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Article

Biorefinery Approach for Cassava Peels: A Review

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Abstract — Sustainability of energy has always become an issue globally as current energy supplies are depleting gradually. Humans were too dependent on natural gasses as a source of energy before, which brought us to this crisis as they are non-renewable energy and take up to a million years to recover. Not only that, prolonged utilization of this type of energy brought deterioration to our environment. Biofuels are one of the renewable energy sources that are favoured in the industry nowadays. They have the potential to replace non-renewable energy while simultaneously decrease the environmental damage. Sourced from various agricultural residues and other plant substances, lignocellulosic materials are capable of being converted to non-renewable energy due to their lavish availability through three basic steps, pre-treatments, enzymatic hydrolysis and fermentation. This review seeks to observe the prospect of cassava peels as a source for biofuels production and other value-added products such as formic acid, levulinic acid, glycolic acid and vanillin.

Keywords — Biofuels; lignocellulosic biomass; cassava peels; chemical derivatives; pre-treatments

INTRODUCTION

Natural gas as a continuous source of energy is impractical for the long term as it is non-renewable, causing environmental drawbacks such as polluting and endangering our already contaminated world. Scientists are searching for alternatives energy sources, and to date, biofuels have shown a high potential to replace natural gases as they are ergonomic, non-toxic and most importantly, biodegradable [1]. Biofuels such as bioethanol could be generated from lignocellulosic biomass, which is easily acquired from agricultural residues, energy crops, forestry residues, or yard trimmings [2]. The production of biofuels reduces the greenhouse effect and consciously helps preserve our world by minimizing waste materials. Cassava peels is an example of residual from agricultural practices. Renewable energy created from it is also known as second-generation bioethanol because non-edible sources are used, considered more suitable as renewable energy than first-generation bioethanol made up from food sources. This is because the latter is prone to face issues like energy consumption, utilization of arable lands, and also initiate fuel versus food debate [3]. According to Wiloso et al. [4], second-generation bioethanol worked better than fossil fuels for two radical impact categories: global warning and net energy output. Today, cassava is grown by more than 8 million farmers in Asia, spanning around 4.2 million hectares[5]. As the processing of cassava usually involves the flesh itself, instead of throwing away its peels and other discarded by-products, it could undergo biorefinery processing to convert it to value-added products. A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, heat, and value-added chemicals from biomass [6]. Biofuels is a renowned example of a biorefineries product. Conversion of these residuals to biofuels is made possible due to the high amounts of lignocellulosic materials in it. However, before it is converted, cassava peels will first be pre-treated and undergo enzymatic hydrolysis to form fermentable sugar and then processed to bioethanol through the fermentation process [7]. Alongside bioethanol, cassava peels could be utilized by converting it to other useful chemical derivatives such as formic acid, levulinic acid, glycolic acid, and vanillin through biorefineries. The chemical properties of the components of lignocellulosic make them a substrate for enormous biotechnological value [8].

Cassava and Its Peels

Manihot esculenta Crantz or more commonly known as cassava or tapioca is one of the biggest agricultural crops harvested primarily in many countries of Asia, Latin America, and Africa [9]. Cassava roots are believed to originate from Brazil. It quickly became one of the favourite crops due to its high content of carbohydrates which is 40% more than rice and 25% more than maize [10].

Not only that, but they also only require minimum care and still can flourish and survive in harsh weather. Cassava is known as emergency crops, eaten during hard times such as war and crops eaten by the low-income family. It is a necessary component of food, accounting for a significant amount of daily caloric consumption. [11]. Cassava can grow in many soil types, with the exception of heavy or saturated soils. It prefers sunny places and thrives in tropical and subtropical climates with high temperatures [12]. According to Jansson et al. [13], cassava is known as the fifth most important plant-based starch globally.

Fig. 2 shows a simple cross-section of cassava, whereas it consists of the starchy flesh, central vascular fibre, and the peels, which are usually made up of the cortex and the periderm. Nartey (1973) [14] has reported that the thickness of the peels lies around 1 to 4mm and counts approximately 10-12% of the total dry matter of the root.

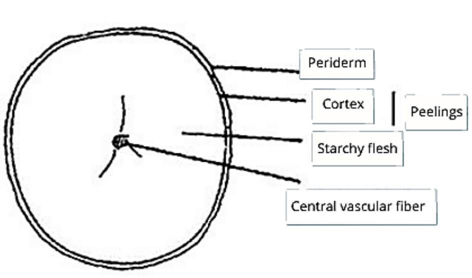

Fig. 2: Cross-section of cassava [15].

Cassava peel is the remnants that are mostly produced by industry from the pre-cleaning process, which consists of peel (composed of cracked bark), inner peel (between cortex layer and central cylinder) and cassava tips [16].

Agricultural crops of cassava are being processed to various products by separation of soluble sugars and fibres, by which a purified starch is produced, along with its residues which includes peels and bagasse. These remnants are often used for animal feed. However, it causes consequential environmental drawbacks [17]. Therefore, cassava peels or its waste in general appeal more as a source of ethanol production because they are rich in cellulose (37.9%) and hemicellulose (37%), with considerably low lignin content (7.5%) [18]. In another report by [19], the cellulose content in cassava peels reached 43.626%.

Overview of Lignocellulosic Materials

Lignocellulose is one of the basic components that exist in the plant, including cassava peels. Basically, it is comprised of three important constituents, which are cellulose, hemicellulose and lignin (Fig. 3). The composition of dry matter in each of them varies between 30% to 60%, 14% to 40%, and 7% to 25%, respectively. Nonstructural carbohydrates (glucose, fructose, and sucrose), proteins, lipids, and pectin can also be found in small quantities [20]. The first major component, cellulose, can be found at plant cell walls as an unbranched crystalline structured biopolymer. It is made up of several to thousands of units of glucose that are connected by β-1,4-glycosidic bonds. Therefore, pre-treatment is needed to eliminate lignin and hemicellulose that surrounded it to access more cellulose [21]. Hemicellulose is a branched heteropolymer made up of different hexoses, pentoses, D-glucuronic acid and acetylated sugars. Many factors influence the proportions of sugars that make up hemicellulose which includes different seasons, the plant type and the cultivation place itself. Research has shown that chemical hydrolysis of hemicellulose is easier to be done compared to cellulose [22]. Lignin is a product of the condensation of three monomeric phenol alcohols: trans-pcumarylic, trans-p-coniferylic, and trans-p-sinapylic. Its main function in plant cell walls is to protect itself from microorganisms by forming an impermeable structure [23]. However, Kang et al. [24] stated in their studies that high lignin and/or high ash concentrations are unfavourable for bioethanol production. Lignocellulose could be further processed to form various beneficial products such as biofuels, fermentable sugars, beauty masks and many more. The main source of these lignocellulosic materials typically comes from agricultural, industrial waste such as cereal straw, corncob, and potato haulms, including cassava peels. Processing of tuberous cassava as various food products results in the increase of its peels. They are often disregarded and will be left behind. Instead of increasing municipal waste, which could take up to years to dispose of, the high content of starch and lignocellulosic materials in its peels can be utilized to form biofuels, a form of renewable energy. However, in the processing of biofuels, it must first undergo pre-treatments, whether physical, chemical, physicochemical, or biological pre-treatments, to remove cyanide content that naturally presents in cassava as well as the enzymes amenable to the sugars embedded in the cellulose and hemicelluloses component of the peel [25].

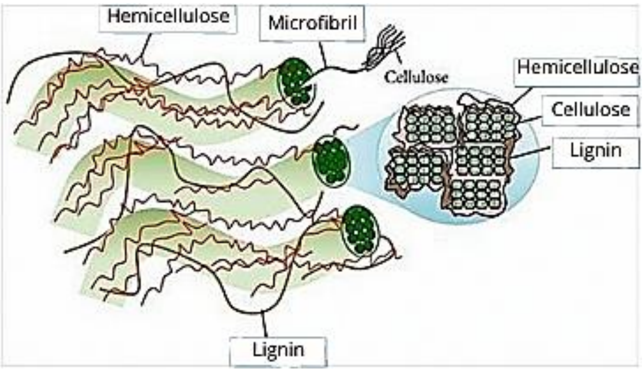

Fig. 3: Structure of lignocellulosic biomass [26].

Pre-treatments of Lignocellulosic Materials

Pre-treatment is a crucial step in the conversion of bioethanol from lignocellulosic materials because it allows the increase of sugar yield. This can be achieved through lignin removal or degradation (Fig. 4). This is because lignins, the amorphous polymer, act as blockades that prevent physical access to cellulose and hemicellulose from microbial or enzymatic degradation. Moreover, lignin is also responsible for the nonproductive adsorption of hydrolytic enzymes and derivatives that are usually toxic to microorganisms may be generated from lignin [20]. Furthermore, cassava peels must undergo pre-treatments to remove cyanide content that is naturally present in cassava, as well as the enzymes amenable to the sugars embedded in the cellulose and hemicelluloses component of the peel [25].

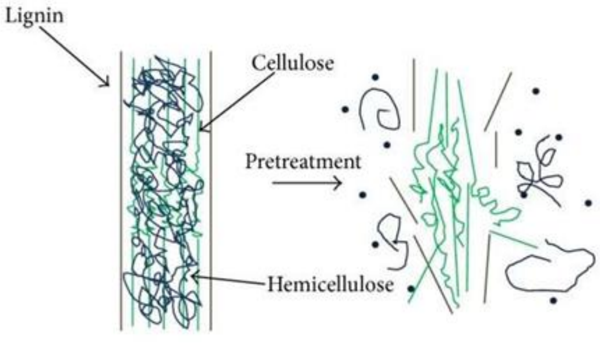

Fig. 4: Deconstruction of lignocelluloses into cellulose, hemicellulose, and lignin [26].

In general, there are four types of pretreatment processes. (Refer to Fig. 5). This includes physical pre-treatments (milling, microwave, extrusion and ultrasonication), chemical pre-treatments (alkaline hydrolysis, acid hydrolysis, ionic liquids, organosolvent and deep eutectic process), physico-chemical pre-treatments (steam explosion, ammonia fibre explosion, CO_2 explosion, and liquid hot water) and biological pre-treatments (whole-cell pre-treatment and enzymatic pre-treatments).

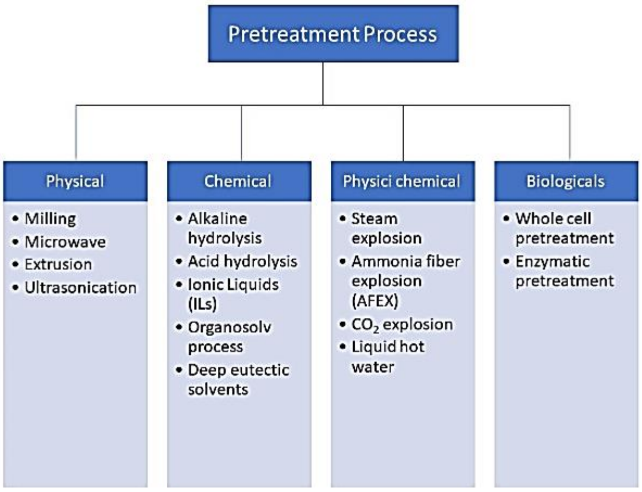

Fig. 5: Various pretreatment processes [22].

The pre-treatment results are affected by ratio constituents of cellulose, hemicellulose and lignin. In contrast, it can be seen that application of dilute acid pre-treatment on sweet gum bark or cornstalks work is inefficient, as opposed to the result of identical pre-treatment on poplar bark trees or corn [27]. Table I shows the suitable pre-treatments used for different biomass.

Physical methods functioned to escalate pore size and surface area of lignocellulosic biomass as well as deescalate the degree of polymerization and crystallinity of cellulose. Milling pre-treatment is usually used, and for the greater result, it can be combined with the enzymatic hydrolysis process [27].

Chemical pre-treatment using acid and alkaline are essentially the most popular pre-treatment method. The process of hydrolysis is enhanced, resulting in more yield of fermentable sugar. Sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) are the two types of concentrated acid that are predominant acids used to treat lignocellulosic biomass. For instance, sulfuric acid pre-treatment is commonly used for poplar, switchgrass, spruce, corn stover and cassava peels. On the other hand, alkaline pre-treatment worked by saponifying lignocellulosic materials and breaking of lignin-carbohydrates linkages. This allowed higher removal of lignin and generated a low-toxicity compound [28]. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are the common alkaline solutions used in a pre-treatment. In accordance to studies by Ovueni et al. [29], pre-treatment with the acid solution, particularly H2SO4, worked the best for cassava peels as it yielded the highest reducing sugar (190.04 mg/mL), followed closely by pre-treatment with an alkaline solution, NaOH which yielded 132.7 mg/mL of reducing sugar while ethanoic acid warranted the least amount of reducing sugar at 51.5 mg/mL.

The physicochemical technique involves a hybrid approach in altering physical parameters, the chemical bonding (bond cleavage) and intermolecular interactions of lignocellulosic biomass. The force of temperature and pressure that works in tandem in a chemical process will break down the network of lignocellulosic biomass [30].

In their studies, Vasco-Correa et al. [31] stated that biological pre-treatment of lignocellulosic biomass employed the ligninolytic potential of certain microorganisms such as fungi and bacteria as a way to reduce the recalcitrance of the feedstock and enhance its digestibility by hydrolytic enzymes. Biological pre-treatment is an eco-friendly method and requires less energy consumption. The utilization of live microorganisms such as white-rot, soft rot and brown fungi results in the removal of lignin and hemicellulose without compromising cellulose content. In addition, some particular microorganisms that exist in nature are capable of hydrolyzing cellulose and hemicellulose [27].

TABLE I
DIFFERENT PRE-TREATMENT USED FOR DIFFERENT BIOMASS

Pre-treatment used	Biomass	References
Physical	Corn stover	[27].
Chemical	Poplar, switchgrass, spruce, corn stover, cassava peels	
Physicochemical	Switchgrass	
Biological	Wheat straw, woodchip	

Current Status of Biomass (Cassava) in Malaysia

As in Fig. 6, after the pre-treatment process, it will undergo hydrolysis and further fermentation for bioethanol production. Generally, bioethanol can be obtained from pre-treated lignocellulosic biomass by using either one of two ways, acid hydrolysis or enzymatic hydrolysis. Acid hydrolysis is a chemical method that involves the usage of either dilutes or concentrated sulfuric, or other acids. Acid hydrolysis of lignocellulosic biomass using the dilute acid solution can be carried out using high temperature, e.g., 180 °C, short retention time, e.g., 5 minutes, or lower temperature, e.g., 120 °C but up to 60 minutes of retention time, which is longer. Concentrated acid hydrolysis makes use of low temperatures and can yield high sugars [31]. However, the drawbacks include the formation of gypsum from the neutralization process, cause high corrosion to the equipment used, and hazardous to be handled due to the usage of high concentration of acid (30% to 70%) [32][31]. Enzymatic hydrolysis is a biological process carried out by (hemi) cellulolytic enzymes such as cellulose or hemicellulose enzymes. Madadi et al. [33] reported that the usage of enzymatic hydrolysis is arguably more suitable due to several advantages, which include low toxic compound generation, high product yield, and less chemical requirements. The specific enzyme is needed to carry out the hydrolysis process of pre-treated biomass in order to break down polymers to their monomers, fermentable sugars. The most common enzyme used is cellulase. In order to carry out enzymatic hydrolysis optimally, few parameters such as the pH and temperatures need to be controlled monitored closely. Swiatek [34] stated that 50°C and 4.0 to 5.0 are the optimal temperature and pH range, respectively.

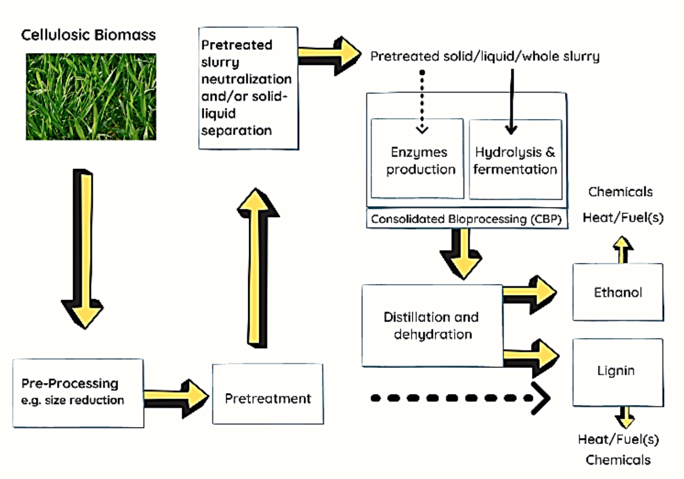

Fig. 6: Bioethanol processing from lignocellulosic biomass [35].

Cellulase reacts to cellulose according to several specific steps. Endoglucanases, cellobiohydrolases, and β-glucosidase, which are components of cellulase enzymes acted on homopolymer cellulose in order to degrade it. Firstly, endoglucanases will randomly hydrolyze internal β-(1-4)-glycosidic bonds in the cellulose chain. Then, cellobiohydrolases will cleave off cellobiose units from the end of the chain, and lastly, β-glucosidase will convert cellobiose into glucose [20]. The summarise of the mechanism is portrayed in Fig. 7.

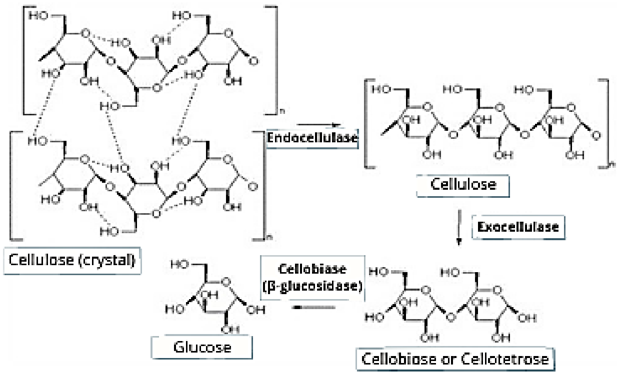

Fig. 7: Cellulase mechanism [36].

According to the Malaysia Department of Agriculture [37], Malaysia recorded about 2,876 hectares of cassava grown in 2019 and producing about 42,285 metric tonnes of the crop. Malaysia makes use of cassava as a food product in textiles industries and paper production. Besides that, it is also used in the production of certain chemicals such as acetone, alcohol and acetic acid. However, the processing of cassava from different industries must result in abundant waste as they are mainly focused on the root and starch. Therefore, the peels are usually discarded.

Asides from that, the major plantation in Malaysia is oil palm. Oil palm processing also generates substantial residues such as palm empty fruit brunches, oil palm frond, palm pressed fibres, oil palm trunks, palm kernel shells and others [38]. Although oil palm possesses a significant amount of lignocellulosic biomass, the high amount of lignin in the oil palm waste makes it less desirable. Table II shows the comparison between the contents of cellulose, hemicellulose and lignin for oil palm and cassava, respectively. Asides from palm oil residues, cassava has the potential to be converted to bioethanol as well. Moreover, cassava grows faster compared to palm oil. While palm oil only begins to produce after around 42 months after it has been planted, cassava only needs 8 to 18 months, depending on the weather and climate [39][40]. They did not require as delicate care compared to palm oil plantations. Thus, its potential as a bioethanol producer should be considered.

TABLE II
CHEMICAL COMPOSITION OF CASSAVA PEELS AND PALM OIL EMPTY FRUIT BUNCH

Type of Lignocellulosic Materials	Cellulose	Hemicellulose	Lignin	References
Palm Oil Empty Fruit Bunch	28.3 ± 1.0%	36.6 ± 0.6%	35.1± 0.8%	[41]
Cassava Peels	37.9%	37.0%	7.5%	[42]

Cellulosic Biomass to Other Chemical Derivatives

Chemical compositions obtained from cassava peels can be converted into other chemical derivatives such as glucose, formic acid, levulinic acid, glycolic acid and ferulic acid via biorefineries processes. In turn, valuable bio-based products can be produced, thus increase the sustainability of cassava processing industries.

Glucose

Glucose or dextrose can be obtained from lignocellulosic biomass through the hydrolysis process either by enzymes or acid [43][44]. Cassava peels, due to the high amount of residual starch in them, also can be converted into sugar. Research conducted by Bayitse et al. [45] discovered that glucose recovery could rise up to 80% through enzymatic hydrolysis using a mixture of cellulase and beta-glucanase enzymes. Arantes and Saddler [46], through their study, described enzymatic hydrolysis of cellulose as a heterogeneous reaction system in which cellulases in an aqueous environment react with the insoluble, macroscopic and structured cellulose, containing highly ordered and less ordered regions. Hemicellulose and cellulose are broken down via hydrolysis during dilute acid pre-treatment, and soluble sugars are obtained [47]. As such, alternative sugar can be produced or be made as a base material in biorefinery.

Formic Acid

Glucose obtained from cassava peels can also generate valuable by-products, which are formic acid (FA) and levulinic acid (LA). This is because formic acid can be generated from the hydrolysis process of lignocellulose biomass, catalyzed by acid reaction[48]. In Fig. 8, conversion to produce FA and LA is illustrated. Glucose that is produced from the cellulose of cassava peels can be further processed by hydrolyzing it to 5 - hydroxymethylfurfural (HMF) and dehydrated to levulinic acid and formic acid. On the other side, C5 (pentose sugars) from hemicellulose can be decomposed into xylose which can be dehydrated into furfural [49]. Besides that, FA can be produced from formyl group cleavage or aldehyde group hydrolytic fission of furfural [49]. As a weak acid used for energy storage and chemical synthesis, FA has unique properties such as nontoxicity, favourable energy density, and biodegradability [50]. In general, many industries utilize FA such as textiles, pharmaceuticals and food chemicals [51]. Besides that, FA application as fuel is also very large. FA can decompose at high temperatures, and FA can produce hydrogen gas which acts as a hydrogen donor in water or another solvent [52]. Because of its unique properties, FA has the potential for hydrogen storage that can be used as fuel for fuel cells technology.

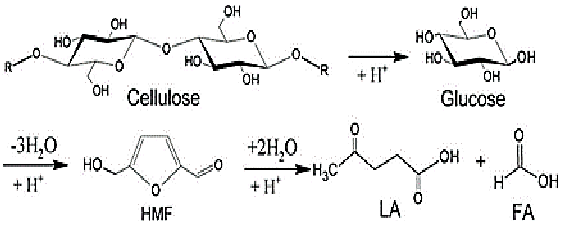

Fig. 8: Conversion of cellulose to levulinic acid and formic acid [53].

Levulinic Acid

Levulinic acid (LA) is one of the two chemicals that can be produced from the glucose of cassava peels. Much like formic acid, LA is accessible through the hydrolysis of lignocellulosic biomass at elevated temperatures (100–250 °C) using acid catalysts. In the presence of an acid catalyst and at elevated temperatures, the cellulose fraction is depolymerized to glucose, which is subsequently converted into 5-hydroxymethylfurfural (HMF) and finally to LA and FA [54]. A study from Kang et al. [55] found out that isolating the cellulose from its biomass before the hydrolysis process began can increase the LA and HMF production yield. Levulinic acid is a commodity chemical that finds applications for several purposes, such as the source of polymer resins, animal feed, food as well as components of flavouring and fragrance industry, textile dyes, additives, extenders for fuels, antifreeze products, antimicrobial agents, herbicides and plasticizers.

Glycolic Acid

Glycolic acid (GA) is another chemical that can be derived from cassava peels. Dapsens et al. [56] reported a pathway to create glycolic acid is through the aid of a Lewis-acid catalyst through a 1,2-hydride shift pathway, fortuitously converting glyoxal into GA. Besides that, G Iglesias et al. [56] concluded that the selected catalyst displays excellent reusability and stability under continuous flow operating conditions, showing high potential for being scaled up to industrial production. Alternatively, glycolic acid can be produced through an oxidation pathway from renewable biomass feedstock, such as glycerol or its derived chemical dihydroxyacetone (DHA), as illustrated in Fig, 9. This hydroxy acid is commercially employed in a wide variety of applications, e.g., as a synthon in organic synthesis, as an agent for chemical cleaning and metal chelation, as a formulation in cosmetics (skincare), and in the fabrication of polyesters such as polyglycolide and the hybrid poly- (lactide-co-glycolide). Furthermore, the high biodegradability and biocompatibility of these polymers make them ideal for biomedical applications, [57] such as tissue engineering [58] or for the synthesis of absorbable sutures [15].

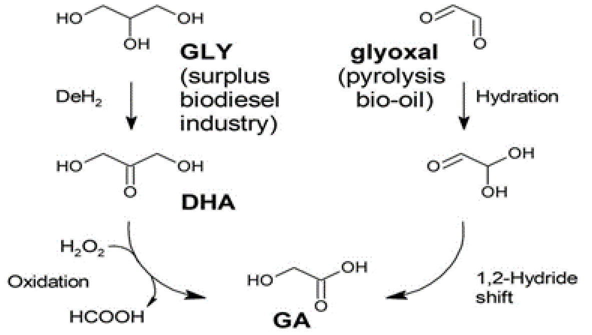

Fig. 9: Reaction pathways to produce glycolic acid [56].

Ferulic Acid

Cellulosic biomass, including cassava peels, is always intended to undergo pre-treatments in order to get rid of recalcitrant components such as lignin, as well as to provide easier access to cellulose and hemicellulose. Through pre-treatment methods, some phenolic compounds from the cassava peels are produced. Ferulic acid (FA) is one of the phenolic compounds resided in lignin that is released as a by-product from the pre-treatment process, either by pre-treatment with strong alkali or through enzymatic hydrolysis [59]. Ferulic acid is also a brilliant precursor for the production of vanillin, a highly valuable aromatic and flavour component in today's market. Fig. 10 demonstrates the pathway of vanillin from ferulic acid. First, FA is converted into feruloyl SCoA (reduced feruloyl coenzyme A) using ATP (adenosine triphosphate) and CoASH (reduced coenzyme A). Then, the water and CH3COSCoA (reduced acetyl coenzyme A) molecule is removed in order to convert feruloyl SCoA into vanillin. Originally, vanillin was extracted from Vanilla pods (*Vanilla planifolia*), known as natural vanilla, and available at a high price compared to synthetic vanilla. Bioconversion of ferulic acid to vanillin represents an attractive opportunity to replace synthetic vanillin with a bio-based product that can be labelled "natural", according to current food regulations [60]. Moreover, ferulic acid is a suitable candidate for biovanillin production, as it is less toxic compared to other precursors.

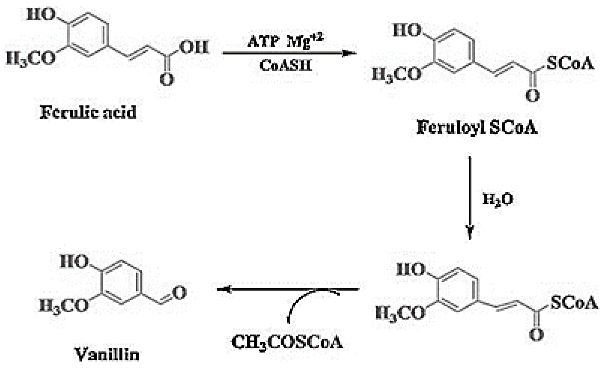

Fig. 10: Ferulic acid to vanillin through bioconversion [61].

CONCLUSION

Cassava peels have a formidable potential for bioethanol production. The valorization of these waste materials to bioethanol serves to conserve and preserve our world and helps control waste management, especially in developing countries, where cassava is mainly produced. As such, careful considerations and further research can be explored in order to conduct it on a commercial scale. However, possible barriers, namely insufficient infrastructures, high costs and lack of knowledge, should be overcome to ensure smooth production. Furthermore, substantial research and study are imperative to choose a type of pre-treatments that worked best with cassava peels to make sure high-quality bioethanol with the highest yield could be produced. Besides that, cassava peels' potential to produce chemical derivatives such as glucose, formic acid, levulinic acid, glycolic acid and vanillin from ferulic acid should be explored further as they are highly sought-out in current industry and market. Consequently, revealing further opportunities for cassava peels as a possible economic value.

RECOMMENDATIONS

Cassava peels have a good prospect as a source for biofuels production and other value-added products such as formic acid, levulinic acid, glycolic acid and vanillin. Due to different compounds present in cassava peels, the utilization of different enzymes for the hydrolysis process can be further explored. This review also broadened the approach to handle waste management in agroecosystems.

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