Catalytic Upgrading of Thermochemical Intermediates to Hydrocarbons: Conversion of Lignocellulosic Feedstocks to Aromatic Fuels and High Value Chemicals

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Table of Contents

Executive Summary

The principal objective of this project was to develop a fully integrated catalytic process that efficiently converts lignocellulosic feedstocks (e.g. bagasse, corn stover, and loblolly pine) into aromatic-rich fuels and chemicals. Virent led this effort with key feedstock support from Iowa State University. Within this project, Virent leveraged knowledge of catalytic processing of sugars and biomass to investigate two liquefaction technologies (Reductive Catalytic Liquefaction (USA Patent No. 9,212,320, 2015) and Solvolysis (USA Patent No. 9,157,030, 2015) (USA Patent No. 9,157,031, 2015)) that take advantage of proprietary catalysts at temperatures less than 300ºC in the presence of unique solvent molecules generated in-situ within the liquefaction processes.

Reductive Catalytic Liquefaction combines a biomass slurry, catalyst, and in-situ generated solvent in a continuous-stirred tank reactor. Extraction and subsequent stabilization of solubilized biomass components take place in the same reactor step. In the Solvolysis process, biomass liquefaction and product stabilization occur in two separate steps. Both of these liquefaction technologies generated volatile oxygenated intermediates that can be converted to aromatics over a modified ZSM-5 catalyst in Virent's Catalytic Oxygenates to Aromatics (COTA) process. Using appropriate fractionation, the combined liquefaction/COTA process can provide aromatic-rich reformate as blend stock for renewable gasoline or jet fuel. Alternatively, this biomass-derived reformate can be processed to generate paraxylene (a precursor for generation of Polyethylene terephthalate, PET) and benzene (a precursor for the generation of nylon, polystyrene, polycarbonates, and polyurethanes).

Experimental work for this DOE funded project started in October 2011 and was completed in September 2015. This project identified the Solvolysis technology to be effective for the solubilization of three lignocellulosic feedstocks (bagasse, corn stover, and residual wood) and demonstrated the integration of Virent's Solvolysis technology with Virent's COTA process to generate aromatic-rich hydrocarbon products for use in fuels or high value aromatic chemical applications. A fully integrated lab-scale biomass to aromatics process was designed, built, and operated to demonstrate operability with a 2000 hour lifetime run within the project. Data collected from the lifetime run was used to establish a baseline yield (liquid fuel product per dry tonne of biomass) for the integrated process and a profited cost estimate for production of this liquid fuel product.

Overall, through the course of the project the technology moved from an early concept to a fully-integrated pilot plant which successfully demonstrated a 2000 hour lifetime run. The integrated lifetime run highlighted opportunities for continued development and process optimization. The solvolysis process approach shows great potential in a new area of biomass based bio-fuels and bio-based chemicals.

Significant improvement in operability, yields, and economics of the technology is expected by:

1. increasing the soluble carbon from deconstruction and evaluating methods to better access and process the lignin fraction of the biomass,

2. developing cost effective ash control via improved harvesting methods, improved conditioning schemes to remove ash, and increasing contaminant tolerance of the catalytic material, and
3. improving catalytic reactor performance through reduced catalyst cost, improved stability, and improved catalyst activity.

Fundamental Research and Development

Fundamental research work was conducted on both the liquefaction/hydrodeoxygenation (HDO) and COTA processes. Results from this work provided the foundation for the down select of the liquefaction/HDO technology and feedstock for the process development of the integrated process. During this phase of the project, safety upgrades were required to ensure all work with benzene was performed according to federal and state standards. Aromatic selectivity improvements were investigated for the COTA process with model feedstocks and then with oxygenates derived from lignocellulosic feedstocks.

Feedstock

The project utilized three lignocellulosic biomass feedstocks including single-pass harvested corn stover (Birrell, Karlen, & Wirt, 2014), supplied by Iowa State University (ISU, Ames, IA), loblolly pine forest residuals (Burnside, 2010) supplied by Catchlight Energy LLC. (Federal Way, WA), and sugarcane bagasse supplied by the Louisiana State University Ag Center (Baton Rouge, LA). Feedstocks were all shipped to ISU and prepared by grinding the material and air drying them overnight (Figure 1 pictures the three feedstocks after grinding). The pine and corn stover were ground to less than 1/4” and the bagasse was ground to less than a 1/8”. The particle size distribution of the ground materials was determined by sieving, and the distributions are shown in Figure 2.

Figure 1. Pictures of the Three Biomass Feedstocks Utilized in this Project

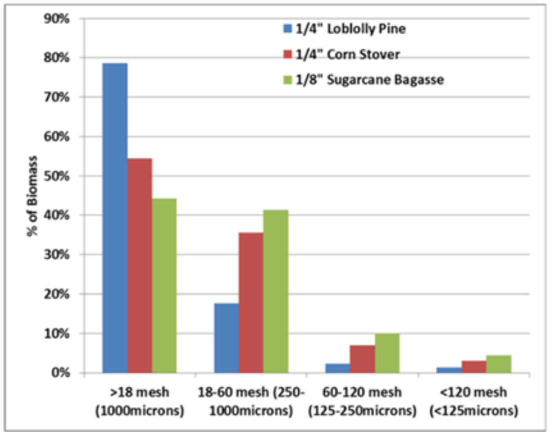

Figure 2. Particle size distribution of the three feedstocks

Samples of the three feedstocks were sent to Galbraith Lab (Knoxville, TN) in order to determine water content and dry carbon, hydrogen, nitrogen, and oxygen (CHNO Analysis), with the results shown in Table 1. Internal Virent analysis, based on NREL biomass analytical methods (NREL, 2010) and updated where applicable, were conducted to determine ash, extractives, cellulose, hemicellulose, and lignin content of the three feedstocks, with the results summarized in Figure 3. Figure 3 shows that pine contains higher amounts of cellulose and lignin, and the lowest amount of ash. Both the corn stover and bagasse contain significant amounts of ash components as well as higher amounts of hemicellulose respectively. The corn stover has the highest amount of extractives, while the bagasse has the highest amount of ash.

Table 1. CHNO Analysis of Feedstocks from Galbraith

All Values in Weight Percent	Pine Forest Residuals	Single Pass Corn Stover	Sugarcane Bagasse
Water Content	7.97	10.25	5.8
Ash	0.7	4.25	10.03
C	51.1	46.44	45.77
H	5.94	5.59	5.47
O	42.22	43.33	38.7
N	<0.5	<0.5	<0.5
S	<0.05	0.065	<0.05
Cl	0.036	0.315	0.0266

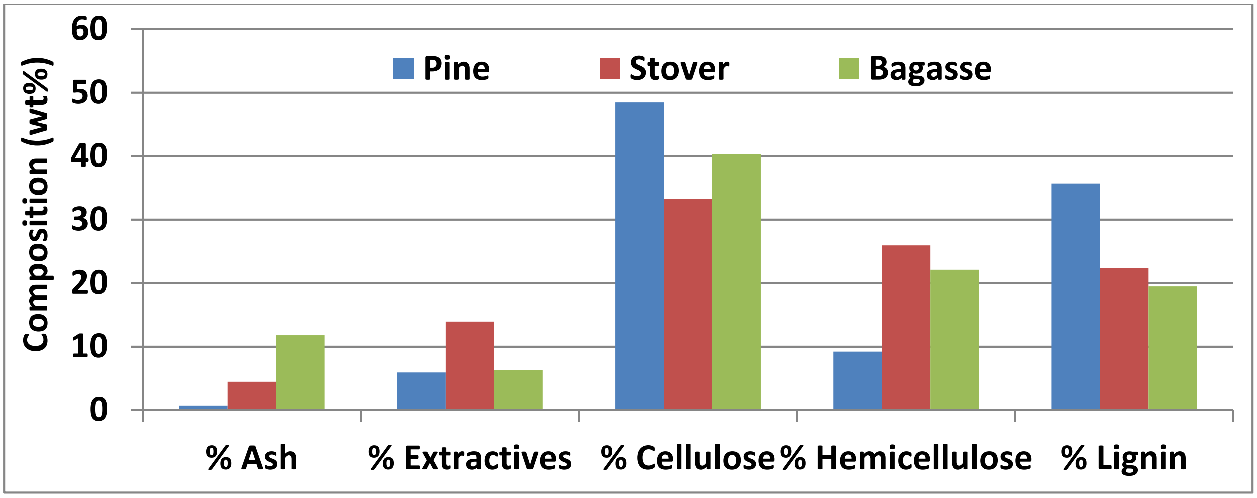

Figure 3. Composition of three feedstocks

Liquefaction/HDO Technologies Evaluations

Initially, Virent proposed to use Reductive Catalytic Liquefaction (RCL) as the liquefaction/HDO technology for this project. The RCL technology utilized a CSTR with biomass feedstock, catalyst, and solvent in the one reactor. The desired oxygenated intermediate products were removed from the system as vapor phase products (USA Patent No. 9,212,320, 2015). During time between submission of the project proposal and the start of the project, Virent discovered alternative liquefaction/HDO technology where the liquefaction was conducted by passing solvent over a fixed bed of biomass, and the resulting solubilized biomass was then passed over the catalytic reactor system containing the HDO catalyst which hydrodeoxygenated the solubilized biomass components. The two-step liquefaction/HDO technology was termed the Solvolysis process (USA Patent No. 9,157,030, 2015). While both liquefaction/HDO technologies utilize similar catalysts and generate similar products, the different processes configurations can impact catalyst utilization and the overall complexity of the process. Both systems were evaluated and the Solvolysis process was down-selected for the process development tasks of the project. Presented below are summaries of the evaluation of the two liquefaction/HDO technologies.

Reductive Catalytic Liquefaction

The RCL process provides methods for making biomass-derived fuels and chemicals, as shown in Figure 4. The method generally provides a feed stream comprising a solvent, H_2 and a biomass component comprising cellulose, hemicellulose and/or lignin. The solvent is generated in-situ and consists of a mixture of oxygenated compounds generated from the liquefaction and catalytic hydrodeoxygenation of the biomass.

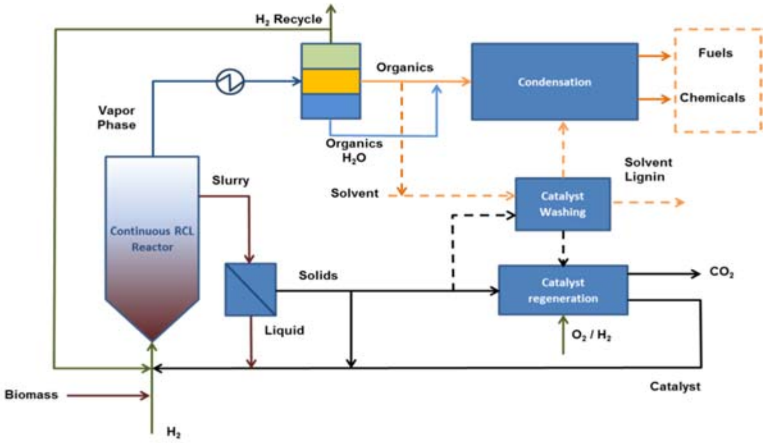

Figure 4. Process flow diagram of reductive catalytic liquefaction of biomass.

In the deconstruction reactor, the biomass feed stream catalytically reacts with hydrogen and a catalyst at a temperature (120°C to 350°C) and a pressure (300 psig to 2500 psig) to produce a product stream comprising of a vapor phase, liquid phase and a solid phase. The vapor phase is comprised of one or more volatile oxygenated hydrocarbons, volatile hydrocarbons, as well as water vapor. The liquid phase contains water and less volatile oxygenated hydrocarbons. The solid phase comprises unreacted biomass component, primarily lignin, and the slurry catalyst. In the continuous liquefaction reactor, solid biomass is deconstructed producing soluble oxygenates including sugars, sugar alcohols, sugar degradation products, and depolymerized lignin compounds. As these components are exposed to the catalyst, the oxygen content of the sugar derived species is reduced as depicted in Figure 5. The partially hydrodeoxygenated biomass components form an in-situ generated solvent which: 1) enhances biomass deconstruction, 2) improves the solubility of deconstruction products – particularly the lignin derived components, and 3) can be further deoxygenated to produce volatile mono- and di-oxygenated compounds. These volatile mono- and di-oxygenated components exit the deconstruction reactor as a condensable gas product.

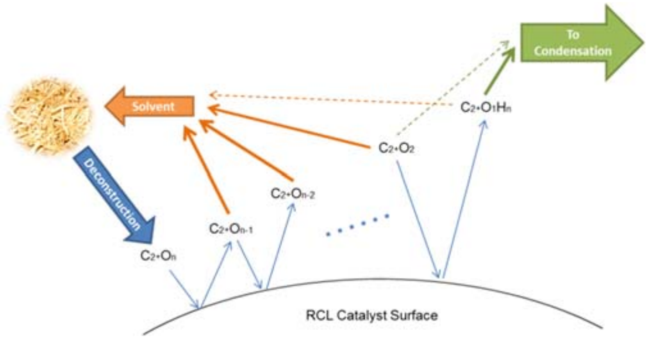

Figure 5. Reaction pathways of reductive catalytic liquefaction of biomass.

A number of reactions occur in order to liquefy the complex mixture of cellulose, hemicellulose and lignin. The cellulose and hemicellulose are deconstructed from their long sugar chains and undergo hydrolysis followed by dehydration of hydroxyl groups and hydrogenation. Side reactions occur such as condensation and cyclization, but are minimized. It is proposed that lignin β-O-4, α-O-4, and C-O bonds are being cleaved to reduce the lignin molecular weight down to a soluble size. The molecules are stabilized in the liquid phase allowing for them to be further processed.

The volatile oxygenated hydrocarbons are separated from the liquid phase and solid phase via vaporization. The vapor stream forms both an organic and aqueous phase when condensed. The overhead aqueous phase contains significant amounts of oxygenated hydrocarbons and is combined with the overhead organic phase. The phases are then catalytically reacted in the presence of a ZSM-5 condensation catalyst within the COTA process to produce a mixture of aromatics and paraffins.

The solid deconstruction catalyst and unreacted biomass solids are separated from the liquid phase, washed and regenerated in the presence of oxygen or hydrogen to remove carbonaceous deposits and unreacted biomass. The regenerated deconstruction catalyst is then reintroduced to the biomass feed stream in the slurry reactor.

Virent modified an existing small scale slurry reactor system to run RCL. Figure 6 shows a photo of this system and details the routes of biomass, solvent, liquid product, and gas. The slurry reactor utilizes a series of automated hoppers, which allow for high concentration slurries (greater than 20 wt %) to be fed to the reactor. Solid-liquid separation was perfomed with a gravitational settler which allowed for the continuous recycle of solid catalyst back to the reactor. Three phases, including biomass, catalysts, liquids, and gases were transported through the various reaction and separation steps. Used catalyst and unreacted biomass could be recycled back to the CSTR deconstruction reactor.

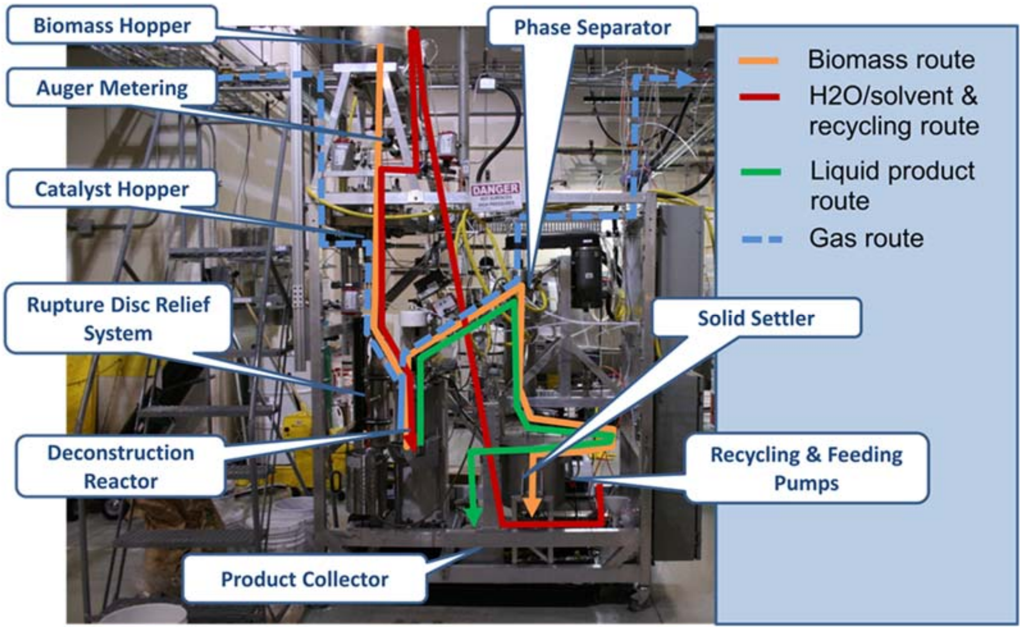

Figure 6. Virent's RCL Reactor system

Figure 7 shows the high level schematic of Virent's RCL pilot plant configuration. Ground up corn stover (<20 mesh) was injected into the slurry reactor that contained an HDO catalyst and solvent. Hydrogen was bubbled into the slurry reactor. Two streams exited the slurry reactor system: (1) a vapor phase stream containing condensable and non-condensable gases (2) a slurry phase material that contained catalyst, aqueous phase product, and potential solid phase biomass. The vapor phase stream passed through a water-cooled condenser and a three phase separator to separate gaseous, organic, and aqueous phases. The gas phase stream flowrate was measured after passing through a pressure control valve, and the composition of this stream determine by an online gas chromatograph. The organic and aqueous phase stream flowrates were measured by weight and were then analyzed to determine the form of the oxygenated hydrocarbons. The slurry phase was sent to the liquid/solid separator where the aqueous-phase solvent was recycled back to the reactor. The solids from the settler contained catalyst and unreacted biomass. The catalyst was regenerated via an oxidative regeneration and then recycled back to the reactor through the lock hopper system.

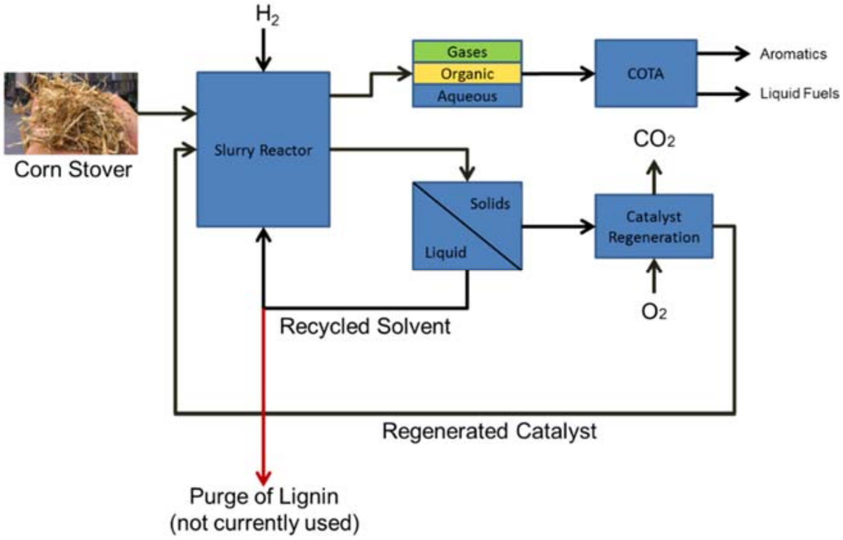

Figure 7. Schematic of RCL Configuration

Figure 8 shows the composition of the aqueous phase streams collected from the condensed vapor stream and the bottoms (recycle stream). The overhead aqueous stream contained significant amount of propanol, ethanol, methanol as well as acetone and propionaldehyde. The less volatile oxygenates (diols, acids, and poly-oxygenates) were concentrated in the bottoms.

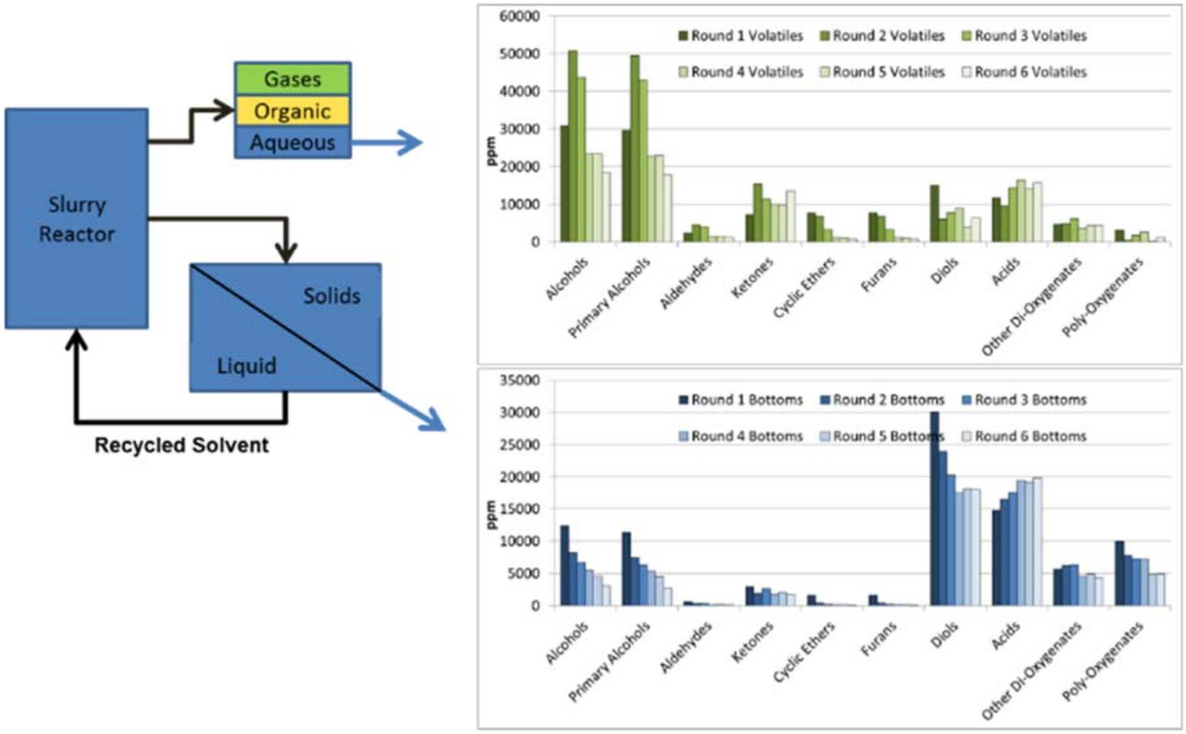

Figure 8. Aqueous Phase Analysis for the Reductive Catalytic Liquefaction of corn stover

Figure 9 shows a gas-chromatograph of the generated organic phase, which indicates that a range of products were generated from both the carbohydrate and lignin fractions of the biomass. This figure shows the presence of longer chain alcohols, cyclic ethers, and oxygenated cycloparaffins derived primarily from the carbohydrate fraction of the biomass. Higher molecular components derived from lignin such as phenols were also observed. Figure 10 shows that besides lignin-derived phenols, the heavier fraction also contained long chain hydrocarbons thought to be derived from the extractive fraction of the biomass.

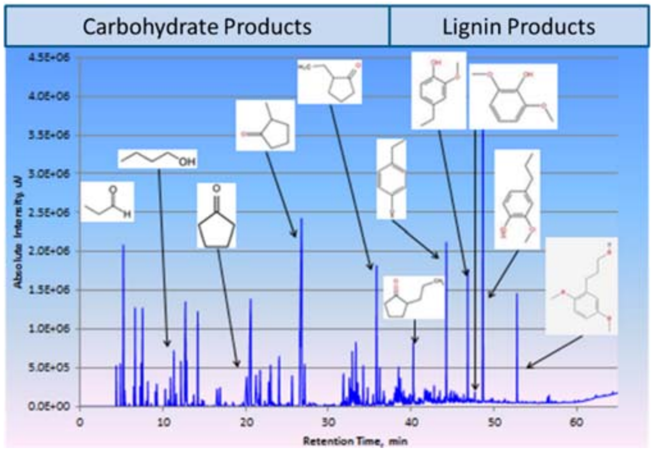

Figure 9. Organic Phase Analysis for the reductive catalytic liquefaction of corn stover

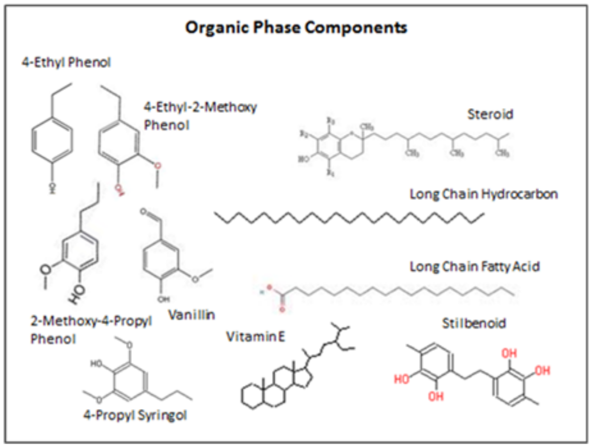

Figure 10. Lignin and extractive-derived organics for the reductive catalytic liquefaction of corn stover

Solvolysis

An alternative liquefaction/HDO technology is the Solvolysis process shown in Figure 11. Virent has successfully developed and demonstrated the technology of Solvolysis to deconstruct a wide range of lignocellulosic biomass into soluble compounds as feedstocks for Virent's BioForming® process. Within the Solvolysis process, biomass is fed to a Solvolysis reactor where it is contacted by an in-situ generated solvent at temperatures of 200 – 350°C. Liquefied biomass is fed to a HDO catalyst with the addition of external hydrogen. In a separation step, hydrogen is recycled back to HDO reactor, an aqueous-phase stream contains the in-situ generated solvent is recycled to the Solvolysis reactor, a slip stream of the aqueous-phase stream is combined with the organic phase generated in the process and fed to the COTA process to produce aromatic hydrocarbons.

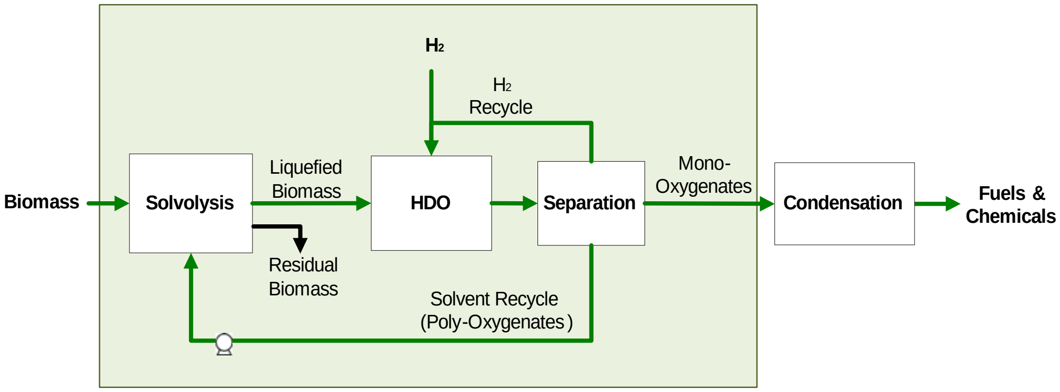

Figure 11. Process flow diagram Solvolysis Process

The Solvolysis chemistry, detailed in Figure 12, can be described as:

- Deconstruction of cellulose and hemicellulose in raw biomass that has a high degree of polymerization (100-10,000 monomer units) into soluble sugar oligomers and monomers
- Hydrodeoxygenation of the soluble carbohydrates to shorten the molecular chain length to 3-6 carbon atoms, and partially remove oxygen as water or carbon dioxide.
- Upgrading of lignin through depolymerization and hydrogenation/hydrogenolysis to produce monomeric, partially de-functionalized phenolics, cresolics and aromatics.

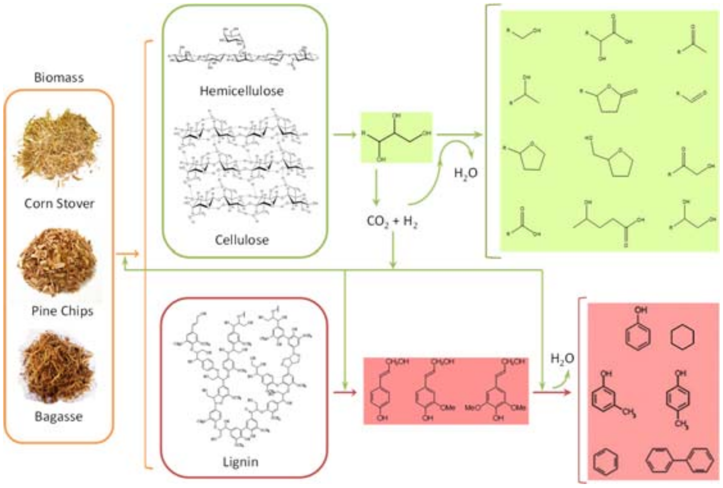

Figure 12. Reactions within Solvolysis Process.

Biomass liquefaction has been demonstrated with various solvents, however, many processes depend heavily on external solvent supply and solvent recycle efficiency. In addition, few of those liquefaction processes use solvent mixtures that contain more than three different compounds, which considerably limits the solvent performance. (US Patent No. 5,730,837, 1994). Solvolysis internally recycled solvent does not need an external supply, and the solvent itself is a mixture of alcohols, ketones, furans, phenolics, etc. which leverages the advantage of multiple functional groups. Figure 13 shows the major species and compounds existing in the in-situ recycled solvent as identified by GC. Figure 14 shows a GC-GC chromatogram of Solvolysis aqueous products which identified some of the unquantified species as aromatics.

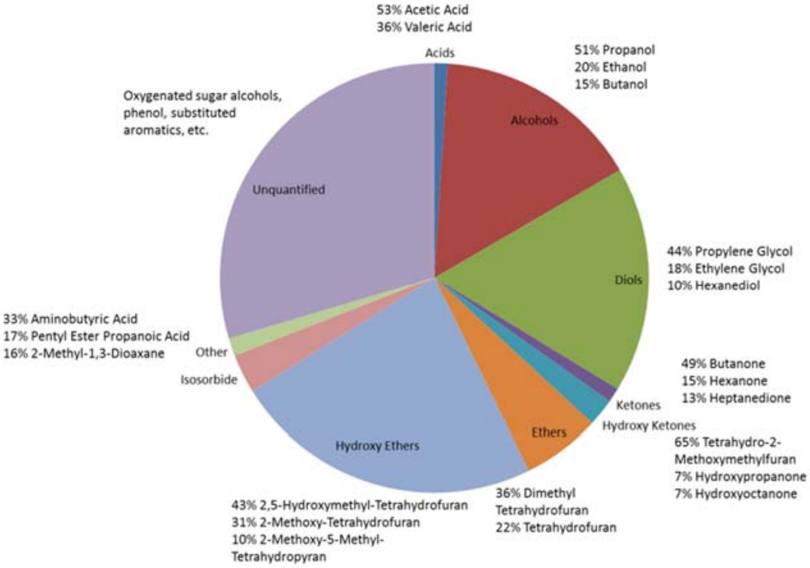

Figure 13. Prevalent species found in the Solvolysis aqueous solvent in weight% (Percentages are shown for the major constituents within each functional group). Almost a third of this stream weight basis could not be quantified.

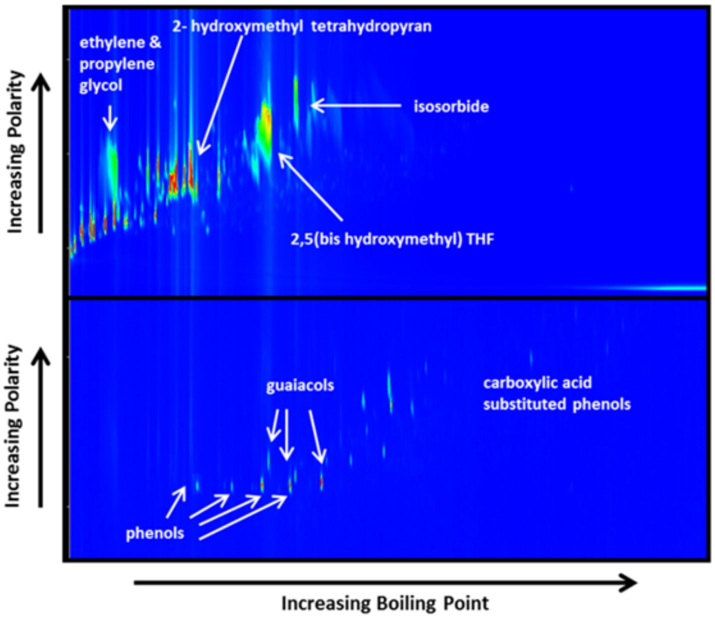

Figure 14. GC-GC of Solvolysis aqueous products (internal recycled solvent).
(a) GC-GC chromatogram of Solvolysis aqueous showing the various compounds identified in the solvent aqueous and (b) Substituted aromatics species identified but not quantified in Solvolysis aqueous.

High amount of alcohols, diols and hydroxy ethers present in the solvent improve the liquefaction potential of the solvent. Although unquantified, the presence of substituted aromatics that also are known to improve overall biomass liquefaction. When these species are not present or at low concentrations, decreased levels of biomass conversion were observed. Many of these species are theoretically derived from the carbohydrate fraction of the biomass, while the aromatics are presumed to be derived from the lignin structure.

The Solvolysis process combines deconstruction, depolymerization, and hydrodeoxygenation reaction pathways to produce a mixture of oxygenates that have an oxygen to carbon ratio of approximately 0.2:1. In the continuous liquefaction reactor, solid biomass is deconstructed and produces a variety of soluble oxygenates including sugars, sugar alcohols, sugar degradation products, organic acids, and depolymerized lignin compounds. As these components are exposed to the HDO catalyst, the oxygen content of the sugar-derived species is reduced. Furthermore, organic acids, generated by the Solvolysis process, significantly enhance hydrolysis and depolymerization of cellulose, hemicellulose and lignin at moderate temperatures. The combination of compounds in the recycle stream reduces cross-linking condensation reactions that occur in typical hydrothermal treatment of biomass and biopolymers.

Virent conducted proof of concept experiments in a modified pilot plant with a Solvolysis reactor. Figure 15 shows a PFD for the process. Biomass was loaded into the Solvolysis reactor. For initial solvent production, corn syrup was pumped directly into the HDO reactor with hydrogen co-feed, bypassing the biomass. Effluent from the column was cooled and separated into a gas and liquid phase, and was recycled back through the HDO catalyst. Once a sufficient amount of solvent was inventoried, the feed pump was shut off, the solvent flow was switched to flow through the Solvolysis reactor, and the Solvolysis reactor was ramped to liquefaction temperatures utilizing a protocol develop to maximize biomass liquefaction. Effluent from the Solvolysis reactor flowed through HDO and the separator. Gas phase products were discharged from the reactor system, and the organic phase products was collected. Net aqueous phase products were collected for future processing with aqueous product recycled back to Solvolysis reactor as liquefaction solvent.

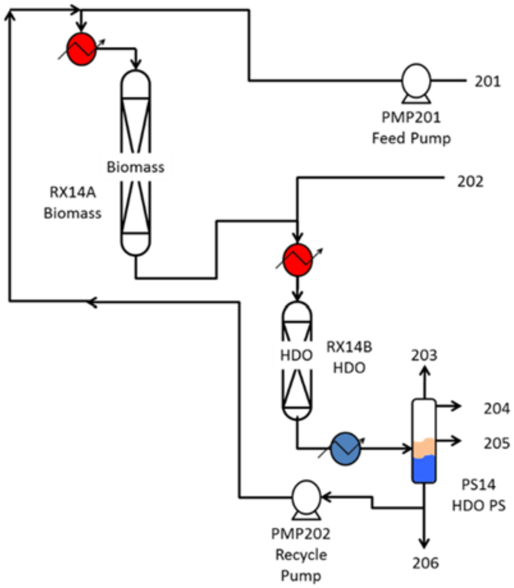

Figure 15. PFD for Solvolysis Process

Figure 16 shows a photo of the 1-inch Solvolysis reactor. This reactor was loaded with the feed biomass and an inert co-load (alpha alumina). The co-load was added to ensure good flow characteristics as the biomass is converted. Figure 29 details the biomass and co-load before liquefaction and the solids unloaded from the Solvolysis reactor after liquefaction. The unloaded solids contained non-structural carbonaceous material as well as inorganic ash. Oxidative regeneration of this material removed the carbon by oxidation and freed the ash from the co-load.

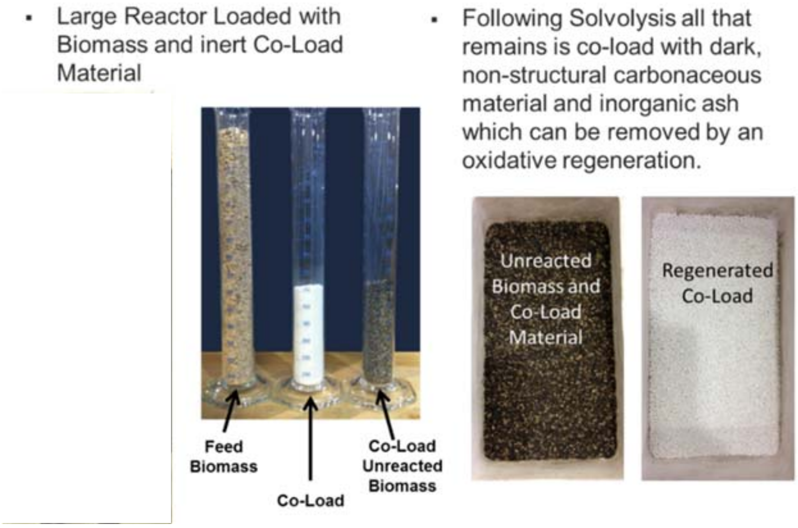
- Large Reactor Loaded with Biomass and inert Co-Load Material
- Following Solvolysis all that remains is co-load with dark, non-structural carbonaceous material and inorganic ash which can be removed by an oxidative regeneration.

Figure 16. Solvolysis reactor before and after liquefaction

Figure 17 shows an example of the mass and carbon balance for an initial experiment utilizing loblolly pine. The carbon balance accounted for carbon added to system with the solvent and biomass and also accounted for carbon in the product gases, organic phase, and aqueous phase.

Additionally, carbon was removed from the system during the washing step, deposition of carbon on the HDO catalyst (determined by monitoring of the oxidative regeneration), and carbon removed with the co-load (un-reactive biomass).

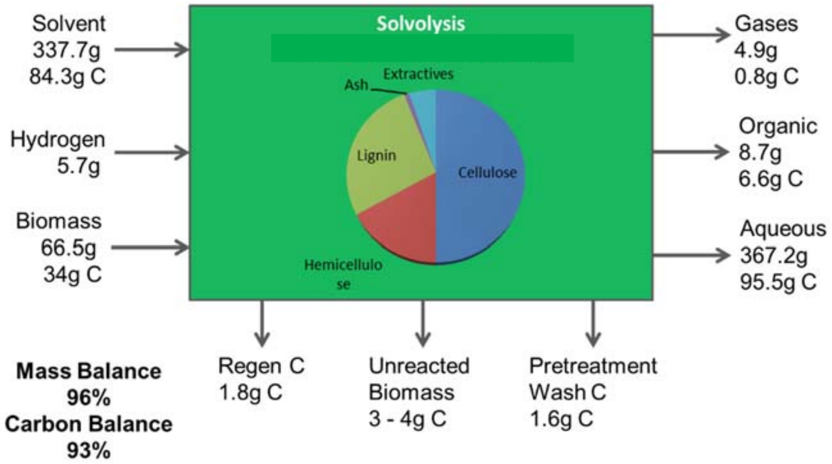

Figure 17. Mass and Carbon Balances for the Solvolysis of Loblolly pine

Liquefaction/HDO Technologies Down Select

Both the RCL and Solvolysis technologies proved to be effective biomass liquefaction. Due to budget and time constraints, it was necessary to down select one technology for process development activities as well as the integration tasks. The two liquefaction/HDO processes were evaluated and compared using key criteria: fundamental chemistry, equipment sourcing, process development needs, system operability, extent of biomass deconstruction, carbon conservation to the product stream and catalyst utilization. A synopsis of the detailed review against the above criteria is shown in Table 2.

Table 2: Comparison of RCL and Solvolysis Processes

Category	RCL	Solvolysis	Advantage
Fundamental Chemistry: Lignin repolymerization potential	Low due to direct interaction with stabilization catalyst	Medium due to transport between deconstruction and stabilization processes	RCL
Fundamental Chemistry: Solvent	Contains more highly oxygenated species	Contains more monooxygenates and partially deoxygenated sugar species	Neutral
Equipment Sourcing	Challenging since the lab-scale slurry pump and control at required process conditions is extremely difficult to source	Straightforward since the fixed bed extraction unit is standard	Solvolysis
Process Development Needs	Poor since the low solids content required for the slurry pump design to work is in direct conflict with project objectives	Good since the process accommodates a range of biomass particle sizes and biomass-to-solvent ratios. This approach also allows for improved integration due to closer scale matches with the downstream condensation process.	Solvolysis
System Operability: Opportunity to Improve Catalyst Lifetime	Limited due to direct contact between catalyst and biomass	High since the system allows for inclusion of a 'cleanup' step between deconstruction and stabilization processes	Neutral
Biomass Deconstruction Extent	>90%	>90%	Neutral
Carbon Conservation	Not as high	Higher	Solvolysis

In reviewing the comparison of the Solvolysis process to the RCL process, key metrics included reactor configuration and catalyst utilization for each process configuration. The two processes are very similar in regard to catalyst compositions and product compositions, with a main variation of separating the biomass deconstruction and the catalyst stabilization systems. The separation of these two processes allows for greater evaluation of the biomass deconstruction chemistry and the interaction with the stabilization catalyst in a practicable manner for a laboratory environment. In both processes, catalyst usage affects key parameters used in the calculation of production economics.

Virent has demonstrated commercial catalyst lifetimes of ~1 year for the stabilization/HDO reactor using both sucrose and glucose based feedstocks. In a separate project validated by the Department of Energy, Virent demonstrated improved catalyst lifetimes compared to the RCL process using corn stover-derived hydrolysates that were purified prior to contact with stabilization catalysts. This resulted in significantly lower catalyst costs per gallon liquid product compared to the RCL process.

Initial testing of the RCL process provided limited information for catalyst lifetimes and biomass deconstruction chemistry. The separation of the processes demonstrated via the Solvolysis process showed improvements over the RCL process baseline in both catalyst lifetimes and biomass throughputs. Incorporation of a Solvolysis reaction scheme, with the ability to separate the system allowing for greater system knowledge and the potential to purify the cellulosic hydrolysates prior to catalyst contact have large benefits. The catalyst costs of processing cellulosic oxygenate can approach those of conventional sugar processing as development progresses.

Based on advantages outlined in Table 2 and the expected improvement on overall process economics, it was decided to move forward utilizing the Solvolysis process as the preferred liquefaction/HDO technology for this project.

Safety Upgrades

Mixed oxygenates derived from the liquefaction/HDO process are upgraded to an aromatic-rich BioFormate® product utilizing Virent's COTA process. A project objective was to investigate maximizing the amount of benzene that could be generated within the integrated process. Due to the potential of high concentrations of benzene, it was necessary to assess and upgrade Virent's facility to allow safe and healthy operations of the aromatics process. A full safety assessment was conducted to determine the necessary capital upgrades and control procedures required to ensure the work within the project involving benzene was performed according to federal and state environmental, health and safety standards. Recommended engineering and administrative controls were implemented prior to starting work on aromatics selectivity.

Figure 18. Walk-In Hood

Based upon the results of third party evaluation, Virent's canopy enclosures did not provide the necessary engineering controls to support safe production of concentrated benzene streams (i.e. >5%) in a continuous process. Safety upgrades were required prior to startup of COTA process studies. Based on third party recommendations and subsequent results of a Hazard Identification (HAZID) study conducted by the Virent Particularly Hazardous Substance (PHS) Readiness Committee, the project team determined that a ventilated walk-in fume hood was required. This walk-in fume hood required minor HVAC modifications to mitigate employee exposure risks associated with COTA process work. The necessary walk-in fume hood was installed and commissioned during the first quarter of 2013. Figure 18 is a photo of the installed hood. Virent was able to safely operate the pilot plant within this fume hood as required for progression of project research. The safety updates enabled Virent to meet federal and state regulatory standards, as well as Virent's internal standards.

Aromatic Selectivity

Virent has shown that oxygenates generated by the catalytic hydrodeoxygenation of biomass-derived feedstocks (sugars and biomass hydrolysates) can be reacted in the presence of water over a Virent modified ZSM-5 catalyst in a vapor-phase reactor system to produce aromatics and paraffins (USA Patent No. 8,017,818, 2011) (USA Patent No. 8,350,108, 2013). The acid condensation catalyst used in the COTA process is based on ZSM-5, a zeolite that was developed in the 1970's by Mobil Oil (Yurchak, 1988) and has since been deployed in several industrially significant processes such as methanol to gasoline (MTG), fluid catalytic cracking (FCC), and in aromatics processing applications including selective toluene disproportionation (STDP) (Venuto, 1994).

There is evidence based on the nature of the feedstock and the properties of the resulting product streams that numerous reaction pathways occur in parallel across the ZSM-5 catalyst. In many cases, it is likely that the observed reaction products are the result of interactions with non-observed intermediates/co-catalysts located within the zeolite pores (Haw, Song, Marcus, & Nicholas, 2003).

Identified pathways include:

- Dehydration of alcohols and diols to alkenes and alkadienes,
- Diels-Alder condensation of dienes and olefins,
- Oligomerization of olefins,
- Aldol condensation of carbonyls,
- Eneone cracking to generate carboxylic acids and olefins,
- Ketonization reactions between organic acids to yield a ketone and carbon dioxide,
- Aromatization with associated generation of hydride reducing equivalents, and
- Hydride transfer to unsaturated species including alkenes, ketones, and acids.

Figure 19 shows a simplified reaction network that summarizes a portion of the reaction pathways. Two overriding trends are evident. First, all oxygenates are generally routed through an alkene (olefin) pool which can be considered pseudo equilibrated in terms of carbon chain length with restricted branching due to the ZSM-5 pore structure. Second, for alkanol conversion, the alkenes are both converted to aromatics, resulting in the generation of hydride reducing equivalents, and act as acceptors of the reducing equivalents to produce alkanes. A key understanding is that unsaturated oxygenates can also accept the reducing equivalents to form saturated species which can then undergo dehydration. For example, ketones are hydrogenated to alcohols by accepting the reducing equivalents provided by aromatization reactions. This hydrogen transfer has a major impact on the stoichiometry of the conversion process.

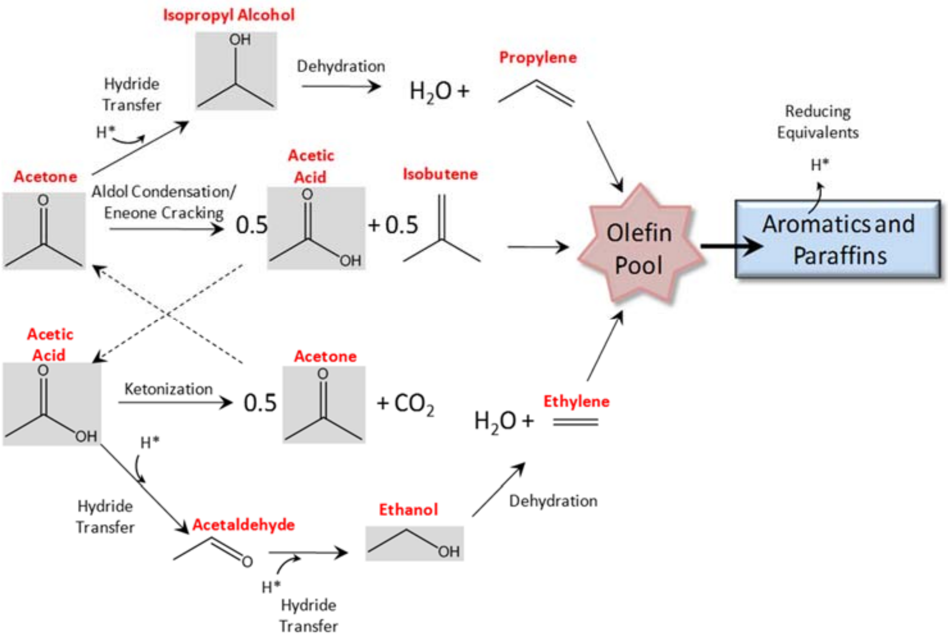

Figure 19. Deoxygenation and Condensation Pathways across ZSM-5

The COTA process is operated as a gas phase, swing bed reactor system. Similar systems have been deployed for several commercial processes.

Early in the project, the aqueous and organic phase products generated from corn stover in RCL were converted to hydrocarbon products in the COTA process. Figure 19 shows the distribution of hydrocarbon products from this process. As shown in Figure 19(a), high yields of aromatic hydrocarbons, including deconstructed lignin compounds, can be achieved using liquefied biomass. From an operational perspective, resulting olefin and mono-oxygenate products can be recycled to acid condensation to improve aromatics yield.

Figure 19(b) shows that C7 to C9 aromatic hydrocarbons are dominant aromatic products. These compounds can be drop-in blends to gasoline and/or jet fuels or precursors for chemical production. Figure 19(a) shows that aromatics were the largest product class with 46% of the RCL feed carbon (corn stover basis) being recovered as aromatics.

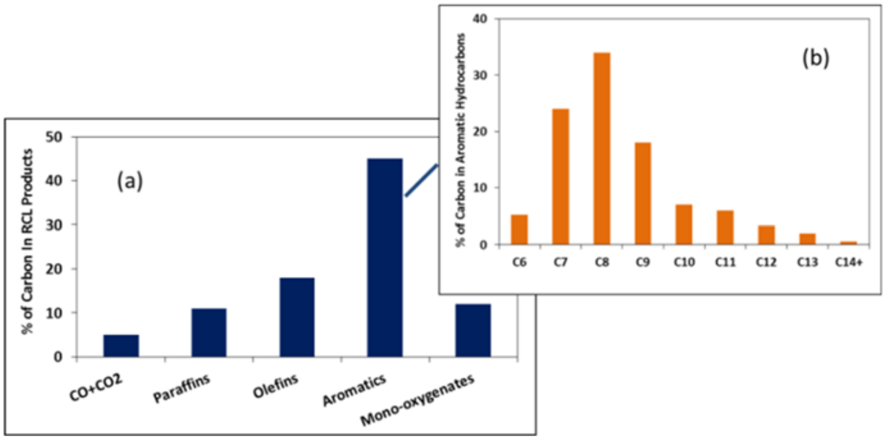

Figure 19. Aromatic hydrocarbons produced with COTA processing of RCL products.(a) Overall carbon yields of acid condensation products; and (b) carbon distribution of aromatic hydrocarbons.

A major milestone of the project was to increase the aromatic selectivity within the COTA process over the baseline of 67wt% of the liquid hydrocarbon product. For both model and Solvolysis feeds, the goal of this milestone was to increase this selectivity from 67% to greater than 84%.

Initial work for this study utilized a model feedstock that mimics the hydrolysate generated from the Solvolysis process. Figure 20 shows the major components in hydrolysate generated from loblolly pine in the Solvolysis process. Table 3 shows the composition of the model feed that contains a primary alcohol, cyclic ether, as well as phenol to mimic lignin compounds.

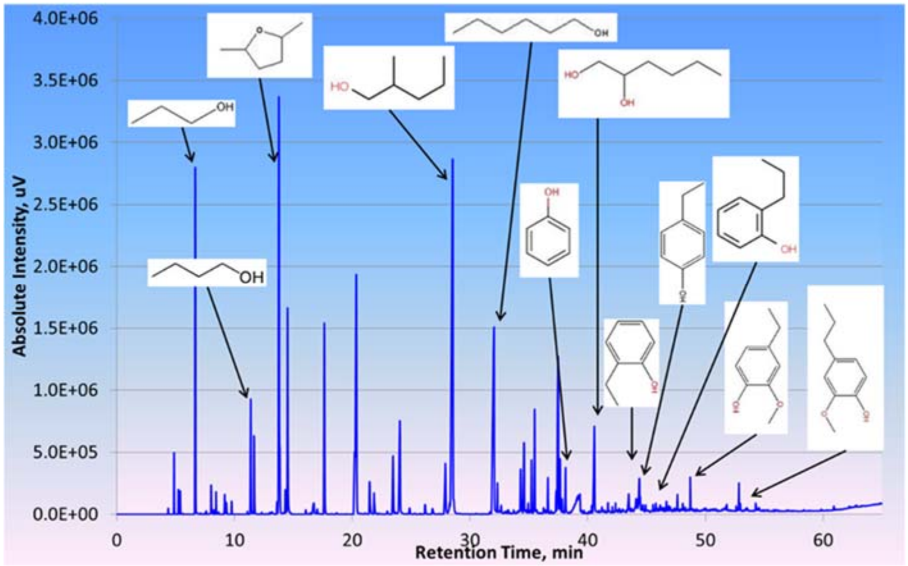

Figure 20. Cellulosic feedstock distribution in internally produced hydrolysates

Table 3. Model Feed Composition

Model Feed Components	Weight %
Ethanol (95%)	10
1-Propanol (99%)	10
2- Methyltetrahydrofuran (99%)	20
2-Methoxy Phenol (Guaiacol 98%)	5
Hexane	5
Water	50

The overall yield and aromatics selectivity results for both the cellulosic hydrolysate and model feeds are detailed in Figure 21. Similar yields were observed with both cellulosic and model feed components, both conserving >60% of the feed carbon to a usable product with selectivity to aromatics of greater than 88%, exceeding the milestone of 84%.

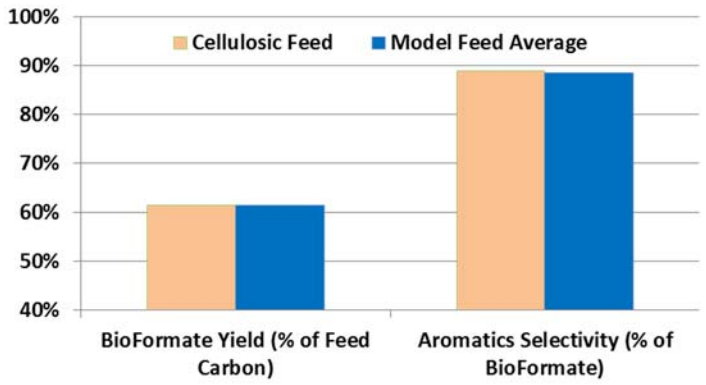

Figure 21. Bioformate Yields and Aromatics Selectivity with both Model and Cellulosic Feeds

A general product distribution can be seen in Figures 22 and 23 for this study. Figure 22 shows similar carbon chain length of the products for both feedstocks. There are 2 primary regions, C_3-C_4 and C_6-C_{10}. The lighter components (C_3-C_4) are largely light paraffins and the heavier components (C_6-C_{10}) are predominantly aromatics.

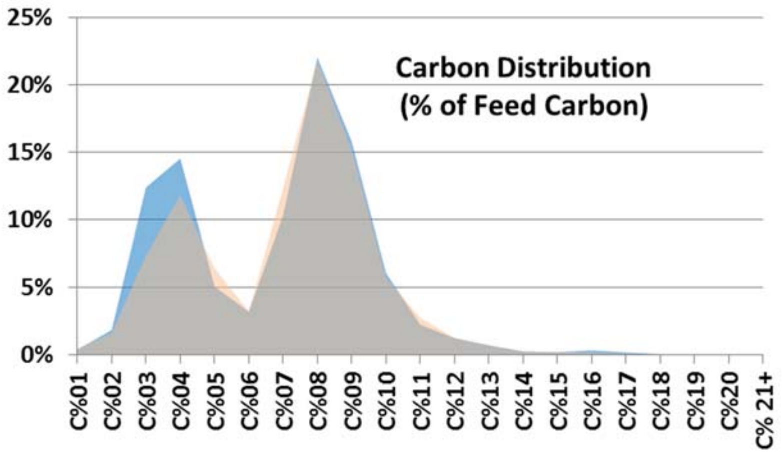

Figure 22. Total Carbon Distribution with both Model and Cellulosic Feeds

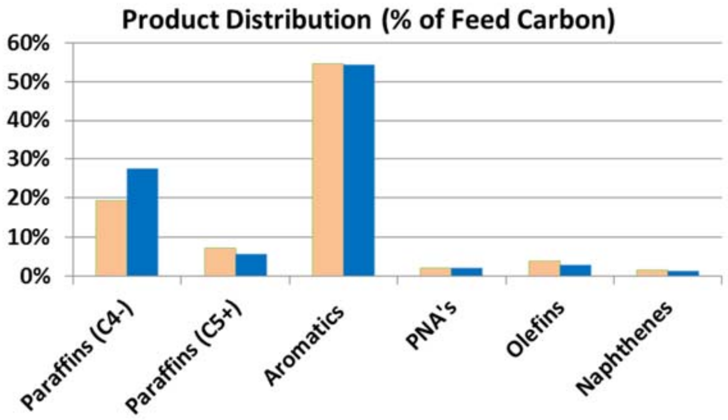

Figure 23. Product Distribution of both Model and Cellulosic Feeds

A breakdown of the aromatics carbon number can be seen in Figure 24. This distribution shows a large amount of toluene (C_7) and mixed xylenes (C_8) are present as well as an appreciable amount ethyl-methyl benzene and tri-methyl benzene (C_9 aromatics) for both feedstocks.

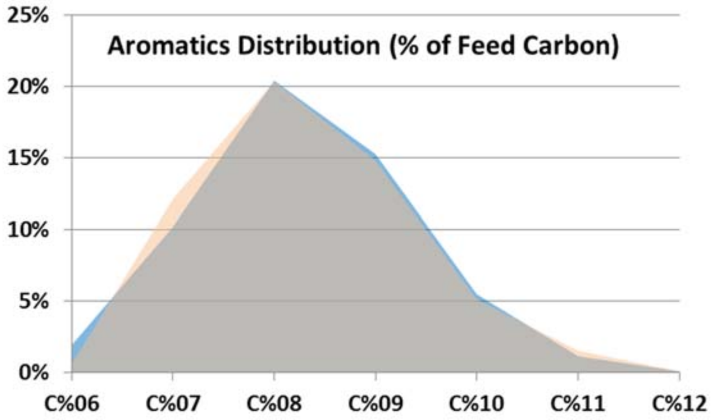

Figure 24. Aromatics Distribution of both Model and Cellulosic Feeds

Process Development

Biomass Deconstruction and Feedstock Down select

Process studies were conducted to investigate the effects of liquefaction temperature, time and solvent recycle rate. These studies used the process flow configuration shown in Figure 15.

Information from this parameter study was utilized to design experiments to achieve greater than 90% biomass conversion for the three investigated biomass feedstocks. The overall conversion results are shown in Figure 25. High yields of aqueous phase products were achieved with production of some organic (~10% of carbon from biomass) and gas (<10% carbon from biomass) phase products. Each of the three feedstocks presented high liquid yields of products to be processed by COTA.

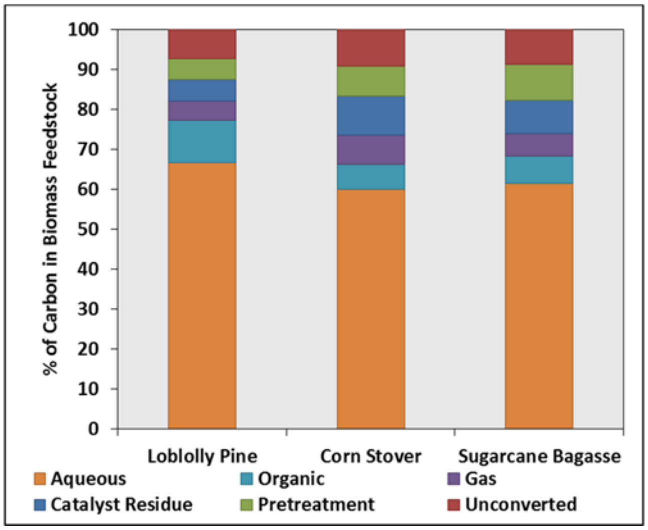

Figure 25. Deconstruction product profile for each of the biomass species through pretreatment and deconstruction

Each of the solubilized biomass materials were then processed in a once through COTA system as shown below in Figure 26 to generate a highly aromatic stream. The overall conversion results are shown in Figure 27.

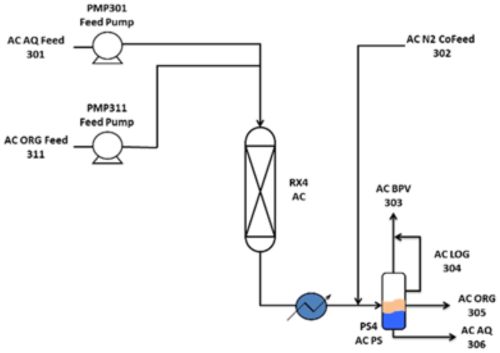

Figure 26. COTA System with no recycles

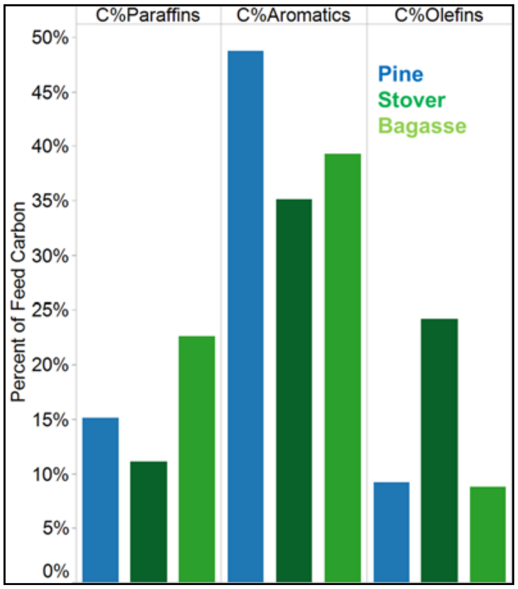

Figure 27. Product Yields through Acid Condensation

High yields of aromatics were produced with each of the biomass materials with loblolly pine having the greatest yield (~50%). The stover and bagasse generated more olefins and paraffins, respectively. Recycle of the olefins would allow for increased yields of aromatics while the paraffins are generally considered gas losses depending on chain length. Acid condensation results indicate the flexibility to handle a variety of feed components.

Virent has continued to work with many 3rd parties in understanding the overall cost structure and supply chain for various biomass based feedstocks. The overall feedback is in general agreement with the trends shown below in Figure 28 from a study completed by the National Academy of Sciences and Engineering. The main areas of comparison of feedstocks are overall price, availability, supply chain development, and the physical and chemical composition of the biomass in relation to the compatibility with the Solvolysis process. Overall, woody biomass has a current supply chain in place which supports the current lumber and paper/pulp industries which can support larger scale biofuel facilities. Also, woody biomass has a relatively low cost point and a low ash composition, both favorable to this catalytic approach.

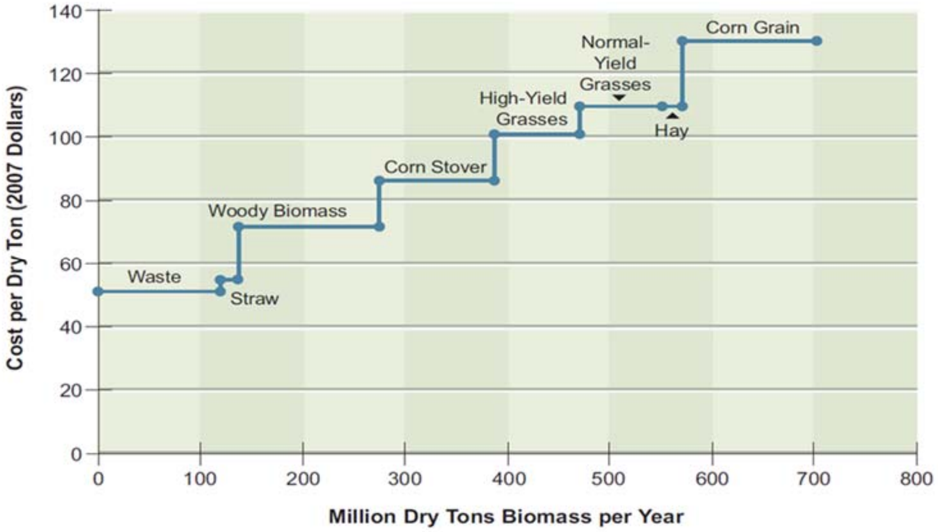

Figure 28. Supply costs of various biomass feedstocks (National Academy of Sciences, 2009)

Attributes covered above from feedstock characterization, biomass deconstruction, product upgrading and overall economics focus was utilized to down select feedstock use to woody biomass material, more specifically loblolly pine for the remainder of the project.

Pilot Plant Upgrades

An important milestone for this project was to conduct a 2000 hour demonstration run of the integrated Solvolysis/COTA process. This milestone required the usage of a consistent biomass feedstock and a single catalyst loading for HDO and COTA for the duration of the run. It was necessary to upgrade Virent's pilot plant capabilities to achieve this milestone. Virent conducted a design review of the Solvolysis process and generated a design for a larger scale Solvolysis pilot plant. The flexibility of the new design allowed for three major steps/components that can be inter-connected or operated separately as desired. The three major steps include: biomass deconstruction, contaminant removal and stabilization.

Figure 29 shows a photo of the deconstruction section of the finished pilot plant.

Figure 29: Deconstruction Section of Solvolysis Pilot Plant

The Solvolysis pilot plant was commissioned in the first quarter of 2015. The unit was run for nearly 40 days at a biomass conversion of greater than 70% (design case). No operational issues were observed in the first campaign, with minor channeling/wall effect issues resolved through adjusting co-load shape, co-load ratio, and adding an internal piece to the reactor to aid in compression. Figure 30 shows a typical progression within the deconstruction reactor where the loblolly pine was digested. Figure 31 shows that the measure biomass conversion observed during this commissioning stage exceeded the expected conversion for the chosen extraction temperature profile.

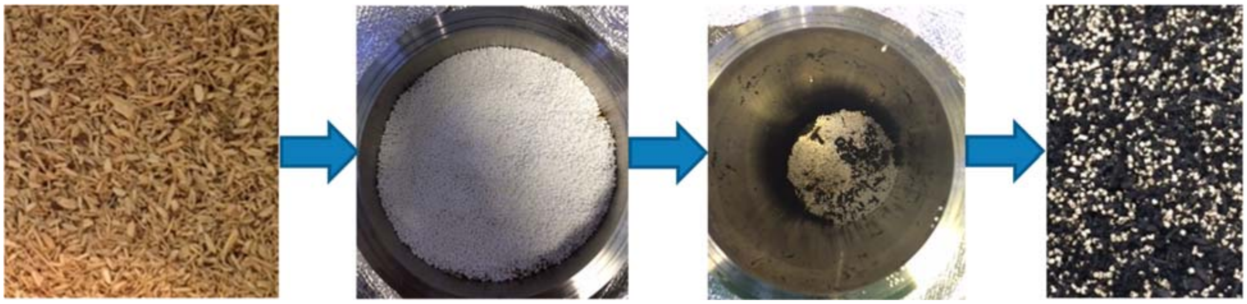

Figure 30 Typical Progression of the Biomass Digester.
From Left to right: ¼" biomass chips to be loaded; loaded reactor prior to Solvolysis; biomass reactor following Solvolysis; unloaded biomass and co-load after a successful extraction.

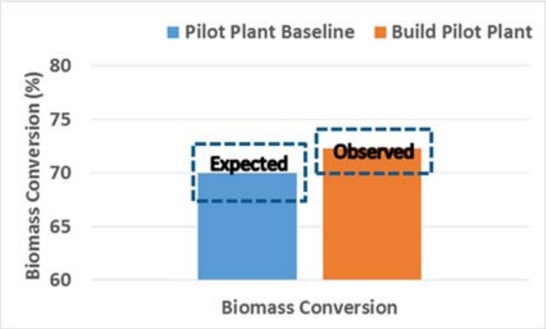

Figure 45. Biomass Conversion results with the build VS previous baseline performance at identical operating conditions at smaller bench scale;

Demonstration Run 2000 Hours

A major task for this project was to conduct a 2000 hour run of the integrated process to convert a cellulosic biomass (loblolly pine) to an aromatic rich BioFormate® product. Prior to the stability run, the longest an HDO catalyst was run in Solvolysis process service was approximately 860 hours. The COTA system was run for a shorter time due to limited volumes of Solvolysis product. The stability run utilized the Solvolysis pilot plant discussed above that contained the Solvolysis digestion reactor and the primary HDO stabilization reactor system. The pilot plant was integrated with a secondary HDO pilot plant to condition the intermediate stream for processing in the COTA reactor system. The goal of this task was to run the process for 2000 hours of cumulative time on stream utilizing single loadings of catalyst for each of the reaction steps (HDO stabilization, HDO finishing, and COTA). A biomass conversion of 70 wt% was targeted to maintain operability of the integrated process for 2000 hours.

Experimental

HDO and COTA Catalyst

A Virent HDO and COTA catalyst was utilized for both the stabilization and conditioning steps.

Process Conditions

Figure 32 shows the PFD for the Solvolysis/HDO laboratory unit. Sized loblolly pine (1/4 inch) was loaded with co-load material (alpha alumina) into a 2L Parr reactor (1 of 3 reactors). The HDO catalyst was loaded in 1" OD reactors. There were a total of three stabilization HDO reactors on the plant, but only one was on-stream at a time, the other two were either being regenerated or were idle (at temperature and pressure). A supply (~30 gallons) of HDO aqueous solvent produced from previous Solvolysis/HDO operations with loblolly pine was utilized as the initial solvent for the stability run. The HDO aqueous solvent was continuously fed to the biomass Parr reactor with an additional internal recycle of HDO aqueous product also being fed to the biomass Parr reactor. All of the product from the biomass Parr reactors was fed to the HDO reactor, along with a co-feed of H_2.

Once per day, a fresh biomass Parr reactor would be loaded and brought into service. The biomass Parr reactors were loaded with both loblolly pine and Al_2O_3 spheres. The Al_2O_3 spheres provided improved flow distribution and reduced pressure drop within the biomass Parr reactors as the biomass is solubilized. Once all pressures and flow rates were stable, the Parr reactor would undergo a temperature program that involved ramping the temperature for a set amount of time. Once the temperature program was completed, the biomass Parr reactor was cooled down and the next biomass Parr reactor, containing fresh biomass and co-load, was brought on service and the process was repeated. The biomass Parr reactor coming off process service was purged with N_2 to push as much remaining liquid as possible through to the HDO process. The wet residual biomass (and co-load) was unloaded from the Parr reactor and dried in an oven overnight at to remove all the entrained liquid. A mass balance was conducted over the time frame of the biomass digestion in the Parr reactor, defined as a weight check, and the mass of entrained liquid was accounted for within the mass balance along with the mass of the dried residual biomass.

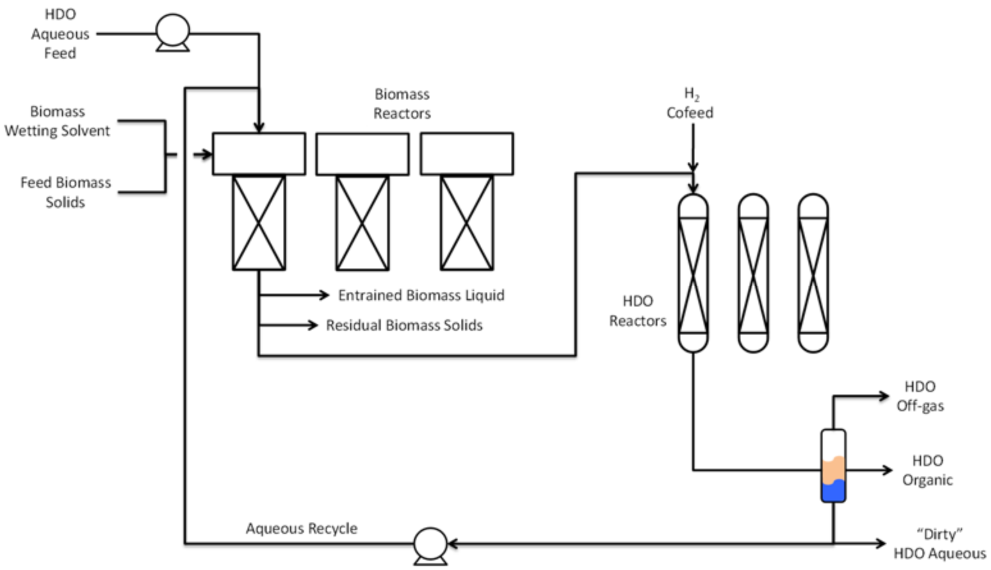

Figure 32. PFD of the Solvolysis/HDO Laboratory Unit

The COTA process was fed the aqueous product as well as the light organic stream generated in the Solvolysis unit. The organic product from the Solvolysis unit was distilled before COTA processing to remove the heaviest fraction of the total HDO organic. The two feeds were fed into the COTA reactors at an appropriate ratio based on production rates in the Solvolysis process.

Solvolysis/HDO was run for a total of 2,160 hours (90 days) and was down several times due to carbon buildup within the reactor inlets and process lines between the biomass reactors and the HDO reactors. The carbon build-up issue could have been alleviated by having less tubing distance between Parr Digesters and HDO reactors or by larger diameter tubing (with less restrictions at elbows, valves, and other restrictions). COTA was run for a total of 2,088 hours (87 days) and was only down twice to remove ash deposits that were accumulating in the preheat section of the reactors.

Results and Discussion

Solvolysis - HDO

Figure 33 shows the level of biomass conversion throughout the stability run. The biomass conversion remained constant throughout the run (~70% on a mass basis and ~60% on a carbon basis). There was not a discernable trend of the biomass conversion with respect to the HDO catalyst time on stream. This is a very important and positive observation since the possibility of HDO catalyst deactivation was a significant concern.

The difference between the mass and carbon bases of biomass conversion highlights the increasing carbon content of the residual biomass. The residual biomass was predominantly composed of lignin and consequently had a higher carbon content than the fresh biomass. The carbon content of the fresh loblolly pine was measured at 51.1 wt% on a dry basis. The carbon content of the residual biomass was measured at 67.8 wt% on a dry basis. As a point of comparison, phenol has a carbon content of 76.6 wt% and guaiacol has a carbon content of 67.7wt%. Both of these components are typical lignin monomers.

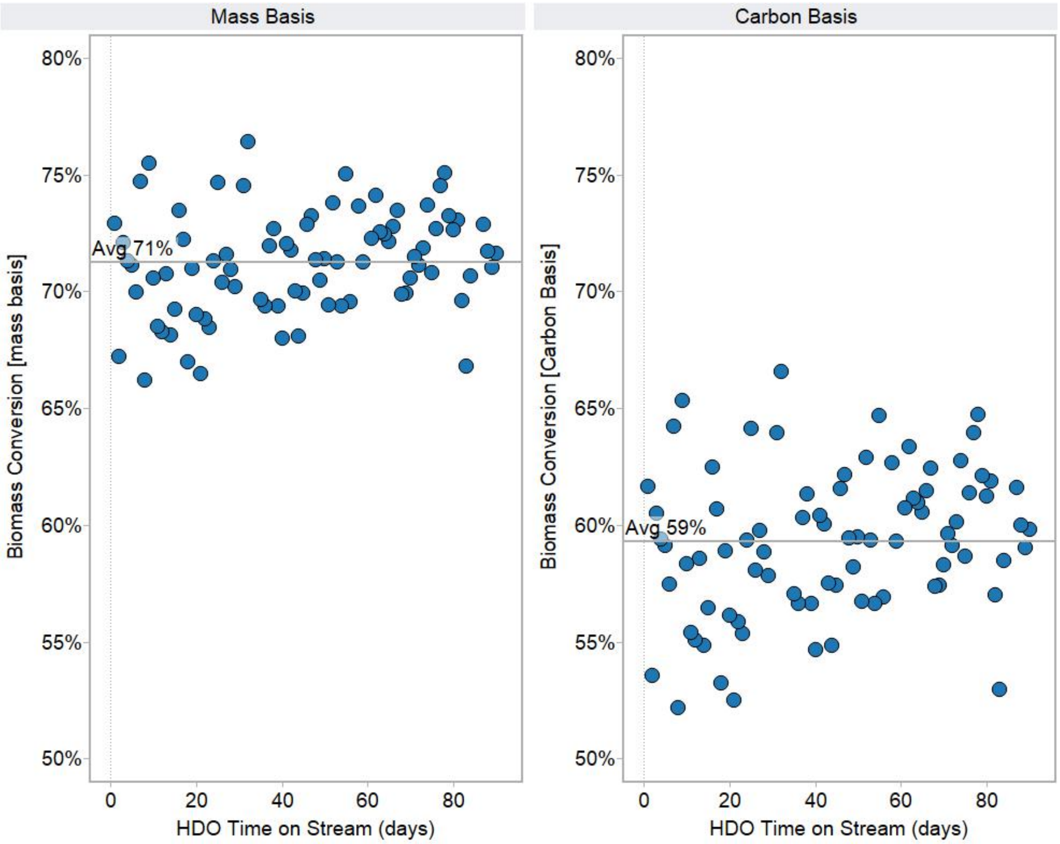

Figure 33. Biomass Conversion (mass basis on left, carbon basis on right) as a Function of the HDO Catalyst Time on Stream

The HDO catalyst did not show signs of long term deactivation during the 90 days of operation. The HDO catalyst also did not show any significant performance loss due to short term deactivation (primarily due to coking, or carbon accumulation on the catalyst). The distribution of products did not change significantly during the cycles and the trend lines for all but mono-oxygenates were statistically insignificant. The rate of mono-oxygenates decreased at a rate of 0.7% per day. On process cycle times for the HDO catalysts were generally 4 days long with some cycles extended to 5 days. Catalyst performance did not suggest that the cycles needed to be this short, however, the amount of carbon removed during the regenerations made it favorable from an operability point of view to limit the HDO cycle times to 4 or 5 days.

COTA

The aqueous product from 2nd stage HDO and the fractionated organic product from Solvolysis/HDO were together fed into the AC system. The product yields on a carbon basis as a function of the COTA catalyst time on stream are shown in Figure . The product distribution between paraffins and aromatics was as expected with the composition of the material being fed into the COTA system. The yield to coke on the COTA catalyst was higher than is usually observed with sugar feedstock HDO products. The coking rate was 3-5% of the inlet carbon for the biomass-derived oxygenates, whereas typical carbon yield of coke is 0.5-3% for sugar-derived oxygenates.

The yield of COTA contaminants shown in red on Figure 34 consist of unconverted reaction intermediates which is inclusive of olefins, dienes, cyclic olefins, naphthenes, and oxygenates. The level of COTA contaminants was as expected at the beginning of the run at ~0.5% of the feed carbon. The contaminants increased at a rate of ~2x versus previous long term COTA experiments with sugar feeds. The yield of COTA contaminants after 90 days was over 10%, a rate of increase just over 0.1% per day. In contrast, the rate of increase of COTA contaminants for stability runs with clean sucrose feedstocks are about 0.04% per day. As the COTA catalyst deactivated over time, due to de-alumination of the zeolite, the extent of conversion was decreased and increasing levels of unconverted intermediates were observed in the product. This was mitigated to an extent by increasing the temperature of the COTA reactors during the run, which is done in all stability runs. The more rapidly increasing yield of COTA contaminants during this stability run was primarily a consequence of an increasing rate of coking or short term deactivation.

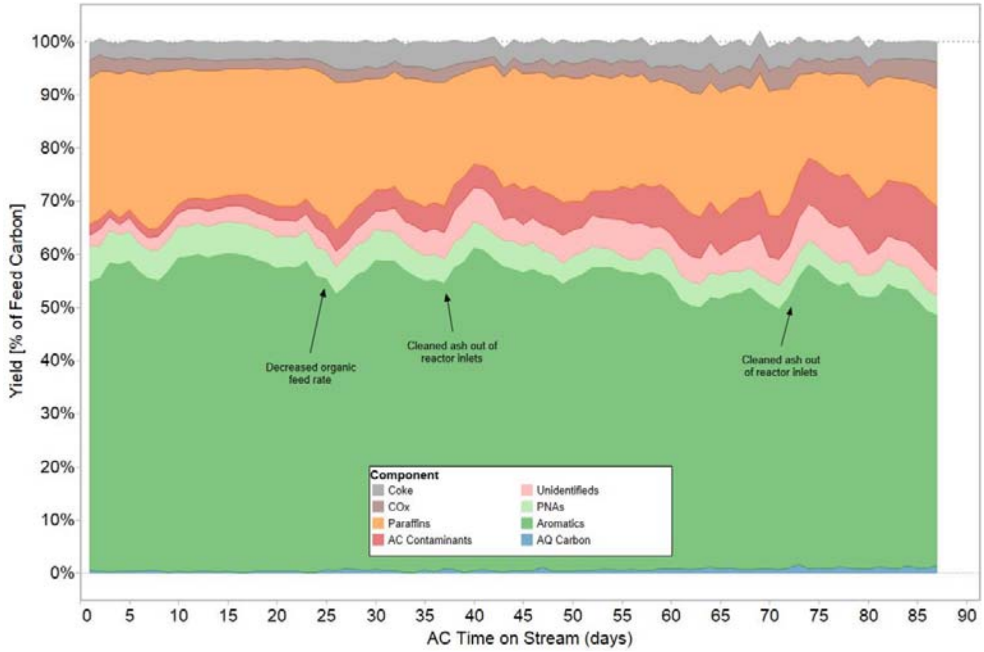

Figure 34. Carbon Yields of Products from the AC Process as a Function of the AC Catalyst Time on Stream

Initially, the rate of deactivation was comparable to experiments with clean sucrose feedstock at ~0.1 g COTA catalyst / g feed C. At the end of the run the rate of deactivation had increased almost 5x from the start of run rate. Previous stability runs with clean feedstocks have not shown a significant change in the short term deactivation rate. One potential cause of this behavior is ash deposits on the COTA catalyst were eliminating active sites, either physically by blocking pores or chemically by neutralizing acid sites, and reducing the tolerance of the catalyst to coke. In the conceptual commercial scale plant design we do not foresee this as a major problem as the ash should not be fed forward into the COTA reactors as it would be removed in distillation prior to COTA. These separations were not incorporated on the demonstration pilot plant and the ash removal would need to be confirmed in future work.

Conclusions from 2000 hour Demonstration Run

Through the course of the stability run, there were no obvious signs of long term deactivation of the HDO catalyst which gives an initial indication that the HDO catalyst is stable for a longer duration. The primary HDO catalyst required frequent regenerations to maintain good operability during the stability run. Cycle times up to 5 days were tested, although 4 days were used more consistently during the stability run. The regeneration requirements for the HDO catalyst contributed significantly to the capital and operating expenses of this process and more testing should be performed to determine the exact regeneration requirements. Further investigation should be completed to optimize the HDO catalyst cycle time. The coking of the HDO catalyst can be affected by changes to either the HDO catalyst itself or the process condition changes to either the HDO or Solvolysis reactors.

The presence of ash in the biomass feedstock and the associated buildup of ash within the process is a concern. Most ash components on the primary HDO catalyst appeared to have reached an equilibrium when analyzed at the end of the stability run, except for P, which appeared as if only the first half of the catalyst bed had reached the equilibrium point. It is unclear what additional impacts a longer stability run would have had in respects to P on the HDO catalyst. In addition to the ash causing chemical changes to the HDO catalyst activity, the ash had also caused physical blockage of flow within the preheat sections of the COTA reactors.

Distilling the heaviest fraction of the HDO products will remove the majority of the ash reducing any issues with the COTA reactors. This distillation step was not practiced during the 2000 hour run but was factored into the conceptual design of the commercial scale plant. In addition to removing the inorganic ash components from the HDO products, the distillation step will remove the heavy non-volatile organic components out of the HDO product. The distillation would remove the need for the second HDO step as residue would be greatly reduced.

Overall, the Solvolysis/HDO stability run was successful in demonstrating the technology for an extended period of time. Further development will be needed in order to improve the economics of the process by increasing the yield to final product (higher biomass conversion), improving the process throughput, and reducing the regeneration requirements of the catalysts.

Techno-economic and Life Cycle Analysis

Commercial Model

An integrated process model was created in Aspen Plus V8.6 simulation software as part of the project to evaluate the expected process at a commercial scale of 2,000 dry MT loblolly pine input per day. This section describes the process design for the conversion of lignocellulosic biomass to advanced biofuels. The model incorporated all aspects of a commercial process from feedstock through final hydrocarbon products, as well as OSBL unit operations such as utilities and boiler/turbogenerator. See Figure 35 for the process section considered for this integrated process model.

The Aspen model has over 70 components that represent a majority of the compounds found in the experimental data. Process conditions and reported yields/results were based on experimentally derived data. All costs were projected in 2014 dollars. The next sections briefly describe the major process operations.

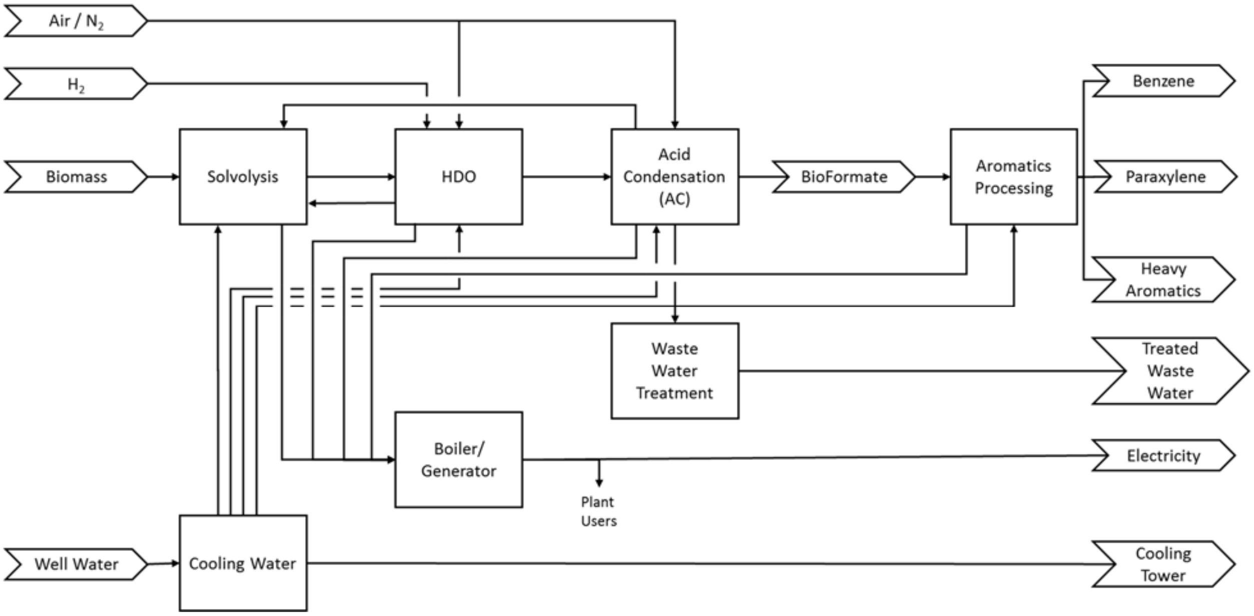

Figure 35. Final configuration PFD for converting biomass into final hydrocarbon products.

Solvolysis

The milled biomass is pumped into the 1st stage of the Solvolysis reactor, where it is mixed with hot solvent that is being recycled around that particular stage. A portion of the biomass, mostly hemi-cellulose, is solubilized in this first stage and removed with the liquid solvent and eventually fed into the HDO reactor. The remaining biomass is then fed into the second stage of the Solvolysis reactor which operates in the same fashion as the 1st stage, only at a higher temperature. In this stage, any remaining hemi-cellulose a portion of the cellulose is removed from the biomass into the solvent. Finally, the biomass is fed into the 3rd stage which operates at the highest temperature and the remaining cellulose and a portion of the lignin is removed. The residual biomass is then removed from the reactor, washed with water to recover entrained solvent, and then fed into a combustor/boiler/turbogenerator that provides heat for the process as well as electricity.

Hydrodeoxygenation (HDO)

The solvent stream from the Solvolysis reactor is fed into the HDO reactor, containing a fixed catalyst bed in the presence of hydrogen gas. The sugars and a portion of the lignin are converted into a mixture of alcohols, ketones, cyclic ethers, alkanes, acids, water, and other oxygenated compounds. A portion of the liquid product is recycled back to the Solvolysis reactor, while the remainder of the liquid product is sent forward to the COTA reactors once the heaviest fraction of components is removed via distillation.

COTA (Acid Condensation (AC))

The volatile liquid products from the HDO catalytic reactor are vaporized and then fed into the COTA fixed bed catalytic reactors. These reactors convert the mixture of oxygenates into a mixture of hydrocarbons, primarily aromatics and alkanes, with water also produced as a by-product.

Aromatics Processing

Aromatics processing represents a typical set of processes used throughout the refining industry to convert a mixture of aromatic chemicals (in this case, BioFormate® product) into primarily para-xylene and benzene. For this model, the aromatics processing section involved 5 distillation columns, two reaction steps, and a crystallization unit to purify the para-xylene. The two reaction steps are xylene isomerization and transalkylation. Xylene isomerization primarily performs two functions for the incoming feed of C_8 aromatics. One is to dealkylate the ethyl benzene into ethane and benzene, and the other is to re-equilibrate the ratio of the three xylene isomers (of which para-xylene is depleted from the crystallization step). The transalkylation reaction step receives a mixed feedstock of C_7 and C_9/C_{10} aromatics and the primary purpose is to perform transalkylation chemistry to convert these aromatics into an equilibrium distribution, which contains additional benzene and xylenes. A model of this aromatics processing operation was developed at Virent and typical industrial performance of the individual unit operations was applied in order to predict what the ultimate yields of final products (i.e. para-xylene, benzene, etc.) would be obtained given a particular yield and composition of BioFormate® product being fed into aromatics processing.

Wastewater Treatment:

A wastewater stream is produced in this design that must be treated before it is safe to discharge back to the environment. The wastewater stream is processed via anaerobic digestion and aerobic digestion to digest organic matter in the stream. Aerobic digestion produces a cleaned water stream that will be safe to discharge to the environment and a sludge that is primarily composed of cell mass. This sludge is also burned in the boiler/combustor system.

Combustor/Boiler/Turbogenerator:

The combustor, boiler, and turbogenerator process section utilizes the various by-product and process waste streams to produce steam and electricity. The combustion of the recovered lignin, WWT sludge, WWT biogas, and process fuel gas produce enough steam and electricity to ensure the process is energy self-sufficient. Excess energy is available, above the plant needs, and is used to produce electricity for export to the grid.

Utilities and Storage:

All process water, cooling water, and electricity requirements throughout the process are modeled and tracked in the utilities section. Steam requirements and balances are accounted for in the combustor/boiler system. Cooling water used throughout the process is designed for a 28°C supply temperature.

Total Capital Investment

The techno-economic analysis included the three steps described above (Solvolysis, HDO, and COTA) required to convert raw biomass (loblolly pine) into BioFormate® product (mixed aromatics).A capital cost and operating cost were calculated in the program.

Greenhouse Gas Analysis

The life cycle analysis (LCA) of the Virent Solvolysis process utilized the 2015 GREET.NET (ANL, 2015) platform. GREET.NET uses the net process inputs and outputs from the integrated Aspen V8.6 process model. The process inputs are summarized below and include feedstock, catalyst, and hydrogen. This section also summarizes the key output material streams which includes the gasoline and diesel cuts and electricity export. The LCA results indicates a baseline case of 7.9 kg CO_2e/MMBtu of liquid fuel. The analysis indicates a reduction of 92% versus the petroleum gasoline baseline of 97.5 kg CO_2e/MMBtu.

It is important to note that in the base case, this process does not consume external grid electricity. Rather, combustion of remaining lignin, fuel gas and heavy liquids produces sufficient electricity and steam to meet process demands as well as provides a significant export of electricity. Also, note that Poplar was utilized as a surrogate for loblolly pine as data sets for loblolly pine were not available in 2015 GREET.net

Project Management

Project Planning

At the outset of the project, a comprehensive Project Management Plan was assembled and a Project Work Plan created. There was frequent and transparent reporting to DOE on the project and technical performance. The Virent project team hosted periodic calls and prepared quarterly reports which were shared amongst the Virent and DOE team members. Quarterly technical and financial reports were filed with the DOE project team as prescribed in the contract documents and Virent provided DOE with project highlights suitable for public dissemination.

Reporting & Control

Reports and deliverables were provided in accordance with the Federal Assistance Reporting Checklist following the instructions included therein. Additionally, the Principal Investigator and Project Manager hosted Advisory Committee meetings to discuss the state and goals of the project.

Throughout the project a project management team was responsible for reporting and controlling the project. This consisted of the following monthly and quarterly tasks:

- Quarterly reporting. Reporting consisted of a PMP, narrative, and SF-425. These reports were completed quarterly and on-time throughout the project.
- Milestone reports. The milestone reports were submitted throughout the project to provide background information regarding each individual milestone as the Phoenix project team achieved them and to serve as a deliverable marking the completion of the milestone.
- Budget Control. The project management team adhered to the budget and communicated with the DOE project team to seek guidance and approval whenever changes were required to meet the project milestones.
- The project team met monthly via teleconference throughout the project to discuss the current state of the project, share progress, and discuss future work.

Project Scope Change

A scope change was necessary to shift the focus from RCL to Solvolysis in order to successfully complete the Pilot Plant Upgrades task and 2000 hour demonstration run of the system. Through discussion of various factors including availability of equipment, process development needs, carbon conservation, and techno-economic analysis the DOE and the Virent project team agreed to move forward with the scope change. The change of scope allowed for the successful completion of all project milestones within budget and the project period.

Peer Review

During the project period two Project Peer Review meetings were hosted by the Bioenergy Technologies Office (BETO) in 2013, 2015 and 2017. All meetings were attended by Virent personnel and the project was reviewed by the DOE, members of the public, industry advisors, and members of the academic community. Virent presented upon the current state of the project, took questions, and responded to questions posed by the reviewers.

Final Reporting

Final reporting will conclude with the submission of this report and the required forms outlined in the Federal Assistance Reporting Checklist. The final reporting documentation will consist of:

- This final technical report.
- Patent certification (DOE 2050.11)
- SF-425 covering the entire span of the project.
- Final property report (SF-428 & SF-428B).

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