PNNL-27848

Pacific Northwest
NATIONAL LABORATORY

Final Report for the Project Characterization and Valorization of Aqueous Phases Derived from Liquefaction and Upgrading of Bio-Oils

July 2018

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U.S. DEPARTMENT OF ENERGY

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Executive Summary

The Characterization and Valorization of Aqueous Phases Derived from Liquefaction and Upgrading of Bio-Oils project developed processes to extract value from the organics within aqueous streams derived from biomass direct liquefaction processes. The focus of the project was twofold. First, we characterized a diverse set of aqueous streams from numerous processes and feedstocks. The characterization effort served to inform this project toward development around the most prevalent compounds to maximize versatility and impact. We analyzed diverse streams from hydrothermal liquefaction of lignocellulosic, algal, and waste feedstocks; catalytic fast-pyrolysis aqueous phases; fast-pyrolysis aqueous phases; and aqueous phases produced by hydroprocessing of fast-pyrolysis bio-oil. Second, thermochemical catalytic processes were developed to convert aqueous-phase organics into useful products. These processes focused mostly on organic acids and specifically acetic acid, which was found to be ubiquitous from the characterization effort. A $La_xZr_yO_z$ catalyst was discovered and developed for the ketonization of acids to ketones in the condensed aqueous phase. A dual-bed steam reforming process was developed to convert acids and other organics to hydrogen for bio-oil hydroprocessing. The dual-bed reforming process consisted of a ketonization step followed by a steam reforming step with Co as the active metal. The dual-bed process significantly reduced the rate of coke deposition versus direct steam reforming of the organic acids and beneficially produced CH_4 below the equilibrium value. Finally, we demonstrated direct conversion of aqueous-phase organics to olefins over a $Zn_xZr_yO_z$ catalyst.

Each thermochemical catalytic process was demonstrated with process-derived aqueous mixtures. Model compounds were used to benchmark performance and optimize conditions, but emphasis was placed on utilizing “real” aqueous streams whenever possible. A liquid-liquid extraction process using methyl tert-butyl ether as the solvent was developed to segregate dissolved inorganic species and sugars from desirable light oxygenates such as acids and alcohols. Furthermore, a carbon treatment to remove color bodies was employed after it was found the presumably heavy organic chromophore species deactivated catalysts. These economic separation processes allowed for the successful demonstration of stable catalytic processing in the condensed-phase ketonization, dual-bed reforming, and direct olefin production processes for tens to hundreds of hours, which were limited only by the quantity of feed available.

Techno-economic analysis of these processes demonstrated the impact possible when capturing “waste” organics as valuable products. The condensed-phase ketonization process for converting aqueous stream acids to ketones followed by reduction and dehydration to olefins sold as a co-product resulted in the reduction of the minimum fuel selling price by about 13% compared to the anaerobic-digestion, aqueous-phase treatment base case ($3.74 to $4.29/GGE). The dual-bed reforming process was commensurate in price to the anaerobic digestion base case ($4.24 versus $4.29/GGE). However, the need for external natural gas to produce hydrogen for bio-oil hydroprocessing was eliminated, thereby lowering the carbon impact of the process.

While this project generated groundbreaking accomplishments toward realizing the potential of gaining value from aqueous-phase organics, significant future opportunities exist. These opportunities include:

1. *Advanced Separations* – Concentrating and segregating organic compounds from the aqueous phase by chemical functional groups to allow directed chemical transformations. Investigations into new solvents for liquid-liquid extraction or development of a simulated moving bed chromatography process would avoid the need to distill large amounts of water.

2. *Hydrothermally Stable Catalysts* – Understanding the reason for the hydrothermal stability of the $La_xZr_yO_z$ catalyst developed by this process would lead to the development of other similar catalysts. Other new types of catalysts composed of mixed metal oxides with known hydrothermal stability (e.g., $V_2O_5 + ZrO_2$) prepared hydrothermally should also be explored. Finally, carbon catalysts combined with metal oxides may produce catalyst supports that overcome the sintering challenges associated with metals loaded onto a carbon support alone.
3. *Oxidative Thermochemical Process* – Processes that focus on converting phenolic compounds using oxidation reactions would be beneficial. Many of these reactions lack hydrothermally stable catalysts, which could be developed by this project. Methods to oxidatively convert phenolics selectively to ring -ened products such as succinic acid or adipic acid could create value-added chemicals or additional fuels. Complete catalytic oxidation could be explored as a low-cost method to clean up wastewater. Complete oxidation reactions may also be of interest to current wastewater treatment plants in the pursuit of destroying recalcitrant organic species such as hormones.
4. *Techno-Economic Evaluations and a Wastewater Guiding Document* – Comparing costs for a generic, non-specific process to separate and convert aqueous-phase organics to value-added products would bound potential new processes. A semi-quantitative analysis would assist in determining the lowest concentration of organics that can be recovered economically. For example, for acetic acid, the concentration at which recovery becomes uneconomic is likely between 1 and 5 wt% as our liquid-liquid extraction process could readily extract 5 wt% but was challenged by the 1 wt% found in algal-derived HTL aqueous phases. Furthermore, a wastewater valorization and disposal guiding document for the bioenergy community would be beneficial as no standard overview of relevant contaminants, associated ASTM tests, and cleanup processes exists.

Capturing and extracting value from even relatively dilute aqueous streams with diverse organic and inorganic constituents will greatly improve the economic viability of future biorefineries. Furthermore, technologies developed for these challenging freestreams will find interest in other existing processes such as at wastewater treatment plants, chemical plants, and petroleum refineries. The U.S. Department of Energy's national laboratories are uniquely positioned to develop materials and processes for these "waste" streams, which can benefit the bioenergy community as well as other industrial stakeholders.

Acronyms and Abbreviations

AC	activated carbon
AD	anaerobic digestion
CHG	catalytic hydrothermal gasification
GHSV	gas hourly space velocity
ICP	inductively coupled plasma
LLE	liquid-liquid extractor
MFSP	minimum fuel selling price
MTBE	methyl tert-butyl ether
PNNL	Pacific Northwest National Laboratory
SMBC	simulated moving bed chromatography
TEA	techno-economic analysis
TIC	total installed cost
UDP	upgrading demonstration plant
USDA	U.S. Department of Agriculture

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1.0 Introduction

The processing of biomass to fuels and chemicals invariably involves water, which may be present in the biomass feed entering a process or may be created during processing. Some oxygenated organic compounds report to the aqueous phase along with dissolved inorganic compounds. A substantial amount of the biogenic carbon may report to the aqueous phase depending on the process employed. Figure 1.1 presents three conversion processes that create aqueous phases with organic compounds present. While the concentration and identity of the organic compounds change depending process factors such as feedstock, direct liquefaction process, and conditions employed, some compounds such as acetic acid are ubiquitous in biomass aqueous phases. Thus, while processes must be tailored to a specific aqueous stream, general development of processes is feasible by focusing on the commonality of the streams.

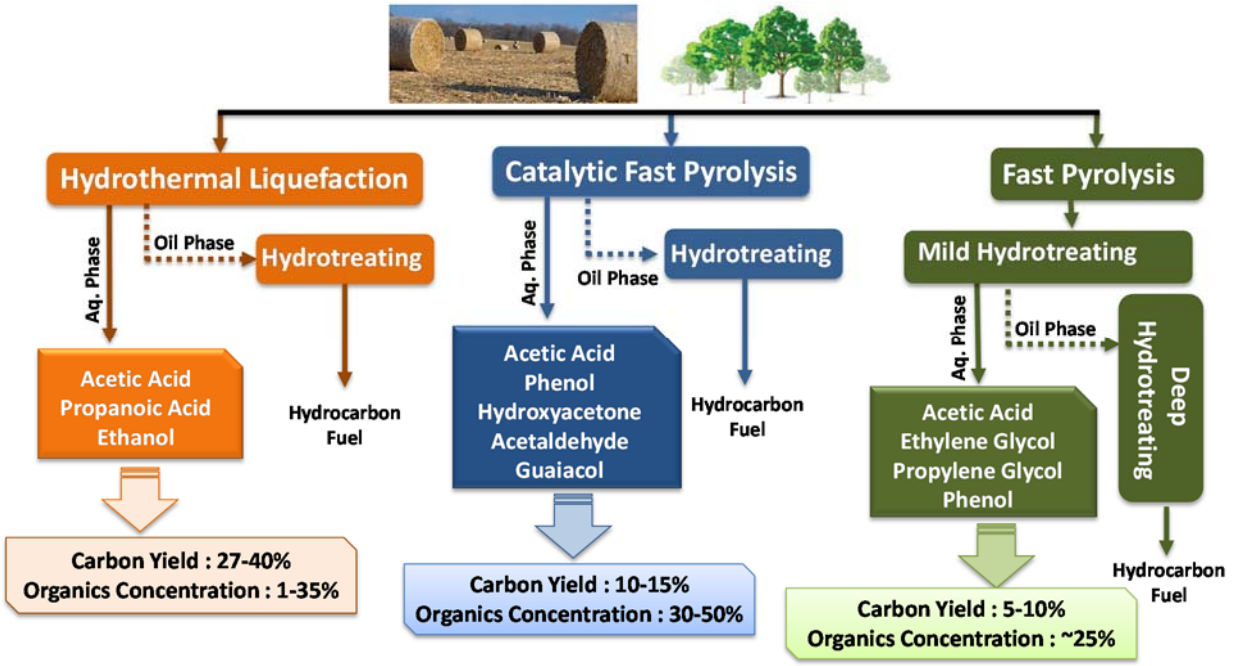

Figure 1.1. Direct Biomass Liquefaction Processes with Aqueous Streams that Contain Significant Amounts of Biogenic Carbon

At the beginning of this project, the state-of-the-art in valorizing aqueous phases was anaerobic digestion (AD), which creates a medium-BTU fuel gas composed of approximately 50:50 (vol) CH_4:CO_2. The gas typically is burned as process heat, which is a low-value proposition. An alternative technology for valorizing aqueous phases is catalytic hydrothermal gasification (CHG). CHG uses a Ru catalyst to quickly gasify organic compounds catalytically in the condensed phase at sub-critical but nonetheless high temperature and pressure (350°C, 3000 psig) (Elliott et al. 2009). Similar to AD, the CHG product is a medium-BTU fuel gas typically burned for process heat. Beyond these options for capturing heat, most aqueous streams were considered waste with the organics contained therein of little-to-no value. However, at the outset of this project, little was known about the composition or concentration of the various aqueous phases as many reports either completely disregarded them or reported a simple carbon yield "lost" to the aqueous phase. Thus, the characterization task was an important contribution to development of the processes devised for valorizing the aqueous streams.

Biological and thermochemical methods have been considered for valorizing aqueous streams. AD may be considered a biological method that is robust and well understood, although many of the components in biomass aqueous phases may pose special challenges (Appels et al. 2008). The National Renewable Energy Laboratory began investigations into biological conversion of direct liquefaction aqueous streams around the time this project began (Beckham 2017). Reports of thermochemical valorization efforts outside of CHG generally were not available. Wastewater cleanup methods such as supercritical water oxidation were studied previously but generally the products of these processes were carbon dioxide and not value-added products (Matatov-Meytal and Sheintuch 1998). Many of the thermochemical processes focused on processing aqueous "waste" streams noted needs for more robust catalysts capable of the harsh conditions experience with water at high temperature.

The goal of this project was twofold. First, we focused on quantifying the organic and inorganic constituents of numerous aqueous phases generated from the direct liquefaction of biomass to obtain critical characterization information that previously had been overlooked. Second, we initiated efforts to devise new valorization methods that could capture and create value from the organics present in the aqueous phase. The characterization efforts have been published in peer-reviewed journals. The dearth of previously available information is readily identified when considering the first characterization paper published by this project has about 42 citations in only three years (2015–2018). The characterization efforts also served to focus the thermochemical valorization methods developed by this project. Specifically, a focus on the most ubiquitous compounds—organic acids—was undertaken to make the developed technologies as widely applicable as possible. We also focused on process-derived mixtures to demonstrate that these technologies were applicable to real streams and not merely model compounds. The realization that the organic compounds are often dilute and require concentration and cleaning facilitated the inclusion of separations research into the project. Specific accomplishments of this project include:

1. Publication of four aqueous phase characterization peer-reviewed journal articles to inform the bioenergy conversion community.
2. Development of a liquid-liquid separation process with demonstrated ability to concentrate and purify streams with acid concentrations as low as 5 wt% to produce feedstocks suitable for conversion processes.
3. Development of a hydrothermally stable condensed-phase ketonization catalyst that has demonstrated stable operation with hydrothermal liquefaction (HTL)-process derived feed for 100 hours, ending only when all of the available feed had been consumed. Tests using model compound have been demonstrated for over 1000 hours.
4. Development of a dual-bed steam reforming process to convert organic acid-rich streams to hydrogen with significantly less carbon deposition on the catalyst versus direct steam reforming of acids at industrially relevant steam-to-carbon ratios.
5. Development of a process for producing olefins from a cleaned aqueous fraction leveraged from technology originally developed for clean ethanol conversion to isobutene under the Indirect Liquefaction Project
6. Development of techno-economic models demonstrating that the production of value-added side products such as olefins reduce the minimum fuel selling price (MFSP) of fuel dramatically by 20% even when transportation costs are included.
7. Development of techno-economic models demonstrating that hydrogen production from aqueous-phase organics is commensurate with the cost of implementing AD but requires no external fossil carbon, thereby diminishing carbon impact on the environment.

2.0 Future Opportunities

Developing processes for aqueous-phase valorization is a proposition uniquely suited to the U.S. Department of Energy's national laboratories. Industry views these streams as waste with significant technological breakthroughs needed for implementation. Indeed, this project developed and demonstrated some of these breakthroughs (e.g., the hydrothermally stable metal oxide catalyst and the dual-bed reforming concept). Significant work remains that can continue to improve these processes and inform the private sector about the opportunities extract value from waste streams. Areas warranting further investigations are described in this chapter.

2.1 Advanced Separations

The concentration of organic compounds, the separation of sugars and anhydrosugars from phenolics and other organics (e.g., light acids and alcohols), and the removal of dissolved solids will likely be necessary to generate desirable feed streams for advanced chemical transformation processes. As demonstrated by this project, liquid-liquid extraction is an attractive method for concentrating organic compounds and segregating sugars and dissolved inorganic compounds. Pervious investigations used methyl tert-butyl ether (MTBE) as the liquid extractant, but better solvents likely exist. The extract solvent may be selected with a low heat of vaporization to minimize energy input during the distillation recycle and may have lower solubility in water than MTBE. Further work on liquid-liquid extraction as it pertains to the investigation and development of solvents is warranted.

Simulated moving bed chromatography (SMBC) is another option practiced commercially that could be developed in the pursuit of rendering "waste" aqueous phases suitable for further processing. SMBC uses several chromatographic columns. At the start, an aqueous-phase feed may be passed through a column containing immobile media, causing the targeted species to adhere to the media. Upon saturation, an eluent solvent then would be passed through the column, releasing the targeted species and capturing the targeted compounds. By combining numerous adsorption columns in parallel and staggering the times that feed and eluent enter a column via port switching, a continuous "moving bed" process may be implemented without the physical challenges of moving solid chromatographic material. Figure 2.1 is a schematic diagram of such an SMBC process. Research in this area would require the investigation of existing and potentially new chromatographic media. Media may be designed with affinities for sugars, acids, or other functional groups to facilitate separations while being resistant to degradation or competitive adsorption with dissolved solids. The opportunity to change phases from the aqueous to an organic phase through selection of appropriate eluent may also be possible, facilitating reactions that would be less corrosive to equipment and catalysts and elevated kinetics on many catalysts.

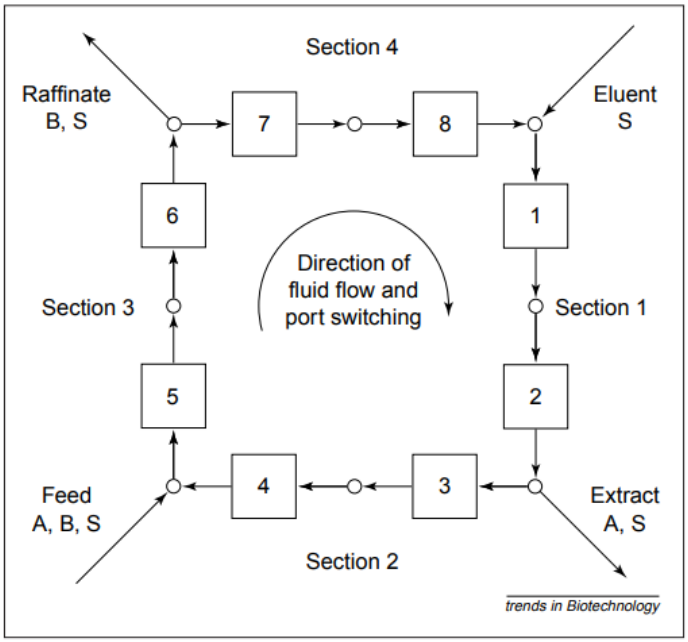

Figure 2.1. Schematic Representation of a SMCB Separation Process, that Uses Several Chromatographic Columns with Feed and Eluent Flow Controlled through Inlet and Outlet Port Switching to Selectively Separate Desired Components in the Aqueous Phase. Figure from Juza et al. (2000).

2.2 Hydrothermally Stable Catalyst Development

Significant opportunities exist to develop methods to prepare catalysts that are hydrothermally stable under relevant aqueous-phase conditions for thousands of hours. As shown in Figure 2.2, some materials such as TiO_2, ZrO_2, and carbon are more intrinsically stable in hot liquid water than siliceous materials such as SBA-15 and MCM-41 or silicoaluminates such as zeolites. TiO_2, ZrO_2, and carbon serve as excellent starting points. However, as shown in our recent work (Lopez-Ruiz et al. 2017), even these materials undergo changes under hydrothermal conditions. For example, pure amorphous or even tetragonal ZrO_2 will convert quickly in hot water to monoclinic ZrO_2. Including hydrothermal synthesis steps in the preparation of new materials with intrinsically greater hydrothermal stability (such as ZrO_2 or TiO_2) will lead to novel hydrothermally stable catalysts and supports. By creating materials under hydrothermal conditions, we will be able to create supports and catalysts with stable pore volumes, surface areas, and active sites. These supports and catalysts will already be stable under hydrothermal conditions because they were prepared under these conditions. Specific examples across several material classes expanding upon this idea and identifying new promising avenues of research are discussed below.

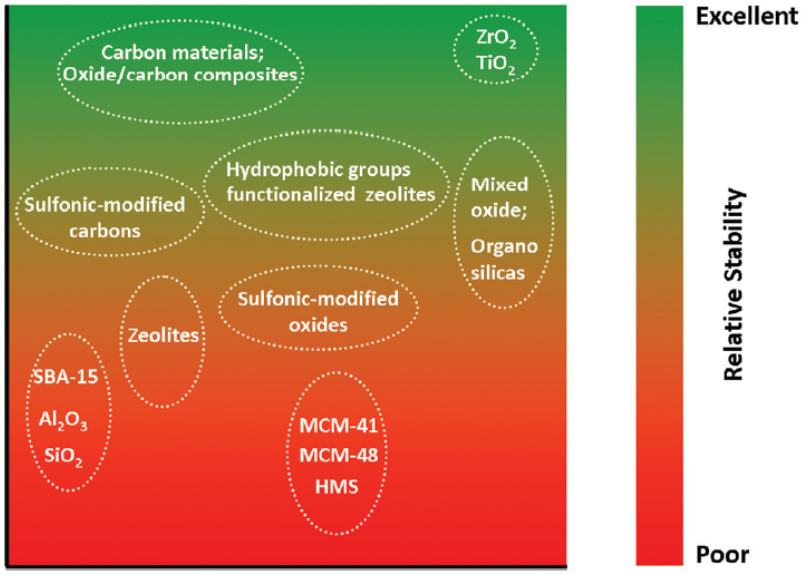

Figure 2.2. Relative Stability of Various Materials in Hot Condensed Water above 200°C. Taken from Xiong et al. (2013).

Hydrothermal synthesis of mixed metal oxides is well established. Indeed, zeolites are prepared via hydrothermal synthesis techniques. Challenges arise when zeolites are used in water at higher temperature than their preparation temperature. The hydrothermal precipitation of ZrO_2 from aqueous salts is also known in the literature (Khollam et al. 2001). Water directly hydrolyzes Zr salts, often creating fine (i.e., nanoscale) monoclinic structures. Recent work at Pacific Northwest National Laboratory (PNNL) demonstrated that amorphous mixed metal oxides of $La_xZr_yO_z$ co-precipitated by conventional means converts rapidly from an amorphous solid to a tetragonal structure in hot condensed water (Lopez-Ruiz et al. 2017). Surprisingly, the $La_xZr_yO_z$ catalyst maintained its high surface area (80 to 90 m^2/g) even after more than 100 hours of operation at 300°C in an aqueous mixture of 10% acetic acid. Questions that arise from observing the stability of $La_xZr_yO_z$ include:

1. Do other metal oxides such as TiO_2 or CeO_2 also impart stability?
2. What is the effect of oxidation state (e.g., Ce_2O_3 versus CeO_2)?
3. Can coordinatively unsaturated sites be created by intimately mixing cations with other valence states to create Bronsted acidity and mimic silicoaluminates? For example, could Nb^{+5} or Y^{+3} be intimately dispersed with Zr^{+4} to create –OH groups in the pursuit of a hydrothermally stable Bronsted acid catalyst?

New methods for synthesizing formed reactor-scale stable mixed metal oxide catalysts are also needed for performance evaluation under process-relevant conditions and commercial applications. Conventional catalyst-forming technologies generally rely on binders to construct macroscopic multi-functional bodies from catalyst powders. However, common binders such as boehmite often are unstable in hot liquid water, which can rapidly compromise the physical integrity of catalyst particles. Furthermore, these binders could negatively impact the properties of active catalytic components for instance via pore blocking and chemical reaction. Intimate mixing of metals may be generated via co-precipitation or sol-gel methods. Work at Oak Ridge has recently focused on the Alginate gelation method to create custom design forms of oxides (see Figure 2.3), which may be converted to carbides, another important class of catalysts increasingly recognized for their suitability as bioprocessing catalysts Sullivan et al. 2016.

Figure 2.3. Metal Oxide Spheres Recently Created at Oak Ridge National Laboratory via the Alignate Method

We believe development of hydrothermal pre-treatment steps either before or after the shaping of the macroscopic oxide catalysts should be employed to facilitate phase changes prior to application. By creating designed forms, we can start to measure relevant structural properties such as crush strength and attrition resistance. These properties are not always directly tied to catalytic properties but are important to commercial practitioners to make sure catalysts may be loaded and unloaded from industrial reactors without being crushed or forming significant amounts of dust/fines. Furthermore, the synthesis techniques employed are cost-effective methods that industry considers commercially viable for manufacturing-scale production.

2.2.1 Carbon

Carbon in its various forms is well known to possess excellent hydrothermal stability. New methods for creating carbon materials with hierarchical pore structures including macropores, mesopores, and micropores have been developed recently (Figure 2.4) (Estevez et al. 2013).

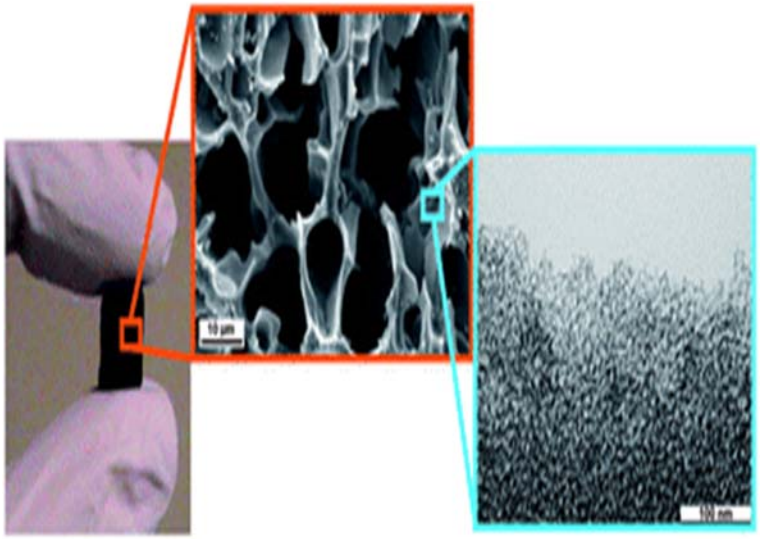

Figure 2.4. Carbon Monoliths (left) with Hierarchical Pores Demonstrated by the Macropores (center) and Mesopores (right) Shown in the Micrographs. Taken from Estevez et al. (2013).

Whereas other mesoporous materials such as SBA-15 lose their surface area and pore volume under hydrothermal conditions, we expect the inert nature of carbon will maintain its form even under aggressive acidic or basic conditions at high temperature. To date, these materials have been used as carbon dioxide scrubbers and in fuel cell applications, but only limited investigations of their use as catalyst supports have been reported. Investigating these hierarchical carbon materials as hydrothermally stable catalyst supports is a significant opportunity future research. The materials—glucose, colloidal silica, and ice—used to produce the hierarchical carbons are relatively inexpensive.

Another new area for exploration is the formation of carbon/metal oxide hybrid materials. We believe it may be feasible to "encapsulate" other metal oxides into a carbon structure that is stable, possesses wide pore openings, and maintains a high surface area. For example, niobia was recently shown to possess improved hydrothermal stability when prepared with carbon (Xiong et al. 2013). The application of ZrO_2, TiO_2, WO_3, MoO_3, or the preparation of carbides of tungsten and molybdenum may be feasible by the co-deposition approach. Work at Oak Ridge National Laboratory has demonstrated that oxide–carbon nanocomposites via a hexamethylenetetramine/urea gelation method. We propose the development of hydrothermal metal oxide gelation or deposition processes to incorporate metal oxides with carbons. Successful development of the hydrothermal processes to "attach" metal oxides to the carbon will result in a stable carbon backbone upon which metal oxides will be uniformly exposed to the reaction mixture. These carbon/metal oxide hybrid materials will possess wide pore diameters allowing access to even large reactants such as sugar monomers and oligomers.

2.2.2 Supported Metal Catalysts

Significant opportunity also exists to create new noble and base metal catalysts with improved hydrothermal stability by supporting metals on the metal oxides or hybrid carbon-metal oxide supports discussed above. Elkasabi et al. (2017) demonstrated that controlling pH during metal deposition onto metal oxides increases the "anchoring" of metals through strong metal-support interactions even under hydrothermal conditions. Another option is to co-deposit metals with carbonaceous materials as described above, then perform controlled oxidation to expose metal sites, followed by a reductive step to create stabilized "islands" of metals. Previous work with noble metals supported on carbon for gas phase applications suggests the carbon supports may facilitate the reduction of the metals. It may therefore be possible to "encapsulate" metals near to the surface of carbon and reduce them to metallic valences while keeping them anchored in place. For example, the encapsulation of Ru may be applied to CHG catalysts so the concentration of Ru may be reduced from the current state of the art of ~8 wt% while maintaining equivalent activity.

2.3 Oxidative Thermochemical Processes

One specific application for metal-supported hydrothermally stable catalysts is for thermochemical oxidation reactions. Oxidation could be useful to convert phenolic compounds (e.g., ring-open catechol) or to completely remove organics from an aqueous stream as a cleanup process (Figure 2.5).

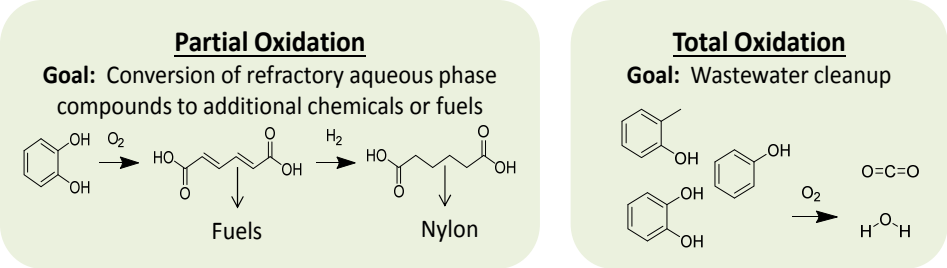

Figure 2.5. Representative Examples of the Condensed-Phase Partial and Total Oxidation Reactions

Two important criteria for condensed-phase oxidation catalysts are physical and chemical stability in hot acidic solutions and a demonstrable activity for prolonged use at elevated temperatures (Matatov-Meytal and Sheintuch 1998). The $La_xZr_yO_z$ catalyst has demonstrated stability in hot acidic water at 300°C, making it an ideal catalyst support for oxidation active materials (e.g., V_2O_5 or CuO). Total oxidation reactions are a potential method for treating wastewater. Partial oxidation will be investigated as a route to forming high-value chemicals such as dicarboxylic acids. There are biological agents adept at partial oxidations resulting in ring opening (Beckham et al. 2016.) Mechanistic investigations suggest phenol and catechol oxidatively ring-open to dicarboxylic acids (Devlin and Harris 1984). Controlling the extent of oxidation through temperature, O_2 partial pressure, and selective catalysts are parameters that could be explored. This concept is ripe for catalyst screening experiments to yield new materials.

2.4 Techno-Economic Evaluations and a Wastewater Guiding Document

The concept of developing an aqueous-phase guiding document for valorization and/or cleanup options that transcends any one given conversion process has received general feedback from stakeholders. The envisioned document would provide economic guidelines for when carbon recovery and sale is likely to be economically beneficial. Process agnostic techno-economic analysis (TEA) could outline aqueous-phase CAPEX[1] and OPEX[2] processing cost envelopes versus the price for chemicals to define economic opportunities (Figure 2.6).

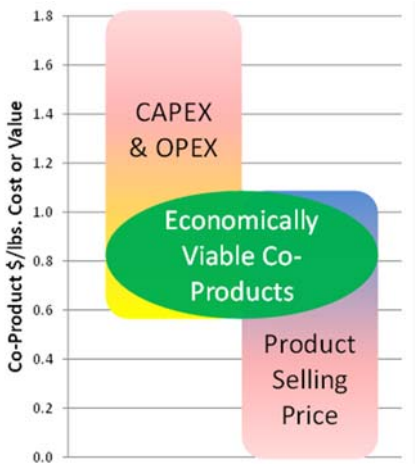

Figure 2.6. Example of Envisioned Economic Guidance for Stakeholders

[1] CAPEX = capital expenditure
[2] OPEX = operational expenditure

Furthermore, bracketing the lower range of when organic compound recovery is likely economically viable would be helpful. In this project, algal and waste HTL streams were not deemed to be suitable feedstocks because recovery of the <1 wt% acetic acid was not feasible. However, fast-pyrolysis aqueous phases received independently from Karlsruhe Institute of Technology and the U.S. Department of Agriculture (USDA) with about 5 wt% acetic acid could be readily converted to olefins. The minimum concentration of organics that may be recovered will be a function of the product selling price, but understanding the economic tradeoffs on recovery would be a significant achievement.

Finally, we expect the guiding document could provide general guidance for wastewater treatment options. Wastewater treatment options and discharge regulations are highly regional, but the envisioned document could provide context to begin a wastewater treatment plan for a novice to process planning. No such short primer on wastewater treatment and disposal is known to exist.

3.0 Technical Achievements

The remainder of this report provides technical highlights of project accomplishments. The characterization, separations, and catalytic processes developed by this project as well as the TEA of the separation and catalytic processes developed are covered below.

3.1 Characterization

The characterization task of this project sought to fill an identified gap in the open literature regarding the organic and inorganic constituents present in the aqueous phases generated from biomass conversion processes. To fill identified knowledge gaps, studies were initiated to quantitatively characterize the aqueous-phase constituents from a variety of feedstocks and processes. The aqueous phases identified for analysis included:

1. Fast-pyrolysis, bench-scale hydrotreating (Panisko et al. 2015)
2. Lignocellulosic feedstock HTL (Panisko et al. 2015)
3. Algal feedstock HTL (Maddi et al. 2016)
4. HTL of agricultural waste, wastewater treatment plant solids, and biomass grown on waste-stream effluents (Maddi et al. 2017)
5. Catalytic fast pyrolysis[3]
6. Demonstration-scale units.[4]

Selected results of the characterization studies are summarized below.

3.1.1 Fast-Pyrolysis, Bench-Scale Hydrotreating

Fast-pyrolysis, bench-scale hydrotreating resulted in an aqueous phase with a very low amount of carbon (Panisko et al. 2015). The total carbon in these aqueous phases was generally less than about 0.45 wt% carbon. Of the carbon present, nearly all existed as inorganic carbon (e.g., dissolved carbon dioxide). The low concentration of organic carbon was likely due to highly efficient conversion within the relatively small (nominally 30 cm^3) bench-scale hydrotreater. Low molecular weight oxygenates are known to convert to gas under hydrotreater conditions (Elliott 2007).

Fast-pyrolysis bio-oil hydroprocessing is conducted in multiple stages to first stabilize the bio-oil at lower temperature prior to a second stage conducted at higher temperature to remove oxygen (Zacher et al. 2014). The aqueous phase after a low temperature bio-oil stabilization step over a Ru/C catalyst contained 18 to 27 wt% organics (Elliott 2007). Thus, it may be possible to stabilize bio-oil, separate the aqueous phase to perform directed catalytic conversion on the organic compounds, and continue deoxygenation of the bio-oil at diminished hydrogen consumption.

[3] Journal article in preparation
[4] Unpublished results

3.1.2 Lignocellulosic Feedstock Hydrothermal Liquefaction

HTL of terrestrial feedstocks such as wood or switchgrass resulted in aqueous phases with generally a 1 to 2 wt% concentration of carbon (Panisko et al. 2015). Glycolic acid, acetic acid, and propionic acid were identified as the major constituents. Inductively coupled plasma (ICP) analysis of the HTL lignocellulosic aqueous product revealed about 2000 to 7000 ppm of Na present. The high concentration of Na resulted from the addition of $Na(CO_3)$ to the HTL feed slurry to buffer the pH of the HTL reaction. Potassium was present at levels of 400 to 1400 ppm in samples generated by processing switchgrass. Samples derived from wood contained only 150 to 180 ppm of potassium.

While the concentration of organic compounds in the aqueous phase from HTL is low, the yield of C to the aqueous phase is substantial. Zhu et al. (2014) found that 39.9% of the C fed to HTL process reported to the aqueous phase. Furthermore, it is likely that in an industrial process, the HTL aqueous product would be recycled to create the slurry of the lignocellulosic feedstock. The HTL samples analyzed in Panisko et al. (2015) were from a single pass except for the "CS8" sample, which was recycled twice. Previous work performed by PNNL for the North American Biotechnology Council showed that recycle of the HTL aqueous phase did indeed result in an increase in concentration of organics.[5] This project extrapolated a proposed concentration in FY 2014 based on the North American Biotechnology Council report and data published by Zhu et al. (2014). Thus, HTL of the lignocellulosic feedstock aqueous phase was identified as a promising stream for valorization because it represents a significant amount of the biomass carbon as well as a relatively low water concentration stream.

3.1.3 Algal Feedstock Hydrothermal Liquefaction

HTL is uniquely suited to process wet feedstocks such as algae into transportation fuels. The HTL aqueous phase produced from algae typically contains 20 to 35% of the total carbon entered into the system (Maddi et al. 2016). The concentration of carbon in the aqueous fraction was on the order 1.4 to 3.4 wt%. In this effort, a two-dimensional gas chromatography method using the time-of-flight mass spectroscopy method was developed and reported (Maddi et al. 2016). Similar to lignocellulosic HTL aqueous products, light organic acids such as acetic acid and propionic acid were among the most prevalent compounds. In contrast, a significant amount of nitrogen present as both NH_3 and nitrogen-containing organic compounds were present. NH_3 was present at concentrations on the order of 0.25 to 0.9 wt% with the total concentration of nitrogen (including NH_3) typically on the order of 0.8 to 1.6 wt%. Many of the nitrogen-containing compounds such as pyridine, n-methyl succinimide, and n-ethyl succinimide have high-value applications as drug and chemical precursors. However, their relatively low concentrations of both oxygen and nitrogen-containing species makes recovery and purification challenging. The concentrations of organic species in the aqueous product due to aqueous-phase recycling to the head of the HTL reactor is not an option for algal feeds. A feedstock produced from algae must be dewatered prior to HTL processing rather than adding water. However, if an appropriate adsorption material were identified in an SMBC process, it is possible that an economically viable recovery technology could be developed provided the products from the separation were sufficiently valuable.

[5] Unpublished PNNL work

3.1.4 Hydrothermal Liquefaction of Agricultural Waste, Wastewater Treatment Plant Solids, and Biomass Grown On Waste Stream Effluents

Waste materials from agriculture or food production and wastewater treatment plant solids represent low-cost streams with the potential to economically produce biofuels. These feeds are often wet, again making HTL particularly attractive for producing biocrude as an intermediate to liquid transportation fuels. The aqueous phase produced by processing grape pomace from wine production, spent grains from brewing beer, and sugar beet tailings from sugar production were investigated (Maddi et al. 2017). The grape pomace produced water with a relatively high concentration of ethanol. While acetic acid was again one of the primary organic constituents in the aqueous phase, sugar beet tailings produced a relatively high concentration of acetic acid at near 1 wt% of the total aqueous product, which may have been due to the carbohydrate rich nature of the feedstock (Nelson et al. 1984). About 30 to 55% of the carbon in the industrial food waste feedstocks were found in the aqueous phase. The grape and beet residues had about 2.5 wt% total carbon concentration in the aqueous phase while the grain from beer production contained only about 1 wt% total.

The aqueous product from the HTL of wastewater treatment sludge produced an aqueous liquid phase similar in many respects to algal feedstocks. While acetic acid is again the major oxygenated compound present, a significant amount of nitrogen (0.4 to 0.8 wt%) also was present. A significant amount of the nitrogen was present as ammonia. Heavy metals such as Ni, Cu, and Pb were not identified in the aqueous phase (detection limit was about 2 ppm). Na and K were present at concentrations ranging from 50 to 5500 ppm in the streams.

HTL aqueous phases produced from algae grown on wastewater effluent as well as oleaginous yeast grown on corn stover lignin were the final feedstocks characterized (Maddi et al. 2017). Some waste streams contain nutrients in which biomass may be grown. Algae grown on wastewater treatment water effluent was similar to other aqueous phases produced by algae (Maddi et al. 2016). Nitrogen is present in the aqueous phase at about 1.2 wt%; most of the nitrogen is present as ammonia. No substantial differences in the aqueous phases generated from algae grown in fresh or salt water were noted. Oleaginous yeast produced water with substantially less nitrogen (0.2 wt%) compared to the algae but a similar amount of organic carbon on the order of about 2 wt%. Inorganic compounds in the oleaginous yeast product included potassium at about 5000 ppm along with sulfur at about 1200 ppm.

3.1.5 Demonstration-Scale Unit Aqueous-Phase Characterization

Three aqueous products generated by HTL and hydroprocessing feeds in demonstration-scale processes at PNNL were collected for analysis. This data is unpublished and presented here for use in future projects. The demonstration-scale samples were selected in part because of concerns that samples characterized at smaller scale (e.g., the bench-scale hydrotreater aqueous samples above) were not representative of products generated at a commercial scale. The three samples selected are listed in and described in Table 3.1.

Table 3.1. Demonstration-Scale Aqueous Samples Characterized

Sample Name	Description
WW06	Aqueous product generated from bench-scale HTL of 50/50 primary/secondary solids from municipal sludge collected from the Detroit wastewater treatment plant.
Upgrading demonstration plant (UDP)-5	Five aqueous products generated from the 30-L catalytic hydrotreating system at PNNL generated by upgrading pine pyrolysis oil supplied by the National Renewable Energy Laboratory.
Modular HTL Skid (MHTLS)	MHTLS aqueous product generated from the HTL of Chlorella algae.

The bulk characterization of each of the streams is shown in Table 3.2. Hydrotreating at the 30-L scale in the UDP-5 material contained only marginally more carbon at 0.15 wt% compared with the smaller scale hydrotreating of bio-oil reported in Panisko et al. (2015).

Table 3.2. Bulk Characterization of the Demonstration-Scale Aqueous Streams

	WW06	UDP-5	MHTLS
Water (wt%)	95.8	99.5	93.7
Carbonyl (mmol/g)	0	0.243	0
Organic Carbon (wt%)	2.2	0.15	2.4
Inorganic Carbon (wt%)	0.22	0.09	-
Total Nitrogen (wt%)	1.2	0.18	0.11
Total Suspended Solids (TSS)(mg/L)	Not Analyzed	10.0	1120
BOD (mg/L)	22900	Not Analyzed	24300
NH_3 (mg/L)	5100	1420	6040
COD (mg/L)	59400	1840	58,900

Dissolved solids in the three streams are presented in Table 3.3 and Table 3.4. Potassium, Na, P, Si, and S were the primary dissolved species identified via ICP for each process. Sulfate and chloride were the primary anions identified.

Table 3.3. ICP Analysis of Cations in the Demonstration-Scale Aqueous Streams

	WW06	UDP-5	MHTLS
K (ppm)	251	15	1363
Na (ppm)	116	72	3469
P (ppm)	8.2	12	24
Si (ppm)	226	108	56
S (ppm)	292	138	455

No detections of the following cations were observed (detection limit 1 ppm): Al, Ca, Fe, Mg, Ag, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Re, Ru, Sr, V, Y, Zn, Ti, Au, Pd, Pt, Rh, Sn, Zr.

Table 3.4. Results from Ion Chromatograph Analysis of Anions in the Demonstration-Scale Aqueous Streams

	Chloride (ppm)	Bromide (ppm)	Nitrate (ppm)	Sulfate
WW06	280	BDL	51	313
UDP-5	31	9.8	12	156
MHTLS	151	BDL	123	894

BDL is below detection limit.

Specific organic species identified in the three larger-scale processes are presented in Table 3.5. As expected based on the total organic carbon analysis above, UDP-5 contains very little organic mater. Similar to other aqueous streams, acetic acid and propionic acid are found to be the major constituents of the WW06 and MHTLS streams. Interestingly, glycerol is also a major component of the MHTLS stream, probably from the hydrolysis of neutral lipids present in the algal feedstocks.

Table 3.5. Results of Ion Chromatograph Analysis of Anions in the Demonstration-Scale Aqueous Streams

Chemical compounds	WW06	UDP-5	MHTLS
Acetic acid (liquid chromatography [LC]) (ppm)	0.55	<0.05	0.259
Propanoic acid (LC) (ppm)	0.08	<0.05	0.107
Butanoic acid (LC) (ppm)	<0.05	<0.05	-
Ethanol (ppm)	0.026	-	0.06
Acetone (ppm)	0.22	0.036	0.16
2-Butanone (ppm)	0.073	-	0.060
2-Butanone, 3-hydroxy (ppm)	0.02	-	0.066
Pyrazine (ppm)	0.045	-	0.038
Acetamide (ppm)	0.15	-	0.04
Cyclopentanone (ppm)	0.009	-	0.006
Pyrazine, methyl (ppm)	0.11	-	0.1
Propanamide (ppm)	0.047	-	0.02
2(3H)-Furanone, dihydro-5-methyl (ppm)	0.026	-	0.21
Phenol (ppm)	0.017	0.024	0.01
2-Pyrrolidinone, 1-methyl (ppm)	0.027	-	0.027
2-Pyrrolidinone (ppm)	0.02	-	0.11
N-methylsuccinimide (ppm)	0.015	-	0.013
3-pyridinol (ppm)	0.038	-	0.023
N-ethylsuccinimide (ppm)	0.016	-	0.024
2-Piperidinone (ppm)	0.06	-	0.055
Glycerol (LC) (ppm)	-	-	0.251
Methyl acetate (LC) (ppm)	-	-	0.262

3.2 Separations

3.2.1 Liquid-Liquid Extraction of Lignocellulosic Hydrothermal Liquefaction Aqueous Product

Results presented in this section are from research undertaken at PNNL.[6]. A cleanup process was designed in which organic compounds extracted from the aqueous phase via liquid-liquid extraction to concentrate the organic compounds and to segregate them from dissolved solids. Carbon treatment also was needed to remove color bodies, which were presumed to be high molecular weight organic compounds. Figure 3.1 is a schematic diagram of the cleanup process.

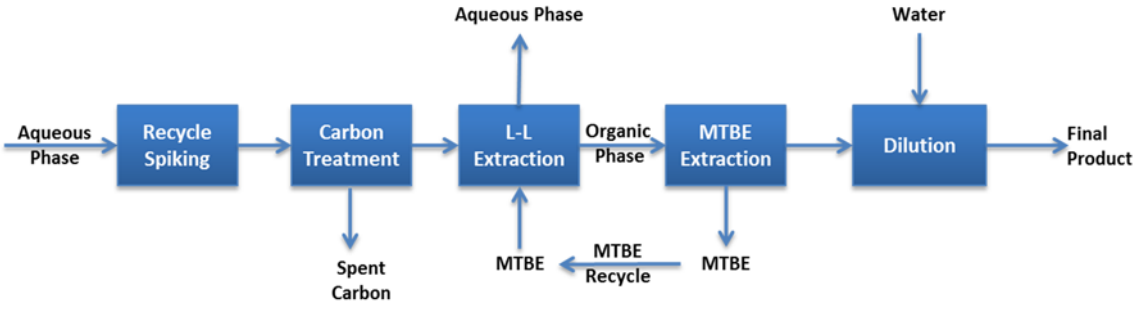

Figure 3.1. Schematic of the Developed Cleanup Process of the Aqueous Fraction Derived from HTL

[6] Article in preparation for submission to *Green Chemistry*

This feedstock simulated an HTL process with aqueous phase recycle as reported by Zhu et al. (2014). Table 3.1 and Table 3.2 detail the resulting organic and inorganic compositions, respectively, after each step of the process. The ketonization feed and steam reforming feed are used as feedstocks below.

Table 3.6 reports the HTL-derived aqueous phase at each point in the cleanup process.

Table 3.6. LC analysis of the Aqueous Fraction derived from HTL Production of Bio-Oil after Each Step of the Cleanup Process

Compound	As Received	Simulated Recycle[a]	Carbon Treated	Aqueous[b]	Organic[b,c]	Ketonization Feed[d]	Steam Reforming Feed[d]
	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]
Xylitol	0.022	0.016	-	0.012	-	-	-
Glycolic acid	0.784	2.242	2.315	2.505	1.256	0.198	0.160
Glycerol	0.044	0.032	0.033	0.040	-	-	-
Formic acid	0.052	0.034	0.017	0.017	0.040	0.005	-
Acetic acid	0.920	22.326	19.360	7.654	63.445	10.176	29.069
Ethylene glycol	0.097	0.975	1.002	1.110	0.264	0.042	-
Levulinic acid	0.035	0.016	-	-	-	-	-
Propionic acid	0.103	3.933	2.332	0.241	11.216	1.751	4.791
Methanol	0.344	2.336	2.249	1.949	0.509	0.043	-
1,2-butandiol	0.026		-	-	0.006	-	-
Ethanol	0.088	0.537	0.394	0.232	0.568	0.080	-
Acetone	0.088	0.053	0.022	0.010		-	-
methyl acetate	0.126	0.045	0.050	-	0.195	-	-
1-propanol	0.026	0.013	0.004	-	0.018	-	-
MEK (2-butanone)	0.032	0.018	-	-	-	-	-
1-pentanol	-	0.043	-	-	-	-	-
3-methyl-2-cyclopentene-1-one	-	0.036	-	-	0.004	-	-
MTBE	-	-	-	2.022	2.911	-	-

[a] Model compounds were added to the HTL process aqueous phase to simulate an HTL-derived aqueous phase that had been recycled numerous times and achieved steady state.
[b] Aqueous and organic phases formed by the addition of MTBE in order to perform the liquid-liquid extraction.
[c] Concentrations are after subjecting the organic phase material to rotary evaporation to remove most of the MTBE solvent.
[d] Water was added to the organic mixture to mitigate process equipment corrosion and achieve desirable steam/carbon ratios

The “As Received” column is the sample generated by the original HTL test. The “Simulated Recycle” column is with the model compounds added to the “As Received” material and shown as “Recycle Spiking” in Figure 3.1. The model compounds were added to simulate a material from an HTL process with water recycle at steady state. Carbon treatment of the Simulated Recycle material resulted in a loss of acetic acid, which decreased from 22.3 to 19.4 wt%, and propionic acid, which decreased from 3.9 wt% to 2.3 wt% due to adsorption with the carbon but little change in other quantified organics. The change in feedstock coloration after carbon treatment was significant as observed in Figure 3.2.

Figure 3.2. HTL-Derived Aqueous Phase As-Received and Untreated (left) and Following Cleanup (right)

Carbon treatment did increase the concentration of Ca, K, Mg, Na, P, and Si, which could likely be mitigated through the use of alternative carbon adsorbents in the future as shown in Table 3.7. Addition of MTBE to the carbon treated aqueous phase resulted in formation of an organic and aqueous layer. The majority of the carboxylic acids and some of the alcohols were carried into the extracting organic phase. Analysis of the aqueous phase showed that a large portion of the acetic acid and propionic acid were removed (decreased to 7.7 and 0.2 wt% respectively). A portion of the MTBE reported to the aqueous phase (2.0 wt%). As expected, the majority of the inorganics remained in the aqueous phase. The organic phase was found to contain mostly acetic acid and propionic acid (63.4 and 11.2 wt% respectively) with all other compounds comprising less than 1 wt%, with the exception of some retained MTBE. The majority of the inorganic compounds remained in the aqueous phase.

Table 3.7. ICP Analysis of the Aqueous Fraction Derived from HTL Production of Bio-Oil after Each Step of the Cleanup Process

Compound	As Received	Simulated Recycle[a]	Carbon Treated	Aqueous[b]	Organic[b,c]	Ketonization Feed[d]	Steam Reforming Feed[d]
	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]
Al	0.98	1.18	4.79	5.30	< 2.0	< 2.0	< 2.0
Ca	74.94	50.31	134.85	139.38	< 2.0	< 2.0	< 2.0
K	725.6	745.9	1959	2351	11.57	< 2.0	3.97
Mg	3.9	3.04	131.15	131.43	< 2.0	< 2.0	< 2.0
Mn	2.98	2.35	3.47	3.66	< 2.0	< 2.0	< 2.0
Na	5237	7043	7321	8576.67	25.25	5.2	22.87
P	<2.0	< 2.0	90.7	98.28	9.37	< 2.0	< 2.0
Sr	1.37	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0
Si	55.3	40.25	88.9	89	8.88	3.34	4.93
S	18.11	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0

[a] Model compounds were added to the HTL process aqueous phase to simulate a HTL-derived aqueous phase that had been recycled numerous times and achieved steady state.
[b] Aqueous and organic phases formed by the addition of MTBE in order to perform the liquid-liquid extraction.
[c] Concentrations are after subjecting the organic phase material to rotary evaporation to remove most of the MTBE solvent.
[d] Water was added to the organic mixture to mitigate process equipment corrosion and achieve desirable steam/carbon ratios

3.2.2 Liquid-Liquid Extraction of USDA Fast-Pyrolysis Aqueous Phase

Fast pyrolysis-derived aqueous product was received from the USDA. Activated carbon (AC) treatment was used to remove coloring agents and diminish the sugar-derivative content of the feedstock. These constituents act as contaminants for downstream synthesis catalysts. For AC treatment, the feedstock was combined with AC (Pacco CTC coconut shell) at a weight ratio of 10:1 (feedstock:AC) and then mixed for 24 hours. Following 24 hours of mixing, the feedstock and carbon were separated by vacuum filtration. AC treatment was done twice to obtain an almost colorless feedstock. After AC treatment, the feedstock was loaded into a continuous liquid-liquid extractor (LLE) with MTBE (Sigma-Aldrich, anhydrous 99.8%). Conditions used for LLE are shown in Table 3.8. Multiple LLE runs were performed in to obtain enough final product to be used as feedstocks for subsequent conversion demonstration (~125 mL). All the LLE runs were combined, water was then added to target a 10 wt% acetic acid feed composition (to maintain a steam:carbon ratio of ~13 to facilitate stable operation), and then MTBE was removed via single-stage distillation. The inorganic and organic compositions of the resulting products are shown in Table 3.9 and Table 3.10, respectively. The extracted aqueous phase was used to produce olefins on the $ZnZrO_x$ catalyst described below.

Table 3.8. Summary of Continuous LLE Operations for Cleanup of the USDA Fast-Pyrolysis Aqueous Phase

Sample	Feedstock: MTBE	Extraction Time [hr]	ICP: K [ppm]	ICP: Na [ppm]	Acetic Acid [wt%]	Propionic Acid [wt%]	Levoglucosan [wt%]
As Received	N/A	N/A	12.34	9.30	4.78	2.88	0.52
AC Treated	N/A	N/A	1559	201.9	3.07	1.95	0.32
LLE 1	3:1	21	2859	347.3	40.38	11.78	0.65
LLE 2	1:1	21	242	34.2	36.50	5.74	BDL
LLE 3	1:1	42	23.5	12.6	43.28	11.76	0.32

Table 3.9. Summary of Feedstock Inorganic Content in the USDA Fast-Pyrolysis Aqueous Phase

Analyte Name	As Received	Carbon Treated	LLE - Organic Combined	Final Feedstock
Al	13.43	2.461	< 10	< 1
Ca	115	84.02	< 10	3.201
Co	2.218	<2	< 10	< 1
Cr	65.66	<2	< 10	< 1
Fe	961	<2	< 10	< 1
K	12.335	1559	24.4	17.21
Mg	17.65	117	< 10	< 1
Mn	38.4	<2	< 10	< 1
Na	9.2995	201.9	13.44	12.78
Ni	108.6	<2	< 10	< 1
P	11.34	95.12	< 10	< 1
Zn	< 2	6.845	< 10	2.497
Si	66.975	43.01	< 10	2.652
S	10.65	65.1	< 10	< 1

Table 3.10. Summary of Organic Compounds in the USDA Fast-Pyrolysis Aqueous Phase

	As Received	Carbon Treated	LLE - Organic Combined	Final Feedstock
Peak Name	[wt%]	[wt%]	[wt%]	[wt%]
Sorbital	0.032	0.021		
Levoglucosan	0.522	0.3175		
Glycolic acid	0.313	0.214		
Glyercol	0.101	0.039		
Formic acid	0.248	0.1205	0.1635	0.187
Acetic acid	4.7835	3.071	8.5225	9.242
Ethylene glycol	0.1755	0.132	0.014	0.015
Levulinic acid	0.0615	0.01	0.014	0.01
Propanoic acid	2.8855	1.951	1.79	1.684
Methanol	2.1135	1.3475		0.137
Ethanol	1.3755	0.718	0.6305	0.674
Propionaldehyde	0.319			
Butanoic acid		0.012	0.022	0.029
Acetone	0.1615	0.049		0.157
methyl acetate	0.692			
1-propanol	0.0555			
Butryaldehyde	0.446			
MTBE			3.2895	0.161
1-butanol	0.3515			
2-cyclopenten-1-one	0.154		0.022	
3-methyl-2-(5H)-furanone	0.02			
2-methylcyclopentanone	0.063			
Furfural	0.186			
1-pentanol	0.096			
3-methyl-2-cyclopentene-1-one	0.1			
4-heptanone	0.051			
m-Cresol	0.02			

3.2.3 Condensed-Phase Ketonization

Work on this project in FY 2014 resulted in the discovery of a $La_xZr_YO_Z$ catalyst with activity and stability for conducting the ketonization reaction in the condensed aqueous phase at nominally 300°C and 1400 psig. Ketonization was most often studied as the reaction of two equivalents of acetic acid reacting to form acetone, water, and carbon dioxide. Further development of the ketonization catalyst was conducted and published by Lopez-Ruiz et al. (2017). As shown in Figure 3.3, an optimum loading of La at about 0.17 mol fraction La/Zr, which corresponds to about 20 wt% La_2O_3. Stable activity was observed in these tests for over 140 hours even under aggressive hydrothermal conditions with 10 wt% acetic acid present as the reactant.

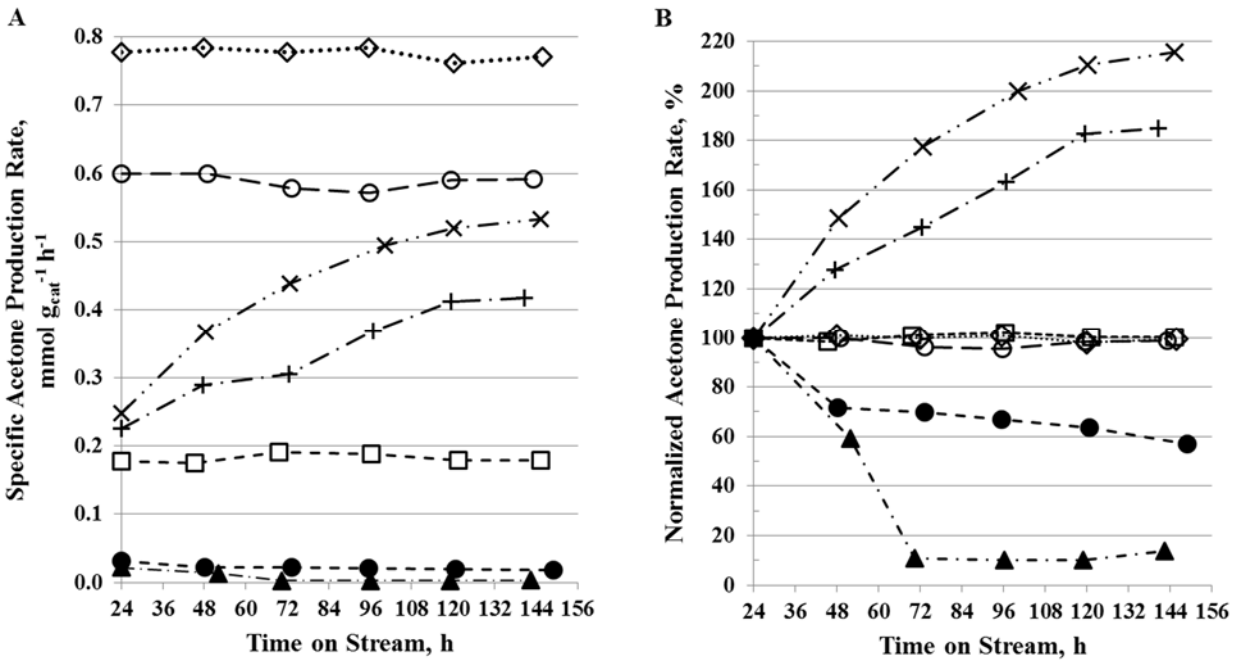

Figure 3.3. Specific Acetone Production Rate (A) and Normalized Acetone Production Rate (B) under Condensed Hydrothermal Conditions (10 wt% acetic acid in water, 9800 kPa, and 568 K) as a Function of Time-on-Stream. Symbol definitions follow: ▲ = La2O3, ● = ZrO2, □ = 0.035 $La_xZr_yO_z$, ○ = 0.10 $La_xZr_yO_z$, ◇ = 0.17$La_xZr_yO_z$, × = 0.20$La_xZr_yO_z$, and + = 0.23$La_xZr_yO_z$. The lines are only meant to help the reader navigate through the results and are not regressions. Taken from Lopez-Ruiz et al. (2017).

3.2.3.1 Model Compound Testing – Effect of Impurities on Condensed-Phase Ketonization

Conversion of aqueous acetic acid to acetone over $La_xZr_YO_Z$ catalyst was shown to be active and stable in the condensed phase for 144 hours with a model feed (Lopez-Ruiz et al. 2017). However, as shown above in Table 3.7, HTL-derived aqueous streams contain several other organic molecules as well as dissolved solids that are likely to affect catalytic stability. For this reason, a systematic evaluation of the effects of cations and organic molecules on ketonization catalyst stability using model feeds was performed. Figure 3.4 illustrates the excellent hydrothermal stability of 15wt% La2O3/ZrO2 with 10 wt% acetic acid in water. No deactivation was observed after about 490 hours. However, when exposed to concentrations of Na similar to those expected in HTL-derived aqueous streams (i.e., 18,000 ppm at 490 hours) the catalytic activity decreased by approximately 50%. Interestingly, when the feed was changed back to Na-free, the activity fully recovered. This suggests that Na did not bind to catalytically active sites on the catalyst but rather changed the binding strength of the acetic acid to the surface of the catalyst. Lower Na concentrations at 10,000 and 5000 ppm produced commensurate decreases in catalytic activity. Speculatively, the Na may be changing the thermodynamic activity coefficient of the acetic acid in solution, resulting in a decrease of the surface concentration of adsorbed acetic acid or acetate on the catalyst surface. When Na is removed from the system, the activity coefficient changes quickly, resulting in the observed increase in the ketonization rate.

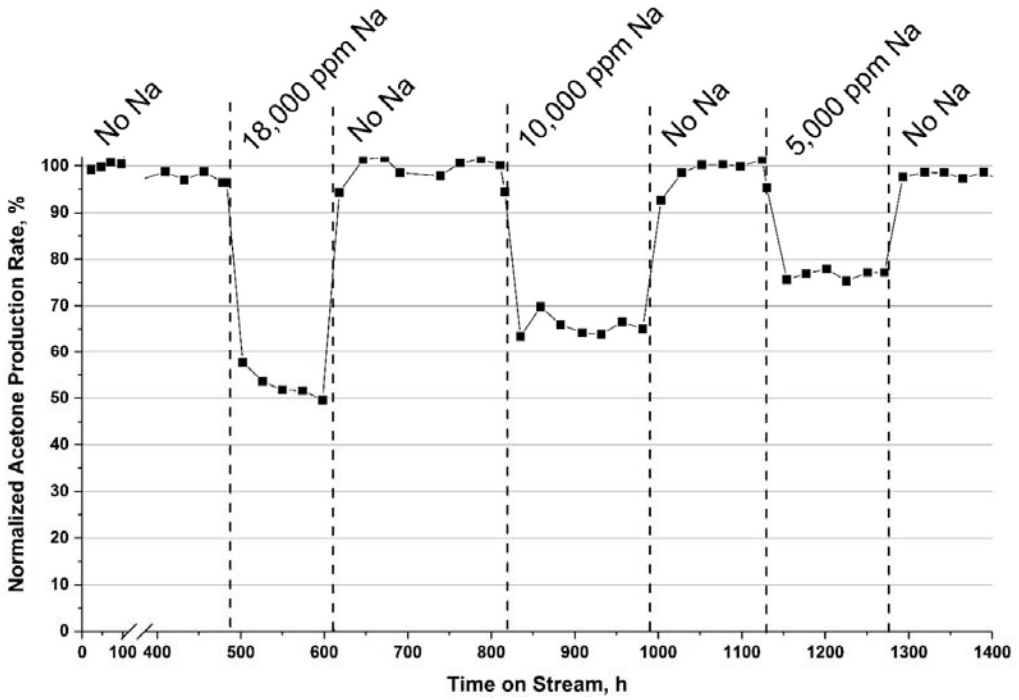

Figure 3.4. Effect of Na Concentration on Normalized Acetone Production Rate during Condensed-Phase Ketonization of Acetic Acid over 15wt% La_2O_3/ZrO_2 (295°C, 1400 psig, 0.03 cm^3/min; feed: 10 wt% acetic acid in water)

Irreversible deactivation behavior was observed when the $La_xZr_yO_Z$ catalyst was exposed to glycolic acid and ethylene glycol as shown in Figure 3.5. Similar to the case when feeding with Na, catalytic activity decreased by approximately 50% when exposed to 10,000 ppm of glycolic acid. However, catalytic activity was not fully recovered upon reintroduction of glycolic acid-free model feed. When adding 10,000 ppm ethylene glycol the catalyst similarly deactivated and the catalytic activity did not recover when model feed without ethylene glycol was used. These results suggest that at least some of the organics molecules present in the HTL-derived aqueous cause irreversible catalyst deactivation.

3.2.3.2 Condensed-Phase Ketonization with Simulated Recycle Aqueous Phase

HTL-derived aqueous feed with constituents detailed in Table 3.6 and Table 3.7 named the "HTL Simulated Recycle" was evaluated over a fresh 15wt% La_2O_3/ZrO_2 catalyst. As shown in Figure 3.6, the catalyst was initially run for 96 hours with model feed to ensure stable operation. After introduction of the HTL-derived aqueous phase the normalized catalytic activity decreased by 90% within 48 hours of operation. The significant loss of activity was attributed to a significant concentration of a variety of both organic and inorganic molecules present in the HTL-derived aqueous feed. Irreversible deactivation of the catalyst was confirmed when the feedstock was changed back to the model 10 wt% acetic acid and only 35% of the original activity was recovered. These results suggest that the HTL-derived feed must be treated to remove organic and inorganic contaminants via the process described above.

Condensed-phase ketonization was evaluated using aqueous product subjected to the cleanup process as feedstock. Water was added to the organic product mixture to mitigate process equipment corrosion via lower acid concentration as well as to match the 10 wt% acetic acid concentration utilized in the model compound studies above and previously reported (Lopez-Ruiz et al. 2017). The composition of the feedstock is shown in Table 3.6 and Table 3.7 and labeled as "Ketonization Feed."

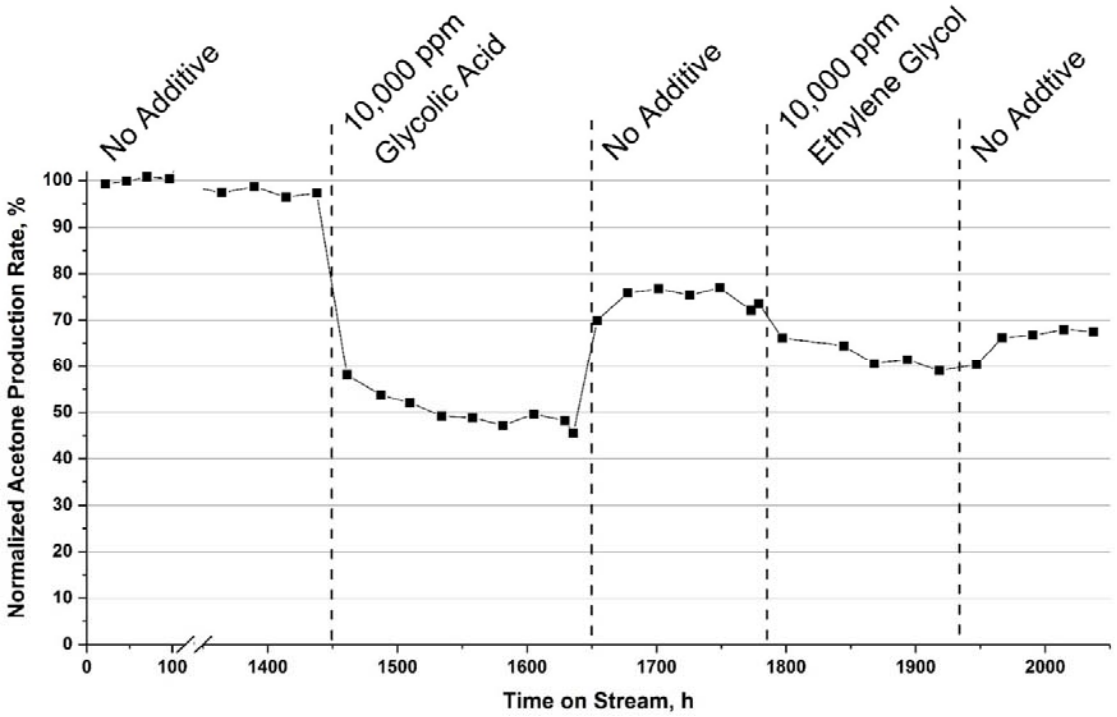

Figure 3.5. Effect of Glycolic Acid and Ethylene Glycol on the Normalized Acetone Production Rate during Condensed-Phase Ketonization of Acetic Acid over 15wt% La_2O_3/ZrO_2 Catalyst (295°C, 1400 psig, 0.03 cm3/min; feed: 10 wt% acetic acid in water)

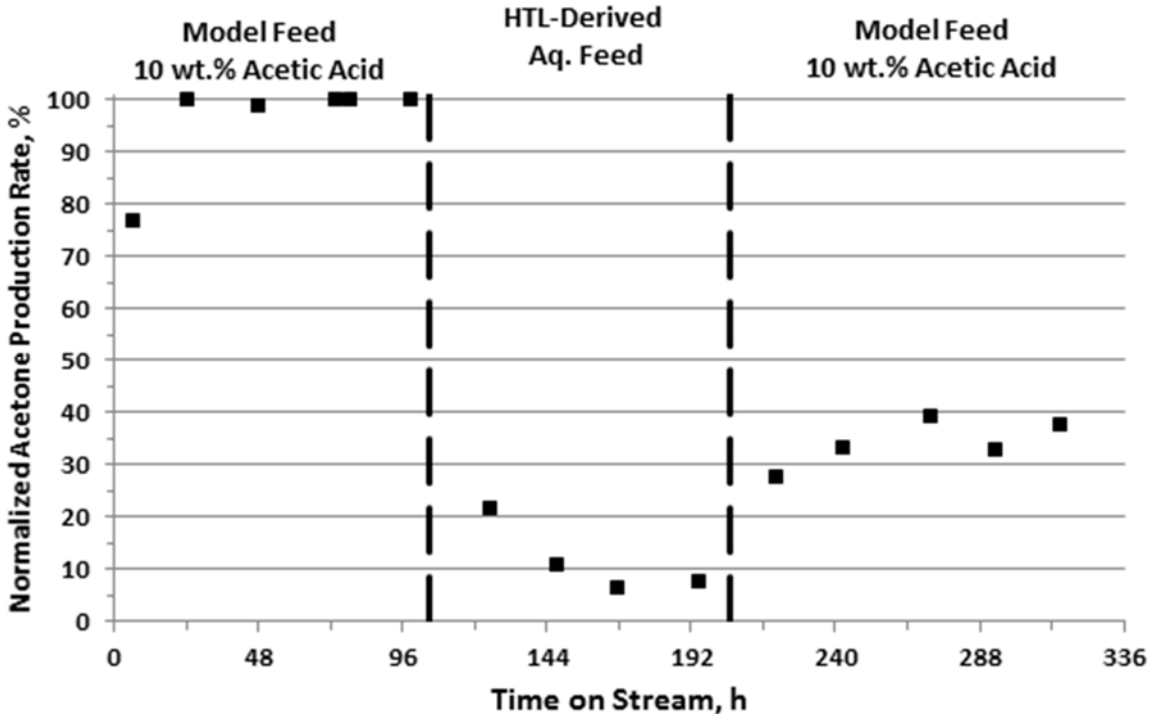

Figure 3.6. Condensed-Phase Ketonization over 15 wt% La_2O_3/ZrO_2 Catalyst using Model Feed and Untreated HTL-Derived Aqueous Phase (295°C, 1400 psig, 0.03 cm^3/min). The composition of the as-received HTL-derived aqueous feed is listed in Table 3.7.

Figure 3.7 illustrates the rate of ketonization of both acetic acid and propionic acid, which is present at 1.8 wt% in the HTL-process derived feed. Compared to the model 10 wt% acetic acid feed, a 10% reduction in the total ketonization activity was observed relative to when using model feed containing only a similar concentration of acetic acid (10 wt%). The 10% reduction in catalytic activity can likely be attributed to the addition of propionic acid (1.8 wt%) to the HTL-derived feedstock. The cross-ketonization of acetic and propionic acids to form methyl ethyl ketone has been reported to be slower than the ketonization of two equivalents of acetic acid (Smith et al. 2016). Thus, the observed lower rate of the total ketonization may be due to the intrinsically slower rate of ketonizaiton with propionic acid. Regardless, complete recovery of the catalyst was observed when the reactor feed was returned to model feed, demonstrating that the loss of activity was indeed reversible. The results with HTL-derived feedstock is superior to the 90% loss of activity observed with feed not subjected to the cleanup process, which also was found to cause significant irreversible catalyst deactivation (Figure 3.6). Thus, the cleanup process resulted in a superior feedstock which could be processed stably for nearly 100 hours.

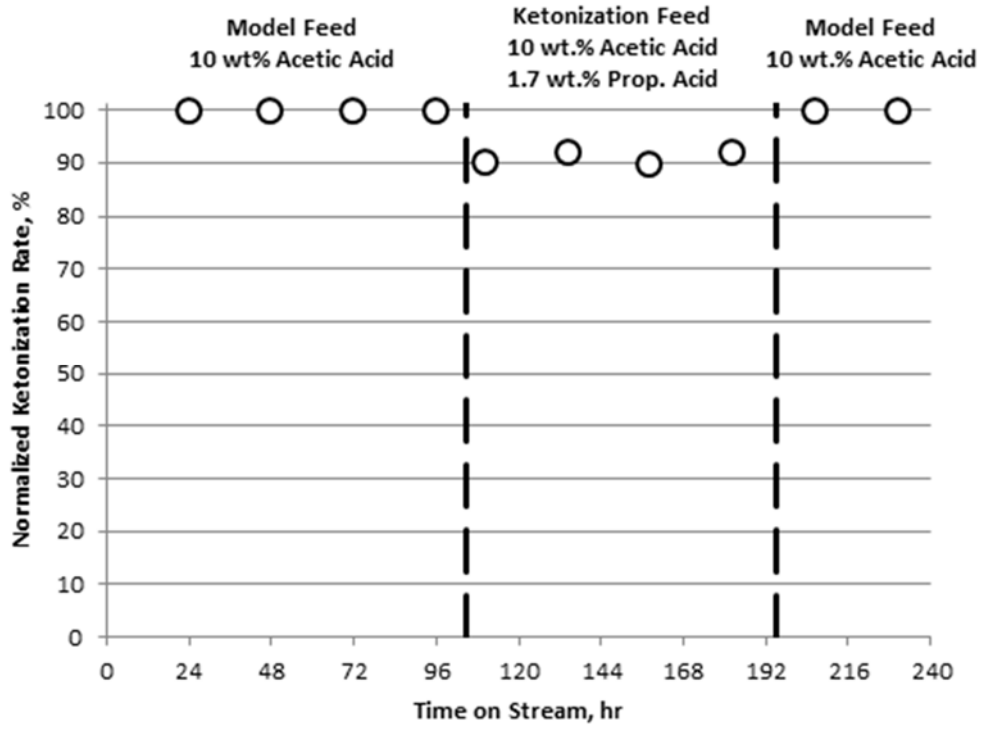

Figure 3.7. Condensed-Phase Ketonization over 15 wt% La_2O_3/ZrO_2 Catalyst using Model Feed and Treated HTL-Derived Aqueous Phase (295°C, 1400 psig, 0.03 cm^3/min; feed: 10 wt% acetic acid in water)

3.3 Catalytic Processing

3.3.1 Dual-Bed Steam Reforming

One path towards valorizing the organic compounds found in various aqueous products is through steam reforming to create hydrogen. The hydrogen would be used to upgrade the bio-oil or biocrude generated to a liquid transportation fuel blendstock. The usual carbon source to produce hydrogen envisioned in a bio-refinery is from natural gas, which has been an economically viable feedstock in recent years. However, by using the aqueous-phase organics to produce hydrogen, a significant amount of greenhouse gases could be eliminated by using renewable carbon versus presumably fossil-derived natural gas.

Initial efforts under this project were published in Xing et al. (2016). A surrogate aqueous phase intended to be representative of the product generated from mildly hydrotreating or stabilizing fast pyrolysis bio-oil was tested. The aqueous-phase surrogate contained several compounds, including acetic acid, phenol, ethylene glycol, and propylene glycol. The amount of water present was 73 wt%, which equated to a 3.5 steam-to-carbon ratio. The surrogate aqueous phase was steam reformed over several different metals supported on $MgAl_2O_4$. Rh, Pt, Ru, Ir, Co, and Ni were tested. A 5 wt% Rh catalyst was found to be the most active catalyst studied. Ni and Co catalysts with 15 wt% loadings on $MgAl_2O_4$ were active, but required gas hourly space velocities (GHSV) at about one-half the rate of the Rh catalyst to achieve 50% conversion. Thus, the Rh catalyst was about twice as active as the Ni or Co catalysts. While all catalysts tested showed some coke formation, the rate of coke formation on the Rh and Co catalysts were about one-fifth the rate of formation on the Ni catalyst. A substantial finding of the study included observation of an elevated yield of hydrogen with the Co catalyst. At 100% organic compound conversion, the Co catalyst gave a hydrogen yield of 94% compared to 74% and 79% for the Rh and Ni catalysts, respectively. The reason for the high hydrogen yield was discovered to be the low methanation activity for Co, which produced sub-equilibrium levels of CH_4. The fact that the Co produced CH_4 at levels lower than equilibrium is significant as it diminishes or eliminates the need for a higher temperature methane steam reformer following the aqueous-phase reforming step, which would substantially lower costs in a bio-refinery.

Fundamental understanding of the low methanation activity on the Co catalyst was ascertained through model compound experiments using ethylene glycol with complimentary density functional theory calculations. The results of this study were published by Mei et al. (2015). Model compound steam reforming studies with ethylene glycol confirmed that CH_4 selectivity was below the level indicative of thermodynamic equilibrium (Figure 3.8).

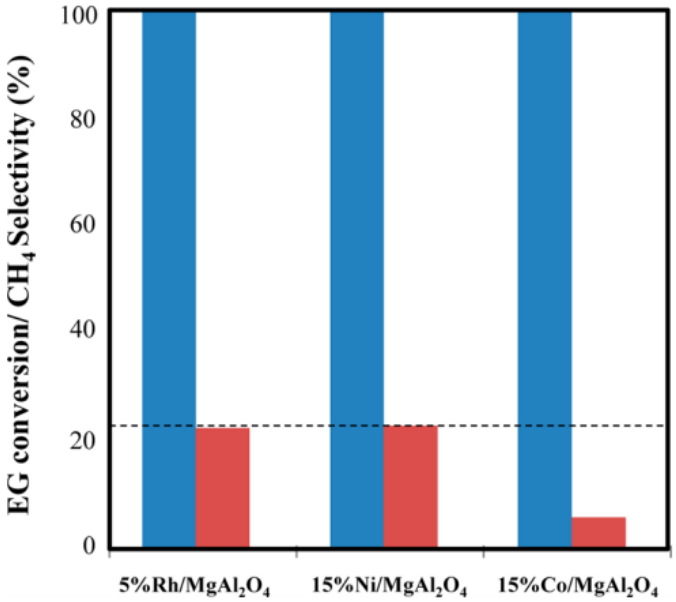

Figure 3.8. At 100% Ethylene Glycol Conversion, the CH_4 Selectivity of the 5% Rh and 15% Ni Catalysts are Indicative of Concentrations at Thermodynamic Equilibrium (dashed line) while the 15% Co Catalyst Exhibits Lower CH_4 Selectivity. Taken from Mei et al. (2015).

Density functional theory calculations on Rh (111), Ni (111), and Co (0001) surfaces revealed that that the low activity for the Co catalyst may be due to the final hydrogenation of adsorbed surface CH_3 to CH_4. The Rh, Ni, and Co catalysts have similar barriers to forming CH_x species up until the formation of CH_3 (Figure 3.9).

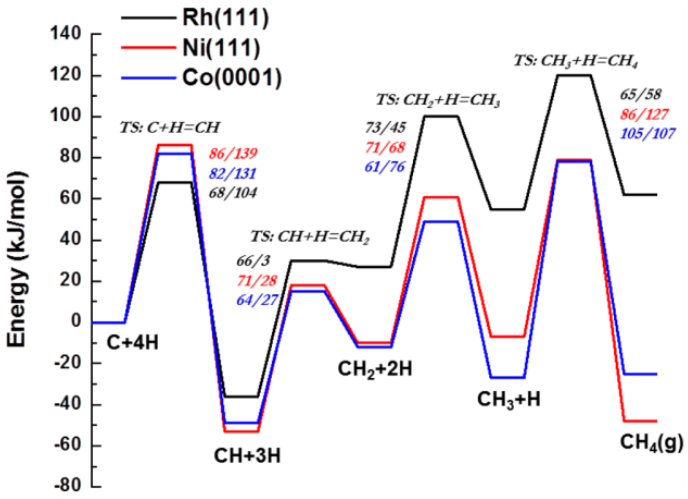

Figure 3.9. Potential Energy Diagram of Methanation on Rh (111), Ni (111), and Co (0001) Metal Surfaces. The listed numbers are forward/reverse activation barriers for each elementary step. Taken from Mei et al. (2015).

The final surface reaction of CH_3 + H → CH was found to be about 20% higher than Ni and about 60% higher than Rh. This suggests that while surface coverage of CH_x is similar for all three catalysts, the methane formation rate is kinetically controlled on the Co catalyst due to a high activation barrier towards the terminating final addition of hydrogen on Co.

Acetic acid is ubiquitous in the numerous aqueous phases characterized by this project. It also is extremely challenging to steam reform because of its propensity to form coke. A new process to steam reform acetic acid was developed by this project and reported by Davidson et al. (2017). Co was again used as the reforming catalyst due to its low propensity for forming methane as described above. The scheme illustrated in Figure 3.10 shows method to first ketonize acetic acid to acetone, followed by steam reforming of the acetone to produce hydrogen in a dual-bed reforming process. The same yield of hydrogen is possible through the modified ketonization/acetone reforming scheme when one assumes the water produced by the ketonization step is involved in the subsequent reforming step. Indeed, in an industrial process, it may be possible to feed less steam and gain the associated energy savings because an equivalent of water is generated during the ketonization reaction.

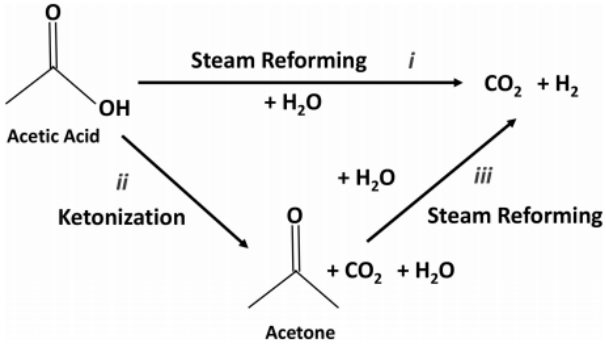

Figure 3.10. Direct Steam Reforming of Acetic Acid Results in a High Rate of Coke Deposition on the Catalyst Surface. In contrast, the rate of coke deposition when reforming acetone is lower. By first ketonizing acetic acid to acetone, it is possible produce the same amount of hydrogen in a manner with significantly improved stability. Taken from Davidson et al. (2017).

The dual-bed steam reforming process developed by this project and reported by Davidson et al. (2017) resulted in a dramatic improvement in catalyst and process stability. As shown in Figure 3.11 directly steam reforming acetic acid resulted in a substantial amount of coke deposition, even to the point that the packed-bed reactor employed for the experiment began to have an increase in pressure due to plugging.

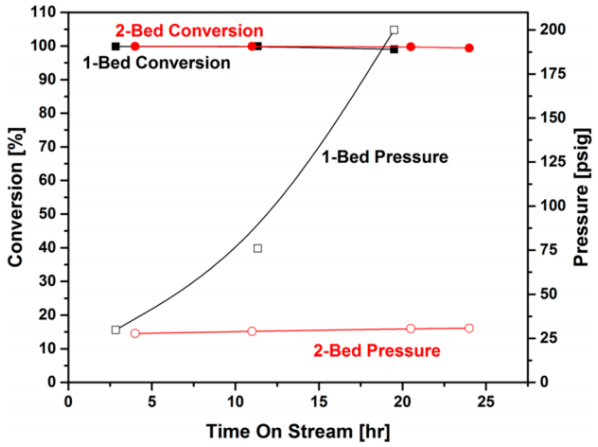

Figure 3.11. Results from Converting Acetic Acid to Hydrogen in a One-Bed (15 wt% Co/CeO_2 - steam reforming only) and Two-Bed (CeO_2 bed followed by 15 wt% Co/CeO_2 ketonization and steam reforming in sequential reaction beds) Configuration. The increase in pressure in the one-bed scenario is indicative of bed plugging through the formation of substantial amounts of coke. Taken from Davidson et al. (2017).

Combining the ketonization and steam reforming functionality was not sufficient to mitigate coke formation. The one-bed results in Figure 3.11 used a 15 wt% Co catalyst supported on CeO_2. CeO_2 is a known ketonization catalyst. In the two-bed scenario, CeO_2 was employed as a ketonization catalyst prior to the 15 wt% Co/CeO_2 catalyst. Ketonizing the acetic acid to acetone prior to the reforming catalyst allowed stable operation of the reactor for over 25 hours; whereas, without the ketonization step, the reactor plugged on about 20 hours. While further work is required to fully demonstrate the combined ketonization/steam reforming concept is suitable for commercial implementation, these initial results were exceptionally promising and demonstrated a method to convert recalcitrant but ubiquitous acetic acid to hydrogen.

3.3.2 Single-Step Conversion of Cleaned Aqueous Product to Isobutene-Rich Olefin Product

Demonstration of the cleanup efficiency and suitability of a cleaned fast-pyrolysis aqueous feedstocks obtained from fast-pyrolysis feedstock for the production of olefins over a recently developed $Zn_xZr_yO_z$ catalyst was performed (Smith et al. 2016; Dagel et al. 2016). The feed, consisting primarily of acetic acid and propionic acid, was converted to a mixed C_4 and C_5 branched olefin stream. The cleanup process and constituents of the feed are detailed above and tabulated in Table 3.8, Table 3.9, and Table 3.10. As shown in Figure 3.12, mostly isobutene was formed due to the acetic acid-rich feed composition. In principle, produced olefins can then be oligomerized to a high octane gasoline, jet, or diesel fuel in a subsequent step using solid acid catalysts. Or, the isobutene, in this case, can be separated and sold as valuable chemical product. To better illustrate the reaction mechanism, in Figure 3.13, results when using a similar HTL-derived feedstock as a function of GHSV are presented. Acetone and 2-butanone are intermediates produced as acetic acid and propionic acid undergo ketonization reactions. As the GHSV is decreased these ketone intermediates undergo condensation reactions, thus resulting in branched C_4 and C_5 olefins. For the run shown in Figure 3.13, only a small amount of C_5 olefin is formed as a result of the

propionic acid undergoing ketonization because its concentration in the feedstock is low. At around 170 hours on stream, acetone breakthrough indicative of catalyst deactivation was observed. A mild oxidative regeneration was performed and catalyst activity was fully restored. Catalytic deactivation that occurred was attributed to coking of the catalyst which is what we observed when using model feed compounds.

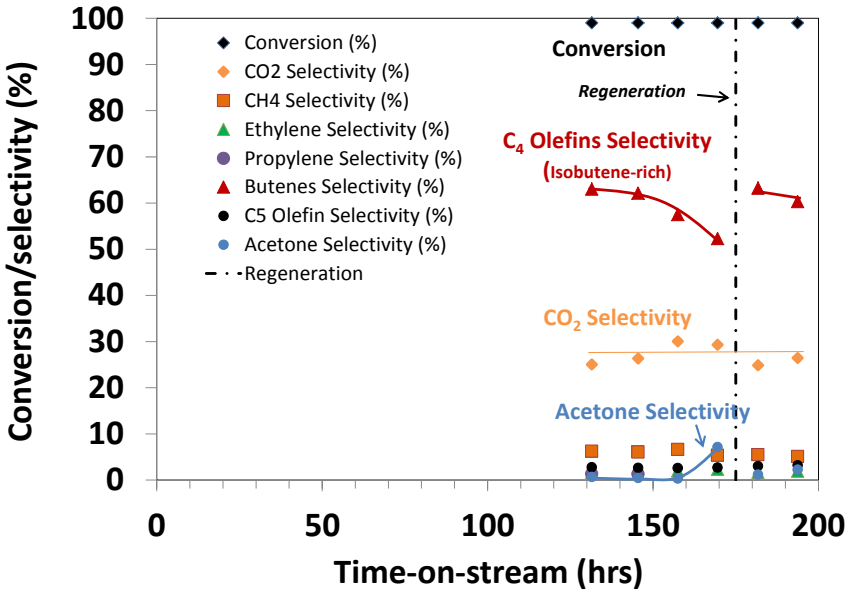

Figure 3.12. Time-on-Stream Performance for Conversion of the Cleaned Up Fast-Pyrolysis Derived Aqueous Product from USDA over $Zn_1Zr_{2.5}O_x$ (450°C, 1 atm, 1300 hr^{-1}, S/C = 13 (mol); major feed constituents were acetic acid = 9.2%, propionic acid = 1.7%). At ~170 hours on stream acetone breakthrough occurred, which is indicative of catalytic deactivation. Mild oxidation of the catalyst was performed to restore its catalytic activity.

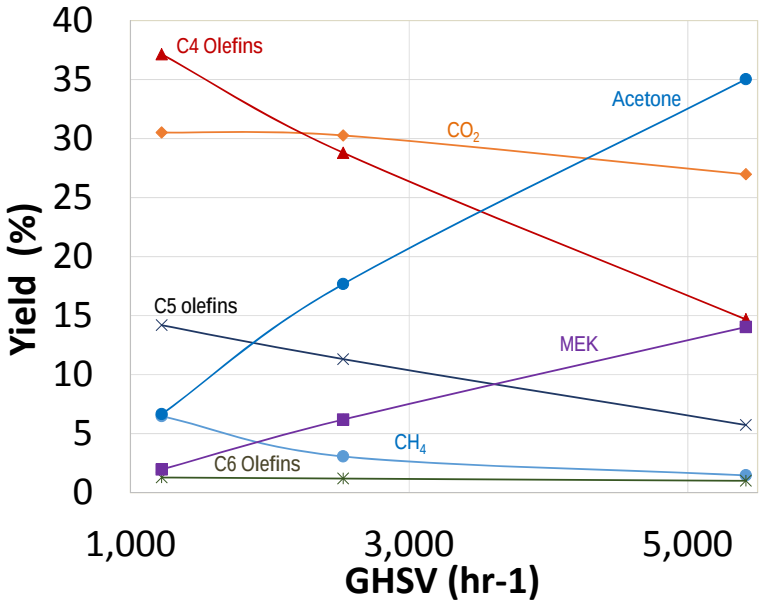

Figure 3.13. Conversion of Cleaned Up HTL-Derived Feedstock over $Zn_xZr_yO_z$ Catalyst (450°C, 1 atm, S/C = 2.8 (mol); major feed constituents were acetic acid = 29%, propionic acid = 5%; <1% other products formed include ethene, propene, alkanes, and CO)

3.4 Techno-Economic Analysis

A TEA was performed for an HTL process employing three different schemes for aqueous phase utilization. The three processes modeled were namely 1) AD, which generates medium-BTU fuel gas and is presented as a baseline case for comparison; 2) condensed-phase ketonization with subsequent reduction and dehydration to form olefins; and 3) ketonization-coupled steam reforming to produce hydrogen.

Techno-economic costing results for the total installed costs (TIC) for the three processes are shown in Figure 3.14. TIC costs for all three systems are comparable and all within about 5% of total cost. For all three cases, the largest component of capital cost was the cost of the HTL reactor system at $184 MM. The TIC for treatment of the aqueous phase is 80, 99, and 80 $MM for the benchmark AD, condensed-phase ketonization, and dual-bed steam reforming cases, respectively. Included in the condensed-phase catalytic conversion and ketonization/steam reforming processes are costs for wastewater treatment in addition to the conversion operation unit operations. Wastewater treatment is required as not all of the organics are converted to products and thus require disposal. The inorganic salts will also require disposal.

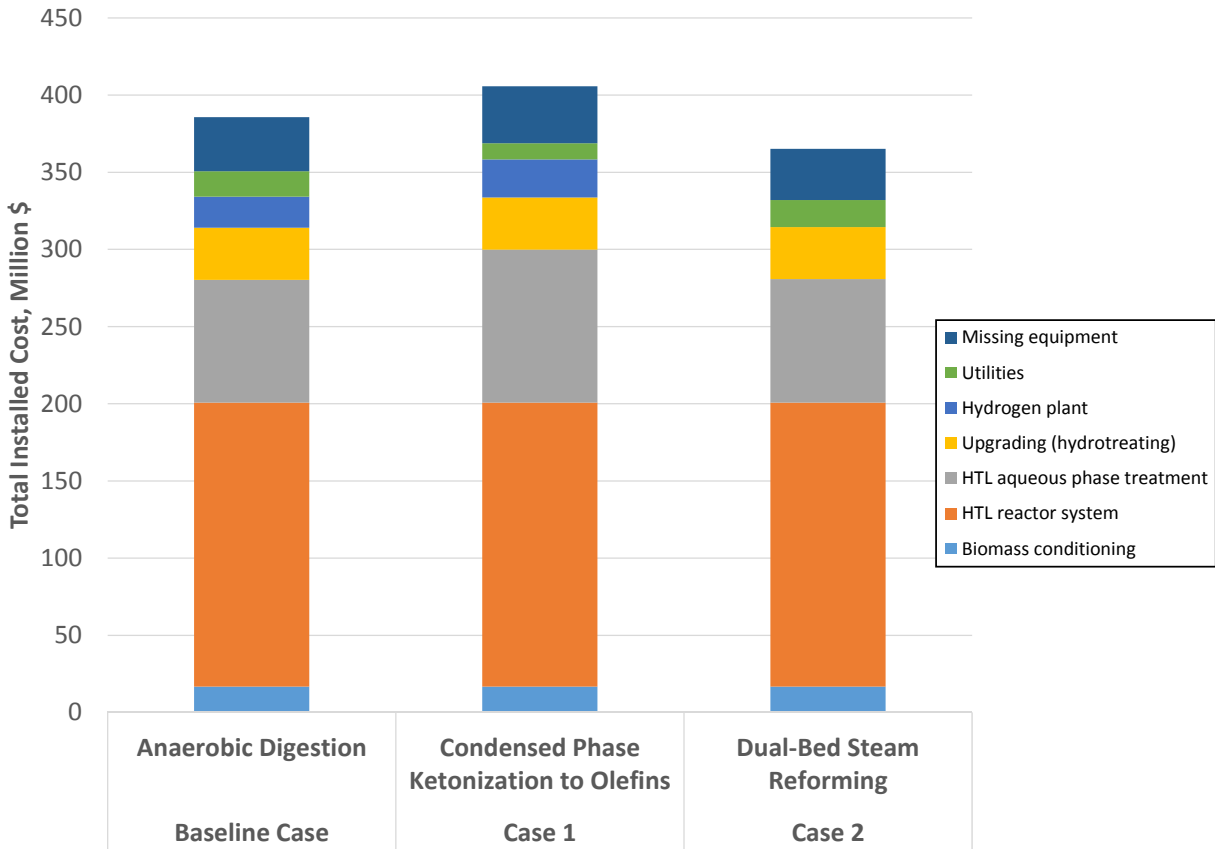

Figure 3.14. Total Installed Cost Results for Baseline Case (AD), Condensed-Phase Ketonization with Reduction and Dehydration to Produce Olefins (Case 1), and Dual-Bed Steam Reforming (Case 2)

Estimates for the production costs on a MFSP basis of the fuel were also obtained and results are shown in Figure 3.15.

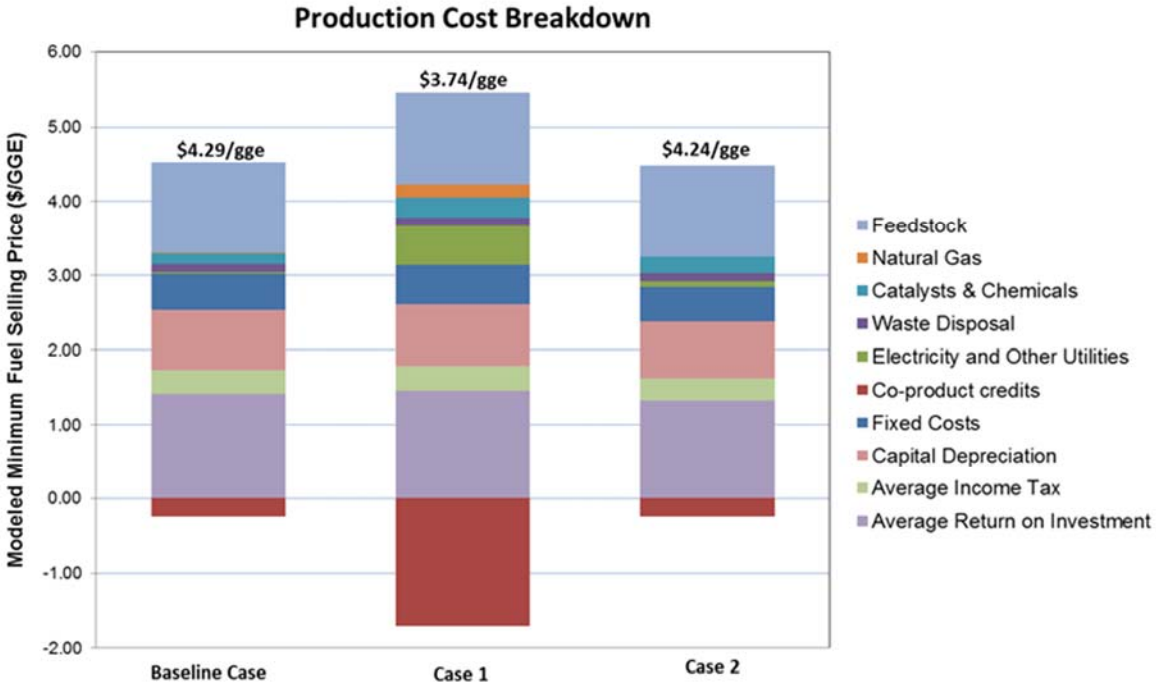

Figure 3.15. Production Cost Breakdown and Final Fuel Selling Price (in dollars per gallon of gasoline equivalent: $/GGE) for AD (baseline case), Catalytic Conversion to Produce Olefins (Case 1), and Steam Reforming (Case 2)

For all three processes, the highest operating cost was when the woody feedstock was used for hydrothermal processing. Both the condensed-phase ketonization and dual-bed steam reforming cases had higher catalyst and chemical costs at $0.32/GGE and $0.27/GGE, respectively, relative to the baseline AD case at $0.17/GGE. The condensed-phase ketonization required more natural gas for hydrogen production ($0.19/GGE) as compared to the baseline AD case ($0.01/GGE). Higher utility costs ($0.55/GGE) were required for the condensed-phase ketonization, compared to baseline AD ($0.32/GGE). However, the added benefit of salable co-products ($1.97/GGE compared to the baseline case of $0.26/GGE) ultimately made the catalytic condensed-phase ketonization system the most appealing. While the steam reforming system did eliminate the need for natural gas and a hydrogen plant separate from the reformer accounted for in the aqueous-phase treatment plate, these savings ($0.01/GGE on natural gas and $0.04/GGE on capital depreciation) left the system with negligible differences to the baseline case. Taken together, TEA analysis found that condensed-phase ketonization of the aqueous phase formed during bio-oil production was attractive economically due to the sale of value-added co-product olefins. The dual-bed steam reforming approach did save on capital costs; however, differences in the final production costs are negligible compared to the AD system. The dual-bed steam reforming approach would be attractive in a scenario where the desire to significantly reduce or eliminate external non-renewable carbon inputs.

4.0 Project Accomplishments

4.1 Publications

Mei D, VM Lebarbier Dagle, R Xing, KO Albrecht, and RA Dagle. 2015. “Steam Reforming of Ethylene Glycol over $MgAl_2O_4$ Supported Rh, Ni, and Co Catalysts.” ACS Catalysis 6(1):315-325. DOI: 10.1021/acscatal.5b01666

Panisko EA, TW Wietsma, TL Lemmon, KO Albrecht, and DT Howe. 2015. “Characterization of the Aqueous Fractions from Hydrotreatment and Hydrothermal Liquefaction of Lignocellulosic Feedstocks.” *Biomass & Bioenergy* 74(March 2015):162-171. 10.1016/j.biombioe.2015.01.011

Maddi B, EA Panisko, KO Albrecht, and DT Howe. 2016. “Qualitative Characterization of the Aqueous Fraction from Hydrothermal Liquefaction of Algae Using 2D Gas Chromatography with Time-of-Flight Mass Spectrometry.” *Journal of Visualized Experiments* 109(October 2016):e53634. https://doi.org/10.1016/j.biombioe.2016.07.010

Maddi B , EA Panisko, TW Wietsma, TL Lemmon, MS Swita, KO Albrecht, and D T Howe. 2016. “Quantitative Characterization of the Aqueous Fraction from Hydrothermal Liquefaction of Algae.” *Biomass & Bioenergy* 93(July 2016):122-130. DOI: 10.1016/j.biombioe.2016.07.010

Xing R, VM Lebarbier Dagle, MD Flake, L Kovari , KO Albrecht, CA Deshmane, and RA Dagle. 2016. “Steam Reforming of Fast Pyrolysis-Derived Aqueous Phase Oxygenates over Co, Ni, and Rh Metals Supported on $MgAl_2O_4$.” *Catalysis Today* 269(February 2016):166-174. DOI: 10.1016/j.cattod.2015.11.046

Davidson SD, KA Spies, D Mei, L Kovarik, I V Kutnyakov, XS Li, VM Lebarbier Dagle, KO Albrecht, and RA Dagle. 2017. “Steam Reforming of Acetic Acid over Co-supported Catalysts: Coupling Ketonization for Greater Stability.” *ACS Sustainable Chemistry & Engineering 5*(10):9136-9149. DOI: 10.1021/acssuschemeng.7b02052

Lopez-Ruiz JA, AR Cooper, G Li, and KO Albrecht. 2017. “Enhanced Hydrothermal Stability and Catalytic Activity of $La_xZr_yO_z$ Mixed Oxides for the Ketonization of Acetic Acid in the Aqueous Condensed Phase.” *ACS Catalysis* 7(10):6400-6412. https://pubs.acs.org/doi/10.1021/acscatal.7b01071

Maddi B , EA Panisko, TW Wietsma, TL Lemmon, MS Swita, KO Albrecht, and DT Howe. 2017. “Quantitative Characterization of Aqueous Byproducts from Hydrothermal Liquefaction of Municipal Wastes, Food Industry Wastes, and Biomass Grown on Waste.” *ACS Sustainable Chemistry & Engineering* 5(3):2205-2214. DOI: 10.1021/acssuschemeng.6b02367

Cai Q, JA Lopez-Ruiz, AR Cooper, J Wang, KO Albrecht, and D Mei. 2018. “Aqueous-Phase Acetic Acid Ketonization over Monoclinic Zirconia.” *ACS Catalysis* 8(1):488–502. DOI: 10.1021/acscatal.7b03298

Davidson SD, JA Lopez-Ruiz, Y Zhu, AR Cooper, KO Albrecht, and RA Dagle. 2018. “Clean up and Catalytic Upgrading of Hydrothermal Liquefaction-Derived Aqueous Phase into Fuels and Chemicals.” *ACS Sustainable Chemistry & Engineering, to be submitted*

4.2 Presentations (presenter denoted in bold)

Albrecht KO, RA Dagle, and DT Howe. 2015. “Characterization and Valorization of Aqueous Phases Derived from Liquefaction and Upgrading of Bio-Oils.” DOE Bioenergy Technologies 2015 Project Peer Review, March 27, 2015, Alexandria, Virginia. https://www.energy.gov/sites/prod/files/2015/04/f22/thermochemical_converion_albrecht_231310.pdf

Albrecht KO, AR Cooper, JG Frye, Y Zhu, D Mei ,Lopez- JA Ruiz, TL Lemmon, and DN Tran. 2015. “Condensed Phase Ketonization of Organic Acids Produced by the Hydrothermal Liquefaction of Lignocellulosic Biomass.” AIChE 2015 Spring Meeting, April 27, 2015, Austin, Texas.

Albrecht KO, AR Cooper, JA Lopez-Ruiz, HM Job, JG Frye, and DN Tran. 2015. “Condensed Aqueous Phase Ketonization of Organic Acids Produced by the Hydrothermal Liquefaction of Lignocellulosic Biomass.” 24th North American Catalysis Society North American Meeting, June 6, 2015, Pittsburgh, Pennsylvania.

Cai Q, JA Lopez-Ruiz, AR Cooper, KO Albrecht, J Wang, and **D Mei**. 2015. “Effects of Solvents on Acetic Acid Ketonization over Zirconia Catalysts.” 24th North American Catalysis Society North American Meeting, June 16, 2015, Pittsburgh, Pennsylvania.

Cai Q, JA Lopez-Ruiz, AR Cooper, KO Albrecht, J Wang, and D Mei. 2015. “Effects of Solvents on Acetic Acid Ketonization over Zirconia Catalysts.” 2015 Pacific Coast Catalysis Symposium, September 18, 2015, Richland, Washington.

Cooper AR, KO Albrecht, JA Lopez-Ruiz, JG Frye, and DN Tran. 2015. ”Condensed Aqueous Phase Ketonization of Organic Acids Produced by the Hydrothermal Liquefaction of Lignocellulosic Biomass.” American Chemical Society Meeting, August 17, 2015, Boston, Massachusetts.

Lopez-Ruiz JA, AR Cooper, JG Frye, HM Job, and KO Albrecht. 2015. “Development of Hydrothermally Stable Catalysts for the Thermochemical Conversion of Carbon-Containing Aqueous Streams into Fuels and Chemicals.” Pacific Coast Catalysis Society Meeting 2015, September 17, 2015, Richland, Washington.

Lopez-Ruiz JA, AR Cooper, Frye J G, Job H M, Albrecht K O 2015. "Development of Hydrothermally Stable Catalysts for the Catalytic Conversion of Biomass-Derived Chemicals" TC Biomass, November 1, 2015, Chicago, Illinois.

Lopez-Ruiz JA, AR Cooper, JG Frye, HM Job, and KO Albrecht. 2015. “Condensed Phase Ketonization of Organic Acids Produced by the Hydrothermal Liquefaction of Lignocellulosic Biomass.” TC Biomass, November 4, 2015, Chicago, Illinois.

Lopez-Ruiz JA, AR Cooper, JG Frye, HM Job, and KO Albrecht. 2015. “Development of Hydrothermally Stable Catalysts for the Thermochemical Conversion of Carbon-Containing Aqueous Streams into Fuels and Chemicals.” PNNL Postgraduate Research Symposium, August 14, 2015, Richland, Washington.

Maddi B, EA Panisko, TW Wietsma, TL Lemmon, MS Swita, KO Albrecht, and DT Howe. 2015. “Poster - Quantitative Characterization of the Aqueous Byproduct from Hydrothermal Liquefaction of Algae.” 2015 AIChE Annual Meeting, November 11, 2015, Salt Lake City, Utah.

Maddi B. 2015. "Pyrolytic Fractionation of Oleaginous Algae to Produce Triglyceride-Specific Bio-Oil of Fuel Value." 2015 AIChE Annual Meeting, November 12, 2015, Salt Lake City, Utah.

Spies KA and RA Dagle. 2015. "Warm Syngas Clean-up Process Development: Multi-Contaminant Removal using Sorbents and Ir-Ni Tar Reforming Catalyst." TCBiomass, November 6, 2015, Chicago, Illinois.

Cai Q, JA Lopez-Ruiz, AR Cooper, KO Albrecht, J Wang, and **D Mei**. 2016. "Mechanistic Insights into Aqueous Phase Acetic Acid Ketonization over Monoclinic Zirconia." 252nd ACS National Meeting. August 23, 2016, Philadelphia, Pennsylvania

Davidson SD, KA Spies, IV Kutnyakov, V Dagle, KO Albrecht, and RA Dagle. 2016. "Steam Reforming of Bio-Derived Oxygenates: Coupling Ketonization for Greater Stability." PNNL Postdoctoral Symposium, July 12, 2016, Richland, Washington.

Davidson SD, KA Spies, V Dagle, KO Albrecht, and RA Dagle. 2016. "Steam Reforming of Bio-Derived Oxygenates: Coupling Ketonization for Greater Stability." TCS Biomass 2016, on November 3, 2016, Chapel Hill, North Carolina.

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Lopez-Ruiz JA, AR Cooper, Q,Cai D Mei, and KO Albrecht. 2016. "Kinetic Investigation of the Ketonization of Biomass-Derived Carboxylic Acids under Hydrothermal Conditions over Stable ZrO_2-Based Catalysts." 252nd American Chemical Society National Meeting & Exposition, August 8, 2016, Philadelphia, Pennsylvania.

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Maddi B, EA Panisko, TW Wietsma, TL Lemmon, MS Swita, KO Albrecht, and DT Howe. 2016. "Quantitative Characterization of Aqueous Byproducts from Hydrothermal Liquefaction of Municipal Wastes, Food Industry Wastes, and Biomass Grown on Waste." TCS biomass 2016, November 1, 2016, Chapel Hill, North Carolina.

Cai Q, JA Lopez-Ruiz, A Cooper, J Wang, KO Albrecht, and **D Mei**. 2017. "Fundamental Insights into Aqueous Phase Acetic Acid Ketonization over Monoclinic Zirconia." 25th North American Catalysis Society North American Meeting, June 8, 2017, Denver, Colorado.

Davidson SD, JA Lopez, IV Kutnyakov, XS Li, V Dagle , KO Albrecht, and RA Dagle. 2016. "Steam Reforming of Bio-Derived Oxygenates: Coupling Ketonization for Greater Stability." 25th North American Catalysis Society North American Meeting, June 5, 2017, Denver, Colorado.

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Davidson SD, JA Lopez-Ruiz, J Saavedra Lopez, M D Flake, V Dagle, KO Albrecht, and RA Dagle. 2017. "Direct Conversion of Aqueous Phase Bio-Oil to Olefins." PNNL Postgraduate Research Symposium, July 26, 2017, Richland, Washington.

Lopez-Ruiz JA, AR Cooper, D Mei, and KO Albrecht. 2017. "Mechanistic Investigation of the Ketonization of Biomass-Derived Carboxylic Acids under Hydrothermal Conditions over Stable ZrO_2-Based Catalysts." 25th North American Catalysis Society Meeting, June 8, 2017, Denver, Colorado.

Lopez-Ruiz JA, AR Cooper, SD Davidson, Y Zhu, RA Dagle, and KO Albrecht. 2017. "Development of ZrO_2-Based Hydrothermally Stable Catalysts for the Catalytic Upgrading of Biomass-Derived Aqueous Streams." PNNL Postgraduate Research Symposium, July 26, 2017, Richland, Washington.

Lopez-Ruiz JA, A Cooper, SD Davidson, Y Zhu, RA Dagle, and **KO Albrecht**. 2017. "Development of Catalytic Processes for the Upgrading of Aqueous Biomass-Derived Carboxylic Acids into Fuels and Chemicals." TC Biomass 2017, September 21, 2017, Chicago, Ilinois.

Lopez-Ruiz JA, AR Cooper, MH Engelhard, L Kovarik, T Varga, G Li, and **KO Albrecht (Invited Speaker)**. 2018. "A Hydrothermally Stable $La_xZr_yO_z$ Catalyst for the Upgrading of Biomass-Derived Carboxylic Acids in the Presence of Condensed Water." American Chemical Society National Meeting and Expo, March 21, 2018, New Orleans, Louisiana.

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5.0 Summary

Aqueous phase “waste” streams are challenging because of the diversity of their organic and inorganic constituents and, at times, the low concentrations of organic compounds that are expensive to capture. This project demonstrated that it is possible to valorize these aqueous phase organics either by producing value-added co-products such as olefins or by offsetting the need for external fossil-derived sources of carbon. MFSP may be dramatically lowered through the production of co-products. The production of hydrogen via thermochemical routes was found to be no more economically intensive than with the state-of-the-art AD process included in many current TEAs. Separation of the aqueous streams to concentrate organics and diminish or remove dissolved inorganics are important steps in the overall design processes to facilitate directed catalytic conversions that can be operated in a stable manner.

While this project made significant progress over its duration towards economically feasible processes, opportunities exist for developing even greater valorization methods. Advanced separation processes with improved LLE solvents or using simulated moving bed chromatography would avoid energy intensive distillation of water. The development of metal oxide, carbon, or hybrid (carbon + metal oxide) catalysts and supports based on materials developed by this project would find wide ranging interest in the catalysis community. The development of oxidation processes based on these supports would be beneficial for converting phenolics and other recalcitrant organic compounds.

Finally, TEA analysis of generic processes with consideration of the value of potential co-products would help to bound which aqueous phases are candidates for valorization and how much processing could be endured without sacrificing economic viability. This TEA analysis coupled with an overview of wastewater disposal considerations (e.g., contaminants, ASTM tests, and cleanup methods) would be a valuable resource. Future support in these areas has the potentially to positively impact the bioenergy community and other industrial stakeholders in areas such as wastewater processing and catalysis.

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