

## Ferulic acid From Lignocellulosic Biomass: Review

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### Abstract

Lignocellulosic materials are important natural renewable resources. Wood, the predominant source is among the most extensively exploited engineering materials. This is because it is low in cost, renewable and strong and it requires low processing energy. Wood and other lignocellulosic material consists of flexible cellulose fiber assembled in an amorphous matrix of lignin with a hemicellulosic polymer. Agricultural residues, water plants, grasses and other plant substances are sources for lignocellulosic materials. These materials are unique in their chemical compositions as well as their chemical, physical and mechanical properties. They consist mainly of cellulose, hemicellulose, lignin and a small amount of extractives. A number of different pretreatment methods of lignocellulosic materials to release lignin, cellulose and hemicellulose are addressed such as chemical pretreatment, steam pretreatment and biological pretreatment. Ferulic acid, one of the phenolic compounds in lignin which are released after pretreatment, can be further utilized for many industrial purposes. Biotransformation of phenolic compounds like ferulic acid usually carried out by various microorganisms into value added commodities have been identified.

**Keywords:** lignocellulosic, phenolic compound, ferulic acid

### I. INTRODUCTION

Lignocellulosic biomass is not only renewable resources but also the most abundant source of organic components in high amounts on the earth, cheap and huge potential availability. To date, extensive research on effective

utilization of lignocellulosic material has been carried out and en-going.

Lignocellulosic biomass is referred as plant biomass that is composed of cellulose, hemicellulose and lignin. The composition of these materials varies. The major component is cellulose (35-50%), followed by hemicellulose (20-35%) and lignin (25%). Proteins, oils and ash make up the remaining fraction of lignocellulosic biomass [1]. Cellulose is a high molecular weight linear polymer of  $\beta$ -1,4-linked D-glucose units which can appear as a highly crystalline material [2]. Hemicelluloses are branched polysaccharides consisting of the pentoses D-xylose and L-arabinose, and the hexoses D-mannose, D-glucose, D-galactose and uronic acids [3]. Lignin is an aromatic polymer synthesised from phenylpropanoid precursors [4]. Lignins are divided into two classes, namely "guaiacyl lignins" and "guaiacyl-syringyl lignins", differing in the substituents of the phenylpropanoid skeleton. Guaiacyl-lignins have a methoxy-group in the 3-carbon position, whereas syringyl-lignins have a methoxy-group in both the 3-carbon and 5-carbon positions. Softwoods generally contain more lignin than hardwoods [3]. Compositions of certain lignocellulosic biomass are listed in table 1.

Table 1: Composition of some agricultural lignocellulosic biomass.

	Composition (% dry weight basis)		
	Cellulose	Hemicellulose	Lignin
Corn fiber	15	35	8
Corn cob	45	35	15
Rice straw	35	25	12
Wheat straw	30	50	20
Sugarcane	40	24	25
bagasse			

Lignocellulosic biomass includes many different types, which may be grouped into four categories: various agricultural residues (straw, hulls, stems, and stalks), deciduous and coniferous woods, waste from pulp and paper industry and herbaceous energy crops. Extensive research has been completed on conversion of lignocellulosic materials to other products like ethanol, butanol, ferulic acid and etc. A number of pretreatment methods have been described to fractionate, solubilize, hydrolyze and separate cellulose, hemicellulose and lignin components [5-8]. Pretreatment is an important procedures for practical

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cellulose conversion processes. The goal is to break the lignin seal and disrupt the crystalline structure of cellulose.

## II. PRETREATMENT OF LIGNOCELLULOSIC MATERIALS

The effect of pretreatment of lignocellulosic materials has been recognized for a long time [9]. The purpose of the pretreatment is to remove lignin, hemicellulose, reduce cellulose crystallinity and increase the porosity of the materials. Pretreatment can be divided into physical, physico-chemical, chemical and biological pretreatments.

### Physical treatment

Physical treatment can be mechanical comminution or pyrolysis. The mechanical comminution includes combination of chipping, grinding and milling to reduce cellulose crystallinity. The power requirement of mechanical comminution of agricultural materials depends on the final particle size and the waste biomass characteristics [10]. Pyrolysis pretreatment are conducted under temperature greater than 300° C. Cellulose will rapidly decomposes to produce gaseous products and residual char [11-12]

### Physico chemical pre treatment

This method can be divided to three major groups which are steam explosion (hydrolysis), ammonia fiber explosion (AFEX) and CO<sub>2</sub> explosion.

Steam explosion is the most commonly used method for pretreatment of lignocellulosic materials [13]. It is usually worked together with H<sub>2</sub>SO<sub>4</sub> (or SO<sub>2</sub>) or CO<sub>2</sub> to improve enzymatic hydrolysis, decrease the production of inhibitory compounds, and lead to more complete removal of hemicellulose [33]. In this method, chipped biomass is treated with high-pressure saturated steam and then the pressure is swiftly reduced, which makes the materials undergo an explosive decompression. The material is exposed to temperature of 160-260°C for several second to a few minutes before exposed to atmospheric pressure. These may cause hemicellulose degradation and lignin transformation due to high temperature, thus increase the cellulose hydrolysis. The factors that affect steam explosion pretreatment are residence time, temperature, chip size and moisture content [14]. Optimal hemicellulose solubilization and hydrolysis can be achieved by either high temperature and short residence time (270°C, 1 min) or lower temperature and longer residence time (190°C, 10 min) [14]. Recent studies indicate that lower temperature and longer residence time are more favorable [15].

AFEX pre treatment is similar with steam explosion. The difference of the process is usage of liquid ammonia instead of steam itself. Typical process of AFEX includes of 1-2 kg of liquid ammonia at temperature 90°C with residence time of 30 min. It can be used for the pretreatment of many lignocellulosic materials including alfalfa, wheat straw, wheat chaff [16], barley straw, corn stover, rice straw [17], municipal solid waste, softwood newspaper, kenaf

newspaper [18], coastal Bermuda grass, switchgrass [19], aspen chips [20], and bagasse [18]. AFEX process is not very effective for the biomass with high lignin content such as newspaper (18-30% lignin) and aspen chips (25% lignin). The hydrolysis yields of AFEX-pretreated newspaper and aspen chips were reported as only 40% and below 50%, respectively [21]. Disadvantage of this process is, liquid ammonia produced after processing have to be recycle in order to reduce cost and protect the environment.

CO<sub>2</sub> explosion is hypothesized to form carbonic acid during the pretreatment of lignocellulosic biomass and as such increase the hydrolysis rate. Zheng et al. (1998) found that CO<sub>2</sub> explosion was more cost-effective than ammonia explosion and moreover, did not cause the formation of inhibitory compounds that would occur in steam explosion process.

### Chemical pretreatment

Chemical pretreatment of lignocellulosic can be divided to 5 types of pretreatment. Ozonolysis, acid hydrolysis, alkaline hydrolysis, oxidative delignification and organosolv process are the types of chemical pretreatment.

Ozonolysis pretreatment has the following advantages: (1) it effectively removes lignin; (2) it does not produce toxic residues for the downstream processes; and (3) the reactions are carried out at room temperature and pressure [23]. However, a large amount of ozone is required, making the process expensive.

Acid hydrolysis usually used concentrated acid such as H<sub>2</sub>SO<sub>4</sub> and HCl. The dilute sulfuric acid pretreatment can achieve high reaction rates and significantly improve cellulose hydrolysis [24]. There are primarily two types of dilute acid pretreatment processes: high temperature (Temperature greater than 160°C), continuous-flow process for low solids loading (5-10% [weight of substrate/weight of reaction mixture] [25-26] and low temperature (Temperature less than 160° C), batch process for high solids loading (10-40%) [24],[27]. However, concentrated acids are toxic, corrosive and hazardous and require reactors that are resistant to corrosion. In addition, the concentrated acid must be recovered after hydrolysis to make the process economically feasible [28]. Furthermore, a neutralization of pH is necessary for the downstream enzymatic hydrolysis or fermentation processes.

Alkaline hydrolysis uses dilute NaOH which will cause swelling, leading to an increase in internal surface area, a decrease in the degree of polymerization, a decrease in crystallinity, separation of structural linkages between lignin and carbohydrates, and disruption of the lignin structure [29]. This pretreatment was found to be effective for the hydrolysis of straws with relatively low lignin content of 10-18% [30], but these pretreatment was not effective for softwood with lignin content greater than 26%[31]

Oxidative delignification is carried out by using H<sub>2</sub> O<sub>2</sub>. About 50% lignin and most hemicellulose are solubilized by 2% H<sub>2</sub>O<sub>2</sub> at 30°C within 8 h, and 95% efficiency of glucose production from cellulose was achieved in the subsequent

saccharification by cellulase at 45° C for 24 h [32]. Oxidative delignification has been found to increase dissolution of lignin and cellulose crystallinity.

In the organosolv process, an organic or aqueous organic solvent mixture with inorganic acid catalysts (HCl or H<sub>2</sub>SO<sub>4</sub>) is used to break the internal lignin and hemicellulose bonds. The organic solvents used in the process include methanol, ethanol, acetone, ethylene glycol, triethylene glycol and tetrahydrofurfuryl alcohol [34], [35]. After pretreatment, the solvent is removed in order to prevent from inhibitory of the growth of organisms.

### Biological pretreatment

In biological pretreatment processes, microorganisms such as brown-, white- and soft-rot fungi are used to degrade lignin and hemicellulose in waste materials [36]. White-rot fungi like *P. chrysosporium*, are the most effective basidiomycetes for biological pretreatment of lignocellulosic materials [37]. It can produce lignin-degrading enzymes, lignin peroxidases and manganese- dependent peroxidases to delignify wood and to decompose the lignin polymer to yield vanillin, vanillic acid, ferulic acid, coniferyl aldehyde, guaiacylglycerol [54-55].

Enzymatic hydrolysis also can be carried by both bacteria and fungi, which can produce cellulase. The cellulase system usually consist of three extracellular hydrolytic enzyme: an endoglucanase which hydrolyzes the internal glycosidic linkages of cellulose; an exocellobiohydrolase which releases cellobiose units from the non-reducing end of the polymer; and a fl-glucosidase which hydrolyzes cellobiose to glucose. Bacteria belonging to *Clostridium*, *Cellulomonas*, *Bacillus*, *Thermomonospora*, *Ruminococcus*, *Bacteriodes*, *Erwinia*, *Acetovibrio*, *Microbispora*, and *Streptomyces* can produce cellulase. [40]. Fungi that have been reported to produce cellulase include *Sclerotium rolfisii*, *P. chrysosporium* and species of *Trichoderma*, *Aspergillus*, *Schizophyllum* and *Penicillium* [38,39]. Fig 2 shows the cellulose microfibrils that can be attack particularly by bacteria or fungi.

Biological pretreatment was previously reported as a safe and environmental friendly method for lignin removal from lignocellulose [40].

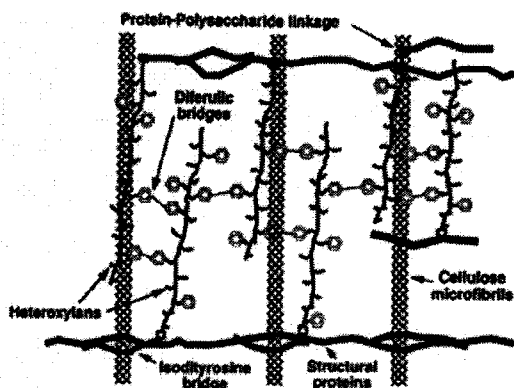


Fig 2 : Model for corn fiber cell walls.[41]

### III BIOTRANSFORMAATION OF FERULIC ACID FROM LIGNOCELLULOSIC BIOMASS

Biotransformation or biocatalysis encompasses the field of microbial transformations of organic or inorganic compounds which result in a change of chemical structure. The processes are now used for the preparation of very valuable specialty chemicals for the pharmaceutical, agricultural, flavor and fragrance, nutritional and chemical industries. Such processes are also exploited for the preparation of commodity chemical substances on an enormous industrial scale.

Ferulic acid is the major cinnamic acid found in the cell wall of woods, grasses and corn hulls [42]. It is widely distributed in higher plants where it is ester-linked to polysaccharide compounds. It plays important roles in plant cell walls including protein protection against pathogen invasion and control of extensibility of cell walls and growth [43]. Ferulic acid endows structural rigidity and strengthens cell wall architecture by cross-linking pentosan chains, arabinoxylans and hemicelluloses, rendering these components less susceptible to hydrolytic enzymes during germination [47].

The efficient pretreatment followed by enzymatic hydrolysis removal of ferulic acid from cell wall materials has been demonstrated and furthermore the acid can be exploited to produce value added aromatic compounds. List of some ferulic acid content in lignocellulosic biomass are listed in table 2.

Table 2 : List of ferulic acid content from lignocellulosic biomass.

Types of lignocellulosic biomass	Content of ferulic acid g/kg	Reference
Corn kernels	1	[44],[45]
Refine wheat	0.05	[46]
Wheat flour	0.5	[46]
Turmeric	1.5	[46]
Paddy straw	0.05	[80]

Ferulic acid also has been used as a 'lignin phenolic substrate' to model microbial degradations of aromatic compounds from chemical and petroleum industrial wastes [48-50]. Aromatic microbial metabolites of ferulic acid are also important flavor constituents in beer, wine, soy sauce, and fruit juices [81,82]. The great abundance of ferulic acid in nature has prompted several investigations into the potential for using ferulic acid as a starting material for microbial or enzymatic synthesis of useful aromatic chemical compounds [51]. Numerous studies on aerobic or anaerobic biotransformations of ferulic acid have been reported [42], [47], [57]. Some bacteria, fungi and yeast involve in ferulic acid biotransformation are listed in Table 3.

Table 3 : List of bacteria, fungi and yeast that involve in biotransformation of ferulic acid.

Organism	Reference
1. <i>Aerobacter sp</i>	[58]
2. <i>Bacillus sp</i>	[59]
3. <i>Escherichia coli</i>	[60]
4. <i>Nocardia sp</i>	[61]
5. <i>Aspergillus niger</i>	[61],[62]
6. <i>Candida intermedia</i>	[63]
7. <i>F.solani</i>	[63]
8. <i>Penicillium frequentans</i>	[61],[62]
9. <i>Saccharomyces cerevisiae</i>	[61],[62],[63]
10. <i>H. capsulata</i>	[63]
11. <i>Fusarium coeruleum</i>	[63]
12. <i>Hansenula anomala</i>	[61],[62],[63]
13. <i>Pestotatia palmarum</i>	[64]
14. <i>Rhizopus arrhizus</i>	[61],[62]

Conversions of ferulic acid to commercially valuable aromatic aldehydes like vanillin have been described [52-53]. Beside production of vanillin, biotransformation of ferulic also can give various of product such as coniferyl alcohol, cinnamic acid, caffeic acid and etc.

The major pathway of ferulic acid metabolism can be divide into decarboxylation and reductive conversion as in fig 3A-D. A number of products are formed from this decarboxylation and reduction process from ferulic acid which can be categorized as a value added product.

### Decarboxylation of ferulic acid

In the mechanism reported, the initial step of ferulic acid catabolism is catalyzed by a decarboxylase, and the formation of 4-hydroxy-3-methoxystyrene (4-vinylguaiacol) is observed (Fig. 3A). This process has been discovered in many fungi and yeast [65-67] and some bacteria [67-69]. The proposed mechanism for the decarboxylation catalyzed by ferulic acid decarboxylase involves the initial enzymatic isomerization of ferulic acid to a quinoid intermediate (Fig. 3), which subsequently decarboxylates spontaneously [61]. This mechanism is in accordance with the observation that a *para*-hydroxyl group is required for the decarboxylation process.

Phenolic acid decarboxylases of *Lactobacillus plantarum* [70], *Saccharomyces cerevisia* [71], *Bacillus subtilis* [72] and *B.pumilus* [83] have been characterized. Lee *at al* (1998) has demonstrated the transformation of ferulic acid by *B. pumilus*, which can produce 9.6 g/l of 4-vinylguaiacol from 25g/l ferulic acid corresponding to a molar yield of 49.7%. *Pseudomonas sp.* has been reported can produced 4-vinylguaiacol beside vanillic and protocatechuic acid [85]. Furthermore, *Fusarium solani* [66] and *Bacillus coagulans* [86] have been found to metabolized 4-vinylguaiacol to vanillin, vanillic acid, and protocatechuic acid.

### Reduction of ferulic acid

In the second phase of the mechanism, side-chain of ferulic acid is reduced and dihydroferulic acid is formed (Fig 3B). It can be conducted under aerob or anaerobic conditions.

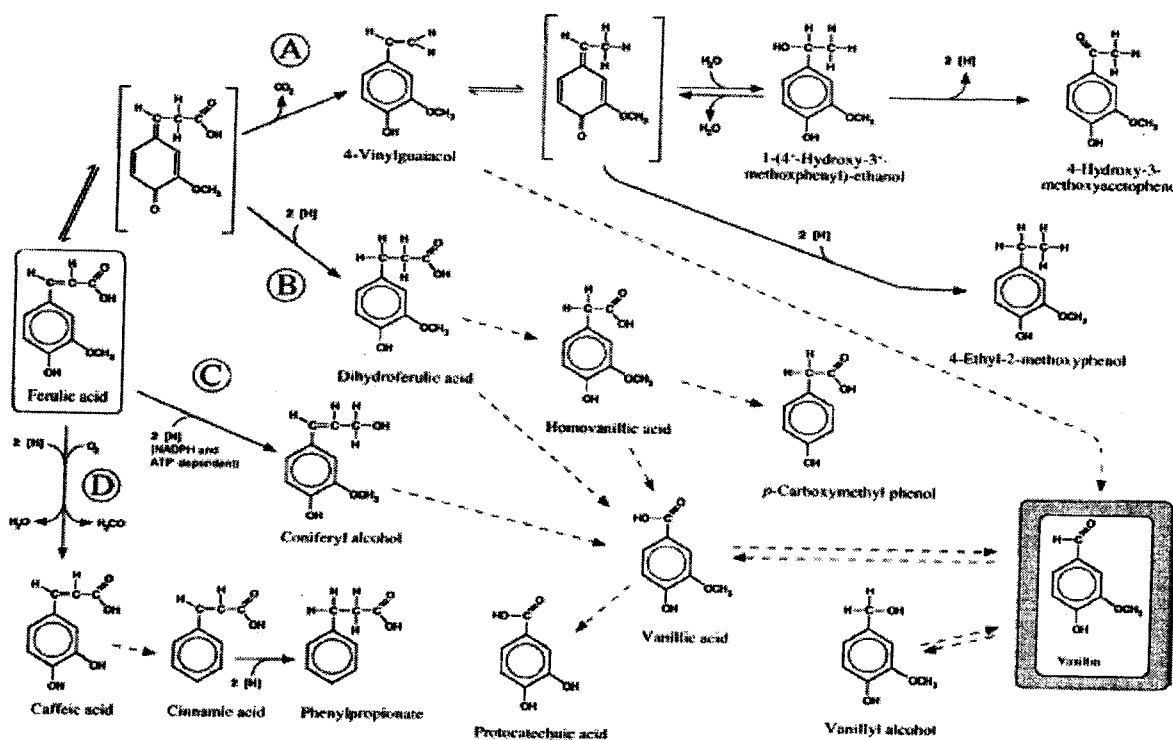


Fig 3A-D. Decarboxylation (A) and reductive conversion (B-D) of ferulic acid to yield vanillin.

Anaerobic degradation of ferulic acid can be carried by *Saccharomyces cerevisiae* [65], and *Lactobacillus plantarum* [73] while under aerobic condition, usually carried by *Phanerochaete chrysosporium* [74] and *Pseudomonas fluorescens* FE2 [75]. The mechanism of side-chain reduction was proposed to proceed via hydride attack

of a quinoid intermediate, initiated by an isomerization analogous to the decarboxylation reaction [42]. In *W. succinogenes*, dihydroferulic acid is further metabolized to homovanillic acid, *p*-carboxymethyl phenol, and vanillic acid [87].

Fig 3C shows another reductive degradation mechanism leading to coniferyl alcohol, which is further degraded to vanillic acid, vanillyl alcohol, and methoxyhydroquinone, has been identified in *Trametes* sp. [76], *Sporotrichum pulverulentum* [77] and *Pycnoporus cinnabarinus* [78]. Conversion of vanillic acid to protocatechuic acid followed by ring-degradation is a common biodegradative pathway in microorganisms [89]. Resting cells of *Rhodotorula rubra* [89] has been reported to convert ferulic acid to vanillic acid, then to guaiacol and protocatechuic acid under aerobic conditions. Vanillic acid with combination of two filamentous fungi can produce vanillin. This two step of biotransformation to vanillin are using two filamentous fungi which is *Aspergillus niger* in the first step to transform ferulic acid to vanillic acid and *Pycnoporus cinnabarinus* in conversion of vanillic acid to vanillin with a molar yield of 88% and 22% respectively [56]. The biotransformation was promoted by cellobiose, which diminishes the concurrent decarboxylation of vanillic acid to a by product, methoxyhydroquinone.

The demethylation of ferulic acid to caffeic acid (Fig 3D) is a common biotransformation reaction. Phenylpropionate is formed by side-chain reduction from cinnamic acid. *Enterobacter cloacae* [79] plays the main role in O-demethylated process to yield caffeic acid which is further dehydroxylated to cinnamic acid. Beside that, a facultative anaerobe *Enterobacter* DG-6 is also capable in O-demethylation of ferulic acid to caffeic acid under either anaerobic or aerobic conditions. Anaerobically, caffeic acid is metabolized to cinnamic acid by ring dehydroxylation. Cinnamic acid is then reduced to phenylpropionic acid which is subsequently metabolized to phenylacetic acid. Aerobically, caffeic acid is oxidized to protocatechuic acid [88].

Many biotransformation methods can convert ferulic acid into useful phenolic aromatic chemical compounds of value. The product such as vanillin is one of the most importance flavor and fragrance in the world market, vinylguaiacol as biodegradable polymer feedstock chemical and dimeric products of potential value as drugs. Sources of ferulic acid which is from lignocellulosic biomass are easily to extract with minimum cost required, therefore importance metabolite from ferulic acid can be performed by selected microorganisms.

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