Cellulosic Biomass Sugars to Advantaged Jet Fuel – Catalytic Conversion of Corn Stover to Energy Dense, Low Freeze Point Paraffins and Naphthenes

Final Report for

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Lead Organization - Virent, Inc.

Subcontractors: National Renewable Energy Laboratory, Idaho National Laboratory, Northwestern University

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Summary

Executive Summary

The purpose of this project was to demonstrate the technical and commercial feasibility of producing liquid fuels, particularly jet fuel, from lignocellulosic materials, such as corn stover. This project was led by Virent, Inc. (Virent) which has developed a novel chemical catalytic process (the BioForming® platform) capable of producing "direct replacement" liquid fuels from biomass-derived feedstocks. Virent has shown it is possible to produce an advantaged jet fuel from biomass that meets or exceeds specifications for commercial and military jet fuel through Fuel Readiness Level (FRL) 5, Process Validation. This project leveraged The National Renewable Energy Lab's (NREL) expertise in converting corn stover to sugars via dilute acid pretreatment and enzymatic hydrolysis. NREL had previously developed this deconstruction technology for the conversion of corn stover to ethanol. In this project, Virent and NREL worked together to condition the NREL generated hydrolysate for use in Virent's catalytic process through solids removal, contaminant reduction, and concentration steps. The Idaho National Laboratory (INL) was contracted in this project for the procurement, formatting, storage and analysis of corn stover and Northwestern University developed fundamental knowledge of lignin deconstruction that can help improve overall carbon recovery of the combined technologies. Virent conducted fundamental catalytic studies to improve the performance of the catalytic process and NREL provided catalyst characterization support. A techno-economic analysis (TEA) was conducted at each stage of the project, with results from these analyses used to inform the direction of the project. Over the course of this ~ 4 year project, began in Q4 of 2011, DOE conducted three on-site validations—termed Benchmark, Intermediate, and Final—as well as a Stage-Gate review which was conducted after the first 2.5 years of the project.

Major accomplishments of the project included:

- Successful integration of NREL's deconstruction technology with Virent's catalytic processing technology.
- Production of a jet fuel product having enhanced properties as compared to conventional and other renewable jet fuels (freeze point, energy density, and stability)
- Reduction in cash cost for generating desired liquid product by ~50% over the length of the project.
- Reduction in capital cost per gallon by >10% from Benchmark case to Final case.
- Development of lower cost catalysts for both catalytic steps utilized by Virent's technology.
- Identification of configurations for the generation of liquid fuels at costs that would meet goals set by DOE's multi-year program plan.

Several challenges were identified that once solved would further improve overall yields and reduce costs.

These challenges include the need for:

- More economical methods to remove catalyst contaminants from the raw biomass and resulting hydrolysate.
- Methods that further reduce or eliminate costs of enzyme in the deconstruction step.
- Materials and reactor configurations that would improve catalyst costs and lifetimes.
- Enhanced carbon yields to liquid products through stabilization and catalytic processing of solubilized lignin components.

Project Summary and Major Accomplishments

The major challenge of this project was to find optimal methods to merge NREL's deconstruction technology with Virent's catalytic conversion technology. Figure 1 shows a schematic of the initial combination of the technologies. NREL's technology was developed to demonstrate the conversion of lignocellulosic biomass to ethanol while Virent's BioForming technology was first developed using purified commercial sugars such as cane sugar, beet sugar, and corn syrup.

NREL's deconstruction technology utilizes a dilute acid pretreatment of the biomass, followed by an enzymatic hydrolysis step to generate a hydrolysate that contains a mixture of monosaccharides. The hydrolysate must then be treated to remove solids and contaminants before it can be fed to Virent's catalytic process. In the combined process, purified hydrolysate is fed to a catalytic reactor where a portion of the oxygen is removed from the oxygenated feed compounds. The resulting mixture of partially deoxygenated compounds is then fed forward to Virent's distillate process to be condensed to higher carbon number species in the distillate range and remove residual oxygen. The resulting non-oxygenated hydrocarbons mixture is then fractionated by boiling point to generate fuels that can be used in gasoline, jet and diesel.

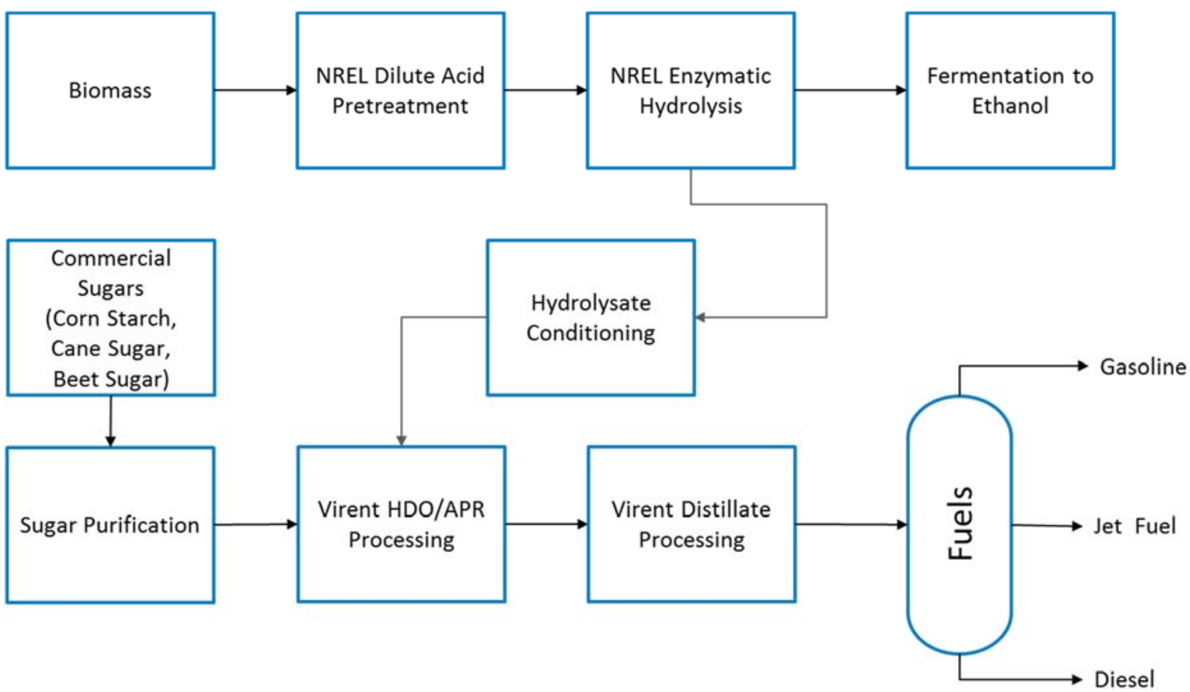

Figure 1. High level process flow diagram (PFD).

Role of Project Partners

Figure 2 shows the organizational structure for the project. Virent was the lead organization with support from NREL, INL, and Northwestern.

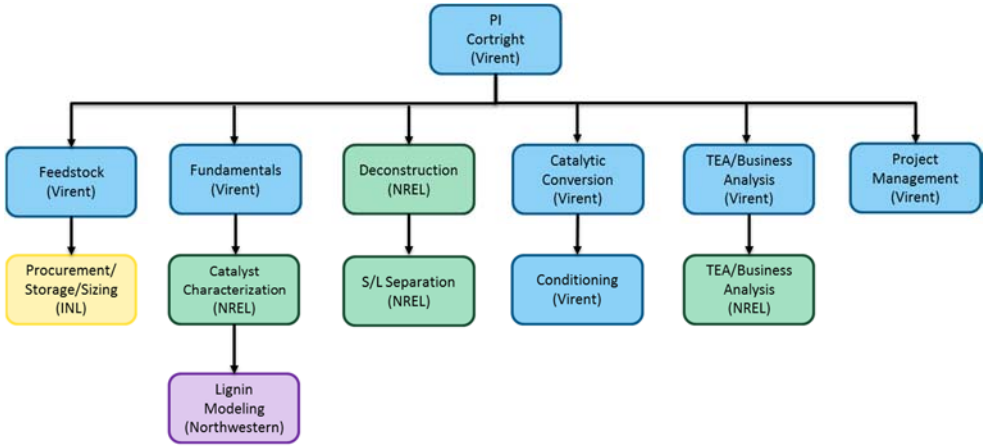

Figure 2. Project organizational structure.

The project was led by Virent with Dr. Randy Cortright (Virent's CTO and Founder) as the Principal Investigator (PI). The project organization was then broken down into different workgroups to align with the Work Breakdown Structure (WBS) that is summarized as follows:

- Feedstock
  - Virent contracted corn stover procurement with INL
  - INL procured corn stover, shipped the corn stover to their location where it was stored, sized, and shipped to NREL
- Fundamentals
  - Fundamental work focused primarily on catalyst development, understanding of deactivation mechanisms, and lignin chemistry
  - Virent in conjunction with NREL (led by Matt Yung) conducted catalyst development studies
  - The research group of Linda Broadbelt conducted theoretical studies of the deconstruction and reactivity of lignin components
- Deconstruction
  - NREL (led by Rick Elander and Eric Kuhn) conducted the necessary work for the different deconstruction steps (deashing, pretreatment, and hydrolysis).
  - NREL also worked on removing solids before shipment of hydrolysate to Virent.
- Conversion
  - Virent conducted process studies (hydrolysate clean-up, catalytic processing, and final product processing) on samples provided by NREL as well as model feedstocks.
  - This work was conducted by Liz Woods, John Kania, and Matt VanStraten at Virent
- TEA
  - Virent (Bob Rozmiarek, Dan Komula) led TEA activities in conjunction with NREL (Mary Biddy)
- Project Management
  - Virent led the project management for the project. Project Managers through the project were Lisa Kamke, Liz Woods, and Bob Rozmiarek.

Background of Virent's APR and BioForming Catalytic Technology for Generation of RPN Jet Fuel

Virent discovered in 2006 that it is possible to produce "direct replacement" fuel range hydrocarbons from sugars utilizing catalytic conversion technology. Process development has significantly expanded the range of potential feed molecules, reduced the process complexity, and verified the advantaged position of the products within the existing infrastructure. Figure 3 illustrates the general concepts of converting biomass-derived oxygenates (i.e., sugars) to liquid fuels. The overall goal of this process, illustrated in Figure 3, is to reduce the oxygen content and increase the average carbon chain length. The process line-up uses two different catalytic steps in series: (1) aqueous-phase reforming/hydrodeoxygenation (APR/HDO) to deoxygenate highly oxygenated feedstocks of high reactivity to lower oxygenated compounds with moderate reactivity and (2) dehydration-oligomerization (DHOG) condensation to condense the products from the APR step to increase the carbon chain length of the feed molecules (<6) to that required for jet fuel (Approximately C_9-C_{19}).

The feedstock flexibility of the APR/HDO and DHOG steps originates from catalytic systems that promote general reaction classes, in contrast to the specific reactions typical of enzyme catalyzed reactions.

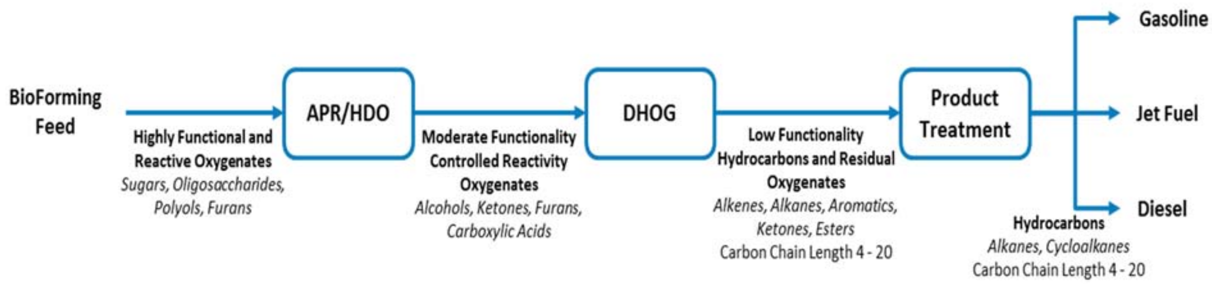

Figure 3. BioForming process for converting oxygenated feedstocks to hydrocarbon liquid fuels.

Aqueous-Phase Reforming/Hydrodeoxygenation (APR/HDO) Chemistries

This project initially utilized APR chemistry within the first catalytic step to transform corn stover derived oxygenates to jet range hydrocarbons. Figure 4 shows the two general APR reactions: (1) reforming reactions to generate in-situ hydrogen and (2) hydrodeoxygenation (HDO) reactions that remove oxygen as water.

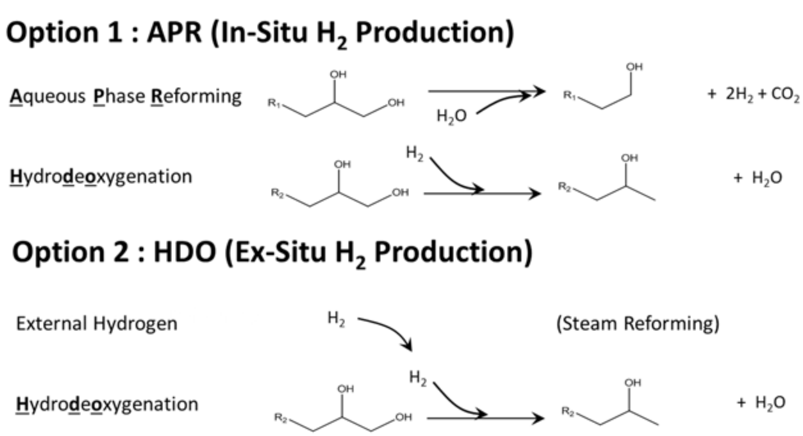

Figure 4. Reactions within APR and HDO catalytic conversion.

(1) Reforming to produce hydrogen. The APR technology was discovered at the University of Wisconsin as a method to produce hydrogen from oxygenated intermediates under liquid phase conditions. This

reaction, shown on the top in Figure 4 has been described extensively [1, 2]. Hydrogen and carbon dioxide are generated from terminal hydroxyls or carbonyls, shortening the carbon chain by a single carbon in each reaction cycle. These reactions may be repeated until the molecule is consumed or may be terminated after one or more reaction cycles. If the process requires all the necessary hydrogen to be generated from this *in-situ* reforming step, then up to a third of the carbon in the feed will be converted to byproduct, carbon dioxide, and this carbon will not be available for use in the final hydrocarbon product. As will be discussed below, this project investigated the use of ex-situ hydrogen that alleviates the loss of carbon due to in-situ hydrogen generation and improves the overall yields of solubilized biomass to the desired liquid products.

(2) Hydrodeoxygenation removes oxygen as water as shown in Figure 5. Oxygen is removed from the various oxygenated feedstocks utilizing hydrogenolysis and dehydration reactions. Oxygen removal also occurs via self-condensation of polyoxygenated compounds resulting in the formation of cyclic ethers (e.g., methyl tetrahydrofuran). Other reaction products observed include organic acids (formed by reaction of aldehydes with water) and carbonyl species (mostly ketones) generated by the dehydrogenation of alcohols. A typical HDO product contains alcohols (20-35% of carbon), ketones (5-10%), cyclic ethers (10-15%), carboxylic acids (2-5%), and paraffins (5-15%), and partially reacted polyols. With the APR process, 25-35% of the carbon is converted to carbon dioxide. Products from the HDO step are more thermally stable than the feed, which is imperative for downstream processing. In particular, the increased thermal stability decreases non-specific reaction rates that form tar-like deposits which can cause operational problems and result in loss of yield.

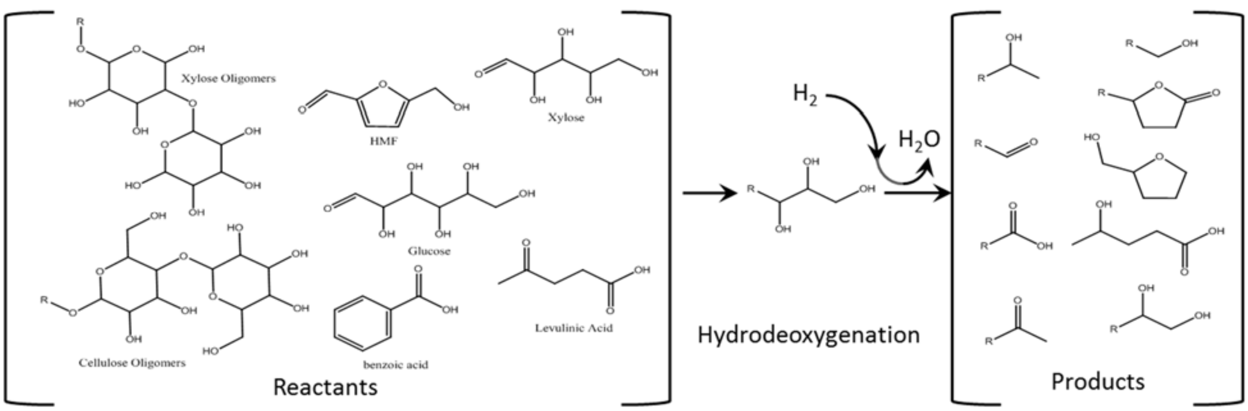

Figure 5. Representative reactants and products within the HDO catalytic conversion step.

Dehydration/Oligomerization Chemistry (DHOG)

It has been shown [3] that it is possible to dehydrate alcohols to form olefins and then generate longer chain hydrocarbons via oligomerization. These existing catalytic systems are limited by the necessity to remove water from the olefins before further processing due to the water sensitive catalysts used. Virent found that it was possible to convert a mixture of alcohols and other oxygenated hydrocarbon molecules over a single reactor in the presence of water. The mechanism of this early work indicated that both dehydration and oligomerization were taking place in this reactor and Virent defined this as a DHOG reactor system. Subsequent studies utilizing the mixture of oxygenates derived from the APR/HDO reactor system, showed that longer chain compounds were generated via reactions other than the dehydration/oligomerization reaction set. Figure 6 illustrates four distinct condensation pathways observed in the DHOG reactor system.

These pathways include:

- Diels-Alder condensation of dienes and olefins,
- Oligomerization of olefins,
- Aldol condensation of carbonyls, and
- Ketonization reactions between organic acids to yield a ketone and carbon dioxide.

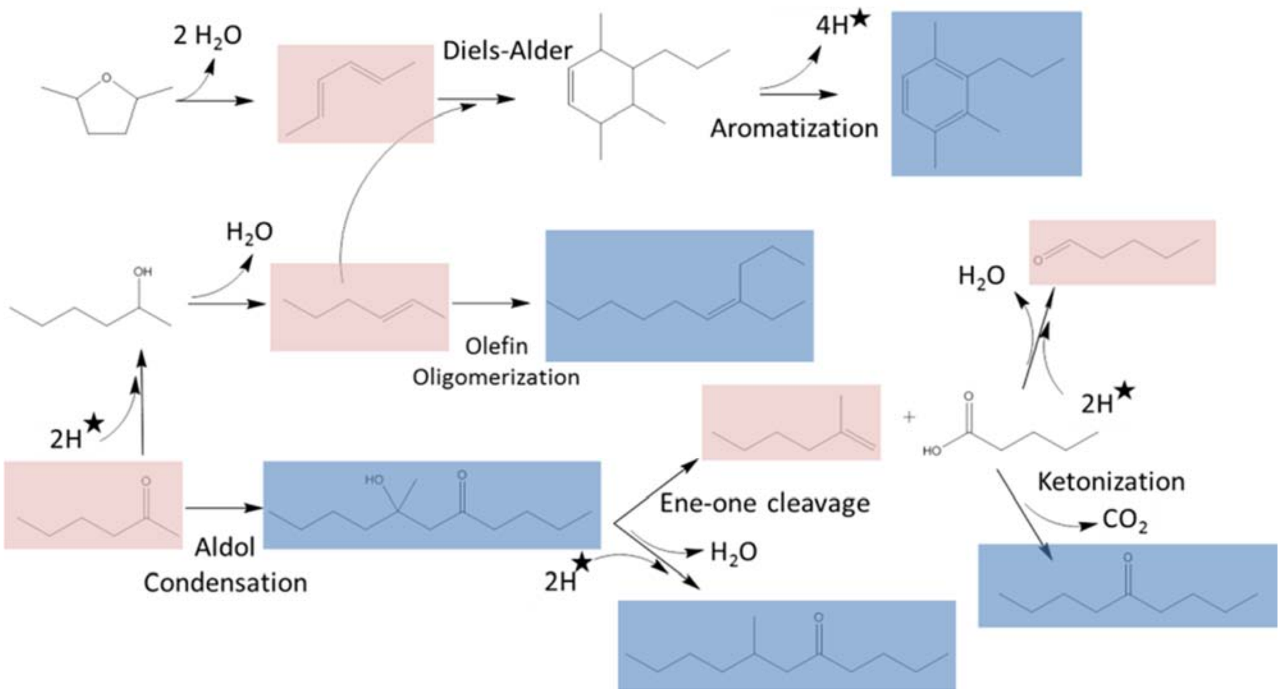

Figure 6. Condensation and deoxygenation pathways in DHOG.

Figure Note: Reactants highlighted in pink are directly suitable for participation in condensation reactions while products highlighted in blue are converted to jet range products by hydrofinishing.

As shown in Figure 3, APR/HDO products are passed to the DHOG reactor to complete the reactions necessary to generate jet range hydrocarbons. The mixture of mono-, di-, and in some cases tri-oxygenated compounds generated in the APR/HDO can be condensed to longer carbon chain materials in the presence of water in the DHOG reactor system.

To generate a finished jet fuel, the DHOG product goes through a hydrofinishing step to remove residual oxygen and saturate the DHOG product. The finished product is then fractionated into gasoline, jet fuel, and diesel cuts. Although the hydrofinishing and fractionation steps are generally required to produce ASTM compliant fuels, the finishing step was not developed further in the project per project guidelines. The finishing step has been previously demonstrated at Virent using a robust, commercially available hydrofinishing catalyst.

Table 1 shows advantages in freeze point, volumetric density, and thermal stability for Virent generated jet fuel samples including corn-stover derived jet fuel generated in this project (in bold text). The table shows Wright-Patterson Air Force Research Laboratory (AFRL) fit-for-purpose testing results for the Virent generated samples (Hydrodeoxygenated Synthesized Kerosene (HDO – SK)) and compares these results to Jet A-1 specification, JP-8 (military grade jet fuel), and a Fischer-Tropsch derived synthetic paraffin kerosene (F-T SPK). The Virent generated samples include one generated using corn syrup as a feedstock (outside the project scope) and the corn stover derived jet fuel generated in this project. The lower freeze point has advantages for use in polar flights, the higher density allows for greater flight distances per volume of fuel loaded, and the higher thermal stability allows the fuel to be used more extensively in engine cooling activities. This fit-for-purpose testing was done outside project.

Table 1. Fit-for-Purpose technical evaluation form Wright Patterson

Specification Test	Jet A-1 Spec Requirement	HDO-SK	HDO-SK	F-T SPK	JP-8
BioForming Feedstock	-	Corn Syrup	**Project Corn Stover**	-	-
Aromatics, vol %	≤25	0.2	**0.2**	0	18.8
Heat of Combustion, MJ/Kg	≥42.8	43.3	**43.3**	44.3	43.3
Distillation:					
IBP, °C		160	**146**	144	159
10% recovered, °C	≤205	177	**172**	167	182
20% recovered, °C		183	**190**	177	189
50% recovered, °C		207	**227**	206	208
90% recovered, °C		258	**280**	256	244
EP, °C	≤300	284	**300**	275	265
Residue, % vol	≤1.5	1.4	**2***	1.5	1.3
Loss, % vol	≤1.5	0.5	**0**	0.9	0.8
Flash point, °C	≥38	53	**NA**	45	51
Freeze Point, °C	≤-47	<-60	**<-60**	-51	-50
Density @ 15°C, kg/L	0.775 - 0.840	0.812	**0.813**	0.756	0.804
Cetane Index (calc.)		44.5	**46.1**	64.2	44.2
JFTOT @325C, dP	≤25	<1	**<1**	<1	280
Color Rating	<3	2	**2**	2	4A

Utilization of External Hydrogen – Impact on Yields

Virent initially proposed to utilize in-situ generated hydrogen via the APR chemistry to convert oxygenated feedstocks to liquid fuels. As shown in Figure 4, for every two molecules of hydrogen generated, one atom of carbon from the oxygenated feedstock is converted to carbon dioxide. Figure 7 shows the stoichiometry for converting a sugar (glucose) to a non-oxygenated jet range hydrocarbon ($C_{14}H_{30}$) for the case with in-situ hydrogen generation. This figure shows that up to one third of the carbon in the feedstock, would be lost to carbon dioxide and not available to be incorporated into desired liquid fuel product if in-situ hydrogen is required.

Figure 7 shows that utilizing external hydrogen would eliminate the loss of feed carbon to carbon dioxide, improving the overall yield of feedstock to the liquid fuels. The continued availability of low-cost natural gas in the United States provides the potential of low cost hydrogen availability through steam methane reforming. This *ex-situ* generated hydrogen is utilized in an HDO reactor system (with appropriate catalyst) to reduce the oxygen content of the feedstock via HDO. Figure 7 shows the theoretical yield of glucose to a jet range paraffin ($C_{14}H_{30}$) increases from 0.31 lb of $C_{14}H_{30}$ per lb of glucose to 0.47 lb of $C_{14}H_{30}$ per lb of glucose moving from *in-situ* hydrogen generation to utilizing ex-situ hydrogen. Figure 7 shows that 0.46 kg of H_2 (0.015 lbs H_2 per lb of glucose consumed) would be required in the theoretical case with *ex-situ* hydrogen generation.

$$\text{In-Situ } H_2: \quad 3.68\ C_6H_{12}O_6 = C_{14}H_{30} + 7.5\ CO_2 + 6.5\ H_2O$$

$$\text{Ex-Situ } H_2: \quad 2.33\ C_6H_{12}O_6 + 15\ H_2 = C_{14}H_{30} + 14\ H_2O$$

Representative Jet Fuel Molecule	Internal H_2 (lbs glucose / gal) {lbs HC/lb glucose}	External H_2 (lbs glucose / gal) {lbs HC/lb glucose}	Theoretical H_2 Requirement (kg H_2 /gal)
$C_{14}H_{30}$	20.8 {0.31}	13.6 {0.47}	0.46

Figure 7. Influence of internal vs. external hydrogen on yields (HC- hydrocarbon)

Summary of Results

Figure 8 shows the improvement in production cost, including capital recovery (refer to Task C – Techno-economic Analysis for a description on capital recovery calculation methodology), over the life of this project. The cost numbers are based on validated results from Benchmark, Intermediate, and Final validation runs. Major cost reductions were observed from improved catalyst performance, utilization of less expensive catalytic materials, and hydrogen utilization. Yields from the initial Benchmark validation run were 63 gallons per dry tonne of corn stover. This yield exceeded the proposed yield of 42 gallons per tonne for the Benchmark. A major factor for the higher yields in the Benchmark case was the utilization of externally generated hydrogen within the catalytic process, as well as higher than proposed yields of convertible oxygenates from the deconstruction process.

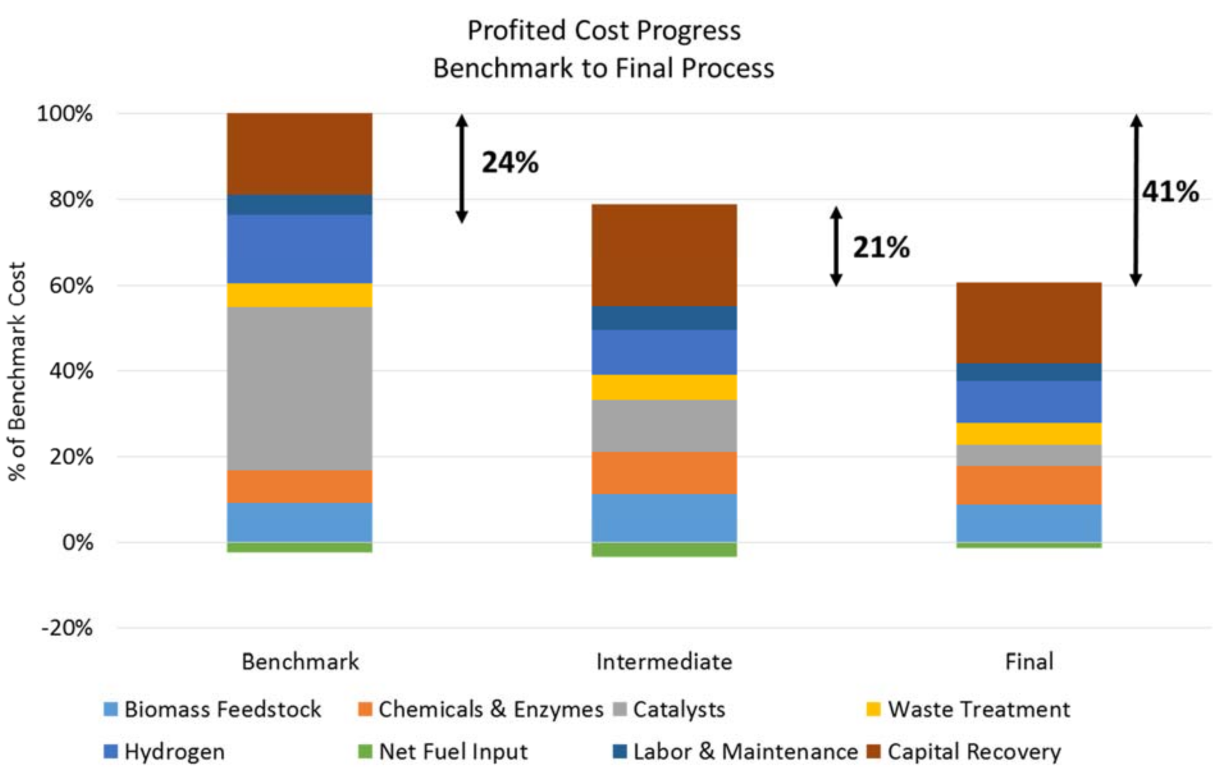

Figure 8. Profited cost of production progress from Benchmark to Final process.

After benchmarking the combined NREL deconstruction/Virent BioForming process, fundamental and process studies were conducted to improve the overall economics of converting corn stover to liquid fuels. These studies focused on three specific areas:

1. **Effective Carbon Utilization**
    a. Increasing soluble carbon yields from deconstruction and evaluating methods to access the lignin fraction of the biomass.
    b. Maximizing recovery of carbohydrate carbon into the hydrolysate stream through deconstruction and hydrolysate conditioning.
    c. Adjusting process configuration, catalyst formulations and operating conditions to maximize carbon conversion to liquid fuel products with enhanced jet fuel selectivity.
2. **Cost Effective Ash Control**
    a. Utilizing harvesting methods to reduce feedstock variability and non-structural ash content.
    b. Developing biomass pretreatment methods to minimize structural and non-structural ash in the deconstruction process.
    c. Evaluating alternative hydrolysate conditioning schemes to reduce costs while maintaining carbon content and reducing contaminant levels.
    d. Increasing contaminant tolerance of the catalyst materials leading to improved catalyst lifetimes.
3. **Improved Catalytic Reactor Performance**
    a. Reducing catalyst costs through reduction in catalyst material costs and extended catalyst lifetimes.
    b. Conducting deactivation mechanism studies and altering reactor configuration and catalysts to address catalyst deactivation.
    c. Evaluating catalyst support materials and reaction conditions to a minimize catalyst degradation due to severe hydrothermal environment in the reactor systems.
    d. Extending catalyst cycle times through process optimization.

After benchmarking the process with NREL's dilute acid/enzymatic hydrolysis technology, it was proposed to reduce the cost of the deconstruction step using a two-step acid pretreatment that would reduce enzyme loads and provide acceptable feedstock to the BioForming process. While acceptable hydrolysate quality was generated from this two-step acid pretreatment process, the cost of generating the hydrolysate was higher than the Benchmark case with no improvement in overall carbon yields to liquid products. The project moved to an alternative deconstruction approach that utilized an alkaline pretreatment, followed by a weak acid pretreatment, and enzymatic hydrolysis step. The promise of this alternative deconstruction route was that a significant amount of the lignin was solubilized in a form that would allow further catalytic processing and result in improved yields of corn stover to liquid fuel product. The alkali pretreatment also significantly removes ash components from the corn stover and reduces the load on hydrolysate clean-up processes which follow the deconstruction steps. While preliminary results from this alkaline pretreatment line-up showed promising results, the Intermediate validation run resulted in xylose and glucose yields much lower than expected.

The lower yields of convertible carbon in the Intermediate case were offset by improvements in catalyst performance (catalyst cost and lifetime) as shown in Figure 8 above. Data from the Benchmark and Intermediate validation runs were presented at a Stage Gate review with independent reviewers in February of 2014. The decision from the Stage-Gate was to reduce the scope of the project by discontinuing development work on the alkali pretreatment step at NREL.

The final budget period of the project focused on improving Virent's BioForming process utilizing hydrolysate provided by NREL. During this final budget period, Virent optimized hydrolysate clean-up, further improved catalyst performance, improved utilization of external hydrogen, and reduced capital for the overall process. Final validation was conducted on the overall process in April of 2015. Figure 8 above shows further improvement of both cash and profited cost over the Benchmark and Intermediate cases. In addition, other experimental work performed suggested that a lower cash cost of could be achieved, which further approaches the DOE target [(4)].

Selectivity to jet fuel was an important project metric with a targeted selectivity of 65 mass % of the liquid product.

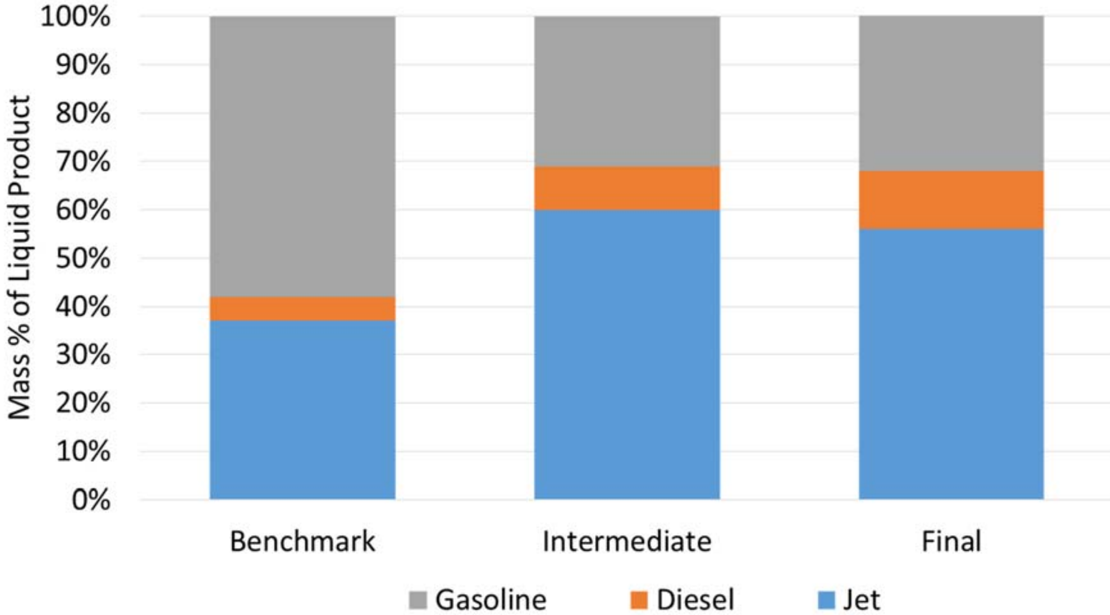

Figure 9. Mass selectivity to fuel fractions.

Figure 9 shows the mass % of the different liquid products from beginning to end of the final project. The initial Benchmark case shows a jet fuel selectivity of 36 mass % with an improvement to 60 mass % for the Intermediate case. The Final validation selectivity was measured at 56 mass %. The jet fuel selectivity had little influence on the overall economics as both gasoline and diesel by-products have similar value to jet fuel and would be in high demand.

The project was executed using a Work Breakdown Structure (WBS). The activities, methods, and results are reported starting with Fundamental Research and Development and moving forward through the WBS structure.

Task A: Fundamental Research & Development

Subtask A.1: Catalyst Fundamentals

A.1.1: Virent Catalyst Fundamentals

Improving the overall economics of the process required improving the performance of the catalysts and the catalytic reactors within the BioForming system. Primary improvements were necessary in catalyst lifetime and reduction in catalyst material costs.

Catalyst Development – HDO

Developing an understanding of catalyst deactivation mechanisms for the HDO catalyst was critical in improving HDO catalyst lifetimes. Due to the nature of the feedstock and reaction conditions, a number of potential deactivation mechanisms were identified. With these deactivation mechanisms in mind, Virent conducted fundamental studies that lead to a Generation II HDO catalytic system with better lifetimes as well as lower costs.

Initial studies were conducted using the Generation I HDO catalysts used in the Benchmark, Intermediate, and Final validation runs. Over the course of the project, Virent developed a lower cost alternative for the Generation I HDO catalyst system.

Catalyst Development – DHOG

Fundamental investigations were conducted over the DHOG catalyst system to further understand the DHOG chemistry such as the effects of feedstock composition on yields and stability. Furthermore, work was conducted to find cost-effective catalytic materials for the DHOG reactor system as well as determine the ability to regenerate the DHOG reactor system.

DHOG Catalyst Screening:

In this project, over 20 different catalyst formulations were tested as DHOG catalyst using a model feedstock. These materials were compared to the performance of the baseline DHOG catalyst used in the Benchmark studies. Figure A.1.1.1 shows the yields of different products generated during the processing of a model feedstock at the same reactor conditions. Catalyst A is the baseline catalyst and three other catalyst formulations were found to exhibit equal or better jet fuel yields. Catalyst B, C, and D all utilize lower cost materials and are commercially viable to produce. Catalyst B was thought to be the easiest to scale-up, and was used for subsequent stability runs and in the Final validation process line-up.

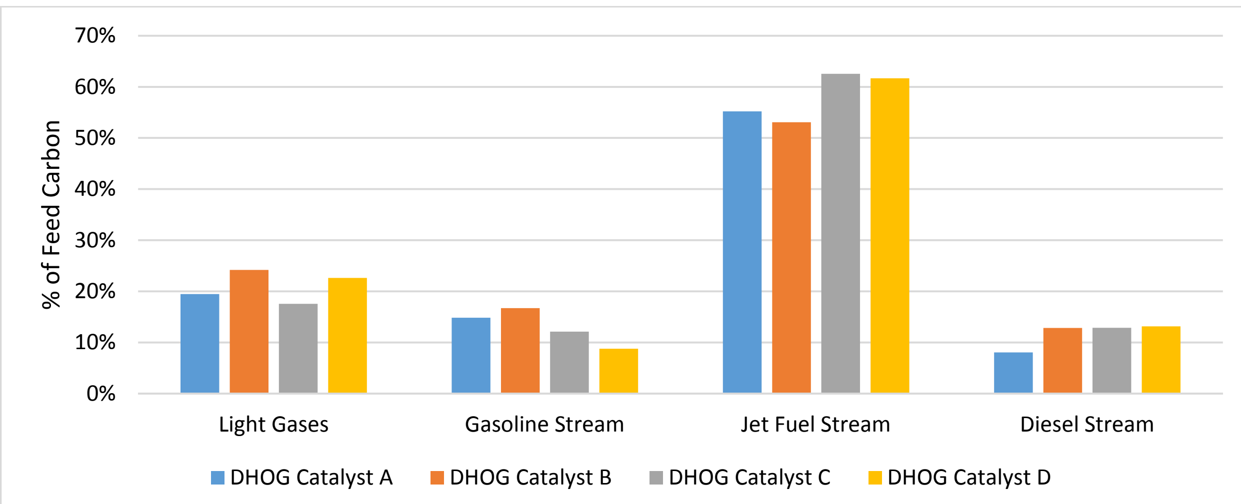

Figure A.1.1.1: Stream breakdown high conversion DHOG catalysts

A.1.2: NREL Catalyst Fundamentals

Part of NREL's contribution to the project was to provide catalyst characterization for prepared catalyst samples. Techniques utilized by NREL included:

- X-ray powder diffraction (XRD)
- X-ray photoelectron spectroscopy (XPS)
- Temperature programmed reduction (TPR)
- Temperature programmed oxidation (TPO)
- Scanning electron microscopy (SEM)
- Energy dispersive spectroscopy (EDS)

The catalyst characterization results provided understanding of the catalyst material chemistry for both as prepared catalysts and spent catalysts. For example, XRD results (not provided) showed how catalyst morphology changed under reaction conditions for a lower cost catalyst formulation. The results of XPS analysis (see Figure A.1.2.1) also suggested a stronger surface coverage of a modifier at the bottom of the reactor compared to the top of the reactor. The results indicated that with reduction, both the active metal and modifier can be converted to a metallic form and concentrated at the surface.

Figure A.1.2.2 provides an example of SEM and EDS characterization of Virent's Generation I HDO catalyst after operation with corn stover hydrolysate. The EDS mapping showed the presence of the active metal, support modifier, as well as evidence of contaminants from hydrolysate that have deposited on the catalyst surface. The catalyst characterization results provided understanding of the catalyst material chemistry for both as prepared catalysts and spent catalysts.

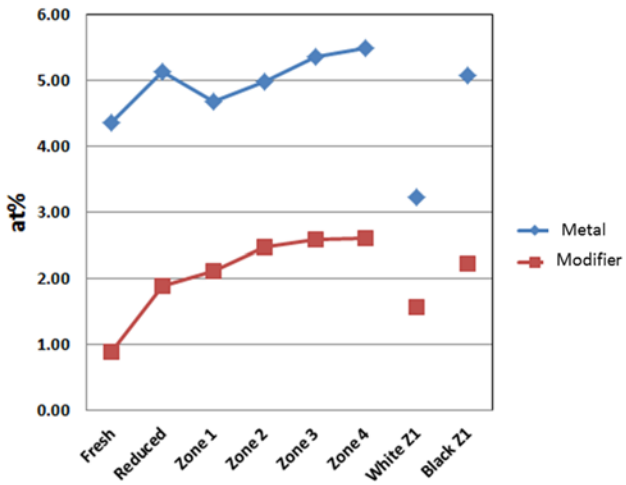

Figure A.1.2.1. XPS Analysis of Generation II HDO Catalyst (Fresh and Spent)

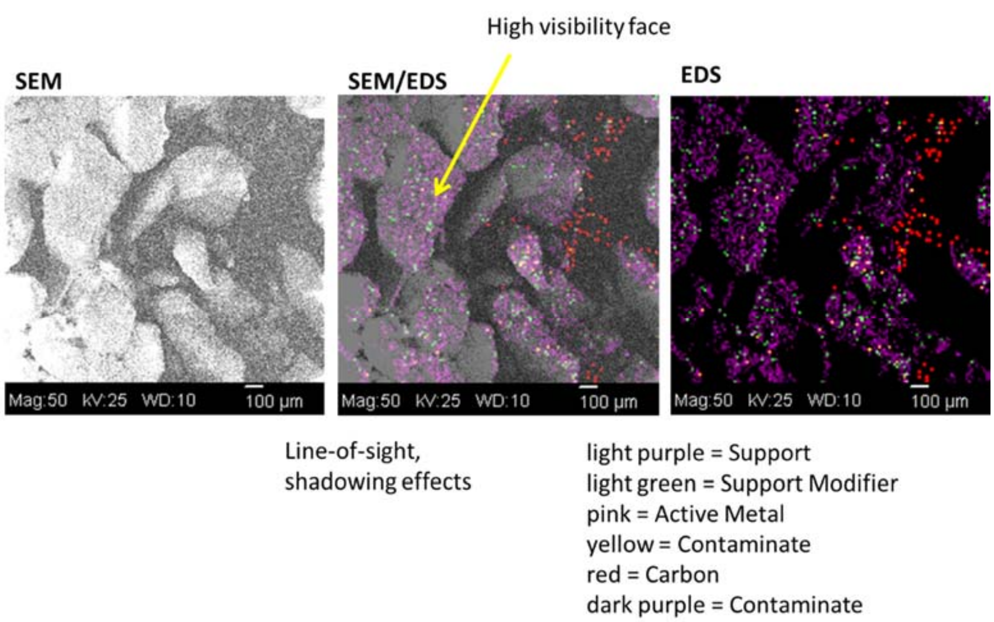

Figure A.1.2.2. SEM and EDS Analysis of Generation I HDO Catalyst after Processing Hydrolysate

Subtask A.2: Modelling Lignin Chemistry

The chemical behavior of cellulose and hemicellulose are reasonably well understood during weak acid pretreatment and enzymatic conversion steps of this project. However, there is not nearly as much understanding of the chemistry of lignin reactivity (depolymerization/polymerization) under acidic environments. Linda Broadbelt's research group at Northwestern University worked within this project to develop fundamental understanding of the reactivity of two α-O-4 model compounds, benzylphenyl ether (BPE) and 1-(phenoxyethyl)benzene (PEB) utilizing a quantum chemical model based on density functional theory (DFT) and microkinetic modeling based on a proposed mechanism involving nucleophilic attack on the α-carbon. This study was published in ACS Sustainable Chemistry and Engineering (6).

Task B: Process Development

Subtask B.1: Benchmark Process Validation

The first process development task for this project was to benchmark the performance of Virent's catalytic BioForming process using corn stover-derived hydrolysate from NREL's demonstrated deconstruction process (consisting of pretreatment and enzymatic hydrolysis). The Benchmark process line-up shown in Figure B.1.1 consisted of the following steps: (1) utilizing corn stover that was procured and sized by INL, (2) deconstruction of corn stover via the NREL's dilute acid pretreatment and enzymatic hydrolysis process steps, (3) separation of the liquid hydrolysate from solids, (4) ion-exchange to remove catalyst contaminants from the hydrolysate, (5) concentration of the hydrolysate, (6) feeding the concentrated hydrolysate into Virent's catalytic reactor steps, with products from the HDO step being condensed in Virent's DHOG reactor to generate longer chain hydrocarbons, (7) and a final hydrofinishing step to remove residual oxygen containing compounds and distillation to fractionate the resulting hydrofinished hydrocarbons into gasoline, jet fuel, and diesel fractions. Details of each of these steps are provided below.

Initial validation of this Benchmark process was conducted in March 2012 with subsequent repeat Benchmark validations in conjunction with the Intermediate validation in January 2014 and the Final validation in April 2015. The following sections lay out the steps and results of the initial Benchmark validation as well as the repeat validations.

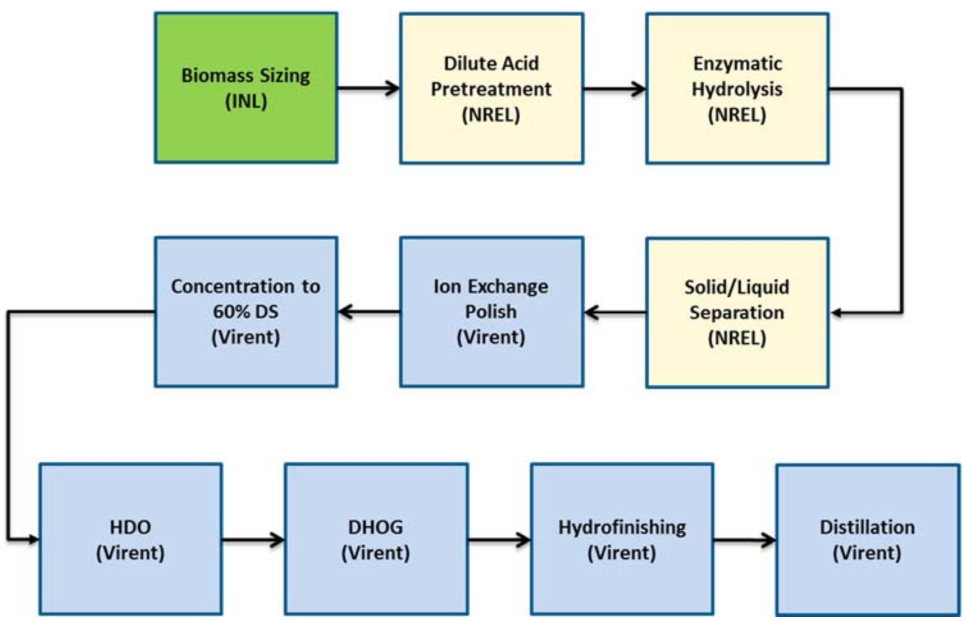

Figure B.1.1: Biomass deconstruction schematic

B.1.1: Biomass Deconstruction

B.1.1.1 Biomass Collection and Preprocessing (INL)

INL was subcontracted to procure necessary feedstock (both single and multi-pass corn stover), supply single pass corn stover to NREL for processing; characterizing test materials for proximate and ultimate analysis, higher and lower heating value, ash content, and ash composition; performing compositional analysis (cellulose, hemicellulose, and lignin) using the NREL NIR model; and grinding, drying and storing the remaining single-pass and multi-pass stover for supply to NREL and Virent as needed over the course of the project.

Table B.1.1.1.1 shows analysis of the as received corn stover. It should be emphasized that this project used only the single-pass corn stover collected by INL in 2011. Table B.1.1.1.1 shows minor deviations in extractives, xylan, acetate, lignin, and ash content with the largest deviation noted in moisture content throughout the project period. The increase in moisture is easily explained by adsorption of atmospheric moisture during storage. These deviations in feedstock composition may have played a role in the decreasing yields of hydrolysate for the three Benchmark validation runs.

Table B.1.1.1.1 Chemical analysis results from single-passed corn stover used in this study for the three Benchmark validation runs.

Date of Validation Experiment	Mar-12	Jan-14	Apr-15
Moisture content (wt. %)	5%	9%	9%
Sucrose (%, dry wt.)	0%	1%	1%
Soluble extractives (organic) (%, dry wt.)	14%	13%	13%
Glucan (Cellulose) (%, dry wt.)	36%	36%	36%
Xylan (%, dry wt.)	21%	22%	22%
Arabinan (%, dry wt.)	4%	3%	3%
Mannan + Galactan (%, dry wt.)	2%	2%	2%
Acetate (%, dry wt.)	3%	2%	2%
Lignin (%, dry wt.)	15%	17%	17%
Protein (%, dry wt.)	2%	3%	3%
Ash (%, dry wt.)	6%	5%	5%

B.1.1.2 Dilute Acid Pretreatment, Enzymatic Hydrolysis, and Solid/Liquid Separation (NREL)

Figure B.1.1.2.1 shows photos of equipment utilized at NREL for the dilute acid pretreatment and enzymatic hydrolysis steps (Benchmark configuration). The single-pass corn stover was first impregnated with sulfuric acid in NREL's Scott Reactor. The impregnation involved contacting corn stover with a 0.8 wt. % sulfuric acid solution, mixing for 1 hour at 60 °C, followed by squeezing out excess solution with a Vincent screw press. Targeted sulfuric acid content was 2 wt. % in the squeezed solids (at 25 – 30% total solids loading). Pretreatment of the impregnated solids was conducted in NREL's 200 kg/day horizontal pretreatment reactor operated at 158°C and 85 psi with a residence time of 5 minutes. Pretreated slurry from multiple days of pretreatment operations were pooled and charged to NREL's 2000 L Dynamic Impregnator vessel, which was operated as a jacketed, high-solids enzymatic hydrolysis paddle reactor. The pretreated slurry was pH-adjusted to 4.8 – 5.2 range with KOH and diluted to a nominal total solids loading of 20%. Novozymes Ctec2 was added (20 mg protein/g cellulose+xylan) and the hydrolysis allowed to take place over 62 hours. Enzymatic hydrolysis slurry was harvested and stored under refrigeration until bulk solids removal was performed. Solid-liquid separation was performed by direct filtration in the Q-120 basket centrifuge followed by concentration of the hydrolysate stream utilizing vacuum evaporation.

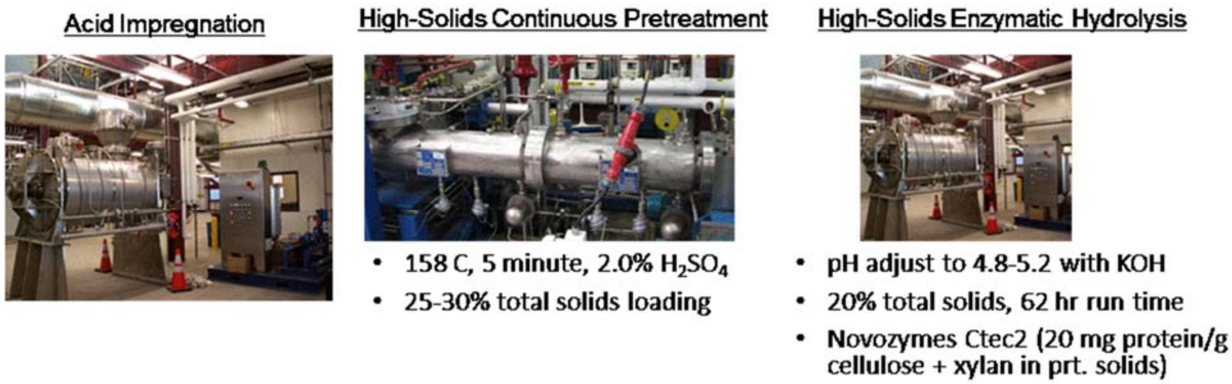

Figure B.1.1.2.1: NREL pretreatment and enzymatic steps equipment and conditions

Table B.1.1.2.1 shows total sugar recovery yields for the three Benchmark validations in comparison to the target values. While all three Benchmark runs exhibited solubilized carbon yields greater than proposed from both cellulose and hemicellulose, it was found that the yields from cellulose decreased significantly between the first and second run. This suggests that aging of the stored corn stover may influence the digestibility of the corn stover resulting in overall lower carbon yields for the digestion step along with a commensurate decrease in carbon yields for the overall process.

Table B.1.1.2.1 Total sugar recovery yields from the three Benchmark runs

Total Sugar Recovery Yields	Benchmark Targets	Mar-12	Jan-14	Apr-15
Glucose from Glucan (% of theoretical)	80%	84%	78%	75%
Xylose from Xylan (% of theoretical)	85%	80%	80%	79%
Solubilized carbon from cellulose (% of theoretical)	83%	93%	86%	84%
Solubilized carbon from hemicellulose (% of theoretical)	95%	98%	97%	96%

B.1.2: Purification

Hydrolysate purification

The catalytic process steps of Virent's conversion technology are adversely affected by both ash components contained in the delivered corn stover as well as by components added during the deconstruction step (sulfuric acid, hydrolysis enzymes, and potassium hydroxide (KOH)). Figure B.1.2.1 shows the level of compounds found in the hydrolysate provided by NREL for the Benchmark validation runs. The Benchmark validation runs used the 20 mg protein loading per g cellulose (referred to as low enzyme loading). Figure B.1.2.1 shows that the hydrolysate contains significant amount of organic nitrogen, potassium (from the neutralization step), sulfate (from the pretreatment step), and silica.

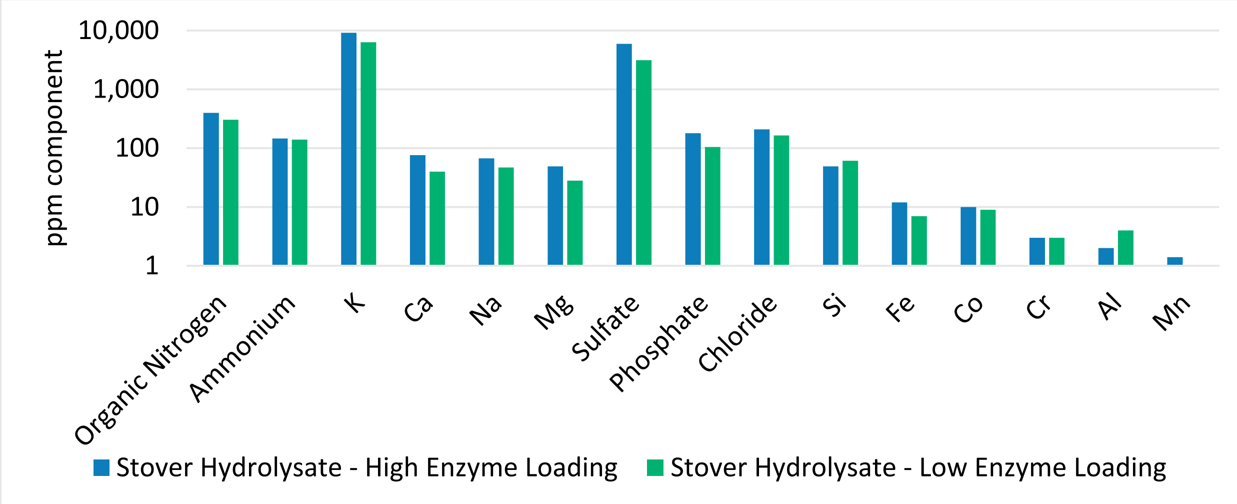

Figure B.1.2.1: Selected inorganic component profiles for stover hydrolysate batches

Virent utilized the process steps shown in Figure B.1.2.2 to treat the hydrolysate as received from NREL for the Benchmark validation runs. In this line-up insoluble solids are removed to avoid plugging of downstream ion-exchange columns. A bench-top barrel filter was used to remove insoluble solids greater in diameter than 1.2 µm.

The filtered hydrolysate was then fed to a series of ion exchange beds. Three ion exchange resins were found to sufficiently remove key contaminants such as sulfate and potassium. A strong acid resin was used to remove cations, a weak base resin was used to remove anions and a mixed bed resin unit was used for a final polish of the hydrolysate.

Figure B.1.2.2: Virent's Benchmark purification process

The final purified product contained primarily glucose and xylose. Organic acids other than acetic acid were removed by ion exchange and some volatiles were removed in evaporation, leaving mostly sugars and HMF. Silicon levels were the highest among remaining contaminants due to its amorphous, non-ionic form making ion exchange ineffective for the its removal. Silicon contaminant is a concern due to its tendency to precipitate in areas where vapor phase service begins leading to plugging of equipment. Other remaining contaminants such as sulfur have been found to cause catalyst deactivation even at the low levels observed in the product. To extend catalyst lifetime and prevent equipment plugging further optimization of the feed conditioning process is required and was investigated in the later parts of the project.

B.1.3: Catalytic Conversion

The catalyst and reactor configurations used for Benchmark validations were selected based upon previous experience with model feeds, primarily food-grade corn syrup, and some limited experimentation with biomass-derived hydrolysates from pine and corn stover.

The Benchmark validation catalytic process included an HDO reactor coupled to a DHOG reactor and distillation column. The HDO system was run with a catalyst that contained a precious metal, modified with base metals on a support. The DHOG reactor was operated with a catalyst that contained a precious metal, modified with base metals on a support. While similar in composition to the HDO catalyst system, the DHOG catalyst utilized different modifying metals. Products from the DHOG reactor were sent to a distillation column to separate the gasoline range components and distillate range components. The distillate range components were separated in a second distillation column and the bottoms were collected for subsequent hydrofinishing and fractionation to generate jet fuel and diesel fractions.

The hydrofinishing step was necessary to remove residual oxygen as well as saturate olefins and aromatics. This hydrofinishing step was outside the scope of the project, but necessary to meet the specification for jet fuel. A commercial hydrofinishing catalyst was run at commercial temperatures, pressures and flowrates, to generate the final fuels for quality testing. The same system was used for the hydrofinishing steps in the Intermediate and Final validation runs.

Carbon recoveries for the purification and catalytic conversions steps were determined from measurements of flow rates and the carbon content of the various streams. The liquid product streams were analyzed utilizing a boiling point gas chromatograph column and the various fractions broken out as being part of the gasoline, jet fuel, or diesel range. Table B.1.3.2 shows the selectivity to the different liquid fuel products for the three Benchmark cases.

Table B.1.3.2 shows the combine yield of liquid fuel in gallons per dry U.S. tonne of corn stover. Over the three Benchmark runs, this yield decreased from 63 gallons per tonne to 58 gallons per tonne. This decrease was primarily attributed to the lower carbon yields from the deconstruction steps (discussed previously) with a secondary loss to carbon in gas phase products of the BioForming process.

Table B.1.3.2: Benchmark validation run product selectivities and yields

	Mar-12	Jan-14	Apr-15
Selectivity (Mass %)			
Jet Fuel	37	39	44
Diesel	5	4	5
Gasoline	58	57	52
Gallons/dry US Tonne of Corn Stover	63	60	58

Subtask B.2: Intermediate Phase Process Development

After establishing the performance of Benchmark process line-up, it was proposed to leverage the feedstock flexibility of Virent's catalytic technology to increase the levels of biomass solubilization (i.e., increase the yield) at reduced enzyme loadings and potentially lower processing cost. This approach would both increase product yields as well as decrease overall operational and capital costs of the integrated process. As shown below, two alternative methods of pretreatment were investigated: (1) an alternative pretreatment that will significantly lower and perhaps eliminate the use of enzymes or (2) enhance the solubilization of the lignin and increasing the overall yields of the process.

It was found during the benchmarking phase of the project that compounds either entering the system with the biomass or added during deconstruction would be detrimental to the downstream catalytic processes. Several hydrolysate purification technologies were investigated during this Intermediate phase stage including: (1) alternative ion-exchange configurations; (2) ion-exclusion methods; and (3) agglomeration and clarification methods.

Catalyst development activities were conducted to reduce the cost of the catalyst system by identifying lower cost materials that had better activity, selectivity to desired products, and longer lifetimes. Both the HDO and DHOG catalyst systems were investigated in these activities.

At the end of the Intermediate phase, a Stage Gate was conducted with DOE to guide the direction of the second phase of the project.

B.2.1: Biomass Deconstruction

B.2.1.1 2-Stage Acidic Pretreatment to Reduce Enzyme Usage

The Intermediate case originally outlined in the project proposal envisioned the use of a more severe 2-stage acidic pretreatment to achieve greater amounts of acid-catalyzed hydrolysis of cellulose and therefore reduce the enzyme usage needed to achieve high levels of conversion of cellulose to glucose and other forms of convertible carbon from cellulose. Although initial work on this two-stage pretreatment concept looked technically promising in terms of achieving good soluble carbon yields at reduced enzyme loadings, the techno-economic analysis showed that high costs caused by inclusion of a separation step after the first pretreatment stage along with a second high temperature/pressure pretreatment reactor were prohibitive for achieving the overall product cost targets.

The project moved to an alternative deconstruction process strategy that used an alkaline pre-processing step prior to acid pretreatment as a technology with potential of meeting the Intermediate case yield and cost targets (Figure B.2.1.1.1). Initial work to develop the alkaline pretreatment concept originally occurred within NREL projects sponsored by the Department of Energy (DOE) Bioenergy Technology Office (BETO) core R&D program as well as the National Advanced Biofuels Consortium (NABC) project.

Advantages of this line-up include:

1. Alkaline pretreatment removes ash (including silica) and lignin in "black liquor" while retaining most of the structural carbohydrates in insoluble solids fraction.
2. Potential of recovering solubilized lignin from the "black liquor" and processing to fuels to improve carbon yields of the overall process.
3. Lignin removal is known to improve subsequent enzymatic saccharification
4. The single stage acid pretreatment would solubilize most of the hemicellulose and portions of the cellulose and reduce enzyme use.
5. Enriched cellulose content in pretreated solids (due to partial lignin removal, near-complete acetate and hemicellulose removal) would allow for effective enzymatic saccharification and low enzyme loadings.

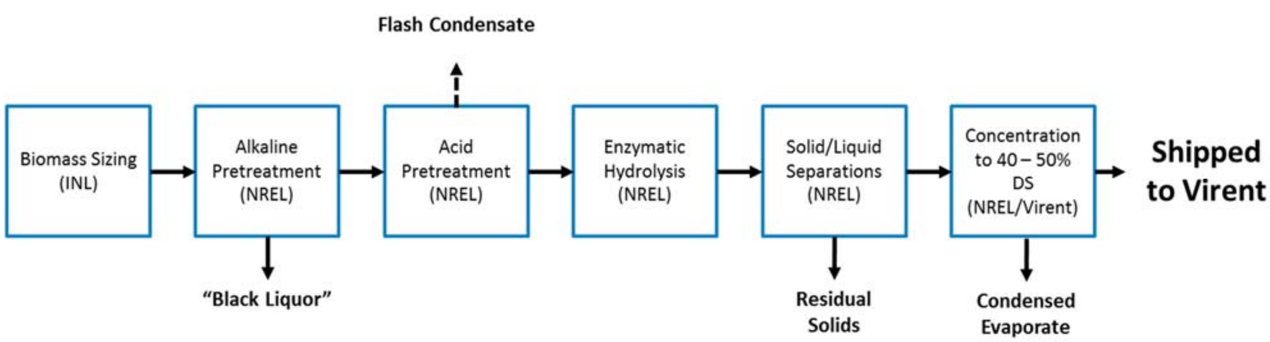

Figure B.2.1.1.1. Alternative deconstruction line-up utilizing an alkaline pretreatment step

Early results from these projects indicated that the alkaline-acid deconstruction process followed by enzymatic hydrolysis was capable of achieving the Intermediate case deconstruction conversion and cost targets. This deconstruction line-up also held the potential of increased yields of upgradeable soluble carbon from the biomass due to partial solubilization of the biomass acetate and lignin components which are potentially upgradeable in Virent's catalytic upgrading process.

B.2.2: Purification

Solid/Liquid Separation - NREL

After biomass deconstruction, a solid-liquid separation step is required before the solids-free aqueous stream can be further processed in Virent's catalytic upgrading process within the equipment used for the project. The separation of the insoluble lignin residues from these slurries is challenging due to the high concentration of insoluble solids (5-10 wt. %) and the fact that the solids are relatively small (23 µm mean diameter) and deformable. NREL investigated methods for producing a sugar-rich stream from enzymatic hydrolysis slurries that is sufficiently solids-free for downstream processing. In this investigation, a two-step approach, with an initial "bulk" separation, followed by a polishing micro-filtration. The well-established, industrial technologies of centrifugation, vacuum filtration, and pressure filtration were evaluated for the bulk separations step, each with and without flocculant filtration aids.

Purification Progress - Virent

Ion Exclusion – Simulated Moving Bed Technology

An alternative to ion-exchange for removing contaminants from hydrolysate is the use of ion-exclusion technology. Ion exclusion technology is particularly useful if the contaminant levels are high in the feed stream. Ion exchange removes ions in the solution by forming ionic bonds to charged sites at the surface of a resin, displacing the original ions loaded on the resin (See Figure B.2.2.1, left). While Figure B.2.2.1 happens to show removal of anions, cations may also be removed utilizing a cation resin, and if the ion concentrations are low enough a mixed bed resin can be used to remove both anions and cations. Regeneration of the ion-exchange resin requires flushing the system with strong salt, acid, or base solution to remove the adsorbed contaminant ions.

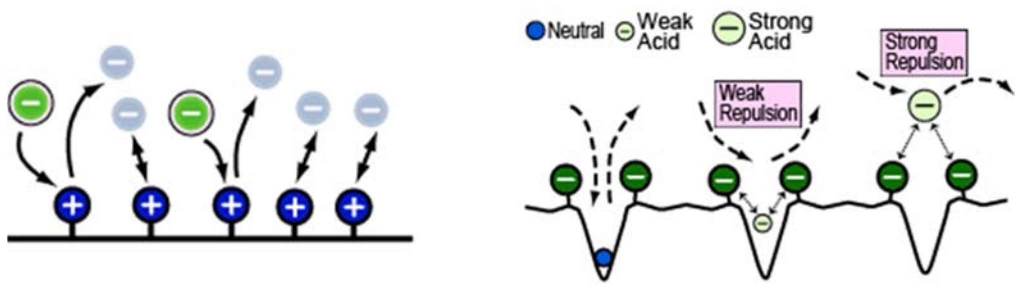

Figure B.2.2.1. Ion-Exchange (left) and Ion Exclusion (right) chemistries

Ion exclusion utilizes charged resins that have sites that repel ions (See Figure B.2.2.1, right). The charge of the solution must be balanced, so ionic salts are excluded.

Ion exclusion chemistry can be utilized in conjunction with simulated moving bed (SMB) technology to separate charged species (solubilized ash components) from non-charged species (oxygenated organics) in the hydrolysate feedstocks. The concept is that feed is injected into a countercurrent system of flowing liquids and moving resin. For ion exclusion the nonpolar components of the feed (sugars) are held up and move within the resin and the polar compounds (ash) are rejected by the resin and move with the flowing liquid. With sufficiently good separation performance, the polar compounds are removed from the system in a raffinate stream without loss of the desired non-polar compounds. A desorbant is added to system and depending on concentration will displace the nonpolar compounds from the resin back to the fluid phase. The purified nonpolar compounds are then recovered in the extract stream.

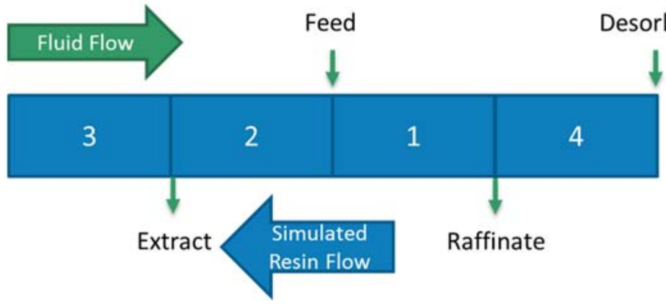

Figure B.2.2.2. Simulated moving bed principles

While it is impractical to actually mechanically flow the resin in the system, this resin flow can be simulated by utilizing a switching valve system that moves the position of the feed, raffinate, desorbant, and extract from bed to bed and simulate the moving the resin.

SSMB Results

To explore the SMB concept within the project, Virent bought a pilot scale sequentially simulated moving bed (SSMB) unit designed and built by ProSep for feedstock purification. When combined with a mixed bed ion-exchange finishing bed, the SSMB did exhibit better performance for ash removal compared to a multi-bed ion-exchange as shown in Figure B.2.2.3. This figure shows improved removal of silicon and nitrogen compounds.

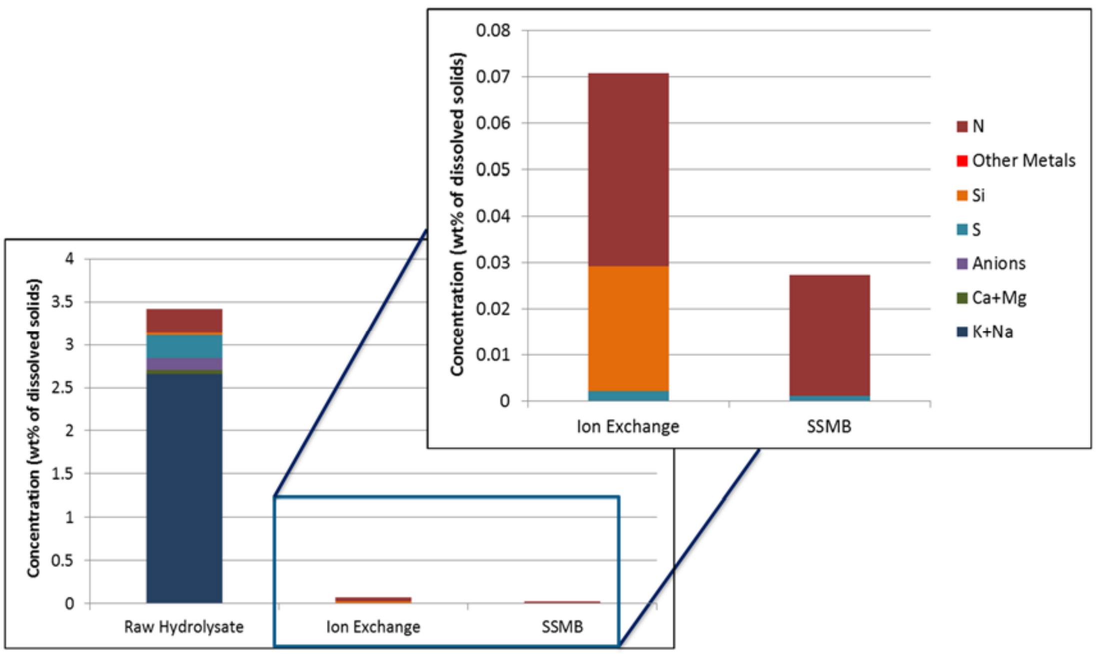

Figure B.2.2.3: Ash reduction comparison ion exchange vs SSMB

B.2.3: Catalytic Conversion

Reactor Design and Modeling

The HDO reactor system is unique in that the hydrodeoxygenation step requires the reaction of hydrogen with a large range of oxygenated compounds in the presence of water. The hydrodeoxygenation reaction is highly exothermic and a temperature rise is observed in an adiabatic reactor. It is important to understand how to control the reaction such that the temperature rise is not too fast resulting in undesired reactions (or potential reaction run away) within the reactor.

While process work and the validation runs were conducted on pilot plants that contain 1 inch reactors, Virent also has 2 inch reactors available that can be run in an adiabatic mode. Using instrumentation and control logic, Virent was able to configure a 2 inch reactor to run adiabatically by maintaining a constant temperature in the radial direction by controlling heat loss or gain across the reactor wall. The reactor is equipped with an internal thermocouple that provides continuous monitoring of the temperature at the center of the reactor. Each heated section can be controlled such that temperature of reactor wall is the same as the temperature of the internal thermocouple, resulting in no loss or gain of heat through the walls of the reactor.

Virent used this system to study the reactor characteristics for the HDO reactor system. A reactor preheater was used to control the temperature of the reactor feed to the desired inlet temperature. Conversion across the reactor can be controlled by either adjusting the inlet temperature or feed concentration. Figure B.2.3.4 shows the experimental temperature rise across the reactor for three extents of conversion of the model feedstock. The conversion was controlled by increasing the inlet temperature of the inlet reaction mixture.

Two reactor models were developed in Aspen to predict the observed temperature rise as a function of inlet temperature and extent of conversion. Figure B.2.3.4 shows that both of these models do a reasonable job of predicting temperature rise across the reactor. The results shown in Figure B.2.3.4 suggest that these models would be useful in reactor scale-up as well as reactor control.

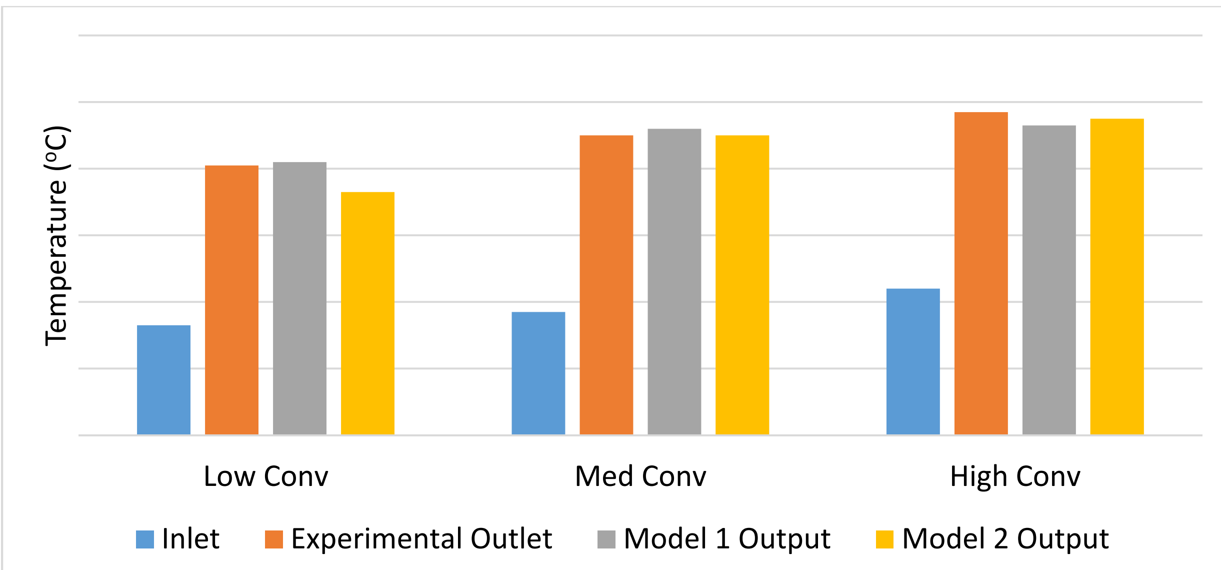

Figure B.2.3.4 Experimental and modelled temperature rises across a 2" adiabatic reactor

B.2.4: Intermediate Validation

Based on process work during Budget Period 1, an Intermediate validation run was conducted using the process line-up shown in Figure B.2.4.1. The validation run utilized the corn stover collected and sized from the start of the project and used for both the repeat Benchmark run as well as the Intermediate configuration. This corn stover was pretreated with alkaline followed by a dilute acid pretreatment and enzymatic hydrolysis at NREL for the Intermediate validation. NREL separated the generated hydrolysate from the solid fraction and then concentrated to 50 wt. % dissolved solids via evaporation. The concentrated hydrolysate was shipped to Virent where contaminants were removed using SSMB technology followed by an ion exchange polishing step. Since water was added during processing in the SSMB a second concentration step was conducted on the cleaned hydrolysate before being fed to Virent's HDO catalytic reactor, with products from the HDO step being condensed in Virent's DHOG reactor to generate longer chain hydrocarbons that are subsequently hydrofinished to remove residual oxygen. A final distillation step was completed to fractionate the resulting hydrofinished hydrocarbons into gasoline, jet fuel, and diesel fractions. Details of each of these steps are provided below.

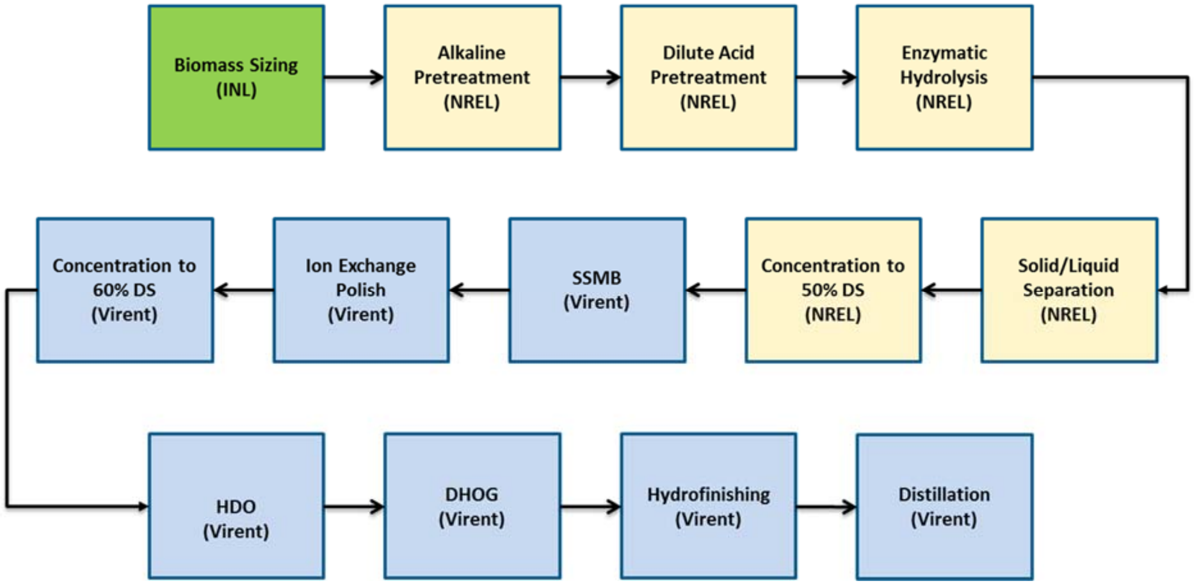

Figure B.2.4.1: Intermediate validation process line-up

Table B.2.4.1 shows analysis of the as received corn stover utilized in January 2014 validation run. The Intermediate target values were set based on the analysis of the Benchmark validation run conducted in March 2012. As mentioned previously, a difference in moisture content was observed due to storage.

Table B.2.4.1 Chemical analysis results from single-pass corn stover used in the Intermediate validation

Date of Validation Experiment	Benchmark Jan-2014	Intermediate Targets	Intermediate Actuals Jan-2014
Moisture content (wt. %)	9%	5%	9%
Sucrose (%, dry wt.)	1%	0%	1%
Soluble extractives (organic) (%, dry wt.)	13%	14%	13%
Glucan (Cellulose) (%, dry wt.)	36%	36%	36%
Xylan (%, dry wt.)	22%	21%	22%
Arabinan (%, dry wt.)	3%	4%	3%
Mannan + Galactan (%, dry wt.)	2%	2%	2%
Acetate (%, dry wt.)	2%	3%	2%
Lignin (%, dry wt.)	17%	15%	17%
Protein (%, dry wt.)	3%	2%	3%
Ash (%, dry wt.)	5%	6%	5%

B.2.4.1 Alkaline/Dilute Acid Pretreatment, Enzymatic Hydrolysis, and Solid/Liquid Separation (NREL)

Alkaline/acid pretreatment and enzymatic hydrolysis processes were conducted for the Intermediate validation. The yields of solubilized carbon from both the cellulose and hemicellulose fractions were lower than expected from this Intermediate case deconstruction line-up. Solubilized carbon from cellulose was 19.8% lower for the Intermediate case compared to the equivalent Benchmark yield. Solubilized carbon from hemicellulose was 17.5% lower for Intermediate case compared to the Benchmark yield. While the solubilized carbon from the Intermediate deconstruction validation run was lower than targeted, subsequent work and analysis suggest that the alkaline pretreatment would provide appropriate yields and economics for a viable process. This will be discuss in more detail below.

B.2.4.2: Purification

The ion removal strategy was changed from ion exchange to ion exclusion in an SSMB due to the high cost of regeneration chemicals at large scale within the former strategy. The entire configuration is presented in Figure B.2.4.2.1.

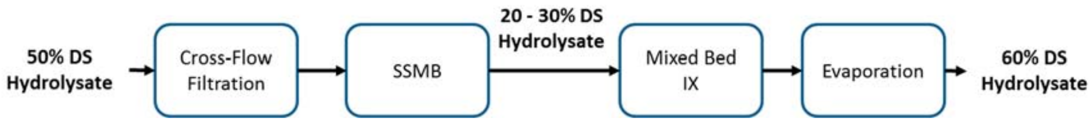

Figure B.2.4.2.1: Virent Intermediate purification process

Table B.2.4.2.2 compares the quality of the product from the Intermediate purification process to the Benchmark purification process. Similar low levels were observed for most of contaminants with a significant improvement in Si removal for Intermediate case.

Table B.2.4.2.2: Ash Concentration (ppm) comparison for Benchmark and Intermediate hydrolysates

	Ca	K	Na	P	S	Si
Benchmark – April 2014	0.5	0.7	BDL	0.6	5.5	232.5
Intermediate – April 2014	2.2	BDL	BDL	1.5	7.3	BDL

B.2.4.3: Catalytic Conversion

An alternative process line-up was investigated for the catalytic conversion steps in the Intermediate validation. Compared to the Benchmark validation, this new line-up utilized two HDO steps with different HDO catalysts and reaction conditions in each step. This Intermediate case also altered the DHOG reaction conditions. These changes resulted both in improvement on the overall liquid yield from the hydrolysate compared to Benchmark configuration (See Figure B.2.3.2), and improved selectivity to jet fuel was also observed. Figure 2.2.17 shows a 15% improvement on liquid fuel yields over the catalytic process steps with a 50% improvement in jet fuel selectivity.

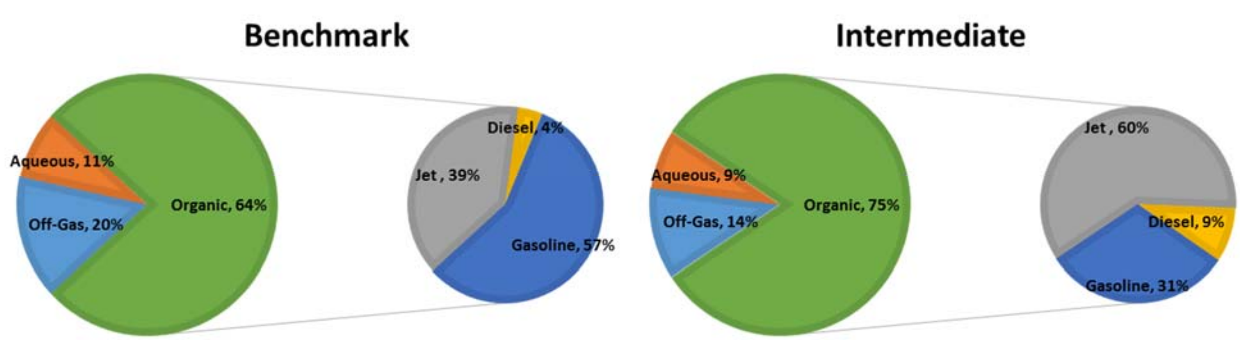

Figure B.2.3.2 Comparison of liquid yields and jet selectivity between Benchmark configuration and Intermediate configuration

An overall yield decrease was observed from the Benchmark case to the Intermediate case. This was attributed primarily to the lower carbon yield from the deconstruction steps as the catalytic conversion yields were actually higher in the Intermediate case. Even with the lower yield of liquid fuel for the Intermediate case, Figure 8 above shows a decrease in the cash cost of production between the Benchmark and Intermediate cases. The improvement in cash cost can be attributed to improved catalyst performance and improved hydrogen utilization in the Intermediate case. After the lower than expected yields from the alkali pretreatment deconstruction line-up, NREL reinvestigated the deconstruction technology and determined that higher yields were possible from enzymatic hydrolysate step of the alkali/weak acid pretreated materials by adjusting conditions for the weak acid pretreatment step.

The alkaline pretreatment process was advantageous to the overall design as it decreased ash content in the hydrolysate stream and showed great potential to reduce the capital and operating cost of hydrolysate conditioning steps. A sensitivity study was conducted to understand the opportunities for utilizing all solubilized biomass carbon and considered approaches to recover and upgrade these biomass intermediates in the BioForming process. Using pilot scale studies that had successfully demonstrated the use of either ion exchange or ion exclusion to recover carbon from black liquor stream produced from alkaline pulping of woody biomass, cost estimates were developed that considered utilization of carbon from the streams using similar design approaches and cost estimates [(7, 8)]. The initial analysis considered the impact of recovering only the carbon of the solubilized lignin fraction as well as recovery of all of the residual solubilized carbon from the biomass. The study indicated that with successful recovery of the carbon, there is the potential to move the profited cost of production towards $3/gge for hydrocarbon blendstocks.

Subtask B.3: Final Phase Process Development

A stage-gate review for the first phase of the project was conducted in February 2014 at NREL with four external reviewers. Virent, with support from the deconstruction and TEA teams from NREL, presented results through the Intermediate validation. Virent also provided a business plan to DOE and the reviewers. After review, the project had a modest scope reduction. Virent continued process work with the hydrolysate provided by NREL and proceeded with process development for the Final validation in April 2015. During this second budget period, Virent focused on catalyst development on the HDO and DHOG system as reported in Subsection A.1 and the interaction of new catalyst formulations with treated hydrolysate.

Ash removal remained one of the main challenges in combining NREL's dilute acid pretreatment/enzymatic hydrolysis deconstruction technology with Virent's catalytic processing technology. While utilizing ion-exclusion/SSMB technology provided a good hydrolysate for processing, this technology added significant capital expense. An alternative strategy for removing ash components is to use a pretreatment protocol before deconstruction to reduce ash content in the hydrolysate, and then utilize ion-exchange to remove the rest of the ash components. Figure B.3.1 shows the line-up utilized for the Final validation of the project utilizing this concept. While the major components of this line-up are similar to the Benchmark line-up, process changes were made within both the purification and catalytic processing sections. These process changes are discussed below.

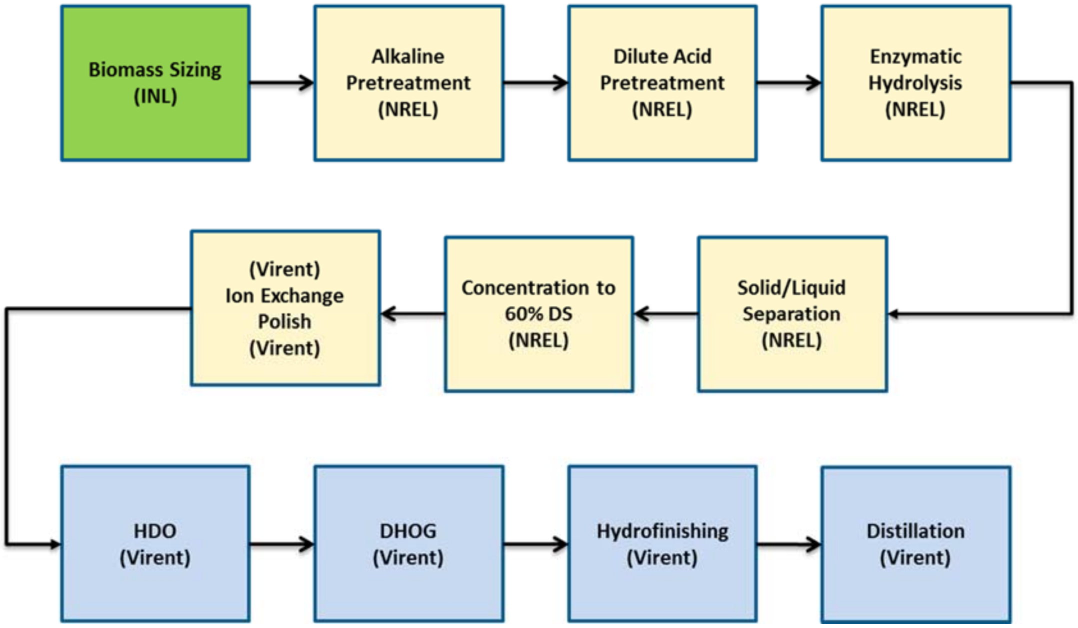

Figure B.3.1: Process line-up for Final validation

B.3.1: Biomass Deconstruction

Dilute Acid Pretreatment, Enzymatic Hydrolysis, and Solid/Liquid Separation (NREL)

The feedstock preparation and pretreatment conditions used in the Final validation campaign are depicted in pictures in Figure B.3.1.1. The general deconstruction protocol for these runs involved feedstock impregnation, followed by pretreatment in the 1 ton/day horizontal reactor, enzymatic hydrolysis in 4000 L high solids enzymatic hydrolysis reactors, bulk solids removal with a filtering basket centrifuge, filtering with cartridge filters, and concentration via vacuum assisted evaporation. Approximately 1000 L of clarified, concentrated hydrolysate was shipped to Virent for each of three hydrolysate production runs, including the Final validation.

The actual glucose and xylose yields in acid pretreatment were 7% and 71%, respectively, which fell below the proposed values of 11% and 78%. The recovered carbon from glucan and xylan in acid pretreatment were 8.2% and 86%, respectively, which fell below the proposed values of 12% and 94%. The enzymatic hydrolysis proposed and actual yields were 82% and 74.1%, respectively, for glucose and 38% and 37.6%, respectively, for xylose. The proposed and actual yields for the overall process were 84% and 74% for glucose, respectively, and 80% and 76.6%, respectively, for xylose. The proposed and actual recovered carbon yields from glucan in the overall process were 93% and 83.8%, respectively, and 98% and 94.6% from xylan, respectively.

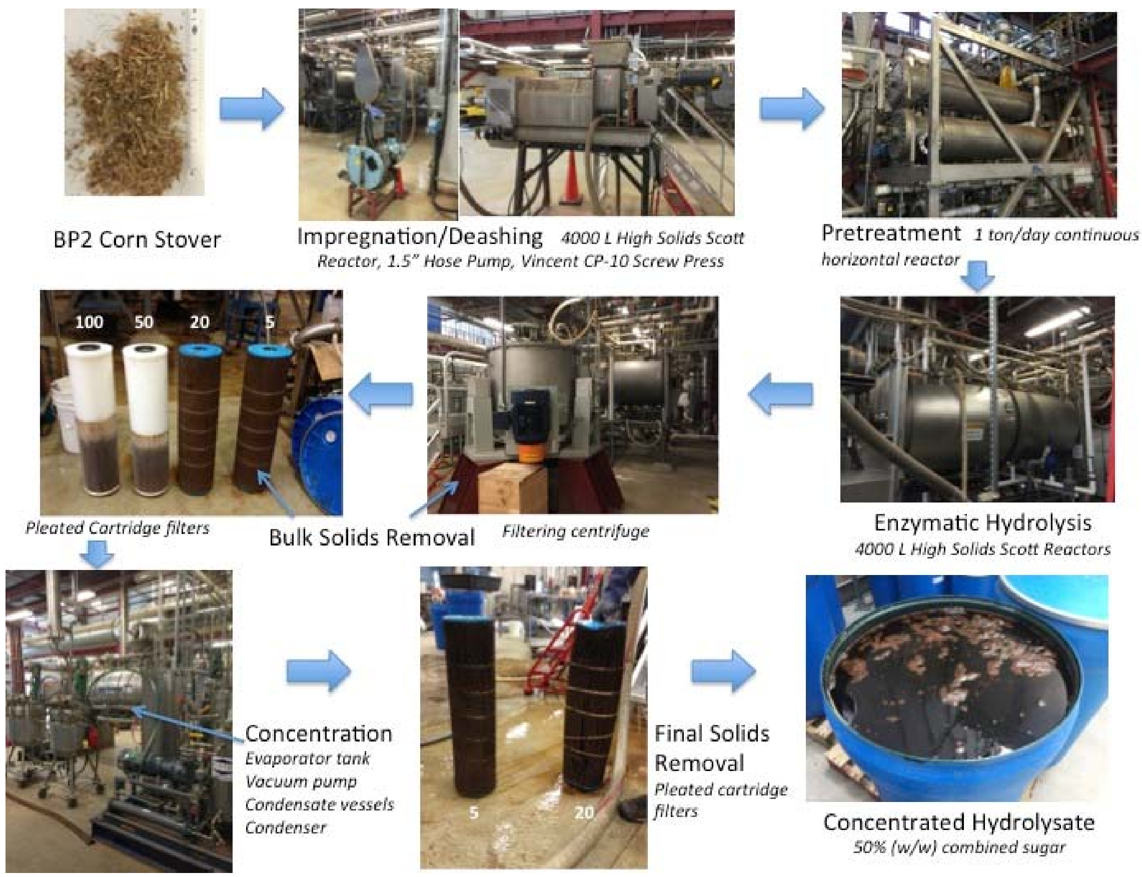

Figure B.3.1.1. Deconstruction process flow pictures of concentrated hydrolysate production for the Final validation and January 2015 production run. Numbers above or below the pleated cartridge filters represent the filter pore size in microns. The concentrated hydrolysate production process for the May and October 2014 campaigns differ in the bulk solids removal step, which was only conducted in the filtering centrifuge for these runs.

B.3.2: Purification

Figure B.3.2.1 shows the line-up used for purification of the hydrolysate for the Final validation. In this line-up residual solids in the hydrolysate were removed using a Pall RAMS cross-flow filtration unit. This filtration is a necessary lab practice due to formation of solids during shipment and storage. It is not expected that this additional filtration will be necessary for a fully integrated process and is not part of the TEA model.

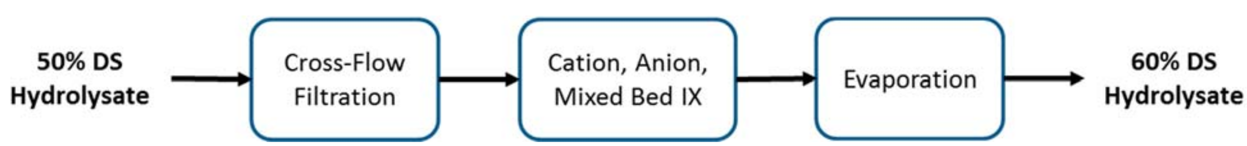

Figure B.3.2.1 Virent Final purification process

Ash removal was conducted using a series of cation, anion and mixed bed ion exchange columns. The ion exchange beds proved effective not only at removing ash components, but also removing trace amounts of high molecular weight materials that were creating operational problems within the catalytic reactor system.

Table B.3.2.2 compares the quality of the product from the three purification processes. Similar low levels were observed for most of contaminants. The major difference is the lower Si concentrations in the

Intermediate and Final products as well as the higher level of phosphorous in the final Benchmark validation product.

Table B.3.2.2: Ash concentration (ppm) comparison for Benchmark and Intermediate hydrolysates

	Ca	K	Na	P	S	Si
Benchmark – April 2015	0.0	23	0.9	92.1	8.0	242.7
Intermediate – April 2014	2.2	BDL	BDL	1.5	7.3	BDL
Final – April 2015	0.0	0.0	0.0	1.1	10.5	20.2

B.3.3: Catalytic Conversion

The line-up of the catalytic process used for the Final validation run was similar to the Intermediate validation configuration, with the Final Validation line-up utilizing two HDO reactor steps. The first HDO step utilized the catalyst formulation used in the Benchmark case. In the Final validation, the second HDO step utilized the Intermediate formulation that consisted of a precious metal modified with different base metals on a support. A lower cost formulation was used in the DHOG reactor for the Final validation that utilized a modified precious metal on a modified support (DHOG Catalyst B from Subtask A.1).

Testing before the Final Validation indicated a 27% increase in liquid product yield across the catalytic processing configuration from the feed hydrolysate compared to Benchmark configuration. This translated to an overall yield (gallons per ton of corn stover) improvement of 26% over the Benchmark configuration. The Final validation yields were lower such that overall yield improvement over the Benchmark validation was 7%. Figure 8 shows improved profited cost of production between the Intermediate and Final validation cases. This improvement was due to improved yields and decreased catalyst cost.

Task C: Techno-economic Analysis

Subtask C.1: Benchmark Process Validation

The Benchmark process configuration was validated three times, initial validation in March 2012, as a reference check during the Intermediate validation in January 2014, and again during the Final validation in April 2015. TEA was successfully completed for each the Benchmark configuration for each validation, and the results will be discussed in the following sections.

Subtask C.2: Intermediate and Final Target Process Economic Development

Throughout the project Virent and NREL increased the robustness of the Aspen model and incorporated all comments/suggestions from the validation teams.

Commercial Model

As part of the project an integrated process model was created in Aspen V7.3 to evaluate the expected process at a commercial scale of 2,000 dry MT corn stover input per day. This section describes the process design for the conversion of lignocellulosic biomass to advanced biofuels. The design was based on the integration of Virent‘s novel catalytic conversion technology (BioForming) with NREL based deconstruction technologies for corn stover. This 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. The model and TEA output were used in the project to help determine progress and aid in guiding the research and development.

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 2007 dollars. The next sections briefly describe the major process operations.

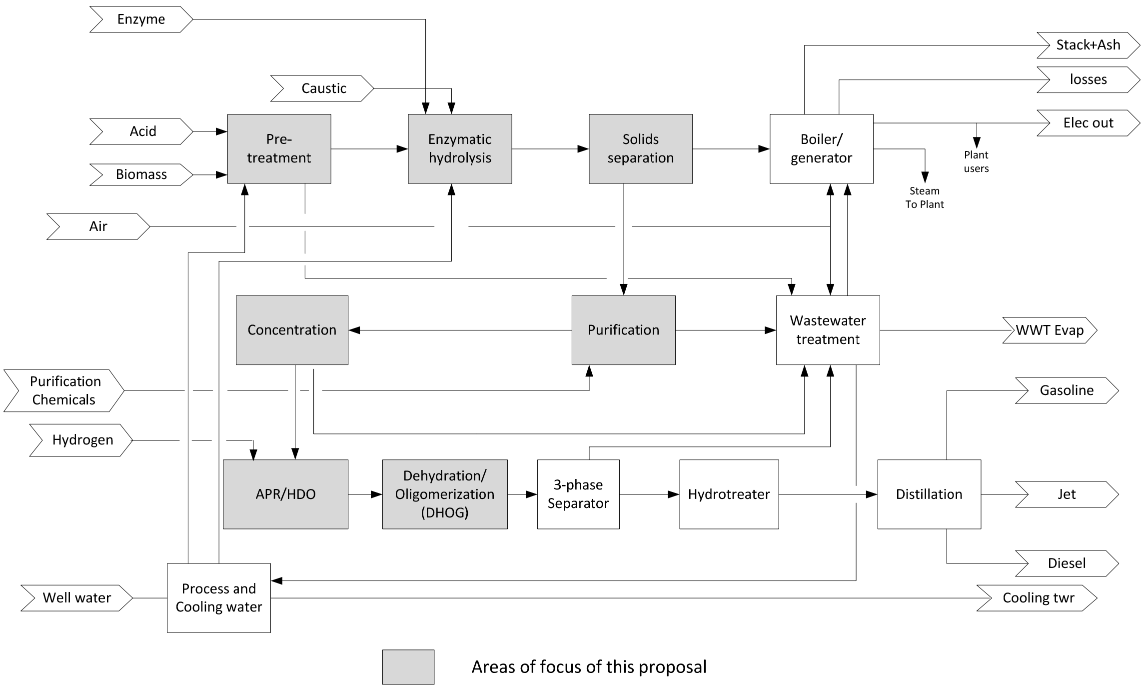

Figure C.2.1. Final configuration PFD for converting biomass into final hydrocarbon products.

Pre-treatment and Enzymatic Hydrolysis:

Milled corn stover enters the process into the pre-treatment reactor receiving system which is then followed by a vertical vessel with a long residence time for steam-heating and potential acid impregnation of the biomass. The biomass is discharged via a pair of plug screw feeders and sulfuric acid is added at a loading of 24.5 mg/g dry biomass (2.5 wt. % catalyst value). The streams from both screw feeders are recombined via a transport conveyor and are delivered to the pretreatment reactor. This single horizontal reactor vessel is operated at 158°C and 83 psi. The yields from the pretreatment reactor are based on the demonstrated conversion for the 2010 NREL state of technology (SOT). The discharge from the pre-treatment reactor is then cooled and condensed. The hydrolysate slurry is further diluted and cooled with fresh water to hit a solids loading target of 20 wt% total solids. The slurry is neutralized with caustic (KOH) to a pH of 5 in the conditioning step. The whole slurry is sent on to enzymatic hydrolysis where purchased enzyme at a loading of 20 mg protein/g cellulose is used. Saccharification is carried out for 3.5 days producing yields based on results from the 2010 NREL SOT for biochemical conversion to ethanol.

Hydrolysate conditioning steps:

The hydrolysate exits the enzymatic hydrolysis step and enters a pressure filter system for solid liquid separation. The solids leave the pressure filter system at 35 wt% and are sent on to the boiler combustion system. The recovered liquid from the filter (pressate) continues to the triple effect evaporator where the syrup is concentrated to 60 wt% water by utilizing steam from the boiler system. The overhead vapor for each effect is collected and condensed. The collected liquid is recycled back to the pretreatment reactor to control the solids loading (at 30 wt% total solids) with the remainder sent back to the process water return.

The filtered and concentrated syrup is processed using fixed bed ion-exchange resin technology where the bulk of the soluble ash components are removed. The soluble carbon product stream leaving the upgrading process contains 60wt% water. The raffinates and regeneration solutions produced during the purifications, which contain mainly extractives and soluble lignin is sent on to wastewater treatment (WWT).

The pressure filter system capital cost and design assumptions are based on a vendor quote for the biochemical conversion design of the hydrolysate filter press solid/liquid separation step (utilized in 2011 earlier SOT cost estimates). The cost of the triple effect evaporator is based on an NREL cost in the sugar model design. Other purification capital cost estimates are based on in-house values from Virent vendor quotes and equipment design.

BioForming Conversion Process and Product Separation/Recovery

The purified hydrolysate enters the HDO reactor, containing a fixed catalyst bed in the presence of hydrogen gas. The sugars are converted into a mixture of alcohols, ketones, cyclic ethers, alkanes, acids, water, and other oxygenated compounds. The organic liquid and gas phases are sent forward to the DHOG reactor. The DHOG reactor contains a fixed catalyst bed and produces a mixture of alkanes, alkenes, and mono-oxygenates with a targeted carbon range of C8-C24.

The DHOG reactor product is separated in a flash separation vessel and the organic liquid phase fed forward to the hydrofinishing reactor. In this final reaction, the organic liquid reacts over a fixed catalyst bed in the presence of hydrogen gas to remove any remaining oxygen in the product as well as saturate alkenes to alkanes. The product from the hydrofinishing reactor is sent to product fractionation, where the hydrocarbon product is distilled into gasoline, jet, and diesel products.

Wastewater Treatment:

A number of wastewater streams are produced in this design that must be treated before being recycled back into the process. Condensed boiler blowdown, cooling tower blowdown, and the water recovered from hydrolysate conditioning steps are mixed together. The combined wastewater stream is processed via anaerobic digestion and aerobic digestion to digest organic matter in the stream. Biogas, produced from the anaerobic digestion, is rich in methane and is fed to the boiler/combustor system. Aerobic digestion produces a cleaned water stream that can be reused in the process 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 various by-product and process waste streams to produce steam and electricity. The combustion of the recovered lignin, WWT sludge and biogas, and process fuel gas produces enough steam and electricity to ensure the process is energy self-sufficient. In fact, there is enough excess energy to produce a by-product revenue through the sale of electricity.

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

All capital costs utilized in the pre-treatment and enzymatic hydrolysis sections are consistent with the 2011 Humbird et al. design report [9] and use vendor quotes for similar equipment design and process conditions. The pressure filter system capital cost and design assumptions are based on a vendor quote for the biochemical conversion design of the hydrolysate filter press solid/liquid separation step (utilized in 2011 earlier SOT cost estimates, [9]). The cost of the triple effect evaporator is based on an NREL cost in the sugar model design. All costs and assumptions of the combustor/boiler/turbogenerator section are consistent with the 2011 Humbird et al. design case [9].

The BioForming portion of the TEA includes the necessary purification required to introduce crude hydrolysate into the BioForming platform, conversion of hydrolysate to liquid fuels via the BioForming Platform and final separations necessary to produce liquid fuel blendstocks (gasoline, jet, and diesel). Purification capital cost estimates are based on in-house values from Virent vendor quotes and equipment design. The Aspen simulation provided sizing parameters for the major pieces of equipment and was used to prepare factored capital estimates based on the methods of Peters & Timmerhaus (P&T)[10]. Metrics from

P&T were then used to estimate direct equipment, installation, and indirect costs. The total capital investment (2007 US dollars) was determined by summing the purchased equipment costs, adding a ten percent delivery charge, then multiplying by a factor of 5.93 (value for a fluid processing plant).

Variable Operating Costs

Variable operating costs were determined based on required raw materials (biomass and hydrogen), catalysts, enzymes, deconstruction and purification chemicals, waste handling and disposal charges, by-product credits and labor and maintenance incurred during the production of biobased hydrocarbons.

Return on Capital

An Effective Capital Recovery Factor (ECRF) of 18% is applied to the new capital build. The 18% capital factor is based on the assumptions shown in Table C.2.1. In its simplest form, a capital recovery factor defines the periodic payments, or annuity, of the present value of a loan for the life of the loan. The weighted average cost of capital can be estimated based on the amount of debt and equity that is used to finance the equipment or facility. The tax shelter impact provided by debt is included in the cost of capital. The capital recovery factor calculates the magnitude of fixed payments necessary to cover interest and principal on a loan used for the initial capital investment. The capital recovery factor does not take into account end of life salvage value, federal taxes, working capital or depreciation which are incorporated into the ECRF. Virent utilizes and applies the ECRF to the total capital cost of the project to determine the annual $/gallon required to return a nominal 10% weighted average cost of capital. The ECRF of 18% is applied to the total installed capital.

Table C.2.1. Financial assumptions behind the capital recovery factor used to calculate the profited cost of production.

Tax Rate	35%	**Cost of Debt**	8%	**Cost of Equity**	15%
Plant Lifetime	15 years	**% Debt**	50%	**% Equity**	50%
Salvage Value	0%	**Working Capital**	10%	**Weighted Average Cost of Capital (Nominal)**	10%

Production Cost

Throughout the project, Virent was able to show a reduction in the cost of production of liquid fuels. The cash cost of production includes all costs required to operate the facility including, biomass, chemicals, catalysts, waste disposal and treatment, hydrogen, utilities and labor and maintenance. The profited cost is the cash cost of production plus the return on capital. From the Benchmark to the Final process configuration, there was a 41% reduction on the profited cost of production. A breakdown of the cost of production is shown below in Figure C.2.2 as a function of the initial benchmark cost of production.

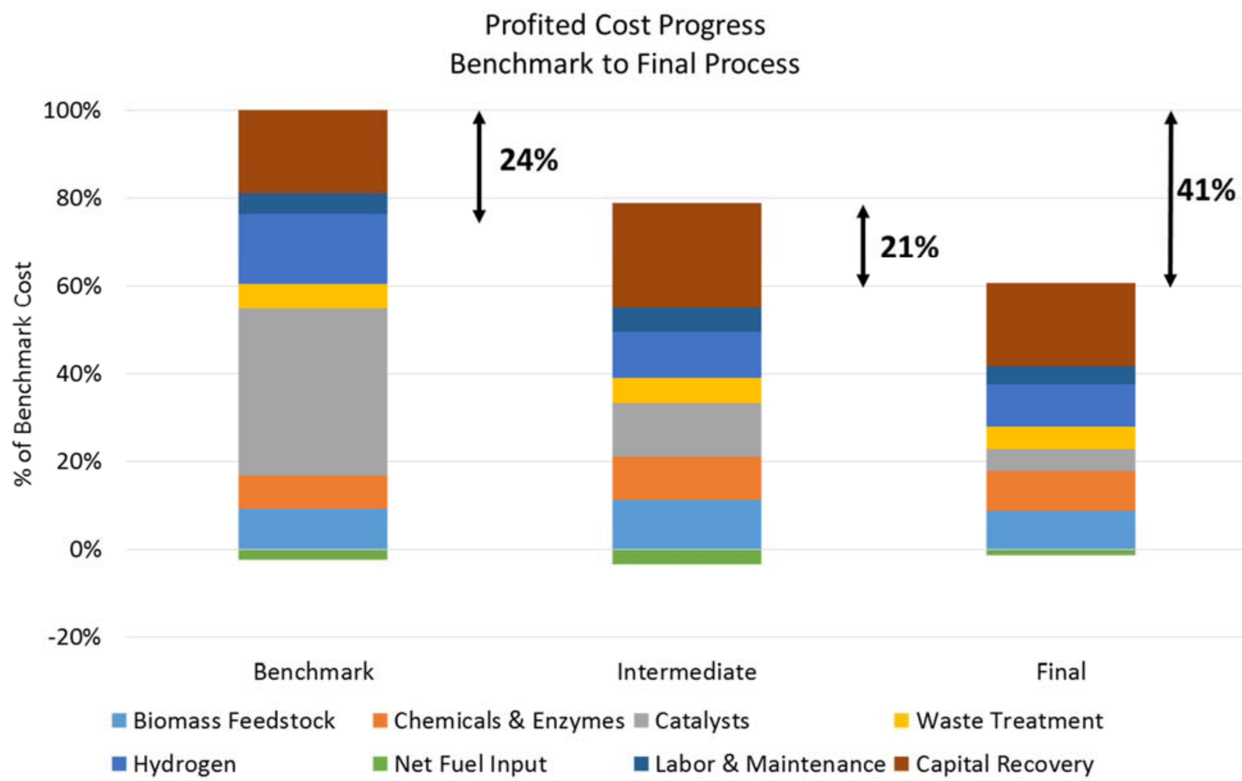

Figure C.2.2. Profited cost of production progress from Benchmark to Final process.

Subtask C.3: Market Analysis & Competitive Position Analysis

Market Sizes and Customer Acceptance

The ultimate market for any biofuel is the national and global refined product markets, which collectively represents over a trillion dollar business. In these markets, the US consumes significant amounts of liquid transportation fuels with a large portion derived from imported crude oil. Table C.3.1 below shows current US demand for gasoline, diesel and jet fuel along with future demand growth projections according to the US Energy Information Administration (EIA)[11].

Table C.3.1. Current US fuel consumption and projected growth.

Fuel Type	Current Consumption 2012 (MMGPY)	Projected Consumption in 2040 (MMGPY)	CAGR (%) 2012 – 2010
Motor Gasoline	133,378	101,373	-1.00%
Jet Fuel	21,845	24,369	0.50%
Distillate Fuel Oil	59,772	70,836	0.80%

Addressing energy security and use within the US Department of Defense (DOD) has been a growing concern of the US Congress and executive branch decision makers. The military services are highly dependent on petroleum-derived fuels for maintaining readiness and executing their missions. The DOD, the largest single fuel consumer in the US, requires substantial amounts of distillate fuels (See Table C.3.2) and devotes significant resources to protecting petroleum interests.

Table C.3.2. US DOD fuel purchases and costs for FY 2012. [12]

	FY 2012 (MMGPY)	Product Cost ($MM)
Jet Fuel	3,521	11,842
Distillates and Diesel	865	2,764
Totals	4,386	14,606

There is a strong current and growing demand for drop-in renewable liquid fuels in the US from industry and government agencies. The joint Navy/DOE and USDA Defense Production Act [13] initiative and the recently announced Fleet to Farm [14] program are two examples of programs designed to create demand and market pull for distillate range fuels from the DOD.

Commercial interest is also strong, with sustainable aviation biofuels routinely cited as a key component of a comprehensive strategy to reduce commercial air carrier emissions. There is also a solid indication of industry and government collaboration to promote the development and production of these types of fuels. The Commercial Aviation Alternative Fuels Initiative (CAAFI) is one example of these joint efforts and Virent has received letters of support from CAAFI. The Midwestern Aviation Sustainable Biofuels Initiative [15] (MASBI) is an example of another collaboration in which Virent participated in an industry led effort focused on delivering sustainable aviation biofuels to the Midwestern US. Virent has also worked in collaboration with Royal Dutch Shell to further develop the BioForming process to produce cost effective distillate fuels, gain certification of the Virent jet fuel through the ASTM certification process, and progress commercialization of the BioForming process. These efforts validate a strong market demand for the bio-distillate products targeted by this project. This project directly addresses the objectives and challenges of all of these collective efforts to promote sustainable, bio based aviation and military grade distillate fuels.

Competitive Advantage

Attractiveness of Technology

The combination of NREL's biomass deconstruction and Virent's BioForming technology is an attractive solution for the production of drop-in hydrocarbon distillate blendstocks for jet fuel and diesel applications. The two parties have already demonstrated the ability to process corn stover into biobased hydrocarbon blendstocks and Virent has shown that fuels produced from traditional carbohydrate sources can be blended with conventional petroleum fuels and meet all ASTM specifications. The attractiveness and competitive advantages of the combined NREL and Virent process versus BTL/FT, HEFA and ATJ is discussed below. The competitive advantages of the combined processes can be broken down into the following categories: (1) process yields, (2) feedstock flexibility, and (3) fuel quality and product flexibility.

Overall Process Yields:

One of the key advantages in the BioForming process is the ability to leverage cheap and abundant natural gas in the US for the production of hydrogen. The use of externally supplied hydrogen in the BioForming process enhances the yields and economics compared to in-situ generated hydrogen or the production of hydrogen from the cellulosic feedstock. Table C.3.3 below sets out expected commercial yields for several competing routes:

Table C.3.3. Estimated process yields of several production routes.

Route	Yields (Gallons/Ton)	Source/Notes:
Virent BioForming	60 - 70	Based on experimental yields with modest continued improvements
Alcohol to Jet	35 – 45	Based on 79 gallons EtOH/ton corn stover [9] and 2.00 gallons ethanol/gallon hydrocarbon.
Biomass to Liquids	50	National Academy of Sciences [16]

Feedstock Flexibility:

One of the main differences in feedstock utilization is that the Virent BioForming process, FT conversion technologies and ATJ can all utilize lignocellulosic biomass feedstocks, whereas HEFA utilizes seed oils, waste oils and algae derived oils. This opens up a large feedstock base compared to HEFA as shown below in Table C.3.4: The fuel production potential is based on the yields shown in Table C.3.3 along with the estimated corn stover available in 2022 from the DOE Billion Ton Study Update (17).

Table C.3.4. Fuel production potential from corn stover.

Technology	Feedstock Base Potential	Fuel Production Potential from Corn Stover (BGPY)
Virent BioForming	Lignocellulosic Biomass	7 – 14
BTL-Fisher Tropsch	Lignocellulosic Biomass	6 – 12
Alcohol to Jet	Lignocellulosic Biomass	5 – 10
HEFA	Seed & Algae Oils, Waste Animal Fats	< 1.5 (from oils not stover)

The BioForming process is also able to process more than just traditional monomeric sugars, which allows for greater optimization of NREL's front end biomass deconstruction with the BioForming process. An example of some of the compounds that Virent has been able to process from NREL's deconstruction technology are shown below in Table C.3.5.

Table C.3.5. Compounds processed in the BioForming process using NREL's deconstruction technology.

Sugars/Sugar Alcohols			Acids	Furans	Aldehydes
Threitol	Mannose	Xylose	Acetic Acid	HMF	Hydroxyacetone
Erythritol	Fructose	Glycerol	Isobutyric Acid	Furfuryl Alcohol	2-Furaldehyde
Rhamnose	Mannitol	Maltose	Levulinic Acid		
Arabinose	Sorbitol	Glucose			
Arabitol	Cellobiose				

Product Output/Quality and Flexibility:

Virent's process, similar to a petroleum refinery is capable of producing a range of hydrocarbons that can be separated into gasoline, jet fuel and diesel blendstocks. This flexibility allows for tailoring the output based on the market conditions and demands. This flexibility is key to helping meet BETO's goal of replacing the whole barrel.

Virent's jet fuel, termed HDO – SK under ASTM certification, provides advantages over other renewable jet fuel pathways and petroleum-derived jet fuel. The broad range of molecules and the generation of paraffins and naphthenes in Virent's final jet fuel product makes it possible to conform to ASTM volatility requirements, unlike fuels with a single or a few molecules that cannot meet the distillation slope requirements of ASTM D7566 for alternative aviation fuels. In addition, the cyclic components produced by the BioForming process provide lower freeze-point and higher density/volumetric energy content than is possible with purely paraffinic fuels produced through FT or HEFA processes. Compared to petroleum fuel, Virent's HDO-SK contains lower sulfur levels, and superior thermal stability due to lower levels of unsaturated compounds, including olefins, dienes, and aromatics. These advantages are highlighted in Table C.3.6.

Table C.3.6. Critical properties for jet fuel and Virent advantages

	ASTM D1655 Requirement	Virent HDO-SK	Petroleum Jet*	FT*	Advantages vs. Petroleum Jet	Advantages vs. Other Renewable Jet
Freeze Point	<-47°C	**<-80**	-44	-51	High cyclics and low n-paraffins → good freeze point	High cyclics and low n-paraffins → good freeze point
Density	775-840 kg/m^3	**812**	806	756		High cyclics → typical density
Thermal Stability Breakpoint	>260°C	**>355°C**	285°C**	>340°C**	Lower levels of unsaturates- olefins, dienes, aromatics → more thermally stable	
Sulfur	<0.3 wt%	**<0.01**	0.08**	<0.01	Lower levels → improved emissions	
T50-T10	15°C	**35**	34	26		Limited component mixtures (not FT) fail the distillation slope requirement
T90 –T10	40ºC	**82**	77	62		Limited component mixtures (not FT) fail the distillation slope requirement

**Commercial sample analyzed for comparison purposes, **Typical*

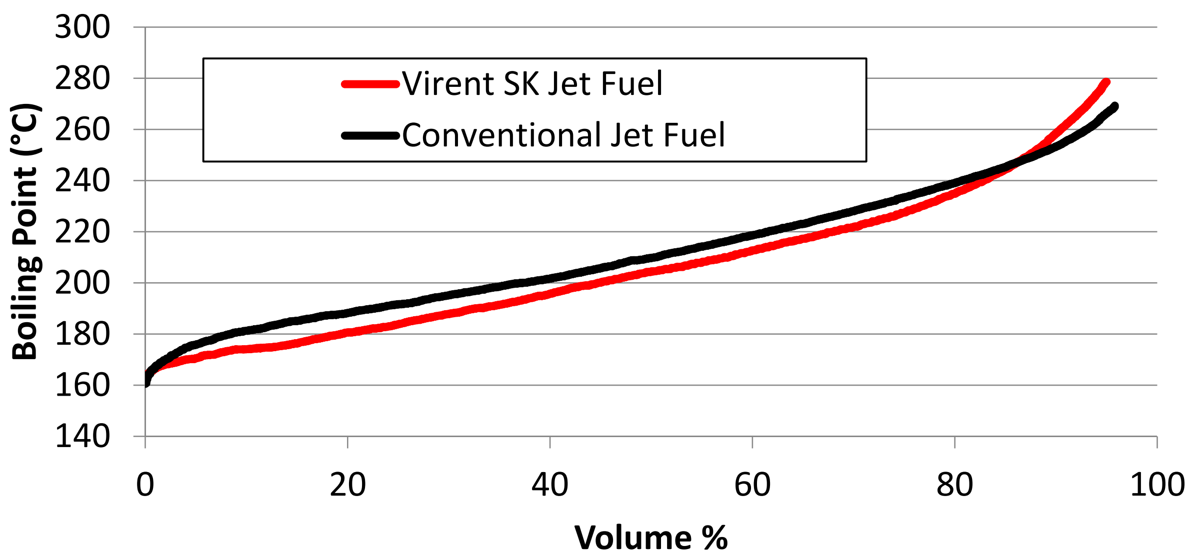

Figure C.3.1. Distillation profile of Virent HDO-SK and petroleum-derived jet fuel

Jet fuel and diesel boiling point ranges have significant overlap, allowing Virent's BioForming distillate process to produce a jet fuel blendstock and a full-range diesel fuel by changing product fractionation to meet the volatility specifications in ASTM D975. The fractionation flexibility of the product is similar to a petroleum refinery, and can be adjusted depending on objectives of the process or demand for each fuel.

Specification testing for a full-range diesel material has been completed by Royal Dutch Shell. The product was shown to have a good cetane number, product density, below normal detection limits of sulfur, and excellent cold flow properties indicated by cloud point measurements.

Unlike traditional Fatty Acid Methyl Ester (FAME) biodiesel products, Virent's BioForm Diesel is a drop-in fuel that does not contain oxygen, so it can be used with existing engines and infrastructure. Additionally, it has higher energy density and does not gel at cold temperatures. Like the jet fuel fraction, the Virent diesel provides a broad range of paraffins and naphthenes similar to petroleum-derived diesel, while biodiesel has a limited range of molecules based on the nature of the oil, grease, or fat used for production.

Table C.3.7. Critical Properties for Diesel Fuel and Virent Advantages

	ASTM D975 No. 2 Diesel Requirement	Virent Diesel	Petroleum Diesel*
Cetane	>40	**49.6**	48.4
Density	>820 kg/m^3	**836**	842
Sulfur	15 ppm (ULSD)	**< 5**	7.5
Cloud Point	--	**-40°C**	-16°C

**Commercial sample analyzed for comparison purposes*

Virent's BioForming distillate process also produces a lighter naphtha cut along with the jet and diesel fractions. This naphtha is a C4-C8 cut very similar to straight-run naphtha from a petroleum refinery, composed of primarily n-paraffins with a smaller amount of iso-paraffins. Results from specification testing completed by Shell indicate the stream could be blended into gasoline similarly to straight-run naphtha, or undergo further upgrading through reforming and isomerization to improve octane.

Extent of Competitive Advantages

A key advantage of the BioForming process is the use of externally supplied hydrogen. The use of externally supplied hydrogen increases yields and profitability of the process. The main source of hydrogen production is from stream methane reforming of natural gas. As depicted in Figure C.3.2 below, the Energy Information Administration is projecting that natural gas prices will stay low relative to oil prices in the US for the next 25 years as shown below making deployment of Virent's technology advantageous for a significant period of time going forward.

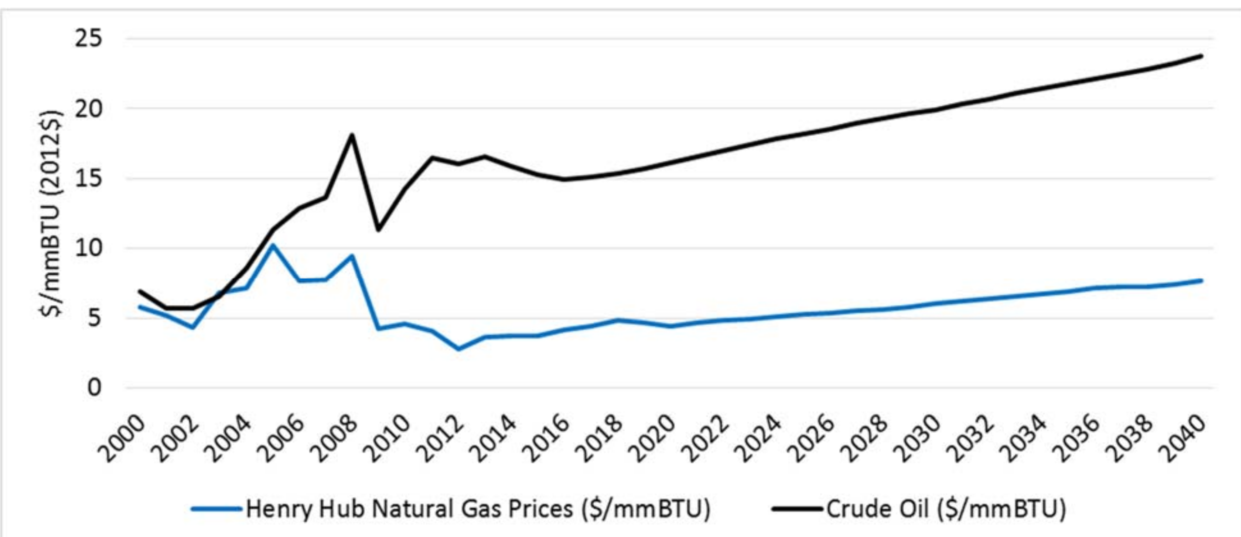

Figure C.3.2. Historic and projected crude oil and natural gas prices in the US [11].

Another key competitive advantage is Virent's extensive portfolio of intellectual property. The BioForming process is well protected until at least 2025 – 2030 by currently issued patents in the US and around the world. Similar to traditional catalytic technologies, the BioForming process also includes significant trade secrets, technique and know-how associated with its catalysts and operating conditions. Through improvements and advancement of the technology, Virent will continuously add additional intellectual property to ensure a competitive advantage for the production of renewable fuels.

Subtask C.4: Technical & Financial Viability of Scale-up

Barriers to Entry

Despite the demand for renewable fuels in the US, there are several barriers to commercial entry of cellulosic biofuels, including; fuel certification volumes and timelines, technology validation and scale-up, financing and the biofuel policy environment.

Fuel Certification Volumes and Timelines:

Renewable jet fuel certification requires the production of approximately 100,000 gallons of "neat" renewable fuel to be blended with conventional jet fuel. This production level typically requires an intermediate plant scale (~250,000 – 1,000,000 gallons/year) in order to produce the fuel in a reasonable time frame (< 1 year). The timeline for certification is typically in excess of 24 months and could create a commercial deployment bottleneck.

Technology Validation and Scale-up:

The large capital requirements for commercial scale biofuel plants, the nature of the new technologies, the need for certification volumes and the need for operability and design parameters typically requires an initial commercial demonstration plant (~250,000 – 1,000,000 gallons/year) deployment prior to full scale commercial production. Despite the smaller scale, these demonstration facilities would still require significant funding (i.e. $10's of millions). This barrier could be overcome by government and industry participation and funding.

Financing:

The capital requirements for full scale commercial plants can be substantial (i.e. $100's of millions) and most biofuel companies do not have the ability to finance the plants on their own. Partnership with major energy companies and grants and loans from federal, state and local governments can help speed up the timeline and reduce the amount of capital that must be raised by traditional debt and equity sources.

Biofuel policy environment:

The Renewable Fuel Standard 2 (RFS2), enacted as part of the 2007 Energy Independence and Security Act is the legislative driver for the biofuels industry in the US. However, the changing US energy landscape, RFS2 program fraud, and production and scale-up challenges faced by the advanced biofuels industry, have all inspired an ongoing debate both inside and outside the government regarding the efficacy of this law. While the RFS2 is still a major driver, concern over the Environmental Protection Agency's (EPA) implementation of the law and the possibility of further legislative action contribute to an air of uncertainly regarding the future of the program. This uncertainty has a chilling effect on further private investment in this industry, especially in the nascent advanced biofuels sector. Similar arguments could be made around California's Low Carbon Fuel Standard and foreign carbon trading schemes (in the EU and Australia) intended to mitigate climate change through increased use of renewable energy resources like biofuels. Stable governmental policy provisions are essential, therefore, to foster the rapid growth of advanced biofuel technologies like those being developed under this project.

Technical Feasibility and Risks

Feasibility

Virent and NREL have successfully demonstrated the technical feasibility of producing distillate range hydrocarbon blendstocks from corn stover at pilot scale. NREL has operated its pilot plant in order to provide cellulosic hydrolysates to Virent. Virent has in turn processed these samples in pilot plants, producing ~1 liter/day of fuel products. In order to implement the combined technologies at commercial scale an integrated demonstration plant would need to be constructed.

Business Risks

There are several identified business risks associated with the deployment of cellulosic biofuels. These risks are generally considered outside the control of companies like Virent and NREL, but can still represent a significant risk to successful commercial deployment.

1) **Prolonged depression of crude oil prices**: A prolonged depression of crude oil prices would weaken the ability of cellulosic biofuels to compete with traditional fossil based fuels, particularly without any renewable credit or carbon pricing mechanism.
2) **Prolonged elevated NG prices:** A key advantage of the BioForming process is the ability to increase process yields through the use of externally supplied hydrogen, the majority of which is obtained from steam methane reforming (SMR) of natural gas. Prolonged elevated natural gas prices would take away this advantage and would make competing with fossil based fuels and other renewable fuels more difficult.
3) **Biomass Price Escalation and Sourcing Issues**: As cellulosic biofuel and bioenergy plants become more prevalent, an increase in feedstock demand could cause difficulty in sourcing low cost feedstock. As the supply chain for cellulosic feedstocks is still in its infant stages, it can also be difficult to fully estimate the cost of obtaining large feedstock volumes required for commercial facilities and could drive price volatility.
4) **Financing:** Commercial scale biofuel plants will require a significant capital investment ($100's of millions). The ability to access financing on reasonable terms will be a significant factor in the deployment of cellulosic biofuel facilities, particularly for unproven technologies
5) **Policy Uncertainty:** Sustained governmental biofuel policy provisions are essential to the rapid growth of advanced biofuel technologies like those being developed under this project. The repeal or diminishment of those policies will effectively remove any incentives for the current fuels industry to support biofuels development and commercialization.
6) **Emerging Technologies:** As with all emerging industries, there is a risk that another new technology could become the lowest cost producer.

Technical Risks

The business risks associated with commercial deployment of these technologies are outside of Virent and NREL's control. The key technical risks can be solved with more work and are identified along with mitigation strategies to provide cost effective ash removal, effective carbon utilization within the biomass and enhance feedstock viability.

Task D: Project Management

Subtask D.1: Project Planning

At the outset of the project, several Project Management Plans were put together to form the Integrated Project Plan. There was frequent and transparent reporting to DOE on the project and technical performance. The project team hosted periodic calls and prepared quarterly reports which were shared amongst the team members. Quarterly technical and financial reports were filed with the DOE project team as prescribed in the contract documents and the project team provided DOE with project highlights suitable for public dissemination. Technical and logistical information was prepared for the validation team to validate the Benchmark case, the Intermediate Case, the Stage Gate review, the Final Target case validation, and for project closeout.

The key assets used for communication for this project consisted of a Web-hosted project workspace, email, conference calls, and web meetings. Detailed technical and project reporting took place within the project team members. Reports and other deliverables were provided in accordance with the Federal Assistance Reporting Checklist following the instructions included therein.

Subtask D.2: Reporting & Control

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 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.

Milestone 1: Benchmark Process Validation

The Benchmark Process Validation was performed at the National Renewable Energy Laboratory (NREL) February 6 – 22, 2012 and at Virent in Madison, Wisconsin, March 5 – 9, 2012. The on-site initial validation of Virent's project was deemed successful. The purpose was to confirm the Benchmark performance and cost estimates of Virent's process for producing jet fuel from lignocellulosic biomass. The on-site validation process followed the procedures described in the Validation Plan for biochemical conversion process improvements made under DOE Funding Opportunity Announcement (FOA) DE-FOA-0000337, "Integrated Process Improvements for Biochemical Conversion of Biomass Sugars: From Pretreatment to Substitutes for Petroleum-based Feedstocks, Products and Fuels."

The primary objective of the initial validation was to verify Benchmark experimental data and cost information provided in Virent's proposal TEA tables. Experimentally, the objective was to confirm the performance of Virent's initial jet fuel production process, thus verifying information in the Benchmark columns of the proposal TEA tables to satisfy FOA Technical Merit & Feasibility Requirements – Criterion 1. In terms of costs, the objective was to assess the reasonableness of Virent's process engineering and techno-economic analysis methods and cost estimates and related supporting documentation to confirm the acceptability of the cost information in the Benchmark column of the proposal TEA tables to satisfy FOA Commercialization/Business Plans and Economic Analysis – Criterion 2.

Validation team members established that NREL and Virent facilities for the project were of sufficient size and scope to provide Virent with the requisite capabilities and resources necessary to fulfill the terms of the award. The Virent project team effectively demonstrated to validation team members its benchmarking experiments and thoroughly explained its process costing methodologies. The project personnel were forthright in answering the validation team's many questions and providing additional supporting information or materials when requested. Experiments demonstrated satisfactory reproducibility and analytical data quality, and incorporated appropriate quality control measures and reasonable data rejection criteria.

This initial validation resulted in proposed revisions to Benchmark values and also identified potential changes in intermediate and final targets in the TEA tables that the validation team found to be reasonable and warranted. The suggested revisions to Benchmark performance and future targets were directly based on experimental results obtained during the initial validation coupled with Virent's increased understanding of the conversion process and its economics since the proposal was submitted.

The validation team had several recommendations for Virent to continue to improve confidence in generated experimental data and modeled cost projections for its project. In particular, the validity of data normalization procedures used in working up deconstruction and upgrading data needed to be confirmed, and data reduction processes and key performance calculations needed to be better documented. In addition, a few methods needed to be clarified and several experimental and cost model assumptions needed to be verified. Progress in addressing those recommendations were described in quarterly reports.

Milestone 2: Final Process Validation

The Final Process Validation took place at NREL over the course of February and March 2015 and subsequently at Virent over the first two weeks in April 2015. The Virent portion of the validation consisted of a Virent validation team which performed the work and an NREL/DOE validation team which monitored and documented the work. The NREL and Virent validations repeated the Benchmark case and validated the Final Process configuration case both from an operational and TEA perspective. The Final validation report has yet to be released but early indications are that the validation was a success within acceptable expectations for such a multi-year process development project.

Subtask D.3: Hold Stage Gate Review

A stage gate review was held at NREL in February 2014.

Concluding Remarks

The purpose of this project was to demonstrate the technical and commercial feasibility of producing liquid fuels, particularly jet fuel, from corn stover.

Major accomplishments of the project included:

- Successful integration of NREL's deconstruction technology with Virent's catalytic processing technology.
- Production of a jet fuel product having enhanced properties as compared to conventional and other renewable jet fuels (freeze point, energy density, and stability)
- Reduction in cash cost for generating desired liquid product by ~50% over the length of the project.
- Reduction in capital cost per gallon by >10% from Benchmark case to Final case.
- Development of lower cost catalysts for both catalytic steps utilized by Virent's technology.
- Identification of configurations for the generation of liquid fuels at costs that would meet goals set by DOE's multi-year program plan.

Several challenges were identified that once solved would further improve overall yields and reduce costs.

These challenges include the need for:

- More economical methods to remove catalyst contaminants from the raw biomass and resulting hydrolysate.
- Methods that further reduce or eliminate costs of enzyme in the deconstruction step.
- Materials and reactor configurations that would improve catalyst costs and lifetimes.
- Enhanced carbon yields to liquid products through stabilization and catalytic processing of solubilized lignin components.

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