Mini-review

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# Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass

Charles M Cai,[a,b] Taiying Zhang,[a] Rajeev Kumar[a] and Charles E Wyman[a,b*]

## Abstract

**Furfural is a natural precursor to furan-based chemicals and has the potential to become a major renewable platform chemical for the production of biochemicals and biofuels. However, current industrial furfural production relies on relatively old and inefficient strategies that have hindered its capacity, and low production yields have strongly diminished its competitiveness with petroleum-based alternatives in the global market. This mini-review provides a critical analysis of past and current progress to enhance furfural production from lignocellulosic biomass. First, important chemical and fuel products derived from the catalytic conversion of furfural are outlined. We then discuss the importance of developing integrated production strategies to co-produce furfural with other valuable chemicals. Furfural formation and loss chemistries are explored to understand effective methods to improve furfural yields from pentosans. Finally, selected relevant commercial and academic technologies that promise to improve lignocellulosic furfural production are discussed.**

**Keywords:** furfural; fuel precursor; lignocellulosic biomass; biorefinery; biofuels; biochemicals

## INTRODUCTION

Environmental awareness of the need to replace fossil resources with renewable alternatives has fostered research to enhance production of suitable biomass-based platform chemicals.[1] In recent years, furfural has received renewed attention as a potential platform for production of biofuels and biochemicals. In a study supported by the US Department of Energy, furfural was selected as one of the top 30 platform chemicals that could be made from biomass with two of its derivatives, levulinic acid and furan dicarboxylic acid, in the top 10.[2] Furfural is a natural dehydration product of xylose, a monosaccharide often found in large quantities in the hemicellulose fraction of lignocellulosic biomass, from which it is almost exclusively produced. In theory, any material containing a large amount of the pentose (five carbon) sugars arabinose and xylose can serve as a raw material for furfural production.[3]

Industrial production of furfural was practiced starting in 1921 by the Quaker Oats company using oat hulls, corn cobs, and sugar cane bagasse, but due to limited demand and high maintenance costs,[4] yield and production methods have not improved significantly since about the 1980s.[3] Currently, about 300–700 Ktons of furfural is produced worldwide annually, the majority coming from China.[5,6] Significant improvements to both yield and production strategy are needed for furfural and its derivatives to compete with petroleum-based products as a renewable alternative. For example, the current price of crude oil is about \$100 per barrel (about \$683 $t^{-1}$ at 38° API gravity), and in order for furfural and its derivatives to be competitive as fuel precursors, its current production cost[6] of about \$1000 $t^{-1}$ must be substantially reduced through yield improvements of at least 46% from raw materials such as bagasse or corn cobs.

In this review, furfural and its catalytic products are introduced. The chemistries of furfural formation and furfural destruction are discussed to gain an insight into effective strategies that could improve furfural yields. Potential co-products from lignocellulosic biomass are identified. Finally, several competing technologies relevant to integrated production of furfural with other products from biomass are described.

## FURFURAL AS A RENEWABLE CHEMICAL AND FUEL PRECURSOR

In addition to attractive thermosetting properties, physical strength, and corrosion resistance[7,8] furfural is a natural precursor to a range of furan-based chemicals and solvents, including methylfuran,[9,10] furfuryl alcohol,[10,11] tetrahydrofurfuryl alcohol,[12,13] tetrahydrofuran,[10,13,14] methyltetrahydrofuran,[10,15] dihydropyran,[4,10,13] and furoic acid.[10,16] Figure 1 outlines some of these potential chemical products from furfural which have high value applications as a fuel or fuel additive.[17] Hydrogenation of the aldehyde group or furan ring remains the most versatile

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* *Correspondence to: Prof. Charles E Wyman, Department of Chemical and Environmental Engineering, Bourns Hall A215 University of California, Riverside, CA 92521, USA. E-mail: cewyman@engr.ucr.edu*

[a] *Center for Environmental Research and Technology (CE-CERT), Bourns College of Engineering, University of California, Riverside, 1084 Columbia Avenue, Riverside, California 92507, USA*

[b] *Department of Chemical and Environmental Engineering, Bourns College of Engineering, University of California, Riverside, 446 Winston Chung Hall, 900 University Ave., Riverside, CA 92521, USA*

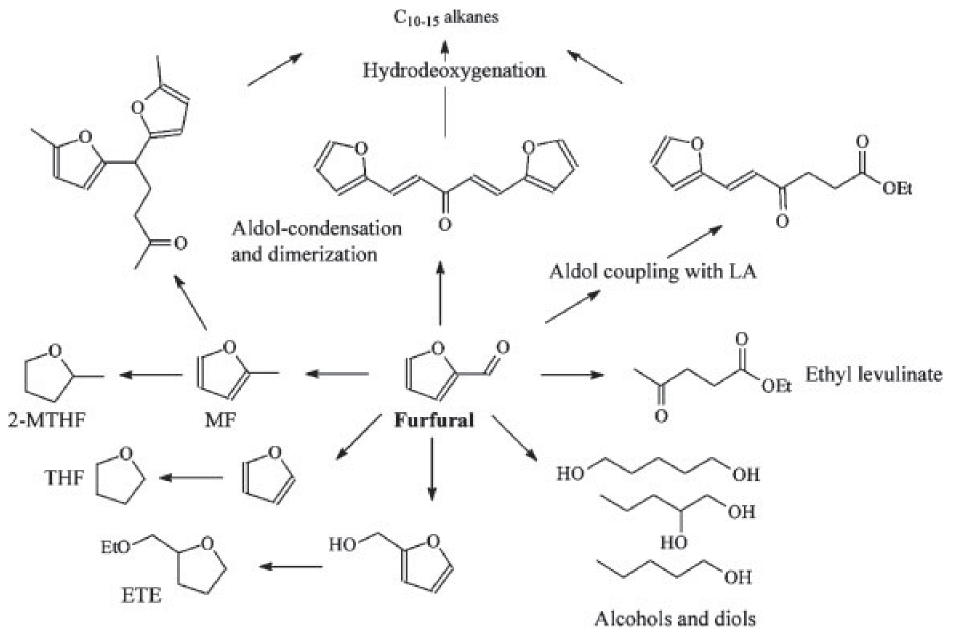

**Figure 1.** Outline of potential chemical and fuel derivatives from furfural by catalytic conversion. (Adapted from Lange *et al.*[17])

reaction to upgrade furanic components and can be employed to synthesize hydrocarbon fuels directly from furan derivatives.[10,18] Cleavage of the furan ring by hydrogenolysis can produce alcohols such as 1,5-pentanediol.

To synthesize longer-chain hydrocarbons from furfural, adduct formation by aldol condensation and dimerization followed by hydrodeoxygenation can produce C8 to C13+ alkanes.[10,19–23] In their review of furfural as a potential biofuel, Lange and co-workers[17] concluded that removing polar groups and reducing volatility of furan products can yield beneficial qualities for blending applications in diesel, whereas unsaturated aromatic derivatives such as methylfuran (MF) and ethyl furfuryl ether (EFE) have octane values and boiling points suitable as gasoline blendstock.

## FURFURAL FROM LIGNOCELLULOSIC FEEDSTOCKS

Lignocellulosic biomass including agricultural and forestry residues is uniquely suited for large-scale production of renewable fuels and chemicals with the potential for minimal environmental impact when properly managed.[24–26] Lignocellulosic biomass is composed primarily of cellulose, hemicellulose, lignin and water-soluble extractives, in order of typical relative proportions.[27,28] Due to the large amounts of enzymes required to overcome the recalcitrance of lignocellulosic biomass, biological approaches to releasing sugars from the cellulose fraction have been particularly challenged.[29]

For many acid-catalyzed pretreatment strategies used to extract sugars from hemicellulose and prepare biomass for biological conversion to ethanol, furfural is considered an inhibiting by-product. However, high severity reaction of lignocellulosic biomass could be employed to produce furfural at higher yields via a purely thermochemical approach. In fact, furfural is produced industrially by acid-catalyzed hydrolysis and dehydration of pentosans in lignocellulosic feedstocks at temperatures ranging from 153°C to 240°C. Pentosans are five carbon (C5) polysaccharides contained in the hemicellulose fraction of lignocellulosic biomass and, for many plants other than softwoods, are composed of complex heteromorphous structures of predominantly xylan (C5) and lesser amounts of arabinan (C5), glucan (C6), mannan (C6), galactan (C6), acetic acid, and uronic acids.[29,30] Table 1 outlines the approximate pentosan content of several plants and agricultural residues potentially suitable for furfural production. Those that have higher pentosan content allow for higher mass yields of furfural and are typically favored in commercial furfural production. Today, bagasse and corn cobs account for more than 98% of all feedstocks used to manufacture furfural because they are relatively high in pentosan content, inexpensive, and readily available from sugarcane and corn processing plants, respectively.[31]

However, since pentosans only contribute a portion of the total composition of lignocellulose, the sole production of furfural from these residues would be wasteful, inefficient and uneconomic. Cellulose is the largest fraction of lignocellulosic biomass consisting of fibrous bundles of repeating glucan units. As amorphous hemicellulose is far more acid-labile than crystalline cellulose, pentosans are hydrolyzed and dehydrated to furfural much sooner than glucans from cellulose.[32–35] Thus, acid-catalyzed production of furfural from biomass often leaves behind a solid residue containing glucan and lignin. Figure 2 outlines a diverse range of potential co-products that could be made from lignocellulosic biomass in addition to furfural.

Processes that can target production of valuable chemical products from all major fractions of lignocellulosic biomass will greatly improve process economics and could potentially synergistically facilitate both chemical and biological production strategies. Vedernikovs, a Latvian professor and creator of the Vedernikovs furfural process, had stated that furfural production is not economically viable without a low-cost feedstock and co-production of other higher-value chemicals from the remaining lignin and cellulosic residues.[31,37] For example, sugars extracted from the glucan-rich residue recovered from furfural production could be used to produce 5-HMF, levulinic acid[38] or bioalcohol,[37] and the remaining lignin could be used for manufacture of

**Table 1.** Pentosan content of plants and agricultural residues that could be employed for furfural production, listed in order of decreasing pentosan content

| Plant material | Pentosan content (%) |
|---|---|
| Corn cobs | 35 |
| Almond husks | 30 |
| Rye straw | 30 |
| Oat hulls | 29 |
| Cottonseed hulls | 28 |
| Barley straw | 25 |
| Birchwood residues after felling | 25 |
| Sugarcane bagasse | 25 |
| Sunflower husks | 25 |
| Wheat straw | 24 |
| Flax shives | 23 |
| Hazelnut shells | 23 |
| Birchwood logs | 22 |
| Eucalyptus wood | 20 |
| Rice hulls | 17 |
| Maple wood | 16 |
| Pinewood | 8 |
| Peanut shells | 3 |

Table adapted from O'Brien.[31]

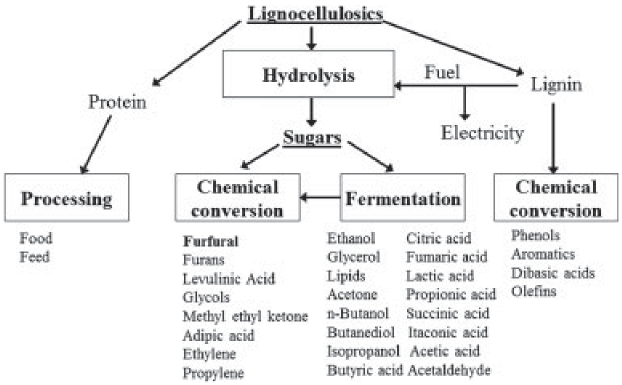

**Figure 2.** Conversion of sugars, lignin, and protein in lignocellulosic biomass for the integrated production of fuels, chemicals, materials, heat, power, food, and feed. (Adapted from Wyman.[36])

aromatics, olefins, dibasic acids, and even carbon fiber (Fig. 2).[39–42] Acetic acid and formic acid are also secondary products from biomass,[5,45] which have also been shown to provide catalytic properties to furfural formation. Due to the structural and compositional differences between each fraction, integrated production strategies may benefit from being able to efficiently fractionate biomass to improve co-product yields. Burning solid residues for energy as practiced in many processes that have since been abandoned would be one of the least viable options.

## FURFURAL FORMATION AND DESTRUCTION CHEMISTRY

The formation of furfural from pentosans can be understood in terms of consecutive hydrolysis and dehydration reactions of xylan or arabinan. Following the introduction of a water molecule to break the glycosidic bond (hydrolysis) and form xylose or arabinose, three water molecules are then released from the respective sugars to form furfural (dehydration). Although various open and closed chain sugar intermediates have been proposed,[3,46–49] the precise reaction mechanism is still not completely understood.[50,51] As shown in Fig. 3, recent thermodynamic simulations by Nimlos and co-workers[52] favored energetics of the closed-chain formation of a dehydrofuranose intermediate by ring contraction of the $O_2$-protonated pyranose. This proposed model was determined to have the lowest energy barrier for furfural formation in the presence of a strong Brønsted acid such as $H_2SO_4$ but does not represent the only valid model, especially in the presence of other catalysts.

Marcotullio and de Jong[51] favored an open-chain mechanism, as shown in Fig. 4, that involves the rate-limited formation of a 1,2-enediol intermediate (2 in Fig. 4) from xylose in the presence of halide salts. They found that the presence of halide ions (such as Cl−, Br−, or I−) in an acidic xylose solution greatly increased the rate of enolization and subsequent dehydration reactions (5, 6, and F in Fig. 4) and that furfural selectivity was greatly improved by the presence of a combination of chlorine and iodine (halide) ions that enhance the enolization and dehydration steps, respectively. Similarly, Binder and co-workers[50] suggested a mechanism in which xylose undergoes a 1,2-hydride shift in the presence of chromium(II and III) chloride catalysts (Lewis acids) to form xylulose (3 in Fig. 4), which they found to be more predisposed to form furfural than xylose by way of the proposed open-chain mechanism. Their study suggested that xylulose dehydration could be a more selective pathway to furfural formation and that Brønsted and Lewis acids play uniquely different roles in promoting hydrolysis and dehydration reactions of xylan.[53] For arabinose, furfural formation rates have been found to be much slower than with xylose and are often neglected in furfural yield calculations due to the relatively small amount of arabinose in lignocellulose.[3]

Despite differences in the proposed mechanism, the general reaction sequence shown in Fig. 5 provides a useful representation of the formation pathway of furfural from pentosans and the competing loss reactions during and after furfural formation. If furfural is allowed to remain in the catalytically active aqueous phase at higher temperatures, hydrolytic fission of the aldehyde group by hydrogen ions at low pH occurs and produces formic acid.[54,55] Also in Fig. 5, reaction losses are further complicated by the minor loss of furfural due to self-polymerization (furfural resinification) and the major loss of furfural by cross-polymerization reactions with sugar intermediates (furfural condensation).[3,48] Consequently, greater furfural losses occur in the active aqueous phase when higher concentrations of pentoses are present in the solution.[3]

For furfural destruction, Marcotullio and co-workers[56] determined that furfural loss in dilute sulfuric acid at 150–200°C could be expressed by a first-order model with an activation energy of 125.1 kJ $mol^{-1}$ for an Arrhenius temperature dependence on the hydronium ion activity. However, it was suggested that the same model could not be applied to other acid catalysts such as HCl where both the hydronium and chlorine ions play roles in the degradation kinetics. Several breakdown products were detected, but not all were identified. Although their study confirmed early findings by Dunlop[55] regarding the first-order loss approximation, the Dunlop study did not account for variations in the second dissociation constant of sulfuric acid and reported a lower 83.7 kJ $mol^{-1}$ activation energy. Also, unlike Dunlop's

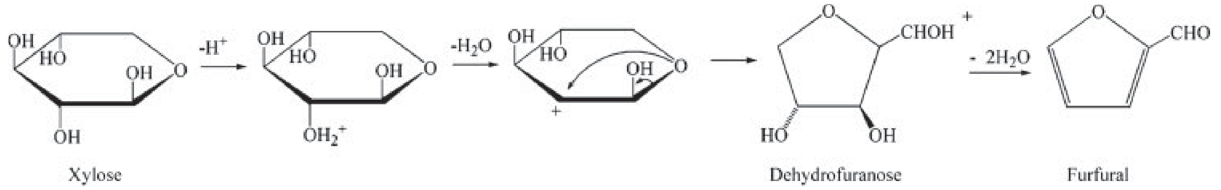

**Figure 3.** Proposed closed-chain mechanism for furfural formation from xylose by $O_2$ protonation and ring contraction to a dehydrofuranose followed by consecutive dehydration. (Adapted from Nimlos *et al*.[52])

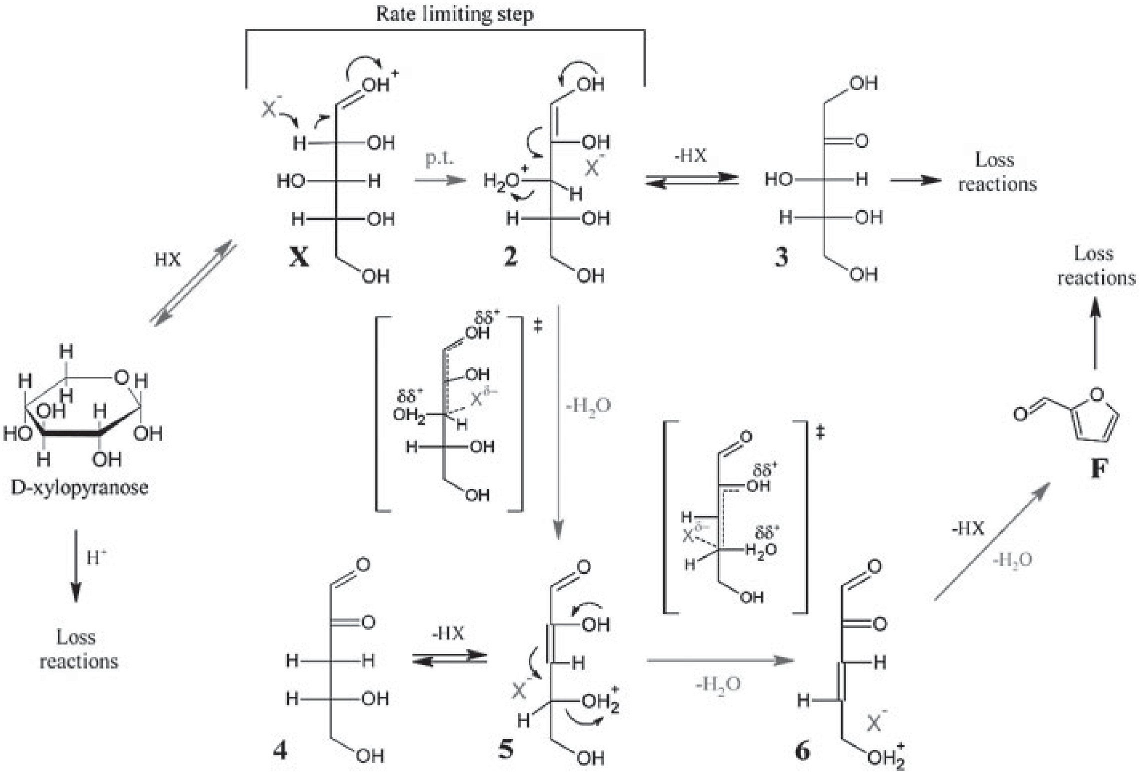

**Figure 4.** Proposed open-chain mechanism of furfural formation by 1,2-enediol formation (2) and dehydration (5 and 6) in the presence of halides, denoted by X-. (Taken *verbatim* from Marcotullio and de Jong.[51])

findings, formic acid formation and furfural polymer products in the study by Marcotullio and co-workers were found to be minimal.

Inconclusive mechanisms to describe furfural formation and the incomplete understanding of pathways responsible for furfural losses show the pressing need to focus more efforts in this area. Only complete chemical analysis of degradation products produced from both furfural and xylose will conclusively determine the contribution and origin of the degradation species. Determination of accurate formation and loss reaction mechanisms and rates for various catalytic environments and reaction conditions in a process model could help define potentially fruitful routes for continued research and process improvements to enhance yields.

## IMPROVING FURFURAL YIELDS

Industrial furfural yields from sulfuric acid digestion of lignocellulosic residues followed by steam striping have remained at or below 50% (molar) of theoretical. One of the first attempts to improve furfural yields was undertaken by Brownlee[57] through application of a two-step process that first hydrolyzed the pentosans in a heated acid solution before the wet matter was subjected to superheated steam that continuously extracted furfural and removed moisture. The resulting increase in the hydrogen ion concentration due to a loss of water and higher temperatures led to a significant reduction in reaction time. The Quaker Oats Company adopted a continuous version of this process to obtain yields of 55%.[3]

A more effective strategy to improved furfural yields is to remove furfural from the catalytically active phase soon after it forms.[3] In line with this reasoning, boiling or otherwise extracting furfural from the aqueous phase represented the first effective approaches to improving furfural yields. Since furfural forms a minimum-boiling azeotrope with water, separation of furfural vapors can occur by azeotropic distillation in the presence of steam at much lower temperatures. In another technique, by continually boiling the solution, furfural vapors are unable to re-enter solution, and unwanted side-reactions are reduced. Zeitsch developed the SupraYield® process which used slow depressurization at high temperatures (240°C) to keep the reactants in a boiling state that recovered more furfural, with the result that furfural yields of 50–70% of theoretical could be realized. More recently, Mandalika and Runge[58] applied these concepts in a batch reactive distillation (BRD) approach[59] in which a continuously heated batch reactor

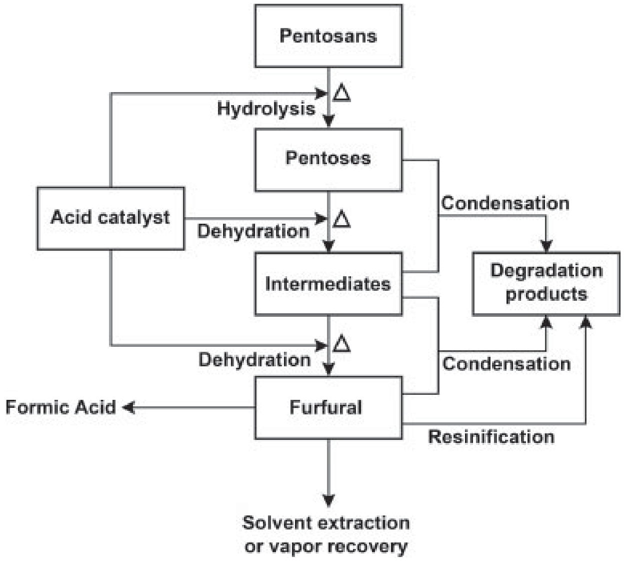

**Figure 5.** Reaction sequences for obtaining furfural from pentosans and loss reactions. (Adapted from Vedernikovs *et al.*[37])

was fitted with a throttle valve that released the vapor contents over the course of the reaction, allowing the solution to boil under depressurization and furfural to escape from the reactor as it was produced, resulting in upwards of 80% yield from wood chips.

Sproull and co-workers [63] proposed that organic solvents such as methyl isobutyl ketone,[60,61] tetrahydrofuran,[21,62] alcohols, and others can be successfully applied to improve yields by extracting furfural into a separate organic phase during furfural production in biphasic reaction schemes. Amiri and co-workers[64] then compared several extracting solvents and their performance using rice straw and found tetrahydrofuran to achieve higher furfural yields in a biphasic system due to its exceptional extraction efficiency. Such biphasic approaches are advantageous in their ability to capture furfural in the organic phase and protect it from attack by hydronium ions to form degradation products. The biphasic approach can also assist in furfural recovery by avoiding costly distillation from water, particularly with low-boiling solvents such as tetrahydrofuran (b.p. 66°C). On the other hand, the need for costly recovery operations to recycle the solvent, the reduction of effective solids loading to maintain a distinct organic phase in the reactor, higher operating pressures from their additive properties, safety hazards, and high solvent costs are some of the disadvantages to the biphasic approach. Gürbüz and co-workers[65] used lignin-derived alkylphenol solvents to address these issues. They achieved a furfural yield of 75% of theoretical using a xylose solution derived from corn stover hydrolysis in a biphasic solvent system with 0.25 mol $L^{-1}$ HCl and 2-*sec*-butylphenol at a high aqueous/organic mass ratio of 6.67:1. However, saturation of the aqueous solution with NaCl was necessary to increase partitioning of the aqueous and organic phases and further promote the xylose dehydration reaction.[66] The presence of salts would also elevate the boiling point of water when recovering aqueous co-products and introduce a processing challenge for post-reaction processing of the salt-saturated aqueous phase.

In an effort to find more environmentally friendly alternatives to mineral acid catalysts, the application of solid metal chloride catalysts has shown promise. As mentioned earlier, halide ions, especially $Cl^-$, appear to promote enolization (step 2 in Fig. 4) and improve the selectivity and yield of furfural from xylose.[51] Acidic metal chlorides such as $CrCl_2$, $CrCl_3$, $ZnCl_2$, $MgCl_2$, $FeCl_3$, and $AlCl_3$ demonstrated the ability to catalyze xylose dehydration and furfural degradation beyond what was achieved using dilute sulfuric acid at the same pH, thereby revealing that the activity of the metal chlorides was not governed solely by its Brønsted activity.[50,53,67] In light of this, vom Stein and co-workers[68] obtained furfural yields of 71% of the theoretical maximum from a xylose solution using $FeCl_3$ as an aqueous-phase catalyst in a biphasic reaction with 2 mol $L^{-1}$ tetrahydrofuran and water to prevent furfural loss. It is worth mentioning that the addition of 20% NaCl was needed to obtain a phase partition to achieve the highest furfural yields and furfural yields decreased to 37% when beechwood hydrolysate was used instead of xylose. More recently, by supplementing $FeCl_3$ with a mixture of seawater (NaCl + water) and acetic acid in a semi-continuous reaction, Mao and co-workers[5] obtained a 72% furfural yield of theoretical directly from processed corn cobs. By introducing a weak Brønsted acid with a strong Lewis acid, the hydrolysis of xylan and dehydration reactions to furfural can be enhanced by conversion of xylose to xylulose.[69] Both groups also demonstrated that the catalyst-containing aqueous phase can be recycled without a significant loss of furfural yield.

Heterogeneous solid catalysts can eliminate the need for catalyst recovery altogether. Various zeolite-based catalysts and ion-exchange resins[70,72] with strong Brønsted acidic sites (over Lewis sites) have been shown to improve selectivity towards furfural,[71] whereas the combined presence of Lewis acid sites helped to reduce the energy barrier for xylose to xylulose formation.[69] Many of these catalyst systems, however, may require organic solvents to extract furfural, introducing the issues discussed above, and catalyst deactivation can occur by the coking of the micro-porous surfaces by insoluble polymers and degradation products. Furthermore, since it is not possible to flow solid biomass through these heterogeneous catalysts, the additional pretreatment needed and further discussion are beyond the scope of this paper.

## INTEGRATED FURFURAL PRODUCTION STRATEGIES FROM LIGNOCELLULOSIC BIOMASS

In modern furfural plants, large digesters (about 1.5 × 8 m) are used to contain agricultural residues for conversion. Typically, sulfuric acid is used as the catalyst, and steam is employed for digester heating and furfural stripping.[3] Due to the corrosiveness of sulfuric acid and the resulting residues, expensive metals are needed for containment, and the process is not environmentally attractive.[3,5,71] Heavy furfural losses are also sustained in industrial production methods from by-product formation and inefficient recovery due to a high steam-to-furfural ratio.[3,73] For Huaxia/Westpro plants currently operating in China, 25–35 tons of steam is consumed per ton of furfural at about a 50% yield of theoretical pentosan content.[6] Remarkably, these plants are estimated to make $1–2 million in profits each year with the sale of higher value by-products contributing to a significant portion of their revenues.[6] Thus, integrated production recovers value from a relatively inefficient process.

Table 2 lists a number of lignocellulosic furfural production strategies proposed by some commercial and academic research projects along with comparisons to some historical benchmark processes. The furfural production book by Zeitsch[3] describes many of the older furfural-only technologies such as those

**Table 2.** Selected technologies for the production of furfural and co-products from lignocellulosic biomass to enhance total revenues through integrated processes

| Company /group /process | Process type | Operating temperature (°C) | Catalyst | Substrate | Furfural yield (% theoretical) | Co-products | References |
|---|---|---|---|---|---|---|---|
| Quaker Oats | Batch/aqueous | 153 | $H_2SO_4$ | Oat hulls | <50 | N/A | 3 |
| Quaker Oats | Continuous/ aqueous | N/A | $H_2SO_4$ | Bagasse | 55 | N/A | 3, 57 |
| Huaxia/ Westpro | Continuous/ aqueous | 160–165 | $H_2SO_4$ | Corn cobs | 35–50 | Methyl alcohol, acetone, acetic acid, levulinic acid | 3, 31 |
| Vedernikovs | Continuous/ aqueous | 188 | $H_2SO_4$ | Wood chips | 75 | Acetic acid, ethanol | 37, 44, 74 |
| Zeitsch/ SupraYield® | Continuous/ aqueous | 240 | $H_2SO_4$ | N/A | 50–70 | N/A | 3, 31 |
| Biofine | Continuous/ aqueous | 190–200 | $H_2SO_4$ | Paper sludge and waste residues | 70 | Levulinic acid, formic acid, char | 43, 75, 76 |
| Abatzoglou and co-workers | Continuous/ aqueous | 190–240 | $H_2SO_4$ | Hardwood saw dust | 65 | Hexose solution | 77 |
| Lignol | Continuous/ organosolv | 180 | $H_2SO_4$ | Wood chips | >4 | Glucose, xylose, lignin | 78 |
| de Jong and Marcotullio/MTC | Continuous/ aqueous | 180 | $H_2SO_4$ | Straw | 85[a] | 5-HMF, cellulosic residues | 43 |
| Mandalika and Runge | Batch/aqueous | 170 | $H_2SO_4$ | Poplar wood chips | 80 | Cellulosic residues | 58 |
| Alonso and co-workers | Batch/organic | 170 | $H_2SO_4$/ Mordenite | Corn stover | 81/87 | Levulinic acid | 79 |
| Mao and co-workers | Batch/aqueous | 190 | Acetic acid/$FeCl_3$ | Corn cobs | 73 | Cellulosic residues, lignin | 5, 80 |

[a] estimated from model.

by Agrifurane, Escher–Wyss, Rosenlew, Supratherm, Stake, Suprayield, and Voest–Alpine and discusses their innovations and disadvantages. This section will focus on more recent advances in the production of furfural integrated with co-production of other products from biomass.

Vedernikovs and co-workers proposed a concept for co-producing hemicellulosic furfural with cellulosic ethanol. The original process achieved furfural yields of 75% by injecting small amounts of strong acid and applying salts to ensure differential catalysis of hydrolysis and dehydration reactions.[44] Further evolution to a two-step hydrolysis process resulted in a claimed seven-fold reduction in degradation of the cellulose residues and provided sufficient material to sustain bioethanol co-production.[37] However, the high temperature reactions could increase the enzymatic recalcitrance of the remaining residue, and furfural carry-over could inhibit biological fermentations. In 2006, a commercial-scale furfural plant was built in Iran to Vedernikovs specifications.[74]

Another commercially viable furfural process patented in 1990 is the Biofine process.[75] Primarily designed for production of levulinic acid from hexoses released from paper pulp waste, furfural was also reportedly recovered at 50–70% yield.[76] Their process outline and the furfural yields reported indicated that a furfural stripping step helped reduce degradation reactions. In a commercial plant in Caserta, Italy, paper mill sludge was processed by this process at 3000 t year$^{-1}$. The acid solution used was recycled, and a large amount of formic acid was also produced due to its equimolar formation with levulinic acid from 5-HMF. Importantly, recovery of furfural and levulinic acid from the reaction by stripping or distillation will require boiling large amounts of water and result in substantial energy demand.

Also in 1990, Abatzoglou and co-workers[77] reported 65% furfural yields and 30% recovery of fermentable hexoses in a single-stage continuous plug-flow reactor using wood sawdust with dilute sulfuric acid as the catalyst. The reactor could handle suspensions of up to 13 wt% sawdust, and at the higher reaction temperatures of 190–240°C, reaction times were only 20–120 s. Despite lower hexose yields, this work represented some of the earlier efforts to co-produce furfural with cellulose that could be enzymatically hydrolyzed to hexoses. It also demonstrated the successful application of a plug-flow reactor to handle higher solids concentrations, and the reaction could be optimized using smaller scale batch reactions.

Lignol Energy Corporation (since 2001) used an ethanol–organo solv process to fractionate recalcitrant wood chips in their pilot plant in Burnaby, Canada. This process relied on enzymatic hydrolysis of the fractionated cellulose and subsequent fermentation to produce ethanol.[78] Because they determined that just producing bioethanol may not be economically favorable, production of furfural from the pentoses and other valuable chemicals from the extracted lignin was highly desirable, especially when co-fermentation of pentoses was not possible.[43] However, their reported furfural concentrations were low when using ethanol, and alternative solvents must be explored to target furfural production from xylans. The acetic acid recovered as a product in this process could also serve a potential catalytic role.[78]

De Jong and Marcotullio[43] proposed a reactor design called the Multi-Turbine-Column (MTC) that continuously hydrolyzed and dehydrated straw while simultaneously stripping furfural product in a counter-current design. Furfural was then extracted by toluene and vacuum distilled at 83°C to high purity. Up to a 10 wt% straw slurry could be safely loaded into the reactor. Application of a counter-current design minimized product accumulation and reduced cross-polymerization reactions. From their simulation data, furfural yields were estimated to be about 85% in a 10 Kt $y^{-1}$ model.[43] Anticipated co-products included methylfurfural and cellulose–lignin residues. Although their model demonstrated economic feasibility, important assumptions such as furfural yield, solvent recovery, and energy consumption greatly impacted the economics.

As mentioned earlier, Mandalika and Runge[58] used batch reactive distillation to achieve >85% furfural yields from hybrid poplar, miscanthus, switchgrass and corn stover. The reaction vessel operated isothermally and slowly released the vapors containing furfural product from the reactor head space while inducing internal boiling to reduce loss reactions. A coil submerged in an ice-bath condensed the vapors into a collection beaker for analysis. They found that reactions with pure xylose solutions led to lower yields (75%) than reactions with biomass (>85%) or hemicellulose hydrolysates extracted from biomass (88%). It is likely that the higher initial concentration of xylose in the pure samples triggered greater furfural losses. The co-product of this reaction was porous lignocellulosic residues enriched in cellulose and lignin for potential conversion into fuels and chemicals.

Recently, novel application of a single phase co-solvent system using $\gamma$-valerolactone as both a solvent and a potential product was applied to produce levulinic acid from 6.6 wt% corn stover.[79] With HCl as the catalyst, open boiling of the reaction media resulted in the highest furfural yields (81%), whereas a closed batch reaction resulted in the highest levulinic acid yields (66%) from corn stover. However, total yields of furfural plus levulinic acid as co-products were considerably lower due to the inherent differences in recalcitrance between the hemicellulose and cellulose fractions, suggesting that a two-stage reaction may be necessary to obtain high yields of both. The highest furfural yield (87%) was obtained using a solid acid catalyst (Mordenite) at a high loading of 0.9 g catalyst per 1 g of corn stover. $\gamma$-Valerolactone also solubilized most of the biomass as well as the lignin, possibly allowing lignin recovery for conversion into products.

The last entry in Table 2 refers to recent work by Mao and co-workers[80] on the digestion of corn cobs using both acetic acid and $FeCl_3 \cdot 6H_2O$ solid catalyst in a semi-batch reactor system. Sieved corn cobs (5–10 mm) were soaked in $FeCl_3$ and saltwater solution and loaded into a tubing-bomb reactor system with a liquid-to-solid ratio of 0.6:1. A mixture of acetic acid and steam was then delivered to the reactor to heat the contents and strip away the furfural product over the course of the reaction. Notably, a 73% furfural yield and 80% delignification were achieved. The remaining cellulosic residue was then steam exploded through a valve in the reactor bottom to produce highly digestible material for enzymatic hydrolysis. The cost and recyclability of the solid catalyst still needs to be determined, and deposition of trace iron compounds on the remaining residues may inhibit enzyme and biological activity.

Such advances in production strategies lend insight into key process features that enhance integrated furfural production. The ability to achieve high yields of furfural and co-products from each major fraction of lignocellulosic biomass is particularly vital. Catalysts that reduce the energy barrier for xylose dehydration will improve selectivity to furfural. Efficient removal or protection of furfural to reduce degradation losses will facilitate process optimization and lower recovery costs and waste treatment. Finally, to have wide-scale application, an integrated lignocellulosic process must be agnostic toward a number of leading feedstocks, and the ability to achieve high yields with more recalcitrant woody feedstocks would further expand the potential impact. It is also vital that the process be capable of handling high solids loadings to keep energy costs as low as possible.

## CONCLUDING REMARKS

Furfural is a promising renewable platform chemical for production of biochemicals and biofuels from low cost and abundant lignocellulosic biomass. Furfural is a natural precursor to furan-based chemicals and is primarily manufactured from the acid-catalyzed hydrolysis and dehydration of lignocellulosic pentosans at moderate temperatures. Catalytic hydrogenation of furfural remains the most versatile reaction to upgrade furanic components and can synthesize hydrocarbons directly from furfural to serve as fuels. The mechanisms involved in the formation of furfural are still unclear as both open and closed chain intermediates have been proposed in the presence of Lewis or Brønsted acids. Furfural losses can occur from both resinification and cross-condensation reactions with sugar intermediates.

Modern commercial production is inefficient (25–35 t steam $t^{-1}$ furfural) and suffers from low yields (<50 mol% of theoretical). Various strategies to improve furfural yields were discussed, including the removal of furfural into the vapor phase, the extraction of furfural from the catalytically active aqueous phase using biphasic solvent systems, and application of reusable or recoverable solid catalysts. Emphasis must be placed on the importance of directly using lignocellulosic biomass as the expectation that pure sugars can be extracted is likely to result in excessive costs for the entire process. Finally, recent integrated strategies were discussed in which co-production of other high-value products in addition to furfural was a central theme to fully utilize all of the feedstock and improve process economics. Overall, advances are still needed to improve our understanding of the underlying chemistries of furfural formation and loss under various catalytic environments to develop efficient production strategies that integrate biomass deconstruction, lignin recovery, sugar dehydration, and product recovery. With success, furfural can become a viable renewable alternative to manufacture many current petroleum-based products at a large commercial scale.

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