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# Hybrid Catalytic Biorefining of Hardwood Biomass to Methylated Furans and Depolymerized Technical Lignin

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S Supporting Information

**ABSTRACT:** A robust method is needed to achieve high yield all-catalytic conversion of recalcitrant lignocellulosic biomass to transportation fuels while maximizing carbon utilization from raw substrates. To accomplish this, we developed an integrated strategy that combines homogeneous and heterogeneous reactions with a treatment-extraction step to coproduce 2-methylfuran (MF) and 2,5-dimethylfuran (DMF) directly from hardwood poplar while maintaining high catalyst activity. In the first step, poplar wood chips were treated with dilute $FeCl_3$ in THF−water at subpyrolytic temperature to yield 93.5% furfural (FF) from xylan and 66.0% 5-hydroxymethylfurfural (HMF) from glucan. Concurrently, a highly pure lignin powder was obtained from the liquor by precipitation upon room temperature vacuum recovery of THF from the water. Afterward, FF and HMF were extracted from water into an organic phase consisting of toluene and 1,4-dioxane treated with $Ca(OH)_2$. A second hydrodeoxygenation reaction using Cu−Ni/$TiO_2$ catalyst yielded 87.8% MF from FF and 85.6% DMF from HMF. Characterization of the lignin product showed its molecular weight to be reduced by an order of magnitude from its native state as well as complete removal of its native β-aryl ether linkages without hydrogen input or further heterogeneous catalytic processing. A 60% cumulative yield of MF, DMF, and lignin products from the available carbon (xylan+glucan+lignin) in poplar was achieved, rivaling more mature cellulosic ethanol strategies.

**KEYWORDS:** Biomass, Fractionation, Hydrodeoxygenation, Biofuels, Lignin
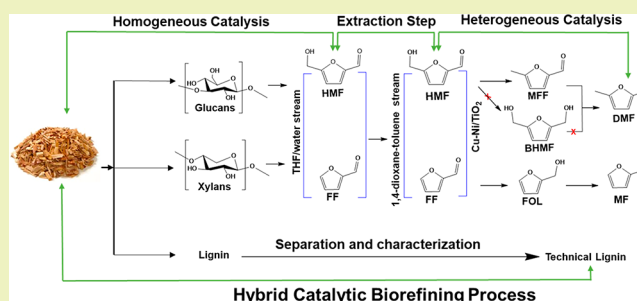
## ■ INTRODUCTION

Economic conversion of second generation lignocellulosic feedstocks to transportation fuels has been an ongoing quest to alleviate our dependence on petroleum and other fossil resources.[1,2] Using first generation feedstocks such as corn-derived sugars and cane sugar syrups to produce fuel ethanol poses food, water, and land sufficiency concerns, whereas second generation feedstocks including forestry and agricultural residues and energy crops can provide an abundant, inexpensive resource for sustainable production of renewable transportation fuels.[3] Purely catalytic conversion of second generation feedstocks can produce fungible fuels provided high enough fuel yields can be achieved to be economic.[4]

Henceforth, a continuous integrated strategy is critically needed that can achieve (1) high yield production of renewable platform fuel precursors furfural (FF) and 5-hydroxymethylfurfural (HMF), (2) extraction of the furanic compounds, which are highly sensitive to acid/base moieties, from the raw liquor into concentrated organic streams, and (3) robust hydrodeoxygenation (HDO) of both FF and HMF to methylated furan fuels.[5−7] Several reports,[8−17] including our past studies,[18] have demonstrated effective HDO of FF and

**Scheme 1. Process Flow Diagram of Integrated Hybrid Catalytic Conversion of Lignocellulosic Biomass to Methylated Furans and Technical Lignin**[a]
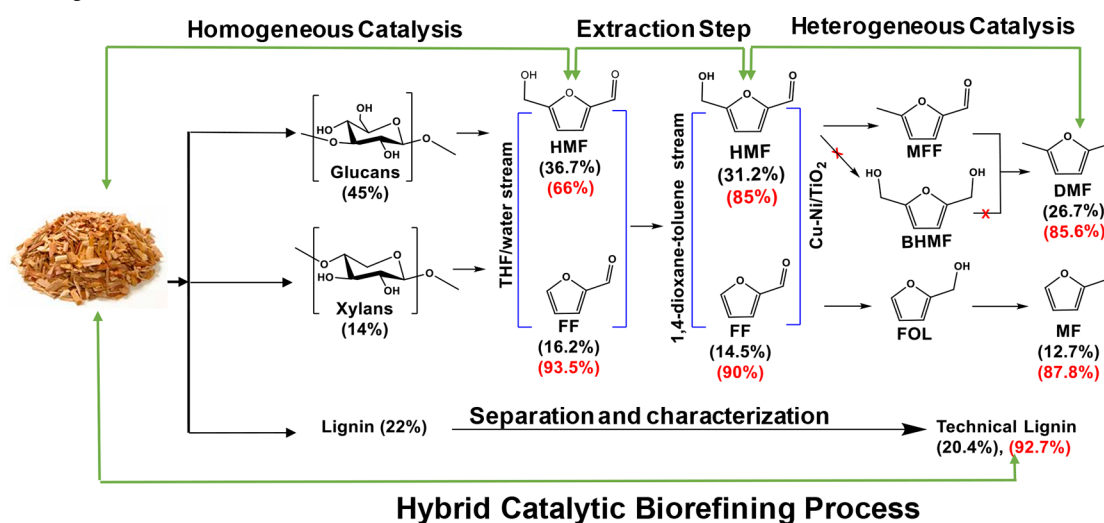


[a]Percentage values reported below to each component black indicate the % theoretical yields based on carbon after each step from the glucans (45%), xylans (14%), or lignin (22%) found in hardwood poplar whereas parenthesized yields values in red indicate individual molar yields achieved at each step.

HMF to methylated furans with promising yield; however, to the best of our knowledge, no previous reports showed HDO of extracted FF and HMF from pretreated lignocellulose biomass over a stable supported non-noble metal catalytic system.[7,16,19−21] The reported HDO methods are unable to achieve high yields from raw biomass streams due to significant catalyst poisoning, mass transport limitations, and the need for treatment of inorganic ions, and typically require expensive highly purified sugar feedstocks to be compatible with exotic supported noble-metal catalysts.[22−26]

Almost all advanced biofuel platforms based on biological platforms only convert the carbohydrates to fuels while the lignin (15−30% by weight) is used as a low value boiler fuel to generate process heat and power. Furthermore, because lignin-rich residues from biological processes are typically unrefined, their value is limited to well under $50/dry ton, the price of coal.[27] Because nearly half the energy of some biomass varieties, such as hardwoods, is contained in their lignin, higher value uses for lignin can dramatically enhance the economic competitiveness of cellulosic biofuels.[28,29] Thus, a promising route to improve the economics is development of efficient methods to extract and depolymerize lignin from biomass as a refined "technical" grade product before it is subject to degradation, condensation, and contamination as an byproduct that also interferes with carbohydrates conversion.[29]

Here, we present a high yield integrated strategy for processing raw hardwood poplar and converting its sugars directly into fungible fuels while achieving higher total carbon utilization from the production of technical lignin. Specifically, we employed a hybrid catalytic strategy that combines homogeneous and heterogeneous methods, as outlined in Scheme 1, to coproduce (1) the high octane gasoline-range blendstocks methylfuran (MF) and dimethylfuran (DMF) at high fuel yields comparable to ethanol fermentation and (2) low molecular-weight technical lignin directly from pretreated poplar wood chips. The strategy presented here maintains high molar yields at each step, achieving an overall combined fuel

and lignin yield of 60% from the theoretically available xylan, glucan, and acid-insoluble lignin present in the raw material.

## ■ MATERIALS AND METHODS

Poplar wood was kindly provided by the National Renewable Energy Laboratory (NREL, Golden, CO) and was milled to obtain less than a 1 mm particle size using a laboratory mill (Model 4, Arthur H. Thomas Company, Philadelphia, PA). The composition of poplar wood was measured to be $45 \pm 0.5\%$ glucan, $14 \pm 0.3\%$ xylan, and $22 \pm 0.2\%$ K-lignin using NREL laboratory analytical procedure in triplicates.[30] Other materials needed for biomass composition to total 100% were not characterized in this study as small amounts were difficult to quantify using HPLC. THF (>99% purity, Fischer Scientific, NJ) was used in all the CELF pretreatment reactions. Hydrated ferric chloride catalyst was purchased from Sigma-Aldrich (St. Louis, MO, US). 1,4-Dioxane and toluene (HPLC grade, Fisher Chemicals) were used as solvents for FF and HMF extraction from CELF stream and further for HDO reactions. In some runs FF (99.9% pure, Sigma-Aldrich) and HMF (99.9% pure, Sigma-Aldrich) were used as starting materials for HDO reactions. $Cu(NO_3)_2 \cdot 3H_2O$ (purity 99%, CAS: 10031-43-3, Aldrich, NJ), $Ni(NO_3)_2 \cdot 6H_2O$ (purity 99.99%, Aldrich, St. Louis, MO) and $TiO_2$ (P25, Batch No. 4161060398, NIPPON AEROSIL Co., LTD, Evonik, Degussa GmbH) materials were used as precursors for synthesizing the $Cu(5\%)−Ni(5\%)/TiO_2$ catalysts. Detailed catalysts synthesis procedure and characterization techniques were reported in our earlier publications.[31]

**Poplar Wood Pretreatment.** All biomass pretreatment reactions were performed in a 1 L Hastelloy Parr reactor (236HC Series, Parr instruments Co., Moline, IL) equipped with a double-stacked pitch blade impeller rotated at 200 rpm. The biomass reaction method employed is called Cosolvent Enhanced Lignocellulosic Fractionation (CELF) that employs THF as a miscible cosolvent with water to significantly enhance solubilization of biomass and improve selectivity of FF and HMF over water-only reactions. THF−water concentrations were varied from 1:1 (THF 50% v/v) to 7:1 (THF 87.5% v/v). Biomass solid loadings were 5 wt % (40 g) based on dry weight and were calculated based on the total mass of the reaction mixture. A 1 wt % loading of $FeCl_3 \cdot 6H_2O$ catalyst was added based on its equivalent anhydrous mass in the THF−water cosolvent. Then, the contents of the reaction were soaked overnight at 4 °C. All the pretreatment reactions were heated using a 4 kW fluidized sand bath

(Model SBL-2D, Techne Princeton, NJ), and temperature was controlled to within ±1 °C measured by an in-line thermocouple (Omega, K-type). The sand bath was preheated to 380 °C to maintain heat-up time less than four minutes. At the end of each reaction, the reactor was quenched in a large water bath at room temperature. The solids were then separated from the hydrolyzate using vacuum filtration through a glass fiber filter paper (Fischer Scientific, Pittsburgh, PA). The final mass and density of liquid fractions were measured for mass balance and yield calculations. The liquid fractions were analyzed by HPLC.

**HMF and FF Extraction from CELF Stream to 1,4-Dioxane-Toluene.** After homogeneous CELF reaction, CELF liquor contained FF, HMF, and solubilized lignin as well as other inorganic ions such as iron ions and Cl⁻. Therefore, CELF liquor was first neutralized to pH 7 by adding slightly more than stoichiometric amounts of $Ca(OH)_2$ (Figure S2). Toluene was added at 1:5 mass ratio to the neutralized CELF liquor and the mixture was sonicated for 30 min. The solids from the CELF stream were removed by vacuum filtration through porous paper filter media and then THF was removed and recovered by rotary evaporation at room temperature. 1,4-Dioxane was then added to the mixture to induce phase separation and the liquids were sonicated for 10 min to improve total extraction. After this step, more than 90% of FF and 80−85% of HMF were extracted from CELF stream to 1,4-dioxane−toluene (1:1 ratio) organic phase. Organic phase was separated from aqueous phase by decanting and used for secondary HDO reaction over Cu(5%)−Ni(5%)/TiO₂ solid catalysts. For better reactivity comparisons, FF and HMF concentration in 1,4-dioxane−toluene (or) toluene stream were concentrated to 0.5 and 0.25 g in 25 mL respectively, in each reaction by adding additional FF and HMF. Prior to HDO reaction, Cu(5%)−Ni(5%)/TiO₂ catalysts were reduced at 450 °C for 3 h. Without exposure to air, 0.3 g of reduced catalysts was transferred into a 100 mL stainless-steel Parr micro benchtop reactor (4590 Series, Parr instruments Co., Moline, IL) containing 1,4-dioxane−toluene(1:1) and (or) toluene extracted FF and HMF stream. The reactor was initially flushed with H₂ and then pressurized with H₂ gas. Next, the reactor temperature was raised to set values (200 to 240 °C), and reactions were conducted for 0.5−8 h.

**Catalyst Recyclability Study.** 1,4-Dioxane−toluene organic layer containing extracted FF and HMF was reacted in a 100 mL stainless-steel Parr reactor with 0.3 g of freshly reduced catalyst at 450 °C for 3 h. In all recycle studies, required amounts of pure FF and HMF were added to as extracted 1,4-dioxane−toluene stream to maintain the same concentrations to 0.5 and 0.25 g in 25 mL, respectively. The reactor was flushed with H₂ and then pressurized with H₂ to 35 bar. Each reaction was conducted for 2 h at 220 °C. After completion of the reaction, the reactor was cooled by quickly lowering it into a room temperature water bath (25 °C) and depressurizing in the fume hood. Then the catalyst was separated from the liquid by filtration and dried at 105 °C for 3 h and then reused in four recycle experiments without washing (or) regeneration. Regeneration of the used catalysts was performed via calcination at 450 °C for 5 h followed by reduction with pure H₂ at 450 °C for 3 h.

**Analytical Procedures.** After pretreatment, obtained liquid samples containing C6, C5 sugars, HMF, FF, levulinic acid (LA), and formic acid were analyzed by an Agilent 1200 HPLC system with a Bio-Rad Aminex HPX-87H column and RI detector along with appropriate calibration standards and with an 5 mM sulfuric acid as an eluent flow rate of 0.6 mL min⁻¹. The chromatograms were integrated using Empower 2 software package. After HDO reactions, solid catalysts were separated and the liquid portion was analyzed by gas chromatography (Agilent Technologies 7890A; column: DB-WAX Ultra Inert, 30 m long × 0.320 mm internal diameter × 0.5 μm) equipped with FID detector using the following program: hold at 30 °C for 1 min, increase from 30 to 100 °C at a ramp rate of 10 °C min⁻¹, hold at 100 °C for 2 min, increase from 100 to 250 °C at a ramp rate of 25 °C/min, 0 min hold, increase from 250 to 325 °C at a ramp rate of 25 °C min⁻¹, and 1 min hold at 325 °C. Yields of the final product were quantified by using calibration curves of standard samples in the gas chromatograph. Mass balances accounting for >95% of the carbon content were obtained in all experiments. Reactant conversion and product yield were calculated as follows:

FF (or) HMF conversion%

$$= \left(1 - \frac{\text{moles of unreacted substrate (FF or HMF)}}{\text{moles of substrate before reaction}}\right) \times 100$$

(1)

$$\text{yields} = \frac{\text{moles of the product produced}}{\text{moles of HMF (or) FF before reaction}} \times 100$$

(2)

## ■ RESULTS AND DISCUSSION

In the first step, poplar wood chips were reacted and liquified in cosolvent mixtures of tetrahydrofuran (THF) with water containing dilute FeCl₃; this homogenous reaction step is also known as the CELF pretreatment process.[32] During this reaction, both C5 and C6 sugars found within the hardwood were both hydrolyzed to monomers and then codehydrated to the fuel precursors FF and HMF, respectively (Scheme 1). The high performance of the first homogeneous catalytic step was owed to unique THF−water−biomass interactions during CELF pretreatment that has been shown to enhance cellulose[33] and lignin[34] solubilization, whereas the mild Lewis acidity of FeCl₃ promotes the kinetically favorable open-chain dehydration of sugar monomers to FF and HMF.[35,36] FF and HMF losses to LA and formic acid were minimized by optimizing reaction conditions applying the following optimization strategy.

We optimized CELF liquefaction reactions over a range of temperatures and reaction times, first while maintaining a 3:1 THF:water ratio of the co-solvent mixture, we determined that 180 °C for 20 min duration resulted in maximum FF/HMF yields and solids liquefaction, while keeping LA formation low, as shown in Figure S1. We then optimized the reaction based on the cosolvent concentration by performing reactions from 1:1 THF:water to 7:1 THF:water ratios, achieving the highest yields at a 4:1 co-solvent ratio with resulting yields of 93.5% FF and 66.0% HMF simultaneously, as shown in Figure 1. To our best knowledge, these FF/HMF yields are the highest reported to date starting from biomass achieved using a one-pot process. Simultaneously, the CELF reaction at these optimized reaction conditions further resulted in over 94% total biomass solids
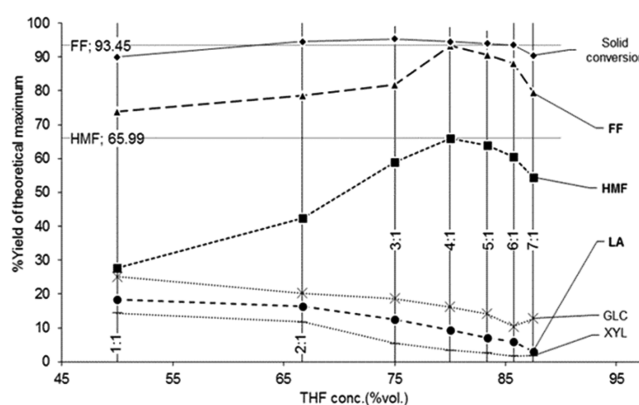


**Figure 1.** Dependence of yields of FF and HMF from poplar wood chips and total liquefaction/solids conversion on THF:water (1:1 to 7:1, v:v) concentrations. Reaction conditions: 180 °C, 20 min, and 1 wt % FeCl₃ loading. Legend: FF, furfural; HMF, 5-hydroxymethylfurfural; LA, levulinic acid; XYL, xylose; and GLC, glucose.
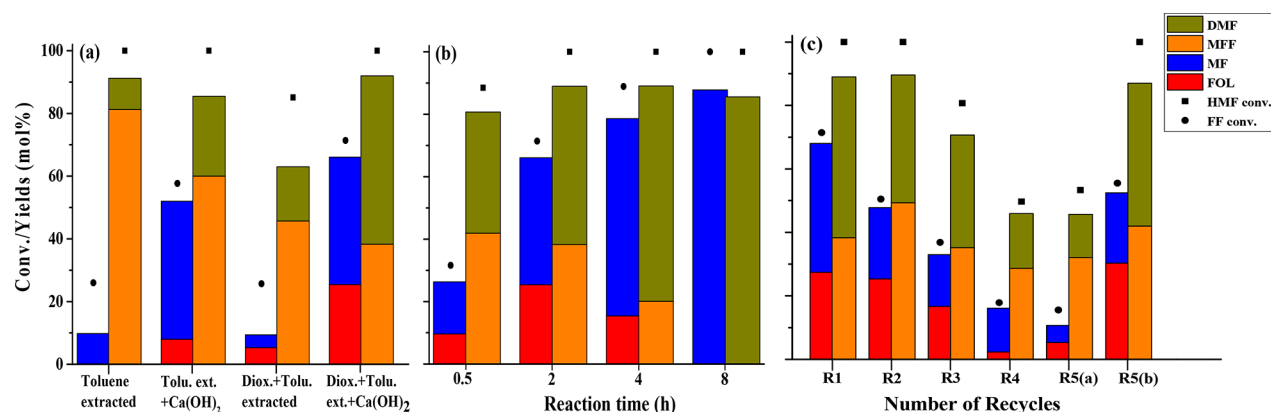
**Figure 2.** (a) HDO of toluene and 1,4-dioxane−toluene extracted FF and HMF reactions. Reactions were conducted with 25 mL of toluene (or) 1,4-dioxane−toluene extracted FF(0.5 g) and HMF(0.25 g) stream with 0.3 g of catalyst [Cu(5%)−Ni(5%)/TiO$_2$] loadings, 0.1 of Ca(OH)$_2$ = 0.1 g, temperature of 220 °C, H$_2$ pressure of 35 bar and at 2 h. (b) As a function of time FF and HMF conversions over Cu−Ni/TiO$_2$ catalysts. Reactions were conducted at 25 mL of 1,4-dioxane−toluene extracted FF(0.5 g) and HMF(0.25 g), 0.1 g of Ca(OH)$_2$, 0.3 g of catalyst loading, and H$_2$ pressure of 35 bar (at 25 °C). (c) 1,4-Dioxane−toluene extracted FF and HMF conversion and product yields as a function of recycles, R, over Cu(5%)−Ni(5%)/TiO$_2$ catalysts. Prior to regeneration (before R5), each catalyst was calcined at 450 °C for 5 h and reduced at 450 °C for 3 h under H$_2$ flow (50 mL/min). For the 6th recycle experiment, 0.1 g of Ca(OH)$_2$ was added during the reaction. Reaction conditions were a 25 mL of 1,4-dioxane−toluene extracted FF(0.5 g) and HMF(0.25 g) stream, catalyst loading of 0.3 g, temperature of 220 °C, H$_2$ pressure of 35 bar (at 25 °C), and 2 h reaction time.

solubilization primarily due to the solubilization of both sugar and lignin fractions. After a neutralization step, the dissolved lignin would later be precipitated as a fine solid powder upon removal and recovery of low boiling THF from the CELF liquor. This purified extracted biomass lignin can be identified as "CELF lignin" with a recovered mass yield that was similar to our previous reports.[37,38] The lower temperatures required for the CELF reaction compared to other thermochemical approaches such as pyrolysis affords CELF the ability to reduce undesirable co-product formation while selectively producing furfurals that are considered valuable platform chemicals for the production of renewable fuels and chemicals.[39,40] The sub-pyrolytic conditions further minimize any solid tar or char formation and the CELF reaction does result in gas production to simplify downstream processing.

After CELF reaction, Ca(OH)$_2$ was added to treat the CELF liquor, not only to neutralize the acidic moieties but also to help precipitate iron hydroxide ions (Figure S2). The recovered iron hydroxides could then be converted back into iron chloride by acid treatment to be reused.[35,41] Ca(OH)$_2$ was selected as it is inexpensive, abundant, and low hazardous and was also reported to be an excellent extracting agent for lignin from pretreated biomass stream at pH above 8.[42,43] However, in this study, we elected to neutralize the CELF liquor to pH 7 as a means to terminate any further acid−base catalyzed reactions in the CELF liquor to prevent loss of FF and HMF.[44] Iron hydroxide and Cl$^−$ species could detrimentally influence subsequent recovery of FF and HMF by extraction from the CELF liquor to an organic phase and also hurt catalyst stability in downstream processing. Following base treatment and THF recovery of the CELF liquor, we found that toluene addition as an organic extractant resulted in immediate phase splitting (organic/aqueous phase) and further precipitated remaining soluble lignin and maintained inorganic ions in the aqueous phase. However, the resulting HMF (<60%) and FF (<80%) extraction from the aqueous phase using toluene alone was poor due to the polar nature of HMF. In order to improve the extraction of FF and HMF into the toluene, we found that addition of 1,4-dioxane to the toluene−aqueous phase system

followed by sonication dramatically improved FF (∼90%) and HMF (80−85%) extraction into the resulting 1,4-dioxane−toluene phase.

Though the extraction efficiency of HMF and FF increased with addition of 1,4-dioxane, it is important to note that some Cl$^−$ ions can also be extracted into 1,4-dioxane due to its polar nature. Without further purification, extracted FF and HMF from CELF liquor was reacted over Cu−Ni/TiO$_2$ catalysts under HDO conditions. In our earlier reports, Cu(5 wt %)−Ni(5 wt %)/TiO$_2$ was shown as an active, selective, and stable catalyst for HDO of pure FF and HMF to methylated furans (i.e., MF and DMF).[31] Characterization of the Cu−Ni particles on TiO$_2$ revealed that TiO$_2$ promoted the formation of a near surface alloy containing 80−85% of Cu and 15−20% of Ni. The low amount of Ni at the catalyst surface enhanced reactivity compared to monometallic Cu by promoting H$_2$ dissociation, while maintaining the inherent selectivity of Cu catalysts.[31,18]

Furthermore, strong Ni−TiO$_2$ interactions promoted stability of the catalysts against performance degradation by metal sintering. Usually, HDO of FF to MF occurs through furfuryl alcohol (FOL) as an intermediate, whereas HMF to DMF occurs through either MFF or BHMF as an intermediate (Scheme 1).[45] For the Cu−Ni/TiO$_2$ catalyst, HMF conversion to DMF was observed to occur through MFF as an intermediate instead of BHMF.[31] The catalytic HDO of FF and HMF extracted from the CELF liquor was first considered as a function of solvent composition. Following HMF and FF extraction using pure toluene, HDO was executed at 220 °C where 26% of FF and 100% of HMF conversion were observed after 2 h. However, the total yield of desired products was low: FOL+MF (9.8%) and MFF+DMF (91.2%). It is assumed that the lower catalytic reactivity in toluene, compared to our previous studies in pure 1,4-dioxane, was due to the nonpolar nature of toluene. The HDO activity derived from 1,4-dioxane−toluene extracted FF and HMF streams was lower than for toluene alone, where diminished MF yields and HMF conversion were seen in Figure 2a.

While comparing the catalytic activity results of pure FF and HMF in 1,4-dioxane−toluene stream (Figure S4-left) with 1,4-dioxane−toluene extracted stream (Figure 2a), significant difference in conversions and product yields were observed without further treatment. It was hypothesized that the diminished catalytic performance observed using 1,4-dioxane−toluene extraction, as compared to toluene alone, was due to 1,4-dioxane driven extraction of trace $Cl^-$ ions from $FeCl_3$ originating from the prior pretreatment step. To neutralize acidic species and minimize $Cl^-$ extraction by the organic phase, acidic species in the 1,4-dioxane−toluene extracted FF and HMF stream were neutralized by $Ca(OH)_2$. The addition of 0.1 g of $Ca(OH)_2$ to 25 mL of extracted liquid was identified as the optimum quantity to promote catalytic activity and selectivity in FF and HMF HDO, as shown in Figure S3 and Figure 2a, where 70% and 100% conversion of FF and HMF and 41% and 51% MF and DMF yields were achieved, respectively. Adding the same amount of $Ca(OH)_2$ to the toluene extracted stream also promoted catalytic reactivity and selectivity, although Figure 2a shows that the influence of $Ca(OH)_2$ was not as significant as it was on the 1,4-dioxane−toluene extracted stream. As known, 1,4-dioaxne is more polar in nature and it can easily polarize (or activate) the carbonyl groups in furanic compounds and further facilitate hydrogenation reaction on metal active sites, whereas nonpolar natured toluene could not polarize these carbonyl groups. Thus, decreased activities were observed in the case with toluene compared to 1,4-dioxane−toluene solvent.[46,47]

To demonstrate that $Ca(OH)_2$ likely promoted reactivity by neutralizing the influence of $Cl^-$ ions, NaCl in water solution was added to a pure 1,4-dioxane−toluene solution containing FF and HMF followed by executing the HDO reaction (Figure S4). However, a significant drop in catalytic activity was observed in the presence of NaCl. Separate experiments performed with the addition of water without NaCl showed no significant reduction reactivity,[46] supporting the hypothesis that $Ca(OH)_2$ addition was necessary to neutralize and fix $Cl^-$. Thus, it is observed that 1,4-dioxane and toluene are needed to maximize HMF and FF extraction efficiency from the CELF liquor, whereas $Ca(OH)_2$ neutralization minimized the influence of extracted $Cl^-$ ions on the catalytic process.

HDO of 1,4-dioxane−toluene extracted FF and HMF was conducted as a function of temperature and time to optimize MF and DMF yields, see Figure S5 and Figure 2b. Though it was observed that MF and DMF yields were maximized at 240 °C, a significant loss of HMF to unwanted byproducts (not MFF or DMF) was observed, suggesting that reaction at lower temperature and longer time would optimize DMF and MF yields. Figure 2b shows the conversion and product yields from HDO of 1,4-dioxane−toluene extracted FF and HMF at 220 °C with the addition of 0.1 g of $Ca(OH)_2$ as a function of time. It was observed that after 8 h reaction time, MF yields of 87.8% and DMF yields of 85.6% could be achieved.

To examine the stability of the catalyst, recycle experiments were conducted where reactions were executed for 2 h, followed by separation of the catalyst and introduction of freshly separated HMF and FF. Four sequential recycles (R1−R4) were executed without additional treatment of the catalyst or $Ca(OH)_2$ addition, followed by regeneration of the catalyst via calcination and reduction before a fifth recycle (R5) and the addition of 0.1 g of $Ca(OH)_2$ during a sixth recycle (R6). From R1 to R4, FF conversion dropped by ∼20% in each cycle, whereas HMF conversions were similar in R1 and R2

case but dropped for the R3 and R4 cycles. The significant drop in FF conversion compared to HMF could be caused by weaker adsorption of FF on catalyst active sites as compared to HMF. HMF adsorption occurs through carbonyl (C=O) and alcohol (C−OH) groups on catalyst active sites, whereas FF has only one carbonyl group. As a result of this difference in adsorption energy of HMF and FF and the catalyst, $Cl^-$ adsorption more effectively blocks FF adsorption and conversion as compared to HMF. This effect was more significant after the first recycle (R1) due to some of the catalysts active sites already positioned by $Cl^-$ ions (R2 to R4). Further, to identify whether the decay in reactivity was caused by $Cl^-$ ions or more tradition mechanisms such as coking or sintering, Figure 2c shows results for R5, where the catalyst was regenerated, compared with R6, where additional $Ca(OH)_2$ was added. It clearly observed that the loss in activity is caused by presence of $Cl^-$ ions in the 1,4-dioxane−toluene stream instead of carbon deposition or metal sintering and that this could be addressed simply by adding $Ca(OH)_2$ in each recycle. Noteworthy is the crucial role of $Ca(OH)_2$ addition not only to improve conversion of raw organic streams but also to neutralize the chlorinated acids, and enhanced the extraction of lignin to aqueous phase.[43] Further, it was reported that pretreatment of lignin by adding $Ca(OH)_2$ efficiently controlled the melting and agglomeration of lignin particles by eliminating the cross-linking reactions between phenolic −OH, −CHO, and −COOH groups by forming calcium hydroxyl phenoxides, phenolic calcium carboxylates, and phenolic alcohols.[42]

The lignin was then precipitated from the CELF hydrolyzate, after recovery of THF by distillation, prepared at the conditions optimized for producing FF and HMF (180 °C, 20 min, 4:1 THF/water, 1% $FeCl_3$). The molecular weight, relative abundance of the lignin interunit linkage (e.g., β-O-4) and monolignol compositions (e.g., S/G ratio), and the contents of free hydroxyl groups in lignin were determined by gel permeation chromatography (GPC), heteronuclear single quantum coherence (HSQC), and ^{31}P nuclear magnetic resonance (NMR) techniques, respectively. The functionality and molecular weight of the CELF lignin were then compared to native-like cellulolytic enzyme lignin (CEL) isolated from poplar wood, with the results presented in Table 1.

Figures S6 and S7 present the aromatic and aliphatic regions of HSQC NMR spectra of CEL and CELF lignin, respectively. In the aliphatic regions, β-aryl ether (β−O−4) was the dominant interunit linkage in poplar CEL along with minor amounts of phenylcoumaran (β−5) and resinols (β−β). However, only peaks associated β−β bonds were barely detected above the noise level while the remaining peaks for β−O−4 and β−5 were not apparent in CELF lignin. This result was further reinforced by the semiquantitative analysis of HSQC spectra shown in Table 1 that probably provides the most important insights into the current lignin characterization. The cleavage of β−O−4 linkages in lignin is usually accompanied with repolymerization reactions under acid conditions.[48−51] Sannigrahi et al. reported the depolymerization by fragmentation of β−O−4 structures through a benzyl carbocation intermediate and polymerization by acid-catalyzed condensation between electron-rich carbon atoms such as aromatic $C_6/C_5$ and the benzyl carbocation as the predominant reactions in acid-catalyzed pretreatments.[50] Meanwhile, β−5 units could be converted to stilbenes through loss of the γ-methylol group as formaldehyde.[52] Although complete

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**Table 1. Molecular Weight, Relative Abundance of Lignin Subunits and Interunit Linkages, and Free Hydroxyl Groups in CEL (native) and CELF lignin**

| Lignin Characteristics | CEL (native) | CELF lignin |
|---|---|---|
| Lignin subunits and interunit linkages (% of S +G) | | |
|    Syringyl (S) | 61.0 | 54.9 |
|    Guaiacyl (G) | 39.0 | 45.1 |
|    p-Hydroxybenzoate | 15.7 | 12.6 |
|    S/G ratio | 1.56 | 1.22 |
|    $\beta$-aryl ether ($\beta$−O−4) | 55.5 | 0 |
|    Resinols ($\beta$−$\beta$) | 6.2 | 1.47 |
|    Phenylcoumaran ($\beta$−5) | 4.9 | 0 |
| Lignin molecular weights (g/mol) | | |
|    Weight-average molecular weight | 11451 | 1245 |
|    Number-average molecular weight | 2701 | 770 |
| Polydispersity index (PDI) | 4.2 | 1.62 |
| Hydroxyl groups (mmol/g lignin) | | |
|    Aliphatic OH | 6.25 | 1.68 |
|    $C_5$ substituted OH | 0.21 | 1.96 |
|    Guaiacyl OH | 0.35 | 0.70 |
|    p-Hydroxyphenyl OH | 0.32 | 0.23 |
|    Carboxylic acid OH | 0.12 | 0.42 |

removal of $\beta$−O−4 interlinkages in lignin could be achieved under conventional organosolv pretreatments at harsh pretreatment conditions,[53] one of the advantages of using THF as the water cosolvent is that THF could preferentially solvate lignin and the THF/water cosolvent mixture could act as a "theta" solvent to prevent lignin aggregation or repolymerization while facilitating lignin solubilization.[34]

GPC results indicated that CELF lignin had much lower weight-average molecular weight ($M_w$) and number-average molecular weight ($M_n$) compared to CEL, suggesting significant lignin depolymerization during CELF pretreatment. The polydispersity index (PDI) that indicates the distribution of molecular mass in lignin suggested that CELF lignin had a much higher uniformity or narrower molecular weight distribution than CEL. The $^{31}$P NMR technique was applied to determine the proportion of different types of hydroxyl groups in CELF lignin after appropriate phosphitylation.[54] As shown in Table 1, the dominant aliphatic hydroxyl group signal in CEL was significantly reduced by ~73% after CELF reaction; on the other hand, the contents of phenolic OH, and especially the $C_5$ substituted OH, were much higher in CELF lignin compared to CEL. The drop in aliphatic OH could be due to the above-mentioned loss of $\gamma$-methylol group as formaldehyde.[48] In addition, the oxidation of aliphatic hydroxyl groups might have occurred as evident by the dramatic increase in the carboxylic OH content. The increase in total phenolic OH supports the HSQC NMR data indicating significant cleavage of lignin interunit linkages during CELF pretreatment. The relatively low content of aliphatic OH and high content of phenolic OH are desired features for potentially using CELF lignin as good antioxidant.[55]

## CONCLUSIONS

In summary, high yield coproduction of CELF lignin and methylated furans directly from poplar wood chips are reported here by hybrid combination of homogeneous catalysis followed by heterogeneous catalysis, respectively. In the first homogeneous reaction step, the CELF reaction was performed

with THF−water mixture containing 1 wt % $FeCl_3$ at 180 °C for 20 min to achieve the highest coproduction yields of FF (93.5%) and HMF (66.0%). The unique interactions among biomass, THF, and water enabled enhanced solubilization of cellulose and lignin in the THF−water system followed by dehydration of sugars to FF and HMF. The resulting furfurals were then efficiently partitioned and concentrated into a $Ca(OH)_2$ neutralized 1,4-dioxane−toluene stream for HDO over Cu−Ni/$TiO_2$ catalysts. Surface-rich Cu in Cu−Ni bimetallic particles promoted selective HDO of FF and HMF to 87.8% MF and 85.6% DMF, respectively, at 220 °C. Compared to poplar CEL, CELF lignin had significantly lower molecular weight and higher phenolic OH contents. The cleavage of $\beta$−O−4 interlinkages under acid conditions, along with the unique interactions between lignin and THF−water system are the major mechanisms of lignin breakdown during CELF pretreatment.

## ASSOCIATED CONTENT

**ⓈSupporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b01930.

> Optimization of reaction temperature and reaction time for production of HMF, FF, and LA from poplar wood; FF and HMF extractions from CELF stream to 1,4-dioxane−toluene phase; $Ca(OH)_2$, chloride ions, and temperature effects on HDO of 1,4-dioxane−toluene extracted FF and HMF stream; aromatic and aliphatic regions of 2D HSQC NMR spectra of CEL and CELF lignin as well as characterization data (PDF)

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**Notes**

The authors declare no competing financial interest.

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