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Review

An Overview on Production of Lignocellulose-Derived Platform Chemicals Such as 5-Hydroxymethyl Furfural, Furfural, Protocatechuic Acid

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Abstract: Furan derivatives such as 5-hydroxymethyl furfural (HMF) and furfural (FA) and aromatic acids such as protocatechuic acid (PCA) represent the most essential classes of intermediates derived from lignocellulosic biomass. These bio-based compounds are potential feedstocks for producing bio-based chemicals and fuels. However, the derivatives of these bio-based compounds are useful in their antioxidative, antibacterial, and anti-aging activities. Protocatechuic acid (PCA, 2,3-dihydroxybenzoic acid), derived from lignin biomass, is also one of the essential bio-derived aromatic intermediates with an active acid and hydroxyl group, which can elevate it into an important class of potential platform chemicals for the production of value-added chemicals, such as HMF and furfuryl alcohol (FAL). The platform compounds are indeed the most used furan-based feedstocks since their chemical structure allows the preparation of various high-value-added chemicals. The related catalytic techniques are well known for the upgradation of biomass into these platform chemicals and their conversion into value-added chemicals. In this short review, we aim to briefly discuss biomass conversion into FA, HMF, and PCA and related heterogeneous catalytic processes. In addition, a few potential ongoing research trends are also proposed to provide some ideas for the further preparation of bio-based innovative derivatives in a much more green, simple, efficient, and economical way.

Keywords: 5-hydroxymethyl furfural; furfural; protocatechuic acid; bio-based feedstocks

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1. Introduction

In the current era, petroleum is the primary source to fulfill global energy demands. Most of the fuel (~+85%) and chemicals (~+96%) in the world are produced from traditional non-renewable fossil resources such as natural gas, petroleum, and coal, which provide significant contributions to the speedy development and prosperity of human society [1–3]. On the other side, progressively increasing global demands are most responsible for the depletion of these fossil resources, given the growing concerns about environmental pollution and greenhouse gas emissions. Renewable biomass would be the best option to meet the increasing energy demands in order to lessen dependence on non-renewable fossil fuels [1,2,4,5]. All biomasses are carbon sources, including waste materials, wood, crops, grasses, agricultural residues, and urban waste. They are widely available resources that represent the most viable alternative for the sustainable production of biofuels and bioderived chemicals [4–7]. Schematic representation for lignocellulose to value added shown in Figure 1.

FA is a derivative of pentose sugar (C5, hemicellulose biomass), HMF is a vital derivative of C6, lignocellulose biomass, and PCA (phenol derivative) [8,9] can be derived from lignin biomass. As per DOE USA, FAL and HMF have been recognized in one of the top platform chemical lists due to their significant potential for various applications [10]. HMF is a bio-based platform chemical that can be used as a building block for the production of a wide range of compounds with diverse applications [11,12]. HMF exhibits comparative properties with PEF, which can be derived from fossil resources. However, it has been very difficult to produce HMF from fossil resources [11,12]. So far, HMF production from

lignocellulose biomass is the best way. Similarly, the production of FA from bio-based feedstocks will be more beneficial than from petroleum-based sources [13]. In the case of PCA, it can be derived from lignin using an enzyme-based catalyst system.

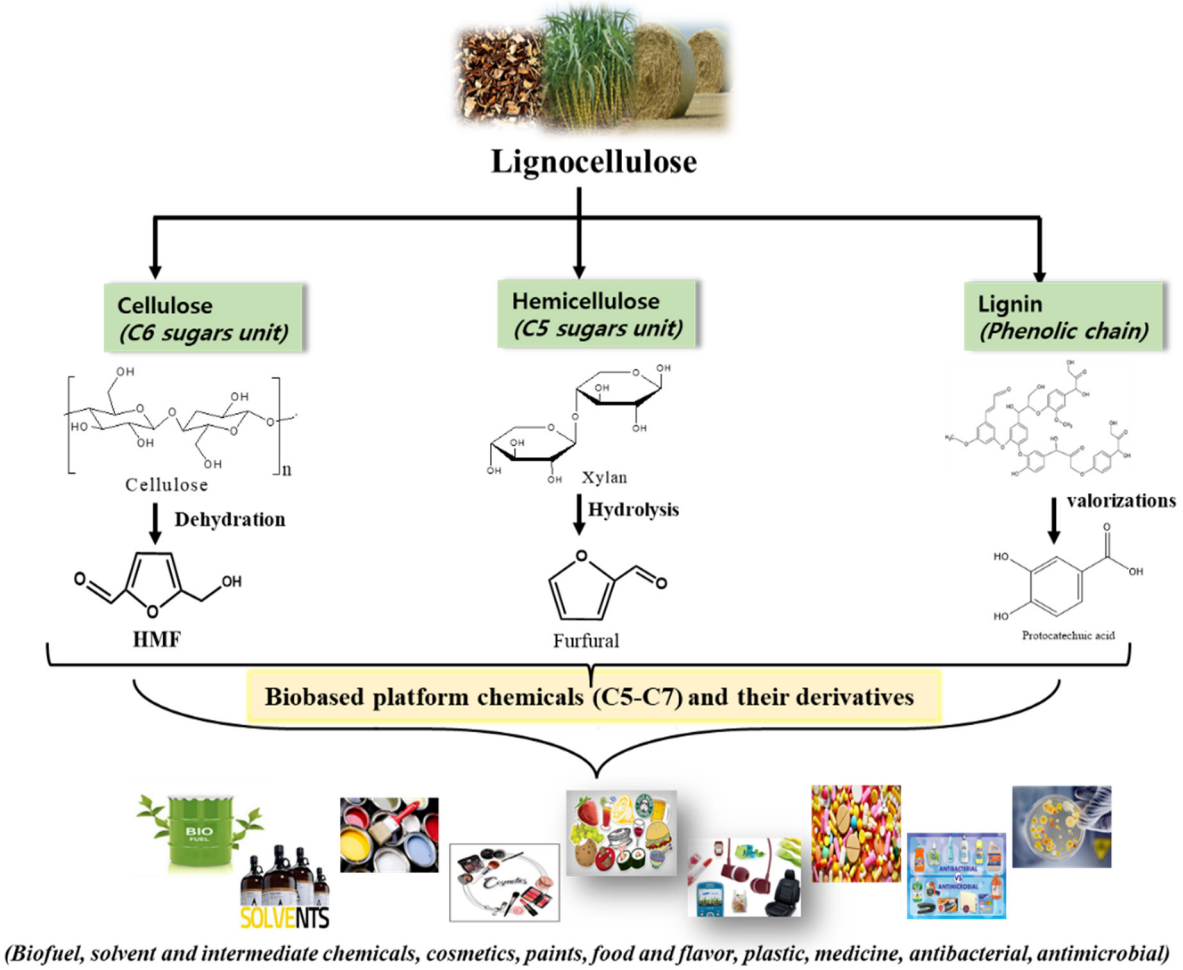


Figure 1. Bio-based feedstocks into platform chemicals and their application.

These bio-based compounds possess a very reactive functional group, and their properties (such as biodegradable, non-corrosive, non-carcinogenic, miscible in water, safety in handling, promising chemical intermediate etc.) make them potential platform chemicals. For the deconstruction of biomass feedstocks, a catalytic treatment is the first choice for researchers. For instance, when lignocellulose is deconstructed into cellulose, hemicellulose, and lignin fractions, these initial biomass fractions can be subsequently converted into platform chemicals for their conversion into target molecules, added-value chemicals, solvents, and materials [1,7,14,15].

The catalytic conversion processes involve deoxygenation (mostly hydrogenation and hydrotreating oxidation), isomerization (skeletal rearrangement), CH activation, CC cleavage, and dehydrogenation. These conversion techniques are being widely utilized due to the presence of reactive ox-functional groups. This review briefly summarizes the recent research on the catalytic conversion of hemicellulose into FA, hexose sugar into HMF, and lignin into PCA and their transformation into value-added products.

2. Biomass-Derived Platform Chemicals

2.1. 5-Hydroxymethylfurfural (HMF)

HMF has been produced by acatalytic or non-catalytic route: dehydration of hexoses, sugars, or acid-catalyzed hydrolysis, or dehydration of cellulose [3,15–17]. The growth of

the worldwide market for HMF is expected to reach multimillion USD in 2030 [18]. In the list of worldwide manufacturers, industries AVA Biochem, Robinson Brothers, Penta Manufacturer, NBB Company, Sugar Energy, Beijing Lys Chemicals, Xuzhou Ruisai Technology, and Wutong Aroma Chemicals are the leading key players for the production of HMF and its utilization in derivatives (2,5-dimethylfuran (DMF), levulinic acid (LA), g-valerolactone (GVL), 5-hydroxymethyl-2-furan carboxylic acid (HMFCA), 2,5-diformylfuran (DFF), 5-formylfuran carboxylic acid (FFCA), and 2,5-furandicarboxylic acid (FDCA) [19]. The Schematic representation of HMF into value-added products is nicely summarized by Xu and co-workers [14]. Please see Figure 2 for derivatives of HMF. AVA biochemuseswaste sugar cane for the production of HMF [20]. As per the report in [15], most industries consider sugar cane waste for the production of HMF because sugar cane waste is very cheap and easily available worldwide. Most industries aim to increase HMF production capacity to ~1000 KTA per annum (kilometric tons) for the use of HMF. In HMF production processes, the formation of unwanted humin as a side product significantly affects the cost of the overall process, and the separation process consumes excessive energy [17]. However, the formation of HMF is not only reactive but also highly unstable due to the presence of a reactive aldehydic group. In an economic aspect, the utilization of cheaper waste biomass (i.e., vegetables, fruits, cooked rice, bread, pasta, and beverage waste) as starting feedstock would be essential for industrial-scale productions [11,17,21]. Sugarcane or any other food-squeezing waste (waste from fruit juice industries) is cheaper, receiving significant attention for the industrial-scale production of HMF and other platform chemicals.

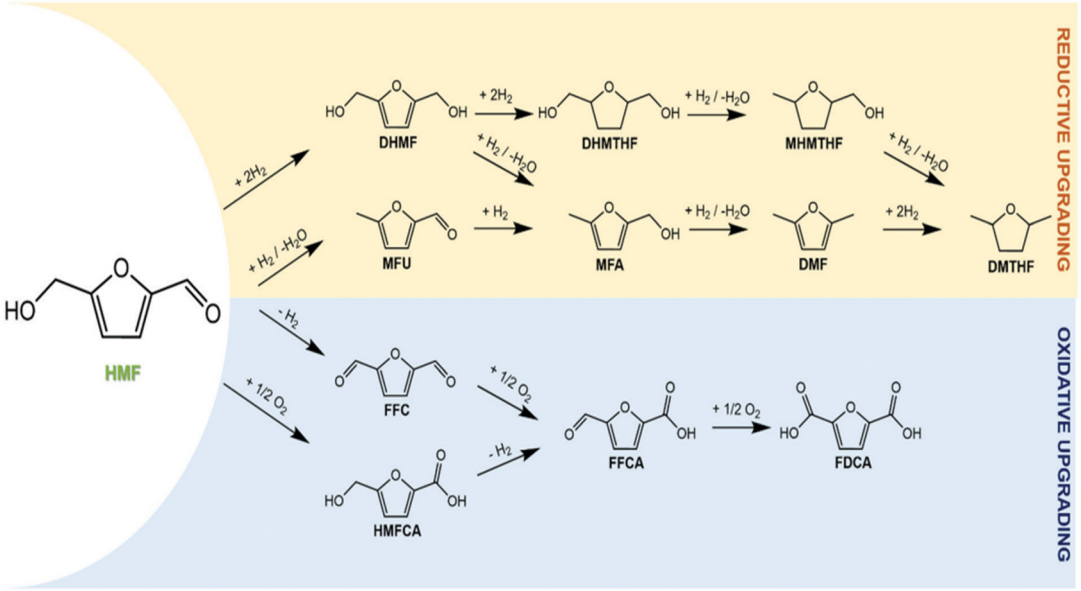


Figure 2. Catalytic transformations of HMF into added-value chemicals. (Figure was adopted ref. [17] with copyright permission).

Catalytic systems (homogenous, heterogenous, enzyme, and photocatalytic) have been employed for the synthesis of HMF from hexose sugar (including glucose, fructose, mannose, galactose, cellobiose, sucrose, starch, xylose, and arabinose) [17,22]. Most of the studies are based on the utilization of fructose rather than glucose. However, the utilization of glucose for the selective production of HMF, although challenging, is more worth while than fructose conversion. Glucose conversion reactions can follow several side paths and produce unwanted side products due to the stable cyclic structure of glucose (aldose). Among the catalytic techniques, heterogeneous catalysts are advantageous over other catalytic systems (easy separation, handling, recyclability, and safety). As per the literature, using a solid acid catalyst is beneficial in sugar dehydration. Solid acid catalysts such as ion-exchange resins, hetero-poly acids, niobic acid, niobium phosphate, vanadium phosphate,

sulfated zirconia, Amberlyst-15, and acid-functionalized materials such as carbon and mesoporous silica, etc. are recommended in these conversions [17,22,23]. However, the separation of solid catalysts from solid biomass residue and humin after the reaction is a cost-effective process. In most of the cases, HMF yield was found to be higher (<90%). However, the separation process for HMF after synthesis is challenging due to the formation of humin as a side product. Unfortunately, most synthesis methods are less cost-effective for producing HMF from fructose selectively. Aqueous phase production of HMF tends not to proceed well due to the formation of side products via the rehydration of HMF as well as the condensation of HMF and/or fructose to form unwanted humin polymers. However, side products such as LA and formic acid (FA) formed during HMF production due to the rehydration of HMF. HMF yield was improved by using nonpolar organic solvents. In the case of polar solvents, the formation of water during sugar dehydration affects the selectivity of HMF through subsequent rehydration and condensation reactions. Most organic solvents (BuOH, DMSO, hexane, alcohols, and ionic liquids) are not easily separable from the HMF product [24–26]. Hence, HMF recovery is more complicated. In brief, the synthesis of HMF is considered a simple approach; however, a wide range of catalysts have been investigated in these conversions. The separation process for HMF is very tedious, which can significantly affect the recovery yield of HMF throughout the process [24–26].

Dumesic and co-workers suggest an efficient approach to using a biphasic solvent system, in which HMF yield improves over a homogenous catalyst [27]. They use NaCl salt as an electrolyte to extract HMF from the water phase into the organic phase. Morales and co-workers conducted a similar study using niobic acid and H_3PO_4-treated tantalum oxide hydrate catalysts in a biphasic water-2 MIBK solvent system [28]. Davis and co-workers also investigated the combination of Sn-Beta with HCL in a water–THF solvent system for the high-yield production of HMF [29]. In addition, different types of sugar feedstocks (glucose, fructose, mannose, galactose, cellobiose, sucrose, starch, xylose, and arabinose) are utilized to produce a higher yield of HMF in a water-THF system [23,30]. An immiscible solvent system aims to prevent HMF from rehydration and condensation reactions due to water formation during sugar dehydration and enhances HMF yield. Noteworthy, recovering HMF from organic solvent is difficult [31]. Instead of HMF recovery from organic solvent, efficient utilization of HMF/solvent crude into another useful product can be more effective from an economic point of view, as suggested by Upare and co-workers [32,33]. Upare and co-workers demonstrated an efficient integrated process for producing HMF derivatives (DMF, DHMF, and poly (2,5-furandimethylene succinate)) from fructose. In this two-step integrated process, fructose was first dehydrated to HMF using an immiscible BuOH solvent and an acidic resin catalyst (Amberlyst-15). The immiscibility of BuOH can prevent HMF from being produced by water during reactions. This efficient process offers easy separation of catalyst and unreacted fructose from the crude product (HMF/BuOH), which was directly utilized in the synthesis of DMF (fuel with the same properties as BuOH), DHMF (intermediate), and poly (2,5-furandimethylene succinate) with a higher yield [33]. Figure 3 represents the schematic representation of the integrated process from glucose to HMF and derivatives, and Figure 4 represents the integrated process for the HMF form cellulose and HMF derivatives. In addition, the catalyst was simply separated from the unreacted fructose by washing it with water after the first reaction. The recyclability, efficiency, and extended operation afforded by this process make it particularly favorable environmentally and industrially and establish it as a new method for producing HMF derivatives.

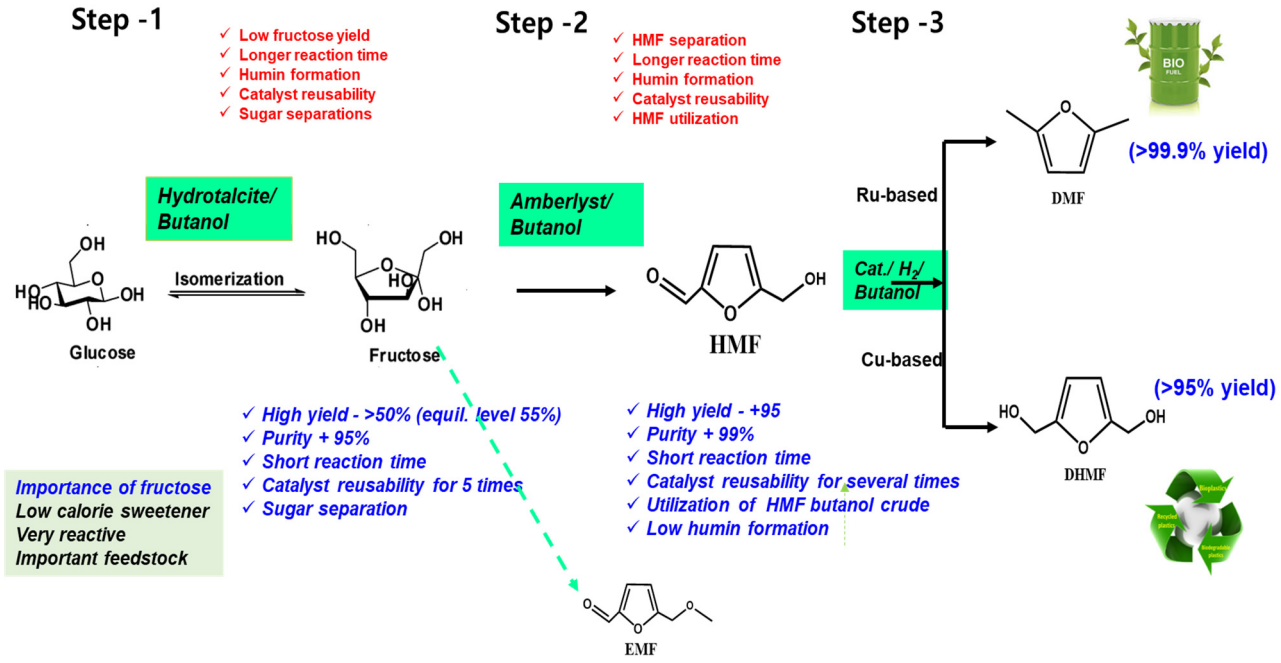


Figure 3. An integrated process of glucose isomerization into HMF and derivatives [32,33].

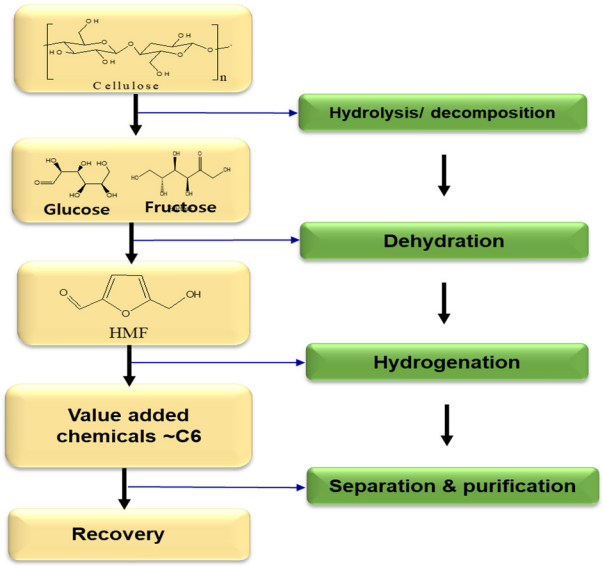


Figure 4. An integrated process of cellulose into HMF and derivatives.

2.2. Furfural (FA)

FA is an important platform where chemicals can be converted into fuel and chemicals. FA is mainly derived from hemicellulose biomass (xylan) and pentose sugars. The US DOE already approved it in the list of top 30 platform chemicals due to its wide range of derivatives and applications in various fields for numerous uses, such as intermediates and solvents in fine chemicals, flavoring agents, cleansing agents, antiseptics, polymers, cosmetics, refineries, automotive, construction, foundries, pharmaceuticals, paints, coating, agriculture, and others. As per the report [34], furfural is very useful in various refractory materials (bricks, fiberglass, and ceramic composites), and its demands are expected to increase in the growing construction industry. However, furfural is a selective solvent for the refinement of lubricants and rosin and raw material for the formulation of polymers (Nylon 66 and 6). Similar to FA, furfuryl alcohol (FAL) (a derivative of FA) has the same potential for various applications. The growing research activities for utilizing FAL in

cosmetics, plastics, and resins are increasing, which would enhance the demands and consumption of FA and FAL and are likely to boost the global market in the upcoming years. Global demand for FA is expected to reach 954.36 million USD by 2030, with a compound annual growth rate (CAGR) of ~7.0%. The main industries holding the global FA market are Illovo Sugar Africa (Pty.) Ltd., Linzi Organic Chemical Inc. Ltd., Trans Furans Chemicals BVBA, Central Romana Corporation, DalinYebo, Hebeichem, KRBL Ltd., and Silva Team S.p.A., LENZING AG [34].FA is directly involved in the production of more than 100 useful chemicals [34]. The main derivatives, pentanediols, FAL, tetrahydrofuran, maleic anhydride, and 5-Methlytetrahydrofuran (MTHF), are manufactured on a commercial scale [34,35]. The Schematic representation ofFA into value-added products is nicely summarized by Xu and co-workers [14]. By considering growing demands, FA production capacity must increase to multiple levels. However, the synthesis of FA-form pentose sugar and xylan hydrolysis and dehydration have been well explored. Few technologies related to the use of homogenous catalysts (carboxylic acid and mineral acids) are less efficient, producing low yields for FA due to humin formation, and are also limited due to high energy consumption, safety concerns, separation issues, etc. As with HMF, the aldehyde group in FA is very reactive; hence, the controlled formation of FA from bio-based feedstock is complicated.

To address these critical issues, several researchers and the science community are focusing on developing FA production techniques based on heterogenous catalysis, by which productivity and separation efficiencies can be somehow improved. For improvement, the utilization of additives such asionic liquids and supercritical CO_2 extraction techniques has been suggested. Arundhati and co-workers nicely summarized the catalytic studies and processes for the production of FA-form hemicellulose feedstocks (sugars such as xylose, arabinose, glucose, galactose, mannose, etc.) [36,37]. Several reviews found that the list of homogenous and heterogenous catalysts and their activities for FA production is well summarized [17]. Catalytic transformations of FA into value added chemicals shown in Figure 5. Among the hemicellulose feedstocks, xylan (derived from wood and crops) is composed of xylose units, commonly used for laboratory-scale catalyst testing for FA productions to achieve a maximum of 70~80% of FA yield (theoretical). As per reports, high temperatures are necessary to obtain a higher yield of FA. So far, most solid acid catalyst systems (with and without modification) have been utilized in these important conversion processes. The catalyst system includes Zeolites (Sn-Beta, HY-faujasite, H-mordenite, and H-ferrierite), solid acid oxides (TiO_2, ZrO_2, SnO_2, and Al_2O_3, SiO_2/Al_2O_3, etc.), acidic resin catalysts (Nafion SAC-13, Nafion-117, Amberlyst-15, and Amberlyst-70), phosphate-based materials (SAPO-5, SAPO-11, SAPO-40, and SAPO-44), sulfonated materials (Carbon, graphene oxide, metal oxide, etc.), and mixed catalyst systems [23,38,39]. In brief, catalysts with Brønsted acid sites are promising candidates for FA synthesis from pentose sugars, and the combination of Lewis acid sites and Brønsted acid sites is important in the two-step mechanistic process of hemicellulose [23]. However, diffusion issues can affect catalytic efficiency for both reactants and products. In solution, using a material with a higher surface area and a higher porosity has been strongly recommended, by which the activity of the process will enhance through improved adsorption and desorption efficiency and also help overcome catalyst deactivation with improved recyclable efficiency. Together with heterogenous catalyst systems, biphasic solvent systems (H_2O/methyl isobutyl ketone (MIBK), H_2O/toluene, and dimethyl sulfoxide (DMSO)) are also recommended for improvement in catalytic and separation efficiencies [37]. Upare et al. have developed a sulfonated graphene oxide catalyst that has excellent catalytic activity for the synthesis of FA (86.4% yield) from xylan with reusable activity [40]. Schematic representation for xylan to FA and its derivatives shown in Figure 6. This approach demonstrated the presence of Brønsted acid (SO_3H) sites together with other oxy-functional groups, which are very important in such types of biomass conversion processes. However, the same group has demonstrated superior catalyst systems for the production of pentanediols from FA.

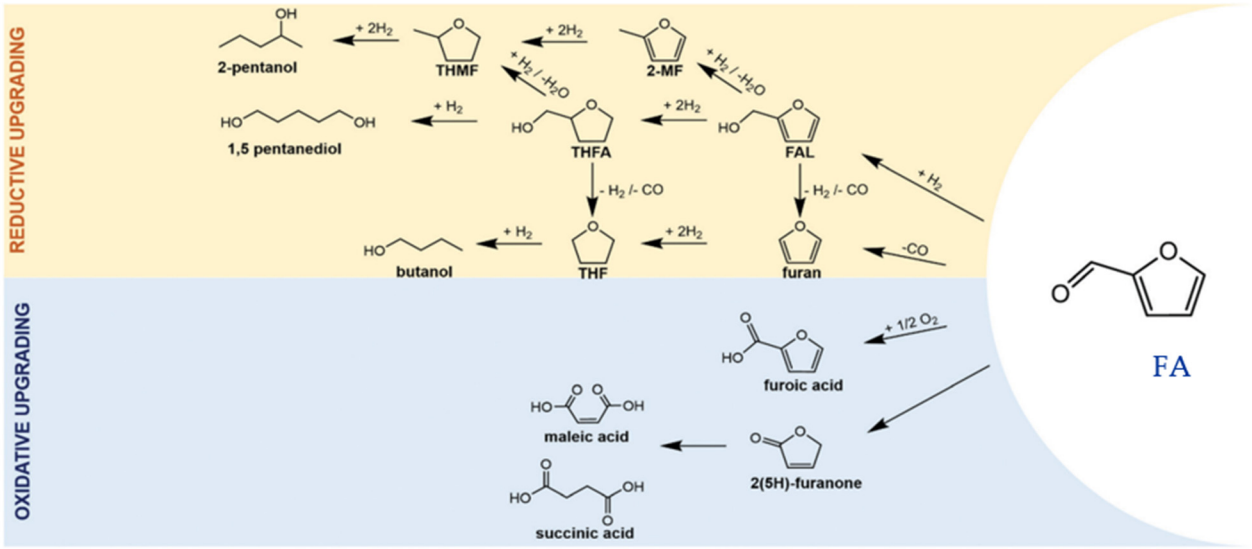


Figure 5. Catalytic transformations of FA into value-added chemicals (Figure was adapted from ref. [17] with copyright permission).

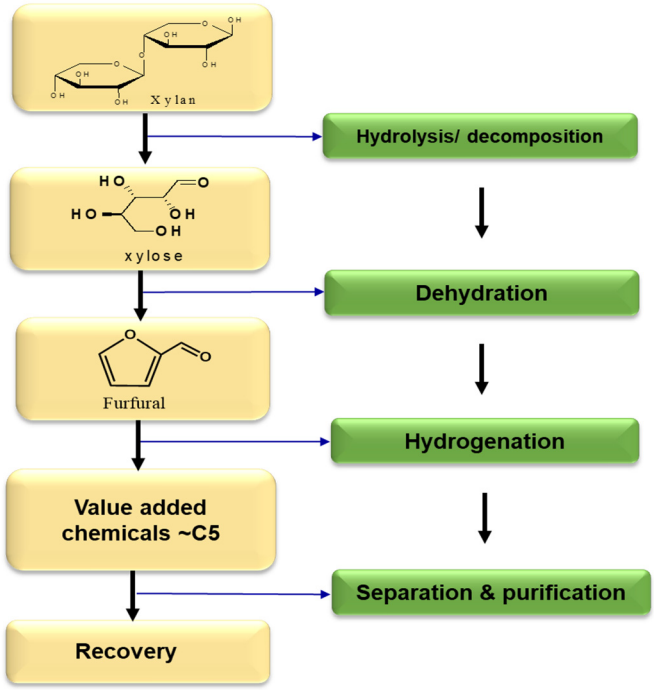


Figure 6. An integrated process Xylan into FA and derivatives.

Of course, several steps are involved in the commercial-scale production of FAL from initial biomass feedstocks (agricultural residue, woody biomass) [36]. However, the yield of FA is limited due to several side reactions associated with the initial residual feedstocks, and it consumes lots of energy. For efficient production of FA, larger-scale operations must be modified to achieve higher yields (>80% based on xylose) with less energy consumption. However, the following are the challenges associated with conventional FA production: lower yields due to undesired side reactions affect the yield of FA by 45–55%. The use of pentose sugars instead of initial biomass can improve the efficiency of processes. In addition, other important factors should be addressed (such as high-energy equipment, equipment corrosion due to the use of mineral acid, catalyst and product separation and reusability, pollution, and minimizing side reactions) [36]. At present, AVPA technology

and Chemtex technology are the most efficient technologies for manufacturing FA with minimal problems [36]. AVPA technology, based on acid vaporization and acidification based on a fluidized bed reactor system, involves steps for acid vaporization, acidification of biomass, and FA recovery. Chemtex technology is based on the hydrolysis of biomass with a dilute acid, followed by FA extraction and purification using organic solvents.

2.3. Protocatechuic Acid (PCA)

An aromatic acid, PCA, is a type of widely distributed naturally occurring phenolic acid with similar structural compositions to gallic acid, caffeic acid, vanillic acid, and syringic acid; these are well-known antioxidants. Most aromatic chemicals are derived from fossil-based feedstocks, prompting the emission of greenhouse gases [41]. Chemical structure of PCA displayed in Figure 7. Among aromatic chemicals, protocatechuic acid (PCA, 3,4-dihydroxybenzoic acid) is a dietetic phenolic acid that occurs in nature and widely exists in our daily diet and surrounding plants. PCA has been reported to possess antioxidative, antibacterial, and anti-aging activities [42–49]. Phenolic compounds are considered secondary metabolites derived from phenylalanine via the shikimic acid pathway. Many studies have been conducted on PCA and its derivatives (esters, aldehydes, etc.), and it has been reported for its potential properties, such as antioxidant activity, antibacterial activity, antidiabetic activity, and anti-aging activity [45,50]. Wang and co-workers also reported the anti-inflammatory effect of PCA on LPS-stimulated BV2 microglia [51]. Apart from its pharmacological significance, PCA is used as a building block for synthesizing plastics, polymers, bio-based active films, and food packaging applications [52]. Liu and co-workers reported that 0.5% and 1% PCA-incorporated chitosan film in food packaging increased the film's mechanical and antioxidant properties and could be applied as a potential active packing material for food preservation [53]. Sun and co-workers reported that the composite polymer of protocatechuic acid and aniline functions as an electrode with excellent electrochemical activity [54]. So far, the production capacity of PCA has not grown much, and it is expected to reach 17 million USD by 2030 due to its potential applications in various fields. Most industries are producing PCA by enzymatic route from bio-based feedstocks such as vanillin. The industries Aktin Chemical, Henan Lyle Wormwood, Taizhou Zhongda Chemical, and Xi'an Seaso are the key players in the worldwide production of PCA [49,55].These industries produce PCA form vanillin.

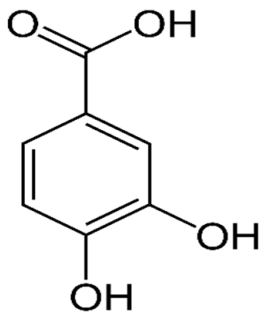


Figure 7. Chemical structure of protocatechuic acid.

2.3.1. Synthesis of PCA from Lignin and Plants

Lignin is the most abundant aromatic biopolymer and has great potential as an aromatic source to produce bio-based products. The schematic representation is shown in Figure 8. Lignin is a natural amorphous and three-dimensional complex branched polymercomposedmainly of three primary precursors: *p*-coumaryl, coniferyl, and sinapylalchohols [16,56,57]. Nguyen et al. studied the depolymerization of lignin using the co-upgrading of ethanol-assisted depolymerized lignin (EDL) into PCA and polyhydroxyalkanoic acid (PHA) without any separation process [58]. The study reported that an engineered *Pseudomonas putida* KT2440 strain was utilized to convert the depolymerized lignin into PCA and PHA, resulting in a 17.5% (*w*/*w*) yield of PCA of total lignin monomers

and a 21.26% yield of PHA (*w*/*w*) of dry cell weight from 0.5 mL of EDL, showing the potential of lignin valorization into PCA. Zhang and co-workers have nicely studied the valorization of lignin into PCA and other aromatic acids [9]. PCA can be chemically synthesized through alkaline fusion of vanillin or direct extraction from plants. Depending on the origin of non-renewable petroleum resources, chemical methods have several drawbacks, such as the destructive effects on the environment of toxic chemical hydrochloride and the harsher reaction conditions requiring a high temperature of up to 250 °C [59]. As for the direct extraction method, solvent extraction using organic solvents from plants is the most common and efficient method for PCA production [60]. However, the direct extraction method revealed a low yield, thus rendering economic infeasibility. For example, a study of PCA extraction by the supercritical carbon dioxide method reported that only 64.09 g/g of PCA was extracted from *Scutellariabarbata* D. Don [61]. Therefore, the biosynthesis of protocatechuic acid is more economical to meet its demand for various applications. Recent metabolic engineering offers a new perspective to overcome the limitations of chemical methods while at the same time aiming to achieve an effective strategy to produce "natural" PCA. In a study conductedto produce "natural" PCA in *Pseudomonas putida* KT2440 via multilevel metabolic engineering strategies by Jin Li and co-workers, it was reported that the engineered *Pseudomonas putida* KT2440 strain produced 12.5 g/L of PCA from glucose fermentation [62].

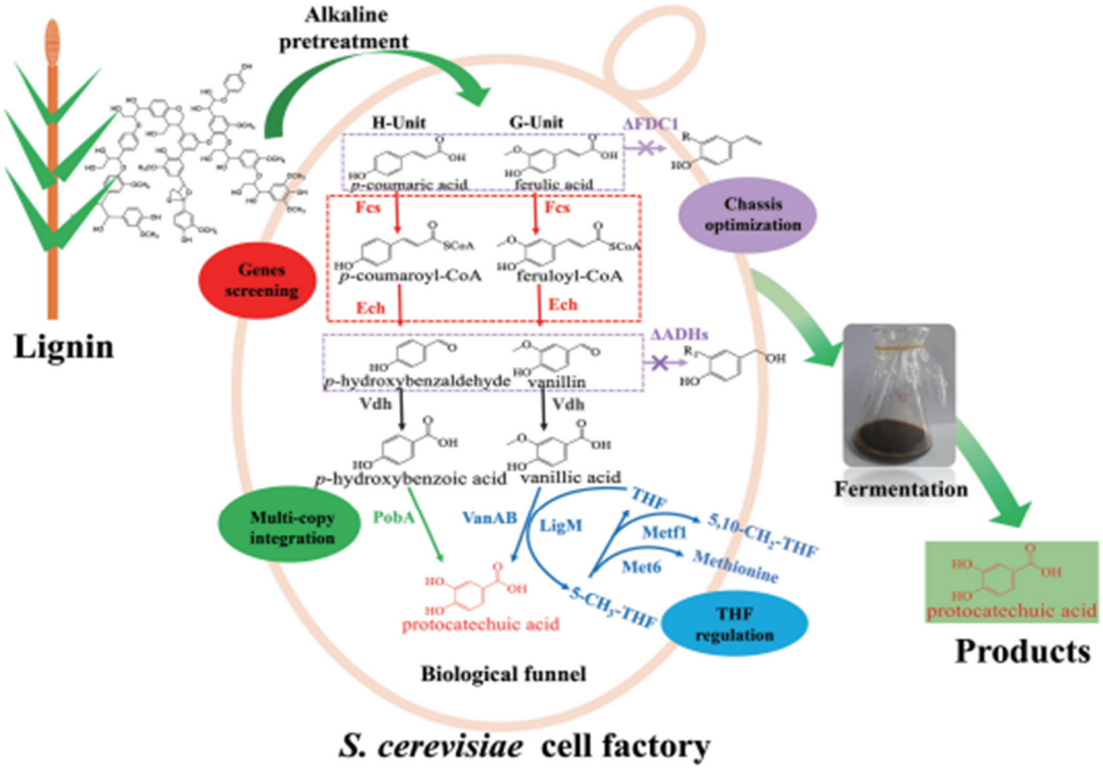


Figure 8. Pathway of *S. cerevisiae* cell factory for production of protocatechuic acid from lignin.

Strategies such as chassis optimization, gene screening, multi-copy integration, and tetrahydrofolic acid metabolism regulations are involved in the biological funnel paths for lignin oligomers in the S. cerevisiae cell factory (denotation; Fcs-4-coumarate-CoA ligase; Ech -enoyl-CoA hydratase/aldolase; Vdh—vanillin dehydrogenase; PobA—p-hydroxybenzoate hydroxylase; VanAB- vanillic acid O-demethylase oxygenase; LigM-vanillic acid O-demethylase oxygenase. THF -tetrahydrofolic acid) (adopted form with copyright permission, [9]).

2.3.2. Protocatechuic Acid Derivatives

PCA is a promising compound, but the derivatives of phenolic acids have been reported to improve their hydrophobicity for various industrial applications, as reported by Maria Figueroa-Espinoza [63]. Esterification of PCA with alkyl alcohol shown in Figure 9. Furthermore, the efficiency of the antioxidant properties of phenolic acids is dependent on their structure, volatility, heat stability, and pH sensitivity [64]. According to Decker, the solubility of the phenolic acids in relation to the site of oxidation is an essential factor to be considered [65]. Because of the relatively low solubility of phenolic acids in aprotic media, applications for these natural antioxidants in oil-based applications (e.g., foods and cosmetics) are limited. The hydrophobicity of phenolic acids can be enhanced by chemical or enzymatic lipophilization. This is achieved by esterifying the carboxylic acid function of the phenolic acid with an alcohol to obtain an amphiphilic molecule, which should maintain its original functional properties (antioxidant, antimicrobial, etc.) [66,67]. PCA derivatives can be synthesized in several ways, and the most common method is esterification with various alcohols. Nihei and colleagues described the synthesis of alkyl esters of PCAs by an acid-catalyzed one-step esterification reaction using dicyclohexylcarbodiimide (DCC) as an activating agent [67]. The study reported that the antimicrobial and antifungal activity against *Saccharomyces cerevisiae* of alkyl esters of PCAs is comparable with alkyl gallates (3,4,5-trihydroxybenzoates) and increases with each additional CH_2 group. The reason for such an increase in activity may be due to the increased lipophilicity of alkyl 3,4-dihydroxybenzoates, which affects their movement across the membrane [68].

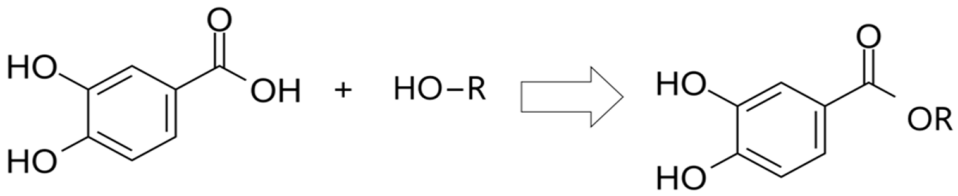


Figure 9. The esterification of PCA with alcohol to produce PCA derivatives (longer-chain alkanes) Adopted form with copyright permission [67].

2.3.3. Effects of PCA Derivatives

As described by Cho and co-workers, through in vivo tests, the derived alkyl esters of PCA have been reported to exhibit antioxidant and skin-brightening effects [69,70]. The schematic representation is shown in Figure 10. The study showed that PCA derivatives contribute to down-regulating the extracellular and intracellular melanin contents in B16 melanoma cells compared to non-conjugated PCA. Furthermore, the study investigated the antioxidative effect of these PCA derivatives by evaluating their free radical scavenging ability. It was found that longer chains of PCA derivatives decreased oxidative stress more effectively than non-conjugated PCA, especially PCA derivatives conjugated with C-5 alcohol and C-6 alcohol. These studies suggested that an increase in hydrophobicity of PCA derivatives due to the conjugating alkyl esters improves the delivery of PCA derivatives into the cells, which enhances the pharmacological activities of PCA. Daré and co-workers proposed an explanation for this effect based on the electron-donating enhancement caused by the alkyl chain leading to a well-stabilized phenoxyl radical. Moreover, Daré and co-workers reported that alkyl esters of PCA exhibit an anti-aging effect by preventing photodamage in UVB-irradiated L929 fibroblasts [71]. However, some enzymatic routes are already reported in the literature for the derivatization of PCA into value-added products [72].

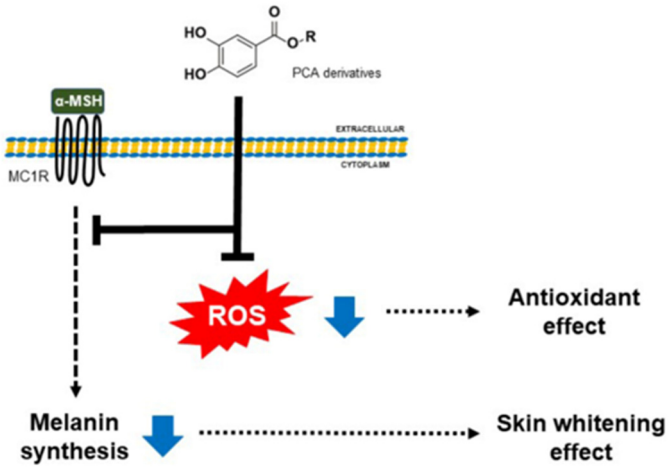


Figure 10. Schematic representation for anti-melanogenesis and antioxidant effects exerted by PCA derivatives for brightening of skin mediated by inhibiting the melanin synthesis induced via α-melanocyte-stimulating hormone in B16 melanoma cells. Adapted from [70].

3. Summary and Perspective

Bio-based feedstocks are cheap and renewable. More effective technology must be created in order to make use of these plentiful resources. The development must be involved with the design of an efficient catalyst system with scale-up capacity. Similarly, a pilot or commercial-scale reaction and separation system must be wellequipped with a feasible facility that requires less energy consumption. A deep understanding of the biomass valorization process is necessary to understand the catalysts and reactions involved, characterize the feedstock, and identify the products of biomass valorization. Developing biorefinery processes could be a huge breakthrough in minimizing research gaps, leading to a closed-loop bioeconomy that reduces waste while increasing output. All biomass-derived chemicals, HMF, FA, and PAC, have significant potential for various applications. This review summarizes the different approaches for the production of these important chemicals. So far, laboratory-scale investigation data are quite sufficient for the development of scale-up processes. Still, from an application point of view, we need more improvement to achieve these platform chemicals more cheaply for their utilization to fulfill growing world energy needs.

For commercial scale development, several factors need to be considered: cheaper catalysts, reusability, cheaper feedstocks, higher yield production of the desired product with minimal waste, reactors and equipment that are easy to handle and require less energy consumption, controlled pollution, bio-based feedstocks that are cheaper and easily available all the time, efficient separation processes, knowledgeable operating staff, etc.

Future research for bioderived substrates should target the development of efficient conversion processes that could offer selective production of target products with higher yield without wastage and lower energy consumptions; these conversion processes can be either catalytic or non-catalytic. In the case of catalytic processes, comprehensive knowledge of the mechanistic pathway of reaction involved on the surface of catalysts, tailoring the morphology of the catalysts, and experimental and theoretical studies will lead to improved performance and practical application in industry. This review will be extremely representative and contribute to promoting international biorefinery innovations.

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