatment features involving the reduction of crystallisation, breakage of lignin, and hemicellulose degradation. This process has a strong effect on fibrous biomass. NH_3 is a pre-treatment agent, where ammonia recycled percolation (ARP) flows recoverable aqueous NH_3 over the reactor encompassing biomass. ARP is helpful for eliminating lignin without sodium and sulphur contaminants. ARP applies for biomass such as paper pulp waste with 5% digestibility and noticed improvement from 41 to 75% with H_2O_2, and hardwood like oak wood shown 6%–85% total lignin removal (Aditiya et al., 2016).

Wet oxidation pre-treatment involves a high pressure of 500–2000 kPa and 170-200 °C for 10–15 min. Lignocellulosic materials degrade in wet oxidation treatment with fewer inhibitors, where the process removes lignin and lowers cellulose crystallinity to provide a better condition for enzymatic hydrolysis and fermentation. In clover and ryegrass mixtures, high conversion efficiency with 75.5% glucose yield was noticed (Martín et al., 2008). The wet air oxidation process observed about 89% lignin removal and 69.77% hemicellulose solubility in rice husk (Banerjee et al., 2009).

A supercritical fluid is one of the advanced technologies for bioethanol production. The most used supercritical fluid for coffee decaffeination is CO_2 (Zabot, 2020). The advantages of supercritical fluid in mass transfer (gas) and solvation (fluid) are lesser inhibitory products, efficient lignin elimination at low temperature, non-acidic, and non-corrosive, thus making supercritical fluid a favourable process for bioethanol production than ARP and steam explosion.

4.2. Hydrolysis

Hydrolysis separates long-chain carbohydrates with adding water. The process is typically catalysed through enzymes or acids to convert carbohydrates into simple sugars and is an essential step that affects the subsequent fermentation method for bioethanol production.

4.2.1. Acid hydrolysis

Dilute acid hydrolyse and degrade lignocellulosic biomass for fermentation. Dilute acid utilises 1% acid concentration for biomass degradation and obtained 50% product yield, mainly glucose. Dilute acid hydrolysis produces reasonable yields but forms inhibitory products as the byproducts (e.g., acetate, furfural, hydroxybenzaldehyde, and 5-hydroxymethylfurfural), which are harmful to fermenting microorganisms. Sulphuric acid hydrolysis of bamboo produces ethanol (Sun et al., 2013). The organic fraction of municipal solid waste containing starchy and lignocellulosic materials produce ethanol (Mahmoodi et al., 2018). Compared to dilute acid, concentrated acid gives a better sugar yield. However, concentrated acid requires high safety precautions for handling as it is highly hazardous to humans and the environment. Although the process has a shorter period, concentrated acid can corrode the production equipment.

4.2.2. Enzymatic hydrolysis of lignocellulosic materials

Lignocellulose mainly consists of cellulose, hemicellulose, and lignin, which degrade using enzymes. Cellulose has glucose chains connected by 1,4-β-glycosidic bonds. Cellulose is created by hydrogen bonding with the chains, which contribute to the degree of crystallinity. The nature of cellulose crystallinity affects the hydrolysis process, including slow hydrolysis and low enzyme adsorption. The amorphous region in cellulose is easier to break down compared to the crystalline area. Cellulase is the enzyme for breaking down cellulose. The enzymatic activity of cellulase can be classified into endoglucanases (EC 3.2.1.4), exoglucanase (EC 3.2.1.91), and β-glycosidase (EC 3.2.1.21). In endoglucanase, the formation of 1,4-β-D-glucanohydrolase chooses the cellulose with less crystallinity. The hydrolysis in endoglucanase occurs by connecting the β-1,4 cellulose bond with water molecules. 1,4-β-D-glucan cellobiohydrolase in exoglycanase degrades the cellulose structure and alters both end chains to form two glucose units, mainly cellobiose. A smaller unit monomer is expected to be used for fermentation, and cellobioses are treated by β-glucosidase, which attacks cellobioses to produce glucose (Srivastava et al., 2018).

Hemicellulose hydrolyses easily due to its amorphous nature. The main component of hemicellulose is xylan. About 10%–15% of the hemicellulose is xylan in softwoods and 10%–35% in hardwoods. Endo-β-1,4-xylanase (EC 3.2.1.8) and β-xylosidase (EC 3.2.1.3.7) are used to break down xylan. Endo-β-1,4 xylanase reduces xylan into shorter chains. The subsequent process that reduces oligosaccharides uses β-xylosidase to obtain xylopyranose (Naidu et al., 2018).

Lignin adsorbs protein to form a bond and later precipitates with protein in an aqueous solution. Lignin has cellulosic fibres, which lowers the access of cellulose to cellulases. However, lignin resists cellulases enzymatic activity, causing low hydrolysis quality. Therefore, lignin elimination must be achieved to increase the hydrolysis efficiency by cellulase. In lignin removal, micro cellulose fibres are separated to provide better access for cellulases. Hemicellulases could degrade hemicellulose structure into monomers but are not favourable for cellulose hydrolysis. Galactose, xylose, mannose, and xylooligosaccharides are the hydrolysis products of hemicellulose, which act as inhibitors to β-glucosidase and cellulase.

4.2.3. Enzymatic hydrolysis of starch-containing biomass

Starch is the primary source of carbohydrates with different chemical structures and properties than carbohydrates. In starch, the structure of glucose is associated with α-glucosidic bonds. Thus, starch consists of linear α-1,4-linked glucan-amylose and another similar α-1,6 linkage-amylopectin. Amylose is a linear polymer with 6000 glucose units, amylopectin has lesser glucose units of 10–60, and α-1,6 linkage comprises 15–45 glucose units. Amylases are the amylolytic enzymes that degrade the glucose linkages present in starch. Amylases can be classified into four groups based on their function: endoamylases, exoamylases, debranching enzymes, and transferases. The inner region of amylose and amylopectin contains α-1,4-glycosidic bonds hydrolysed by endoamylase. α-amylase (EC 3.2.1.1) can break down α-1,4-glycosidic bonds to produce shorter and varied length products. Glucose and maltose are released as α-amylase works randomly (Balakrishnan et al., 2019).

Exoamylase is the second amylase that aims at the outer part of amylose and amylopectin. Glucoamylase (amyloglucosidase; EC 3.2.1.3) and α-glucosidase (EC 3.2.2.20) are exoamylases that can degrade α-1,4 and α-1,6 bonds. Another example of exoamylase is β-amylases (EC 3.2.1.2), restricted to break down α-1,4-glycosidic bonds. In hydrolysis, glucoamylase exhibits an improved action on polysaccharides, and α-glucosidase works on maltooligosaccharides. The hydrolysis products of exoamylase include glucose and maltose as low structures.

Debranching enzymes toil on α-1,6 glycosidic bonds on various fragments of polysaccharides. An example of the debranching enzyme is isoamylase (EC3.2.1.68), which only degrades α-1,6-linkages in amylopectin. Pullulanase type I (EC3.2.1.41) degrades the α-1,6 linkages in amylopectin and pullulan. Another debranching enzyme, pullulanase type II, degrades both α-1,4 and α-1,6-glycosidic bonds to produce maltose and maltotriose. The final group of amylases is transferases, which transfer molecules to form a new glycosidic bond. The new α-1,4 glucosidic bond formation is catalysed by amylomaltase (EC2.4.1.25) and cyclodextrin glycosyltransferase (EC 2.4.1.19). Enzymes also form cyclodextrin rings with 6–8 units of glucose connected by α-1,4 bonds (Balakrishnan et al., 2019).

4.3. Fermentation

Fermentation exhibits metabolic action utilising the fermentation agent to produce bioethanol. Hydrolysate is presented to a precise fermentation agent (i.e., bacteria or yeast) to degrade or break down sugar compounds. A glucose-fermenting bacterium (e.g., *Z. mobilis*) prefers glucose-containing rich hydrolysate to produce bioethanol. Fermentation mainly depends on the supporting conditions, such as temperature and pH range, particularly for microbe sustainability. Mesophilic organisms are involved in fermentation within the temperature of 303–311 K. The pH values need to be 6.5–7.5 to sustain bacterial growth. But fungi require an acidic environment (3.5–5.0 pH). Other elements essential in the fermentation process include microbial growth and genetic stability, inhibitor tolerance, productivity, and bioethanol yield. *Z. mobilis* is the most common bacterium that converts glucose, sucrose, and fructose into bioethanol. *S. cerevisiae* consumes hexoses like glucose and fructose. Bacteria's use results in poor productivity and requires proper handling as bacteria are susceptible to acidic and inhibitors. *P. stipitis* BCC15191 was adopted as a fermenting agent for bioethanol from sugar cane bagasse (Muhamad et al., 2021). In separated hydrolysis and fermentation (SHF), the hydrolysis is carried in period time followed by a fermentation process. Sugarcane leaves are agricultural residues transformed to bioethanol through SHF (Jutakridsada et al., 2017).

In simultaneous saccharification and fermentation (SSF), the hydrolysis process uses the enzyme to free the sugars and ferment those sugars immediately to bioethanol exclusive of segregation. This approach stops the monomers reduction after hydrolysis. SSF is said to produce greater bioethanol yield. Fermentation helps in solving the hydrolysis inhibitions, hence making it a desirable method. A study revealed that the SSF method uses fewer enzymes, has a faster production period, and requires a smaller number of reactors. Thus, low cost is involved as sugar releasing, and fermenting processes occur concurrently (Szambelan et al., 2018). Another alternative fermentation method for bioethanol production is simultaneous saccharification and co-fermentation (SSCF). This method uses the varied culture of microbes to start the continual method without separating sugar, using different substrates and sterilisation. SSCF efficiently produces bioethanol from corn stover, municipal solid wastes, and sugar cane bagasse (Chen et al., 2017).

Consolidated bioprocessing (CBP) is another alternative process to produce bioethanol from cellulosic materials. The process involves self-cellulase production, substrate hydrolysis, and hexose and pentose fermentation, which occur in the same reactor using certain microorganisms capable of performing these tasks. Compared to SHF, the CBP method offers better advantages in lower production costs due to the reduced number of steps and no extra acquisition of enzymes, improved adaptation performance, and less energy required for bioethanol generation (Cripwell et al., 2020). *T. reesei* is a cellulolytic type of fungi that naturally secretes enzymes that can degrade lignocellulosic materials. Many fungi like *F. oxysporum*, *N.crassa*, *Paecilomyces sp.*, and bacterium *C. thermocellum* are appropriate for CBP. However, the CBP process still needs to improve due to the low ethanol conversion rate and low ethanol yield. Several efforts have been made to the CBP method to produce bioethanol, which focuses on the genetic modification of microorganisms to lower production costs. Two modification paths are consolidated bioprocessing I (CBP-I) and consolidated bioprocessing II (CBP-II). CBP-I alters cellulolytic microbes to produce bioethanol, and it is recognised as a preliminary development step. The importance of different fungi towards modifying the strains in category I include *T. reesei*, *F. oxysporum*, *Aspergillus spp.* (*A. sojae*, *A. niger*, *A. oryzae*, and *A. terreus*), and *Rhizopus spp.* (*R. koji*, *R. oryzae*, and *R. stolonifera*). CBP-II highlights the modification of genes, particularly ethanologenic microbes, to provide cellulolytic properties. CBP-II focuses on exhibiting engineered microbes' capability to develop exo- and endoglucanases to ferment saccharides, along with sustainable growth ability by depending only on carbon sources. Many bacteria like *E. coli*, *K. oxytoca*, *Z. mobilis*, and yeasts like *C. shehatae*, *P. tannophilus*, *S. cerevisiae*, *P. stipitis*, have been modified for CBP-II (Kumari and Singhal, 2019).

4.4. Distillation

Distillation is the process used for separation and purification. The ethanol solution obtained from fermentation must be purified to separate the water and produce superior quality ethanol known as anhydrous ethanol. Generally, the water content is removed from distillation by utilising different boiling points of the mixtures. The mixture is heated, and once it reached the 78.2 °C boiling point, ethanol vaporises and is parted from other components. Anhydrous ethanol has 99.5% of ethanol with less than 0.5% aqueous content.

4.4.1. Adsorption distillation

Adsorption distillation (AD) uses the variance in molecular dimensions of the ethanol–water mixture to capture extra aqueous content. AD separates ethanol from the mixture using a molecular sieve based on the size of the sieve's opening. Ethanol molecules of 4 Å in diameter detached from aqueous molecules using a 3 Å diameter sieve, as water molecules are 2.5 Å in diameter. Two molecular sieve beds are required in a typical AD process. Water vapour occupies the voids of the molecular sieve for the first bed and is adsorbed until the maximum quantity of water molecules are absorbed by the bed, separating dehydrated and anhydrous ethanol. After the bed is occupied with water, the hydrated bed is replaced with a fresh bed from an automatic or control throttle. The bed is reused multiple times in the absorption process due to its regenerative property. Besides, the absorbent material (zeolite) is also reusable. Although the materials are cheap and environmentally friendly, they cannot be regenerated. A high temperature (228 °C) for 2–4 h is required for sieve regeneration (Aditiya et al., 2016). Copper exchanged LTA zeolite membranes enhanced the water flux for ethanol dehydration (Xu et al., 2019).

4.4.2. Azeotropic distillation

Azeotropic distillation can be performed with adding tertiary chemical constituents (entrainers) in the azeotropic binary mixture, in which the mixture violates Raoult's law. Adding entrainers change the relative volatilities of azeotropes, and the entrainers can be reclaimed by decantation, distillation, or other recovery processes. This process is also used for the removal of water from the ethanol–water blend. The third substance (entrainer) is added to the mixture, resulting in a ternary azeotrope, then flows to a decanter for recycling before it is returned to feed the mixture in the distillation column. The typical chemical substances used are cyclohexane and benzene; however, benzene possesses carcinogenic properties. Other entrainers used to generate anhydrous ethanol are toluene, propanone, diethyl ether, isooctane, hexane, pentane, heptane, and polymers (Zhao et al., 2017b). Azeotropic distillation involves high costs, especially for maintaining a large stream of entrainer flow for continuous circulation, hence increases distillation costs and energy input. A harmful entrainer like benzene is undesirable to produce anhydrous ethanol as the substance damages human health and the environment.

4.4.3. Chemical dehydration

Anhydrous ethanol is conventionally produced through the dehydration of hygroscopic chemical substances. These substances are added to the ethanol–water mixture, allowing the substances to hydrate with water. The commonly used substance is calcium oxide (CaO) or quicklime. The substance reacts with water and forms calcium hydroxide, and ethanol is formed at the top. Dehydration by quicklime is usually carried out at the water-to-quicklime ratio of 1:4.2. Distillation or thorough filtration is necessary for the complete removal of CaO in the mixture. Calcium hydroxide can be reversed to produce CaO through the reaction with water, and the recycled CaO can then be used in the subsequent batch to produce ethanol. Quicklime dehydration requires a massive amount of energy due to high temperatures during anhydrous ethanol production. Glycerol, ethylene glycol and quicklime were employed to produce anhydrous bioethanol from sweet potatoes as alternate dehydration agents (Silva et al., 2019).

4.4.4. Diffusion distillation

The separation by diffusion is accomplished by the internal voids of gas, followed by condensation. The blend is vaporised after reaching boiling point, and the diffusion influences the inert gas's volatility and diffusivity. The pre-distillation blends containing ethanol and water were examined. The blend containing isopropanol-methanol-water and binary isopropanol-water was examined at different evaporation conditions, inert gases, the variance of condensation, and the wetted-wall column's annular widths (Singh and Prasad, 2011). Ethanol determined with a diffusive micro-distillation device from fermented sugarcane substrates (Brasil et al., 2020).

4.4.5. Extractive distillation

Extractive distillation (ED) is a standard method used by chemical and pharmaceutical industries due to its high purity in isolating components from a mixture, which is achieved by adding a non-volatile solvent. Solvent addition is essential to separate the components. The high volatile components are present at the column's topmost, whereas the less volatile constituents are present at the column's bottom. Separation occurs due to the difference in volatility. The lighter component is extracted first, and the heavy component enters the second column for distillation, with the solvent for separation. Solvent recycling occurs in the second column, where the recovered solvent can be used in the primary column through a continual ED method. This process was used in the second world war to produce pure butadiene and toluene. Dielectric constant behaves as the polarity property adjacent to the heavy constituent for the interaction to occur. In the binary azeotrope mixture, the light and heavy components are estimated by the boiling point. For instance, there is only a slight variance in ethyl acetate and ethanol (77 °C and 78.3 °C), respectively. Dimethyl sulfoxide, N, N-dimethylformamide, and N-methyl-2-pyrrolidine with dielectric constants of 48.9, 36.71, and 32, correspondingly. Ethanol is the hefty constituent attributable to a nearer dielectric constant value of 25.7, while ethyl acetate exhibits a 6.02 dielectric constant. However, the overall cost efficiency does not align with the energy required for ED with a liquid solvent. The regular ratio of 1:5 is the mixture feed to solvent, which requires much energy. Glycerol and ethylene glycol are used as entrainer for the azeotropic distillation of ethanol. The hazardous nature of the solvent is also a drawback for this method. For instance, ethylene glycol is used for anhydrous ethanol generation, but it is toxic to human health (Pan et al., 2019).

4.4.6. Membrane distillation

Membrane distillation (MD) involves mass transfer with specific components from a mixture through a semi-permeable membrane. The membrane blocks the feed through the surface tension, in which the volatile constituent passes through the membrane. MD is practically used for seawater desalination, dairy processing, volatile component separation, and wastewater treatment (Tibi et al., 2020). The most common membrane materials are organic polymers, gases, liquids, ceramics, and metals. Polypropylene is the membrane material (Himma et al., 2016). The temperature of 20 °C difference between the distillate and the bioreactor. In forward osmosis membrane distillation (FOMD), the temperature difference is 15 °C (Parveen and Hankins, 2021). Anhydrous ethanol is produced by pervaporation, another type of membrane process. MD and pervaporation can be distinguished based on the material. MD uses microporous and non-wetting membranes, whereas pervaporation applies thick polymer membranes. MD forces the permeability from the partial pressure difference

Table 4
Various sources with the process, ethanol efficiency and GHG emission reduction.

Source	Method	Efficiency	GHG emission reduction
Sugarcane	Pressing & fermentation	41%	82%
Sugar beet	Crushing & fermentation	12%	28–66%
Corn grain	Dry milling & fermentation	62%	35–56%
Wheat	Dry milling & fermentation	53–56%	40%
Corn stover, switchgrass, bagasse	Simultaneous saccharification/co-fermentation	35%	83–88%

among the membrane pores. MD selects the membrane materials based on their characteristic feature and distillation process applications. But in pervaporation, the permeability force from the slight vapour pressure due to the condensation of the permeate vapour and the material selection depends on the affinity intake to the membrane (Chen et al., 2018a; Zouhair et al., 2021).

4.4.7. Vacuum distillation

Vacuum distillation (VD) produces anhydrous ethanol by reducing the pressure lower than 1.66 psi to interrupt the ethanol–water azeotrope mixture. The interruption in the azeotrope system leads to the partition that can be conducted in two columns, where moderate pressure is maintained at the first column, and low pressure is applied at the second column. VD was modified to MD to obtain favourable properties of VD and MD. The factors influencing ethanol distillation are pore size, membrane materials, feed temperature, mixture characteristics, and cycle flow rate. The membranes utilised include polypropylene, polytetrafluoroethylene, and polyvinylidene fluoride (PVDF) with different pore sizes. The theoretical data were similar to experimental data. The theoretical model based on Aspen Plus was predicted with vacuum distillation performance in a rotating packed bed. The factors of mass transfer rate, liquid hold-up, gas, mass and energy balance were considered (Li et al., 2017). MD can be conducted at low pressure and temperature. The selection of membrane materials is a tremendous challenge as membrane fabrication requires high energy, technology, and manufacturing costs.

5. Bioethanol as biofuel and other applications

Bioethanol is a colourless, flammable, polar solvent and deemed non toxic. Ethanol has vapour density of 1.59 and a specific density of 0.79. Ethanol exhibits a flash point of 55°F, the boiling point of 173°F, auto-ignition temperature of 793°F. Bioethanol provides benefits as a renewable energy source with sustainable production. This high quality of fuel can reduce air pollution and improve automobiles' performance by increasing engine speed and decreasing engine torque. Blending the bioethanol with gasoline shows the differences in smoke and flame characteristics as compared to unblended gasoline. Higher the ethanol content less the visible black smoke and orange flame formation. The energy density is lower than gasoline, which determines higher amounts of fuel required in volume and mass to perform a corresponding work. The octane number of bioethanol is higher than gasoline, allowing an engine to raise its compression ratio and thermal efficiency. Thus, bioethanol is an alternative for petrol in automobiles and can be mixed with gasoline.

Bioethanol is used in many forms. For example, 5%–10% ethanol is added to diesel for diesel engines, 10%–85% ethanol is mixed with petrol for internal combustion engines, and 1%–100% ethanol is substituted with petrol for flexible fuel vehicles. The number of flexible-fuel vehicles on the roads has continuously increased. In Latin America, the sales reached 400,000 vehicles per year and about 1,500,000 in the United States. Meanwhile, Europe and Sweden recorded 15,000 vehicles fuelled with 85% ethanol (E85) (Khuong et al., 2016). Bioethanol is a transportation fuel used directly or combined with gasoline, known as gasohol. In India, E10 is the most common bioethanol blend containing 10% ethanol and 90% gasoline. Meanwhile, Brazil used a blend of 24% ethanol and 76% gasoline. Bioethanol provides 35% more oxygen content than gasoline, which provides efficient combustion in the vehicle engine, resulting in decreased NO_X, hydrocarbons, and particle emission values. The subsequent combustion CO_2 is not an extra released gas to the environment. The CO_2 emission is captured by plants and used in photosynthesis reactions. Thus, there is no rise in net CO_2 amount in the atmosphere.

In the bioethanol production process, the performance of ethanol from various feedstocks is assessed in terms of process efficiency, defined as the ratio of the energy content of ethanol produced to energy content of the biomass. The process is also used to evaluate greenhouse gas (GHG) emission reduction. The commercial process based on simple pre-treatment of feedstock and fermentation of the juice of sugarcane and corn grain achieves an energy efficiency of 41% and 62% with GHG reduction of 82% and 35%–56%. The pre-treatment method is substituted with coproducts like distillers grains during dry grind in the ethanol production plant. Lignocellulosic material with pre-treatment and fermentation like simultaneous saccharification and co-fermentation have 35%–48% ethanol efficiency with 10% power produced from residues and GHG reduction of 83%–88% depending on the coproduct used (Badwal et al., 2015). The summary of commercial feed stocks used for ethanol production process with efficiency and GHG emission reduction by utilising the coproducts for supplementing the heat process or using coproduct as an animal feed compared to using total process energy from fossil fuels is described in Table 4.

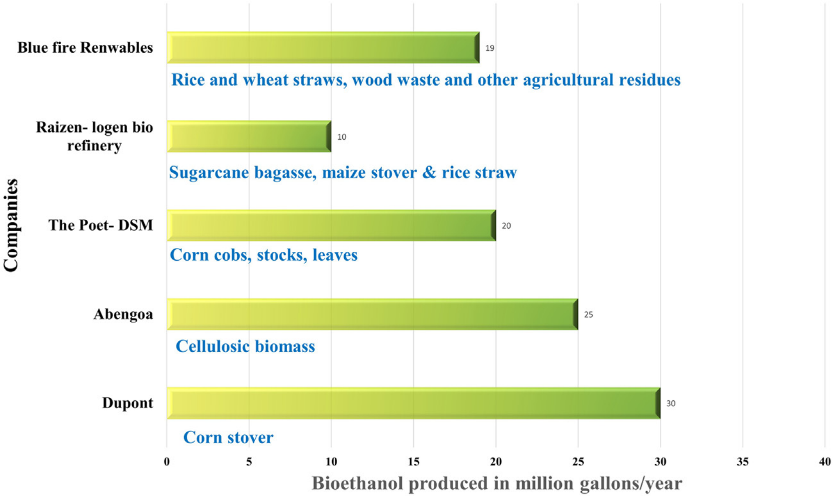

Fig. 7. Sources used by companies to produce bioethanol.

World major companies and commercial plants used for bioethanol production as biofuel is described in Fig. 7. In Brazil, sugarcane is used as feed stock to produce 193 million gallons/year of bioethanol by BP company. Other company Algenol biotech produced 253 million gallons/year of bioethanol using algae in Florida (Pandiyan et al., 2019).

The most common fuels utilised by flexible fuel vehicles (FFV) are unleaded gasoline and ethanol fuel. Ethanol fuel is used in blends with gasoline from 5%–85%. The most common blends are E85 (85% bioethanol, 15% gasoline), E20 and E10. Blends with a higher bioethanol concentration are used in FFV that can operate the mixtures until 85% bioethanol (E85). Bioethanol is converted into ethyl tertiary butyl ether (ETBE) with a 15% blend with gasoline (Sarris and Papanikolaou, 2016). Anhydrous ethanol is approximately 10 per cent useable in traditional combustion vehicles, while blends are 100 per cent in flexible fuel engines. Ethanol is used on fuel cell vehicles to avoid combustion pollution and reduce greenhouse gas emissions. In indirect ethanol fuel cells, ethanol is converted to hydrogen and CO utilised as a fuel in high temperature fuel cells (solid oxide or molten carbonate). At low-temperature fuel cells like polymer electrolyte membrane fuel cells (PEMFC), the CO is converted to hydrogen and carbon dioxide by water gas shift reaction and cleaned to bring CO level below 10 ppm before feeding to fuel cells. In direct ethanol fuel cells (DEFC), ethanol in anhydrous or diluted or vapourised form is directly fed to the anode chamber, and the air is supplied to the cathode chamber of the cell. Ethanol at the electrode/electrolyte interface is oxidised to form protons, CO_2 and electrons besides intermediates/partially oxidised products such as acetaldehyde and acetic acid. Protons are transported through the membrane and electrons flow through the electrical circuit. The transported protons react with oxygen in air at cathode/electrolyte interface to form water. In Direct ethanol fuel cells (DEFC), ethanol is used in the fuel cell instead of methanol. As, the ethanol is a hydrogen rich liquid with higher specific energy of 8.0 kWh/kg than methanol (6.1 kWh/kg). Ethanol utilisation would overcome hydrogen's storage and infrastructure challenges for fuel cell applications (Badwal et al., 2015).

Ethanol is used in medicines like acetaminophen, iron supplements, ranitidine, furosemide, mannitol, phenobarbital, trimethoprism/sulfamethoxazole, and cough medicine. Ethanol is the alcohol used in alcoholic drinks such as beer, brandy or whiskey. Ethanol is soluble in water and is an ideal solvent for various products like perfumes, deodorants, hair sprays, and industrial items such as lacquers, varnishes and paints. Ethanol prevents oily and watery layers from separation by forming an emulsion.

Ethanol is also used in cosmetics, de-icers, drugs, lacquers, polishes, plastics, plasticisers, mouthwashes, liniments, and window cleaners. Other critical ethanol applications in medicine are a topical anti-infective drug and an antidote for methanol and ethylene glycol poisoning. Ethanol is a solvent to dissolve polar and non-polar compounds and as an intermediate to produce chemicals like acetic acid, diethyl ether, ethyl amines, and ethyl esters. Ethanol is used to produce hand sanitisers and medicinal wipes due to its antibacterial and antifungal properties. Ethanol is used as antiseptics and disinfectants that kill organisms by denaturing their proteins and dissolving their lipids effectively against bacteria, fungi, and viruses. The ethanol-based hand sanitiser is utilised in the pandemic covid-19 situation. Ethanol can be used as rocket fuel in a bio-propellant rocket.

6. Current challenges and opportunities

Energy demand is increasing in many countries, and their high usage of fossil fuels substantially causes environmental pollution and threatens sustainability. There is a need for significant alternative fuel to gasoline; bioethanol. It is a clean, domestic, and renewable fuel similar to gasoline and supports national and global sustainability. Since there is substantial demand for bioethanol in the global market, it has become essential to ensure a systematic, continuous supply of cheap and abundant feedstock to produce bioethanol from renewable resources. However, bioethanol will not be enough to match the energy demand by a sharp increase in population and vehicles and depleting natural resources. But with each generation source of bioethanol, there is an advancement in technology with increasing production potential. Agriculture products used in the first-generation bioethanol that lead to second-generation bioethanol to avoid use of food raw materials for public. Lignocellulosic biomass enables this opportunity and became prominent due to its inexpensiveness. However, pre-treatment and obtaining carbohydrate source is harder than sugar/starch containing biomass. The fine tuning of pre-treatment for different biomass types and development of the economically viable process is required. Hence parameters are optimised to obtain higher ethanol production from lignocellulosic materials. Third-generation bioethanol production is involved in the exploration of algae due to the high content of carbohydrates. Algenol biofuels Inc. developed technology to utilise sunlight trapping microalgal cells as a tiny biorefinery for ethanol production helped by photobioreactors and claimed to produce 6000 gallons of ethanol per acre per year.

Waste utilisation is the most economical process for renewable energy production coupled with benefit the environment. Significant biomass residues and wastes are inevitably produced from different sectors across world. Wastes are the promising feed stock for bioenergy if efficient and economically viable technologies were developed. The biodiesel industry produces 10 wt% of crude glycerol remained as waste. The opportunity of glycerol waste can be converted to bioethanol via a fermentation process using microbes. Glycerol is a good carbon source to transform into ethanol. The production of ethanol depends on pH, transportation of metabolites within and outside the cell, temperature etc. Despite high yields from glycerol fermentation, the slow consumption rates of glycerol and unfavourable productivities are major drawbacks unsuitable for industrialisation. However, the microorganisms such as *E. coli* can be easily altered genetically for large scale application through metabolic engineering.

By 2030, the global vehicle number is expected to be around 1.3 billion, drastically affecting oil reserves and energy demand. Therefore, bioethanol must be produced as a sustainable source of energy and their costs should compete with petrol and diesel. This will ensure a huge market for fuel and take care of hazardous emissions and other environmental issues. Develop a strategy for crop rotation, utilising the agricultural residues and industrial waste and cost optimisation. This requires the national government to adopt special policies regarding relief the taxes, agricultural-based policies and subsidies and proper fuel mandates to encourage bioethanol industries. The biofuel producers have no direct access to customers. Hence, the government should supply different biofuel blends and advertise the benefits of biofuel at petrol/diesel stations. Carbon dioxide emission of fossil fuels and biofuels to the costumers are informed about exemplifying the benefits of biofuels compared to fossil fuel.

7. Conclusion

Bioethanol is one of the best alternative solutions in the attempt to overcome energy and environmental crisis. Bioethanol is an alternative energy source to fossil fuels. Many sources from food crops, agriculture biomass, woody biomass, forest waste and algae biomass are converted into bioethanol. Crude glycerol, an industrial biodiesel byproduct generated, can be efficiently utilised to produce bioethanol. The biological conversion of crude glycerol produces higher-value chemicals. However, there are different methods used for the conversion of crude glycerol into ethanol. Still, there is a need to develop the suitable process of unrefined glycerol to bioethanol from biodiesel processing in large-scale industries to establish eco-friendly and cost-efficient technology. Besides this, some key findings include crude glycerol without pre-treatment by a fermentation process using microorganisms to produce higher bioethanol conversion. The bioethanol utility improves the efficiency of an SI engine and reduces the emission of GHGs to a greater extent to maintain sustainability.

CRediT authorship contribution statement

Chaitanya Reddy Chilakamarry: Conception and design of study, Acquisition of data, Writing – original draft. **A.M. Mimi Sakinah:** Analysis and/or interpretation of data, Writing – original draft, Writing – review & editing. **A.W. Zularisam:** Writing – original draft, Writing – review & editing. **Ashok Pandey:** Analysis and/or interpretation of data, Writing – original draft, Writing – review & editing. **Dai-Viet N. Vo:** Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Aditiya, H.B., Mahlia, T.M.I., Chong, W.T., Nur, H., Sebayang, A.H., 2016. Second generation bioethanol production: A critical review. Renew. Sustain. Energy Rev. 66, 631–653. http://dx.doi.org/10.1016/J.RSER.2016.07.015.

Albert, M.J., 2020. Beyond continuationism: climate change, economic growth, and the future of world (dis)order. http://dx.doi.org/10.1080/09557571.2020.1825334.

Alfonsín, V., Maceiras, R., Gutiérrez, C., 2019. Bioethanol production from industrial algae waste. Waste Manage. 87, 791–797. http://dx.doi.org/10.1016/J.WASMAN.2019.03.019.

Ali, S., Paul Peter, A., Chew, K.W., Munawaroh, H.S.H., Show, P.L., 2021. Resource recovery from industrial effluents through the cultivation of microalgae: A review. Bioresour. Technol. 337, 125461. http://dx.doi.org/10.1016/J.BIORTECH.2021.125461.

de Araujo Guilherme, A., Dantas, P.V.F., Padilha, C.E.de.A., dos Santos, E.S., de Macedo, G.R., 2019. Ethanol production from sugarcane bagasse: Use of different fermentation strategies to enhance an environmental-friendly process. J. Environ. Manag. 234, 44–51. http://dx.doi.org/10.1016/J.JENVMAN.2018.12.102.

Aziati, N.N., Sakinah, M., 2018. Efficient production of succinic acid in immobilized fermentation with crude glycerol from Escherichia coli. J. Homepage 2, 110–118. http://dx.doi.org/10.26656/fr.2017.2(1).156.

Badwal, S.P.S., Giddey, S., Kulkarni, A., Goel, J., Basu, S., 2015. Direct ethanol fuel cells for transport and stationary applications – A comprehensive review. Appl. Energy C 8, 0–103. http://dx.doi.org/10.1016/J.APENERGY.2015.02.002.

Balakrishnan, D., Kumar, S.S., Sugathan, S., 2019. Amylases for food applications—Updated information. In: Energy, Environment, and Sustainability. Springer, Singapore, pp. 199–227. http://dx.doi.org/10.1007/978-981-13-3263-0_11.

Banerjee, S., Sen, R., Pandey, R.A., Chakrabarti, T., Satpute, D., Giri, B.S., Mudliar, S., 2009. Evaluation of wet air oxidation as a pretreatment strategy for bioethanol production from rice husk and process optimization. Biomass Bioenergy 33, 1680–1686. http://dx.doi.org/10.1016/J.BIOMBIOE.2009.09.001.

Barbosa, T.P., Eckert, J.J., Roso, V.R., Pujatti, F.J.P., da Silva, L.A.R., Horta Gutiérrez, J.C., 2021. Fuel saving and lower pollutants emissions using an ethanol-fueled engine in a hydraulic hybrid passengers vehicle. Energy 235, 121361. http://dx.doi.org/10.1016/J.ENERGY.2021.121361.

Ben Atitallah, I., Antonopoulou, G., Ntaikou, I., Alexandropoulou, M., Nasri, M., Mechichi, T., Lyberatos, G., 2019. On the evaluation of different saccharification schemes for enhanced bioethanol production from potato peels waste via a newly isolated yeast strain of wickerhamomyces anomalus. Bioresour. Technol. 289, 121614. http://dx.doi.org/10.1016/J.BIORTECH.2019.121614.

Boboescu, I.Z., Damay, J., Chang, J.K.W., Beigbeder, J.B., Duret, X., Beauchemin, S., Lalonde, O., Lavoie, J.M., 2019. Ethanol production from residual lignocellulosic fibers generated through the steam treatment of whole sorghum biomass. Bioresour. Technol. 292, 121975. http://dx.doi.org/10.1016/J.BIORTECH.2019.121975.

Boboescu, I.Z., Gélinas, M., Beigbeder, J.B., Lavoie, J.M., 2018. High-efficiency second generation ethanol from the hemicellulosic fraction of softwood chips mixed with construction and demolition residues. Bioresour. Technol. 266, 421–430. http://dx.doi.org/10.1016/J.BIORTECH.2018.06.056.

Bórawski, P., Bełdycka-Bórawska, A., Szymańska, E.J., Jankowski, K.J., Dubis, B., Dunn, J.W., 2019. Development of renewable energy sources market and biofuels in the European Union. J. Clean. Prod. 228, 467–484. http://dx.doi.org/10.1016/J.JCLEPRO.2019.04.242.

Brant, L.M.S., de Freitas Júnior, J.E., Pereira, F.M., Pina, D.S., Santos, S.A., Leite, L.C., Cirne, L.G.A., Alba, H.D.R., de Araújo, M.L.G.M.L., Pimentel, P.R.S., de Carvalho, G.G.P., 2021. Effects of alternative energy and protein sources on performance, carcass characteristics, and meat quality of feedlot lambs. Livest. Sci. 104611. http://dx.doi.org/10.1016/J.LIVSCI.2021.104611.

Brasil, M.A.S., Gomes, L.H., Kamogawa, M.Y., Basso, L.C., 2020. Ethanol determination in fermented sugarcane substrates by a diffusive micro-distillation device. J. Microbiol. Methods 178, 106085. http://dx.doi.org/10.1016/J.MIMET.2020.106085.

Buchori, L., Djaeni, M., Ratnawati, R., Retnowati, D.S., Hadiyanto, H., Anggoro, D.D., 2020. Glycerolysis using KF/CAO-mgo catalyst: Optimisation and reaction kinetics. J. Teknol. 82, 109–116. http://dx.doi.org/10.11113/JT.V82.14585.

Burniol-Figols, A., Cenian, K., Skiadas, I.V., Gavala, H.N., 2016. Integration of chlorogenic acid recovery and bioethanol production from spent coffee grounds. Biochem. Eng. J. 116, 54–64. http://dx.doi.org/10.1016/J.BEJ.2016.04.025.

Ccopa Rivera, E., Yamakawa, C.K., Saad, M.B.W., Atala, D.I.P., Ambrosio, W.B., Bonomi, A., Junior, J., Rossell, C.E.V., 2017. Effect of temperature on sugarcane ethanol fermentation: Kinetic modeling and validation under very-high-gravity fermentation conditions. Biochem. Eng. J. 119, 42–51. http://dx.doi.org/10.1016/J.BEJ.2016.12.002.

Ćetković, J., Lakić, S., Živković, A., Žarković, M., Vujadinović, R., 2021. Economic analysis of measures for GHG emission reduction. Sustain 13 (2021), http://dx.doi.org/10.3390/SU13041712, 13, 1712.

Cha, Y.L., Yang, J., Park, Y., An, G.H., Ahn, J.W., Moon, Y.H., Yoon, Y.M., Yu, G.D., Choi, I.H., 2015. Continuous alkaline pretreatment of miscanthus sacchariflorus using a bench-scale single screw reactor. Bioresour. Technol. 181, 338–344. http://dx.doi.org/10.1016/J.BIORTECH.2015.01.079.

Chaitanya Reddy, C., Khilji, I.A., Gupta, A., Bhuyar, P., Mahmood, S., Saeed AL-Japairai, K.A., Chua, G.K., 2021. Valorization of keratin waste biomass and its potential applications. J. Water Process Eng. 40, 101707. http://dx.doi.org/10.1016/j.jwpe.2020.101707.

Chaudhary, N., Ngadi, M.O., Simpson, B., 2012. Comparison of glucose, glycerol and crude glycerol fermentation by escherichia coli K12. J. Bioprocess. Biotech. http://dx.doi.org/10.4172/2155-9821.S1-001.

Chen, H., Cai, D., Chen, C., Wang, J., Qin, P., Tan, T., 2018a. Novel distillation process for effective and stable separation of high-concentration acetone–butanol–ethanol mixture from fermentation–pervaporation integration process. Biotechnol. Biofuels 111 (2018), 11. http://dx.doi.org/10.1186/S13068-018-1284-8, 1–13.

Chen, W.C., Lin, Y.C., Ciou, Y.L., Chu, I.M., Tsai, S.L., Lan, J.C.W., Chang, Y.K., Wei, Y.H., 2017. Producing bioethanol from pretreated-wood dust by simultaneous saccharification and co-fermentation process. J. Taiwan Inst. Chem. Eng. 79, 43–48. http://dx.doi.org/10.1016/J.JTICE.2017.04.025.

Chen, W.H., Lo, H.J., Yu, K.L., Ong, H.C., Sheen, H.K., 2021. Valorization of sorghum distillery residue to produce bioethanol for pollution mitigation and circular economy. Environ. Pollut. 285, 117196. http://dx.doi.org/10.1016/J.ENVPOL.2021.117196.

Chen, S., Xu, Z., Li, X., Yu, J., Cai, M., Jin, M., 2018b. Integrated bioethanol production from mixtures of corn and corn stover. Bioresour. Technol. 258, 18–25. http://dx.doi.org/10.1016/J.BIORTECH.2018.02.125.

Chilakamarry, C.R., Mahmood, S., Saffe, S.N.B.M., Arifin, M.A.B., Gupta, A., Sikkandar, M.Y., Begum, S.S., Narasaiah, B., 2021a. Extraction and application of keratin from natural resources: a review. Biotech 3, 11. http://dx.doi.org/10.1007/s13205-021-02734-7.

Chilakamarry, Chaitanya Reddy, Sakinah, A.M.M., Zularisam, A.W., Pandey, A., 2021b. Glycerol waste to value added products and its potential applications. Syst. Microbiol. Biomanufacturing 2. http://dx.doi.org/10.1007/s43393-021-00036-w.

Cho, D.H., Shin, S.J., Bae, Y., Park, C., Kim, Y.H., 2011. Ethanol production from acid hydrolysates based on the construction and demolition wood waste using Pichia stipitis. Bioresour. Technol. 102, 4439–4443. http://dx.doi.org/10.1016/J.BIORTECH.2010.12.094.

Choi, W.J., Hartono, M.R., Chan, W.H., Yeo, S.S., 2011. Ethanol production from biodiesel-derived crude glycerol by newly isolated Kluyvera cryocrescens. Appl. Microbiol. Biotechnol. 89, 1255–1264. http://dx.doi.org/10.1007/s00253-010-3076-3.

Chol, C.G., Dhabhai, R., Dalai, A.K., Reaney, M., 2018. Purification of crude glycerol derived from biodiesel production process: Experimental studies and techno-economic analyses. Fuel Process. Technol. 178, 78–87. http://dx.doi.org/10.1016/J.FUPROC.2018.05.023.

Chong, T.Y., Cheah, S.A., Ong, C.T., Wong, L.Y., Goh, C.R., Tan, I.S., Foo, H.C.Y., Lam, M.K., Lim, S., 2020. Techno-economic evaluation of third-generation bioethanol production utilizing the macroalgae waste: A case study in Malaysia. Energy 210, 118491. http://dx.doi.org/10.1016/J.ENERGY.2020.118491.

Chong, C.T., Loe, T.Y., Wong, K.Y., Ashokkumar, V., Lam, S.S., Chong, W.T., Borrion, A., Tian, B., Ng, J.H., 2021. Biodiesel sustainability: The global impact of potential biodiesel production on the energy–water–food (EWF) nexus. Environ. Technol. Innov. 22, 101408. http://dx.doi.org/10.1016/j.eti.2021.101408.

Chowdhary, K., Prasad, U., Sharma, S., 2018. Role of Fungi in Biorefinery: A Perspective. Springer, Cham, pp. 1–20. http://dx.doi.org/10.1007/978-3-319-90379-8_1.

Chozhavendhan, S., Devi, G.K., Jayamuthunagai, J., Bharathiraja, B., Kumar, R.P., Raman, J.K., 2019. Conversion of Glycerol to Valuable Products, Horizons in Bioprocess Engineering. Springer, Cham, http://dx.doi.org/10.1007/978-3-030-29069-6_8.

Cofré, O., Ramírez, M., Gómez, J.M., Cantero, D., 2016. Pilot scale fed-batch fermentation in a closed loop mixed reactor for the biotransformation of crude glycerol into ethanol and hydrogen by Escherichia coli MG1655. Biomass Bioenergy 91, 37–47. http://dx.doi.org/10.1016/J.BIOMBIOE.2016.04.015.

Cripwell, R.A., Favaro, L., Viljoen-Bloom, M., van Zyl, W.H., 2020. Consolidated bioprocessing of raw starch to ethanol by Saccharomyces cerevisiae: Achievements and challenges. Biotechnol. Adv. 42, 107579. http://dx.doi.org/10.1016/J.BIOTECHADV.2020.107579.

Ethier, S.E., 2010. Producing omega-3 polyunsaturated fatty acids from biodiesel waste glycerol by microalgae fermentation.

Fernandes, B.S., Dias, O., Costa, G., Neto, A.A.K., Resende, T.F.C., Oliveira, J.V.C., Riaño Pachón, D.M., Zaiat, M., Pradella, J.G.C., Rocha, I., 2019. Genome-wide sequencing and metabolic annotation of Pythium irregulare CBS 494.86: understanding eicosapentaenoic acid production. BMC Biotechnol. 191, 19. http://dx.doi.org/10.1186/S12896-019-0529-3, 1–17.

Gahlawat, G., Soni, S.K., 2017. Valorization of waste glycerol for the production of poly (3-hydroxybutyrate) and poly (3-hydroxybutyrate-co-3-hydroxyvalerate) copolymer by Cupriavidus necator and extraction in a sustainable manner. Bioresour. Technol. 243, 492–501. http://dx.doi.org/10.1016/j.biortech.2017.06.139.

Gatti, M.N., Cerioni, J.L., Pompeo, F., Santori, G.F., Nichio, N.N., 2020. High yield to 1-propanol from crude glycerol using two reaction steps with Ni catalysts. Catal 10 (2020), 615. http://dx.doi.org/10.3390/CATAL10060615, 10, 615.

Gu, Y., Zhang, Y., Zhou, X., 2015. Effect of Ca(OH)2 pretreatment on extruded rice straw anaerobic digestion. Bioresour. Technol. 196, 116–122. http://dx.doi.org/10.1016/J.BIORTECH.2015.07.004.

Gumienna, M., Szwengiel, A., Lasik, M., Szambelan, K., Majchrzycki, D., Adamczyk, J., Nowak, J., Czarnecki, Z., 2016. Effect of corn grain variety on the bioethanol production efficiency. Fuel 164, 386–392. http://dx.doi.org/10.1016/J.FUEL.2015.10.033.

Guo, Z., Zhang, Q., You, T., Ji, Z., Zhang, X., Qin, Y., Xu, F., 2019. Heteropoly acids enhanced neutral deep eutectic solvent pretreatment for enzymatic hydrolysis and ethanol fermentation of Miscanthus x giganteus under mild conditions. Bioresour. Technol. 293, 122036. http://dx.doi.org/10.1016/J.BIORTECH.2019.122036.

Hassan, S.S., Williams, G.A., Jaiswal, A.K., 2018. Emerging technologies for the pretreatment of lignocellulosic biomass. Bioresour. Technol. 262, 310–318. http://dx.doi.org/10.1016/J.BIORTECH.2018.04.099.

He, S., Muizebelt, I., Heeres, A., Schenk, N.J., Blees, R., Heeres, H.J., 2018. Catalytic pyrolysis of crude glycerol over shaped ZSM-5/bentonite catalysts for bio-BTX synthesis. Appl. Catal. B Environ. 235, 45–55. http://dx.doi.org/10.1016/J.APCATB.2018.04.047.

Hernández, F., Orengo, J., Villodre, C., Martínez, S., López, M.J., Madrid, J., 2016. Addition of crude glycerin to pig diets: sow and litter performance, and metabolic and feed intake regulating hormones. Animal 10, 919–926. http://dx.doi.org/10.1017/S175173111500275X.

Himma, N.F., Anisah, S., Prasetya, N., Wenten, I.G., 2016. Advances in preparation, modification, and application of polypropylene membrane. J. Polym. Eng. 36, 329–362. http://dx.doi.org/10.1515/POLYENG-2015-0112.

Hiremath, A., Kannabiran, M., Rangaswamy, V., 2011. 1, 3-propanediol production from crude glycerol from jatropha biodiesel process. N. Biotechnol. 28, 19–23. http://dx.doi.org/10.1016/J.NBT.2010.06.006.

Hung, H., chai, Adeni, Dayang Salwani Awang Johnny, Q., Vincent, M., 2018. Production of bioethanol from sago hampas via Simultaneous Saccharification and Fermentation (SSF). Nusant. Biosci. 10, 240–245. http://dx.doi.org/10.13057/NUSBIOSCI/N100407.

Jiao, J., Li, J., Bai, Y., 2019. Uncertainty analysis in the life cycle assessment of cassava ethanol in China. J. Clean. Prod. 206, 438–451. http://dx.doi.org/10.1016/J.JCLEPRO.2018.09.199.

Jönsson, L.J., Martín, C., 2016. Pretreatment of lignocellulose: Formation of inhibitory by-products and strategies for minimizing their effects. Bioresour. Technol. 199, 103–112. http://dx.doi.org/10.1016/J.BIORTECH.2015.10.009.

Jutakridsada, P., Saengprachatanarug, K., Kasemsiri, P., Hiziroglu, S., Kamwilaisak, K., Chindaprasirt, P., 2017. Bioconversion of saccharum officinarum leaves for ethanol production using separate hydrolysis and fermentation processes. Waste Biomass Valoriz. 104 (2017), 10. http://dx.doi.org/10.1007/S12649-017-0104-X, 817–825.

Kalia, V.C., Prakash, J., Koul, S., 2016. Biorefinery for glycerol rich biodiesel industry waste. Indian J. Microbiol. 562 (2016), 56. http://dx.doi.org/10.1007/S12088-016-0583-7, 113–125.

Kancelista, A., Chmielewska, J., Korzeniowski, P., Łaba, W., 2020. Bioconversion of sweet sorghum residues by trichoderma citrinoviride C1 enzymes cocktail for effective bioethanol production. Catal 10 (2020), 1292. http://dx.doi.org/10.3390/CATAL10111292, 10, 1292.

Katsimpouras, C., Christakopoulos, P., Topakas, E., 2016. Acetic acid-catalyzed hydrothermal pretreatment of corn stover for the production of bioethanol at high-solids content. Bioprocess Biosyst. Eng. 399 (2016), 39. http://dx.doi.org/10.1007/S00449-016-1618-5, 1415–1423.

Khattab, S.M.R., Watanabe, T., 2021. Metabolic engineering of saccharomyces cerevisiae for efficient conversions of glycerol to ethanol. http://dx.doi.org/10.1101/2021.01.04.425180, bioRxiv 2021.01.04.425180.

Kholif, A.E., 2019. Glycerol use in dairy diets: A systemic review. Anim. Nutr. 5, 209–216. http://dx.doi.org/10.1016/J.ANINU.2019.06.002.

Khuong, L.S., Zulkifli, N.W.M., Masjuki, H.H., Mohamad, E.N., Arslan, A., Mosarof, M.H., Azham, A., 2016. A review on the effect of bioethanol dilution on the properties and performance of automotive lubricants in gasoline engines. RSC Adv. 6, 66847–66869. http://dx.doi.org/10.1039/C6RA10003A.

Kim, E.J., Kim, S., Choi, H.-G., Han, S.J., 2020. Co-production of biodiesel and bioethanol using psychrophilic microalga Chlamydomonas sp. KNM0029C isolated from Arctic sea ice. Biotechnol. Biofuels 131, 13. http://dx.doi.org/10.1186/S13068-020-1660-Z, 1–13.

Kim, S.J., Kim, T.H., Oh, K.K., 2018. Deacetylation followed by fractionation of yellow poplar sawdust for the production of toxicity-reduced hemicellulosic sugar for ethanol fermentation. Energies 11 (2018), 404. http://dx.doi.org/10.3390/EN11020404, 11, 404.

Kim, H.M., Oh, C.H., Bae, H.J., 2017. Comparison of red microalgae (Porphyridium cruentum) culture conditions for bioethanol production. Bioresour. Technol. 233, 44–50. http://dx.doi.org/10.1016/J.BIORTECH.2017.02.040.

Kot, A.M., Błażejak, S., Kurcz, A., Gientka, I., Kieliszek, M., 2016. Rhodotorula glutinis—potential source of lipids, carotenoids, and enzymes for use in industries. Appl. Microbiol. Biotechnol. 100, 6103. http://dx.doi.org/10.1007/S00253-016-7611-8.

Kothari, R., Vashishtha, A., Singh, H.M., Pathak, V.V., Tyagi, V.V., Yadav, B.C., Ashokkumar, V., Singh, D.P., 2020. Assessment of Indian bioenergy policy for sustainable environment and its impact for rural India: Strategic implementation and challenges. Environ. Technol. Innov. 20, 101078. http://dx.doi.org/10.1016/J.ETI.2020.101078.

Kumar, V., Park, S., 2018. Potential and limitations of Klebsiella pneumoniae as a microbial cell factory utilizing glycerol as the carbon source. Biotechnol. Adv. 36, 150–167. http://dx.doi.org/10.1016/j.biotechadv.2017.10.004.

Kumari, D., Singhal, B., 2019. Recent Advancements in Mycodegradation of Lignocellulosic Biomass for Bioethanol Production. Springer, Cham, http://dx.doi.org/10.1007/978-3-030-23834-6_9.

Kut, A., Demiray, E., Karatay, S.E., Dönmez, G., 2020. Second generation bioethanol production from hemicellulolytic hydrolyzate of apple pomace by Pichia stipitis. http://dx.doi.org/10.1080/15567036.2020.1838000.

Lee, J.H., Yoo, H.Y., Lee, S.K., Chun, Y., Kim, H.R., Bankeeree, W., Lotrakul, P., Punnapayak, H., Prasongsuk, S., Kim, S.W., 2020. Significant impact of casein hydrolysate to overcome the low consumption of glycerol by Klebsiella aerogenes ATCC 29007 and its application to bioethanol production. Energy Convers. Manag. 221, 113181. http://dx.doi.org/10.1016/J.ENCONMAN.2020.113181.

Li, Y., Cui, J., Zhang, G., Liu, Z., Guan, H., Hwang, H., Aker, W.G., Wang, P., 2016. Optimization study on the hydrogen peroxide pretreatment and production of bioethanol from seaweed Ulva prolifera biomass. Bioresour. Technol. 214, 144–149. http://dx.doi.org/10.1016/J.BIORTECH.2016.04.090.

Li, W., Song, B., Li, X., Liu, Y., 2017. Modelling of vacuum distillation in a rotating packed bed by Aspen. Appl. Therm. Eng. 117, 322–329. http://dx.doi.org/10.1016/J.APPLTHERMALENG.2017.01.046.

Lu, X., Xi, B., Zhang, Y., Angelidaki, I., 2011. Microwave pretreatment of rape straw for bioethanol production: Focus on energy efficiency. Bioresour. Technol. 102, 7937–7940. http://dx.doi.org/10.1016/J.BIORTECH.2011.06.065.

Luiza Astolfi, A., Rempel, A., Cavanhi, V.A.F., Alves, M., Deamici, K.M., Colla, L.M., Costa, J.A.V., 2020. Simultaneous saccharification and fermentation of Spirulina sp. and corn starch for the production of bioethanol and obtaining biopeptides with high antioxidant activity. Bioresour. Technol. 301, 122698. http://dx.doi.org/10.1016/J.BIORTECH.2019.122698.

Mahmoodi, P., Karimi, K., Taherzadeh, M.J., 2018. Efficient conversion of municipal solid waste to biofuel by simultaneous dilute-acid hydrolysis of starch and pretreatment of lignocelluloses. Energy Convers. Manag. 166, 569–578. http://dx.doi.org/10.1016/J.ENCONMAN.2018.04.067.

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

Manowattana, A., Techapun, C., Watanabe, M., Chaiyaso, T., 2018. Bioconversion of biodiesel-derived crude glycerol into lipids and carotenoids by an oleaginous red yeast Sporidiobolus pararoseus KM281507 in an airlift bioreactor. J. Biosci. Bioeng. 125, 59–66. http://dx.doi.org/10.1016/J.JBIOSC.2017.07.014.

Martín, C., Thomsen, M.H., Hauggaard-Nielsen, H., BelindaThomsen, A., 2008. Wet oxidation pretreatment, enzymatic hydrolysis and simultaneous saccharification and fermentation of clover–ryegrass mixtures. Bioresour. Technol. 99, 8777–8782. http://dx.doi.org/10.1016/J.BIORTECH.2008.04.039.

Maru, B.T., López, F., Kengen, S.W.M., Constantí, M., Medina, F., 2016. Dark fermentative hydrogen and ethanol production from biodiesel waste glycerol using a co-culture of Escherichia coli and Enterobacter sp. Fuel 186, 375–384. http://dx.doi.org/10.1016/J.FUEL.2016.08.043.

Mazaheri, D., Orooji, Y., Mazaheri, M., Moghaddam, M.S., Karimi-Maleh, H., 2021. Bioethanol production from pomegranate peel by simultaneous saccharification and fermentation process. Biomass Convers. Biorefinery 2021, 1–9. http://dx.doi.org/10.1007/S13399-021-01562-2.

Mendoza Martinez, C.L., Saari, J., Melo, Y., Cardoso, M., de Almeida, G.M., Vakkilainen, E., 2021. Evaluation of thermochemical routes for the valorization of solid coffee residues to produce biofuels: A Brazilian case. Renew. Sustain. Energy Rev. 137, 110585. http://dx.doi.org/10.1016/J.RSER.2020.110585.

Methrath Liyakathali, N.A., Muley, P.D., Aita, G., Boldor, D., 2016. Effect of frequency and reaction time in focused ultrasonic pretreatment of energy cane bagasse for bioethanol production. Bioresour. Technol. 200, 262–271. http://dx.doi.org/10.1016/J.BIORTECH.2015.10.028.

Mikulski, D., Kłosowski, G., 2020. Microwave-assisted dilute acid pretreatment in bioethanol production from wheat and rye stillages. Biomass Bioenergy 136, 105528. http://dx.doi.org/10.1016/J.BIOMBIOE.2020.105528.

Mohanty, S.K., Swain, M.R., 2019. Bioethanol production from corn and wheat: Food, fuel, and future. Bioethanol Prod. Food Crop. 45–59. http://dx.doi.org/10.1016/B978-0-12-813766-6.00003-5.

Muhamad, A., Noor, S.F.M., Syahirah, N., Hamid, A.I., Zaidi, M.A.H.M., 2021. Physical factors optimization of saccharomyces cerevisiae fermentation to enhance production of bioethanol: A review. Multidiscip. Appl. Res. Innov 2, 266–277.

Naidu, D.S., Hlangothi, S.P., John, M.J., 2018. Bio-based products from xylan: A review. Carbohydr. Polym. 179, 28–41. http://dx.doi.org/10.1016/J.CARBPOL.2017.09.064.

Nazato, C., Romero, A.de.C., Abdalla, A.L., 2019. Determination of methanol residues in crude glycerol for animal feed by gas chromatography. Sci. Agric. 76, 527–531. http://dx.doi.org/10.1590/1678-992X-2017-0362.

Ngamsirisomsakul, M., Reungsang, A., Liao, Q., Kongkeitkajorn, M.B., 2019. Enhanced bio-ethanol production from Chlorella sp. biomass by hydrothermal pretreatment and enzymatic hydrolysis. Renew. Energy 141, 482–492. http://dx.doi.org/10.1016/J.RENENE.2019.04.008.

Niju, S., Nishanthini, T., Balajii, M., 2019. Alkaline hydrogen peroxide-pretreated sugarcane tops for bioethanol production—a process optimization study. Biomass Convers. Biorefinery 101 (2019), 10. http://dx.doi.org/10.1007/S13399-019-00524-Z, 149–165.

Nomanbhay, S., Hussein, R., Ong, M.Y., 2018. Sustainability of biodiesel production in Malaysia by production of bio-oil from crude glycerol using microwave pyrolysis: a review. p. 11. http://dx.doi.org/10.1080/17518253.2018.1444795, http://mc.manuscriptcentral.com/tgcl.

Novais-Eiras, D., de Carvalho, G.G.P., Leite, L.C., Eiras, C.E., Freitas, J.E.de., Pina, D.dos.S., Ferreira, F.G., Santos, G.T.dos., Grande, P.A., 2018. Crude glycerin in the feed supplementation of lactating goats on pasture. Small Rumin. Res. 168, 39–46. http://dx.doi.org/10.1016/J.SMALLRUMRES.2018.09.001.

Nwachukwu, R.E.S., Shahbazi, A., Wang, L., Ibrahim, S., Worku, M., Schimmel, K., 2012. Bioconversion of glycerol to ethanol by a mutant Enterobacter aerogenes. AMB Express 2, 1–6. http://dx.doi.org/10.1186/2191-0855-2-20.

Nwachukwu, R.E.S., Shahbazi, A., Wang, L., Worku, M., Ibrahim, S., Schimmel, K., 2013. Optimization of cultural conditions for conversion of glycerol to ethanol by Enterobacter aerogenes S012. AMB Express 31 (2013), 3. http://dx.doi.org/10.1186/2191-0855-3-12, 1–10.

Oh, B.R., Seo, J.W., Heo, S.Y., Hong, W.K., Luo, L.H., Joe, M., ho Park, D.H., Kim, C.H., 2011. Efficient production of ethanol from crude glycerol by a Klebsiella pneumoniae mutant strain. Bioresour. Technol. 102, 3918–3922. http://dx.doi.org/10.1016/j.biortech.2010.12.007.

Oh, B.R., Seo, J.W., Heo, S.Y., Hong, W.K., Luo, L.H., Kim, S., Kwon, O., Sohn, J.H., Joe, M.H., Park, D.H., Kim, C.H., 2012. Enhancement of ethanol production from glycerol in a Klebsiella pneumoniae mutant strain by the inactivation of lactate dehydrogenase. Process Biochem. 47, 156–159. http://dx.doi.org/10.1016/J.PROCBIO.2011.10.011.

Oumer, A.N., Hasan, M.M., Baheta, A.T., Mamat, R., Abdullah, A.A., 2018. Bio-based liquid fuels as a source of renewable energy: A review. Renew. Sustain. Energy Rev. 88, 82–98. http://dx.doi.org/10.1016/J.RSER.2018.02.022.

Palacios, S., Ruiz, H.A., Ramos-Gonzalez, R., Martínez, J., Segura, E., Aguilar, M., Aguilera, A., Michelena, G., Aguilar, C., Ilyina, A., 2017. Comparison of physicochemical pretreatments of banana peels for bioethanol production. Food Sci. Biotechnol. 264, 26. http://dx.doi.org/10.1007/S10068-017-0128-9, 993–1001.

Pan, Q., Shang, X., Li, J., Ma, S., Li, L., Sun, L., 2019. Energy-efficient separation process and control scheme for extractive distillation of ethanol-water using deep eutectic solvent. Sep. Purif. Technol. 219, 113–126. http://dx.doi.org/10.1016/J.SEPPUR.2019.03.022.

Pandiyan, K., Singh, A., Singh, S., Saxena, A.K., Nain, L., 2019. Technological interventions for utilization of crop residues and weedy biomass for second generation bio-ethanol production. Renew. Energy 132, 723–741. http://dx.doi.org/10.1016/J.RENENE.2018.08.049.

Parveen, F., Hankins, N., 2021. Integration of forward osmosis membrane bioreactor (FO-MBR) and membrane distillation (MD) units for water reclamation and regeneration of draw solutions. J. Water Process Eng. 41, 102045. http://dx.doi.org/10.1016/J.JWPE.2021.102045.

Patsalou, M., Samanides, C.G., Protopapa, E., Stavrinou, S., Vyrides, I., Koutinas, M., 2019. A citrus peel waste biorefinery for ethanol and methane production. Mol 24, 2451. http://dx.doi.org/10.3390/MOLECULES24132451, 24, 2451.

Pradima, J., Kulkarni, M.R., Archna, 2017. Review on enzymatic synthesis of value added products of glycerol, a by-product derived from biodiesel production. Resour. Technol. 3, 394–405. http://dx.doi.org/10.1016/J.REFFIT.2017.02.009.

Raghavi, S., Sindhu, R., Binod, P., Gnansounou, E., Pandey, A., 2016. Development of a novel sequential pretreatment strategy for the production of bioethanol from sugarcane trash. Bioresour. Technol. 199, 202–210. http://dx.doi.org/10.1016/J.BIORTECH.2015.08.062.

Rajendran, N., Gurunathan, B., Han, J., Krishna, S., Ananth, A., Venugopal, K., Sherly Priyanka, R.B., 2021. Recent advances in valorization of organic municipal waste into energy using biorefinery approach, environment and economic analysis. Bioresour. Technol. 125498. http://dx.doi.org/10.1016/J.BIORTECH.2021.125498.

Razmjoo, A., Gakenia Kaigutha, L., Vaziri Rad, M.A., Marzband, M., Davarpanah, A., Denai, M., 2021. A technical analysis investigating energy sustainability utilizing reliable renewable energy sources to reduce CO2 emissions in a high potential area. Renew. Energy 164, 46–57. http://dx.doi.org/10.1016/J.RENENE.2020.09.042.

Remya, N., Swain, A., 2019. Soft drink industry wastewater treatment in microwave photocatalytic system – Exploration of removal efficiency and degradation mechanism. Sep. Purif. Technol. 210, 600–607. http://dx.doi.org/10.1016/J.SEPPUR.2018.08.051.

Reungsang, A., Sittijunda, S., Angelidaki, I., 2013. Simultaneous production of hydrogen and ethanol from waste glycerol by Enterobacter aerogenes KKU-S1. Int. J. Hydrogen Energy 38, 1813–1825. http://dx.doi.org/10.1016/J.IJHYDENE.2012.11.062.

Samsudin, M.D.M., Mat Don, M., 2015. Assessment of bioethanol yield by S. cerevisiae grown on oil palm residues: Monte Carlo simulation and sensitivity analysis. Bioresour. Technol. 175, 417–423. http://dx.doi.org/10.1016/J.BIORTECH.2014.10.116.

Sarchami, T., Munch, G., Johnson, E., Kiezlich, S., Rehmann, L., 2016. A review of process-design challenges for industrial fermentation of butanol from crude glycerol by non-biphasic clostridium pasteurianum. Ferment 2 (2016), 13. http://dx.doi.org/10.3390/FERMENTATION2020013, 2, 13.

Sarris, D., Papanikolaou, S., 2016. Biotechnological production of ethanol: Biochemistry, processes and technologies. Eng. Life Sci. 16, 307–329. http://dx.doi.org/10.1002/elsc.201400199.

Sarris, D., Sampani, Z., Rapti, A., Papanikolaou, S., 2019. Valorization of crude glycerol, residue deriving from biodiesel- production process, with the use of wild-type new isolated yarrowia lipolytica strains: Production of metabolites with pharmaceutical and Biotechnological interest. Curr. Pharm. Biotechnol. 20, 881–894. http://dx.doi.org/10.2174/1389201020666190211145215.

Sebayang, A.H., Masjuki, H.H., Ong, H.C., Dharma, S., Silitonga, A.S., Kusumo, F., Milano, J., 2017. Optimization of bioethanol production from sorghum grains using artificial neural networks integrated with ant colony. Ind. Crops Prod. 97, 146–155. http://dx.doi.org/10.1016/J.INDCROP.2016.11.064.

Semkiv, M., Kata, I., Ternavska, O., Sibirny, W., Dmytruk, K., Sibirny, A., 2019. Overexpression of the genes of glycerol catabolism and glycerol facilitator improves glycerol conversion to ethanol in the methylotrophic thermotolerant yeast Ogataea polymorpha. Yeast 36, 329–339. http://dx.doi.org/10.1002/YEA.3387.

Seta, K., Suzuki, T., Kiyoshi, K., Shigeno, T., Nakajima-Kambe, T., 2018. Potential use of methane fermentation digested slurry as a low-cost, environmentally-friendly nutrient for bioethanol production from crude glycerol by Klebsiella variicola TB-83D. N. Biotechnol. 44, 1–5. http://dx.doi.org/10.1016/j.nbt.2018.02.014.

Sharma, H.K., Xu, C., Qin, W., 2017. Biological pretreatment of lignocellulosic biomass for biofuels and bioproducts: An overview. Waste Biomass Valoriz. 102 (2017), 10. http://dx.doi.org/10.1007/S12649-017-0059-Y, 235–251.

da Silva, V.Z., Ourique, L.J., de David, C., Ayub, M.A.Z., 2020. Construction of recombinant Klebsiella pneumoniae to increase ethanol production on residual glycerol fed-batch cultivations. Appl. Biochem. Biotechnol. 192, 1147–1162. http://dx.doi.org/10.1007/S12010-020-03397-5.

Silva, J.V., Pardilhó, S.L., Almeida, M.F., Alvim-Ferraz, M.C., Dias, J.M., 2019. Sweet potato bioethanol upgrade using organic and inorganic dehydrating agents. Chem. Eng. Technol. 42, 560–565. http://dx.doi.org/10.1002/CEAT.201800353.

Sim, G.Y., Lee, S.U., Lee, J.W., 2020. Enhanced extraction of phytic acid from rice hulls with enzymatic treatment and production of ethanol from reducing sugars in hydrolyzed rice hulls after extraction of phytic acid. LWT 133, 110111. http://dx.doi.org/10.1016/J.LWT.2020.110111.

Singh, N., Prasad, R., 2011. Fuel grade ethanol by diffusion distillation: an experimental study. J. Chem. Technol. Biotechnol. 86, 724–730. http://dx.doi.org/10.1002/JCTB.2579.

Sittijunda, S., Reungsang, A., 2020. Valorization of crude glycerol into hydrogen, 1, 3-propanediol, and ethanol in an up-flow anaerobic sludge blanket (UASB) reactor under thermophilic conditions. Renew. Energy 161, 361–372. http://dx.doi.org/10.1016/J.RENENE.2020.07.053.

Solarte-Toro, J.C., Romero-García, J.M., Martínez-Patiño, J.C., Ruiz-Ramos, E., Castro-Galiano, E., Cardona-Alzate, C.A., 2019. Acid pretreatment of lignocellulosic biomass for energy vectors production: A review focused on operational conditions and techno-economic assessment for bioethanol production. Renew. Sustain. Energy Rev. 107, 587–601. http://dx.doi.org/10.1016/J.RSER.2019.02.024.

Sönnichsen, N., 2020. Global Biodiesel Production by Country 2020. Worldwide.

Srivastava, N., Srivastava, M., Mishra, P.K., Gupta, V.K., Molina, G., Rodriguez-Couto, S., Manikanta, A., Ramteke, P.W., 2018. Applications of fungal cellulases in biofuel production: Advances and limitations. Renew. Sustain. Energy Rev. 82, 2379–2386. http://dx.doi.org/10.1016/J.RSER.2017.08.074.

Stepanov, N., Efremenko, E., 2017. Immobilised cells of pachysolen tannophilus yeast for ethanol production from crude glycerol. N. Biotechnol. 34, 54–58. http://dx.doi.org/10.1016/J.NBT.2016.05.002.

Suhag, M., Kumar, A., Singh, J., 2020. Saccharification and fermentation of pretreated banana leaf waste for ethanol production. SN Appl. Sci. 28 (2020), 2. http://dx.doi.org/10.1007/S42452-020-03215-X, 1–9.

Suhaimi, S.N., Phang, L.Y., Maeda, T., Abd-Aziz, S., Wakisaka, M., Shirai, Y., Hassan, M.A., 2012. Bioconversion of glycerol for bioethanol production using isolated Escherichia coli SS1. Brazilian J. Microbiol. 43, 506–516. http://dx.doi.org/10.1590/S1517-83822012000200011.

Sun, Z.Y., Tang, Y.Q., Morimura, S., Kida, K., 2013. Reduction in environmental impact of sulfuric acid hydrolysis of bamboo for production of fuel ethanol. Bioresour. Technol. 128, 87–93. http://dx.doi.org/10.1016/J.BIORTECH.2012.10.082.

Sunarno, J.N., Prasertsan, P., Duangsuwan, W., Cheirsilp, B., Sangkharak, K., 2019. Biodiesel derived crude glycerol and tuna condensate as an alternative low-cost fermentation medium for ethanol production by Enterobacter aerogenes. Ind. Crops Prod. 138, 111451. http://dx.doi.org/10.1016/j.indcrop.2019.06.014.

Sunarno, J.N., Prasertsan, P., Duangsuwan, W., Cheirsilp, B., Sangkharak, K., 2020. Improve biotransformation of crude glycerol to ethanol of Enterobacter aerogenes by two-stage redox potential fed-batch process under microaerobic environment. Biomass Bioenergy 134, 105503. http://dx.doi.org/10.1016/j.biombioe.2020.105503.

Suzuki, T., Nishikawa, C., Seta, K., Shigeno, T., Nakajima-Kambe, T., 2014. Ethanol production from glycerol-containing biodiesel waste by Klebsiella variicola shows maximum productivity under alkaline conditions. N. Biotechnol. 31, 246–253. http://dx.doi.org/10.1016/J.NBT.2014.03.005.

Swain, M.R., Krishnan, C., 2015. Improved conversion of rice straw to ethanol and xylitol by combination of moderate temperature ammonia pretreatment and sequential fermentation using Candida tropicalis. Ind. Crops Prod. 77, 1039–1046. http://dx.doi.org/10.1016/J.INDCROP.2015.10.013.

Szambelan, K., Nowak, J., Szwengiel, A., Jeleń, H., Łukaszewski, G., 2018. Separate hydrolysis and fermentation and simultaneous saccharification and fermentation methods in bioethanol production and formation of volatile by-products from selected corn cultivars. Ind. Crops Prod. 118, 355–361. http://dx.doi.org/10.1016/J.INDCROP.2018.03.059.

Tan, I.S., Lee, K.T., 2015. Solid acid catalysts pretreatment and enzymatic hydrolysis of macroalgae cellulosic residue for the production of bioethanol. Carbohydr. Polym. 124, 311–321. http://dx.doi.org/10.1016/J.CARBPOL.2015.02.046.

Tasić, M.B., Konstantinović, B.V., Lazić, M.L., Veljković, V.B., 2009. The acid hydrolysis of potato tuber mash in bioethanol production. Biochem. Eng. J. 43, 208–211. http://dx.doi.org/10.1016/J.BEJ.2008.09.019.

Teigiserova, D.A., Tiruta-Barna, L., Ahmadi, A., Hamelin, L., Thomsen, M., 2021. A step closer to circular bioeconomy for citrus peel waste: A review of yields and technologies for sustainable management of essential oils. J. Environ. Manage 280, 111832. http://dx.doi.org/10.1016/J.JENVMAN.2020.111832.

Tibi, F., Charfi, A., Cho, J., Kim, J., 2020. Fabrication of polymeric membranes for membrane distillation process and application for wastewater treatment: Critical review. Process Saf. Environ. Prot. 141, 190–201. http://dx.doi.org/10.1016/J.PSEP.2020.05.026.

Tinôco, D., Genier, H.L.A., da Silveira, W.B., 2021. Technology valuation of cellulosic ethanol production by kluyveromyces marxianus CCT 7735 from sweet sorghum bagasse at elevated temperatures. Renew. Energy 173, 188–196. http://dx.doi.org/10.1016/J.RENENE.2021.03.132.

Vedovatto, F., Bonatto, C., Bazoti, S.F., Venturin, B., Alves, S.L., Kunz, A., Steinmetz, R.L.R., Treichel, H., Mazutti, M.A., Zabot, G.L., Tres, M.V., 2021. Production of biofuels from soybean straw and hull hydrolysates obtained by subcritical water hydrolysis. Bioresour. Technol. 328, 124837. http://dx.doi.org/10.1016/J.BIORTECH.2021.124837.

Veiga, S., Faccio, R., Segobia, D., Apesteguía, C., Bussi, J., 2017. Hydrogen production by crude glycerol steam reforming over Ni–La–Ti mixed oxide catalysts. Int. J. Hydrogen Energy 42, 30525–30534. http://dx.doi.org/10.1016/J.IJHYDENE.2017.10.118.

Veiga, S., Romero, M., Faccio, R., Segobia, D., Duarte, H., Apesteguía, C., Bussi, J., 2020. Hydrogen-rich gas production by steam and oxidative steam reforming of crude glycerol over Ni-La-Me mixed oxide catalysts (Me = Ce and/or Zr). Catal. Today 344, 190–198. http://dx.doi.org/10.1016/J.CATTOD.2019.02.008.

Vivek, N., Sindhu, R., Madhavan, A., Anju, A.J., Castro, E., Faraco, V., Pandey, A., Binod, P., 2017. Recent advances in the production of value added chemicals and lipids utilizing biodiesel industry generated crude glycerol as a substrate – Metabolic aspects, challenges and possibilities: An overview. Bioresour. Technol. 239, 507–517. http://dx.doi.org/10.1016/J.BIORTECH.2017.05.056.

Wang, Q., Wang, W., Tan, X., Zahoor, Chen X., Guo, Y., Yu, Q., Yuan, Z., Zhuang, X., 2019. Low-temperature sodium hydroxide pretreatment for ethanol production from sugarcane bagasse without washing process. Bioresour. Technol. 291, 121844. http://dx.doi.org/10.1016/J.BIORTECH.2019.121844.

Widayat, Philia J., Farsha, T., Rifaldi, F., 2020. Synthesis of zeolite catalyst from geothermal solid waste for crude glycerol dehydration to acrolein. Key Eng. Mater. 849, 130–136. http://dx.doi.org/10.4028/WWW.SCIENTIFIC.NET/KEM.849.130.

Wu, B., Wang, Y.-W., Dai, Y.-H., Song, C., Zhu, Q.-L., Qin, H., Tan, F.-R., Chen, H.-C., Dai, L.-C., Hu, G.-Q., He, M.-X., 2021. Current status and future prospective of bio-ethanol industry in China. Renew. Sustain. Energy Rev. 145, 111079. http://dx.doi.org/10.1016/j.rser.2021.111079.

Xin, F., Chen, T., Jiang, Y., Lu, J., Dong, W., Zhang, W., Ma, J., Zhang, M., Jiang, M., 2017. Enhanced biobutanol production with high yield from crude glycerol by acetone uncoupled clostridium sp. strain CT7. Bioresour. Technol. 244, 575–581. http://dx.doi.org/10.1016/J.BIORTECH.2017.08.002.

Xu, C., Zhou, C., Wang, S., Huang, A., 2019. Copper-exchanged LTA zeolite membranes with enhanced water flux for ethanol dehydration. Chinese Chem. Lett. 30, 1204–1206. http://dx.doi.org/10.1016/J.CCLET.2019.01.016.

Yan, J., Kuang, Y., Gui, X., Han, X., Yan, Y., 2019. Engineering a malic enzyme to enhance lipid accumulation in Chlorella protothecoides and direct production of biodiesel from the microalgal biomass. Biomass Bioenergy 122, 298–304. http://dx.doi.org/10.1016/J.BIOMBIOE.2019.01.046.

Yang, F., Hanna, M.A., Sun, R., 2012. Value-added uses for crude glycerol–a byproduct of biodiesel production. Biotechnol. Biofuels 5, 13. http://dx.doi.org/10.1186/1754-6834-5-13.

Yu, K.O., Kim, S.W., Han, S.O., 2010. Engineering of glycerol utilization pathway for ethanol production by Saccharomyces cerevisiae. Bioresour. Technol. 101, 4157–4161. http://dx.doi.org/10.1016/J.BIORTECH.2010.01.066.

Yusoff, M.N.A.M., Zulkifli, N.W.M., Sukiman, N.L., Chyuan, O.H., Hassan, M.H., Hasnul, M.H., Zulkifli, M.S.A., Abbas, M.M., Zakaria, M.Z., International Collaboration, 2021. Sustainability of palm biodiesel in transportation: a review on biofuel standard, policy and between Malaysia and Colombia. Bioenergy Res. 14, 43–60. http://dx.doi.org/10.1007/s12155-020-10165-0.

Yuwa-amornpitak, T., Chookietwatana, K., 2016. Development of ethanol production from cooking oil glycerol waste by mutant Enterobacter aerogenes. African J. Biotechnol. 15, 2344–2351. http://dx.doi.org/10.5897/AJB2016.15275.

Zabot, G.L., 2020. Decaffeination using supercritical carbon dioxide. In: Green Sustainable Process for Chemical and Environmental Engineering and Science: Supercritical Carbon Dioxide As Green Solvent. Elsevier, pp. 255–278. http://dx.doi.org/10.1016/B978-0-12-817388-6.00011-8.

Zahid, I., Ayoub, M., Abdullah, B.B., Nazir, M.H., Ameen, M., Zulqarnain Yusoff, M.H.M., Inayat, A., Danish, M., 2020. Production of fuel additive solketal via catalytic conversion of biodiesel-derived glycerol. Ind. Eng. Chem. Res. 59, 20961–20978. http://dx.doi.org/10.1021/ACS.IECR.0C04123.

Zeppini, P., van den Bergh, J.C.J.M., 2020. Global competition dynamics of fossil fuels and renewable energy under climate policies and peak oil: A behavioural model. Energy Policy 136, 110907. http://dx.doi.org/10.1016/J.ENPOL.2019.110907.

Zhao, X., Li, S., Wu, R., Liu, D., 2017a. Organosolv fractionating pre-treatment of lignocellulosic biomass for efficient enzymatic saccharification: chemistry, kinetics, and substrate structures. Biofuels, Bioprod. Biorefining 11, 567–590. http://dx.doi.org/10.1002/BBB.1768.

Zhao, L., Lyu, X., Wang, W., Shan, J., Qiu, T., 2017b. Comparison of heterogeneous azeotropic distillation and extractive distillation methods for ternary azeotrope ethanol/toluene/water separation. Comput. Chem. Eng. 100, 27–37. http://dx.doi.org/10.1016/J.COMPCHEMENG.2017.02.007.

Zhao, X., Peng, F., Cheng, K., Liu, D., 2009. Enhancement of the enzymatic digestibility of sugarcane bagasse by alkali–peracetic acid pretreatment. Enzyme Microb. Technol. 44, 17–23. http://dx.doi.org/10.1016/J.ENZMICTEC.2008.07.011.

Zhao, J., Xu, Y., Wang, W., Griffin, J., Roozeboom, K., Wang, D., 2020a. Bioconversion of industrial hemp biomass for bioethanol production: A review. Fuel 281, 118725. http://dx.doi.org/10.1016/J.FUEL.2020.118725.

Zhao, J., Xu, Y., Wang, W., Griffin, J., Wang, D., 2020b. Conversion of liquid hot water, acid and alkali pretreated industrial hemp biomasses to bioethanol. Bioresour. Technol. 309, 123383. http://dx.doi.org/10.1016/J.BIORTECH.2020.123383.

Zouhair, F.Z., Kabbour, M.R., Ebich, F., Benali, A., el Maadoudi, E., haj Alrashdi, A.A., Bouksaim, M., Lgaz, H., Essamri, A., 2021. Dehydration of bioethanol produced from argane pulp using pervaporation membrane process: Experimental, molecular dynamics and GCMC simulation studies. J. Mol. Liq. 329, 115441. http://dx.doi.org/10.1016/J.MOLLIQ.2021.115441.

Zwirzitz, A., Alteio, L., Sulzenbacher, D., Atanasoff, M., Selg, M., 2021. Ethanol production from wheat straw hydrolysate by issatchenkia orientalis isolated from waste cooking oil. J. Fungi 7 (2021), 121. http://dx.doi.org/10.3390/JOF7020121, 7, 121.