

Review

A Review on the Transformation of Furfural Residue for Value-Added Products

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Abstract: As a by-product of lignocellulosic depolymerization for furfural production, furfural residue (FR) is composed of residual cellulose, lignin, humic acid, and other small amounts of materials, which have high reuse value. However, due to the limitation of furfural production scale and production technology, the treatment of FR has many problems such as high yield, concentrated stacking, strong acidity, and difficult degradation. This leads to the limited treatment methods and high treatment cost of furfural residue. At present, most of the furfural enterprises can only be piled up at will, buried in soil, or directly burned. The air, soil, and rivers are polluted and the ecological balance is destroyed. Therefore, how to deal with furfural residue reasonably needs to be solved. In this review, value-added products for furfural residue conversion are described in detail in the fields of soil culture, catalytic hydrolysis, thermal decomposition, and porous adsorption. The future studies reporting the FR to convert value-added products could find guidance from this review to achieve specific goals.

Keywords: furfural residue; value-added products; waste utilization; lignocellulose

1. Introduction

Furfural, which is also known as furan formaldehyde (C₅H₄O₂), is a high-value platform molecular chemical in the separation and synthesis industry, which can be obtained by high temperature depolymerization and dehydration distillation of lignocellulose like corncob in acidic medium [1]. The industrial process (General production conditions: 160–180 °C, 0.8–1.0 MPa, and 10% sulfuric acid) for furfural production can break down the complex dense structure of lignocellulose, decompose unstable hemicellulose into pentosan, and further generating furfural (as shown in Figure 1). Subsequently, rough furfural emerges with hot steam, which is dehydrated and distilled to produce the refined furfural [2]. The remaining solid waste after furfural production is the FR.

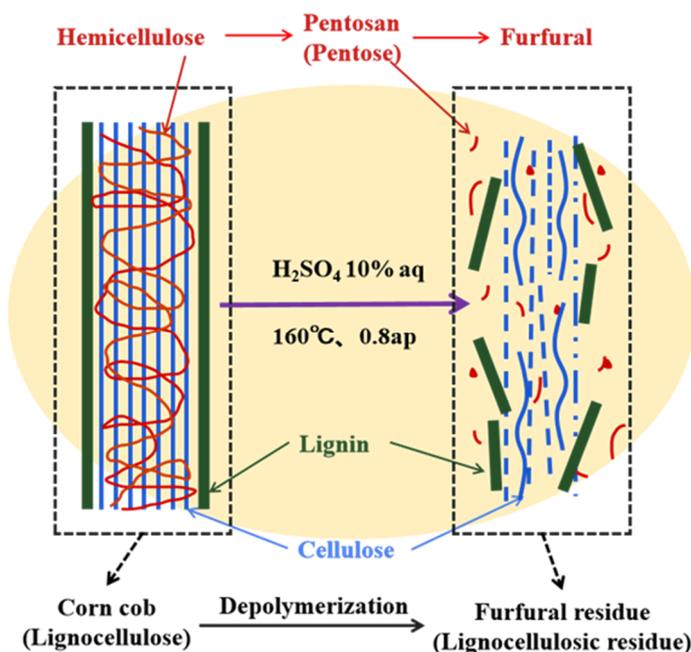


Figure 1. Schematic diagram of furfural production and FR formation.

As a kind of intermediate for the production of various chemical products, furfural has high commercial value and yield demand. However, no direct synthetic method has been found, which can only be extracted by polymerization of lignocellulose. Previous studies have shown that the conversion rate of most furfural factories is only 50% to 60% [3]. As such, one ton of furfural product will produce 10 to 15 tons of underutilized FR. There are more than 200 furfural factories in China [4], according to the annual furfural capacity of 1000 tons per furfural factory. The annual FR output can reach 2 million to 3 million tons. The accumulation of FR occupies a large amount of land and even causes a series of environmental problems such as air, soil, and river pollution [5]. Therefore, how to deal with FR reasonably, and even further reuse it to transform value-added products, is key to achieve non-polluting and high-efficiency production of furfural. This is an urgent problem to solve in industrial production of furfural. For this, this review summarized the different value-added product transformation of furfural from four main research aspects, providing guidance for the correct treatment of FR in practical application.

2. Characteristics and Value-Added Products of FR

The pentose for furfural production usually comes from hemicelluloses of agricultural waste (e.g., corn cobs, straws, and rice husks) and the residue produced by the furfural process is characterized by high salinity, strong acidity, and difficult degradation, which makes it difficult to treat.

As shown in Figure 2, the composition of FR can be observed where most of the hemicellulose for the corn cob is consumed during the furfural production process, and the remaining part exists in the form of short-chain pentose (2.18%). The rest of FR mainly consists of lignin (40.23%), cellulose (38.06%), humic acid (12.35%), trace elements (2.28%), acetic acid (3.55%), and sulfate ion (1.35%). Due to the high temperature catalytic depolymerization and the hydrolysis of unstable hemicellulose, the hydrogen bonds, covalent bonds, and van der Waals forces between cellulose, hemicellulose, and lignin in lignocellulose are broken, which make FR present fluffiness and porous characteristics. Therefore, previous scholars have conducted in-depth studies in different directions on the characteristics of FR, including four research directions of soil cultivation, catalytic hydrolysis, high temperature pyrolysis, and porous adsorption [6]. A variety of value-added products have been developed in different research directions (Figure 3).

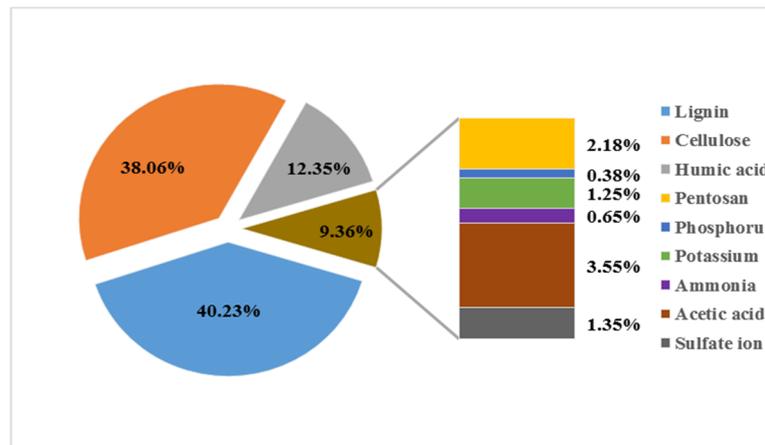


Figure 2. The composition of FR from the corn cob.

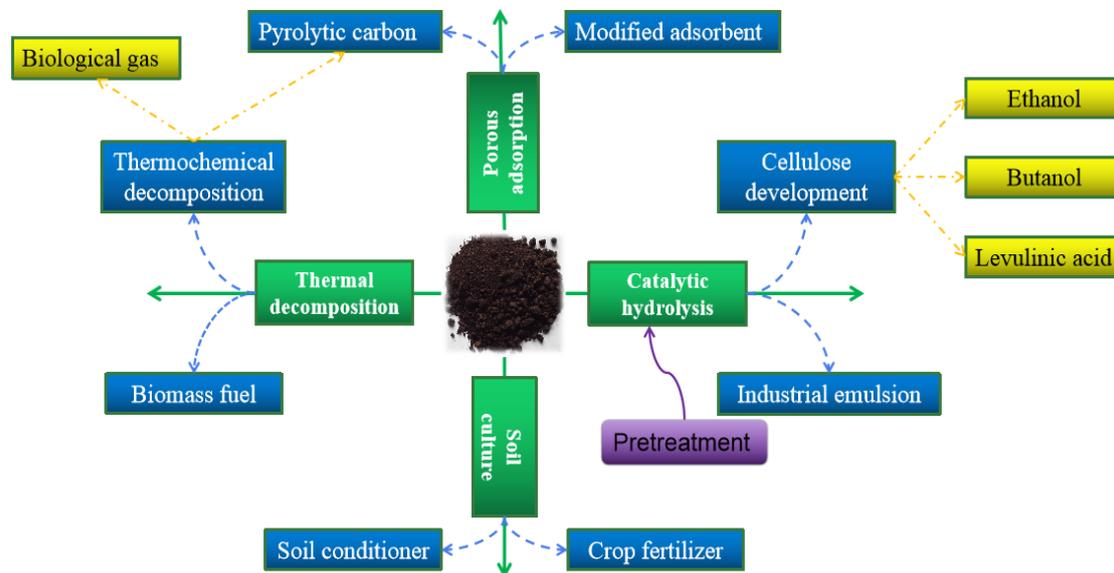


Figure 3. Value-added products of FR in different fields.

- (1) *Soil culture*. Due to the earlier research and more mature technology, FR has been applied to soil culture on a pilot scale. There are two principles to utilize here. One is to neutralize the high alkalinity of saline and desert soils with the strong acidity of FR, or to provide the acidic soil environment for acid-loving plants such as blueberries. The other is to improve the soil structure due to the rich organic matter, and to provide fertilizer for crops.
- (2) *Catalytic hydrolysis*. The proposition of FR hydrolysis and the conversion value-added product comes from the catalytic hydrolysis of lignocellulose. The introduction of the second generation of non-food biofuels makes the hydrolysis of FR into cellulosic ethanol become a hot research topic [7]. Compared with traditional non-food crops (e.g., straw, hay, bagasse, rice husk, wood chips, etc.), the intermolecular forces between the components are weaker in FR, which makes cellulose easier to extract.
- (3) *Thermal decomposition*. FR is used as biomass fuel to generate heat in the early stage of research. With the development of the “bio-refining” concept, biomass pyrolysis as a new technology to optimize the energy structure and reduce greenhouse gas emissions has attracted the attention of government officials. As a potential biomass source, FR has the feasibility to transform biochar due to the fluffy, porous structure and high carbon content [8].

- (4) *Porous adsorption.* The adsorption characteristics of FR are mainly related to its specific surface area, porosity degree, and surface chemical properties, which show adsorption capacity on some material such as methyl blue and methyl violet. In addition, further processing can improve the adsorption property of FR, such as thermal decomposition of biochar described above and modification with a chemical activation [9].

3. Value-Added Products of FR in Soil Culture

3.1. Application of FR in Soil Improvement

As shown in Table 1, FR with a low pH contains abundant organic matter and a variety of nutrient elements required for plant growth. The content of organic matter and the size specific surface area play an important role in maintaining water and fertilizer and increasing microbial activity, when applied to soil [10]. Therefore, the application of FR as a soil conditioner can significantly improve the quality of the soil, which causes scattered soil particles to form pellets, in order to improve the soil structure, change the pH of the soil, and increase the content of organic matter in the soil.

Table 1. Nutrient content of FR.

Nutrients	Total Oxygen	P ₂ O ₅	K ₂ O	Organic Matter	Minerals
Content (%)	0.4–0.8	0.3–0.7	2.8–3.4	76–84	14–16

In China's northeast plain, north China plain, northwest inland, and coastal areas, there are a large number of saline lands [11], which cause perennial soil hardening and fertility decline, form an adverse effect on crop cultivation, and even seriously affect the life and development of people and regions. This brings serious problems to the balanced development of east and west regions of China [12]. Therefore, how to solve the problem of land salinization has always been a concern for people. As a waste product of furfural production, FR can be processed and reused. The organic matter, and the P and K element contained in FR, are not consumed during the furfural process. Meanwhile, the acidity of FR can neutralize alkalinity of saline lands. Therefore, FR has a good prospect as a land improver, which can not only increase soil organic carbon content and improve soil structure, but also neutralize soil alkalinity or provide an acidic soil environment [13].

The effects of FR addition on different soils are summarized in Table 2. Part of Na²⁺ in saline soil can be replaced by Ca²⁺ in FR, which is excluded from soil along with water flow. This reduces the high sodium content in the soil. Meanwhile, the functional groups of phenolic hydroxyl, carboxyl, methoxy, carbonyl, hydroxyl, and quinone generate a negative charge by dissociating in the humification process of organic matter for FR, which increases the attraction to metal cation and regulates the physical and chemical properties of soil [14]. For example, the absorption of Ca²⁺ promotes the formation of soil aggregates, and the absorption of Ni²⁺ and Pb²⁺ passivates the enrichment rate of heavy metals in the soil. A low pH value can dissolve and activate some insoluble substances and increase the content of soluble salt in soil, whereas excessive H⁺ promotes the conversion of N, P, and K elements, which is conducive to the growth of crops. In addition, the mixture of FR and pulverized coal can synthesize new artificial soil for land reclamation with reasonable fertilizer and water management [15].

However, the costs of transportation and labor limit the real application of FR in soil improvement. Therefore, it is necessary to consider the commercial feasibility and social benefit from the cardinality and transport distance required for FR.

Table 2. Improvement effect of FR on different soils.

Materials	Area	Application Effects	References
FR	Yellow River delta saline soil	The contents of organic carbon and N, P, and K elements increased. The pH of soil decreased.	[16]
FR	Hexi corridor saline tidal soil	Soil bulk density and pH decreased. Soil total porosity, aggregate structure, and water content increased, organic matter, and N, P, and K element content increased.	[17]
FR Desulfurization gypsum	Crack solonetz	Soil structure and permeability were improved, which promoted the salt leaching rate, reduced alkalinity, and pH value.	[18]
FR Paper dry powder	Coastal saline soil	The N and P supply capacity was significantly improved to alleviate the effects of salinity and alkali stress on crop growth and nutrient accumulation.	[19]
FR	Alkaline soil in Northern Yinchuan	Soil alkalinity and total salt content decreased. Bulk density and soil porosity increased.	[20]
FR Coal powder	Coal mine subsidence area soil	The shortage of backfill soil in the coal mine subsidence area was solved. The soil after irrigation and desalination is suitable for agricultural production.	[21]
FR	Red mud soil	The pH of soil decreased. The stability of Al, V, and Pb in red mud was improved by inhibiting the leaching of metal elements.	[22]
FR Peat/Sawdust	Blueberry planting soil	Improved the physical and chemical properties of soil and created a slightly acidic environment.	[23]
FR Sulfur	Blueberry planting soil	Increased the content of ammonium and nitrate nitrogen and provided a slightly acidic environment for blueberry planting soil.	[24]
FR	Aeolian sandy soil in the irrigation area	Soil aggregates, rapidly available as N, P, K, and Zn increased.	[14]

3.2. Application of FR in Crop Cultivation

The strong acidity of FR and the high degree of space barrier polymerization of lignocellulose make it difficult to reuse, which result in the waste of nutrients such as cellulose, starch, and organic matter in FR. If these substances are converted into fertilizers that can be absorbed by plants, environmental pollution will be reduced and the reuse of FR will be promoted [25]. At present, the application of FR in crop cultivation is mainly to regulate the growing environment of crops by soil improvement. This can improve crop yield such as blueberry planting and saline planting. The effect of increasing yield on crops with FR fertilizer was listed in Table 3. In addition, some studies showed that artificial substrates made from FR, furnace slag, cow manure, and mushroom residue were feasible for soilless cultivation, and their organic matter content, porosity, moisture content, and rapid available P and K indexes were all in line with crop growth indexes [26–28]. It was also reported that FR could replace the cotton seed shell to produce edible fungus rods, which can solve the pollution risk and improve economic benefits [29]. As a substitute for the fertilizer, the FR is applied to crops, which alleviates the contradiction between supply and demand and realizes the value-added process of pollutants. This process achieves a win-win situation. However, the high salinity and acidity of FR will inevitably affect crops, and further research should be carried out to provide solutions. In addition, FR, as a crop additive with a low cost, high adaptability, and strong practicability, has high practical feasibility. However, currently, most reports are focused on potted plant and small-scale experimental fields, and its practical promotion and application still need to be explored.

Table 3. The effect of increasing yield on crops with FR fertilizer.

Cultivated Crops	Planting Soil	Increasing Rate (%)	References
Beet	Saline soil	16.31	[17]
Rape	Crack solonetz	33.09	[18]
Wheat	Saline soil	208.54	[30]
Corn	Saline soil	118.85	[19]
Rice	Alkaline soil	108.62	[20]
Blueberry	Blueberry planting soil	55.81	[23]
Eggplant	Aeolian sandy soil	3.01	[14]
Tomato	Soilless cultivation	35.23	[26]

4. Value-Added Products of FR in Catalytic Hydrolysis

Due to the complex structure of lignocellulosic biomass, it is usually necessary to break the dense structure of lignin, cellulose, and hemicellulose by pretreatment to achieve efficient hydrolysis. As a by-product of lignocellulosic hydrolysis, FR clearly breaks down its original dense structure and reduces the degree of polymerization among the components, which is equivalent to a pretreatment. Large amounts of cellulose and lignin remain. Figure 4 shows the variation of lignocellulose composition in the process of furfural production for corn cob. The content of lignin and cellulose increased significantly (a total of more than 90%) and only 3.6% of hemicellulose is in the form of pentose because of the breakdown of hemicellulose. Cellulose can be hydrolyzed to produce glucose, which is further converted into value-added products such as levulinic acid, ethanol, butanol, and formic acid [31–33]. Lignin can be used as raw material to produce stabilizers, agricultural dispersants, emulsifiers, adhesives, and composite material [34–36]. Therefore, the conversion of FR into value-added products with catalytic hydrolysis has good commercial prospects.

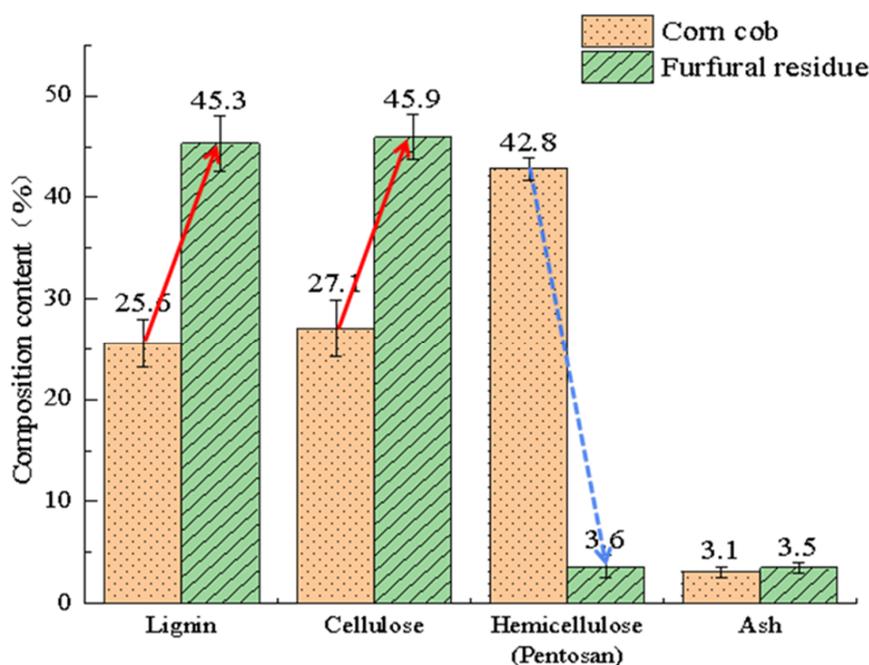


Figure 4. The variation of lignocellulose composition in the process of furfural production for corn on the cob.

4.1. Extraction and Transformation of Lignin and Cellulose in FR

The conversion of lignin and cellulose from FR into value-added products is a potential technology. The original cell wall structure of the corn cob is destroyed by the drastic depolymerization in furfural production, which greatly increases the porosity of FR and makes the extraction of lignin and cellulose

easier. However, lignin is a complex phenolic polymer, which is not easy to be soluted in acidic and neutral solutions, and can only be dissolved in alkaline solutions or organic solvents. This greatly limits the separation of lignin and cellulose [37]. In addition, phenolic hydroxyl groups that can directly affect the physical and chemical properties of lignin and heterogeneous lignin with high protein binding ability are produced by depolymerization and recondensation reactions in furfural production [38]. These substances enable cellulase to be irreversibly adsorbed on lignin, which reduces the efficiency of cellulose extraction and sugar production. Therefore, it is necessary to improve the concentration of cellulose substrates by delignin treatment to reduce the ineffective adsorption of cellulase.

Lignin has a wide range of sources and a low price, whereas the extraction of lignin from FR requires pH regulation and water washing, which increases the technological complexity. Therefore, there are few studies on the extraction of lignin in FR. Wei [39] proposed that alkaline lignin extracted from FRs could be used to synthesize cheap and recyclable industrial emulsion polymerization materials by utilizing lignin's insoluble characteristics in water but soluble characteristics in alkali. The emulsion developed by this method could wrap polystyrene particles in a neutral environment and a release in the alkaline environment, which can avoid the addition of chemical surfactant or emulsifier in traditional emulsion.

As an intermediate in the synthesis of many chemicals, glucose has high economic value. Therefore, the extraction and conversion of cellulose from FR into value-added products have been the research focus for catalytic hydrolysis of FR [37]. Furthermore, cellulose is hydrolyzed into small molecular compounds such as glucose through appropriate cellulase or acid catalysts, further processing it into different value-added products (Figure 5). For example, industrial ethanol and butanol produced by different fermentation processes [40]. Levulinic acid was prepared under high temperature, high pressure, and catalyst [41]. Therefore, how to optimize and improve the related processes and further improve cellulose hydrolysis and glucose conversion is the focus and difficulty of research.

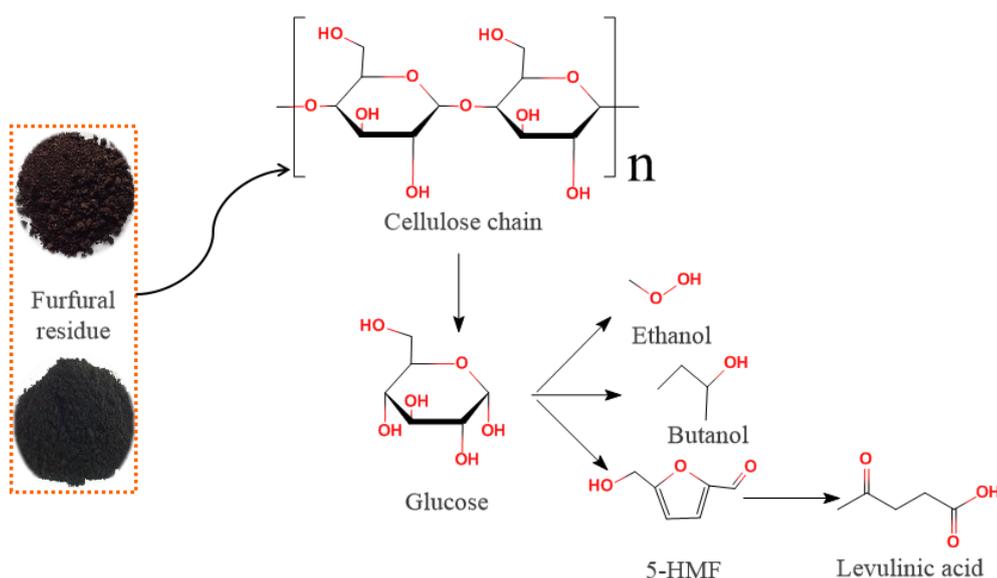


Figure 5. Conversion of cellulose value-added products in FR.

4.2. The Enhancement of Cellulose Hydrolysis with Different Pretreatment for FR

Lignin in FR can be reduced by a different pretreatment, which enhances cellulase accessibility and promotes cellulose hydrolysis and glucose conversion. Currently, some pretreatment methods for FR are applied, such as physical (e.g., ultrasonic, microwave, steam explosion, and high temperature), chemical (e.g., acid and alkali), strong oxidant (e.g., hydrogen peroxide and bisulfite), and combined pretreatment. Alkali pretreatment is widely studied due to the simple operation, remarkable effect, and moderate conditions. The OH^- in the alkaline substance breaks the ester and C-C bonds, which

removes the amorphous region of the biomass (usually composed of lignin and hemicellulose). This accelerates cellulose hydrolysis [42]. This process has a remarkable effect and mature technology, which was suitable for large-scale industrial production.

To further enhance the pretreatment effect, alkali pretreatment is usually accompanied by other treatments, such as alkaline peroxide, alkaline ethanol, alkaline ultrasound, alkaline microwave, etc. Cooperative physical means of alkali pretreatment can break the unstable hydrogen bond in the amorphous area of lignocellulose through vibration, high temperature, and strong pressure, which is conducive to the decrease of alkali and lignin [43]. This method has short pretreatment time and a clear effect, but harsh conditions and high cost. Alkali pretreatment with a strong oxidant was obtained from the bleaching principle in alkaline pulping, which causes the oxidant to sulfonate with lignin to form the sulfonate group of strong hydrophilicity, and then dissolve lignin sulfonate [44]. This kind of alkali pulping technology was used in the industrial paper and the technical methods have been mature. However, the black liquor produced by alkaline papermaking has been an urgent problem to be solved. In addition, some in-depth studies have further optimized the pretreatment conditions of FR. For instance, the addition of ethylenediamine tetraacetic acid can reduce the ineffective decomposition of hydrogen peroxide in the pretreatment of alkaline hydrogen peroxide in order to improve the pretreatment effect [37]. The released lignin usually needs to be washed away with water in traditional furfural pretreatment to prevent the cellulase from adhering to its surface. The lignin sulfonate produced by sulfonation of bisulfite has a lower affinity for cellulase, which eliminates the washing step and saves cost.

4.3. Hydrolysis Principle of Cellulose in Acid or Enzyme

The cellulose hydrolytic product is called hydrolyzed cellulose, which is decomposed into glucose under the action of acids, enzymes, and other factors. The hydrolysis of cellulose with the enzyme is a complex process. At present, the most acceptable enzymatic hydrolysis mechanism is that the cellulose crystallization area is affected by the action of endoglucanase to form a free polysaccharide chain, and the non-reducing end of the polysaccharide chain is further cut into fibrous disaccharide units by cellobiohydrolase. Eventually, glucose is produced via glucoside [45]. The higher substrate sugar yield can be obtained by cellulase hydrolysis, whereas the culture of related hydrolases is more difficult and the input cost is higher. Therefore, the output value after cellulose hydrolysis needs to be evaluated. High-solid enzymes can increase sugar yield and reduce operating costs. The problem is that the mixture produced by FR becomes more viscous in a high solid load, which is not conducive to contact between the enzyme and cellulose. Currently, several additives have been shown to enhance high-solid enzymatic hydrolysis, such as *Gleditsia saponin*, cocktails, etc. [46,47].

Compared to the former, the hydrolysis of cellulose with acid is slightly less efficient in producing sugar, while its cost-effective input and longer service life give it more potential. Cellulose is generally difficult to dissolve in dilute acid, whereas the free hydroxyl group in cellulose will be esterified with an acid radical to form hydrogen sulfate ester in a concentrated acid medium, such as concentrated sulfuric acid, which breaks the connection between the glucose residues and then dissolves the cellulose. By contrast, catalytic hydrolysis of cellulose by solid carbon-based acid is more environmentally-friendly and recyclable. However, the relevant data [48] showed that the yield of reducing sugar for liquid acid was more than 60%, which only took 2 h, and that for carbon-based solid acid is only 30%. It took 10 h to achieve the best results. In summary, the efficiency of cellulose hydrolysis can be improved clearly by optimizing the conditions of acid and enzymatic hydrolysis. However, considering all factors, none of the technologies achieved mass production. The main limitation comes from the capital investment of the technology. Table 4 shows the progress in the process of extracting cellulose from the FR and the conversion process in recent years.

Table 4. The value-added products of cellulose from FR.

Raw Material	Pretreatment	Additives ^a	Value-Added Products	Effects	References
FR	-	Surfactant	Ethanol	Cellulose conversion rate: 78%	[49]
FR	-	-	Ethanol	Ethanol concentration: 73.1 g/L	[50]
Corn kernels					
FR	-	Lactobacillus/Yeast	Ethanol	Cellulose conversion rate: 86.8%	[51]
FR	-	Saponin	Lactic acid	Ethanol production rate: 22.8%	[52]
FR	Alkaline peroxide	-	Ethanol	Lignin extraction rate: 12.6%, Saccharification rate: 86.6%	[53]
FR	Formic acid/Peroxide	-	Glucose	Cellulose production rate: 41.92%	[54]
FR	Alkaline peroxide	Cocktail	Cellulose	Lignin extraction rate: 73.5%	[44]
FR	Green liquor/Peroxide	-	Ethanol	Ethanol concentration: 16.9 g/L	[37]
FR	Green liquor/Ethanol	-	Glucose	Glucose production rate: 90.4%	[55]
FR	NaOH/Peroxide & NaOH/Microwave & NaOH/Ultrasound	Carbon-based solid acid	Glucose	Glucose production rate: 85.9%	
			Reducing sugar	Reducing sugar production rate: 35.7%	
				Reducing sugar production rate: 33.9%	[43]
				Reducing sugar production rate: 33.13%	
FR	-	Sulfuric acid & coal tar acid & activated carbon-based acid	Reducing sugar	Reducing sugar production rate: 66.6%	
				Reducing sugar production rate: 35.7%	[48]
				Reducing sugar production rate: 33.2%	
FR	Alkaline peroxide	Ethylene glycol	Liquefied content	Liquefaction rate: 82.0%	[56]
FR	-	Saponin/High solid enzyme	Glucose	Cellulose conversion rate: 74.8%	[45]
FR	Bisulfite	High solid enzyme	Glucose	Glucose production rate: 99.4%	[5]
FR	-	Saponin	Ethanol	Ethanol concentration: 36.0 g/L	[57]
Cassava residue					
FR	Alkaline peroxide	Saponin/High solid enzyme	Ethanol	Cellulose conversion rate: 82.2%	[58]
FR	Sodium bisulfite	High solid enzyme	Ethanol	Ethanol concentration: 69.1 g/L	[59]
FR	Green liquor/Peroxide	-	Ethanol	Glucose production rate: 99.4%	[60]
Cassava residue				Lignin production rate: 42.0%	
FR	Alkaline peroxide	-	Ethanol	Ethanol concentration: 51.9 g/L	[61]
FR	Alkaline sodium hypochlorite	Activated carbon/Resin	Ethanol	Cellulose conversion rate: 88.6%	[62]
			Butanol	Butanol concentration: 8.48 g/L	

Note: ^a Where there is no emphasis on acids or enzymes, the default is traditional acids or enzymes, which are not listed. & indicates different methods.

5. Value-Added Products of FR in Thermal Decomposition

Thermal decomposition is a new method for the reuse of FR, including the thermogravimetric change, final temperature, and heating rate on product properties and distribution, which broadens the practical application field of FR [63,64]. Currently, the research on the pyrolysis of FR is in the stage of development from theoretical research to the combination of theory and practical application at present.

5.1. Application of FR in Thermal Decomposition

Thermal decomposition is one of the methods of biomass energy utilization, including direct combustion and thermochemical technology. Direct combustion is the most common means of biomass utilization, which burns biomass raw materials directly in contact with air or processes them into specific fuels for use in combustion equipment [65]. Because of the convenience of operation, this technique is an early way to treat FR. However, FR has low calorific value, high moisture content, and high sulfur content, which is not easy to direct combustion. It is necessary to carry out certain pretreatment before heating the boiler or generating electricity for the power plant. For example, the circulating fluidized bed combustion technology has characteristics of stable combustion, strong applicability, and sulfur fixation in the furnace, which can make the FR continuously stable combustion [66]. In addition, multi-fuel co-combustion has been a major topic in direct combustion research because it can improve the combustion performance. As a kind of biomass raw material, FR has also been studied in the co-combustion. The addition of FR can improve combustion efficiency and reduce sulfur gas emission in coal biomass briquette. This is because the FR burned before coal biomass briquette forms a relatively loose gap, which is conducive to the combination of sulfur and the sulfur fixation agent as well as the contact combustion of oxygen and materials [67]. In the co-combustion of furfural residue and oil shale semi-coke, it was found that the effect between them is not simply the superposition of calorific value, but the co-promotion of combustion characteristics through some synergistic action [68].

The thermochemical application of FR mainly includes pyrolysis technology and biomass gasification technology. The former refers to the process of converting raw materials into solid, liquid, and gas three-phase low molecular substances by thermochemical conversion under low oxygen or anaerobic conditions [65]. Biochar or adsorbents from thermal cracking of furfural residue show good porosity and a high specific area (specific area: 567 m²/g, v_{total}: 0.38 cm³/g), which completely meets the basic requirements of activated charcoal, especially clear adsorption effects on various metal ions, methyl blue, and tetracycline [69]. In addition, nuclear magnetic resonance technology can track and scan the whole process of preparing activated carbon from FR, determine the changes of carbon structure, electron transfer, surface chemistry, and adsorption capacity in the process, and provide a theoretical basis for further research on the preparation of economical, practical, diversified, and specialized biomass activated carbon from the pyrolysis of FR [70]. The latter refers to the process of using a small amount of oxygen or oxygen-containing substances as a gasification agent under incomplete combustion conditions to convert the combustible components in raw materials into carbon dioxide, hydrogen, methane, and other combustible gases by means of a high-temperature overheating chemical method. For example, furfural residue and waste fungus sticks were gasified in the absence of oxygen to prepare biomass combustible gas [71].

5.2. Mechanism Analysis of Thermal Decomposition for FR

Thermal decomposition of FR is a complex intermolecular process, it is necessary to analyze the morphological transformation of various substances and functional groups in the thermal decomposition and gasification, which can provide a theoretical basis for the design of efficient pyrolysis devices and in-depth exploration of the pyrolysis characteristics for FR.

Generally, there are four kinds of chemical bonds in lignocellulosic materials [72].

The first type includes the aliphatic series/ aromatic carbon groups in lignin (C–C/C–H).

The second type includes the hydroxyl in cellulose and hemicellulose (–OH).

The third type includes the carbonyl or single carbonyl carbon in lignin and hemicellulose (C=O).

The fourth type includes the ester bond in the hemicellulose carboxyl group (O–C=C).

Most hemicellulose is hydrolyzed for furfural production, which indicates that the change of the remaining hydroxyl group determines the state of cellulose. The structural units of cellulose and lignin in FR are shown in Figure 6a,b. With the increase of temperature, the phenomenon was found by Thermogravimetric Analyzer-Fourier Transform Infrared Spectroscopy (TG-FTIR) that the water in FR first evaporates, which is followed by dehydration and dehydroxylation, and more gaseous products were released with the further increase of temperature. Therefore, the components of FR were separated in the following order: water, a small amount of hemicellulose, cellulose, and lignin [73]. In terms of the generated gas composition, carboxyl can be formed into CO₂, CO, or H₂O. Among them, –OH is cleaved into H₂O, while the lateral C=O bond fracture generates CO₂ or CO and methoxy and methylene produce CH₄. Therefore, the gas products of thermal decomposition are mainly CO₂, H₂O, CO, and CH₄ [74].

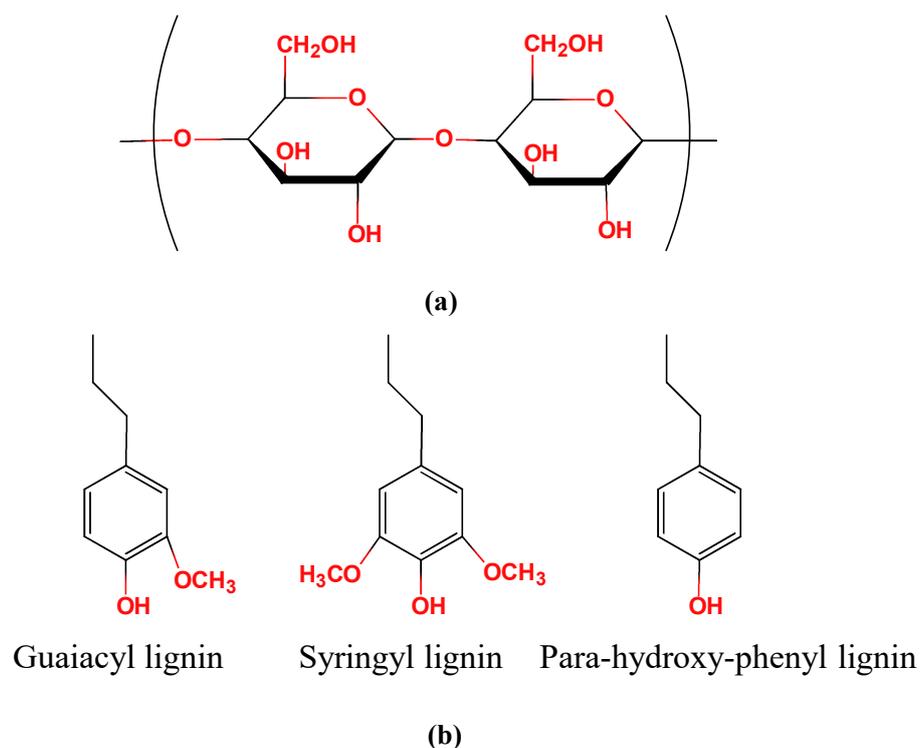


Figure 6. The main composition structure of lignocellulose in FR. (a) Structural unit of cellulose and (b) structural unit of lignin.

In addition, many parallel and serial complex reactions often occur during biomass pyrolysis due to the diversified structure of components, it is necessary to analyze the process by thermogravimetry and simulate the relevant kinetic parameters. In the current biomass pyrolysis kinetic model, the coasts method, dolye method, and the maximum rate atia method are most commonly used [75]. For different pyrolysis types, the models are selected and applied differently, while, for non-isothermal degradation materials such as FR, Coats-Redfern integration is usually applied [76]. Therefore, kinetic models of non-isothermal degradation materials are often selected to establish dynamic models of FR [74,77]. The kinetic model is shown below.

$$f(a) = \frac{ART^2}{E} e^{-E/RT} \quad (1)$$

Additionally, the model is also applicable to the analysis of the co-pyrolysis characteristics of FR and other substances [78].

6. Value-Added Products of FR in Porous Adsorption

Adsorption is a mass transfer process, which is manifested in the adsorption of solid adsorbent to non-electrolyte molecules. For materials with a larger specific surface area, although the internal molecules attract each other, the external molecular forces are not fully exerted. Therefore, some relatively large areas of materials such as water film, activated carbon, and more are often used as adsorption materials in industry [79]. The specific surface area is not the only parameter that determines the adsorption characteristics, but is also related to the chemical properties of surface functional groups.

6.1. Evaluation of Adsorption Capacity of FR

In the production of furfural, most of the hemicellulose in the raw material is removed by hydrolysis, and the obtained FR is mainly composed of structurally altered cellulose, lignin, and a small amount of hemicellulose. From the scanning electron microscope in Figure 7, there are a few gaps and protrusions on the surface of the corn cob, but the overall structure is dense with few channels or porous structures, which presents a smooth layered structure (Figure 7a,b). In contrast, FR has a rougher surface with more particles and a pore size (Figure 7c,d). The surface of the cob becomes wrinkled in furfural production due to the violent depolymerization reaction, which greatly increases the specific surface area.

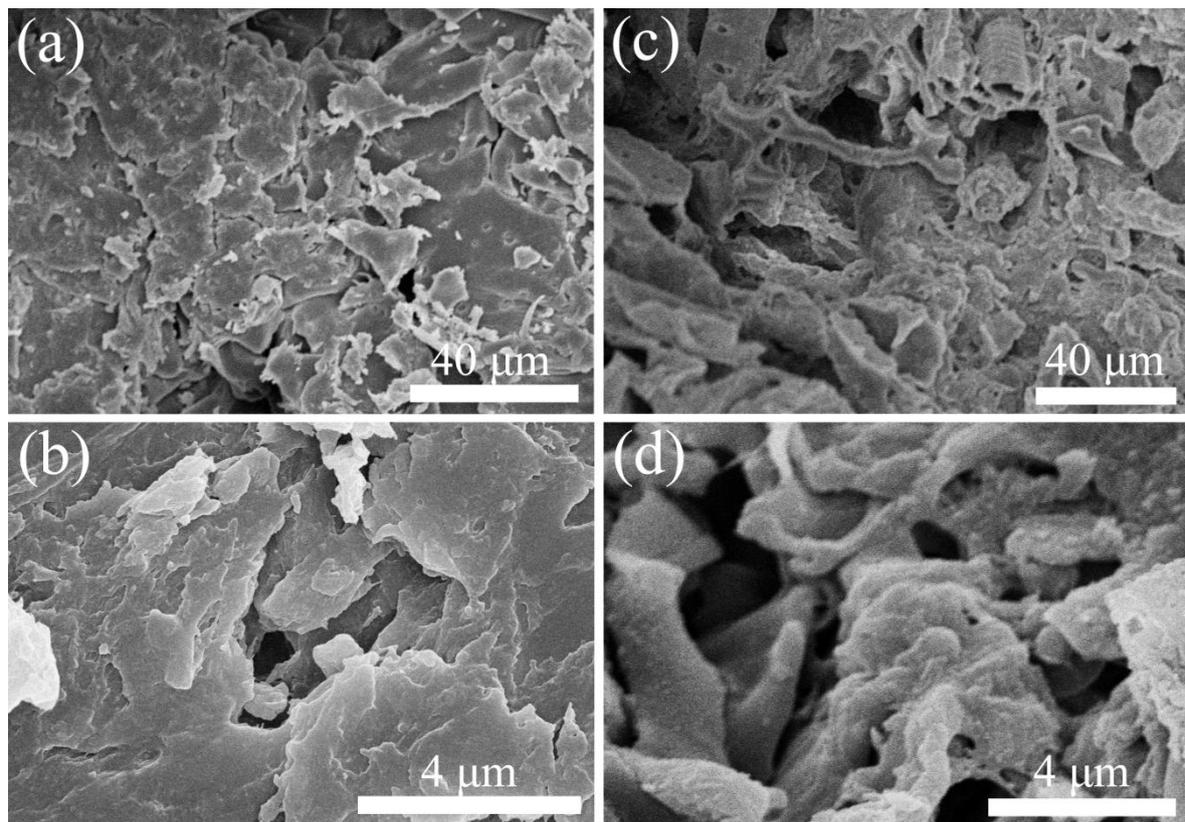


Figure 7. Scanning electron micrographs of corn cob (a,b) and FR (c,d).

On the other hand, there are many nonpolar bonds in the FR, whereas the polar bonds such as carboxyl and hydroxyl are relatively few. According to the principle of similarity and intermiscibility, the adsorbent prepared from FR has weak adsorption on polar molecules such as water, but stronger

adsorption on a nonpolar substance in aqueous solution, which provides a possibility for the adsorption of nonpolar substances in a strong, polar aqueous solution. Furthermore, it is necessary to further activate before preparation of the mature adsorbent product to enhance the adsorption capacity. Currently, the activation of FR are mainly the physical activation method and the chemical activation method. The former has less pollution and lower cost, but the process conditions are harsh, which requires high temperature and low oxygen. The latter is mild and can control the aperture structure and performance by adjusting the activation conditions, but the corrosion resistance of the equipment is high and it is easy to produce pollutants.

6.2. Preparation of Biomass Adsorbent Product from FR

In the development of the early adsorption application for FR, the residue body is simply washed, crushed, and mixed with the adsorbed liquid, and the adsorption effect was evaluated by measuring the residual concentration of the adsorbed substance [80–82]. With the development of technology, FR is often used to prepare highly active biomass adsorbent via further activation by physical and chemical methods.

The physical activation method, which is the pyrolysis technology mentioned in Section 3.1, obtains biomass adsorption carbon with larger aperture and higher mechanical strength by pyrolysis and a polycondensation reaction of organic components in FR. However, the newly formed products in the carbonization process of furfural residue tend to accumulate in the pore diameter, which reduces the adsorption performance of biomass charcoal. Some strategies can reduce this negative effect. For example, the oxidation gas introduced into the thermal carbonization process can effectively remove the residual material and carry out selective oxidation on the highly reactive sites in the FR, which further expands the pore diameter of the carbon structure [83,84]. Microwave and other auxiliary means can also accelerate the internal thermal activation process of activated carbon, which effectively expands the carbonization aperture [85,86]. In addition, Yin et al. [69] proposed a self-activation method of biochar activated by pyrolysis gas of FR. Essentially, the pyrolytic gas generated from the pyrolysis of FR is directly injected into the carbonization reactor to promote the activation of biomass charcoal, so as to produce low cost but high performance biochar.

The chemical activation method refers to the modified biomass carbon adsorbent obtained by mixing furfural residue with a related activator, which is treated by heating, washing, and drying. There are many activators commonly used to modify FR such as zinc chloride [87], basic epichlorohydrin [88], basic isopropanol/citric acid [89], sodium phenolate [90], sodium carbonate [91], and sulfuric acid [4]. The principle is that the functional groups of activated carbon and their own acid and alkali are changed by impregnation, alkali, acid, salt, and other treatment means, so as to mention the adsorption capacity of activated carbon. In addition, the addition of the activator in the carbonization process can release hydrogen and oxygen from FR in the form of water, and inhibit the decomposition of high polymer and the formation of tar [92], which is conducive to the carbonization heating process. This reduces the carbonization temperature and saves energy consumption.

Adsorption capacity is critical for adsorbents. Maximum adsorption per unit is an authoritative measure of adsorption capacity. The preparation methods and maximum adsorption per unit of different types of FR adsorbents were listed in Table 5. The comprehensive analysis of the results shows that the furfural residue has a certain adsorption effect as a biomass adsorption material. It is feasible to prepare high-performance activated carbon by further exploration and development.

High-performance activated carbon has been the most popular and widely used adsorbent, whereas the problem of high prices has not been solved. As a substitute of the adsorbent, cheap FR has good potential research value, which provides the feasibility and reference basis for making the adsorbent from FR.

Table 5. Adsorption effect of FR adsorbent on different substances.

Adsorbed Material	Adsorption Capacity (mg/g)	Activation Method	Reference
Methylene blue Cr ⁶⁺	202.5 7.583	ZnCl/Microwave	[87]
Methylene blue	47.7	-	[80]
Ni ²⁺	19.0	NaOH/Isopropanol/Citric acid	[89]
Pb ²⁺	46.4	-	[81]
Cr ⁶⁺	93.9	NaOH/ Epichlorohydrin	[9]
Cd ²⁺	18.3		
Ni ²⁺	98.2		
Pb ²⁺	34.8	NaOH/Phenol/Formaldehyde	[90]
Cu ²⁺	45.1		
Zn ²⁺	14.7		
Tetracycline	162.0		
Terramycin	335.0	Concentrated sulfuric acid	[4]
Iodine	127		
Methylene blue	59	CaO/KCO ₃ /Microwave	[86]

Note: Heat treatment is not indicated.

7. Conclusions and Future Perspectives

As a by-product of furfural production, FR has been well studied in soil culture, catalytic hydrolysis, thermal decomposition, and porous adsorption due to its composition and structural characteristics. There are many value-added products from FR that have been converted. However, the treatment and reuse of FR remains a challenge and there are two critical reasons for furfural residue to convert value-added products. One reason is that the production of FR only increased but did not decrease due to the limitation of production technology and high intensity operation for furfural enterprises. Another is that the use of FR as raw materials is not an economically viable selectivity and the willingness for furfural enterprise is still low. Hence, the scale operation is the most fatal problem for FR treatment technology. For value-added products in the above research domains, only biomass fuel, soil conditioner, and crop fertilizer can be produced on a large scale, but there are also corresponding problems.

At present, biomass fuel products are the main utilization of furfural residue, but the essence is only the transformation of the pollution source from solid waste to a gas source, which is far from the concept of “green” and “friendly.” Soil conditioner products are severely restricted by objective factors, such as the particularity of the soil to be treated (alkaline soil) and the harsh transportation conditions (transportation distance and transportation location). The crop fertilizer from RF is only suitable for acidophilous soil, which narrows the application range.

Cellulosic ethanol production is the most promising scheme from a range of value-added products for FR conversion. As a high-end clean energy technology, cellulosic ethanol technology is highly expected. Despite this, some obstacles must be overcome, especially the cost. Therefore, it is likely to be a while before cellulosic ethanol can be considered seriously for industrial-scale production. Fortunately, with the improvement of cellulosic ethanol technology, it will become more economical to obtain ethanol from furfural residues. To sum up, there are a variety of value-added products for furfural residue conversion. However, there is a need to rapidly develop new technologies that can break through economic bottlenecks or find other potential applications in future exploration. In addition, it is also of practical significance to improve the production system of furfural from the source, such as to reduce FR production and regulate acidity by improving the production efficiency of furfural and using recyclable catalysts.

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