Electronic supplementary information

Integrated Conversion of Hemicellulose and Cellulose from Lignocellulosic Biomass

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1. Materials and methods

1.1. Open reactor system

A glass apparatus was used for the removal of furfural from the reactive mixture of gamma-valerolactone (GVL), levulinic acid (LA), and sulfuric acid (SA) (Figure S1). Typically 6 g of dry corn stover (obtained through the Great Lakes Bioenergy Research Center (GLBRC)), 90 g of GVL (Sigma-Aldrich >98%), and 10 g of SA solution (Sigma-Aldrich) were added to a 250 mL three-neck flask (i.e., reactor flask). The middle port of the reactor flask was connected to a three-way, 75° angle connecting adapter. A thermometer was added to the top of the connecting adapter to monitor vapor temperature. The sidearm of the connecting adapter was connected to a water condenser, vacuum adapter (left at ambient conditions), and a 250 mL round-bottom flask (i.e., distillation flask), as shown in Figure S1. In a typical experiment (7 h run), water was fed continuously to the reactor flask (0.05 to 0.25 mL min^{-1}) through one port of the reactor flask using an HPLC pump (Lab Alliance Series I) to facilitate the distillation of furfural. GVL was added to the water solution to compensate for the GVL removed during the distillation (the rate of GVL fed depended on the separation achieved in the distillation zone and the temperature used). The remaining port of the reactor flask was used to house a thermocouple, which monitored the temperature of the reactive liquid. The round-bottom flask was surrounded by a heating mantle, and heating tape was wrapped around the reactor flask and three way stem to prevent heat loss to the ambient. At the end of the reaction, the reactor flask was cooled to room temperature, and 0.2 g of sample from both the reactor and distillation flasks were diluted to 1 mL using distilled water, syringe filtered (0.2 μm membrane), and analyzed by HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-87H).

1.2. Closed reactor system

To further increase the yield of LA, 3 g of the remaining mixture from the reactor flask (section 1.1) was added to a 10 mL glass reactor along with water as indicated in the text. The reactor was immersed in an oil bath at 443 K and held for the indicated time. The reactor was then cooled to room temperature, and samples were taken using the procedure outlined in section 1.1.

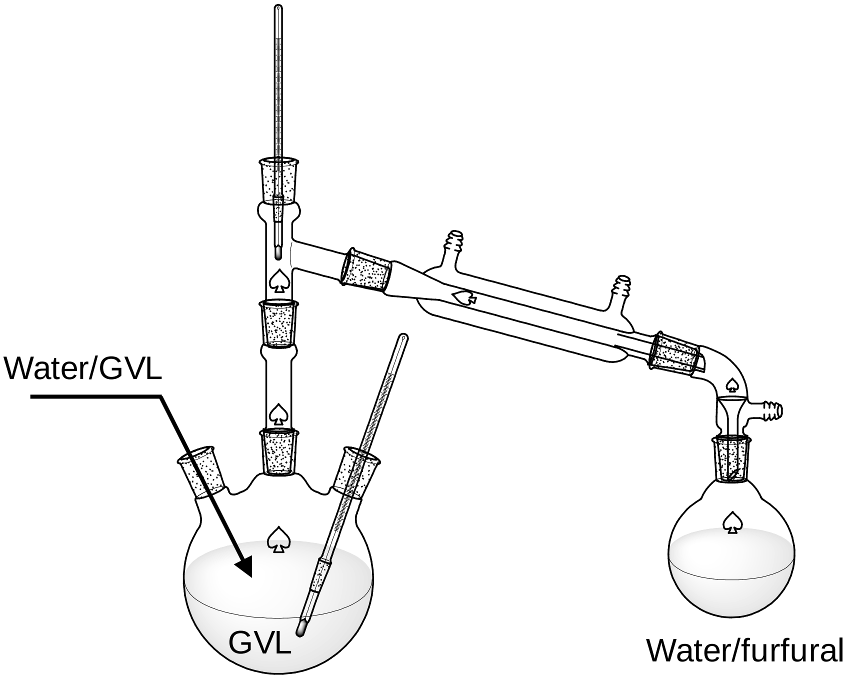

Figure S1: Diagram of apparatus used for open system reactions.

1.3. Glass reactor studies of biomass deconstruction

In a typical experiment, microcrystalline cellulose (5 wt% moisture, average size 20 µm, Sigma-Aldrich), dry corn stover (GLBRC), or alkaline hydrogen peroxide pretreated corn stover (AHP; GLBRC) (*18, 19*) was added to a 10 mL glass reactor to achieve a final cellulose concentration of 2 wt%. GVL and SA solution (Sigma Aldrich) were added to obtain the appropriate SA concentration and GVL/water ratio. For some experiments, kraft lignin (lignin alkali, Sigma Aldrich) was also added. The reactor was immersed in an oil bath at 443 K and held for the indicated time. The reactor was then cooled to room temperature, and 0.1 g of sample was diluted to 1 mL using distilled water, syringe filtered (0.2 µm membrane), and analyzed by HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-87H column). If additional batches of biomass were added, no sample was taken between batches, the reactor was weighed, and another dose of solids (equal to the first addition) was added. The vessel was resealed and a second or third cycle started. Samples were then taken using the procedure outlined above.

1.4. Parr reactor studies of biomass deconstruction

For biomass deconstructions carried out in a Parr reactor, the reactants (cellulose source, GVL, and SA) were added to a 450 mL reactor, then purged with Ar gas three times and heated to 443 K (9 K min^{-1} ramp) with a high-temperature fabric heating mantle. The reactor was maintained at 443 K for the stated time while stirring at approximately 600 rpm. At the end of the reaction time, the heating mantle was removed, and the built-in cooling line cooled the reactor to room temperature. Samples were analyzed as outlined above. The composition of the resulting reaction mixture using 5 wt% of AHP corn stover was 0.05 M furfural and 0.08 M LA.

1.5. Filtration

A ceramic Buchner funnel was used to filter samples with 11 μm filter paper (Whatman Grade 1). When using GVL as solvent, approximately 10 times the volume of distilled water was added to the sample to precipitate the solids, and the resulting solution was filtered as stated above. The filter paper was then removed from the funnel and dried at 353 K in an oven overnight. The weight of the sample was recorded, and the sample was dried until the weight was constant.

1.6. Dual-catalyst bed flow reactor

Hydrogenation of furfural to furfuryl alcohol in presence of LA and GVL, and subsequent hydrolysis of furfuryl alcohol to LA in presence of LA and GVL, were carried out in a dual-catalyst bed flow reactor operating in an up-flow configuration. The first reactor (stainless steel 6.35 mm OD) was loaded with Pt_3Sn/SiO_2 catalyst held between two end plugs of silica granules and quartz wool. The catalyst was reduced in-situ for 2 h at 773 K (1 K min^{-1}) before use. The tubular reactor was fitted inside of an aluminum block and placed within an insulated furnace (Applied Test Systems). Bed temperature was monitored at the reactor wall using a Type K thermocouple (Omega) and controlled using a 16A series programmable temperature controller (Love Controls). The second reactor (stainless steel 12.27 mm OD) was loaded with Amberlyst 70 (Dow chemical company) catalyst mixed with SiO_2 (Sigma-Aldrich) and held between two end plugs of quartz wool. The Amberlyst 70 was rinsed prior to use with distilled water until the pH of the effluent solution stabilized and showed no indication of residual acidity, crushed, and dried overnight at 393 K. The tubular reactor was heated using a heating tape (OMEGA) and insulated with glass wool tape. Bed temperature was monitored at the reactor wall using a Type K thermocouple (Omega) and controlled using a 16A series programmable temperature controller (Love Controls).

The feed to the flow reactor system was introduced into the reactor using an HPLC pump (Lab Alliance, Series I). The commercial feed was a liquid solution of furfural (Sigma-Aldrich >99%), LA (Sigma-Aldrich > 98%) in a mixture of 80 wt% GVL (Sigma-Aldrich >98%) and 20 wt% water. SA (Sigma-Aldrich 0.5 M analytical standard) was used as the mineral acid and $Ca(OH)_2$ (Sigma-Aldrich >95%) was added when SA neutralization was required. In the case of the feed prepared from corn stover (see section 1.4), the SA present in the reaction mixture was neutralized using $Ca(OH)_2$ and the reaction mixture was filtered to remove the $CaSO_4$ generated prior to feeding the solution into the dual-catalyst bed flow reactor. The flow of H_2 during reaction (25 cm^3(STP) min^{-1}) was controlled by a mass flow controller (Brooks Instruments, 5850S). Reactor pressure (35 bar of H_2) was controlled using a back pressure regulator (GO BP-60). The reactor effluent flowed into a vapor-liquid separator wherein the liquid product was collected. Gas phase products were analyzed using an in-line pair of gas chromatographs. A GC-2014 (Shimadzu) equipped with an FID was used for analysis of hydrocarbon products in the gas phase, while CO and CO_2 were quantified using a GC-8A (Shimadzu) with a TCD using helium as a carrier/reference. Liquid samples were taken after both reactors. The concentrations of organic species were quantified using a GC-2010 (Shimadzu) with an FID and HPLC (Waters

2695 system with a Bio-Rad Aminex HPX-87H column and a RI 410 detector). Identification of products was achieved using GC-MS analysis (Shimadzu GCQP-2010).

1.7. Catalyst preparation

A silica-supported Pt/Sn catalyst was prepared by sequential impregnation to reach 3:1 ratio of Pt:Sn. Using $H_2PtCl_6•6H_2O$ as precursor, 5 wt% of platinum was added to Cab-O-Sil (Cabot) by incipient wetness impregnation. Tin was added to the Pt/SiO_2 catalyst by evaporative impregnation of a solution of tributyltin acetate in pentane. After impregnation with tin, the catalyst was dried at 373 K, calcined with flowing air at 573 K (2 h), followed by reduction in flowing hydrogen at 773 K (2 h).

1.8. Levulinic acid production from furfuryl alcohol

Reactions were carried out in 10 mL glass reactors as described in the section 1.2. The feed was 1 wt% furfuryl alcohol (Sigma-Aldrich > 98%) and 2 wt% LA in a mixture of 80 wt% GVL and 20 wt% H_2O. The reactor was immersed in an oil bath at 443 K and held for the indicated time. The reactor was then cooled to room temperature, and samples were taken using the procedure outlined in section 1.1.

2. Additional Data

2.1. Studies of levulinic acid production after distillation of furfural

After using the open reactor system described in section 1.1, the LA and furfural yields that can be obtained after further treatment in a closed reactor were studied at different reaction conditions. It can be seen in Table S1 that after 16 h at 443 K, small quantities of furfural remain in the reactor for reactions using 0.05 M SA, and furfural is completely degraded when using 0.1 M SA. However, when the reaction time is reduced to 2 h, no degradation of furfural is observed for reactions at 0.05 M, while a small extent of degradation is observed for reactions using 0.1 M SA.

Table S1. Furfural (FurOH) and LA yield using a glass reactor (closed system) at 443 K. Feed is the liquid remaining in the reactor flask after distillation at the listed temperature.

		Yield (%)							
	Distillation temperature	After distillation		16 h		16 h + water*		2 h + water*	
SA (M)	(K)	FurOH	LA	FurOH	LA	FurOH	LA	FurOH	LA
0.05	433	1	21	1	23	0	27	1	26
0.05	413	19	15	6	32	5	53	19	39
0.1	413	11	42	0	45	0	53	7	50
0.1	393	43	13	0	53	2	68	31	57

*10 wt% water added to the feed prior to reaction in closed reactor.

At a low acid concentration (0.05 M), the LA yield slightly increased (21% to 23%) when the distilled sample was run for 16 h at 443 K (Table S1). When 10 wt% water was added before reaction in the closed system, the LA yields increased slightly at both 2 and 16 h. This result indicates that C_6 sugars likely degraded to form humins during distillation. At a lower temperature, 413 K, the LA yield increased from 15% to 32% after 16 h at 443 K, and higher yields were obtained when 10 wt% water was added (53%). Higher LA yields were also observed for the samples using 0.1 M SA, equal to 45% and 53% for the samples distilled at 413 and 393 K (and run in the closed reactor for 16 h), respectively. As with the lower acid conditions, LA yields increased to 53% and 68% respectively when 10 wt% water was added to the reaction mixture prior to the reaction in the closed system. For both temperatures, high yields of LA were obtained after only 2 h of reaction, 50% and 57%.

2.2. Studies of the effects of lignin

Lignin reacts with SA during biomass deconstruction, neutralizing part of the catalyst, thereby eliminating the possibility of reutilizing the same SA multiple times. This reduction in SA concentration leads to low yields of furfural and LA. All reactions were carried out for 18 h to maximize the production of LA for feeds containing 2 wt% cellulose. As seen in Table S2, the yield of LA was equal to 57% for the first batch of corn stover (Table S2, entry 1), and it decreased to 27% after the third batch. When microcrystalline cellulose was used instead, the LA yield after the first batch was higher, 78%, and although the yield decreases on subsequent batches, as seen previously (*21*, *27*), the yield was still 58% after the third batch (entry 2). When 2 wt% of kraft lignin was added to the reactor in addition to the cellulose, the LA yield after the first batch was similar to cellulose (entry 2), 75% (entry 3); however, successive batches of cellulose and lignin showed low yields of LA yields, 35% overall after the third batch. When 8 wt% of lignin was added to the cellulose, the LA yield was only 14% after the first batch (entry 4), indicating that lignin is at least partially responsible for the low yields obtained. Finally when the majority of lignin was removed from the corn stover using an AHP pretreatment, the LA yield was 69% after the first batch, and it decreased slightly to 57% after the third batch (entry 5), which is similar to that obtained with microcrystalline cellulose as feedstock (entry 2).

Table S2. Effect of cellulose batches using different feedstocks on formic acid and LA yields. 0.1 M SA, T = 443 K, solvent = 80 wt% GVL/20 wt% H_2O, time = 18 h (glass reactors).

Entry	Feed (wt% per batch)	Feed	1^{st} batch yield (%)		2^{nd} batch overall yield (%)		3^{rd} batch overall yield (%)	
			Formic	Levulinic	Formic	Levulinic	Formic	Levulinic
1	6.6	Corn stover	59	57	45	46	0	27
2	2	Cellulose	31	78	33	68	21	58
3	2/2	Cellulose/Lignin	41	75	7	41	5	35
4	2/8	Cellulose/Lignin	0	14	0	10		
5	5	AHP Corn stover	67	69	49	59	46	57

2.3. Levulinic acid production from furfuryl alcohol

As seen in Table S3, SA, H-ZSM-5, and Amberlyst are good catalysts for the conversion of furfuryl alcohol LA. The highest yield of LA was obtained using H-ZSM-5 at 423 K and 1 h.

Table S3. Furfuryl alcohol conversion to LA in presence of GVL and LA in 80 wt% GVL/20 wt% H_2O.

Catalyst	Temperature (K)	Time (h)	Levulinic acid yield (%)
H-ZSM-5	373	0.5	52
		1	60
		1.5	60
	398	0.5	63
		1	63
		1.5	73
	423	0.5	72
		1	80
		1.5	75
Nafion	398	1	38
Mordenite		1	42
Amberlyst 15		1	61
Sulfuric acid		1	62
Amberlyst 70		1	71

2.4. Levulinic acid production from furfural and levulinic acid mixtures in the dual-catalyst bed reactor flow system

Experiments were carried out in the dual-catalyst bed reactor system described in section 1.6. Figure S2 shows that furfural is initially completely converted with a high yield to furfuryl alcohol (greater than 90%) for more than 70 h time-on-stream over a Pt_3Sn/SiO_2 catalyst. Over the second catalyst bed, H-ZSM-5, the furfuryl alcohol can be completely converted with yields to LA up to 74%; however, the H-ZSM-5 deactivates with time-on-stream, and only 10% furfuryl alcohol conversion is observed after 42 h. The activity over the H-ZSM-5 can be recovered by calcination, but it undergoes rapid deactivation thereafter.

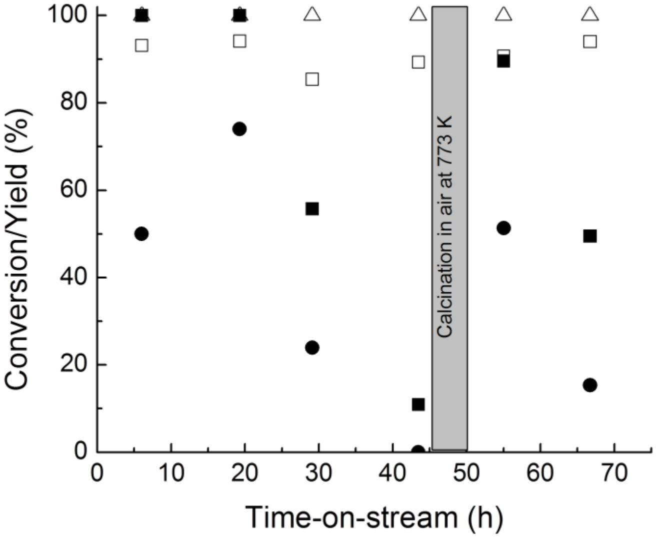

Figure S2. Furfural conversion over Pt_3Sn/SiO_2 (Δ), furfuryl alcohol yield over Pt_3Sn/SiO_2 (□), furfuryl alcohol conversion over H-ZSM-5 (■), LA yield over H-ZSM-5 (●) versus time on stream at 35 bar H_2. First reactor loaded with Pt_3Sn/SiO_2 at 373 K and 0.51 h^{-1}. Second reactor loaded with H-ZSM-5 at 398 K and 0.12 h^{-1}. Feed: 2 wt% furfural in mixture of 80 wt% GVL and 20 wt% H_2O.

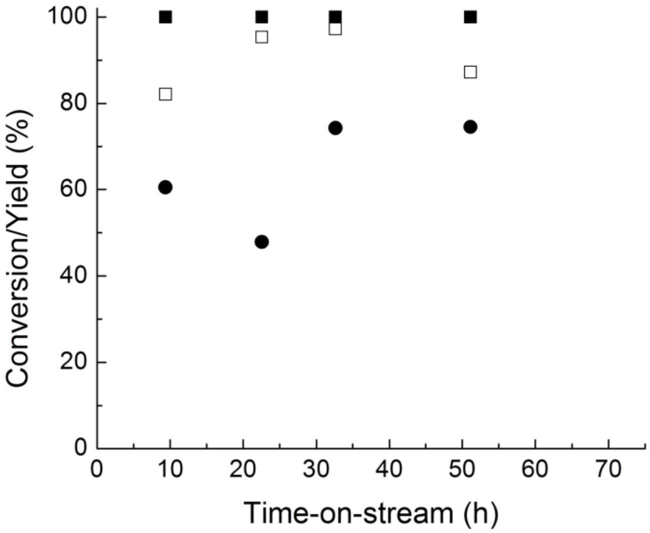

Figure S3. Furfuryl alcohol yield over Pt_3Sn/SiO_2 (□), furfuryl alcohol conversion over Amberlyst 70 (■), LA yield over Amberlyst 70 (●) versus time on stream at 35 bar H_2. First reactor loaded with Pt_3Sn/SiO_2 at 373 K and 0.13 h^{-1}. Second reactor loaded with Amberlyst 70 at 398 K and 0.04 h^{-1}. Feed: 0.5 wt% furfural and 0.8 wt% LA in mixture of 80 wt% GVL and 20 wt% H_2O.

The dual-catalyst bed reactor system was next studied using Amberlyst 70 as the catalyst in the second catalyst bed. Furfural is completely converted over the first bed containing the Pt_3Sn/SiO_2 catalyst, with greater than 80% yield to furfuryl alcohol after 50 h time-on-stream (Figure S3). The furfuryl alcohol was then completely converted over Amberlyst 70 with yields to LA up to 74% over 50 h time-on-stream. The presence of SA significantly decreases the yield of furfuryl alcohol over the Pt_3Sn/SiO_2 catalyst bed (lower than 80%), and the catalyst deactivates with time-on-stream, resulting in furfuryl alcohol yields of less than 10% after 50 h (Figure S4). SA does not affect the stability of Amberlyst 70 bed; however, the yields of LA are only 48%. After neutralizing the SA, Pt_3Sn/SiO_2 completely converts furfural for over 55 h, with a yield of approximately 90% (Figure S5). Furfuryl alcohol is then completely converted over Amberlyst 70 with yields over 75% after 55 h on-stream.

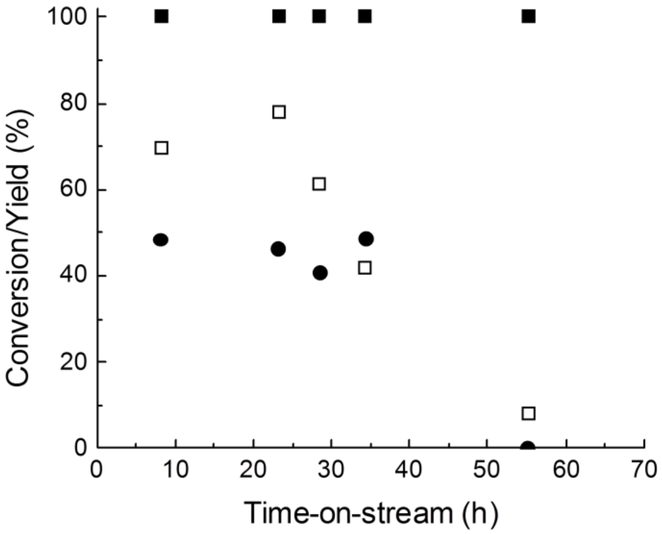

Figure S4. Furfuryl alcohol yield over Pt_3Sn/SiO_2 (□), furfuryl alcohol conversion over Amberlyst 70 (■), LA yield over Amberlyst 70 (●) versus time on stream at 35 bar H_2. First reactor loaded with Pt_3Sn/SiO_2 at 373 K and 0.13 h^{-1}. Second reactor loaded with Amberlyst 70 at 398 K and 0.04 h^{-1}. Feed: 0.5 wt% furfural and 0.8 wt% LA 0.5 wt% SA in mixture of 80 wt% GVL and 20 wt% H_2O.

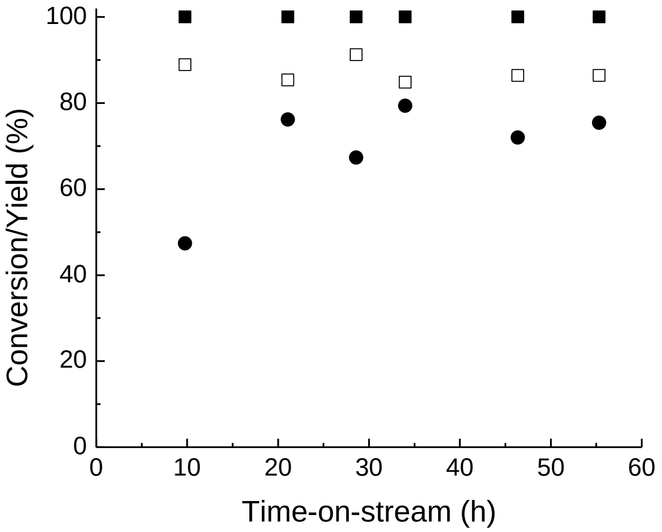

Figure S5. Furfuryl alcohol yield over Pt_3Sn/SiO_2 (□) in neutralized feed, furfuryl alcohol conversion over Amberlyst 70 (■), LA yield over Amberlyst 70 (●) versus time on stream at 35 bar H_2. First reactor loaded with Pt_3Sn/SiO_2 at 373 K and 0.13 h^{-1}. Second reactor loaded with Amberlyst 70 at 398 K and 0.04 h^{-1}. Feed: 0.5 wt% furfural, 0.8 wt% LA, and 0.5 wt% SA in mixture of 80 wt% GVL and 20 wt% H_2O. The SA was neutralized with $Ca(OH)_2$.

3. Process overview, furfural and liquid fuels production

Bioethanol is the most important liquid biofuel in the market today. It has been reported that 59 gallons of ethanol (39 gallons of gasoline equivalent, Table S4, entry 1)) can be produced per ton of corn stover (52% of the theoretical maximum)(*25*). This productivity is similar to the gallons of liquid fuel that can be produced using our closed reactor system at the current yields (entry 2), i.e., 37 gallons of gasoline equivalent (57 gallons of ethanol equivalent according with the energy content). However, high-value chemicals such as furfural, furfuryl alcohol, LA and GVL may also be obtained as final products from our process.

Corn stover is 25.2 wt% C_5 sugars and 41 wt% C_6 sugars. At our current yield of 56% for furfural from C_5 sugars and 61% for LA from C_6 sugars (see entry 3, Table 2 in the main text), 91 kg of furfural and 162 kg of LA can be produced per ton of corn stover. As we demonstrated herein, furfural can be converted to furfuryl alcohol with 95% selectivity over the Pt_3Sn/SiO_2 catalyst, and subsequently furfuryl alcohol can be converted to LA acid with 70% selectivity over Amberlyst 70 (see Figure 2 in the main text) to produce a total amount of 234 kg of LA per ton of dry corn stover. LA can be converted quantitatively to GVL by hydrogenation over a RuSn catalyst (*10, 11*) to produce a total of 196 kg of GVL (97% selectivity). The GVL can be converted to butene (99% selectivity)(*8*) and finally C_{8+} liquid hydrocarbons (95% selectivity)(*8*) to produce 103 kg of liquid hydrocarbons (125.5 MJ/gallon), which is equal to 37 gallons of gasoline equivalent (122.5 MJ/gallon) or 57 gallons of ethanol equivalent (80.1 MJ/gallon) (Table S4, entry 2). The final yield obtained is 47% of the theoretical maximum, which leaves room for further improvements after optimization of the process.

As reported herein, the C_5 fraction of the sugars can be used to produce a high value chemical, furfural, in combination with the production of liquid fuels. At our best conditions for the production of furfural, 126 kg of furfural can be produced per ton of dry corn stover, 78% of the theoretical value (Table 1, entry 1, 79% furfural yield and 99% furfural distilled). However, in this case, low yields of LA are obtained (27%), and only 11.5 gallons of gasoline equivalent are produced (18 gallons ethanol equivalent; Table S4 entry 3). Decreasing the temperature of the distillation leads to lower amounts of furfural that can be achieved but higher amounts of liquid fuels. For example at 413 K (Table 1, entry 2), 131 kg of furfural can be produced per ton of corn stover (81% yield). 101 kg of the furfural produced (77% of the total) are recovered by distillation and can be used in chemical applications, while the remaining 30 kg can be converted to LA, to produce a total amount of 157 kg of LA (according to the yields obtained in the closed reactor after 2 h at 443 K (Table S1, entry 2)), which can be converted to 25 gallons of gasoline equivalent (38 gallons of ethanol equivalent; Table S4, entry 4). Finally, decreasing the distillation temperature to 393 K (Table 1, entry 4) leads to production of 121 kg of furfural per ton of corn stover (75% yield). Of this amount, 52 kg of furfural (43% of the total produced) are recovered by distillation, while the remaining 69 kg can be converted to LA to produce a total amount of 191 kg of LA (according to the yields obtained in the closed reactor after 2 h at 443 K (Table S1, entry 4)), which can be converted to 30 gallons of gasoline equivalent (46 gallons of ethanol equivalent; Table S4, entry 5).

Table S4. Production of furfural, gasoline, and ethanol for the various systems presented in this paper, as compared to previously published data for cellulosic ethanol (row 1) (*25*).

Strategy	Furfural recovered (kg)	Gallons equivalent gasoline	Gallons equivalent ethanol
Cellulosic Ethanol	0	39	59
Closed system	0	37	57
Open system at 433 K	126	11	18
Open system at 413 K	101	25	38
Open system at 393 K	52	30	46