# **ASPEN MODELING OF THE** NARA CONVERSION PROCESSES

# Authors ORGANIZATION



Washington State University

Tom Spink

Thomas Spink Inc. (TSI)

Allan Gao



Washington State University

# **TABLE OF CONTENTS**

LIST OF FIGURES	03
LIST OF TABLES	03
LIST OF ACRONYMS	04
EXECUTIVE SUMMARY	05
INTRODUCTION	06
TASK 1: INTEGRATED PROCESS MODEL	07
TASK 2: PRETREATMENT ANALYSIS MBS AND OXIDATION	28
TASK 3: CO-PRODUCT MODEL DEVELOPMENT	32
TASK 4: DIRECTION OF PROCESS IMPROVEMENTS	34
NARA OUTPUTS	35
FUTURE DEVELOPMENT	35
REFERENCES	36
APPENDIX	. 37





NARA is led by Washington State University and supported by the Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30416 from the USDA National Institute of Food and Agriculture.



Any opinions, findings, conclusions, or recommen-USDA dations expressed in this publication are those of the author(s) and do not necessarily reflect the view of the U.S. Department of Agriculture.

# **LIST OF FIGURES**

FIGURE NO.	FIGURE TITLE	PAGE NO.
AM-Intro.1	Process block diagram of the NARA biorefinery process and process streams detailed in the mass and energy balance.	06
AM-1.1	Primary steps required in the Feedstock Handling Department.	08
AM-1.2	The primary steps required in the Pretreatment Department	11
AM-1.3	The primary steps required in the enzyme production and enzymatic hydrolysis process.	14
AM-1.4	The primary steps required in the fermentation, separation, and upgrading process.	17
AM-1.5	The primary steps involved with co-product production.	20
AM-1.6	The primary steps involved with distribution.	23
AM-1.7	The primary steps involved with boiler operations.	24
AM-1.8	Essential infrastructure items contained in Utilities Department.	27
AM-2.1	Block flow diagram of the WEx pretreatment system. Figure courtesy of Birgitte Ahring and Philip Teller, WSU BSEL.	29
AM-2.2	Process flow diagram of the mild bisulfite pretreatment process.	30
AM-3.1	Process flow diagram representing the unit operations in the co-products generation process.	33
AM-App1	Aspen process flow diagram of the WEx pretreatment process.	37
AM-App2	Aspen Plus process flow diagram of each WEx reactor system.	38
АМ-Арр3	Mild Bisulfite pretreatment process flow diagram generated in Aspen Plus.	39
AM-App4	Aspen Plus process flow diagram of the SSL evaporation process.	40
AM-App5	Aspen Plus process flow diagram of the activated carbon production process.	41

# **LIST OF TABLES**

TABLE NO.	TABLE TITLE	PAGE NO.
AM-1.1	Major inputs/outputs of the Feedstock Handling Department	08
AM-1.2	Mass and energy balance for Feedstock Handling Department	09
AM-1.3	Major inputs and outputs associated with the pretreatment process	10
AM-1.4	Mass and energy balance for the MBS/SPORL pretreatment process	12
AM-1.5	Major inputs and outputs associated with the enzyme production and saccharification process	13
AM-1.6	Mass and energy balance for the enzyme production and enzymatic hydrolysis process	15
AM-1.7	Major inputs and outputs associated with the Gevo Block	16
AM-1.8	Mass and energy balance for the fermentation, separation, and upgrading process	18
AM-1.9	Major inputs and outputs associated with the co-product development	19
AM-1.10	Mass and energy balance for co-product production	20
AM-1.11	Equipment list for Storage and Distribution	22
AM-1.12	Product distribution at a NARA biorefinery	23
AM-1.13	Mass and energy balance for boiler operations	25
AM-2.1	Process parameters used for CapEx and OpEx estimates of MBS and WEx pretreatments	28
AM-2.2	Tradeoff comparisons between Wet Explosion and Mild Bisulfite processes	31

# **LIST OF ACRONYMS**

AC activated carbon

- ATJ alcohol to Jet
- CAPEX capital expenditure
- LCA Life Cycle Assessment
- MBS Mild Bisulfite
- MMBTU Millions British Thermal Units
- BDMT Bone Dry Metric Tonnes
- OPEX operating expenditure
- SPORL Sulfite Pretreatment to Overcome Recalcitrance of Lignocellulose
- SSL spent sulfite liquor
- TEA Techno-economic Analysis
- WEx Wet Explosion



# **EXECUTIVE SUMMARY**

The Aspen Modeling Team created a process flow diagram and a mass and energy balance for the NARA biorefinery in support of the NARA objective to evaluate the technical and economic feasibility of a biochemical process for the conversion of softwood residual into isoparaffinic kerosene (IPK) product for use as a drop-in jet fuel substitute. Researchers at Washington State University and TSI developed a process model in Aspen Plus (AspenTech, Inc.) and Microsoft Excel using process inputs from other NARA teams. The outputs of this model were used to inform other teams in support of a technoeconomic analysis (TEA) and life cycle analysis (LCA) of the NARA process, as well as examine possible process improvements and process integrations.

In this work, the primary output was a set of process flow diagrams, process parameters, and mass and energy balances, which define the NARA conversion process. The described process begins at the plant gate with the reception of forest residuals and ends with the production of IPK, activated carbon, and lignosulfonate. The process was broken into 8 departments, which include:

- 1. Feedstock Handling Reception of wood residuals, sorting and chipping, and pre-processing storage
- **2. Pretreatment** Chipped wood residuals are pretreated using a calcium bisulfite solution, producing a cellulose-rich pulp and a lignosulfonate rich aqueous stream
- **3. Enzymatic Hydrolysis** Pretreated pulp is broken down by cellulase and hemicellulase enzymes to form monomeric sugars, including glucose and xylose
- **4. Fermentation, Separation, and Upgrading** Sugars obtained after enzymatic hydrolysis are used in Gevo's yeast fermentation process to create isobutanol, which is separated and upgraded into IPK
- 5. Distribution Product and co-product storage prior to shipment
- **6. Co-Product Generation** The lignosulfonate stream was evaporated for use as a concrete additive. Residual cellulose and un-used fiber from the woody biomass is dried and pyrolyzed to form an activated carbon product
- **7. Boiler** A hog fuel boiler is used to provide heat from purchased hog fuel and discarded material from the feedstock sorting process. In addition, a volatile gas boiler is used to combust gas produced by the pyrolysis unit in the co-products department and to generate additional steam.
- 8. Utilities An estimate is provided for various utility items required to support a biorefinery, including process and cooling water supply, wastewater treatment, landfill, administration, and other infrastructure

# **INTRODUCTION**

The Aspen modeling team collected data from various operating NARA teams, including the feedstock procurement teams, pretreatment development teams, and Gevo fermentation team to develop a process model, which can be used to understand the NARA process as a whole. The development of a process model is integral to the calculation of capital cost and operating cost estimates and for the construction of a life cycle analysis of the jet fuel product.

In NARA Year Three, the Aspen Modeling Team was brought into the NARA team and participated in creating process models of two pretreatment processes, the MBS and Wet Oxidation pretreatments and to assist in a phase-gate decision to down-select to a single pretreatment process. The Aspen Modeling Team worked with the teams from Catchlight Energy and Washington State University to assess the benefits and drawbacks of each pretreatment process, providing information, which supported the decision to use the MBS/SPORL pretreatment.

In NARA Year Four, work progressed on the development of the integrated biorefinery model and report, with the process overview being finalized as depicted in Figure AM-Intro.1. At the end of the year, the process model and outputs were distributed to the LCA and environmental emissions teams, with outputs being used to assist in the development of CAPEX and OPEX estimates.

In NARA Year Five, the integrated biorefinery model was finalized, and an assessment of alternate production strategies was assessed, including a preliminary analysis of a distributed sugar depot system and the wood milling pretreatment.



Figure AM-Intro.1. Process block diagram of the NARA biorefinery process and process streams detailed in the mass and energy balance.

# TASK 1: INTEGRATED PROCESS MODEL AND NARA BIOREFINERY REPORT

# OBJECTIVE

The objective was to gather process data from the NARA experimental teams and create a process model in Aspen Plus for each of the major departments outlined in Figure AM-1.1. A mass and energy balance was to be created for each department and integrated to form a biorefinery model.

# METHODOLOGY

## **Aspen Plus Properties**

The Aspen Plus thermodynamic properties and model was set up based on thermodynamic properties obtained from the 2011 NREL model (Humbird et al., 2011) for biomass components, including cell mass, enzyme, glucan, xylan, and mannan. Activity coefficients were calculated according to the non-random two-liquid (NRTL) model. The Aspen Plus Software (Aspen Plus v8.6) includes property databases for standard chemicals, such as water, calcium carbonate, and ammonia, which were used in the model.

## Data collection

The data used in the creation of the process model was collected from NARA teams conducting research on feedstock procurement, pretreatment, and conversion. This data was obtained through e-mail request to the teams. The Aspen Modeling Team did not originate any of the experimental data used in the process model.

## Vetting/Internal Review

The process models and outputs, using data obtained from the other NARA teams, were shared with the teams, which originally provided the data to verify accuracy. In addition, the integrated model was shared and reviewed at the 2015 NARA annual meeting by NARA members. The sources from which the Aspen Modeling Team gathered data with are:

- Feedstock Handling Weyerhaeuser/Catchlight Energy, Oregon State University (John Sessions)
- Pretreatment Mild Bisulfite/SPORL Catchlight Energy (Johnway Gao & Dwight Anderson), USDA Forest Service (J.Y. Zhu), Wet Oxidation WSU (Birgitte Ahring)

- Enzymatic Hydrolysis Based on NREL 2011 model for enzyme production and saccharification
- Fermentation, Separation, Upgrading The process details for these operations was provided by Gevo
- Co-Products Activated Carbon WSU (Ian Dallmeyer), Lignosulfonate TSI (Tom Spink)
- Utilities, Distribution, Wastewater Treatment NREL 2011 model and secondary literature review by WSU (Allan Gao, Kristen Brandt)

## RESULTS

The results stated below are a process description of each department, followed by the primary learnings obtained from each of the department process models. This results section will briefly explain the process steps in each department followed by a summary of mass and energy flows

## **Results Layout**

Each department was given a process description, a mass and energy balance, a capital expenditure estimate, an operating expenditure estimate, and an environmental considerations page, which listed possible environmental emissions or flow streams not explicitly accounted for in the process model.

## FEEDSTOCK HANDLING

The Feedstock Handling Department (FHD) receives truckloads of forest residuals (FR) at the entrance to the Integrated Bio Refinery (IBR) and processes the FR feedstock into the appropriate size for pretreatment (1/8" – 3/4"). The department includes systems to weigh, sample, record data, and unload truckloads of FR. It also includes storage equipment to hold unscreened FR large enough to protect the IBR from shutdown due to short-term lack of supply or to take advantage of large supply surges in the summer. Because the unscreened FR includes fines that are high in ash and chunks that are too large for pretreatment, a fines/overs screen and overs chipper are included in this department. The fines are conveyed to the IBR hog fuel boiler and the overs are re-chipped and placed back into the fines/overs screen. A 500-ton self-unloading fines storage prior to the hog fuel boiler and a 5000 ton self-unloading pretreatment feedstock storage are included in this department as well as all conveyors supplying FR to the pretreatment department. All germane conveyors and ancillary equipment is sized for 2200 BDTPD FR delivered to pretreat-

#### ment with inbound FR sized at 2400 BDTPD.

Also included in the department is a system to weigh, sample, record data, unload, and store purchased hog fuel. The entrance and weighing system for hog fuel will use the same system as forest residuals. There will be a dedicated system to unload hog fuel trucks as well as a covered hog fuel storage area. All hog fuel conveyors and those to the hog fuel boiler are included in this department. The major inputs and outputs of the Feedstock Handling Department are listed in Table AM-1.1.

The hog fuel and fines, which is woody material (but not waste) screened from the chipped biomass, are used in the hog fuel boiler to generate steam for the biorefinery. Figure AM-1.1 illustrates the primary steps required in the Feedstock Handling Department.

#### Table AM-1.1. Major inputs/outputs of the Feedstock Handling Department

Inputs	Amount	Unit
Forest Residuals	840,000	BDST/yr
Hog Fuel	250,000	BDST/yr
Electricity	3.2	MW
Outputs		
Screened & Chipped Biomass	770,000	BDST/yr
Fines for Boiler	70,000	BDST/yr



Figure AM-1.1. Primary steps required in the Feedstock Handling Department.

### **Process Steps**

- 1. Truckloads of FR are weighed (in and out), sampled, and data recorded to correctly pay suppliers.
- 2. Multiple truck dumps are employed to unload up to 66,000 truckloads per year.
- 3. An unscreened FR storage pile of 30 days is employed with appropriate conveyors.
- 4. A fines/overs screen with a chipping of the overs via a 200 HP overs chipper.
- 5. A 500 ton fines to hog fuel boiler self-unloading storage
- 6. A 5000 ton FR accepts to pretreatment self-unloading storage
- 7. Purchased hog fuel is weighed, sampled, data recorded to correctly pay suppliers.
- 8. Truckloads of hog fuel are unloaded in dedicated end dumps.
- 9. Hog fuel is stored in a 30 day storage located adjacent to the FR 30 day storage.
  10. Hog fuel is conveyed to the Hog fuel boiler.

### Mass and Energy Balance

A mass and energy balance based on input from the NARA forestry teams was constructed and presented in Table AM-1.2. Forest residuals contain polymeric carbohydrate in the form of glucan, xylan, arabinan, etc., which can be converted into monomeric sugar (glucose, xylose) which can be utilized in fermentation. The purpose of the feedstock handling department is to collect and process enough sugar containing forest residual for downstream conversion into sugar, which can be consumed by yeast in fermentation to create isobutanol. The carbohydrate content of the NARA feedstock is approximately 60%. In addition to the forest residuals, hog fuel is brought into the NARA refinery to run the hog fuel boiler and generate steam. 40 wet tons per hour of hog fuel are consumed, in addition to 9-10 tons per hour of forest residual fines which are of too low quality to be used in pretreatment.

The energy input required for the Feedstock Handling Department is in the form of electricity, which is required to operate the conveyers, truck dumps, and chipper, among other equipment.

### **Environmental Considerations**

In addition to the modeled mass flows, there are additional waste materials that are present in the feedstock handling which may have an environmental impact. These include:

1. Rain runoff into the mill sewer system. The Feedstock Handling Yard will collect rain runoff for treatment prior to discharge to local receiving waters. This runoff will contain waste material from the refinery site, including chemicals, oils, and solid material. For the estimated 50-acre plant site with an average of 40 inches rainfall per year, the amount of rainwater that needs to be treated is equal to Table AM-1.2. Mass and energy balance for Feedstock Handling Department: A) mass and energy balance, B) schematic showing directional flow for each component listed in (A).

Feedstock Handling										
Component	1	2	3	4	5					
	Forest Residual	Hog Fuel	Fines to Boiler	Residual to Pretreatment	Electricity					
Water	67.2	10.0	6.0	61.1						
Glucan	41.0	-	3.7	37.3						
Xylan	5.4	-	0.5	4.9						
Arabinan	1.2	-	0.1	1.1						
Galactan	2.9	-	0.3	2.7						
Mannan	11.5	-	1.0	10.5						
Ash	0.5	-	0.0	0.4						
Insoluble Lignin	28.5	-	2.6	25.9						
Soluble Lignin	0.5	-	0.0	0.4						
Bark	3.5	-	0.3	3.2						
Extractives	5.7	-	0.5	5.2						
Hog Fuel	-	30.0	-	-						
Air	-	-	-	-						
Steam	-	-	-	-						
Elec. (MWhr)	-	-	-	-	3					
Subtotal BDT	101	30	9	92						
BDT/yr	846,059	252,000	76,145	769,914						
Total tons	101	30	9	92						
Total tons/yr	846,059	252,000	76,145	769,914						





151,000 gallons of rainwater per day, or 55.1 million gallons/yr.

- 2. Miscellaneous dust from fine wood particles and road dust. The processing and unloading of forest residuals will generate a significant amount of wood and road dust. This can be partially handled through periodic spraying of the plant area during dry periods for dust suppression.
- 3. Noise from conveyors, mechanical equipment, and mobile equipment
- 4. Debris that may need to be hauled to landfill occasionally. This includes waste material that is sorted prior to chipping and preparation for the pretreatment system.

# PRETREATMENT

The Pretreatment Department uses a calcium bisulfite-based pretreatment liquor, known as the mild bisulfite (MBS) or sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL) process. The pretreatment process occurs at 145 °C at a residence time of 240 minutes and a 4:1 liquor to wood (L/W) loading. The pretreatment department produces two streams: (1) a pulp stream containing the solid carbohydrates and lignin, and (2) an aqueous stream containing soluble monomeric sugars and soluble lignosulfonate, termed the spent sulfite liquor (SSL) stream.

The pulp stream is used in enzymatic saccharification to produce sugar for fermentation, and the spent sulfite liquor is fermented to make use of the soluble sugar, and then processed to become the lignosulfonate product. Major inputs and outputs associated with the pretreatment process are shown in Table AM-1.3. Figure AM-1.2 illustrates the primary steps required in the Pretreatment Department. Approximately 20% of the input mass is solubilized during the pretreatment process, resulting in a lower mass entering enzymatic saccharification than entered. This mass is primarily soluble sugar and lignin in the SSL stream.

### Table AM-1.3. Major inputs and outputs associated with the pretreatment process.

Inputs	Amount	Unit
Screened & Chipped Biomass	770,000	BDST/yr
Calcium Carbonate	27,320	BDST/yr
Sulfur	27,720	BDST/yr
Process steam	116,000	Lbs/hr
Outputs		
Pretreated pulp	606,000	BDST/yr

## **Process Steps**

### **Chemical Production**

- 1. Liquid sulfur is purchased from Pacific Northwest oil refineries and transported in specialty-insulated trucks. A steam heated liquid sulfur tank and steam heated lines are required.
- 2. Liquid sulfur is burned to SO2 under controlled conditions to minimize sulfite and sulfate formation. Sulfur is burned at a 10:1 air to sulfur ratio at 1300 0C to form SO2. The combustion gases, which contain SO2, nitrogen, and small amounts of excess air, are used to generate steam and then contacted directly in the acid adsorption tower.
- 3. A sulfur boiler generates steam (42,600 lbs/hr) from the cooling of the SO2. This is then followed by a cooling tower to further cool and condition the SO2 for entry into the calcium bisulfite acid preparation absorption column.
- 4. Granular calcium carbonate is sourced from mines in the PNW and delivered to plant site by truck, rail, or barge.
- 5. Granular calcium carbonate is mixed with water and combined with the SO2 gas mixture in the acid preparation absorption column. Calcium carbonate is pumped to the top of the column and SO2 enters at the bottom below the first absorption plate. A liquid settling tank is used to settle the acid solids and the cleaned acid is then pumped to the cold acid tank. Carbon dioxide and residual combustion air is vented from the top of the acid absorption column.
- 6. The calcium bisulfite solution is the cooking acid that will be used in pretreatment.

### Pretreatment & Washing

- 1. The cold cooking acid goes through a preheating system where flash vapors (SO2, steam, and volatiles) from the continuous digester are condensed in a 2-stage heat. It is estimated that 50% of the flash energy can be recovered and recycled directly back to the continuous digester by heating the cold acid. The remaining digester's vapor energy is directed to an internal plant hot water recovery system and on to the pretreatment vent scrubbing system.
- 2. The heated cooking acid then enters the digester alongside the softwood residual chips.
- 3. The continuous reactor holds the forest residual chips for 4 hours at 145  $^\circ\text{C}.$
- 4. The forest residual chips exit the reactor through a disk refiner and into a flash tank.
- 5. The flash vapors are used for heat recovery as described in item 1 above.
- 6. The solids from the digester flash tank are recovered and pumped to a multi stage countercurrent washer.
- 7. The countercurrent washer removes 95% of soluble solids, and these soluble solids are sent directly to fermentation. The soluble solids stream consists primarily of sugar, extractives, cooking acid, and lignosulfonate.
- 8. The insoluble solids, termed pulp, is sent to a high-density pulp storage tank and then pumped to the enzymatic hydrolysis department.

### Mass and Energy Balance

A mass and energy balance for the MBS/SPORL process, based on input from the Catchlight Energy and USDA Forest Service, was constructed and is presented in Table AM-1.4.

During the course of pretreatment, the harsh conditions in the pretreatment reactor will break down some of the carbohydrate content in the wood and release monomeric sugar. In addition, some of the lignin in the wood is solubilized and will react with the sulfur compounds in the pretreatment liquor to form a lignosulfonate compound. The soluble sugar and lignosulfonates make up the majority of stream 6, termed "spent sulfite liquor". This liquor contains fermentable sugars, which are used in the fermentation process, and the liquor remnants are processed to make the lignosulfonate co-product.

The pretreated pulp contains the solid portion of the forest residuals, which remains after pretreatment. This pulp has significantly reduced lignin content and is much less recalcitrant compared to the original wood. The treated pulp is sent to enzymatic hydrolysis for digestion into monomeric sugar.

#### **Environmental Considerations**

In addition to the modeled mass flows, there are additional waste materials that are present in the pretreatment department, which may have an environmental impact. These include:



Figure AM-1.2. The primary steps required in the Pretreatment Department

#### Air Discharge

The atmospheric discharge from the pretreatment department includes flows from three separate unit operations that are all combined and directed to a water/caustic scrubber. The vent from this water- caustic scrubber is the single air discharge from the pretreatment department. The unit operations that flow to the pretreatment water-caustic scrubber are described as follows:

- 1. The first of these is the combustion gases from the burning of sulfur to produce sulfur dioxide.
- 2. The second is the carbon dioxide produced from the reaction of calcium carbonate with sulfur dioxide in an aqueous absorption tower.
- 3. The third gas stream is the residual volatile and inert gases remaining from the digester blow gases after the blow gases have been direct contact cooled in the

Table AM-1.4. Mass and energy balance for the MBS/SPORL pretreatment process: A) mass and energy balance, B) schematic showing directional flow for each component listed in (A). Component 59 (Steam Out) not shown in (B).

					Pretreatmer	nt								Caustic
Component	4	5	8	9	10	6	45	6 46	47	59	9 60	$ \mathbf{R} $	-	60
	Forest Residuals	Pretreated Pulp	Sulfur	Calcium Carbonate	Pretreatment Combined Vent	Spent Sulfite Liquor	Electricity	Steam In	Process Water	Steam Out	Caustic In		-	Sulfur 8
Water	61.1	142.6	-	-	1.3	247.8	-	-	321.5	-	-		-	CaCO3 10
CWS/CWR	-	-	-	-	-	-	-	-	3,030.0	-	-			9
Glucan	37.3	35.4	-	-	-	-	-	-	-	-	-			× 1
Xylan	4.9	2.6	-	-	-	-	-	-	-	-	-			
Arabinan	1.1	0.7	-	-	-	-	-	-	-	-	-		Wood	MBS
Galactan	2.7	1.4	-	-	-	-	-	-	-	-	-		4	Pretreat
Mannan	10.5	5.7	-	-	-	-	-	-	-	-	-			
Ash	0.4	0.4	-	-	-	-	-	-	-	-	-			
Insoluble Lignin	25.9	18.5	-	-	-	-	-	-	-	-	-			
Soluble Lignin	0.4	1.7	-	-	-	10.9	-	-	-	-	-			
Bark	3.2	3.2	-	-	-	-	-	-	-	-	-			
Extractives	5.2	0.7	-	-	-	4.6	-	-	-	-	-			45
Glucose	-	0.3	-	-	-	1.8	-	-	-	-	-			e Stm 47
Xylose	-	0.3	-	-	-	2.3	-	-	-	-	-			Water
Arabinose	-	0.1	-	-	-	0.4	-	-	-	-	-			ii
Galactose	-	0.2	-	-	-	1.2	-	-	-	-	-			
Mannose	-	0.7	-	-	-	4.6	-	-	-	-	-			
CaCO <sub>3</sub>	-	-	-	3.3	-	-	-	-	-	-	-			
Sulfur	-	-	3.3	-	-	-	-	-	-	-	-			
Bisulfite	-	0.2	-	-	-	1.4	. –	-	-	-	-			
SO2	-	-	-	-	0.0	-	-	-	-	-	-			
Steam (klb)	-	-	-	-	-	-	-	158.6	-	42.6	5 -			
Elec. (MWhr)	-	-	-	-	-	-	18.0	) -	-	-	-			
Acetic Acid	-	0.3	-	-	-	-	-	-	-	-	-			
Furfural	-	0.2	-	-	-	-	-	-	-	-	-			
CO2	-	0.0	-	-	0.8	-	-	-	-	-	-			
NaOH	-	-	-	-	0.13	-	-	-	-	-	0.1			
Subtotal BDT	91.7	72.2	3.3	3.3	-	27.1	. –	-	-	-	-			
BDT/yr	769,914	606,564	27,720	27,300	-	227,825	-	-	-	-	-			
Total	153	215	3	3	-	275	-	-	-	-	-			
Total tons/yr	1,283,238	1,803,984	27,720	27,300	) –	2,309,320	- (	-	-	-	-			



cold acid stream and then cooled in indirect cold water system heat exchangers. This third steam is a very small flow but worthy of collecting. The pretreatment vent scrubber consumes approximately 100 gpm of process water and 3.0 tons per day of caustic (NaOH)

#### Water Discharge

The water discharge from the pretreatment department includes only miscellaneous wash-down water and the discharge from the vent scrubber mentioned above.

#### Solid Waste Discharge

The calcium carbonate raw material is 1 to 3% inert. This inert material does not react with SO2/water in the absorption tower and needs to be wasted from the acid plant screen and settling basin. This material will be hauled to landfill. The quantity of this discharge will be between 273 and 819 tons per year.

## ENZYME PRODUCTION AND SACCHARIFICATION

In this department, cellulolytic enzymes, namely cellulase and hemicellase, are produced by filamentous fungi consuming glucose and other media nutrients, including ammonia and corn steep liquor, in an aerobic culture. The produced enzymes are then used to break down polymeric carbohydrate in lignocellulose, such as glucan, xylan, and mannan, to create monomeric sugar (glucose, xylose, mannose) that can be consumed by the microorganisms in fermentation.

The saccharification process takes place at 50°C and over 72 hr, during which between 80-85% of the carbohydrate is broken down into sugar. This breakdown continues into the fermentation process, for an estimated total recovery of about 92%. Major inputs and outputs associated with the enzyme production and saccharification process are shown in Table AM-1.5. Figure AM-1.3 illustrates the primary steps required in the enzyme production and enzymatic hydrolysis process.

### **Process Steps**

### **Enzyme Production:**

- 1. Under a license from a respected enzyme company, glucose, SO2, corn steep liquor, ammonia, and water are used in an enzyme fermenter seed train to produce a dense culture of Trichoderma reesei (or other fungal strain capable of producing enzymes) for the production of cellulase and hemicellulase enzymes. The total enzyme loading is 0.044g/g pretreated solids (4.4% (w/w)).
- 2. The fungal strain producing the enzyme produces a large quantity of carbon dioxide, which is exhausted to the fermentation CO2 scrubber.
- 3. The seed fungal culture is inoculated into a larger enzyme production reactor and is induced with sophorose, which begins enzyme production.

 ${\sf Table \, AM-1.5. \, Major \, inputs \, and \, outputs \, associated \, with \, the \, enzyme \, production \, and \, saccharification \, process$ 

Inputs	Amount	Unit		
Pretreated pulp	606,000	BDST/yr		
Produced enzyme	26,000	TPY, 22.5% protein titer		
Outputs				
Glucose	273,000	BDST/yr		
Fermentation residual solids	300,000	BDST/yr		

4. The produced enzyme broth is filtered to remove fungal biomass and used directly in large batch saccharification. Produced enzyme is stored in a tank for use in enzymatic saccharification.

5. The produced enzyme is separated from fungal biomass through a filtration step. The fungal biomass is discarded.

6. The enzyme production plant is required to be sterile to maintain the quality and dependability of the enzyme production process.

#### **Enzymatic Hydrolysis:**

- 1. The pulp stream from pretreatment (80°C, 1.8 pH and 30% consistency) is mixed with water to reach a consistency of 15% and cooled to 50°C, and pH is adjusted by lime to a pH of 5.0. This cooling and pH adjustment is accomplished in an indirect cooled paddle or auger contactor. The cooling water system (CWS) is utilized as the coolant.
- 2. The enzymes are mixed with the pulp at a loading of 4.4% enzyme on biomass in the later stages of the paddle cooler indicated in item 1 and sent to a set of eight saccharification reactors. The saccharification is performed via batch mode.
- 3. The exothermic reaction in saccharification aids in maintaining the reactor temperature. According to the exothermic reaction, a small amount of cooling is required to maintain the reactor temperature at 50°C.
- 4. The hydrolyzed pulp is sent directly to Gevo-based fermentation. The hydrolyzed pulp contains approximately 10% (w/w) monomeric sugars, with significant residual fibers (up to 6% w/w), and the consistency of the solution is similar to a slurry.
- 5. The saccharified solution is stored in a large storage tank prior capable of 12 hours of storage prior to Gevo-based fermentation.

### Mass and Energy Balance

A mass and energy balance for the enzymatic hydrolysis department, consisting of enzyme production and saccharification, was constructed and shown in Table AM-1.6.

Components 11 through 15 are media reagents required to feed the fungal biomass, which creates the cellulase and hemicellulose enzymes. The media is fed to an aer-

obic reactor, which contains the fungal strains, and enzyme is produced continuous and sent to a holding tank. The enzyme is then mixed with the incoming pretreated pulp and placed in enzymatic saccharification for 48 to 60 hours.

Component 16 represents the digested forest residual pulp leaving the enzymatic hydrolysis stirred tank reactors. The hydrolysate consists of monomeric sugar, un-

digested carbohydrate, lignin, and remaining enzyme. The entirety of this stream, which has a consistent similar to a slurry, is used in the fermentation process.

The enzyme production process results in the production of some CO2, which is vented to the atmosphere, represented by component 62.



Figure AM-1.3. The primary steps required in the enzyme production and enzymatic hydrolysis process.

#### Table AM-1.6. Mass and energy balance for the enzyme production and enzymatic hydrolysis process: A) mass and energy balance, B) schematic showing directional flow for each component listed in (A).

				Enz	ymatic S	accharit	ication					
Component	5	11	12	13	14	15	48	49	16	55	56	62
	Pretreated	Corn Steep								Fungal	Process	Saccharification
	Pulp	Liquor	Glucose	Lime	NH3	\$02	Electricity	Steam	Hydrolysate	Biomass	Water	Vent
Water	142.6	-	0.6	-	-	-	-	-	380.0	3.1	226.2	0.1
Glucan	35.4	-	-	-	-	-	-	-	6.4	-	-	-
Xylan	2.6	-	-	-	-	_	-	-	0.5	-	-	-
Arabinan	0.7	-	-	-	-	-	-	-	0.1	-	-	-
Galactan	1.4	-	-	-	-	-	-	-	0.3	-	-	-
Mannan	5.7	-	-	-	-	-	-	-	1.0	-	-	-
Ash	0.4	-	-	-	-	-	-	-	0.4	-	-	-
Insoluble Lignin	18.5	-	-	-	-	-	-	-	18.6	-	-	-
Soluble Lignin	1.7	-	-	-	-	-	-	-	1.6	-	-	-
Bark	3.2	-	-	-	-	_	-	-	3.2	-	_	-
Extractives	0.7	-	-	-	-	-	-	-	0.7	-	-	-
Chucasa	0.2		2 2						22.2			
Giucose Vuloco	0.3	-	5.2	-	-	-	-	-	2.2	-	-	-
Arabinoso	0.3	-	-	-	-	-	-	-	2.0	-	-	-
Arabinose Calastasa	0.1	-	-	-	-	-	-	-	0.7	-	-	-
Galactose	0.2	-	-	-	-	-	-	-	1.5	-	-	-
iviannose	0.7	-	-	-	-	-	-	-	5.8	-	-	-
Lime	-	-	-	0.5	-	-	-	-	-	-	-	-
NH3	-	-	-	-	0.2	-	-	-	0.0	-	-	0.0
CSL	-	0.2	-	-	-	-	-	-	-		-	-
SO2	-	-	-	-	-	0.0	-	-	0.0	-	-	0.0
Enzyme	-	-	-	-	-	-	-	-	1.0	-	-	-
Fungal Biomass	-	-	-	-	-	-	-	-	-	0.8	-	-
Bisulfite	0.2	_	_	-	-	_	-	-	0.2	-		_
Steam (klb)	-	_	-	-	-	_	-	1.0	-	-	_	_
Flec (MWhr)	-	_	-	-	-	_	23	-	_	-	_	_
Acetic Acid	03	_	_	-	_	_	_	_	_	_	_	_
Furfural	0.3	-	-	-	-	_	-	-	0.2	-	_	_
CO2	0.0	-	-	-	-	-	-	-	0.0	-	-	1.9
Iotal BDT	72.2	0.2	3.2	0.5	0.2	0.0	-	-	76.8	-	-	-
BDT/yr	606,564	1,848	26,775	4,368	1,260	168	-	-	645,036	-	-	-
Total	214.8	0.2	3.2	0.5	0.2	0.0	-	-	456.8	-	226.2	-
Total tons/vr	1,803,984	1848	26775	4368	1260	168	-	-	3,837,070	-	1,899,996	-





### **Environmental Considerations**

Additional streams, which are produced by enzymatic saccharification and would need handling in a commercial plant, include:

Air – There is a vent stack that discharges carbon dioxide as a result of the enzyme production. This stream is vented through the enzyme production vent.

Water – The water-caustic scrubber will discharge water (estimated to be 100 gpm) to wastewater treatment.

Solids – The fungal biomass produced as a byproduct of the enzyme production process is separated with a belt press and sent to landfill. A possibility is to send the fungal biomass to the anaerobic digestion process. The fungal species is likely to be a genetically modified organism (GMO) and discharge into wastewater or landfill would have to comply with local and/or federal guidelines.

## FERMENTATION, SEPARATION, AND UPGRADING

The Gevo process consists of three major processes:

- 1. fermentation of softwood-derived sugar into isobutanol;
- 2. separation and purification of the isobutanol; and
- 3. dehydration, oligomerization, and hydrogenation of isobutanol into iso-parafinnic kerosene (IPK).

IPK is a mixture of C12 and C16 alkane hydrocarbons, which can act as a drop-in substitute for jet fuel. The unit operations in this process was designed by Gevo, using input provided by the upstream models of pretreatment and enzymatic hydrolysis, which were designed by the WSU Aspen team. In order to maintain confidentiality of Gevo technology, process details will not be stated in this report. A general process description will be provided along with the overall mass and energy balance of the Gevo operation.

The sugar obtained from enzymatic saccharification is fermented by Gevo's proprietary yeast, which produces isobutanol. The fermentation process occurs at 34 °C and a pH of 4.3 for a period of 48 hours. The isobutanol in the fermentation broth is recovered through use of distillation and then used in an alcohol-to-jet (ATJ) conversion process. The fermentation residuals, which are present in the bottoms of the distillation column, termed FRS, are used in the co-products process to create activated carbon.

The alcohol-to-jet process for the conversion of isobutanol to a long chain hydrocarbon jet fuel is similar to the process for conversion of ethanol to jet fuel. The steps involve dehydration of the alcohol through high temperature removal of the alcohol group to form isobutylene and then a catalyzed process, which reacts units of isobutylene in a chain lengthening reaction to form an unsaturated hydrocarbon. In the final step, hydrogen is used to saturate the molecule resulting in a saturated hydrocarbon with a chain length of C12 to C16.

The estimated yield of IPK from this process is 36 million gallons per year, corresponding to a yield of 46.7 gallons per BDST of input wood (Table AM-1.7).

Table AM-1.7. Major inputs and outputs associated with the Gevo Block.

Inputs	Amount	Unit		
Monomeric Sugar (from SSL)	80,000	BDST/yr		
Monomeric Sugar (from hydrolysate)	390,000	BDST/yr		
Outputs				
IPK	36.0	MM gal/yr		

### Process Steps

- 1. The saccharified pulp biomass containing C6 and C5 sugars, residual unreacted cellulose fibers, and non-sulfonated lignin are used in fermentation by a Ge-vo-GMO yeast to produce isobutanol. The saccharified pulp biomass is produced by the enzymatic hydrolysis department.
- 2. The spent sulfite liquor (SSL) biomass stream containing C5 and C6 sugars is also used in fermentation by a Gevo-modified yeast to produce isobutanol. The spent sulfite liquor is produced by the pretreatment department. The SSL sugars are fermented by the Gevo-GMO yeast to isobutanol separately from the pulp saccharified sugars.
- 3. The fermentation process requires up to 48 hours at 34 °C and a pH of 4.3. Both the SSL sugar stream and the pulp saccharified sugar stream are cooled by indirect cooling from 80°C and 50°C respectively to 34°C. The SSL sugars are adjusted in pH by lime from a pH of 1.8 to a pH 0f 4.3. The pulp saccharified biomass is adjusted from a pH of 5.0 to 4.3 by sulfuric acid.
- 4. The fermentation process is estimated to produce 25.6 TPH of carbon dioxide.
- 5. The separation and purification of the isobutanol from the SSL solution and the pulp biomass stream is done according to Gevo patented processes.
- 6. The SSL stillage and pulp biomass fermentation residual stillage is transferred to the co-products department at 100°C and 7% and 9% solids respectively.
- 7. The separated and purified isobutanol is dehydrated, oligomerized, hydrogenated, and the IPK is purified according to Gevo demonstrated principals and process.
- 8. The model predicts a production of 36.2 million gallons of IPK per year. The produced IPK is sent to the distribution department.





Figure AM-1.4. The primary steps required in the fermentation, separation, and upgrading process.

#### Table AM-1.8. Mass and energy balance for the fermentation, separation, and upgrading process: A) mass and energy balance, B) schematic showing directional flow for each component listed in (A).

Component	c	10	17	10	24	25		20	50	<b>F1</b>	53	F 2
component	Cnont Sulfito	10	1/ Other	18 Combined	24	25	27	28	50	Drocorc	52	55
	Liquor	Hydrolysate	Chemicals	Vent	Wastewater	ІРК	SSL Stillage	FRS Stillage	Electricity	Water	Steam	Natural Gas
Water	267.3	359.3	-	3.3	1.1	-	260.4	444.4	-	0.9	-	-
Glucan	-	6.4	-	-	-	-	-	1.2	-	-	-	-
Xylan	-	0.5	-	-	-	-	-	1.2	-	-	-	-
Arabinan	-	0.1	-	-	-	-	-	1.2	-	-	-	-
Galactan	-	0.3	-	-	-	-	-	1.2	-	-	-	-
Mannan	-	1.0	-	-	-	-	-	1.2	-	-	-	-
Ash	-	0.9	-	-	-	-	-	0.9	-	-	-	-
Insoluble Lignin	-	18.5	-	-	-	-	0.0	18.5	-	-	-	-
Soluble Lignin	9.6	1.3	-	-	-	-	9.6	1.5	-	-	-	-
Bark	-	3.2	-	-	-	-	-	3.2	-	-	-	-
Glucose	1.8	32.1	-	-	-	-	0.4	0.9	-	-	-	-
Xylose	2.3	2.6	-	-	-	-	0.4	0.9	-	-	-	-
Arabinose	0.4	0.7	-	-	-	-	0.4	0.9	-	-	-	-
Galactose	1.2	1.4	-	-	-	-	0.4	0.9	-	-	-	-
Mannose	4.7	5.7	-	-	-	-	0.4	0.9	-	-	-	-
Protein	-	1.4	-	-	-	-	1.4	3.3	-	-	-	-
Acetic Acid	0.9	0.3	-	-	-	-	0.9	0.3				
Furfural	0.1	0.2	-	-	-	-	0.1	0.2				
Other Solubles	8.4	0.8	-	-	-	-	8.4	0.8				
Steam (klb/hr)	-	-	-	-	-	-	-	-	-	-	270.0	-
Elec. (MWhr)	-	-	-	-	-	-	-	-	22.0	-	-	-
Nat. Gas (MM BTU/hr)	-	-	-	-	-	-	-	-	-	-	-	56.5
VOC	-	-	-	0.1	-	-	0.9	2.4	-	-	-	-
CO2	-	-	-	31.9	-	-	-	-	-	-	-	-
Mixed Input	-	-	\$0.45/gal	-	-	-	-	-	-	-	-	-
IPK	-	-	-	-	-	13	-	-	-	-	-	-
Subtotal BDT	29	77	-	-	-	13	23	39	-	1	-	-
BDT/yr	246,011	648,648	-	-	-	112,980	189,084	331,128	-	7,350	-	-
Total tons	297	437	-	-	-	13	283	484	-	1	-	-
Total tons/yr	2,490,911	3,666,936	-	-	-	112.980	2,376,276	4.063.920	-	7,350	-	-



# CO-PRODUCTS

### **Activated Carbon Process**

The activated carbon process produces a powdered activated carbon product, which can be used for a variety of adsorption related applications. In the modeled process, activated carbon is produced from fermentation residual solids (FRS), which is primarily composed of undigested woody residuals (cellulose, lignin, hemicellulose, ash and extractives), and cell mass from fermentation.

Initially, excess moisture is removed from the FRS by use of a belt press and dryer, which is required prior to use of the FRS in a pyrolysis process. The pyrolysis of FRS is performed in a rotary kiln reactor at 700 °C for 1 hr. under an oxygen-free environment. An inert carrier gas, typically nitrogen, is used to carry pyrolysis vapors, which are produced from the more volatile components of the FRS away from the reactor. These pyrolysis vapors are combusted in the volatile gas boiler for heat generation. The residual mass in the reactor after the pyrolysis reaction is a biochar, which is enriched in carbon (70-80% carbon by mass), and represents about 40% of the mass of the input FRS. The biochar is used in a second reaction at 700 °C for 1 hr. which is designed to consume carbon through reaction of carbon with carbon dioxide at elevated temperatures to form carbon monoxide, also known as the Boudouard reaction. This reaction results in the formation of micro and meso-pores in the biochar, increasing the surface area, and 'activating' it. The formed product is activated carbon. The yield of activated carbon from FRS is between 20-25 wt.%.

### **Lignosulfonate Process**

During the course of the mild bisulfite pretreatment, bisulfite ions (HSO3-) from the pretreatment liquor react with lignin present in the biomass. In the acidic environment of the pretreatment process (pH 2.0 or less), an acid catalyzed cleavage of lignin ether bonds occurs, resulting in the substitution of a bisulfite group onto the lignin side chain, forming a lignosulfonate product.

Lignosulfonates are primarily used as plasticizers in the concrete industry, where addition of lignosulfonate into the concrete mixture improves the plasticity of the concrete at low water addition, which improves concrete strength.

In the NARA process, a significant amount of lignosulfonate is produced during the pretreatment reaction and is present in soluble form in the pretreatment liquor or spent sulfite liquor (SSL). The SSL stream contains a significant amount of sugar as well and is used in fermentation prior to being processed into a saleable lignosulfonate product. Major inputs and outputs associated with the co-product development are shown in Table AM-1.9. The primary steps involved with co-product production are presented in Figure AM-1.5.

#### Table AM-1.9. Major inputs and outputs associated with the co-product development.

Inputs	Amounts	Units		
AC: Nitrogen	200,000	BDST/yr		
AC: CO <sub>2</sub>	50,000	BDST/yr		
Outputs				
Activated Carbon	66,000	BDST/yr		
Lignosulfonate	200,000	50 wt.% short tons/yr		

### **Process Steps**

#### **Spent Sulfite Liquor**

- 1. The spent sulfite liquor, obtained from washing of the pretreatment solids, is pumped in to the vapor recompression evaporators (VRE).
- 2. The VRE units evaporate the SSL until it reaches 50% solids.
- 3. The evaporator condensate is discharged directly to wastewater treatment.
- 4. The pH of the SSL is adjusted to 6.5.
- 5. The 50% SSL solution is intended for sale as a concrete additive.

#### **Activated Carbon**

- 1. Fermentation residual solids are obtained from Gevo and excess water is initially removed through a belt press.
- 2. The excess water is directly discharged to wastewater treatment and contains small amounts of sugar as well as organic acids and furfural.
- 3. Residual water in the FRS is removed through a dryer.
- 4. The dry FRS is placed into a rotary kiln reactor for pyrolysis at 700 °C for 1 hour. The reactor is fed with a nitrogen carrier gas at a 1:1 nitrogen to solid mass ratio.
- 5. The generated pyrolysis vapors are burned in a multi-fuel boiler to generate heat and steam for the process.
- 6. The pyrolysis reaction gives a yield of 40% (w/w) biochar. The remaining 60% becomes pyrolysis vapor and is combusted.
- 7. The biochar is subjected to an activation process in which excess CO2 is reacted with the biochar at 700 °C for one hour. The CO2 reacts with carbon in the biochar via the Boudouard reaction to form CO, which is also combusted in the volatile gas boiler. This reaction removes some of the carbon in the biochar to form micro and mesopores to increase the surface area of the activated carbon.
- 8. The heat required for the drying of FRS, pyrolysis reaction, and carbonization activation reaction, are provided by natural gas, consumed at a rate of 58.4 MMBTU/ hr.
- 9. The activation reaction generates a yield of about 55%, which results in 22.5% (w/w) yield of activated carbon based on input FRS.
- 10. The activated carbon is cooled and placed in Supersaks for sale.

### Mass and Energy Balance

A mass and energy balance for the co-products department was constructed based on input from the co-products team at WSU and is presented in Table AM-1.10.

Components 27 and 28 represent fermentation residual stillage and spent sulfite liquor stillage coming from the fermentation process, respectively. These streams contain small amounts of residual sugar in addition to solids, which were undigested and lignosulfonate, which is soluble in the pretreatment liquor.

After processing, the stillage streams leave the department as activated carbon and 50 wt.% lignosulfonate. This process consumes energy in the form of steam and heat from fired heaters (components 58 and 72), and the activated carbon process also requires relatively pure streams of nitrogen and carbon dioxide.

Component 39 represents the volatile vapors, which exit the pyrolysis process to create biochar. The vapor contains a significant amount of heating value and is combusted in the volatile gas boiler in order to generate additional steam for the process.



Figure AM-1.5. The primary steps involved with co-product production.

### **Environmental Considerations**

#### Lignosulfonate Production

### Air discharge

The Lignosulfonate evaporators exhaust inert gases and volatiles organic compounds. Although the discharge is very low, they must be scrubbed with caustic and water to prevent malodors. The scrubber will use 30 gpm of process water and 1.0 tons per day of caustic (NaOH).

### Water discharge

The lignosulfonate evaporators produce a major waste water discharge. This wastewater is the condensate from increasing the fermented spent sulfite liquor (SSL) stillage to 50% total solids. The estimated flow is 1.21 MGD and contains an estimated COD of 4000ppm and BOD of 2000ppm.

### Solid waste discharge

There is no solid waste discharge from the Lignosulfonate production except for a twice per year sludge clean out of the equipment.



Component	77	20	25	26	27		20	/10	67	EO	70	71	73
component	27	28	Snent	30	3/	58	39	43	57	58	/0	/1	12
	Spent Sulfite Liquor Stillage	Fermentation Residual Stillage	Sulfite Liquor Condensate	Activated Carbon	Pyrolysis Boiler Vent	CO2 & N2	Pyrolysis Vapors	Ligno sulfonate	Electricity	Steam	Fired Heater Vent	FRS Filtrate	Natural Gas
Water	260.4	444.4	236.9	-	56.7	-	0.5	23.5	-	-	-	408.9	-
-													
Glucan	-	1.2	-	-	-	-	-	-	-	-	-	1.1	-
Xylan Arabia ar	-	1.2	-	-	-	-	-	-	-	-	-	1.1	-
Arabinan	-	1.2	-	-	-	-	-	-	-	-	-	1.1	-
Galactan	-	1.2	-	-	-	-	-	-	-	-	-	1.1	-
Mannan	-	1.2	-	-	-	-	-	-	-	-	-	1.1	-
Asn	-	0.9	-	-	-	-	-	-	-	-	-	-	-
Insoluble Lignin	0.0	18.5	-	-	-	-	-	0.0	-	-	-	-	-
Soluble Lignin	9.6	1.5	-	-	-	-	-	9.6	-	-	-	1.3	-
Bark	-	3.2	-	-	-	-	-	-	-	-	-	-	-
Monomeric Sugar	2.2	4.7	0.0	-	-	-	-	2.2	-	-	-	-	-
Protein	1.4	3.3	-	-	-	-	-	1.4	-	-	-	-	-
CaOH							-	1.0	-	-	-	-	-
Acetic Acid	0.9	0.3	0.4	-	-	-	-	0.9	-	-	-	-	-
Furfural	0.1	0.2	0.5	-	-	-	-	0.1	-	-	-	-	-
Other Solubles	8.4	0.8	-	-	-	-	-	8.4	-	-	-	2.5	-
Steam (klb/hr)	-	-	-	-	-	-	-	-	-	34.2	-	-	-
Elec. (MWhr)	-	-	-	-	-	-	-	-	10.9	-	-	-	-
Nat. Gas (MM BTU/hr)	-	-	-	-	-	-	-	-	-	-	-	-	58.4
voc	0.9	2.4	-	-	-	-	-	-	-	-	-	-	-
CO2	-	-	-	-	28.3	6.0	2.6	-	-	-	2.6	-	-
NO	-	-	-	-	3.2	-	-	-	-	-	-	-	-
02	-	-	-	-	6.9	-	-	-	-	-	-	-	-
СО	-		-	-	-	-	10.0	-	-	-	-	-	-
N2	-	-	-	-	-	24.0	1.0	-	-	-	-	-	-
Volatile Gases	-	-	-	-	-	-	17.8	-	-	-	-	-	-
A ativista d'Cashau				7.0									
	-	-	-	7.9	-	-	-	-	-	-	-	-	-
L3 (3U%)	-	-	-	-	-	-	-	47.0	-	-	-	-	-
Total BDT	23.4	41.9	0.9	7.9	38.3	30.0	13.6	23.5	10.9	34.2	2.6	9.2	58.4
BDT/vr	196,224	351,540	7.657	66.120	322.056	252.000	114.072	197,484	91.896	287.280	21,924	76.927	490,560





#### **Activated Carbon Production**

#### Air discharge

There are two air discharges from the Activated Carbon Production unit. The first discharge is the gaseous vent from the FRS drum dryer. This is a water scrubber that consumes 100 gpm of process water and the water is directed to waste water treatment. The second air discharge from the activated carbon process is from the nitrogen and CO2 natural gas fired heaters that heat nitrogen for the carbonization step and CO2 for the activation process. These two natural gas combustion streams are combined and directly vented to the atmosphere. There is a small air discharge from the bag house on the top of the activated carbon finish product storage and the supersak bagging operation, but they are deemed inconsequential.

#### Water Discharge

There is a wastewater discharge from the FRS filtrate belt press. This stream is sent directly to wastewater treatment. This is a significant flow to waste water and is estimated to be 2.3 MGD. The BOD and COD from this stream are estimated to be 200 and 400 ppm respectively. There is also vapor produced by drying the belt filter press filtrate to 50% solids in a rotary drum dryer. This vapor flows to a scrubber where it is condensed and scrubbed and the wastewater stream goes to the wastewater treatment plant.

### ater treatment pla

Solid Waste Discharge

There is no solid waste expected form activated carbon production except for frequent clean ups.

#### Table AM-1.11. Equipment list for Storage and Distribution.

# DISTRIBUTION

The Distribution Operation stores and distributes the iso-parafinnic kerosene (IPK) produced by the NARA biorefinery. The co-products storage and handling is detailed in the co-products department.

The distribution department was not modeled in Aspen Plus. Instead, a list of equipment was provided by TSI Inc. (Table AM-1.11). The products are distributed through both rail and truck, with an estimated 75% of product leaving by truck and 25% leaving by rail due to the relatively small volume of product being produced (Figure AM-1.6; Table AM-1.12).

### **Environmental Considerations**

In addition to the listed mass streams, the distribution department has additional streams that require removal or cleaning. Loading trucks or rail cars requires a vented gas system to collect vapor pressure fumes from the empty vessel used for transportation. Additionally, small quantities of wastewater are expected from connecting and securing filling devices.

		Liquid Distribution Cost Estimate			
Item	Process Description	Unit Description	Detailed description	Cost Estimate	Reference
1	IPK Product Storage, 30 days	Two 2.00MM Gallon Tanks	Poly coated Iron and system pipes to	\$ 6,000,000	TSI
			from plant and racks, heated		
2	IPK/IBA Rail loading system	System for single car and unit trains	Scales and automated loading	\$ 2,500,000	TSI
3	IPK/IBA Truck loading system	Multiple Loading stations	Automated loading and billing	\$ 1,500,000	TSI
	Total			\$ 10,000,000	



Figure AM-1.6. The primary steps involved with distribution.

Table AM-12. Product distribution at a NARA biorefiner	y: A	) distribution amounts (	tons	) reflected in <sup>*</sup>	Tables AM-	1.9 and AM-1	.9; B	) schematic of distribution.

	Distributio	n		R	25 IPK		25 IPK
Component	25	36	43		36 Activated Carbon	Distribution	36 Activated Carbon
	101/	Activated	500/10		43 50% Lignosulfonate	Shipping	43 50% Lignosulfonate
	IPK	Carbon	50% LS				
Water			23.5				
ІРК	13.45						
Activated Carbon		7.9					
Lignosulfonate			23.5				
Total BDT/yr	112,980	66,360	197,400				
Total ton/yr	112,980	66,360	394,800				

# BOILER

The boiler provides steam and heat for the entire biorefinery. Based on the earlier process models, a minimum of 415,000 lbs/hr of steam is required to power the entire biorefinery. Hog fuel (35-50% moisture) has an average heating value of 6,000 BTU/lb, equivalent to 12 MMBTU per short ton. This requires the consumption of 35 to 40 tons per hour of hog fuel, depending on the quality of the input fuel.

There are two sources of fuel for the hog fuel boiler: fines which were screened in the feedstock handling department (8.3 TPH) and directly purchased hog fuel (29.7

TPH). Hog fuel is described as a wet mix of coarse chips of bark and wood, which is of too poor quality to process as wood pulp. The fines are forest residual chips that pass through the lower screen in the feedstock handling department, and are too small to be used for pretreatment.

In addition to the hog fuel boiler, a mixed fuel boiler is used to handle pyrolysis vapors from the activated carbon process. The mixed fuel boiler receives the vapors at 700 °C and is co-located near the co-products process unit operations. A special note should be made that the piping to handle these vapors needs to be specialized in order to prevent corrosion as well as condensation of the pyrolysis vapors on the



Figure AM-1.7. The primary steps involved with boiler operations.

pipes. The operational flow of the boiler system is shown in Figure AM-1.7. Mass and energy balance is shown in Table AM-1.13.

### **Environmental Considerations**

#### Air Discharge

The boiler will have a combustion gas discharge from the burning of hog fuel to produce process steam. This discharge is from a bag house that cleans the exhaust gas prior to discharge from the stack. The estimated flow is approximately 303,000 cfm at 320°F. There are two other air discharges associated with the production of steam. One is the combustion of sulfur in the pretreatment department and the other is the combustion of volatile gases from the production of activated carbon. The sulfur combustion gas discharge is reported in the pretreatment department and the volatile gas combustion gas discharge is report in the co products department.

#### Water Discharges

The water discharge from the boiler department is the ion exchange backwash from the boiler feed water and condensate return treatment. These are estimated to be 8% of the total steam production requirement of the biorefinery (550,000 lbs/hr), equal to 0.13 MGD.

#### Solid Waste Discharge

There is one solid waste stream from the boiler department. This is the boiler ash remaining after the complete combustion of the hog fuel. The fines percent ash is 1.97% and the hog fuel percent ash is 6.80%. The total bone dry tons per day to landfill of boiler ash is then 4.3 bpd and from hog fuel is 63.6 BDT.

The solid waste discharge from the volatile gas boiler is described in the co-products department and there is no ash discharge from the sulfur boiler.

	Boiler								
Component	2	3	39	40	41	42	54	55	
	Hog Fuel	Forest Residual Fines	Pyrolysis Vapors	Boiler Water Return	Steam	Boiler Exhaust	Boiler Ash	Combustion Air	
Hog fuel	39	9.06	-	-	-	-	-	-	
Vapors	-	-	24.11	-	-	-	-	-	
Steam	-	-	-	-	207.5	-	-	-	
Electricity	-	-	-	-	-	-	-	_	
CO2	-	-	-	-	-	83.55	-	-	
NOx	-	-	-	-	-		-	-	
со	-	-	-	-	-		-	-	
N2	-	-	-	-	-	315.33	-	316	
02	-	-	-	-	-	20.51	-	84	
Ash	-	-	-	-	-	-	2.34	-	
Water	13	-	-	-	-	30.81	-	-	

Table AM-1.13. Mass and energy balance for boiler operations: A) mass and energy balance, B) schematic showing directional flow for each component listed in (A).



Northwest Advanced Renewables Alliance

# UTILITIES

The utilities department contains a number of essential infrastructure items that although not explicitly modeled, were included in the capital and operating cost estimate. These items are described below, and depicted in Figure AM-1.8.

Electrical Substation: The NARA biorefinery does not produce any electricity. As a result, the refinery needs to be connected to the local power grid to obtain electricity to run the plant. The electrical substation transforms and distributes power from the local grid to the plant.

Gates, Roads, Fence, and Security: The plant site requires gates, roads into and out of the site, fencing, and security.

Cooling Tower: The cooling tower handles heat removal for various process water streams, including water from pretreatment, upgrading of isobutanol to IPK, and cooling of evaporator condensate prior to wastewater treatment.

Potable Water and Sanitary Waste: The people working at the plant site require potable water and disposal of sanitary waste generated at the site.

Mill Compressed Air: Compressed air is required for pneumatic actuators and other process equipment.

Administration and Human Needs Building: This building at the plant site houses the engineers and administrative staff that manage the refinery.

Mill Control & Data System: The mill control and data system manages equipment, flow through processes, and monitors unit operations at the site. Essentially, this is a process control system.

Wastewater Treatment: The wastewater treatment uses aerobic treatment, anaerobic treatment, and reverse osmosis to clean process water used (i.e. from pretreatment and evaporator condensate from SSL) and returns clean water to the plant for re-use. There is an excess of treated wastewater, above the NARA process requirements, that requires discharge to receiving waters.

Landfill: Landfill is required to dispose of solid waste, including boiler fly ash, fungal biomass from enzyme production, and material from the feedstock handling woodyard that is not usable in the NARA biorefinery process. The NARA process has assumed the use of an external landfill site, which accepts solid waste at a tipping fee of \$45/ton.

Process Water Supply & Fire Suppression: The process water supply system pumps fresh municipal water and treated water from the wastewater treatment process

back to the various operations that require it. The fire suppression system includes fire suppression water storage and pumps for the fire suppression system.

# CONCLUSIONS/DISCUSSION

The objective of this task was to provide a mass and energy balance for the core operations of the NARA biorefinery, which converts 770,000 BDST of forest residuals into 36 million gallons of IPK jet fuel, 67,000 TPY of activated carbon, and 200,000 TPY of 50 wt.% lignosulfonate. These operations were successfully modeled, and mass and energy balances provided above and in the Appendices section.

The process to convert forest residuals into jet fuel is long and involved. Our analysis of the equipment required and the chemical and energy consumption for each unit operation suggested that the process is expensive as well. As a result, significant effort is required to find valuable co-products, which can be produced alongside the jet-fuel in order to improve the economic viability of the biorefinery. Future work is required in the area of co-product development, as well as reducing the number of process steps required to get to a product from the woody feedstock.

NARA Northwest Advanced Renewables Alliance



Figure AM-1.8. Essential infrastructure items contained in Utilities Department.

# TASK 2: PRETREATMENT ANALYSIS BETWEEN MILD BISULFITE/SPORL PRETREATMENT AND WET OXIDATION

# TASK OBJECTIVE

The objective was to work with the Catchlight Energy team (mild bisulfite pretreatment) and WSU team led by Dr. Birgitte Ahring (wet oxidation pretreatment) to develop process models which accurately portrayed the chemical usage and utility consumption (steam, electricity) of each pretreatment process, with the intent that the information be used as part of the pretreatment selection process.

## METHODOLOGY

## **Process Modeling**

Primary research data was gathered from Catchlight Energy for the calcium bisulfite pretreatment process and from Dr. Birgitte Ahring and Philip Teller at WSU Tri-Cities for the Wet Oxidation/Wet Explosion (WEx) process. The process conditions were used to create process models for each of the pretreatments based on the same input of 770,000 BDTY of softwood residuals, and a comparison was made starting from feedstock handling and ended with enzymatic saccharification. Table AM-2.1 below presents the process parameters used for the analysis.

The Aspen Plus model generated an estimated CAPEX and OPEX for each of these pretreatment processes based on estimated equipment cost and utility (steam, electricity, chemical) usage.

Note: The Aspen process flow diagrams presented in this section are representative of the process as described in NARA year 3, and may not be representative of the final NARA process.

### Estimation differences between WEx and MBS

The WEx and MBS processes had several differences, which required the Aspen Modeling Team to perform estimations or assumptions which were not obtained from primary research data. In addition, two differences between the processes, which are not self-evident (the pressure of each process and reactor size), are explained in greater detail here.

#### Table AM-2.1. Process parameters used for CapEx and OpEx estimates of MBS and WEx pretreatments

Process Parameter	Mild Bisulfite	Wet Explosion
Temperature	145	185
Residence Time (min)	280	20
Calcium Bisulfte Loading (wt.% on biomass)	6.5	-
Oxygen Loading (wt.% on biomass)	_	5.2
Solids Loading (% w/v)	25	35
Enzyme Loading (wt.% on biomass)	4.4	7.1
Monomeric sugar yield (wt.% of theoretical)	82	82

use of CTec (cellulase) and HTec (hemicellulase) enzymes from Novozymes for their enzymatic saccharification. Catchlight Energy reported their enzyme dosage in wt.% of enzyme solution onto total biomass, i.e. 44 grams of enzyme solution per 1000 grams of pretreated biomass. Dr. Ahring's WSU team reported their enzyme dosage in mg of enzyme protein per gram of glucan content, i.e. 40 mg enzyme protein per 1.0 grams glucan. In order to compare these pretreatments, an assumption of 22.5 wt.% protein titer in Novozymes enzyme solution was made. This resulted in:

- o MBS stated enzyme consumption: 4.4 wt.% onto biomass
- o WEx stated enzyme consumption: 40 mg/g glucan = 177 mg enzyme solution/g glucan. At an experimentally determined glucan content of 40% after pretreatment, this was equal to 71 mg enzyme solution per gram biomass, or a 7.1 wt.% loading onto biomass
- Saccharification yield assumption: No data was provided for the WEx saccharification yield on the NARA feedstock. An assumption was made of 82% yield, the same as the MBS/SPORL process.
- Pressure The MBS/SPORL pretreatment process occurred at the saturation pressure of steam at 145 °C, or 3.5 bar g. The WEx pretreatment process occurred at 185 °C, corresponding to a steam pressure of 12 bar g, requiring oxygen to also be injected at this pressure.
- Reactor size The WEx pretreatment process was modeled as 6 parallel reactors, based on a statement of maximum reactor size by the WSU research team.
- Enzyme consumption estimation: Both pretreatment research groups reported the

# RESULTS

The Aspen Plus process flow diagrams for the WEx and MBS pretreatment processes are presented in Figures AM-2.1 and AM-2.2. At this stage in the work, no capital

cost estimates were performed, but the benefits and tradeoffs of each pretreatment were assessed, and found to be roughly equal in terms of CAPEX. These tradeoffs are listed in the Table AM-2.2, followed by the operating costs associated with each pretreatment.



Figure AM-2.1. Block flow diagram of the WEx pretreatment system. Figure courtesy of Birgitte Ahring and Philip Teller, WSU BSEL



Figure AM-2.2. Process flow diagram of the mild bisulfite pretreatment process



#### Table AM-2.2. Tradeoff comparisons between Wet Explosion and Mild Bisulfite processes

Wet Explosion	Mild Bisulfite
Higher T, P, in reactor	Use of sulfur based pretreatment chem- ical 'dirtier' than oxygen
Requires air separation unit for oxygen generation	Long residence time in pretreatment reactor
Smaller reactors, but requires greater number of reactors	

### **MBS Pretreatment**

- The MBS pretreatment operating cost was predicted to be \$13 MM/yr, primarily in chemical (calcium bisulfite) and steam costs.
- The associated MBS enzymatic saccharification cost for pretreated biomass was predicted to be \$23 MM/yr, with the major cost items being enzyme production inputs (glucose, media) and electricity for compression of air through the aerobic enzyme production reactors

### **WEx Pretreatment**

- The WEx pretreatment operating cost was predicted to be \$15 MM/yr, primarily in purified oxygen (92% v/v O2 required for operation), and steam cost.
- The associated WEx enzymatic saccharification cost for pretreated biomass was predicted to be \$43 MM/yr. The increase over MBS pretreated biomass was due to a higher enzyme loading required to obtain the same sugar yield.

# CONCLUSIONS/DISCUSSION

As pretreatment technologies, both the mild bisulfite and wet explosion technologies are capable of treating softwood residuals effectively such that a high yield of monomeric sugar can be obtained after enzymatic saccharification. However, the MBS pretreatment process holds several advantages over the WEx process, including a lower operating temperature and pressure, a less expensive process chemical, which can be partially recycled, and the ability to scale to larger reactors. As a result, the estimated CAPEX and OPEX values for the MBS pretreatment process were lower than for the WEx process.

# **TASK 3: CO-PRODUCT MODEL DEVELOPMENT**

# TASK OBJECTIVE

The objective was to work with the NARA co-products team to assess possible commercially viable co-products which could be created from the NARA biorefinery 'waste' material and develop process models for each of these processes.

# METHODOLOGY

The two co-products suggested for the NARA biorefinery were lignosulfonate, taken from the spent sulfite liquor (SSL) stream, and activated carbon, produced from the fermentation residual solids stream (FRS). Ian Dallmeyer at WSU performed the research on the activated carbon process, and the process parameters and yields used in the model were taken from his work. Lignosulfonate is an existing commercial product, and the preparation process was taken from literature and information provided by Tom Spink at TSI, Inc.

## RESULTS

Figure AM-3.1 is a process flow diagram representing the unit operations in the co-products generation process. In addition, the process description and operating cost estimate results are stated below.

### **Activated Carbon Process**

The activated carbon process produces a powdered activated carbon product, which can be used for a variety of adsorption related applications. In the modeled process, activated carbon is produced from FRS, which is primarily composed of undigested woody residuals (cellulose, lignin, hemicellulose, ash and extractives), and cell mass from fermentation.

Initially, excess moisture is removed from the FRS by use of a belt press and dryer, which is required prior to use of the FRS in a pyrolysis process. The pyrolysis of FRS is performed in a rotary kiln reactor at 700 °C for 1 hr under an oxygen-free environment. An inert carrier gas, typically nitrogen, is used to carry pyrolysis vapors, which are produced from the more volatile components of the FRS away from the reactor. These pyrolysis vapors are combusted in the boiler for heat generation. The residual mass in the reactor after the pyrolysis reaction is a biochar, which is enriched in carbon (70-80% carbon by mass), and represents about 40% of the mass of the input FRS. The biochar is used in a second reaction at 700 °C for 1 hr which is designed to consume carbon through reaction of carbon with carbon dioxide at elevated temperatures to form carbon monoxide, also known as the Boudouard reaction. This

reaction results in the formation of micro and meso-pores in the biochar, increasing the surface area, and 'activating' it. The formed product is activated carbon. The yield of activated carbon from FRS is between 20-25 wt.%.

The operating costs associated with activated carbon production were estimated to be \$35 MM/yr, with the major costs being the purified carrier gases (N2 and CO2) and natural gas for heating the reactor. Although high, the estimated revenue from activated carbon is between \$90 and \$100 MM per year, based on annual production of 66,000 short tons of activated carbon valued at \$1,500 per ton.

### **Lignosulfonate Process**

During the course of the mild bisulfite pretreatment, bisulfite ions (HSO3-) from the pretreatment liquor react with lignin present in the biomass. In the acidic environment of the pretreatment process (pH 2.0 or less), an acid catalyzed cleavage of lignin ether bonds occurs, resulting in the substitution of a bisulfite group onto the lignin side chain, forming a lignosulfonate product.

Lignosulfonates are primarily used as plasticizers in the concrete industry, where addition of lignosulfonate into the concrete mixture improves the plasticity of the concrete at low water addition, which improves concrete strength.

In the NARA process, a significant amount of lignosulfonate is produced during the pretreatment reaction, and is present in soluble form in the pretreatment liquor, or spent sulfite liquor (SSL). The SSL stream contains a significant amount of sugar as well, and is used in fermentation prior to being processed into a saleable lignosulfonate product.

The processing of the lignosulfonate in SSL in relatively straightforward, and predominately involves the removal of water from the SSL stream. The SSL is dried using vapor recompression evaporation to 50 wt.% solids, after which pH is adjusted by the addition of lime to pH 6.5. This results in the production of 200,000 short tons per year of 50 wt.% lignosulfonate, which can be sold for \$200 per ton for an annual revenue of \$40 MM. The operating cost associated with producing SSL is approximately \$9 MM, with the major costs being electricity for evaporation and lime for pH adjustment.

# CONCLUSIONS/DISCUSSION

The modeled co-product processes produce 67,000 and 200,000 short tons of activated carbon and lignosulfonate respectively, for a total operating cost of \$44 MM,

and bringing in projected revenue of \$140 MM. The NARA project investigated the possibility of several other uses for the byproduct streams of SSL and FRS, including use of lignosulfonate in asphalt, incorporation of lignosulfonate into plastics, and combustion of FRS as an energy source. However, of the possible options, the

production of activated carbon and lignosulfonate offered the least technical and market risk, and as a result were chosen to be the co-products representative of the NARA process.



Figure AM-3.1. Process flow diagram representing the unit operations in the co-products generation process



# TASK 4: DIRECTION OF PROCESS IMPROVE-MENTS AND INTEGRATION WITH OTHER TEAMS

# TASK OBJECTIVE

The objective was to disseminate the learnings from the Aspen process model to other NARA teams, in support of the objective to create a technoeconomic analysis and life cycle analysis for the NARA process, which help us to understand the economic and environmental viability of the process respectively.

## METHODOLOGY

This task was composed of two targets:

- 1. Inform the life cycle analysis teams working NARA of the mass and energy flows in the process in support of their effort to conduct an LCA on the bio-jet produced from the process
- 2. Work with other NARA teams to direct process improvements, which included co-product selection, down-selection of the pretreatment process, use of chemicals in the NARA plant, and assessment of process flows, which affect the environmental impact of the process.

To this end, the Aspen Modeling Team worked and communicated with many teams, including the LCA teams at University of Washington and University of Minnesota, TEA team at TSI and Weyerhaeuser, Co-products team at Washington State University, and the Air Emissions team at Washington State University.

# RESULTS

The following are tasks for which the Aspen Modeling Team provided significant support.

- Creation of the LCA model for bio-jet fuel from forest residuals, showing the bio-jet product meets a 60% greenhouse gas emission reduction compared to conventional petroleum jet.
- Creation of the technoeconomic analysis for the NARA biorefinery
- Assessment of co-product impact and alternative co-products
- Assessment of possible air pollution impacts in the Pacific Northwest as a result of the establishment of a biorefinery.

# NARA OUTPUTS

# PRESENTATIONS

- 1. "Aspen Modeling of Pretreatment", Gao A.H., Spink T., Bule M.V., Chen S. Presented at the NARA 2014 annual meeting
- 2. "The NARA Integrated Biorefinery Report", Gao A.H., Spink T., Chen S. Presented at the NARA 2015 annual meeting

# POSTERS

- 1. "Aspen Plus Process Modeling of NARA Biorefinery Departments", Gao A.H., Spink T., Bule M.V., Chen S. – Presented at the NARA 2014 annual meeting
- 2. "NARA Integrated Biorefinery Report", Gao A.H., Spink T., Chen S. Presented at the NARA 2014 annual meeting

# **FUTURE DEVELOPMENT**

To date, much of the work in the field of renewable energy from lignocellulose has concentrated on the use of agricultural residues, namely corn stover, wheat straw, or bagasse (Kumar, Barrett, Delwiche, & Stroeve, 2009; Searcy, Flynn, Ghafoori, & Kumar, 2007; Somerville, Youngs, Taylor, Davis, & Long, 2010). This is primarily due to two factors: (1) the ease of collection of agricultural residues, which by nature are locally concentrated, and (2) the relatively lower recalcitrance agricultural residues possess due to lower lignin content and a less dense cell structure.

The current work is one of the few studies that examine in depth a process for the conversion of woody biomass into renewable fuels and chemicals. There is significant future potential to build upon the established process model and technoeconomic analysis of NARA biorefinery. Areas in which the WSU Aspen Modeling Team will continue to develop are:

- Technoeconomic analysis of the cost of production of lignocellulosic sugar from woody biomass and possibilities for conversion of sugar into valuable non-fuel bioproducts.
  - o The production of bio-derived jet fuel is a goal that cannot be supported by the economic landscape of today. However, a near term target of utilizing woodbased sugar for the creation of more valuable chemical compounds, including higher alcohols or plastic precursors such as poly-hydroxy-butyrate or poly-lactic acid (Choi & Lee, 1997), may be economically viable but would be predicated on cheap lignocellulosic sugar. As a result, assessment of the cost of producing sugar, and not necessarily end-products, from a variety of feedstocks is essential to understanding where future paths of development may lie.
- Technoeconomic analysis of the integration of a lignocellulosic biorefinery with existing large scale chemical plants, including pulp mills, corn ethanol plants, or large agriculture processing centers.
  - o The greenfield capital cost of a new biorefinery at the NARA scale is prohibitive at best, and a fiscal impossibility at worst. During the course of the NARA project, some work was performed to examine possibilities for integration with defunct pulp mills. Future development should focus extensively on the possibility of converting old industrial plants into biorefineries and the impact on capital cost. In particular, the conversion of smaller facilities to add on biorefinery capabilities could be of much interest, and would support work conducted already on depot-scale conversion of woody biomass.

# REFERENCES

Choi, J.-i., & Lee, S. Y. (1997). Process analysis and economic evaluation for poly (3-hydroxybutyrate) production by fermentation. Bioprocess Engineering, 17(6), 335-342.

- Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., . . . Worley, M. (2011). Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol: dilute-acid pretreatment and enzymatic hydrolysis of corn stover: National Renewable Energy Laboratory (NREL), Golden, CO.
- Kumar, P., Barrett, D. M., Delwiche, M. J., & Stroeve, P. (2009). Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. Industrial & Engineering Chemistry Research, 48(8), 3713-3729.
- Searcy, E., Flynn, P., Ghafoori, E., & Kumar, A. (2007). The relative cost of biomass energy transport. Applied Biochemistry and Biotechnology, 137(1), 639-652.
- Somerville, C., Youngs, H., Taylor, C., Davis, S. C., & Long, S. P. (2010). Feedstocks for lignocellulosic biofuels. Science(Washington), 329(5993), 790-792.

# **APPENDIX**

This appendix contains flow diagrams of the WEx pretreatment process (Figure AM-App1), the WEx reactor system (Figure AM-App2), the Mild Bisulfite pretreatment

process (Figure AM-App3), the SSL evaporation process (Figure AM-App4) and the activated carbon process (Figure AM-App5).



Figure AM-App1. Aspen process flow diagram of the WEx pretreatment process. Sub-blocks (RX-1 to RX-6) are individual WEx pretreatment systems. Oxygen is compressed and mixed with air and steam for injection into each individual pretreatment sub-block. The pretreatment section is divided into 6 blocks due to the requirement for 6 reactors and 6 pressure feed systems into the reactor. After pretreatment is complete, pretreated biomass is placed in a holding tank (B9) prior to being fed to hydrolysis.





Figure AM-App2. Aspen Plus process flow diagram of each WEx reactor system. The Biomass is fed into a set of 6 pre-feed sections and fed through 6 valves into the reactor, as specified by the WSU system design. After the biomass is pretreated (bottom left) the biomass is flashed for heat recovery and cooling and the vent gases are scrubbed.

NARA

Northwest Advanced Renewables Alliance



Figure AM-App3. Mild Bisulfite pretreatment process flow diagram generated in Aspen Plus. The process begins with the creation of the pretreatment liquor. Liquid sulfur is mixed with calcium carbonate and water (initial mixture forming calcium hydroxide) to form calcium bisulfite in the absorbing tower (ABS-TWR). The pretreatment liquor is then used in the pretreatment reactor, and pretreated biomass is flashed through a refiner prior to being used in enzymatic saccharification.





Figure AM-App4. Aspen Plus process flow diagram of the SSL evaporation process. The spent sulfite liquor is fed through a series of two vapor recompression evaporators, which remove about 80% of the water, resulting in a 50 wt.% lignosulfonate product. The dried lignosulfonate is pH adjusted using calcium hydroxide (lime) to pH 6.5 and then cooled and stored for sale.





Figure AM-App5. Aspen Plus process flow diagram of the activated carbon production process. The fermentation residual solids from hydrolysis and fermentation are initially pressed through two belt filters, which removes a majority of the water and soluble solids. The semi-dry solids are then dried (EVAP-1) and de-lumped prior to entering the pyrolysis reactor, where N2 is fed as a carrier gas. After pyrolysis, the biochar is fed to the activation reactor (ACTIVATE) alongside CO2 to form the activated carbon product. Pyrolysis vapors are combusted to provide heat for the system.

