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## Executive Summary

The overall goal of this project is to utilize the Co-Solvent Enhanced Lignocellulosic Fractionation (CELF) as a platform technology to realize transformation of real biomass feedstocks to fungible transportation fuels. CELF is a solvolysis method that seeks to break the cost barrier for biomass deconstruction so that high yield liquid intermediates from both sugars and lignin can be recovered for their subsequent catalytic conversion to fungible transportation fuels. It is important for the DOE EERE mission to focus on supporting platform technologies that enable greater end-to-end utilization of biomass whereby the co-development of both process and catalyst is streamlined. CELF is one of the most competitive platform technologies that uses multifunctional co-solvents THF and water to provide the cleanest intermediate product streams that can allow advanced catalysts to be developed on real feedstocks instead of model compounds.

For this project, we developed a hybrid catalytic process that first applies CELF homogeneous catalysis to convert solid biomass to a liquid stream containing intermediate fuel precursors (FPs) such as furfural (FF) and 5-hydroxymethylfurfural (5-HMF). Afterwards, a second heterogeneous catalytic step was then applied to selectively hydrodeoxygenate (HDO) the FPs produced from biomass into gasoline blendstocks methylfuran (MF) and dimethylfuran (DMF). Concurrently, capitalizing on CELF's efficient lignin extraction capabilities, we further explored production C9+ cyclic hydrocarbons from biomass lignin to improve overall process economics. For the first step, the CELF process was optimized to achieve yields of >95% for FF and >60% for HMF from the xylan and glucan fractions in poplar wood, respectively. For the second step, we created a patent-pending bifunctional Cu-Ni solid catalyst that is tolerant to real product streams from the CELF process and simultaneously produce MF and DMF blendstocks at >80% yields. To provide more market versatility, we further explored the production of 2-pentanol from MF and have achieved >70% yields.

During this project's three year period, we also developed a dynamically informed technoeconomic computer model that helped to guide key project decisions that allowed us to reach a final biofuel selling price (MFSP) of <$3/GGE (gallon gasoline equivalent) and total biomass carbon utilization of 60%. We also determined that the MFSP in our model could be further reduced to below $2/GGE if the value of the lignin-derived aromatic hydrocarbon fuels could be sold at diesel-range prices (>$500/tonne). Our process model was designed to consume 288 tonnes per day of poplar wood chips with minor consumption of hydrogen to produce a range of fuel blendstocks suitable for use in the transportation sector. The project was successful in meeting DOE EERE program criteria for application of an all-catalytic biofuels process to achieve a biofuel selling price target of <$3/GGE as well as to achieve a 60% reduction in greenhouse gas emissions (GHG) compared to conventional fossil petroleum processes.

At project completion, the outlined catalytic process reported total utilization of up to 60% of the carbon found in biomass, rivaling more mature biological cellulosic ethanol technologies at a fraction of the fixed and operating costs. This project also resulted in 7 peer-reviewed publications, 2 provisional inventions, and 1 patent pending.

NOTE: This public version of the document contains redacted text, tables, and figures as indicated within the document.

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# Total Accomplishments toward Project Targets and Objectives

## Summary of Project Objectives and Project Targets

The project was divided into four primary objectives and a milestone/task/sub-task structure defining key performance targets within each objective. The four objectives are summarized:

*Objective 1: Optimize CELF to achieve higher yields of FPs from poplar wood than competing baseline technologies*. First, investigate the optimum THF concentrations using inexpensive sulfuric acid to maximize total FP production. Second, investigate application of metal halide acid catalysts to selectively enhance production of only furfural and 5-HMF in a single reaction. Finally, determine best use of remaining glucan-rich solid product for CELF either by further thermochemical reaction to levulinic acid, or enzymatic digestion to glucose. Thirdly, investigate the recovery of THF by both conventional and unconventional methods from the CELF reaction to minimize THF loss to less than 5% and then recycle the THF to be reused in the CELF reaction and achieve comparable yield targets to fresh THF. The performance targets are shown in Table 1.

**Table 1: Objective 1**

| % theoretical: | FF | HMF | LA |
|---|---|---|---|
| Baseline | 55% | <5% | 60-70% (separate rxn) |
| Target 1.1 | 85% | 20% | 75% (separate rxn) |
| Target 1.2 | 85% | 50% | <8% (single rxn) |

*Objective 2: Develop a heterogeneous catalyst system for selective transformation of furfural and 5-HMF simultaneously to either furanic, alcohol, and/or hydrocarbon fuels.* First, optimize a catalyst to achieve high yield conversion of both furfural and 5-HMF to a potential range of gasoline blendstocks such as methylfuran (MF), dimethylfuran (DMF), MTHF, and DMTHF using hydrogen or a hydrogen donor. Second, optimize the catalyst system to further narrow the range of final fuel products from furfural and 5-HMF into no more than three. Lastly, investigate the production of alcohols produced from furan blendstocks. The expected yields of total fuel products from furfural and 5-HMF is 60% theoretical or higher as outlined in Table 2.

**Table 2: Objective 2**

| % theoretical: | MF+DMF | MTHF+DMTHF | Alcohols | Total Products |
|---|---|---|---|---|
| Baseline | (never attempted) | (never attempted) | <30% | <30% |
| Target 2.1 | 50% | 10% | N/A | 60% |
| Target 2.2 | 10% | <5% | >45% | 60% from Target 2.1 |

*Objective 3: Characterize and valorize lignin extracted from CELF to realize higher value in a true biorefinery than can be realized by use as a boiler fuel.* First, characterize CELF lignin for intrinsically high-value components (low-MW components, phenolics) that can be derived into non-fuel co-products, then recommend a catalytic pathway to produce a fuel product from the remaining CELF lignin. Second, investigate fractionation of CELF lignin to remove high-value components, then optimize conversion of remaining CELF lignin by

oxidative or reductive catalytic fragmentation to a liquid fuel oil. Thirdly, optimize conversion of CELF lignin by selective catalytic hydrodeoxygenation over a copper catalyst to cyclohexyl-alkanes suitable as jet fuel blendstock. The expected outcome is to derive energy value from at least 50% of the lignin extracted by CELF as fuel oil or achieve 50% theoretical yield of cyclohexyl-alkanes from CELF lignin by catalysis. The economics of both pathways would be evaluated and a winning pathway would be selected at end of project.

**Table 3: Objective 3**

| % theoretical: | Bio-oil | Cyclohexyl alkanes |
|---|---|---|
| Baseline | 50% from Kraft lignin | 30% from organosolv lignin |
| Target 3.2 | 50% from CELF lignin | N/A |
| Target 3.3 | N/A | 50% from CELF lignin |

*Objective 4: Design integrated cellulosic biomass conversion processes based on CELF technology to understand technical needs and define opportunities to reduce costs.* First, employ critical yield and product data from Objectives 1-3 to design a working computer model of an integrated biorefinery to carry forth material flow, energy, and economic calculations. Second, optimize process parameters to reduce energy consumption and recommend process steps to minimize THF consumption. Third, produce a non-bridging pumpable high solids wood slurry and demonstrate pumping of the wood slurry in a positive displacement slurry pump up to 300 psig to de-risk commercial deployment of CELF.

Success in these objectives could lower production costs of sustainable transportation fuels that substantially reduce carbon dioxide emissions that contribute to global climate change, improve energy security, and create a new industry that improves domestic rural economies and balance of trade. In addition, the results can provide valuable process options, data, insight, and technical advances for making competitively-priced fuels from major fractions of cellulosic biomass, suggest even more transformational technologies, and accelerate transformation of inexpensive cellulosic biomass into transportation fuels with major societal benefits.

## Summary of Project Accomplishments

### Project Milestone Completion Chart

Based on the project objectives and individual targets, the following accomplishments are summarized as either not met, met, or exceeded in Table 4:

**Table 4:** Project Accomplishments towards Project Milestone Targets

| Milestone | Not Met | Met | Exceeded |
|---|---|---|---|
| 1.1.1 | | X | |
| 1.1.2 | | X | |
| 1.1.3 | | X | |
| 1.2.1 | | | X |
| 1.2.2 | | X | |
| 1.2.3 | | X | |
| GN1 | | X | |
| 1.3.1 | | X | |
| 1.3.2 | | X | |

| | | | |
|---|---|---|---|
| 1.3.3 | | X | |
| 2.1.1 | | | X |
| 2.1.2 | | X | |
| 2.1.3 | | X | |
| 2.1.4 | | | X |
| 2.1.5 | | | X |
| 2.1.6 | | | X |
| 3.1.1 | | X | |
| 3.1.2 | | X | |
| 3.2.1 | | X | |
| 3.2.2 | | X | |
| 3.2.3 | | X | |
| 3.3.1 | | X | |
| GN2 | | X | |
| 3.3.2 | | X | |
| 4.1.1 | | X | |
| 4.1.2 | | X | |
| 4.1.3 | | X | |
| 4.1.5 | | X | |
| 4.2.1 | | X | |
| 5.1 | | X | |

## Detailed Description of Project Outcomes and Results

### Task 1 – Optimize CELF to achieve higher yields of FPs from poplar wood than competing baseline technologies.

For Task 1, we first performed optimization for production of 5-hydroxymethylfurfural (HMF) and furfural (FF) from poplar wood using CELF reaction with dilute sulfuric acid. Combinations of sulfuric acid loadings, temperatures (170-200°C), and reaction times were attempted at a modest 1:1 (vol) THF:water ratio to maximize co-production of HMF and FF. At 1:1 mixtures, we were able to achieve 27% HMF and 76% FF yields of the theoretical maximum at 170°C and 60 min reaction time or 80% FF production and 21% HMF yields at 40 min reaction time which was very close to achieving Milestone 1.1.1 of 20% HMF and 85% FF yields without having to increase solvent loadings. At a higher solvent loadings of 3:1 THF:water ratio, we were able to achieve 22% HMF and 86% FF yields from poplar at 170°C and 60 min reaction time.

We then confirmed conversion of the solid residuals to levulinic acid (LA) and achieved a yield of 75.4 mol%. The reaction conditions were the same as reported previously of 200°C for 1 hour with 2 wt% loading of sulfuric acid[1]. This reaction mechanism occurs by the acid-catalyzed hydrolysis and dehydration of cellulose in the solid residual to HMF and further hydrolysis to LA as the most stable product from this reaction.

**REDACTED TEXT**

**REDACTED FIGURE**

CELF residual solids were reacted at 200°C thermochemical conversion for 1 hr in our 1L Parr reactor. Quantification of LA peaks revealed 73.4 mol% conversion of poplar glucan to LA. As glucose yields from enzymatic hydrolysis greatly exceeded LA yields, it is advised to pursue the former method to maximize glucan utilization of the CELF residuals. We then delivered CELF lignin samples throughout the project to Task 3 for characterization and catalytic valorization. Lignin was extracted from hydrolysate mixture by precipitation of the CELF liquids through boiling of THF. **REDACTED TEXT**

We then performed vacuum distillation from CELF liquor after reaction of poplar wood chips using $FeCl_3$ acid catalyst. We managed to recover 97.2wt% of THF used during the CELF reaction at a 93.5wt% concentration with water (due to the azeotrope). We found that 2.0 wt% of the THF had reversibly hydrolyzed to 1,4-butanediol (BDO) and could also be accounted for in the aqueous phase after THF recovery. Thus, the total recovery of THF and BDO from the CELF process using $FeCl_3$ catalyst was 99.2%. The THF recovered from rotary evaporation of CELF liquids contained 93.5% THF/4% water/0.5% organics (from slippage). Accounting for water content, the recycled THF stream was reused with no detrimental impact to yields producing 91% furfural and 66% HMF yields from poplar wood. These results completed our work for this milestone.

### Task 2 – Develop heterogeneous catalyst system for selective transformation of FF and HMF simultaneously to either furanic, alcohol, and/or hydrocarbon fuels

For this task, we have successfully achieved >60% yields of methyl furan (MF) and dimethyl furan (DMF) from Furfural (FF) and 5-Hydroxy methylfurfural (HMF), respectively, in a single batch reactor. At 200°C, 8h reaction time, under 25 bar $H_2$ pressure (at 25°C), >81.5% and >74% yields of MF and DMF were co-produced from 0.5 g of FF and 0.250 g of HMF, respectively. We used 0.3 g of a Ni(5 wt%) – Cu(5 wt%)/TiO2 catalyst with 25 ml of 1,4-Dioxane as solvent. This was the first demonstration of high selectivity in simultaneous co-processing of HMF an FF to DMF and MF, respectively. Both the active catalyst composition (Ni/Cu) and support (TiO2) were optimized and required to achieve good selectivity and conversion. **In the final iteration of these reactions, we have achieved simultaneous conversion of both FF and 5-HMF to their respective methylated furans at >90% molar yields, the highest reported to date (Ct-F Increasing Yields of Catalytic Process)**. These results can be found in our publications[4-5].

We introduced 1,4-dioxane as the primary carrier solvent for the hydrodeoxygenation (HDO) of FPs to methylated furans instead of isopropanol, due to the undesired reactivity of isopropanol in this environment and incompatibility of IPA with extraction of FF and HMF from CELF hydrolysate. Increasing the catalyst loading (0.050 to 0.300 g) resulted in a loss of 2 to 4 ml of isopropanol in each reaction. We have chosen 1, 4 dioxane as a solvent for further reactions. It is a polar aprotic solvent and is stable under reaction conditions.

FF to MF and FF to THFOL are consecutive reactions that are thought to occur through the intermediate product FOL, where MF and THFOL are produced from FOL by hydrogenolysis and furan ring hydrogenation, respectively. Figure 2-1 shows that MF was selectively produced on monometallic Cu catalysts while Ni catalysts are selective for THFOL at 200°C, regardless of the support. This was due to the strong coordination of the ring and the Ni surface that induces ring hydrogenation. $Cu/Al_2O_3$ catalysts more are active than $Cu/TiO_2$ catalysts, where for $Cu/Al_2O_3$ 80% of FF was converted into FOL (60.7%) and

MF (14.4%) at 1 h and further extending the reaction to 8h led to 72.9% yields of MF. This demonstrates that FOL is an intermediate for MF production on $Cu/Al_2O_3$. The mechanism was different for $Cu/TiO_2$, where FF to FOL and FF to MF occurred simultaneously, resulting in 1.9% of FOL and 10.2% of MF yields at 1h reaction. Further reaction after 8 h on $Cu/TiO_2$ showed a similar product mixture as with 1h, suggesting that FOL was not an intermediate for MF production on $Cu/TiO_2$ or that FOL conversion on MF occurs very quickly on the $Cu/TiO_2$ catalyst. This was evidence that there are unique active catalytic sites at the $Cu/TiO_2$ interface that allow effective conversion of FF to MF with minimal FOL production. THFOL yields were suppressed on Cu catalysts due to repulsive interactions between Cu and the furan ring.

Although, $Cu/Al_2O_3$ was more active than $Cu/TiO_2$, undesired products such as diols and pentanols were obtained at 8h reaction time on $Cu/Al_2O_3$. For $Ni/Al_2O_3$, FF was completely converted to THFOL (54.5%) and MF (30.5%) at 1 h and the product selectivity didn't change after 4 h. Although $Ni/TiO_2$ catalysts are less active than $Ni/Al_2O_3$, 70% of THFOL was achieved by 4h reaction time. Comparing Ni and Cu catalysts, it was clear that Ni promotes ring hydrogenation to form THFOL, while Cu was selective for hydrogenolysis to form the desired product, MF. It also seems that by using $TiO_2$ as a support with Cu, unique reaction pathways to form MF are introduced.

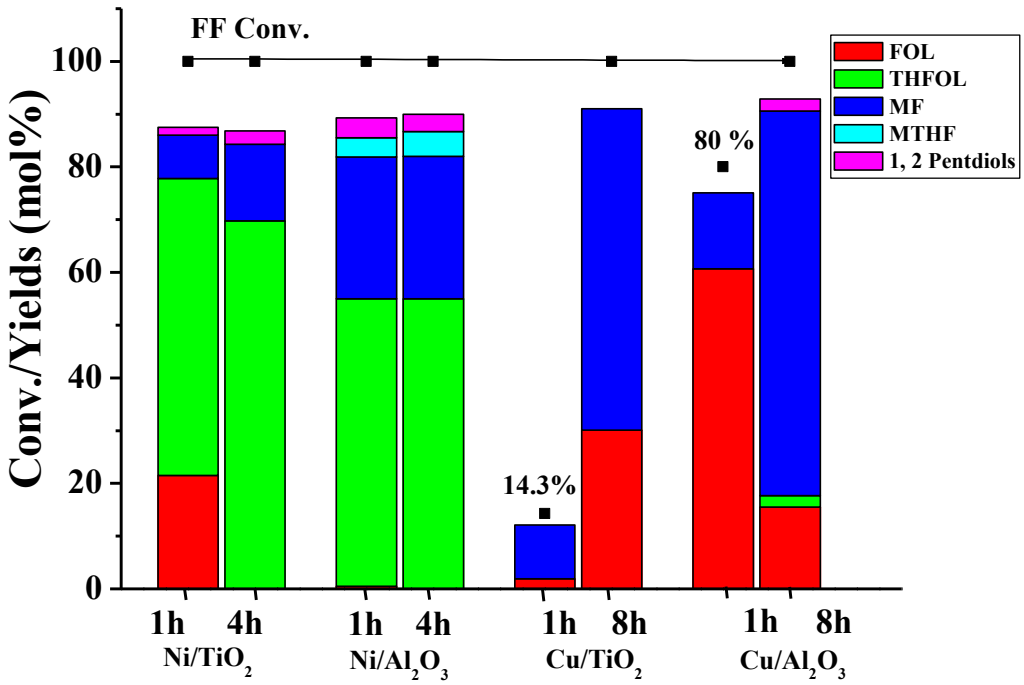



**Figure 2-1.** FF conversion over monometallic Ni and Cu on $Al_2O_3$ and $TiO_2$ catalysts. **Reaction conditions**: FF = 1 g, Catalyst = 0.300 g, Solvent (1, 4 Dioxane) = 25 ml, Temperature = 200° C, Pressure ($H_2$ gas) = 25 bar. FF = Furfural, FOL = Furfuryl alcohol, MF = Methyl furan, THFOL = Tetrahydrofurfuryl alcohol, Others = Pentanols + Pentane diols

Figure 2-2 shows that when using a Cu/Ni alloy catalyst (Cu (5 wt%) –Ni(5 wt%)) the support significantly influenced selectivity in FF conversion. The Cu-$Ni/Al_2O_3$ catalyst was more active than the Cu-$Ni/TiO_2$ catalyst (this was the same trend observed with monometallic Cu), where 100% FF conversion was achieved in 0.5 h reaction time for Cu-

$Ni/Al_2O_3$, whereas 8 h was required for complete conversion on $Cu\text{-}Ni/TiO_2$. However, on $Cu\text{-}Ni/TiO_2$ MF selectivity was increased with increasing FF conversion (by increasing reaction time) resulting in 82.1% yield of MF obtained at 8h over $Ni\text{-}Cu/TiO_2$ catalyst. $Ni\text{-}Cu/Al_2O_3$ catalysts favor furan ring hydrogenation which resulted in increasing THFOL yields with subsequent loss of FOL by furan ring hydrogenation in 2h. This suggests that on the $Ni\text{-}Cu/Al_2O_3$ catalyst, Ni is exposed at the surface. These results are well correlated with XPS (Table 2-1) and TPR experiments, which showed that Ni is at the surface in significant concentration. In the bimetallic catalysts, the percentage of surface metal ratios (Cu/Ni) were calculated from XPS data which showed Cu/Ni surface concentration ratios of 82/17.6 and 48.7/51.3 on $TiO_2$ and $Al_2O_3$ surfaces, respectively. Thus, most of the Ni was covered by Cu for the $Cu\text{-}Ni/TiO_2$ catalyst. This was also confirmed by $Cu\text{-}Ni/TiO_2$ TPR profiles, which show no peaks for Ni in the range of 350 to 450°C. Since $TiO_2$ is reducible metal oxide and Ni is stronger reducing agent than Cu metal, strong metal support interactions (SMSI) occurred between Ni and $TiO_2$, and therefore Ni is closer to the titania interface and Cu is well exposed on the surface. Thus, SMSI enhanced the catalytic activity of Cu-Ni/TiO2 case compared with $Cu/TiO_2$ and the MF selectivity was maintained by surfaces rich copper. Henceforth, $Ni\text{-}Cu/TiO_2$ catalyst are chosen for HMF and co-processing of HMF and FF conversion reactions under same reaction conditions.

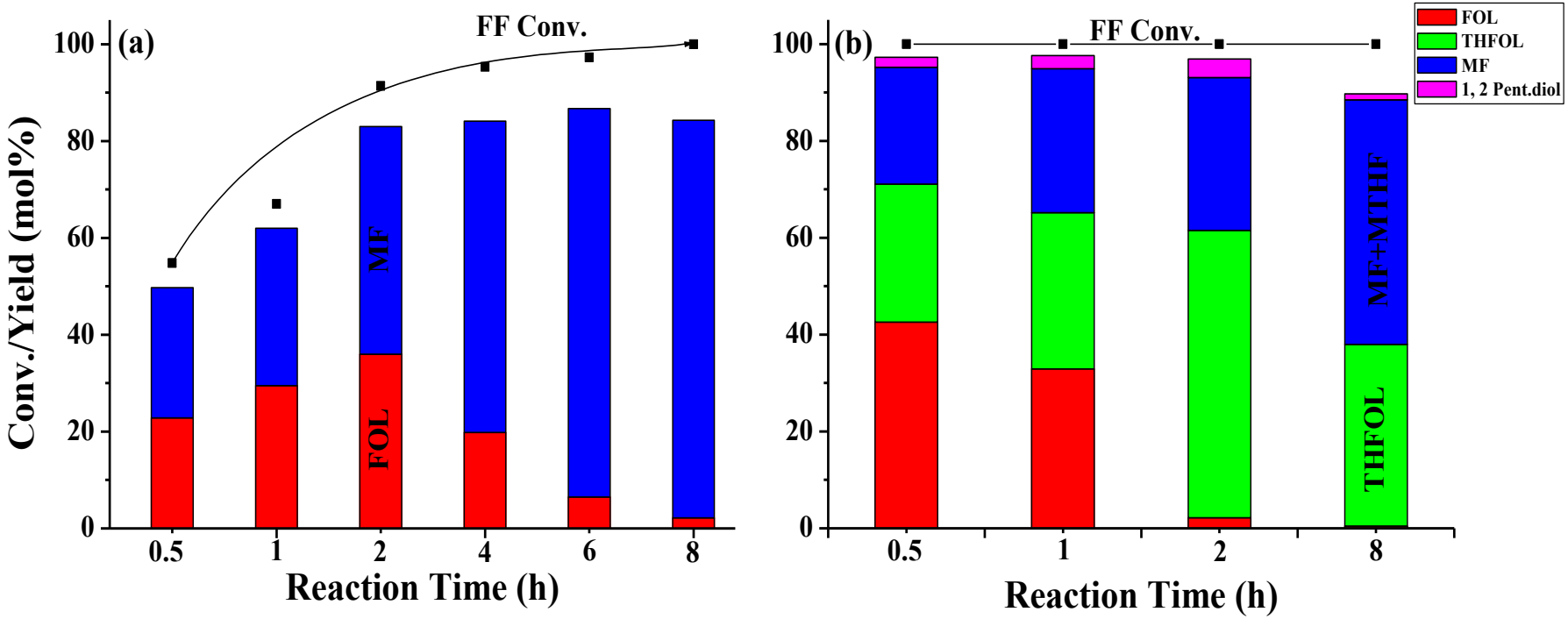


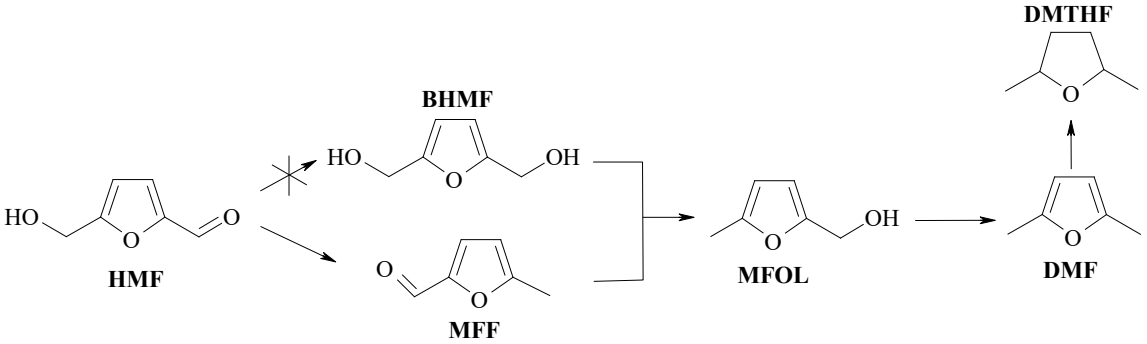

**Figure 2-2.** FF conversion as a function of time over bimetallic supported catalysts. (a)Ni(5 wt%)-Cu(5 wt%)/$TiO_2$ and (b)Ni( 5wt%)-Cu( 5wt%)/$Al_2O_3$

**Reaction conditions**: FF = 0.1 g, Catalyst (a) Ni(5 wt%) – Cu(5 wt%)/$TiO_2$ = 0.300 g, (b) Ni(5 wt%) – Cu(5 wt%)/$Al_2O_3$ = 0.300 g, Solvent (1, 4 Dioxane) = 25 ml, Temperature = 200° C, $H_2$ Pressure = 25 bar. FF = Furfural, FOL = Furfuryl alcohol, MF = Methyl furan, THFOL = Tetrahydrofurfuryl alcohol, Others = Pentanols + Pentane diols.

**Table 2-1.** Surface Cu/Ni ratio from XPS experiments:

| **Catalyst** | **$Cu^{2+}/Cu^{0}$** | **$Ni^{2+}/Ni^{0}$** | **Cu/Ni ($Cu^{o}+Cu^{+1}+Cu^{+2}$)/ ($Ni^{0}+Ni^{+2}$)** |
|---|---|---|---|
| Cu(10 wt%)/$Al_2O_3$ | 37.6/62.4 | - | - |
| Cu(10 wt%)/$TiO_2$ | 47.8/52.2 | - | - |
| Ni(10 wt%)/$Al_2O_3$ | - | 52.4/47.7 | - |
| Ni(10 wt%)/$TiO_2$ | - | 57.5/42.7 | - |
| Cu(5 wt%)-Ni(5 wt%)/$Al_2O_3$ | 38.6/61.4 | 73.7/26.3 | 48.7/51.3 |
| Cu(5 wt%)-Ni(5 wt%)/$TiO_2$ | 33.13/66.9 | 57.5/42.5 | 82.4/17.6 |
| Cu(5 wt%)-Ni(5 wt%)/$Al_2O_3$ | - | - | 47.2/52.8 |
| Cu(5 wt%)-Ni(5 wt%)/$TiO_2$ | - | - | 82.4/17.6 |

The progress of HMF and HMF with FF (co-processing) conversions as a function of time on Ni-Cu/$TiO_2$ catalysts are presented in Figures 2-3(a) and 2-3(b), respectively. DMF and MFF products are primarily observed from HMF conversion in the present reaction conditions, see Scheme 2-1. MFF occurs by HMF hydrogenolysis and DMF was produced from MFF by hydrogenation followed by hydrogenolysis of the carbonyl group. Also, small amounts of MFOL were observed, as it was intermediate in the conversion of MFF to DMF reaction. Ni-Cu/$TiO_2$ catalysts are active and selective for HMF conversion, showing 95.9% conversion of HMF into MFF (30.7%) and DMF (52.2%) in 0.5 h reaction time at 200°C. Further, DMF yields were increased with increasing reaction time and 72.3% of DMF was obtained by subsequent conversion of MFF. Unknown or undesired products were enhanced by prolonging the reaction time to 8h. Co-processing of HMF and FF was executed over the Ni-Cu/$TiO_2$ catalysts using 0.5 g of FF and 0.250 g of HMF under the same reaction conditions as the HMF case. Cu-Ni/$TiO_2$ catalysts showed similar activity and methyl furans (MF + DMF) selectivity, as compared to the separate processing of HMF and FF. Moreover the mechanism towards to methyl furans (MF and DMF) didn't change when co-processing FF and HMF, by comparing the time evolution of intermediate products to the single reactant processing reactions. Though HMF conversion (100%, 2h) was complete at short time, maximum yields of MF (80.3%) and DMF (73.9%) were obtained after 6h. Finally, we achieved our targets with Cu(5 wt%) – Ni(5 wt%)/$TiO_2$ catalysts with 1, 4 dioxane as solvent at 200°C, 25 bar hydrogen pressure, 8h reaction time. This was, to the best of our knowledge, the first example of co-processing HMF and FF to achieve high yields of methyl furans (MF and DMF), and was enabled by a unique interaction of bimetallic Cu-Ni catalysts on $TiO_2$ supports.




**Scheme 2-1**: Hydrodeoxygenation of HMF to its derivatives

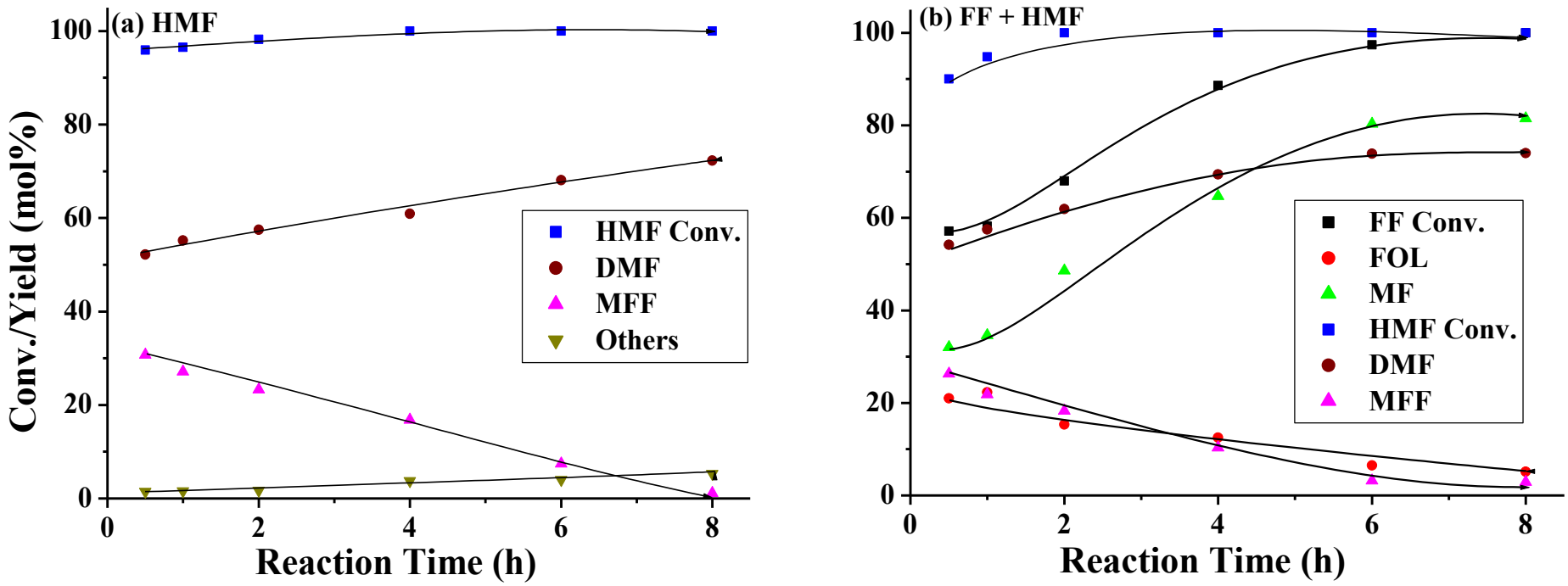



**Figure 2-3.** As a function of time HMF and HMF+FF conversion over Ni(5 wt%)-Cu(5 wt%)/$TiO_2$ catalyst.
**Reaction conditions**: (a) HMF = 0.5 g, (b) FF = 0.5 g and HMF = 0.250 g, Catalyst (Ni(5 wt%) – Cu(5 wt%)/$TiO_2$) = 0.300 g, Solvent (1, 4 Dioxane) = 25 ml, Temperature = 200° C, Pressure ($H_2$ gas) = 25 bar. HMF = 5-Hydroxy methylfurfural, DMF = Dimethyl furan, MFF = Methyl furfural. Others = Tetrahydrofurfuryl alcohol + Pentanols + 1, 2 Pentane diols + Hexane diols

Fuel catalyst recyclability tests were performed. The results in Figure 2-4(b) suggest the catalyst did not lose reactivity. However, selectivity towards MF (methyl furan) dropped with increasing number of recycles, while the FOL (furfuryl alcohol) and THFOL (tetrahydrofurfuryl alcohol) production increased. Regeneration of Cu-Ni/$TiO_2$ significantly increased the MF selectivity to close to the values for the fresh catalyst, although there was also some increase in THFOL (tetrahydrofurfuryl alcohol) formation. This result suggests that calcination/reduction regeneration protocols can be effective in reforming the Cu-Ni surface segregated structures to restore high activity and selectivity for MF formation. However, the regeneration did not completely reverse surface Ni exposure. These results demonstrate superior stability and regenerability for the Cu-Ni/$TiO_2$ catalyst compared to monometallic Cu catalysts.

Monometallic Cu catalyst recyclability studies revealed that Cu/$TiO_2$ (Figure 2-4a) was not as stable as Cu-Ni/$TiO_2$ under FF hydrogenation conditions, and furthermore that regeneration of Cu-Ni/$TiO_2$ resulted in MF selectivity close to that for the fresh catalyst, which was not the case of Cu/$TiO_2$. Because sintering is known to be the primary catalyst degradation mechanism for Cu under FF hydrogenation reaction conditions and lower MF yields are consistent with the decreased Cu surface area observed for Cu/$TiO_2$ after regeneration, it can be concluded that sintering occurred for this catalyst. However, for Cu-Ni/$TiO_2$, stability was enhanced compared to Cu/$TiO_2$ and catalyst regeneration restored MF selectivity to that of the fresh catalyst.

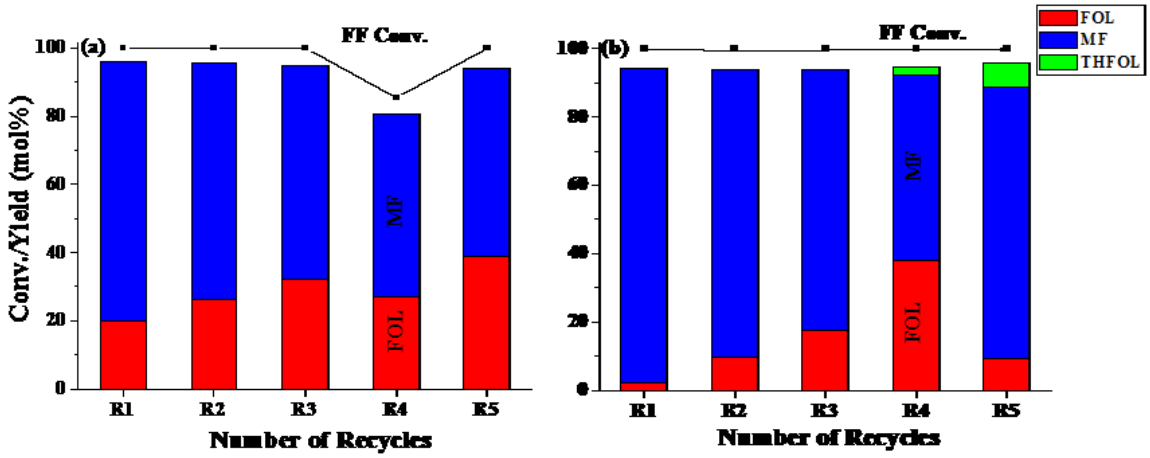



**Figure 2-4.** FF conversion and product yields as a function of number of catalyst recycles, R, for (a) Cu/$TiO_2$ and (b) Cu-Ni/$TiO_2$ catalysts. Reaction conditions: FF loading of 1 g, catalyst loading of 0.3 g, 25 mL of 1,4 Dioxane as solvent, temperature of 200 ºC, $H_2$ pressure of 25 bar, and 8 hour run time.
After R4, both Cu-Ni/$TiO_2$ and Cu/$TiO_2$ catalysts were calcined at 450 °C for 5 hours and reduced at 450 °C for 3 hours under $H_2$ flow (50ml/min) prior to R5

For optimizing the extraction of FF and HMF from the CELF liquor, two initial methods were proposed and had successfully achieved target of >90% extraction of FF and HMF from CELF process. The initial methods are outlined in Figure 2-5 below:

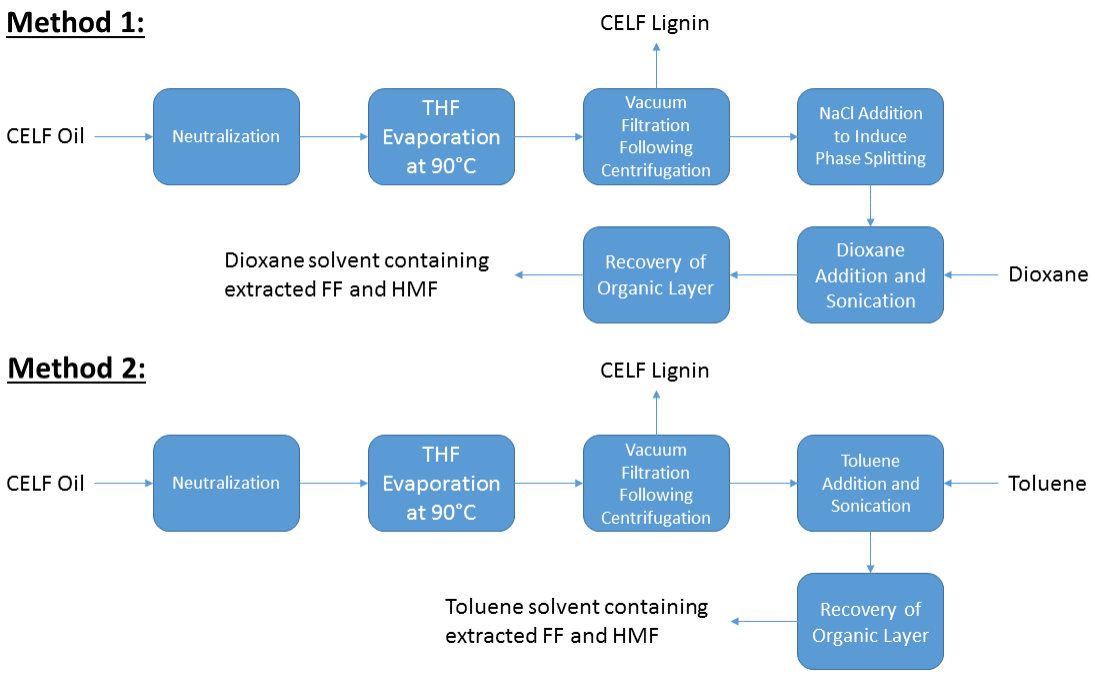



**Figure 2-5.** Two experimental methods validated for the solvent extraction of HMF and FF from the raw CELF liquor stream at over 95% extraction efficiencies.

Method 1: Consisting of phase splitting of dioxane with salt addition.

Method 2: Consisting of solvent extraction by toluene without salt addition.

As mentioned earlier**,** we followed the same reaction conditions to test the recyclability of Cu (5 wt%) – Ni (5 wt%)/$TiO_2$ and Cu (5 wt%)/$TiO_2$ catalysts for HDO (*hydrodeoxygenation*) of FF (furfural) (*see Figure 2-2 below*). Cu (5 wt%) – Ni (5 wt%)/$TiO_2$ showed stable activity and 100% FF conversion for the four consecutive recycle experiments reported in Figure 2-5(b).

**REDACTED TEXT**

**REDACTED FIGURE**

**REDACTED TABLE**

As a result of reaction tuning, our initial attempts had successfully achieved >60% yields of MF and DMF from CELF extracted FF and HMF using the previously described Cu(5%)-Ni(5%)/$TiO_2$ catalyst at 35 bar of $H_2$ pressure and 220 °C reaction temperature for 8 hours. We first optimized the solvent extraction process of FF and HMF from raw CELF liquor/oil stream. First, THF was separated from the CELF liquor by rotary evaporator (rotavap) and the resulting aqueous hydrolysate was vacuum filtered to separate the solid-lignin. The aqueous filtrate contains HMF, FF, soluble lignin, soluble oligomeric sugars, iron hydroxides and chloride ions. Toluene was then added to the obtained aqueous hydrolysate (25 g) to crash out remain lignin

and oligomeric sugars into an aqueous phase. The solids were then separated by filtration and ~95% of FF and 30-35% of HMF were extracted in to toluene phase (organic phase). Further, adding dioxane to biphasic CELF liquor enhanced the organic phase extracted HMF. Then, $Ca(OH)_2$ was added to neutralize and detoxify the CELF extracted-stream from pH-3 to pH-7. The organic phase (toluene+dioxane) was separated from the aqueous-phase and treated with activated carbon to remove chloride ions. The resulted liquid fraction was used for the HDO of FF and HMF reaction on Cu and Cu-Ni on $TiO_2$ and $Al_2O_3$ catalysts. All reactions described below were executed using the extracted FF and HMF from CELF, as just described.

Monometallic Cu catalysts supported on $TiO_2$ and $Al_2O_3$ achieved complete conversions of FF and HMF (Table 2-4). However, FOL was the major product from FF and similar amounts of BHMF and DMF were produced from HMF. The quantified product yields from HMF hydrodeoxygenation (HDO) on Cu catalysts were below 50%, suggesting that HMF degraded into side products under these reaction conditions instead forming the desired products. The addition of Ni to Cu-Ni on $TiO_2$ showed a positive influence on MF and DMF yields. 70.8% yield of MF and 55.8% yield of DMF were obtained from FF and HMF respectively, over a Cu(5%)-Ni(3%)/$TiO_2$ catalyst. Further increasing the Ni loadings to 5% at Cu (5%) on $TiO_2$ resulted greater than 60% yields of MF and DMF. After this first optimization, we were later able to increase the co-production yields of MF and DMF from CELF-extracted FF and HMF to above 80% for both. The final results can be found in our recent publication[3].

**Table 2-4 Product Yields from HDO of CELF Oil Products Temperature Variation**

| S.No. | Catalysts | FF Conv. | Product Yields (mol %) | | HMF Conv. | Product Yields (mol %) | |
|---|---|---|---|---|---|---|---|
| | | | FOL | MF | | BHMF | DMF |
| 1 | Cu(10%)/$Al_2O_3$ | 100 | 73.6 | 11.8 | 100 | 27.8 | 23.4 |
| 2 | Cu(10%)/$TiO_2$ | 100 | 55.1 | 18.3 | 100 | 20.4 | 18.5 |
| 3 | Cu(5%)-Ni(3%)/$TiO_2$ | 100 | 0.0 | 70.8 | 100 | 0.0 | 55.8 |
| 4 | Cu(5%)-Ni(5%)/$TiO_2$ | 100 | 4.2 | 78.9 | 100 | 7.4 | 65.3 |

Reaction conditions: Dioxane and toluene extracted FF and HMF from CELF stream = 25 ml, additives = 0.1 g of $Ca(OH)_2$, Temperature = 220 °C, $H_2$-pressure = 35 bar, Time = 8 h. FF = furfural, FOL = furfuryl alcohol, MF = methyl furan, HMF = 5-hydroxymethylfurfural, BHMF = bis(hydroxymethyl) furan, DMF = dimethyl furan.

For a secondary objective in Task 2, we proposed the potential for conversion of MF to alcohols if that were a more desired transportation fuel. For this independent study, we aimed to and achieved >70% yields of 2-pentanols from MF using a Cu(5%)-Co(5%)/$TiO_2$ catalyst at 35 bar of $H_2$ pressure and 240 °C reaction temperature at 8 hours. In addition, we have also achieved >65% yields of 2-pentanols from FF in one-step reaction over Cu(5%)-Co(5%)/$Al_2O_3$ catalyst at 240 °C, 35 bar $H_2$ pressure at 12 hours reaction time. The full results of this study can be found in our publications[6].

## Task 3 – Characterize and valorize lignin extracted from CELF to realize higher value in a true biorefinery than can be realized by use as a boiler fuel

For Task 3, CELF lignin samples were first isolated under different pretreatment conditions and analyzed for purity and key lignin functional structural features by ash analysis, sugar profiles, and well-established NMR methodologies to select for optimal reaction conditions.
Then, different methods used to isolate CELF lignin from THF liquid phase including dilution, boiling, sonication, filtration and centrifugation were compared. Water dilution factor (5x and 10x) was found to have neglect impact on the CELF lignin molecular weight, inter-linkages distribution, and hydroxyl groups contents (sample 1 vs. 2, 6 vs. 7, and 9 vs. 10 in Table 3-3, 3-4 and Figure 3-1). Similarly, centrifugation and filtration resulted in CELF lignin with very similar structural features (sample 9 vs. 6 and 10 vs. 7). Compared to dilution method, boiling the THF solution generated CELF lignin with much lower molecular weight (sample 3 vs 1 and 2, sample 8 vs. 6, 7, 9 and 10 in Table 3-3). The following sonication further decreases the lignin molecular weight (sample 5 vs. 4 in Table 3-3). 2D HSQC NMR analysis revealed that boiling method slightly decreases the β-O-4 inter-linkages, while sonication further decreases the β-O-4 to a larger extent (sample 8 in Table 3-4). $^{31}$P NMR technique indicated that sonication slightly decreases aliphatic OH content and increases $C_5$ substitute OH content (sample 4 vs. 5 and 8 vs. 6, 7, 9 and 10 in Figure 3-1). In conclusion, sonication proved to be a useful method to further depolymerize the lignin for the following catalytic conversion process

In the reaction conditions listed in Table 3-1 and extraction methods listed in Table 3-2, dilution and boiling are the two methods to precipitate CELF lignin whereas filtration and centrifugation are the solid-liquid separation steps to isolate the precipitated CELF lignin. In dilution method, the hydrolysate was diluted with either 5 or 10 times of water to precipitate the soluble lignin out. In boiling method, the hydrolysate was boiled at 76 $^{O}$C for 3 hours to evaporate THF. The residue was then used to isolate lignin using two different methods: acetone dissolving and sonication. In all the methods, lignin was subjected to 1 L of water wash and 100 mL of diethyl ether wash to remove all the poplar and non-poplar impurities, respectively. NMR data of the characterized lignin samples is shown in Table 3-4 and Figure 3-1.

**Table 3-1.** CELF pretreatment conditions.

| Pretreatment condition | Feedstock | Temperature | Time (min) | Solids loading | THF/water | Acid | Conc. |
|---|---|---|---|---|---|---|---|
| A | Poplar | 160 | 15 | 10% | 1:1 | $H_2SO_4$ | 0.5% |
| B | Poplar | 180 | 30 | 5% | 4:1 | $FeCl_3.6H_2O$ | 1% |
| C | Maple | 160 | 15 | 10% | 1:1 | $H_2SO_4$ | 0.5% |

**Table 3-2.** Extraction methods used to isolate CELF lignin from THF

| Sample | Pretreatment conditions | Extraction method |
|---|---|---|
| 1 | A | Dilution (5x) – Filter |
| 2 | A | Dilution (10x) – Filter |
| 3 | A | Boil – Sonication 0min |
| 4 | B | Boil – Sonication 0min |
| 5 | B | Boil – Sonication 15min |
| 6 | C | Dilution (5x) – Filter |
| 7 | C | Dilution (10x) – Filter |

| | | |
|---|---|---|
| 8 | C | Boil – Sonication 5min |
| 9 | C | Dilution (5x) – Centrifuge |
| 10 | C | Dilution (10x) – Centrifuge |

**Table 3-3**. GPC molecular weight analysis of CELF lignin samples

| Sample | $M_w$ | $M_n$ | PDI |
|---|---|---|---|
| 1 | 3691 | 1837 | 2.01 |
| 2 | 3752 | 1879 | 2.00 |
| 3 | 3036 | 1675 | 1.81 |
| 4 | 2377 | 1483 | 1.60 |
| 5 | 1862 | 1183 | 1.57 |
| 6 | 3850 | 1839 | 2.09 |
| 7 | 3984 | 1873 | 2.13 |
| 8 | 3814 | 1857 | 2.05 |
| 9 | 3772 | 1816 | 2.08 |
| 10 | 3916 | 1871 | 2.09 |

**Table 3-4.** Semi-quantitative information for lignin subunits and inter-linkages of CELF lignin by HSQC NMR technique.

| Sample | Lignin subunits | | | Lignin inter-linkages | | |
|---|---|---|---|---|---|---|
| | Syringyl | Guaiacyl | S/G | β-O-4 | α-O-4/β- 5 | β- β |
| 1 | 54.3% | 45.7% | 1.19 | 16.1% | 1.87% | 5.12% |
| 2 | 55.6% | 44.4% | 1.25 | 15.3% | 2.48% | 4.88% |
| 3 | 59.3% | 40.7% | 1.45 | 15.2% | 1.40% | 4.77% |
| 4 | 93.1% | 6.89% | 13.5 | 0 | 0 | 7.32% |
| 5 | 88.3% | 11.7% | 7.58 | 0 | 0 | 5.38% |
| 6 | 66.5% | 33.5% | 1.99 | 23.3% | 4.31% | 4.76% |
| 7 | 57.6% | 42.4% | 1.36 | 19.8% | 3.21% | 4.55% |
| 8 | 65.5% | 34.5% | 1.90 | 16.6% | 2.69% | 4.59% |
| 9 | 60.2% | 39.8% | 1.51 | 20.0% | 3.11% | 4.55% |
| 10 | 58.6% | 41.4% | 1.42 | 20.6% | 3.37% | 3.83% |

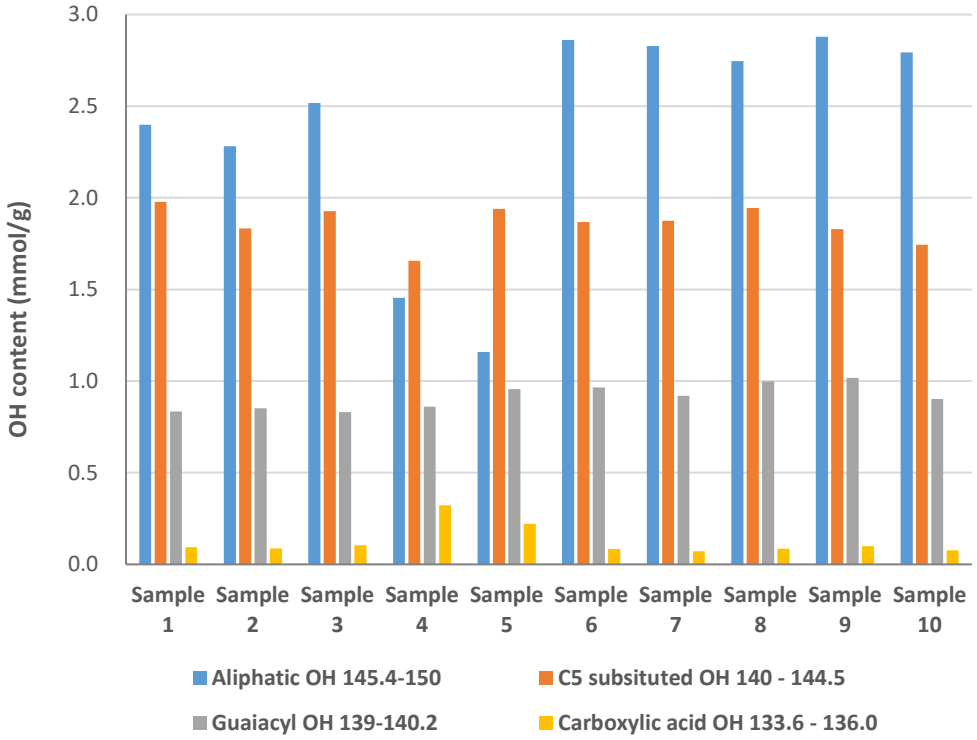



**Figure 3-1**. Hydroxyl group contents of CELF lignin as calculated by $^{31}P$ NMR technique.

For the samples described in Table 3-5, the impact of sonication time and acid catalyst was studied. The CELF lignin samples were all isolated by boiling 100 g of hydrolysate at 76 ºC for 6 hours and then sonicated for the times indicated. All the samples were also neutralized before boiling to prevent unwanted degradation. After boiling, the lignin samples were washed with dimethyl ether and water to remove other impurities. HSQC NMR was then run on the lignin samples. The purpose of the NMR characterization was to determine whether the catalyst ($FeCl_3$) was the major reason causing the cleavage of β-O-4 inter-linkages during CELF reaction. GPC data is shown in Table 3-6, NMR data is shown in Table 3-7 and Figure 3-2. The final results can be found in our publications[7].

**Table 3-5**. CELF pretreatment conditions.

| Pretreatment condition | Feedstock | Temperature | Time (min) | Sonic. t (min) | THF/water | Catalyst | Conc. |
|---|---|---|---|---|---|---|---|
| 1 | Poplar | 180 | 20 | 0 | 4:1 | $H_2SO_4$ | 1 % |
| 2 | Poplar | 180 | 20 | 5 | 4:1 | $H_2SO_4$ | 1% |
| 3 | Poplar | 180 | 20 | 10 | 4:1 | $H_2SO_4$ | 1% |
| 4 | Poplar | 180 | 20 | 15 | 4:1 | $H_2SO_4$ | 1% |
| 5 | Poplar | 180 | 20 | 0 | 4:1 | $FeCl_3.6H_2O$ | 1% |

**Table 3-6**. GPC molecular weight analysis of CELF lignin samples

| Sample | Mw | Mn | PDI |
|---|---|---|---|
| 1 | 1455 | 1011 | 2.01 |

| | | | |
|---|---|---|---|
| 2 | 1375 | 945 | 2.00 |
| 3 | 1372 | 969 | 1.81 |
| 4 | 1357 | 965 | 1.60 |
| 5 | 1447 | 1031 | 1.57 |

**Table 3-7**. Semi-quantitative information for lignin subunits and inter-linkages of CELF lignin by HSQC NMR technique.

| Sample | Lignin subunits | | | Lignin inter-linkages | | |
|---|---|---|---|---|---|---|
| | Syringyl | Guaiacyl | S/G | β-O-4 | α-O-4/β- 5 | β- β |
| 1 | 85.0% | 14.9% | 5.68 | 0 | 0 | 2.75% |
| 2 | 85.1% | 14.8% | 5.73 | 0 | 0 | 3.25 % |
| 3 | 82.0% | 14.0% | 5.86 | 0 | 0 | 2.43% |
| 4 | 86.1% | 13.9% | 6.19 | 0 | 0 | 2.70% |
| 5 | 84.0% | 16.0% | 5.26 | 0 | 0 | 2.08% |

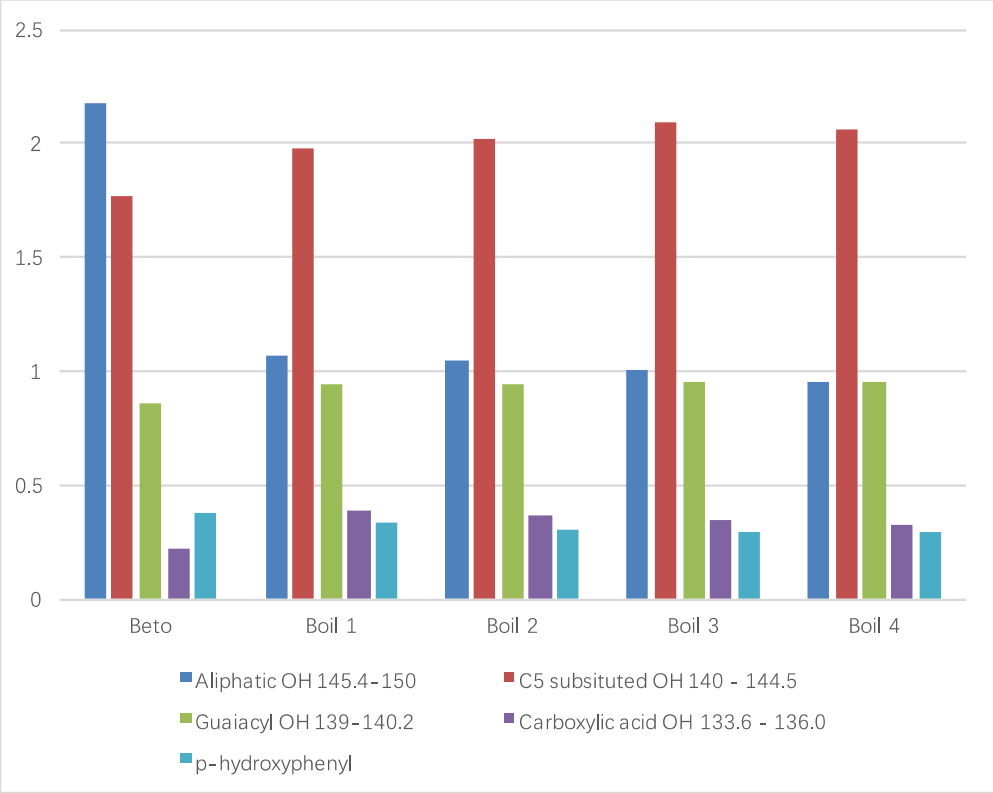



**Figure 3-2.** Hydroxyl group contents of CELF lignin as calculated by $^{31}P$ NMR technique. BETO sample is sample 5 performed at optimum conditions as described in Milestone 1.2.1.

After a deep literature dive, we have selected the following most promising catalysts and solvent systems for the valorization of CELF lignin through two pathways:

**Pathway 1:** Oxidative fragmentation of CELF lignin into bio-oil
The following catalysts system has been proposed from literature and purchased from Sigma.

1). NiO-MoO3/AC (activated charcoal), CoO-MoO3/AC, methanol
2). Iodine – Sodium borohydride, ethanol
3). Pd/C, Pt/C, Ru/C and Rh/C, isopropanol system

**Pathway 2:** Catalytic hydrodeoxygenation of CELF lignin into cyclohexyl alkanes

Copper-doped porous metal oxide (Cu20-PMO) catalyst was synthesized at University of California Riverside (UCR) and delivered to University of Tennessee Knoxville (UTK) as needed during the project.

Solvent –based extraction were applied to fractionate low MW components from CELF lignin from the high MW parts. ~50 mg of CELF lignin was extracted with 10 mL of different solvents (water, acetone, THF, methanol, ethanol, isopropyl alcohol, toluene, commercial 100% gasoline, and diesel) at room temperature for 24 h with data shown in Table 3-8. The undissolved part was isolated by centrifuge and the solid dissolved in liquid phase was separated by rotor evaporation. Both dissolved and undissolved MW parts were subjected to GPC (Table 3-9), HSQC (Table 3-10) and $^{31}$P NMR (Figure 3-4) analysis for molecular weight and chemical functionality. THF was found to fully dissolve the CELF lignin as expected. Gasoline and diesel cannot dissolve CELF lignin at all, and only ~3% and ~7% of CELF lignin was dissolved in toluene and water, respectively. The molecular weights ($M_w$) of CELF lignin dissolved in water and toluene are 512 and 1015 g/mol, and both are lower than the original lignin resource (1536 g/mol). However, their undissolved parts only slightly increase the $M_w$ from 1536 g/mol to 1584 and 1821 g/mol for water and toluene extraction, respectively. On the other hand, ~75% of CELF lignin was dissolved in acetone, and the higher MW parts turn out to be the lignin dissolved in acetone with a molecular weight of 1560 g/mol. The best solvents tested in this study in terms of low and high MW separation are alcohol solvent. Methanol, ethanol and isopropyl alcohol are all well qualified to dissolve the lower MW parts of CELF lignin. For example, ethanol-dissolved CELF lignin known as the low MW parts has a molecular weight ($M_w$) of 1318 g/mol, while the undissolved component has a much higher MW of 3119 g/mol. Further advanced NMR analysis revealed that the low MW fraction had a higher Syringyl and lower Guaiacyl content therefore a higher S/G ratio, while the high MW fraction components had significantly lower amount of p-hydroxylbenzoate. In addition, alcohol dissolved lower MW CELF lignin was also found to have higher aliphatic, phenolic and carboxylic acid OH content.

A precipitative distillation fractionation technique was then applied to fractionate ethanol soluble "low MW" components of CELF lignin using various solvents. Methanol, ethanol, and isopropyl alcohol were identified to dissolved the lower molecular weight (MW) parts of CELF lignin. CELF lignin fractions with different molecular weight were prepared using THF/water mixture as further outlined in the Figure 3-3. A step-wise THF/water fractionation was applied to the "low" MW components by successive dilution of THF by addition of water, and the high MW components was delivered to Milestone 3.2.2. The final results can be found in our publication[8].

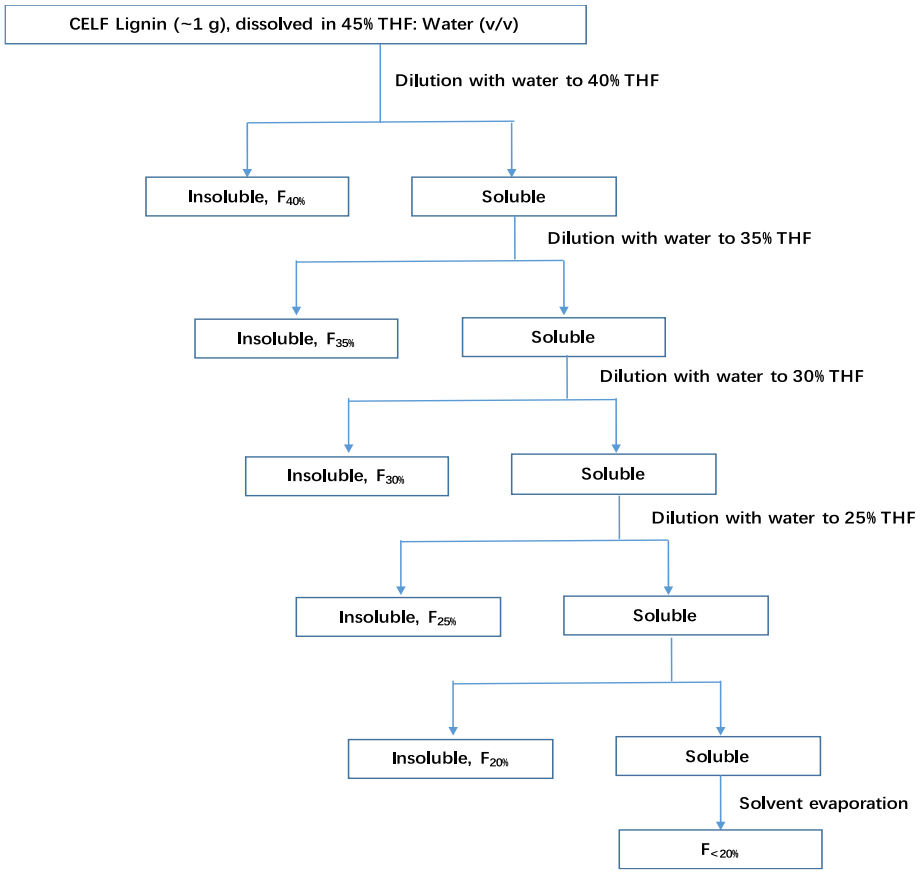



**Figure 3-3.** Lignin fractionation procedures using THF:Water mixture.

Solvent –based extraction was applied to fractionate the low MW components from CELF lignin from the high MW cuts. ~50 mg of CELF lignin was extracted with 10 mL of different solvents at room temperature for 24 h. The undissolved part was isolated by centrifuge and the solid dissolved in liquid phase was rotor evaporated. Both low and high MW parts were subjected to GPC, HSQC and $^{31}$P NMR analysis for molecular weight and chemical functionality.

**Table 3-8.** Solvent used to extract CELF lignin.

| Solvent | Sample weight (mg) | Dissolved weight (mg) | Undissolved weight (mg) |
|---|---|---|---|
| Water | 50.7 | 3.5 | 47.2 |
| Acetone | 50.6 | 37.8 | 19.8 |
| Methanol | 51.6 | 41.2 | 10.4 |
| Ethanol | 100 | 61.2 | 39.8 |
| Isopropyl alcohol | 50.7 | 29.3 | 21.4 |
| Toluene | 52.0 | 1.57 | 50.4 |
| Gasoline (100%) | 52.3 | 0 | 52.3 |
| Diesel | 54.6 | 0 | 54.6 |
| THF | 74.5 | 74.5 | 0 |

**Table 3-9.** GPC molecular weight analysis of solvent-extracted CELF lignin samples.

| Solvent | | $M_w$ | $M_n$ | PDI |
|---|---|---|---|---|
| Original Lignin source | | 1536 | 699 | 2.20 |
| Water | Dissolved | 512 | 199 | 2.57 |
| | Undissolved | 1584 | 839 | 1.89 |
| Acetone | Dissolved | 1560 | 874 | 1.78 |
| | Undissolved | 1156 | 714 | 1.62 |
| Methanol | Dissolved | 1369 | 763 | 1.79 |
| | Undissolved | 2968 | 1493 | 1.98 |
| Ethanol | Dissolved | 1318 | 756 | 1.74 |
| | Undissolved | 3119 | 1434 | 2.18 |
| Isopropyl alcohol | Dissolved | 1009 | 686 | 1.47 |
| | Undissolved | 2332 | 1240 | 1.88 |
| Toluene | Dissolved | 1015 | 630 | 1.61 |
| | Undissolved | 1821 | 874 | 2.08 |
| Gasoline | Dissolved | N/A | N/A | N/A |
| | Undissolved | 1563 | 679 | 2.30 |
| Diesel | Dissolved | N/A | N/A | N/A |
| | Undissolved | 1593 | 653 | 2.44 |
| THF | Dissolved | 1476 | 752 | 1.96 |
| | Undissolved | N/A | N/A | N/A |

**Table 3-10.** Semi-quantitative information for lignin subunits and inter-linkages of ethanol dissolved and undissolved CELF lignin by HSQC NMR technique

| Sample | Lignin subunits | | | | Lignin inter-linkages | | |
|---|---|---|---|---|---|---|---|
| | Syringyl | Guaiacyl | S/G | p-hydroxybenzoate | β-O-4 | α-O-4/β- 5 | β- β |
| Dissolved | 63.8% | 36.2% | 1.76 | 31.4% | 0 | 0 | 0.58% |
| Undissolved | 51.8% | 48.2% | 1.08 | 18.5 | 0 | 0 | 1.34% |

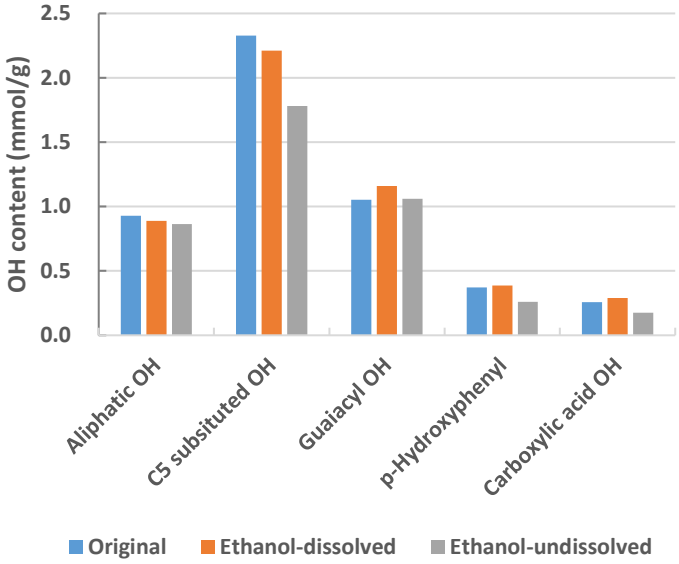



**Figure 3-4**. Hydroxyl group contents of ethanol dissolved and undissolved CELF lignin as calculated by $^{31}P$ NMR technique.

We then further fractionated the ethanol soluble "low MW" lignin fraction by fractional dilution of THF by addition of water. Different concentrations of THF in water ranging from 20 to 45% (v/v) were prepared for further fractionation of the low MW CELF lignin as detailed in Figure 3-3 with GPC data shown in Table 3-11. Higher concentration of THF was found to dissolve higher molecular weight fractions of the ethanol soluble lignin. Consequently, the polydispersity index (PDI) decreases. In conclusion, our proposed strategy for complete fractionation of CELF lignin will be first to extract the water-soluble fraction with $H_2O$ that removes the lowest MW fraction. The water insoluble CELF lignin would then be extracted with ethanol, and the ethanol-dissolved and undissolved part are defined as the low and high MW CELF lignin, respectively. The low MW ethanol-soluble CELF lignin fraction would then be further fractionated by dilution of THF in water. With reduction of THF proportion from 45%, CELF lignin starts to precipitate partially. A higher proportion of THF in water dissolved higher MW fractions of the lignin. The molecular weights of different low MW fractions were in the range of 493 -1353 g/mol for CELF lignin. In summary, the proposed lignin fractionation strategies produced the most number of distinct fractional cuts from original CELF lignin with each unique fraction exhibiting a narrow distribution of MWs and chemical functionalities. **The result is an ability to funnel different MW lignin fractions extracted from biomass to different valorization methods resulting in much higher utilization of lignin to co-products or fuels than without lignin fractionation. (Ct-C Lignin Valorization)**

**Table 3-11**. GPC molecular weight analysis of CELF lignin samples

| Sample | $M_w$ | $M_n$ | PDI |
|---|---|---|---|
| F40 | 1353 | 976 | 1.39 |
| F35 | 1047 | 849 | 1.23 |
| F30 | 928 | 771 | 1.2 |
| F25 | 819 | 708 | 1.16 |

| | | | |
|---|---|---|---|
| F20 | 774 | 686 | 1.13 |
| F<20 | 493 | 394 | 1.25 |
| $H_2O$ soluble | 245 | 113 | 2.17 |

The high-MW fraction of CELF lignin was further subjected to a one-pot catalytic hydrocracking reaction over supported noble metal catalysts in isopropanol system as outlined in Table 3-12. Catalysts used were: Pt/C, Pd/C, Ru/C, and Rh/C. Initial experiments were performed to study the influence of temperature on bio-oil yield. The results suggested that the yield of bio-oil increased and char formation decreased with the temperature increasing from 250 to 350°C. All the catalysts substantially improved the bio-oil formation with Ru/C being the best, yielding 43.5% bio-oils.

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**REDACTED FIGURES**

### *Supplementary Information*

**REDACTED TEXT**

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## Task 4 – Design cellulosic biomass conversion processes based on CELF technology linked with catalytic conversion to fuels and lignin valorization to track progress and define opportunities to reduce costs.

For Task 4, we have decided to complete an overall plant model for the fully integrated plant (not just the CELF process alone) for both the sulfuric acid-based case as well as the FeCl3-based case. This way, we can perform sensitivity analysis on the operating margins of the plant based on the sale of products and cost of input streams to down select the superior process model for a more in-depth development of a single plant model. We scaled the model plant from 288 bone dry tonnes per day (BDTPD) capacity for the first two comparison models built up to 1920 BDTPD (or 80 BDT/hr) for the final plant model that incorporated subsequent changes to solvent extraction, catalytic conversion, and product recovery as informed by development of our experimental results. In this unique arrangement, not only did our computer model evolve over the course of the project, but it also helped us to make key decisions on the types of processes, solvents, and catalysts that minimized fixed costs and reduced the selling price of the final fuels.

Process analysis was first performed to determine the economic viability of metal halide catalyzed CELF process to produce methylated furan gasoline blends from poplar wood and

compare it with sulfuric acid catalyzed CELF process. As we continue to build our process model, it was more logical to first perform a high level sensitivity analysis and overall economic evaluation based on operating margin for the two cases (sulfuric acid vs. metal halide catalyzed plant processes) such we could determine which case was superior. Although our milestones indicate the development of two separate process models, we believe this would no longer be necessary from the cash balance analysis presented here, clearly outlining that the $FeCl_3$-catalyzed case is superior to the sulfuric acid-based plant (Figure 4-2). This way, instead of building two completely separate and full plant models for both cases, we can select the superior process at this stage ($FeCl_3$ catalyzed plant) and put forth our fullest effort to refining one plant model. This process combined experimental data from two studies:

1. Poplar wood to FF and HMF using 4:1 THF-to-water ratio and ferric chloride hexahydrate as the metal halide catalyst ($FeCl_3.6H_2O$)
2. Catalytic conversion of FF and HMF to 2-methylfuran (MF), 2-methyl tetrahydrofuran (MTHF), 2,5-dimethylfuran (DMF), and 2,5-dimethyl tetrahydrofuran (DMTHF) using Ni-Cu bimetallic catalyst supported on $TiO_2$.

The plant capacity was 288 dry metric tons/day of biomass assuming 20% solids loading per ton of total feed. Figure 4-1 shows the first preliminary plant model which includes 4 major areas: pretreatment, lignin extraction and acid regeneration, catalytic upgrading, and product recovery. Ancillary areas such as feed storage and waste water treatment are also included in the design. Newly included is a "salting out" process step (Area 200, Figure 4-1) to enhance lignin precipitation and a base neutralization step to produce $Fe_2O_3$ (rust). Afterwards, HCl is added to $Fe_2O_3$ to regenerate $FeCl_3$ catalyst for reintroduction back to the CELF reaction upstream. Another new process unit added is a room-temperature biphasic extraction vessel (Area 300, Figure 4-1) that utilized dioxane to extract FF and HMF from a salted-out hydrolysate stream into a water-free organic layer that is more suitable for catalytic upgrading to methylated furans. This strategy has been demonstrated in the lab and presents a good first option for partitioning the water/organic layers to support full plant integration of the CELF and Catalytic Upgrading processes. If the MF and DMF yields are less than ideal from this extraction process, we will investigate more expensive distillation/pervaporation methods to de-water our raw effluent.

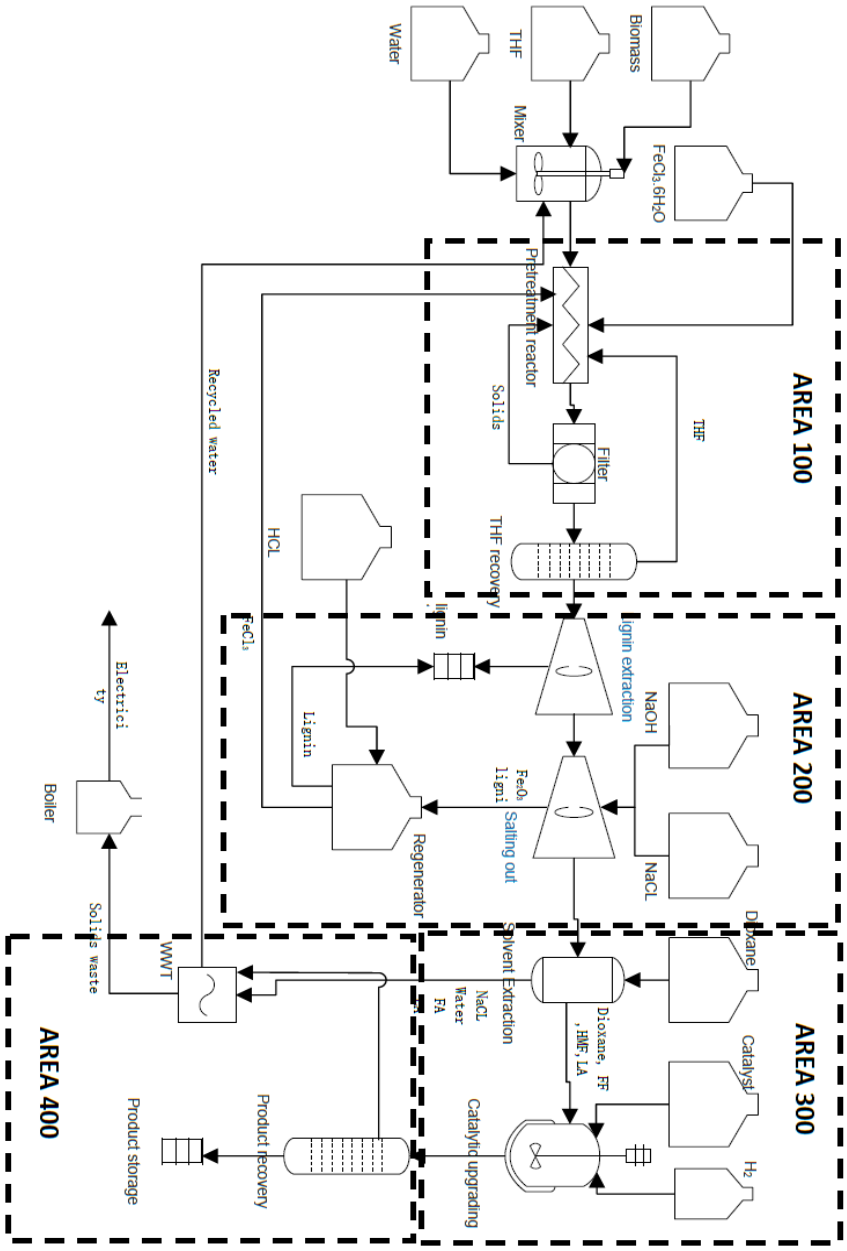


**Figure 4-1** Preliminary process flow diagram for the integrated process using $FeCl_3$ catalyst and integrated THF, dioxane, and $FeCl_3$ recovery loop.

**REDACTED TEXT**

**REDACTED TABLES**

**REDACTED FIGURES**

For calculating MFSP, variable operating costs, fixed operating costs and total capital investment would have to be determined. Table 4-5, shows the summary of the cost associated with different areas in the plant. The colored regions in the table indicate the total equipment cost which are then added with other direct and indirect cost to determine Fixed capital investment (FCI).

*Process and Economic Assumptions:*
The fixed and variable operating costs are based on previous model, however with plant capacity modified from 12 BDT/hr. of raw biomass to 80 BDT/hr. The assumptions involved in calculating MFSP such as discount rate, depreciation method, income tax rate and plant life are directly based of NREL's model. All the calculations for fixed and variable operating costs are based on base case scenario which assumes feedstock cost to be $60/BDT, lignin selling price of $500/tonne and furan selling price of $600/tonne as summarized in Table 4-5.

It is assumed that 40% of the financing would be done by equity and a loan would be taken for remaining 60% at 8% interest for 10years. Table 4.2 illustrates all the assumptions involved in the calculations of MFSP. Since previous reports have been based on $/tonne of furans produced, gasoline API gravity of 0.77 kg/liter is assumed to calculate MSP in terms of $/gallon of furans.

*Analysis:*
The MFSP at the base case scenario was calculated to be $1.91/gallon. The MFSP of $1.91 is lower than $2.15 from NREL's model, the main reason being the by-product credit obtained by lignin valorization. Thus, a sensitivity of MFSP to lignin price was conducted to evaluate the plant economics if lignin is just burnt for fuel ($20/tonne) or it is sold as phenol substitutes ($800/tonne).

Figure 4-4 demonstrated how lignin valorization has a major influence on achieving lower MFSP. **When lignin is burned as a boiler fuel its value can be assumed to be approximately $20/tonne, which results in a MFSP of $3.26/gallon in our plant model. However, when lignin is converted into a high value chemical such as a carbon composite precursor or jet fuel, it could be potentially sold at over $600/tonne which translates into MFSP of $1.63/gallon in our plant model. (Ct-F, Ct-B)** Thus, lignin conversion into high value chemicals is mandatory for sustenance of a biorefinery and compete with low crude oil prices, which are less than $50 per barrel of oil.

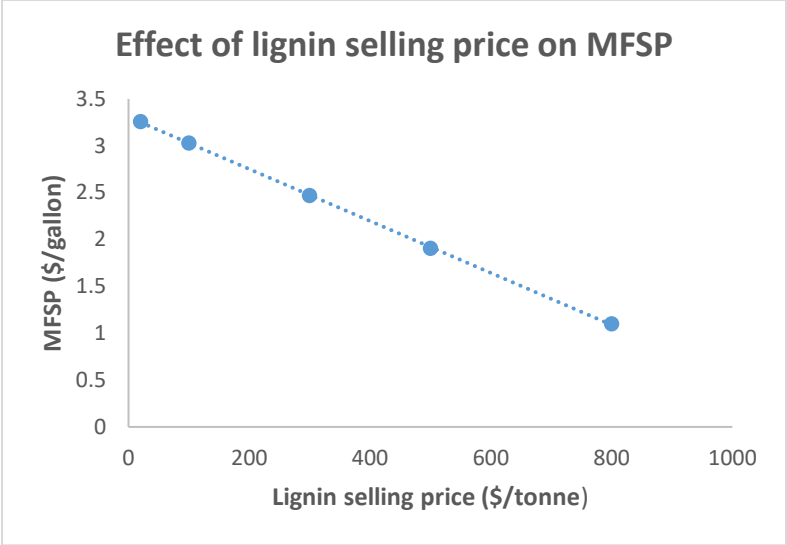


**Figure 4-4** Sensitivity analysis of MFSP to lignin price.

**REDACTED TEXT**

**REDACTED TABLES**

Based on the results of our plant model, we can claim that a >60% reduction in GHG could be achieved inside battery limits (IBL) by our advanced hybrid catalytic biorefinery model compared to an equivalently-sized conventional petroleum refinery due to two major dominating factors: 1) our hydrogen and energy consumption rates were lower than petroleum refineries, and 2) we had achieved a 60% carbon utilization from biomass into final fuel products, thus potentially displacing an equivalent number of fossil carbons.

A secondary objective for task 4 was to develop pumping technologies to insure that a high solids content wood-based slurry could be introduced at the pressures needed by the CELF reaction. This objective would be crucial to allow technology licensing, hand-off, and commercialization with our cost share partner MG Fuels. Due to initial technical difficulties with pump setup and operation at UCR, we have decided ask project cost-share partner MG Fuels, LLC (Northbrook, IL) to perform and complete wood slurry pumping at their pilot facility in Charlottesville, VA where they can operate two 5 GPH high pressure positive displacement (PD) Seepex pumps. The project PI and researcher worked with MG Fuels to complete the work.

The orifice of the MG Fuels PD pump was 2" and needed smaller than 1mm wood chip particle sizes. Thus, UCR prepared 10kg of 1mm wood chips and delivered to MG Fuels to accomplish Milestones 4.2.1. **REDACTED TEXT**

## Products Developed Under Project

### Publications

1. XM, AP, BS, RK, YP, CEW, CMC, AR. 2019. "Characterization of fractional cuts of co-solvent enhanced lignocellulosic fractionation lignin isolated by sequential precipitation". *Bioresource Technology*. 272, 202-208.
2. BS, RK, CMC, CEW, PC. 2019. "Single-step catalytic conversion of furfural to 2-pentanol over bimetallic Co–Cu catalysts". *Reaction Chemistry & Engineering*. 4, 261-267
3. BS, XM, AP, NN, RK, CEW, AR, PC, CMC. 2018. "Hybrid Catalytic Biorefining of Hardwood Biomass to Methylated Furans and Depolymerized Technical Lignin". *ACS Sustainable Chemistry & Engineering.* 6 (8), 10587–10594
4. MDS, CMC, XC, LP, JS. 2018. "Temperature-dependent phase behaviour of tetrahydrofuran–water alters solubilization of xylan to improve co-production of furfurals from lignocellulosic biomass". *Green Chemistry*. 20, 1612-1620.
5. XZM, AP, BS, RK, YP, CEW, CMC, AR. 2018. "Chemical transformations of poplar lignin during co-solvent enhanced lignocellulosic fractionation process". *ACS Sustainable Chemistry & Engineering.* 6 (7), 8711–8718
6. BS, CM Cai, RK, CEW, PC. 2017. "Effects of Cu-Ni bimetallic catalyst composition and support on activity, selectivity and stability for furfural conversion to 2-methyfuran". *ACS Sustainable Chemistry & Engineering*. 6, 2152-2161
7. BS, CM Cai, CEW, PC. 2017. "Support Induced Control of Surface Composition in Cu-Ni/TiO2 Catalysts Enables High Yield Co-Conversion of HMF and Furfural to Methylated Furans". *ACS Catalysis*. 7, 4070-4082.

### Networks and Collaborations

We partnered with Jeremy Smith's group at the Oak Ridge National Lab (ORNL) to simulate the interactions of co-solvents with biomass xylan and how it impacts the production of furfurals from biomass. The result is a peer-reviewed publication in *Green Chemistry* journal (#4 in Publications list).

### Technologies Used

The primary technology used in this project was the CELF process that was invented prior to this project (Patent: WO2014176531).

### New Inventions

1. UC 2017-488-2, titled CATALYST AND PROCESS FOR SIMULTANEOUS CONVERSION OF HYDROXYMETHYL FURFURAL AND FURFURAL TO METHYLATED FURANS, filed as U.S. Prov. App. 62/640,305 on 3/8/2018 with the USPTO, currently pending.
2. UC 2017-488-2, titled HYBRID CATALYTIC BIOREFINING OF HARDWOOD BIOMASS TO METHYLATED FURANS AND DEPLOYMERIZED TECHNICAL LIGNIN, filed as U.S. Prov. App. 62/640,406 on 3/8/2018 with the USPTO, currently pending.

## References:


1. Cai, C. M.; Zhang, T.; Kumar, R.; Wyman, C. E., THF co-solvent enhances hydrocarbon fuel precursor yields from lignocellulosic biomass. *Green Chemistry* **2013,** *15* (11), 3140-3145.
2. Cai, C. M.; Nagane, N.; Kumar, R.; Wyman, C. E., Coupling metal halides with a co-solvent to produce furfural and 5-HMF at high yields directly from lignocellulosic biomass as an integrated biofuels strategy. *Green Chemistry* **2014,** *16* (8), 3819-3829.
3. Seemala, B.; Meng, X.; Parikh, A.; Nagane, N.; Kumar, R.; Wyman, C. E.; Ragauskas, A.; Christopher, P.; Cai, C. M., Hybrid Catalytic Biorefining of Hardwood Biomass to Methylated Furans and Depolymerized Technical Lignin. *ACS Sustainable Chemistry & Engineering* **2018,** *6* (8), 10587-10594.
4. Seemala, B.; Cai, C. M.; Wyman, C. E.; Christopher, P., Support Induced Control of Surface Composition in Cu–Ni/TiO2 Catalysts Enables High Yield Co-Conversion of HMF and Furfural to Methylated Furans. *ACS Catalysis* **2017,** *7* (6), 4070-4082.
5. Seemala, B.; Cai, C. M.; Kumar, R.; Wyman, C. E.; Christopher, P., Effects of Cu–Ni Bimetallic Catalyst Composition and Support on Activity, Selectivity, and Stability for Furfural Conversion to 2-Methyfuran. *ACS Sustainable Chemistry & Engineering* **2018,** *6* (2), 2152-2161.
6. Seemala, B.; Kumar, R.; Cai, C. M.; Wyman, C. E.; Christopher, P., Single-step catalytic conversion of furfural to 2-pentanol over bimetallic Co–Cu catalysts. *Reaction Chemistry & Engineering* **2019,** *4* (2), 261-267.
7. Meng, X.; Parikh, A.; Seemala, B.; Kumar, R.; Pu, Y.; Christopher, P.; Wyman, C. E.; Cai, C. M.; Ragauskas, A. J., Chemical Transformations of Poplar Lignin during Cosolvent Enhanced Lignocellulosic Fractionation Process. *ACS Sustainable Chemistry & Engineering* **2018**.
8. Meng, X.; Parikh, A.; Seemala, B.; Kumar, R.; Pu, Y.; Wyman, C. E.; Cai, C. M.; Ragauskas, A. J., Characterization of fractional cuts of co-solvent enhanced lignocellulosic fractionation lignin isolated by sequential precipitation. *Bioresource Technology* **2019,** *272*, 202-208.