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Reaction Kinetics Based Optimization of Furfural Production from Corncob Using a Fully Recyclable Solid Acid

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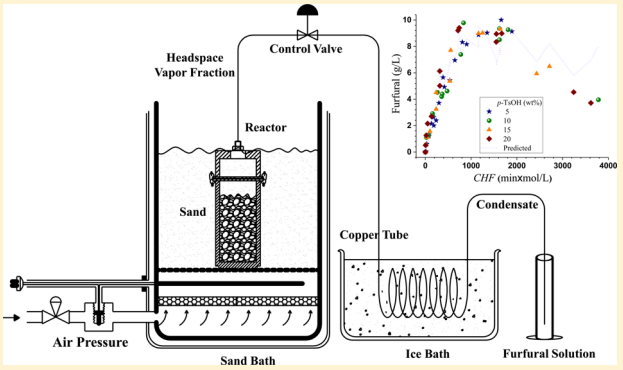
Supporting Information

ABSTRACT: To achieve green processing through recycling catalysts, this study demonstrated a commercial solid acid toluenesulfonic acid (*p*-TsOH) for furfural production from corncob. Acid recyclability study indicate that crystalized *p*-TsOH was highly effective for furfural production. A kinetic based reaction severity, combined hydrolysis factor (CHF), was used to develop a furfural predictive model with the consideration of loss through degradation. Furfural yield of approximately 75% theoretical was achieved in a CHF range between 830 and 1850.



1. INTRODUCTION

Because of concerns over energy shortage and climate change, efficient utilization of natural resources as a sustainable alternatives for producing renewable chemicals and fuels become critically important. Lignocellulosic biomass is an obvious choice to replace petroleum feedstock, because it is the most abundant and potentially low cost from a variety of sources including agricultural and forest residuals as well as high-yield bioenergy crops.[1] For most of the strategies being investigated, platform intermediate furfural, traditionally produced from renewable lignocellulosic biomass, is often employed as a critical feedstock for the sustainable production of value-added chemicals and biofuels.[2−4] In fact, furfural is the valuable and versatile precursor for many furan-based chemicals such as furfuryl alcohol, furoic acid, furan, and tetrahydrofuran, which has well-established chemistry developed since its mass production.[5,6] Furfural is also widely employed to make relatively high energy density and high octane number biofuels such as gasoline, diesel, or jet fuel.[7−9]

The industrial process for the production of furfural was developed in 1921 by Quaker Oats using oat hulls as feedstock in a sulfuric acid aqueous solution at 443−458 K in a batch reactor.[10] The process resulted in a furfural yield of 40−50%. Because of limited demand and high maintenance costs, yield and production methods have not been substantially improved up until the 1980s.[11,12] Conventional batch production of furfural is always accompanied by the side reaction that resulted in low yield. Furfural is a reactive molecule that can undergo condensation with itself and intermediates (glucose, HMF) to form black, resinous products called humins.[13] To address this problem, organic solvents such as alkylphenol solvents,[14] methyl isobutyl ketone,[15] tetrahydrofuran,[16] etc. have been successfully applied to extract furfural into a separate organic phase in biphasic reaction schemes. By comparing several extracting solvents and their performance using rice straw as feedstock, Amiri et al. found that tetrahydrofuran achieved highest furfural yield in a biphasic system due to its exceptional extraction efficiency.[17] However, using a large amount of organic solution can increase the cost for commercial furfural production. Many industrial solvents are known to be hazardous to human health. Furthermore, concerns over flammability and environmental effects due to disposal may prohibit widespread usage of these solvents in industry practice.

At a molecular level, some researchers focus on preparing novel catalyst to influence the 1,2-enediol intermediate, a precursor of furfural, in ways that reduce the formation of humins and improves selectivity toward the production of furfural. Lessard et al. used zeolite catalysis in a continuous two-liquid-phase (aqueous-toluene) plug-flow reactor at 260 °C and 55 atm to achieve both furfural molar yield and selectivity of 98%.[18] Marcotullio et al. investigated different halides in dilute aqueous acidic solutions on furfural selectivity and yield. Their results indicated that the presence of metal halides improved reaction kinetics by promoting the formation of the 1,2-enediol structure, and the highest selectivity and furfural yield, 95.3%

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and 87.5%, respectively, were obtained using a combination of KCl and metal halides.[19]

A more effective strategy to improved furfural yields is to remove furfural from the catalytically active phase soon after it forms. Because furfural forms a minimum-boiling azeotrope with water at higher pressures. This characteristic can be used to extract the lower-boiling furfural-water azeotrope from the reaction mixture and decrease furfural loss. This concept was applied through a batch reactive distillation (BRD) approach in which a continuously heated batch reactor 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 upward of 80% yield from wood chips.[20] In fact, this BRD process is advantageous not only in their ability to improve the furfural yield by protecting furfural from degradation but also in assisting furfural recovery by avoiding costly water distillation from dilute solutions as the distilled furfural solution is highly concentrated.

Solid acids have the advantage of easing chemical recovery[21] and have been used for hydrolyzing cellulosic materials.[22] The novelty of the present study is to demonstrate robust furfural production from corncob using an easily recyclable commercially available solid acid (toluenesulfonic acid (*p*-TsOH)), which exhibited higher catalytic activity than sulfuric acid in water for the hydrolysis of cellulosic materials,[23] with a BRD process. Furthermore, process optimization was achieved using a kinetic based reaction severity, the combined hydrolysis factor (CHF),[24] that can ease process scale-up as demonstrated previously in bioethanol production.[25,26] The goal of the study is to achieve environmentally sustainable production of platform molecules from lignocelluloses using easily recyclable solid acid. Therefore this study is important to the existing furfural production industry to increase process efficiency.

2. MATERIALS AND METHODS

2.1. Materials. Corncob used in this study was kindly provided by Dr. Xuejun Pan of University of Wisconsin-Madison, and it was ground into particles with a size range of 20−40 mesh using a Wiley mill (model no. 2, Arthur Thomas Co, Philadelphia, PA). *p*-TsOH and calcium carbonate were ACS reagent grade and acquired from Sigma-Aldrich (St. Louis, MO). *p*-TsOH is a solid acid that can be easily recovered through commercially proven crystallization technology.[27] Therefore, *p*-TsOH was used as a catalyst instead of mineral acids reported in the literature.

2.2. Reactive Distillation Experiments. Reactive distillation experiments were conducted in a laboratory assembly designed to simulate conditions in a batch reactive distillation process. A 100 mL stainless reactor was fitted with a valve that can be opened to continuously remove a portion of the vapor from the reactor headspace as schematically shown in Figure 1. The stainless reactor was filled with 85 mL of *p*-TsOH solution and 6 g in oven dry (OD) weight ground corncob. Reactions were performed in a sand heating bath (Techne F932D, Techne Inc.) to maintain specified reaction temperature. When mixture was heated to a given temperature, the valve was slightly opened and furfural-water azeotrope was extracted from the reactor through a copper tube that was immersed in an ice bath to condensate the extracted vapor from the reactor headspace. A total of 71 experiments were conducted in a range of reaction conditions (Table S1). The range of acid concentrations studied was 5−20 wt% in 5 wt% increment.

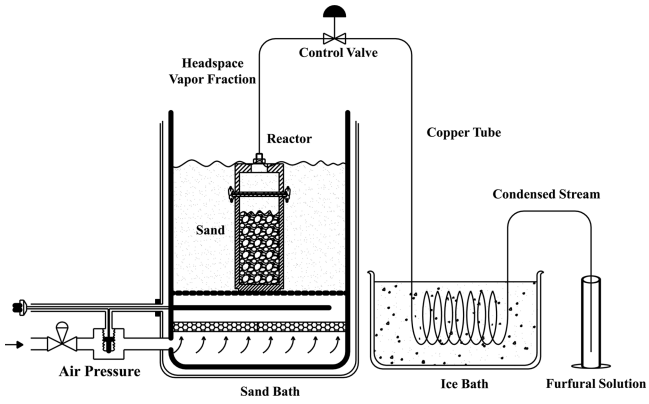

Figure 1. Schematic of the batch reactive distillation system: the vapor fraction is pulled from the headspace and condensed within the copper tubing immersed in the ice bath.

Reactions were conducted at temperatures of 60, 80, 100, 120, 130, 140, 150, abd 160 °C with a reaction time range of 30−90 min in a 20 min increment. The vapor extraction valve was open slightly after the reactor reached the desired reaction temperature. Heat was continuously supplied to the reactor to offset the cooling effect of vapor loss to maintain a nearly constant temperature throughout the reaction. For each experiment, a total of 35 mL (exact) of furfural solution was extracted from the reactor into a beaker. At the end of each reaction, the stainless reactor was cooled with tap water before opening. Solids and freely drainable spent liquor were separated by a Büchner funnel using filter paper (15 cm, slow, Fisher Scientific Inc., Pittsburgh, PA). The collected solids were washed and dried at 55 °C in an oven (Thermo Fisher Scientific Inc.) to constant weight for further analysis. The collected spent liquor and distilled furfural solution were analyzed by HPLC.

2.3. Analytical Methods. The solid samples were hydrolyzed using sulfuric acid in two steps for carbohydrates analyses by the Analytical Chemistry and Microscopy Lab (ACML) at the Forest Products Lab as described previously.[28] Monosaccharides, levulinic acid, furfural, 5-hydroxyl methylfurfural (HMF), acetic acid, and formic acid in pretreatment spent liquor and distilled furfural solution were determined using a Dionex HPLC system (Ultimate 3000) equipped with an RI (RI-101) detector and a UV detector (VWD-3400RS), as described previously.[29]

Furfural yield with respect to the weight of the raw biomass was calculated as follows:

$$Y_{\text{furfural}}(\%) = \frac{m_{\text{furfural}}}{m_{\text{corncob}} \times 0.9529 \times 0.268 \div 0.88 \times 0.64} \times 100\%$$

where m_{furfural} is total weight of measured furfural after reaction assuming no water loss in reaction, m_{corncob} is mass (6 g) of corncob used in reaction; 0.9525 is dry matter content of corncob; 0.268 is the xylan content in dry corncob, 0.88 and 0.64 are the ratios of molecular weight of xylan over xylose and furfural over xylose, respectively.

2.4. Acid Recycling. In the first run similar to the experiments described previously, fresh corncob (6 g) was first mixed with fresh *p*-TsOH solution (85 mL) of 1.18 mol/L, then heated to 150 °C for 30 min. A volume of 35 mL of furfural solution was withdrawn through distillation from the

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reactor into a separate beaker (Figure 1). At the end of the reaction, spent liquor was collected for composition analyses. Residual solids was filtered and washed using deionized water to neutrality for further analysis using deionized water at the end of reaction. After evaporating most of water in all the collected liquid, the acid along with any remaining solids was crystallized at 55 °C in an oven (Figure 2a–c) and reused in the subsequent experiment using fresh corncob. *p*-TsOH was recycled three times to evaluate its catalytic efficacy for furfural production.

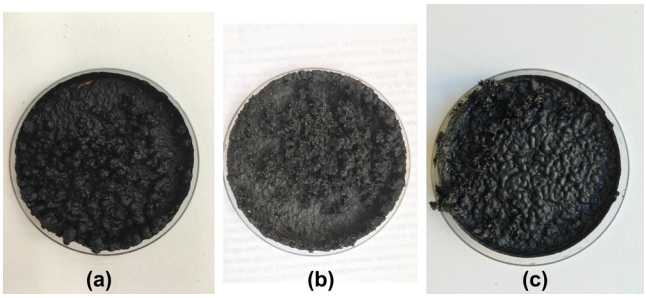

Figure 2. Images of recycled *p*-TsOH along with solubilized lignin and solids of degradation products. Images taken after filtration of solids and evaporation of water: (a) after first cycle of reaction, (b) after second cycle of reaction, and (c) after third cycle of reaction.

2.5. Reaction Severity Based Furfural Predictive Model. Furfural production through dehydration of xylose has been observed to follow first order Arrhenius kinetics.[30−32] However, side reactions can cause furfural loss especially at high reaction severities. This can be attributed to reactions of furfural with itself (furfural condensation) and reactions of furfural with intermediates[13] to form black, resinous loss products called humins.[20,33] Reaction kinetics has been developed for the prediction of furfural yield with good success[13] but not easily usable for process control. Here, we develop a reaction severity based kinetic model that can be easily used for process scale-up design similar to that demonstrated previously for biofuel production.[25,26]

Reaction severity was developed to quantitatively represent the extent of a chemical reaction. The H-factor,[34] an integration of temperature over time (or thermal energy input) is widely used in chemical pulping for process control. For acid hydrolysis of hemicelluloses, a combined severity factor (CSF)[35] was developed by modifying the H-factor but was not used for process control. We developed a kinetic based combined hydrolysis factor (CHF) previously that combined reaction temperature, time, and chemical concentrations to control hemicellulose dissolution.[24] Hemicelluloses are inhomogeneous in terms of rate of chemical reaction partly due to the hierarchical structure of lignocelluloses as observed by several researchers during acid hydrolysis of xylan.[36−38] By using a biphasic reaction model, we successfully predicted wood hemicellulose (xylan) dissolution under acidic conditions using a reaction severity CHF[24,25] as below:

$$X_R = (1-\theta)\exp(-\mathrm{CHF}) + \theta\exp(-f\mathrm{CHF}) \tag{1a}$$

$$\mathrm{CHF} = \exp\left(\alpha - \frac{E}{RT} + \beta C\right)Ct \tag{1b}$$

where X_R is the fraction of xylan remaining in solids; θ is the fraction of slow reaction xylan; f is the ratio of the reaction rates between the slow of fast xylan; E is apparent activation energy; α and β are adjustment parameters; R = 8.314 J/mol/K is the universal gas constant; C is acid molar concentration; T is reaction temperature in degree Kelvin; and t is reaction time in min.

CHF was used for predicting hemicellulose sugar degradation under typical lignocellulosic biomass pretreatment conditions, i.e., milder than those for furfural production, when lumping all sugar degradation (dehydration) into one pool to define one rate constant, k_d, without considering furan degradation.[39] The model performed reasonably well under low to mild severity conditions. For the furfural production study here, we amended this simple model by taking furan (furfural) degradation into consideration using first order kinetics. We ignored furfural degradation through the reaction between xylose and furfural based on the fact that xylose was produced in situ from the corncob through acid hydrolysis, i.e., low xylose in the reaction system, unlike the literature study[13] with xylose readily available as xylose was directly used. Furthermore, furfural concentration in the reactor was also low because of distillation. Then, net furfural production with the consideration of degradation can be expressed

$$\frac{dF}{dt} = k_d(1 - X_R) - k_l F \tag{2a}$$

$$F(0) = 0 \quad \text{at } t = 0 \tag{2b}$$

where $(1 - X_R)$ represents the total amount of xylan dissolved in the hydrolysate and used as an approximation for xylose with the understanding that oligomeric xylose must be low at severities for furfural production; k_d is rate constant of all sugar dehydration reactions; and k_l is the rate constant of furfural degradation reactions. Both of these two rate constants can be expressed using an Arrhenius temperature dependence,

$$k_d = \exp\left(\alpha_d - \frac{E_d}{RT} + \beta_d C\right) \tag{3a}$$

$$k_l = \exp\left(\alpha_l - \frac{E_l}{RT} + \beta_l C\right) \tag{3b}$$

where α_d, α_l, β_d, β_l are adjustable parameters. E_d, E_l are the apparent activation energies.

Substitute eqs 3a and 3b along with eqs 1a and 1b into eq 2a, we can solve the initial value problem of the first order linear differential equation analytically to obtain net furfural production:

$$F = \frac{k_d}{k_l}(1 - e^{-k_l t}) + k_d\left[\frac{1-\theta}{k_l - \frac{\mathrm{CHF}}{t}}(e^{-k_l t} - e^{-\mathrm{CHF}}) + \frac{\theta}{k_l - \frac{f\mathrm{CHF}}{t}}(e^{-k_l t} - e^{-f\mathrm{CHF}})\right] \tag{4}$$

3. RESULTS AND DISCUSSION

3.1. Xylan Dissolution and Net Furfural Production. The results of all 71 experiments were listed in Table S1. Xylan dissolution can be accurately predicted using eq 1a by the CHF (eq 1b) as shown in Figure 3a. Approximately 95% of the xylan was dissolved at CHF = 100 (insert in Figure 3a). The fitting of the residual xylan yield data X_R using eqs 1a and 1b produced

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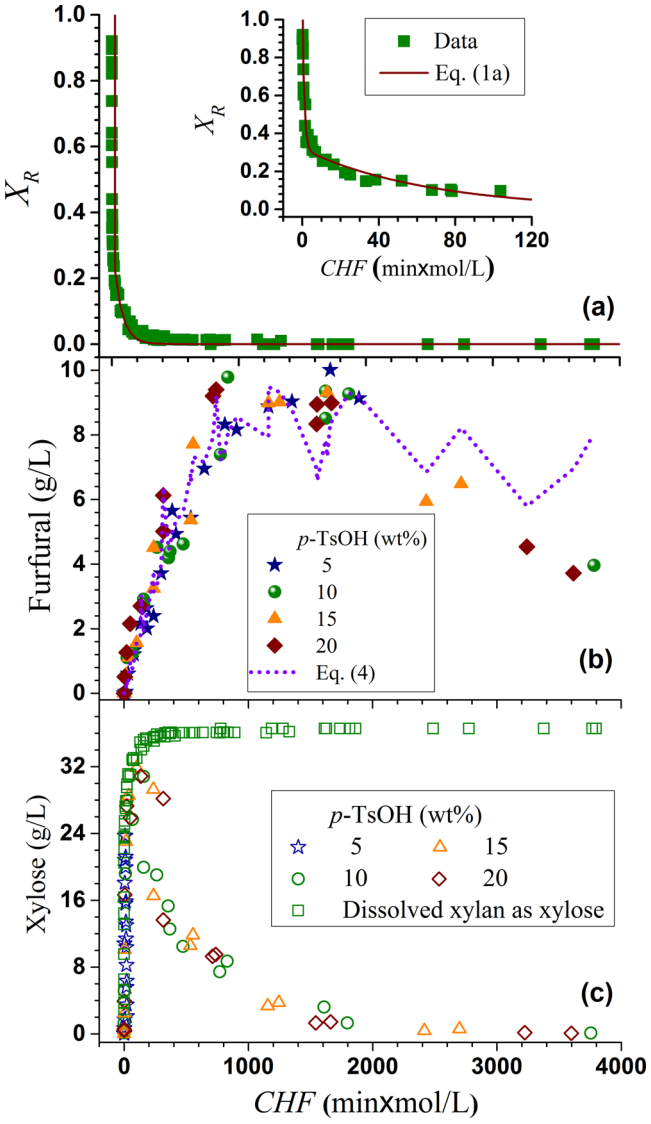

Figure 3. Effects of the combined hydrolysis factor (CHF) on (a) xylan dissolution, (b) furfural production, and (c) xylose concentration in hydrolysate.

the parameters α, β, E, θ, and f as listed in Table 1. Xylan dissolution was initially rapid and followed by a slow phase with increasing reaction severity. The best fit of the results shows that the fraction of slow xylan θ = 0.319, the ratio of reaction rates between the slow and fast xylan, f = 0.015. The results presented in Figure 3a are in agreement with previous studies using aspen and poplar wood.[24,39]

Table 1. List of Fitting Parameters for Xylan Dissolution by eq 1 and Xylose Degradation to Furfural by eq 9

parameters	fitted value	unit
a	35.78	none
β	0	L/mol
E	112400	J/mol
f	0.015	none
θ	0.319	none
α_d	32.30	none
E_d	121000	J/mol
β_d	2.31	L/mol
α_l	37.64	none
E_l	148800	J/mol
β_l	2.84	L/mol

Despite the wide ranges of acid concentration, temperature, and time were used, furfural concentration in the combined condensate and reaction spent liquor (calculated assuming no water loss during reaction) in general can be well correlated by the reaction severity CHF as shown in Figure 3b. Furfural first increased rapidly with the increase in reaction severity CHF, then plateaued between CHF = 830−1850 and subsequently decreased, suggesting furfural degradation dominants at high severities. This is in agreement with the furfural production model, eq 4 that neglected furfural degradation by the reactions between xylose and furfural for the present study. In general eq 4 can predict net furfural production reasonably well (Figure 3b), especially at CHF ≤ 1500 before furfural degradation becomes important. This suggests that eq 4 can be used for process control for furfural production. Furthermore, optimization of furfural production can be achieved by simply using an optimal reaction severity at approximately CHF = 830. This gives a lot of flexibility in scale-up process design as long as the optimal CHF is used, the particular reaction condition such as catalysts concentration and reaction time are not critically important.

The measured xylose concentrations in the hydrolysates agreed very well with the amounts of xyaln dissolved (Figure 3c) at low CHF ≤ 50, suggesting the dissolved xylan was immediately hydrolyzed into monomer xylose validated our assumption that oligomeric xylose in the hydrolysate is minimal. Xylose concentration then decreased rapidly with further increase in CHF due to dehydration into furfural. Xylose was almost undetectable at CHF ≥ 1800, suggesting furfural degradation due to reaction between xylose and furfural can be negligible.

3.2. Xylose Dehydration Reaction Kinetics. Fitting of the measured furfural concentrations using eq 4 resulted in the fitting parameters of α_d, α_l, E_d, E_l, β_d, β_l as listed in Table 1. The activation energy for furfural degradation to humins E_l = 148 800 J/mol > E_d = 121 000 J/mol for xylose dehydration to furfural, and β_l = 2.84 > β_d = 2.31, suggesting using a long reaction time either at a low temperature or low acid concentration can reduce furfural degradation and therefore preferred at a given (optimal) reaction severity for improved process optimization. This can be illustrated in a separate study with four hydrolysis experiments conducted at approximately the same CHF ∼ 1600 with slight variations in temperatures (153−165 °C) but at very different acid concentrations and therefore reaction times. As listed in Table 2, overall the furfural yields from these four experiments did not vary substantially due to similar level of CHF. However, the run with the longest reaction time of 48 min at the lowest acid concentration of 0.28 mol/L resulted in highest furfural yield of 76.4 ± 2.4% theoretical, while the run with the shortest reaction time of 27 min at the highest acid concentration of 1.18 mol/L resulted in the lowest furfural yield of 68.3 ± 5.4% theoretical.

3.3. Glucan Dissolution and Formation of 5-Hydroxymethylfurfural and Levulinic Acid (LA). It is well understood that cellulose goes through four major categories of reaction in furfural production using lignocelluloses:[40] (1) hydrolysis of polymeric cellulose into monosaccharides, (2) isomerization of glucopyranose to fructofuranose, and (3) dehydration of fructofuranose to 5-hydroxymethylfurfural (HMF), and (4) transformation of HMF to levulinic acid

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Table 2. Experimental Concentration of Furfural with Similar CHF

no.	*p*-TsOH (mol/L)	*T* (°C)	time (min)	CHF (min mol/L)	predict C_{fur} (g/L)	experiment C_{fur} (g/L)	experiment yield (%)
1	0.28	165	48	1659	9.94	10.01 ± 0.34	76.4 ± 2.4
2	0.57	160	34	1621	9.93	9.35 ± 0.62	71.3 ± 4.7
3	0.87	156	30	1636	9.58	9.31 ± 0.39	71.0 ± 3.0
4	1.18	153	27	1553	9.28	8.95 ± 0.71	68.3 ± 5.4

(LA). Glucan dissolution was found to increase almost linearly with reaction severity CHF in the range studied, independent of the specific reaction conditions (Figure 4a). HMF

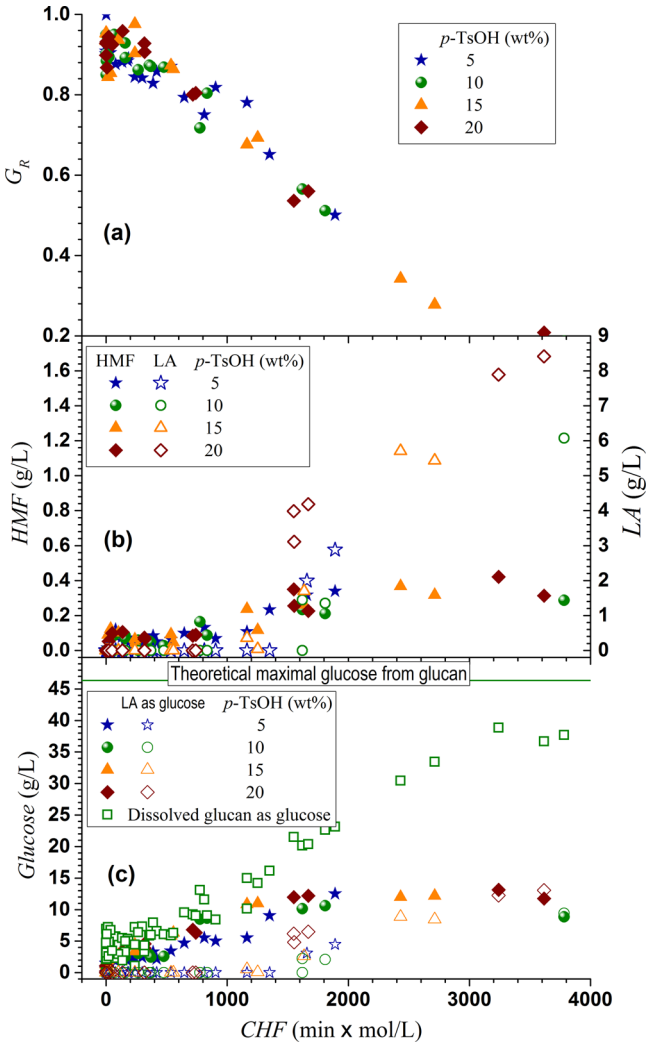

Figure 4. Effects of the combined hydrolysis factor (CHF) on (a) glucan dissolution, (b) HMF formation, and (c) glucose concentration in hydrolysate.

concentrations in the spent liquor increased with reaction severity and then decreased at CHF ≥ 3250 (Figure 4b). Overall HMF concentration was low with a maxima of 0.42 g/L achieved at CHF = 3242. LA formation was almost zero at low CHF ≤ 1600 then increased abruptly. Both the concentrations of HMF and LA correlated with CHF fairly well, suggesting CHF is also a good reaction severity measure for glucose dehydration and HMF degradation though it was developed from xylan dissolution. Our previous study indicated glucan depolymerization by dilute acid prehydrolysis can be predicted by CHF.[41]

LA production was low even at high CHF of approximately 3500 (Figure 4b) relative to the amount of glucose available (Figure 4c). Approximately only one-third of the dissolved glucan were converted into LA, one-third of the dissolved glucan remained as oligomers, another third remained as glucose (Figure 4c). The low LA formation is perhaps due to the low temperatures (mostly below 160 °C) used with the aim to achieve maximal furfural yield.

3.4. Acid Recyclability Study. One of the substantial benefits of using solid acids is its recyclability. In the present study *p*-TsOH was recycled and reused three times as described in the Materials and Methods. The measured furfural concentrations and yields were found not affected by the number of recycles as listed in Table 3. The incomplete

Table 3. Effect of Acid Recycle Times on Furfural Production[a]

acid recycle times	furfural in distillate (g/L)	furfural in spent liquor (g/L)	furfural yield (% theoretical)
fresh	18.5	4.2	76.9
1	17.2	5.2	77.5
2	16.2	2.6	62.4
3	19.8	4.6	82.9

[a]Experiments conducted at *p*-TsOH of 1.18 mol/L and 150 °C for 30 min.

conversion of xylose to furfural in the second cycle resulted in a low furfural yield but a high furfural yield in the third recycle as the unconverted sugars remained with the acid and subsequently converted into furfural.

3.5. Comparison with Literature Study in Furfural Production. The results in this study were compared with those reported recently on furfural production from lignocelluloses. As listed in Table 4, furfural yield of 80% theoretical from a poplar wood was reported when using H_2SO_4 as a catalyst through batch with distillation separation processing.[20] Similar yields of 67.9% and 72.9% from corncob were also reported by Mao at el. when using acetic acid and $FeCl_3$ as catalysts together with the reuse of acetic acid.[42,43] Recently, the conversion of furfural from lignocellulose biomass was investigated using efficient microwave (MW) irradiation. Microwave can interact very efficiently with polar wood molecules, thus allowing a rapid heating of the reaction environment, good yields, and selectivity toward the desired products. It can penetrate lignocellulosic materials and heat the entire volume of the materials rather than just the external surface. When using MW and hydrochloric acid as a catalyst for furfural production from giant reed, a theoretical yield of 70% was achieved.[44] Similar yield of 65% theoretical was also reported from wheat straw with glycine betaine hydrochloride as catalyst.[10] On the other hand, furfural yield of only 53.7% theoretical from corncob was reported using hydrochloride acid as a catalyst.[45] The best furfural yield obtained in the present study was 76.4 ± 2.4% theoretical from corncob higher than

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Table 4. Comparison between This Study and Literature Work on Furfural Production

company /group /process	process type	operating temperature (°C)	catalyst	t (min)	substrate	furfural yield (% theoretical)	co-products
Mandalika and Runge [20]	batch with separation	170	1.6% H_2SO_4	50	poplar wood chips	80	cellulosic residues
Mao et al. [42]	semibatch system with separation	180	3% acetic acid and 20 mM $FeCl_3$	30	corncob	67.9	cellulosic residues
Mao et al. [43]	semibatch system with acetic acid steam	190	2% acetic acid and 60 mM $FeCl_3$	30	corncob	72.9	cellulosic residues
Antonetti et al. [44]	batch with microwave	140	1.68% hydrochloric acid	15	giant reed	70	LA
Liu et al. [10]	batch with microwave	150	glycine betaine hydrochloride	60	wheat straw	65	none
Sánchez et al. [45]	batch with microwave	180	2% HCl	5	corncob	53.7	cellulosic residues
this study	batch with separation	CHF = 1830	p-TsOH	48	corncob	76.4 ± 2.4	LA

most reported studies. This suggests p-TsOH is an effective catalyst for furfural production in terms of yield and recyclability, important to sustainable manufacturing.

4. CONCLUSIONS

This study demonstrated a commercial solid acid, toluenesulfonic acid, as a robust renewable catalyst for the production of furfural from corncob for sustainable biorefinery operations. Acid recyclability study indicated recycled p-TsOH through crystallization was very effective. A combined hydrolysis factor (CHF) was used to develop a predictive model for furfural production from corncob. Excellent agreement between predicted and experimentally measured furfural yield was obtained, suggesting CHF can be used as a scaling factor for process scale-up and control applications. Optimal CHF ranged from 830 to 1850. Verification experiments conducted at CHF approximately 1500 suggested maximal achievable furfural yield was over 75% theoretical.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.6b03243.

List of furfural production experiments conducted and results obtained (PDF)

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Notes

The authors declare no competing financial interest.

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