Final Technical Report
Department of Energy – Office of the Biomass Program

Project Title: Fractionation and Catalytic Upgrading of Bio-Oil
Award Number: EE0006287
Recipient: University of Oklahoma

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Executive Summary

The goal was to develop a biomass conversion process that optimizes fractionation and conversion to maximize Carbon efficiency and Hydrogen consumption to obtain drop-in fuels. Selective fractionation of raw biomass was obtained via multi-stage thermal fractionation to produce different streams that are enriched in a particular chemical family (acids, furanics or phenolics). These streams were later catalytically upgraded in both liquid and vapor phase to perform C-C bond formation and hydrodeoxygenation. Among various upgrading strategies investigated we have identified an effective path in which cyclopentanone is a crucial intermediate that can be derived from furfural and other furanics obtained in high concentrations from this thermal staged process. Cyclopentanone is a very versatile molecule, which can couple with itself to product high quality jet-fuel, or couple with phenolic or furanics to create long chain molecules. These (mono-oxygenated) compounds in the correct molecular weight fuel range can be hydrotreated to direct drop-in fuels. Interestingly, we have found that the conversion of furfural to cyclopentanone is not affected by the presence of acetic acid, and, more interestingly, it is enhanced by the presence of water. These are very significant findings, since water and acetic acid are always present in all streams from the primary conversion stage. These results have allowed to complete detailed life-cycle assessment and techno-economic analysis that have been back-fed to the experimentalists to refine the catalyst selection and process operations with the objective of maximizing C efficiency at minimum H utilization. These combined investigations have opened the possibility of an economically and technologically effective process that could result in commercial fuels produced from renewable sources at a cost that might be competitive with fossil fuels.

Goals and Actual Accomplishments

Goals

The current technologies for bio-oil upgrading, such as in-situ catalytic pyrolysis or ex-situ hydrotreating of pre-formed bio-oil suffer from low C-retention in the fuel range and high H consumption. A fundamental problem with these technologies is that the complex bio-oil presents different problems that cannot be solved with a single solution. Therefore, the goal of our project was to maximize C-retention in the fuel range at minimum H utilization via an effective fractionation strategy combined with catalytic upgrading. Specifically, selective fractionation of biomass pyrolysis products will be approached by two methods, thermal fractionation of raw biomass via torrefaction/pyrolysis, and supercritical solvent extraction of full bio-oil and thermal fractionation cuts. These fractionation strategies will be combined with catalyst design, synthesis, characterization, and testing for C-C bond formation and hydrodeoxygenation upgrading reactions, in the liquid or vapor phase. The experimental results allowed life-cycle and techno-economic analyses that were back fed to the experimentalists to refine the selection of catalyst and process operations with the ultimate objective of maximizing C efficiency at minimum H utilization.

Actual Accomplishment

Staged torrefaction/pyrolysis of lignocellulosic biomass

Lignocellulosic biomass is composed of three main constituents, hemicellulose, cellulose and lignin. The decomposition of these components at high temperature (pyrolysis) will produce bio-oil, which a complicated mixture with hundreds of compounds, which in general belong to three main chemical families, acids, furanics or phenolics. The upgrading of these three chemical families altogether in one step is complicated and resulted in low yield of valuable liquid fuel products.

Therefore, to decrease stream complexity, selective fractionation of raw biomass was obtained via multi-stage thermal fractionation to produce different streams that are enriched in a particular chemical family (acids, furanics or phenolics). Figure 1 shows a diagram of this multi-stage torrefaction process, which products different streams. Each stream will have a different upgrading strategy to maximize the final liquid fuel yield.
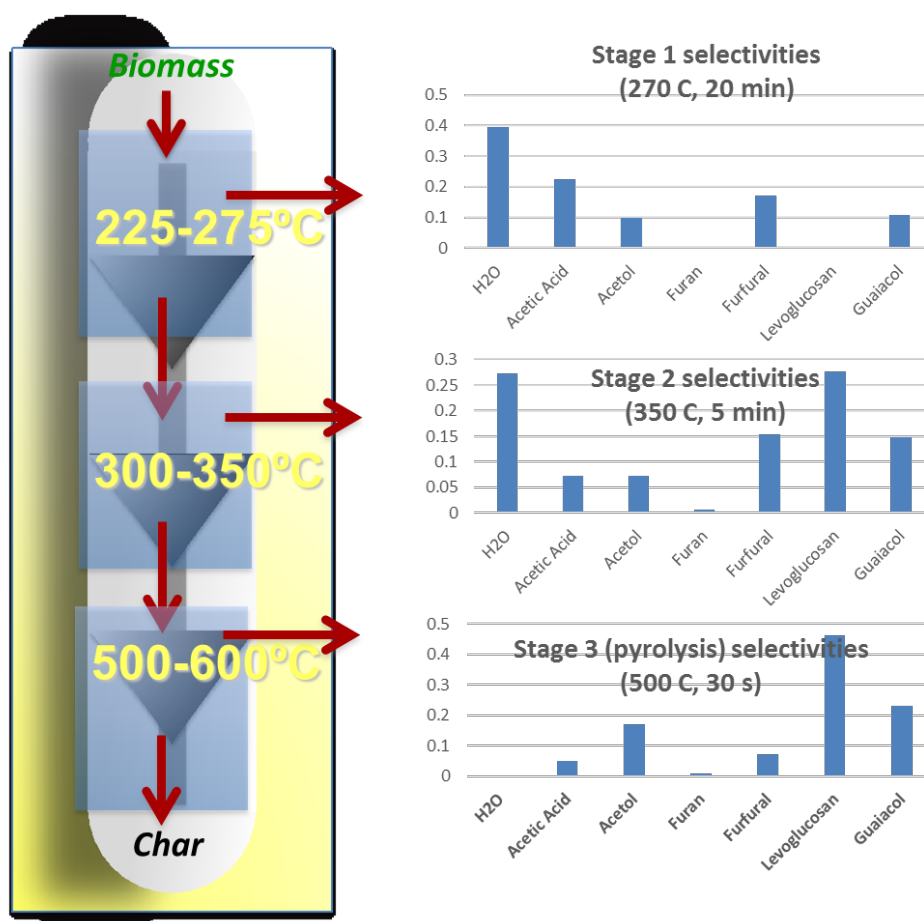
Figure 1. Process scheme for multi-stage torrefaction of biomass

By changing the pyrolysis condition of each stage such as time and temperature, we can manipulate the composition of the resulting stream, these results will be further presented in the activity summary. Furthermore, interestingly, we have also found that the use of activated carbon adsorptive trapping is very effective in enhancing the fractionation efficiency. As shown in Figure 2, the pyroprobe effluent of state 1 passing through activated carbon bed shows large reduction in levoglucosan and methoxyphenols, which are compounds that may deactivate catalyst in subsequent upgrading steps of stage 1.
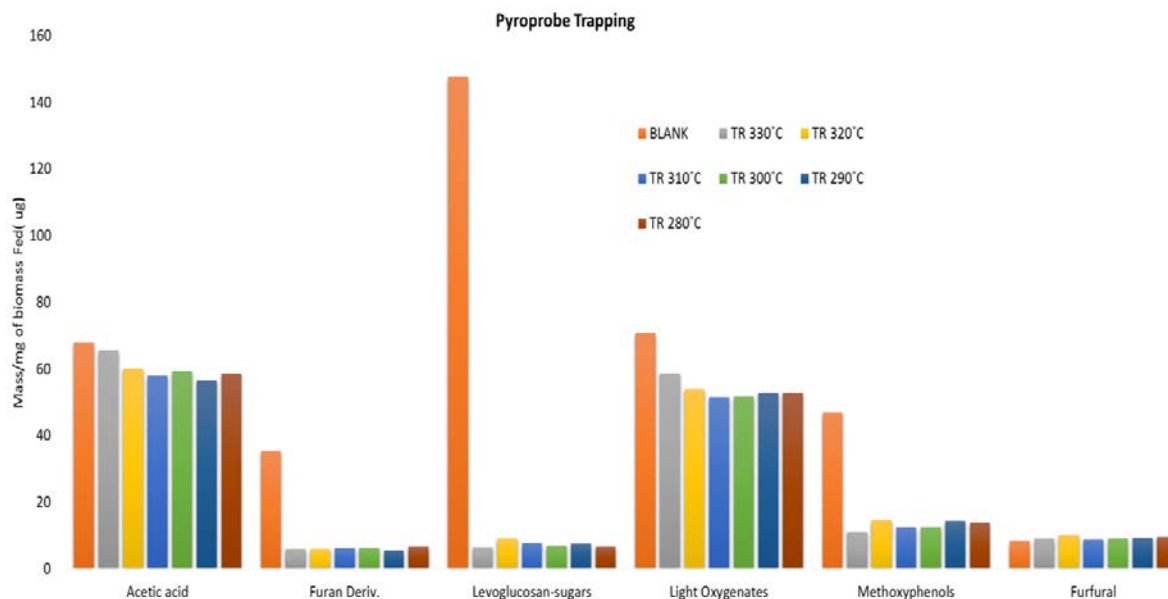
Figure 2. Comparison of trapping the vapor with activated carbon at different temperatures vs. blank (no trap)

Vapor phase upgrading

Different strategies were investigated to incorporate two of the most abundant species from thermal stage streams: Acetic acid and furfural.

A. Acylation reactions over HZSM-5

Based on the previous study of ketonization of acetic acid over HZSM-5, the reaction mechanism was found to involve (1) the formation of acylium ion from acetic acid followed by (2) the C-C coupling between the acylium ion with another acetic acid molecules (as depicted in Figure 3). The rate of step (2) C-C coupling was found to be the rate limiting step with high energy barrier. Therefore, the ketonization of acetic acid requires a high energy barrier, and the maximum yield of this chemistry is only 75% as it will produce CO_2 as a side product.
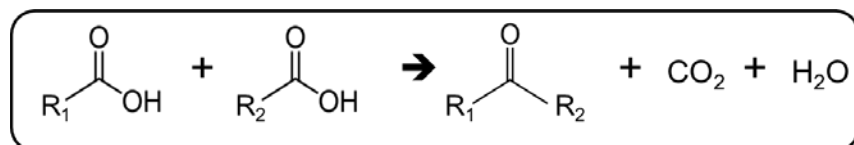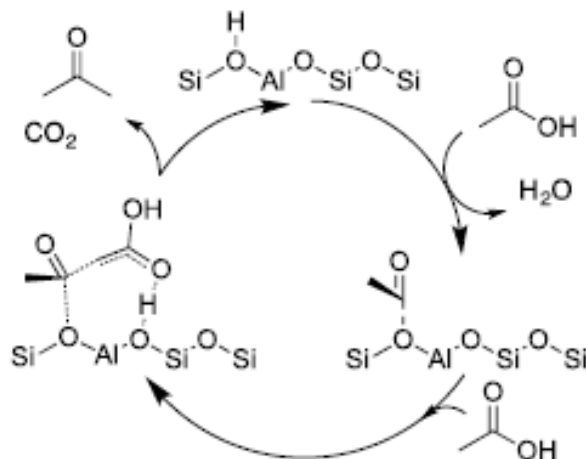
Figure 3. Reaction scheme for ketonization

Therefore, we have proposed an alternative upgrading strategy that uses acetic acid as the acylating agent and use other molecules in bio-oil as the substrates. This strategy has a lower the energy barrier, so that we can operate at lower temperatures, while increasing the total carbon yield of acetic acid to 100%.

Different molecules in bio-oil can be used as the substrate including furfural derivatives and phenolic compounds, since furfural and phenolics are abundant in other torrefaction streams. Furfural was not used as the substrate due to its high activity to polymerization, particularly in the presence of an acid catalyst such as zeolite. Furfural can be easily converted to furan or methyl furan, which are more stable molecules. The reaction schemes for acylation of acetic acid with furan, methyl furan and m-cresol as substrates are shown below.
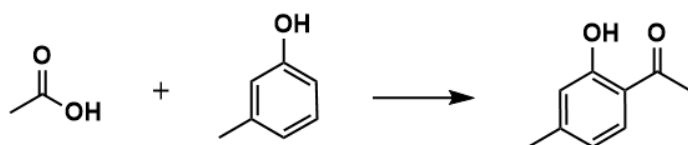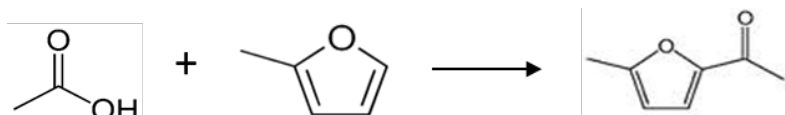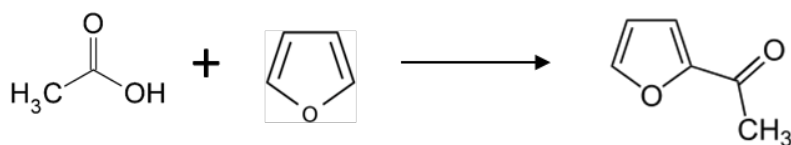
The activity of these substrates above for C-C coupling with acylium ion are different, with methyl furan > furan > toluene, as illustrated in Figure 4.
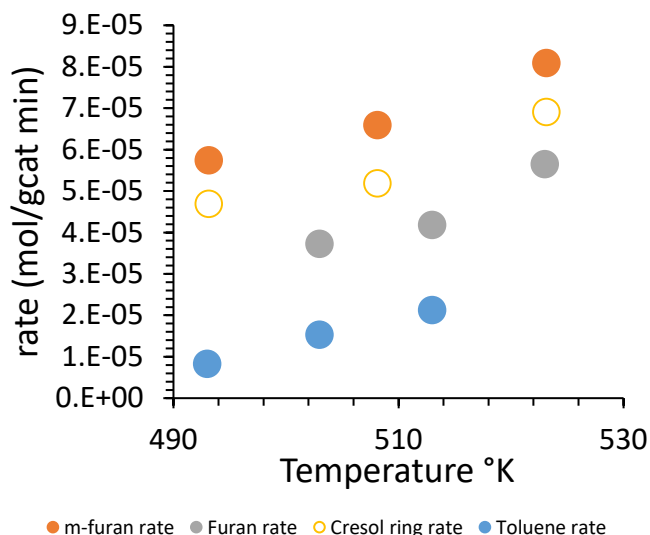
Figure 4. The rate of acylation of acetic acid with different substrate versus temperature. Gas phase reaction, H-ZSM5, Si/Al=40

B. Upgrading of Furfural over Ru/TiO₂

The catalyst Ru/TiO$_2$ was found to be very selective to convert furfural to methyl furan, as shown in Figure 5, methyl furan remained to the main product at increasing space time (W/F).
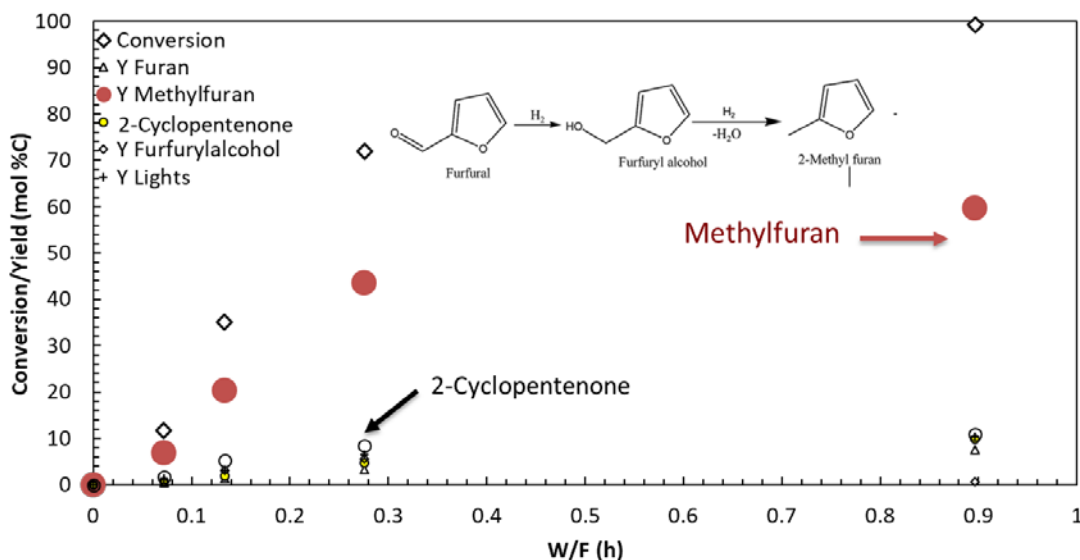
Figure 5. Product Distribution for pure furfural 5% Ru/TiO$_2$, 400°C, atmospheric pressure, under H$_2$, Feeding 0.1 mL/h of furfural and 1800 mL/h of H$_2$

However, interestingly, as we co-feed water with furfural, the selectivity was shifted to cyclopentanone. Water was found to have a positive effect when it reduces the light products formation while increasing the selectivity to cyclopentanone. Cyclopentanone is a very valuable building block for fuel as it is stable and could be converted to jet-fuel via aldol condensation.
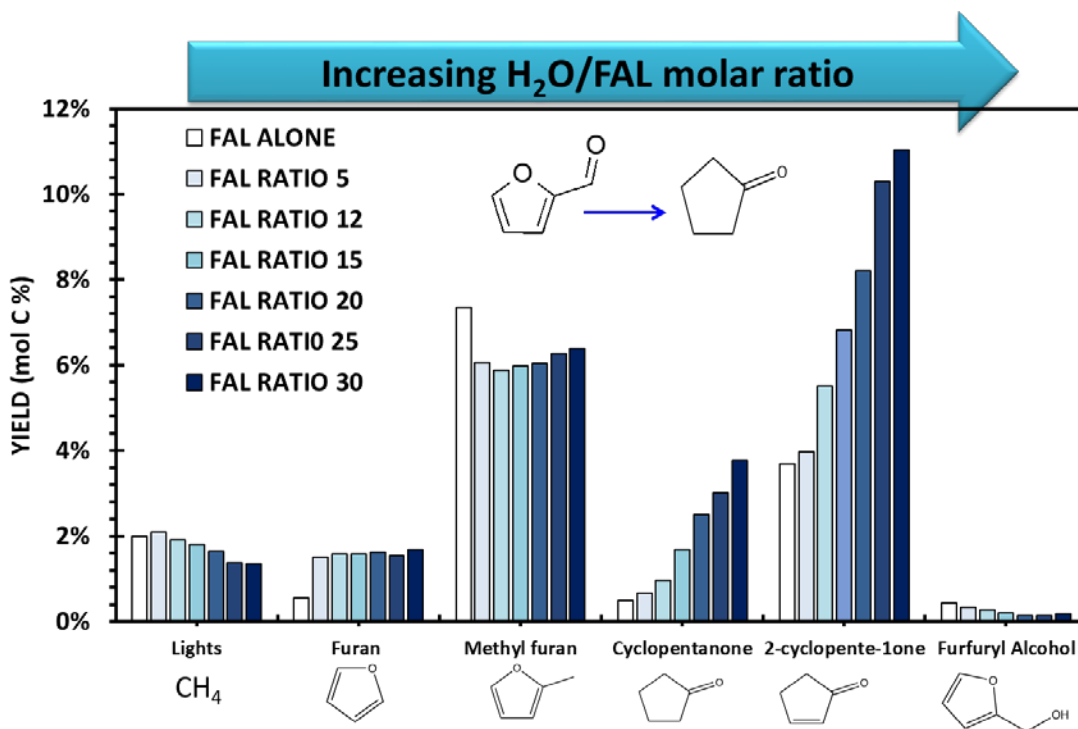
Figure 6. Product Distribution for pure furfural and furfural co-fed with water at different molar ratios over 5% Ru/TiO2, T= 400°C, P= 1 atm, TOS= 30 mins

Liquid phase upgrading

The upgrading strategy for liquid phase is demonstrated in Figure 7. Different chemistries can be used to convert short chain oxygenates into longer chain molecules that fit into the fuel pool.
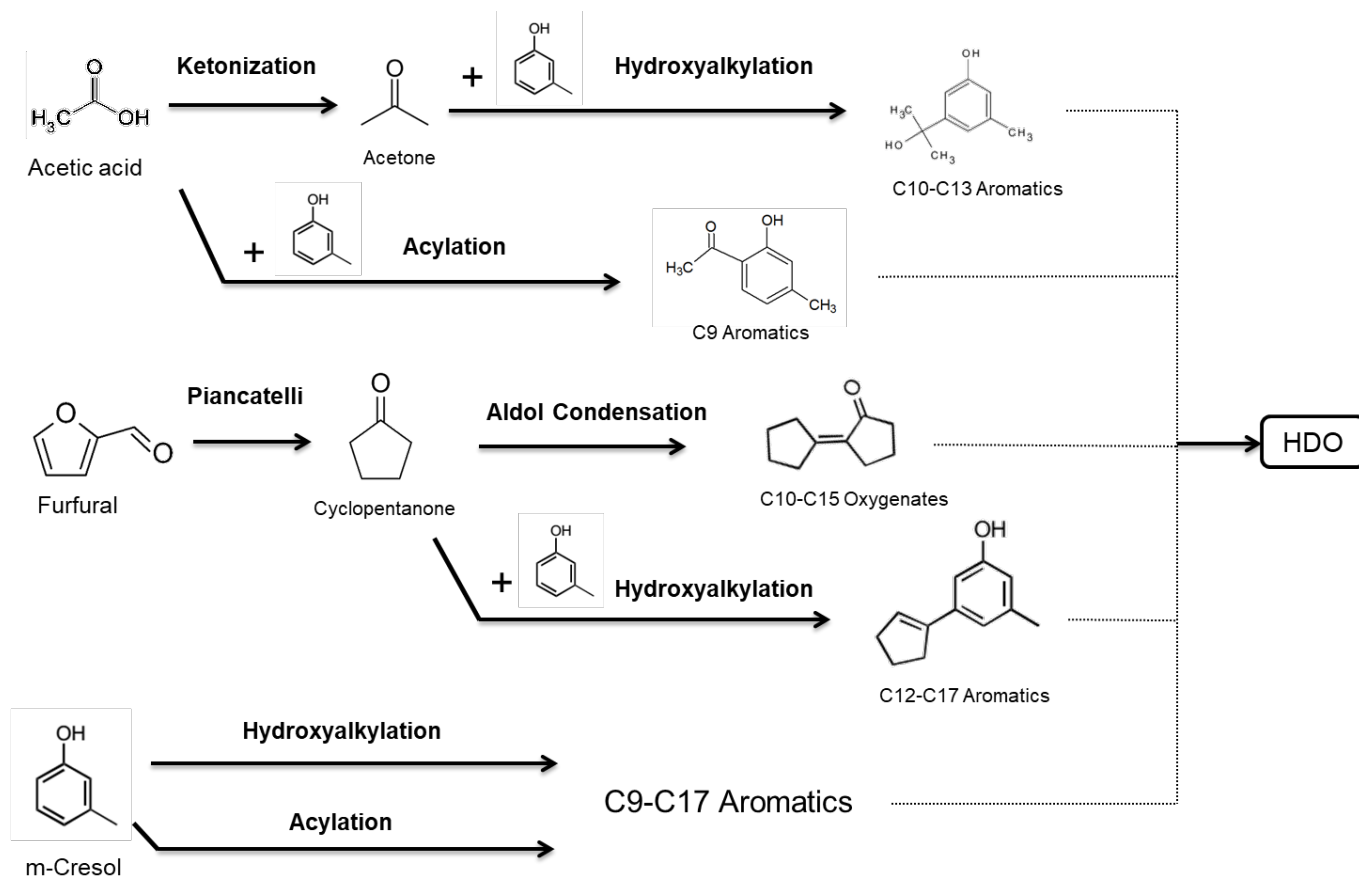
Figure 7. Liquid phase upgrading strategy

A. Acylation of phenolic compounds by acetic acid

Acetic acid was found to be a not very effective acylating agent in liquid phase, but it can undergo esterification with phenol derivatives (with -OH substituent) to create aromatic esters, which are more effective acylating agents, as shown in the scheme below.
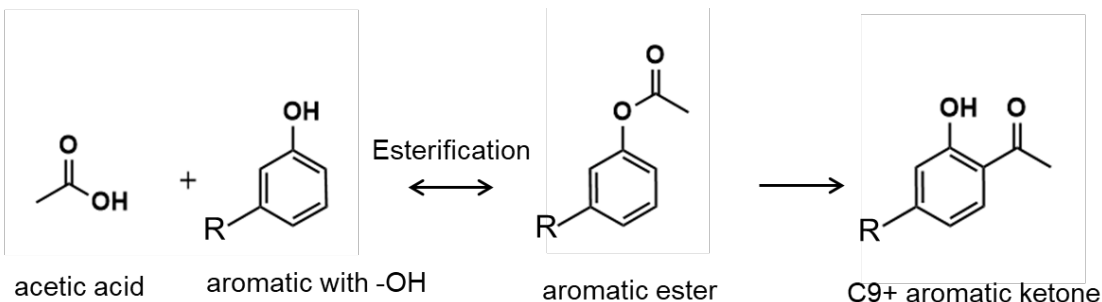
Zeolites were found to be active for this chemistry, in which zeolite beta was the most selective for the final aromatic ketone product, as shown in Table 1.

Table 1. Conversion and selectivity of acylation product. *1g zeolite in 80ml of 1M acetic acid with 8M m-cresol. Temp: 250°C, time: 1h, Pressure: 500 psia N$_2$*

Zeolite	Conversion of acetic acid	Selectivity to ketone product
H-ZSM5 (Si/Al=25)	50%	47%
HY (Si/Al=30)	55%	65%
H-Beta (Si/Al=19)	58%	70%

We have proposed the following strategy. First, we pretreat the 3rd stream with enriched phenolic compounds to enhance the concentration of -OH functionality. This can be done over zeolite catalyst, in which the abundant alkoxy functionality -OR can undergo transalkylation to -OH and -R. Then, the presence of -OH functionality will help esterification with acetic acid to create aromatic esters, which are efficient acylating agents.   The net positive effect of this strategy is to maximize the yield of molecules in the desirable molecular weight range, compatible with fuels.

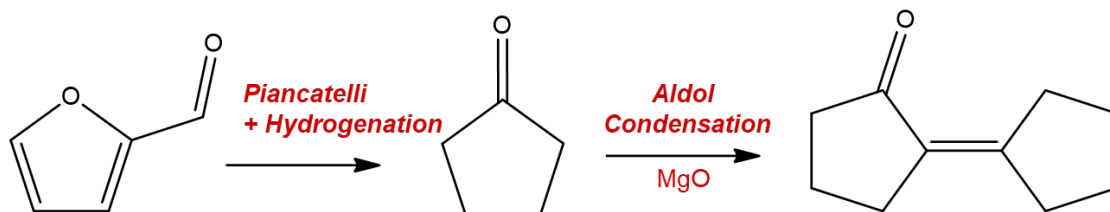B. Liquid phase conversion of furfural to cyclopentanone followed by aldol condensation

Furfural can react via Piancatelli rearrangement to cyclopentanone over Pd-Fe catalyst using water as the solvent, as shown in Table 2.

Table 2. Catalyst: 2%Pd-Fe/SiO2 (1:1) - Solvent: Water, *Temp: 150°C, time: 6h, Pressure: 200-600 psia*

Pressure (psia)	Conversion	Cyclopentanone Selectivity
200	49%	95%
300	79%	93%
600	93%	88%

C. Hydroxy-alkylation of phenolics and cyclopentanone

The hydroxy-alkylation between phenolics and cyclopentanone can create long chain molecules that are very can be further hydrodeoxygenated to hydrocarbons that belong to gasoline and diesel range. The reaction scheme that shows all of the products is illustrated in Figure 8.
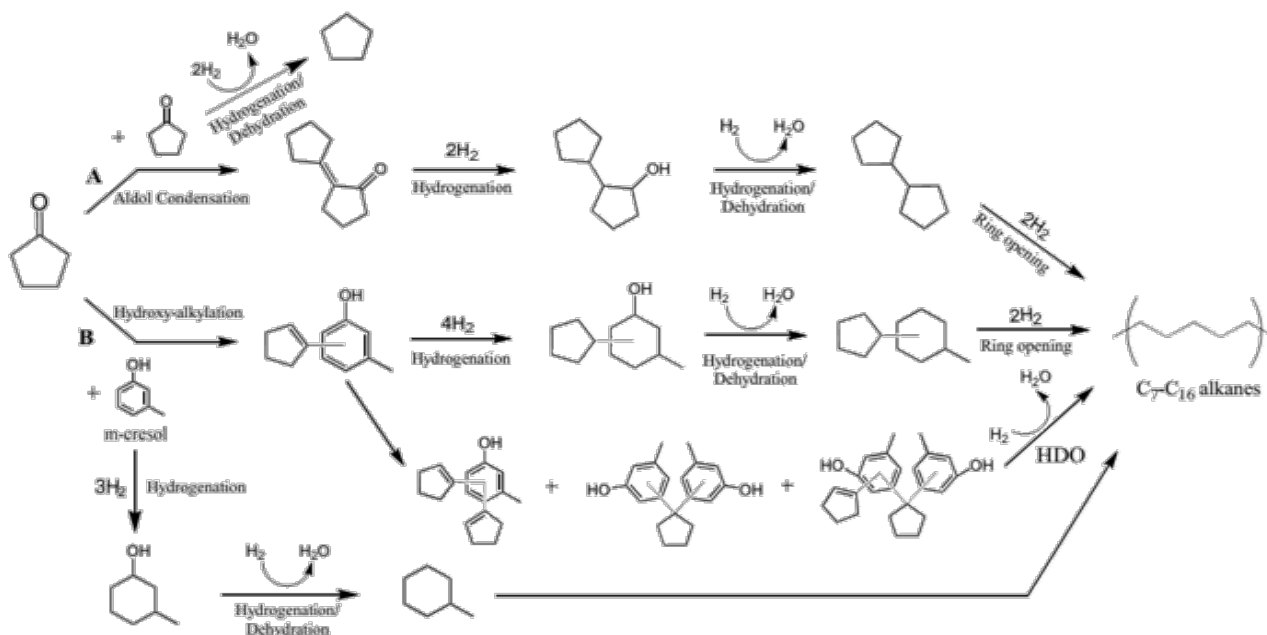

Figure 8. Reaction scheme for hydroxy alkylation between cyclopentanone and m-cresol

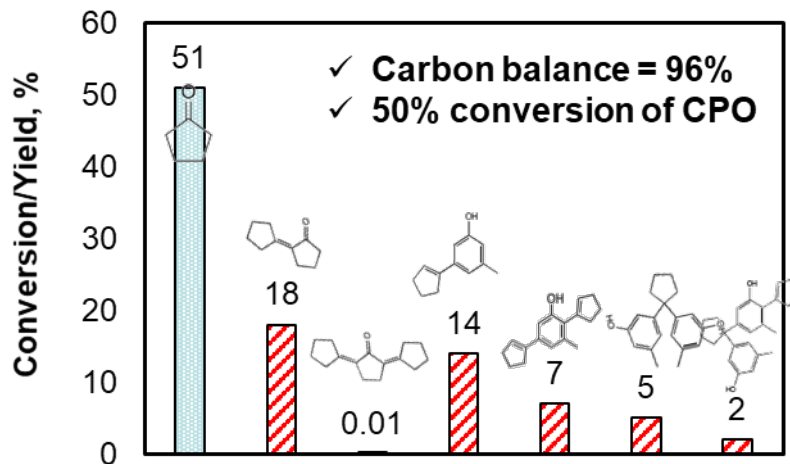The yield of hydroxy alkylation reaction was plotted in Figure 9.

Figure 9. Conversion/Yield of hydroxy-alkylation of cyclopentanone and m-cresol. Catalyst: Amberlyst 36. Reaction condition: 150°C,12 hrs in Decalin

The products after this hydroxy alkylation reaction was fed over Pt/Al_2O_3 for hydrodeoxygenation to hydrocarbons. The yield and selectivity were shown in Figure 10.
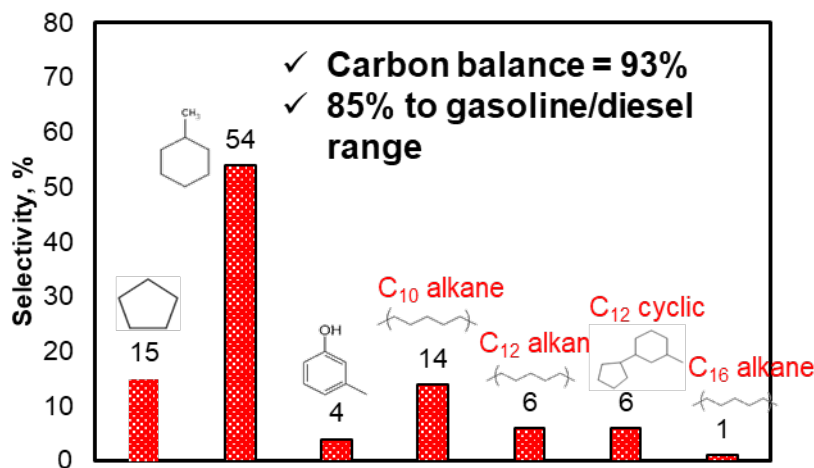
Figure 10. Selectivity of the HDO products.

Life cycle analysis

Different scenarios were compared with the base case (fast pyrolysis at 500°C followed by direct hydrodeoxygenation). This comparison is shown in Figure 11, 12 and Table 3.

We can see that all our multistage strategies reduce process H_2 consumption by ~40% relative to the base case of fast-pyrolysis & HDO. In Multistage System 3, over 47% of total Carbon input is stored in the C6+ liquid products. Multistage Fuel-to-Hydrogen Ratio ranges from approx. 6.4 to 8.0, significantly higher than baseline Fast Pyrolysis & HDO value of 1.2. That is, it can be now concluded that:

- Multistage systems could potentially produce high quality, infrastructure-compatible biofuel capable of achieving over 80% GHG reductions relative to petroleum diesel

- Multistage system 3 has the highest environmental performance of the examined design cases, with promising EROI and GHG emissions profile

- Exogenous fossil-derived H2 constitutes the principle GHG and primary energy burden across all systems

- Analysis suggests that reduction in overall process complexity could be achieved via collapsing the first two torrefaction stages into a single reactor

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Figure 11. Block flow diagram for general torrefaction-based biofuel production process

Figure 12. Carbon chain length distribution of different strategies

Table 3.   Comparison of performance metrics for Multistage Design Cases vs. Fast Pyrolysis & HDO

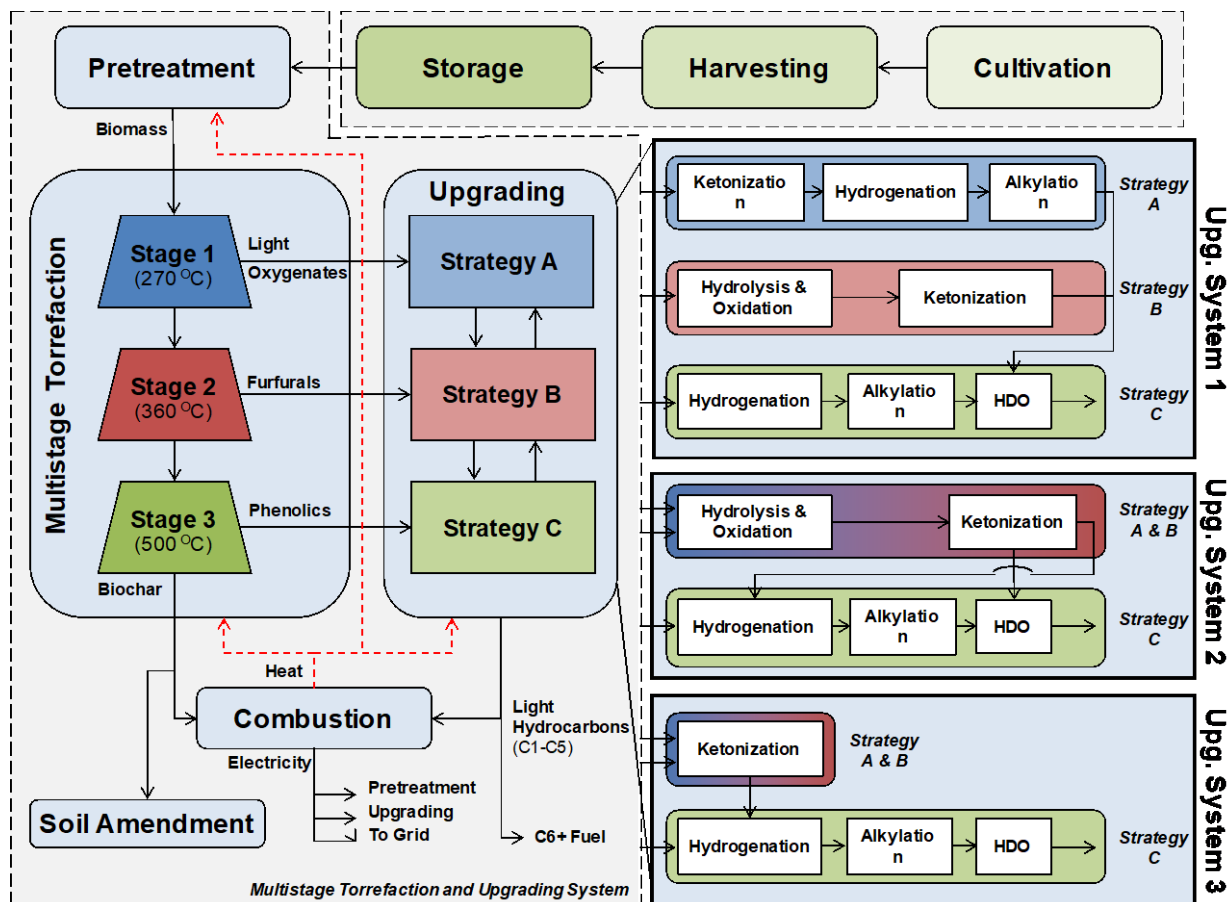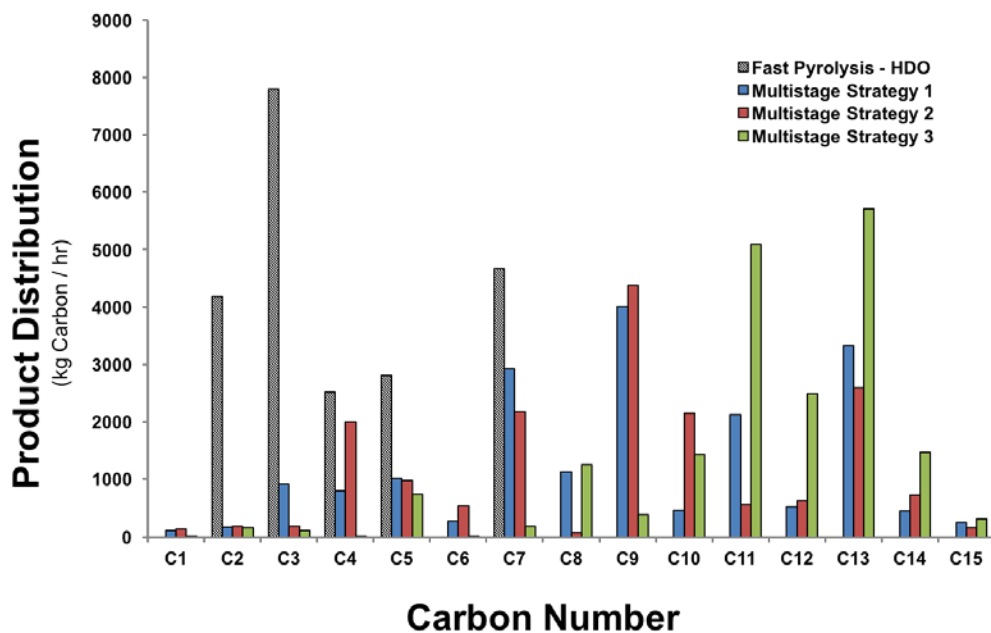| Process Design Parameters & Performance Metrics	*Fast Pyrolysis & HDO*	*Multistage System 1*	*Multistage System 2*	*Multistage System 3*
Absolute Fuel Yield [kg $Fuel_{Carbon}$ / hr]	21981	18451	17461	19358
C6+ Liquid Carbon Yield [kg C6+ $Fuel_{Carbon}$ / hr]	4659	15448	13981	18350
Hydrogen Consumption [kg H_2 / hr]	3875	2339	2195	2295
C6+ Fuel to Hydrogen Consumption [kg C6+ $Fuel_{carbon}$ / kg H_2]	1.2	6.6	6.4	8.0
C6+ Carbon Efficiency [C6+ $Fuel_{Carbon}$ / $Biomass_{Carbon}$) x 100]	12.1	40.1	36.3	47.6
Process Complexity [# Decomp., Upg. Blocks]	(1,1)	(3,8)	(3,5)	(3,4)

Technoeconomic analysis

Technoeconomic analysis was also done for different multi-stage scenarios, as shown below. To synthesize alternative upgrading strategies, we have considered various abundance of chemical functionalities in each fraction. The goal in this TEA investigation was to maximize carbon yield (primary) and minimize H2 consumption (secondary).

We have identified the two key trade-offs, as shown in Figure 14. (1) Carbon yield improvement requires more complex processing, leading to higher capital costs and (2) Design of thermal decomposition conditions must be done in parallel with fraction upgrading system
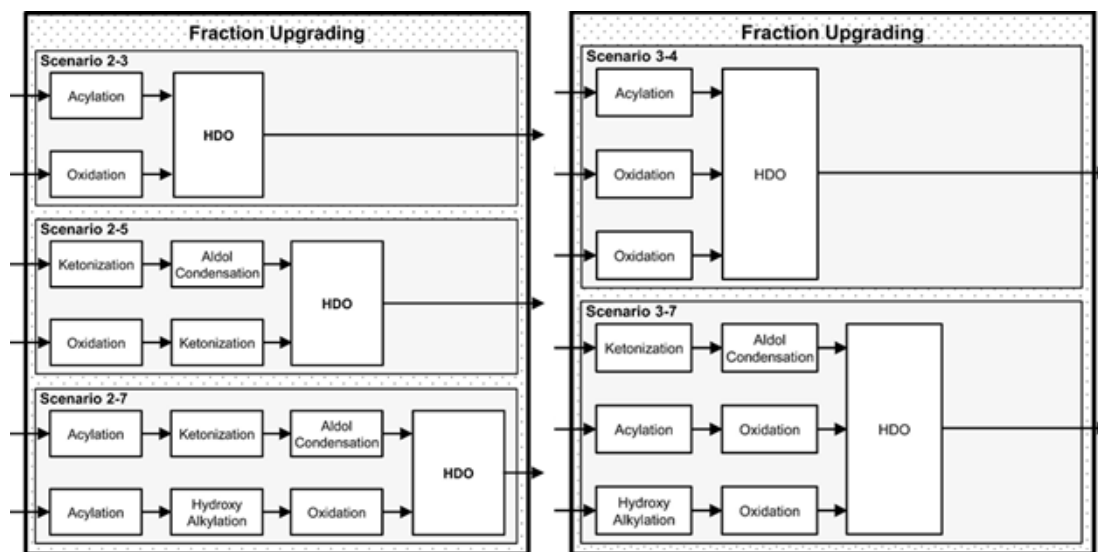
Figure 13. Selected block flow diagram of reactors in a fraction upgrading system.
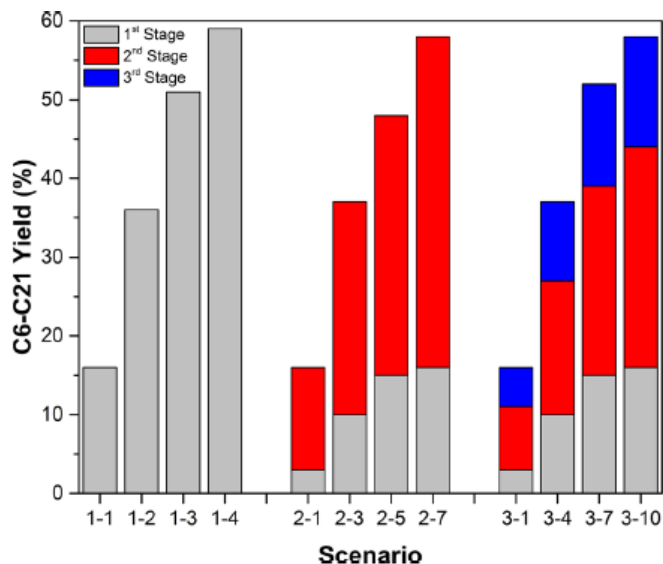
Figure 14. C6-C21 yield for different scenarios.

Conclusion

The goal of the project was successfully accomplished. The C yield to valuable fuel products was significantly improved at lower H consumption, as compared with the base case of fast pyrolysis followed by hydrodeoxygenation. It is very important to first fractionate biomass into different streams, then selectively condense them to make longer and more stable molecules and finally hydrodeoxygenated to remove oxygen and make hydrocarbons. It should be notice that, the project was aimed for general higher quality fuel. If the goal is to make a specific type of fuel, such as gasoline, diesel or jet fuel, the actual process can be easily modified with the chemistries and strategies that we have developed in this project. This is also another great advantage of the study.

Project Activities Summary

The project was implemented by a multidisciplinary research team with combined expertise in catalysis, separation, life-cycle analysis, and techno-economic assessment. The whole project can be illustrated as shown in Figure 15 below.
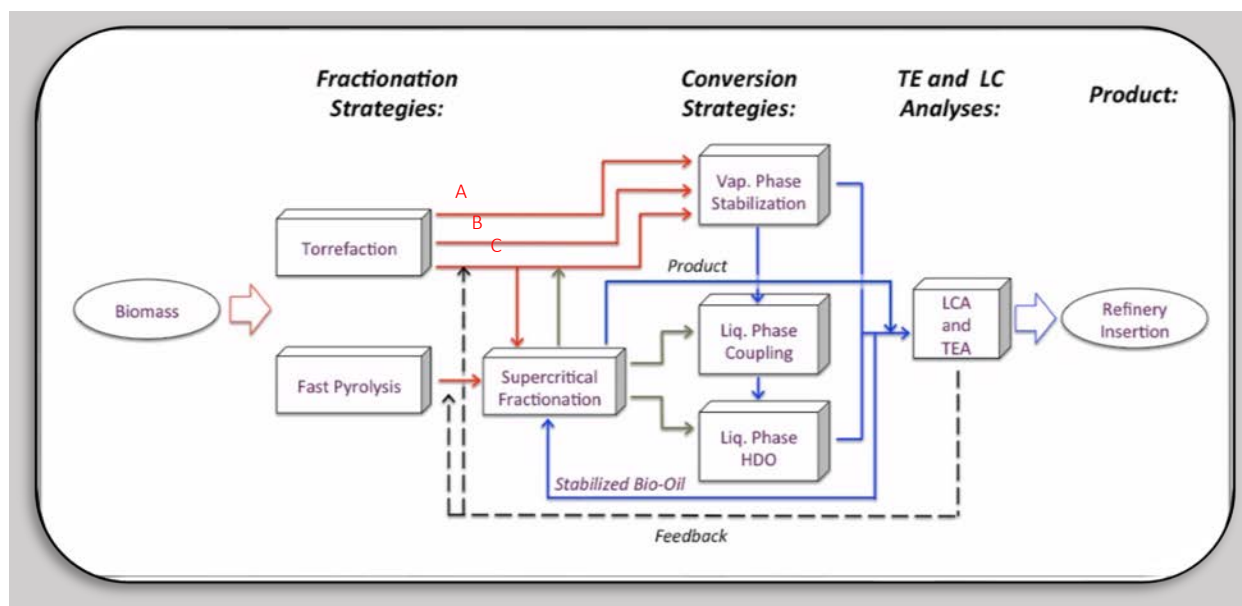
Figure 15. Project overview

* Fractions A, B, and C represent staged pyrolysis fractions rich in small oxygenates, sugar-derived and lignin-derived compounds, respectively.

Thermal fractionation of biomass

Fractions A, B, and C were produced at various temperatures and resident time. At moderate temperatures and times, the most reactive parts in biomass will be destructed to create mostly small oxygenates. On the contrary, higher temperatures and faster heating rates will produce mostly phenolic compounds. These activities were completed by University of Oklahoma.

Supercritical Separation

At Idaho National Lab, different fractions were further refined by supercritical fluid extraction and selective adsorption to divide the primary fractions in purer streams. CO_2 was used as the solvent and has shown high separation efficiency for different bio-oil fractions.

Design of novel catalysts

At University of Oklahoma, different families of catalysts were synthesized and characterized for different feed composition and the upgrading strategies. Different families include:

a)   Basic/acidic oxides, consisting of both pure oxides (e.g. TiO_2, CeO_2) and mixed oxides (Ce-ZrO_2). Oxides that are both reducible (TiO_2) and non-reducible (Al_2O_3) were tested.

b)   Acidic zeolites (e.g. protonated forms of Y, ZSM-5, ZSM-22, and Beta)

c)   Metals and bimetallic catalysts supported on inert supports (e.g. SiO_2, C) (e.g. Ni/SiO_2, Pt-Sn/SiO_2, $Ni-Fe/SiO_2$)

d)   Metals and bimetallic catalysts supported on basic/acidic oxides (e.g. Ru/TiO_2, Ni-Fe/Ce-ZrO_2)

Catalytic upgrading of different bio-oil fractions in vapor and liquid phases

Different strategies for vapor and liquid phase upgrading has been designed and tested at the University of Oklahoma, in which the main goal is to first perform different C-C bond formation chemistries to convert the reactive short chain molecules into longer molecules, followed by hydrodeoxygenation to remove oxygen and create valuable hydrocarbons that can be used as fuels.

Life cycle analysis (LCA) and technoeconomic analysis (TEA)

Analysis of LCA and TEA were performed for continuous improvement and feedback. LCA was studied by University of Pittsburgh and TEA was studied by University of Wisconsin.

List of Publications

Journal publications

- Duong, N. N.; Wang, B.; Sooknoi, T.; Crossley, S.P.; Resasco, D. E., Enhancing the Acylation Activity of Acetic Acid by Forming an Intermediate Aromatic Ester. *Chemsuschem* **2017**, *10* (13), 2823-2832.

- Duong, N. N.; Tan, Q.; Resasco, D.E., Controlling Phenolic Hydrodeoxygenation by Tailoring Metal-Oxygen Bond Strength via Specific Catalyst Metal Type and Particle Size Selection. *Comptes Rendus Chimie* **2017**

- Bui, T. V.; Crossley, S.; Resasco, D. E., C–C coupling for biomass-derived furanics upgrading to chemicals and fuels. Wiley-VCH Verlag and Co. KGaA: 2016; pp 431-494.

- Ghorbanpour, A.; Gumidyala, A.; Grabow, L. C.; Crossley, S. P.; Rimer, J. D., Epitaxial growth of ZSM-5@ Silicalite-1: A core–shell zeolite designed with passivated surface acidity. *ACS nano* **2015,** *9* (4), 4006-4016.

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- Resasco, D. E.; Crossley, S. P., Implementation of concepts derived from model compound studies in the separation and conversion of bio-oil to fuel. *Catalysis Today* **2015,** *257*, 185-199.

- Resasco, D. E.; Wang, B.; Crossley, S., Zeolite-catalysed C–C bond forming reactions for biomass conversion to fuels and chemicals. *Catal. Sci. Technol.* **2016,** *6* (8), 2543-2559.

- Wan, S.; Waters, C.; Stevens, A.; Gumidyala, A.; Jentoft, R.; Lobban, L.; Resasco, D.; Mallinson, R.; Crossley, S., Decoupling HZSM-5 catalyst activity from deactivation during upgrading of pyrolysis oil vapors. *ChemSusChem* **2015**, *8* (3), 552-9.

- Zhang, L.; Pham, T. N.; Faria, J.; Resasco, D. E., Improving the selectivity to C4 products in the aldol condensation of acetaldehyde in ethanol over faujasite zeolites. *Applied Catalysis A: General* **2015**, *504* (Supplement C), 119-129.

- Rozenblit, A.; Avoian, A. J.; Tan, Q.; Sooknoi, T.; Resasco, D. E., Reaction mechanism of aqueous-phase conversion of γ-valerolactone (GVL) over a Ru/C catalyst. *Journal of Energy Chemistry* **2016**, *25* (6), 1008-1014.

- Bui, T. V.; Sooknoi, T.; Resasco, D. E., Simultaneous Upgrading of Furanics and Phenolics through Hydroxyalkylation/Aldol Condensation Reactions. *ChemSusChem* **2017**, *10* (7), 1631-1639.

- Tan, Q.; Wang, G.; Nie, L.; Dinse, A.; Buda, C.; Shabaker, J.; Resasco, D. E., Different Product Distributions and Mechanistic Aspects of the Hydrodeoxygenation of m-Cresol over Platinum and Ruthenium Catalysts. *ACS Catalysis* **2015**, *5* (11), 6271-6283.

- To, A. T.; Resasco, D. E., Hydride transfer between a phenolic surface pool and reactant paraffins in the catalytic cracking of m-cresol/hexanes mixtures over an HY zeolite. *Journal of Catalysis* **2015**, *329*, 57-68.

- González-Borja, M. Á.; Resasco, D. E., Reaction pathways in the liquid phase alkylation of biomass-derived phenolic compounds. *AIChE Journal* **2015**, *61* (2), 598-609.

- Anaya, F.; Zhang, L.; Tan, Q.; Resasco, D. E., Tuning the acid–metal balance in Pd/ and Pt/zeolite catalysts for the hydroalkylation of m-cresol. *Journal of Catalysis* **2015**, *328*, 173-185.

Presentations

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- Duong, N. N.*; Tan, Q.; Resasco, D.E. Elucidating Particle Size Effects on the Hydrodeoxygenation (HDO) of Phenolics by Micro-Pulse Experiments and DFT Calculations. AIChE Annual Meeting in San Francisco, CA. Nov 2016.

- Duong, N. N.*; Wang, B.; Sooknoi, T.; Crossley, S.P.; Resasco, D. E. HBeta zeolite-catalyzed acylation of phenolics in the liquid phase. 252nd ACS National Meeting, Philadelphia, PA, August 2016.

- Herron, J.A.*; Lobban, L.L.; Mallinson, R.G.; Crossley, S.P.; Resasco, D.E.; Maravelias, C.T. Process Synthesis for Biomass Torrefaction. AIChE Annual Meeting, Atlanta, GA, November 16-21, 2014.

- Herron, J.A.; Won, W.; Resasco, D.E.; Maravelias, C.T. A System-level Analysis on Biomass Thermal Fractionation and Catalytic Upgrading Processes. AIChE Annual Meeting, San Francisco, CA, November 13-18, 2016.

- L.M. Petkovic*, D.M. Ginosar, C. Hrbac, S. Lwin, "Fractionation of bio-oils using supercritical fluids," 252th ACS (American Chemical Society) National Meeting, Philadelphia, PA, August 21-25, 2016.

- L.M. Petkovic*, D.M. Ginosar, "Bio-oil fractionation using supercritical fluids," 38th Symposium on Biotechnology for Fuels and Chemicals, Baltimore, MD, April 25-28, 2016.

- L.M. Petkovic*, D.M. Ginosar, "Fractionation of thermally produced bio-oils using supercritical fluids,"250th ACS (American Chemical Society) National Meeting, Boston, MA, August 16-20, 2015.

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- G.G. Zaimes*, N. Vora, D.E. Resasco, S.P. Crossley, and V. Khanna, Environmental life cycle evaluation of multistage torrefaction and pyrolysis for biofuel production, American Institute of Chemical Engineers Annual Meeting, Salt Lake City, UT, November 8-13, 2015.

- G.G. Zaimes*, D.E. Resasco, S.P. Crossley, and V. Khanna. Environmental Impacts of Multistage Pyrolysis-Derived Biofuels: Connecting Experimental Studies with Systems-Level Analysis, International Society for Industrial Ecology Meeting, University of Surrey, Guildford, U.K. July 7-10, 2015.

- G.G. Zaimes*, N. Vora, D.E. Resasco, S.P. Crossley, and V. Khanna, Multistage Torrefaction for Biofuel Production: A life cycle inspired assessment of the Climate-Energy Nexus, Association of Environmental Engineering and Science Professors Meeting, New Haven, Connecticut, June 14-16, 2015.