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Production of 1,000 Gallons of Certified Biojet Fuel through Biochemical Conversion of Softwood Forest Residues

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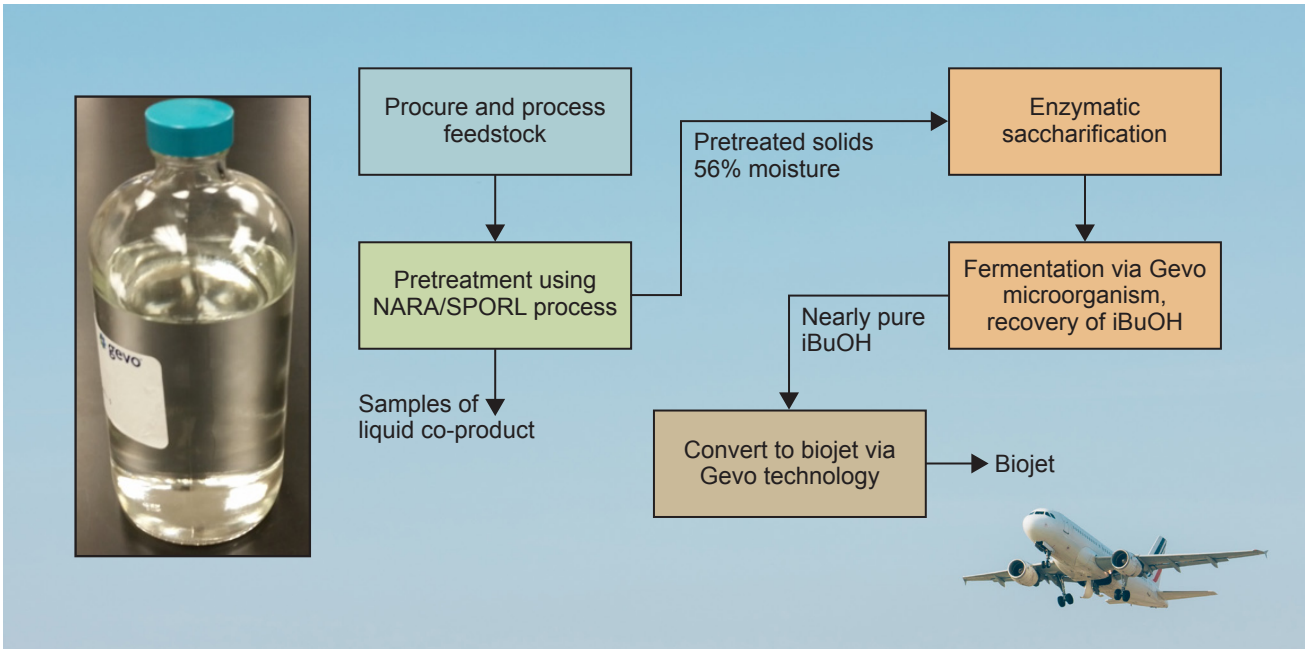

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Abstract

Approximately 1,050 gal of certified biojet fuel was produced utilizing feedstocks of softwood forest slash from the Pacific Northwest and pulp mill reject material from a mill in Washington State, USA. These feedstocks were collected and processed by the team of Northwest Advanced Renewables Alliance (NARA) using technologies developed by NARA partners. This investigation found these feedstocks to be economically sustainable.

Keywords: Biojet fuel, forest residue, biorefinery, SPORL, enzymatic saccharification and fermentation, iso-butanol, iso-paraffinic kerosene

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Contents

Acronyms

AF	aerobic fermenter
API	American Process, Inc.
BDT	bone-dry ton
CHF	combined hydrolysis factor
CIP	clean in place
CSKT	Confederated Salish and Kootenai Tribes
DO	dissolved oxygen
FPL	Forest Products Laboratory
GC	gas chromatograph
HFM	hollow fiber membrane
HPLC	high-pressure liquid chromatography
NREL	National Renewable Energy Laboratory
RDVF	rotary drum vacuum filter
SHR	South Hampton Resources
SIP	steam in place
SPORL	sulfite pretreatment to overcome the recalcitrance of lignocelluloses
VB	viscosity break tank
YC	yeast conditioning tank

Conversion table

English unit	Conversion factor	SI unit
gallon (gal)	3.785412	liter (L)
inch (in.)	2.54×10^{1}	millimeter (mm)
pound, mass (lb)	4.535924×10^{-1}	kilogram (kg)
pound per square inch ($lbf\ in^{-2}$)	6.894757	kilopascal (kPa)
ton (2,000 lb)	9.071847×10^{-1}	metric ton (t)
$T_{°F}$	$T_{°C} = (T_{°F} - 32)/1.8$	$T_{°C}$

Executive Summary

Approximately 1,050 gal (3,975 L) of certified biojet fuel was produced utilizing feedstocks of softwood forest slash from the Pacific Northwest and pulp mill reject material from a mill in Washington, USA. These feedstocks were collected and processed by the team of Northwest Advanced Renewals Alliance (NARA) using technologies developed by NARA partners. This investigation found these feedstocks to be economically sustainable.

This project was sponsored by a US$40 million U.S. Department of Agriculture, National Institute of Food and Agriculture (USDA–NIFA), Coordinated Agriculture Project (CAP). The project had no large capital equipment to accomplish such a task, so toll processers across the country were investigated to find locations that could (1) perform the NARA partners' technologies, (2) have sufficient capacity to handle this large volume, and (3) be available for contracting at a fair cost. Some compromises were required by NARA because available equipment was not necessarily what would be designed for this process and due to the fact that there are multiple toll processers located at far distant locations.

Forest residues were collected by NARA from Weyerhaeuser's Siuslaw site in Oregon, USA, from Muckleshoot Tribal lands in Auburn, Washington, USA, and from CSKT Flathead Tribal lands in Lone Pine, Montana, USA. All material was brought to Lane Forest Products in Junction City, Oregon, USA, where it was screened and rechipped. Overall, 272 green tons (GT) of material was received and 66 bone-dry tons (BDT) was used for further processing.

The pretreatment facility of ZeaChem, Inc., in Boardman, Oregon, USA, was selected to perform the pretreatment of forest residues using sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL). The SPORL technology was developed by the USDA Forest Products Laboratory in collaboration with the University of Wisconsin–Madison. Most of the SPORL development work to date was at the Forest Products Laboratory (a NARA partner) in a batch mode; ZeaChem's process was continuous. ZeaChem's pretreatment equipment was supplied by Andritz, Inc. (Canonsburg, Pennsylvania, USA), so a short trial at Andritz's pilot plant in Springfield, Ohio, USA, seemed the best way to transition to a continuous operation. A two-day trial was conducted to understand the conditions that should be used at ZeaChem and to verify the kinetic-based reaction severity scale-up factor, the combined hydrolysis factor (CHF), developed at the Forest Products Laboratory. Various adaptations were required, including using $Mg(HSO_3)_2$ and H_2SO_4 to make HSO_3^- and SO_2 in the reactor rather than feeding SO_2. Additionally, the residence time and reaction temperature were adjusted to accommodate the equipment based on CHF. Another compromise was to not transport the sugar-containing liquid hydrolyzate from the process. This material is low pH and is therefore a hazardous material for shipping.

The facility of ICM Biofuels, Inc., in St. Joseph, Missouri, USA, was selected to carry out enzymatic saccharification of the pretreated woody material from ZeaChem and the rejected pulp from the Cosmo Specialty Fibers mill in Cosmopolis, Washington, USA. The Cosmo facility uses a sulfite pulping process very similar to SPORL, but at high sulfite loadings, longer reaction times, and a low temperature and uses softwood (hemlock) as their feedstock. Cosmo is interested in the possibility of valorization of their rejected pulp material through this project. In addition to enzymatic saccharification, the resulting sugars were fermented to isobutanol at ICM using Gevo's proprietary microorganism (Gevo, Englewood, Colorado, USA).

Enzymatic saccharification of the SPORL-pretreated forest residue at ZeaChem and Cosmo materials went well at ICM with expected yields. However, issues associated with the filtering of residual solids caused sugar loss, and the storage of sugars induced sugar contamination led to the production of less isobutanol than expected. Approximately 900 gal of isobutanol was produced, about half the amount needed to make 1,000 gal of jet fuel.

A second campaign was conducted at ICM, this time using only Cosmo rejected pulp. Approximately 60 BDT of Cosmo material was obtained. Process changes were implemented at ICM, such as not filtering the solids after saccharification and running low-concentration fermentations. As a result, an additional 1,000 gal of isobutanol was produced.

The lack of a complete distillation system at ICM for the removal of any ethanol in the product limited how much water could be removed by distillation as well. Therefore, another toll processer (Whitefox) was used to remove the water via a membrane process.

Finally, the purified isobutanol was converted to biojet fuel in the Gevo design pilot facility owned and operated by South Hampton Resources in Silsbee, Texas, USA.

The ASTM-certified (ASTM D7566) biojet fuel was blended with Jet A by Alaskan Airlines and flown in their regularly scheduled commercial flights AS04 from Seattle (SEA) to Washington DC (DCA) on November 14, 2016.

Project Objective

The purpose of this project was to demonstrate that conversion technologies developed and researched in the NARA project can indeed convert the woody feedstock selected by NARA to biojet fuel as a blend stock in fuel for commercial airlines. In addition to simply showing that jet fuel could be produced, a quantity needed to be produced that would allow a commercial airline to fly one of their jets on a meaningful flight.

To use the fuel produced by NARA in a commercial flight, the process and final fuel needed to be accepted by the industry. Gevo accomplished this by being instrumental in developing an ASTM certification approved by essentially the entire aviation industry (airline manufacturers, engine manufacturers, airline operators, and many others) (ASTM International 2016). Without this certification process in place, commercial flights with this fuel would be impossible. In addition to spearheading the certification process, Gevo teamed with Alaskan Airlines to fly more than one flight using biojet fuel produced from their corn-based isobutanol. The certification is for biojet from isobutanol in any blend up to 30% with commercial aviation fuel. Given this, and in conversations with airline representatives, a 20% blend of NARA biojet (5,000 gal total) was determined be an appropriate quantity for a significant demonstration flight. For example, an airline company indicated that a Boeing 737 could be flown from Seattle, Washington, USA, to Washington, D.C., USA, with approximately 5,000 gal of blended fuel.

Having established that the original amount of fuel, 1,000 gal, was appropriate, the priorities of making this fuel were also established (for example, whether to insist that the NARA configuration of their member's processes be followed exactly and that engineering scale-up information be developed, or that we produce and collect the various by-products envisioned for the commercial process). To get everyone associated with this project in agreement on boundary conditions, a meeting in Seattle of the various technology stakeholders within the NARA project was convened in January 2015. Included in the meeting were those responsible for all technical aspects of the NARA project. Out of that meeting came a list of five guiding principles for this project:

1. A quantity of 1,000 gal was chosen to enable a blended jet fuel trial by a commercial airline plus useful performance, quality, and composition tests.
2. Several key aspects from the NARA project are to be utilized in production:
   - Feedstock: softwood forest residues from the Northwest region of the United States, primarily Douglas-fir and hemlock
   - Pretreatment: SPORL process as developed by FPL using CHF as the scaling-up factor (Zhu et al. 2012)
   - Enzymatic saccharification: utilizing commercial enzymes from Novozymes and as utilized by USDA–FPL and Gevo on this pretreated material
   - Isobutanol production: via fermentation using Gevo patented organisms and fermentation protocols
   - Jet fuel conversion: via Gevo process
3. Efforts will be made to accommodate the production of representative co-products, but it will not be a priority.
4. Cost and availability of suitable demonstration scale equipment will dominate decisions, so the production process conditions adopted are not optimal.
   - Efforts will be made to determine representative or scalable yields as opportunities present themselves (for pretreatment generally). Specifically, when available, scalable demonstration equipment and procedures will support TEA studies (that is, data for specific scenarios defined by the demonstration will be available to the TEA).
5. An overall optimized yield from wood to biojet fuel is not expected and the overall yield of the trial will be considered NARA confidential.

With these guiding principles, then project could be moved forward knowing what is important to address or include and what is not.

1. Vetting Potential Toll Facilities

Producing 1,000 gal of biojet is a large operation. Even with a production facility operating at peak efficiency, it would require over 20 BDT of wood feedstock to be processed. For this project, we needed to lower yield expectations because the equipment being used was the best available and not specifically designed for the technologies adopted by NARA. In addition, the various processing steps took place at multiple physical sites, further reducing the efficiency of the operations. Neither the NARA project nor the primary developers of the technology generally owned or operated facilities for all parts of the process at this scale of operation. The exception were the Gevo-built isobutanol recovery process at ICM and an isobutanol to biojet fuel demonstration plant at South Hampton Resources (SHR, Silsbee, Texas, USA). However, the rest of the process was not readily available; even the two assets that Gevo built were not available for Gevo to operate themselves.

In an effort to determine what (if any) facilities were available in the country to handle the needs of this project, a comprehensive list of organizations that potentially had equipment suitable for this project was developed. A crude flowsheet showing the various steps in the process was established (Fig. 1.1). Each of these processes likely took place at a different location, as opposed to a commercial operation where most of or all the operations would be on a single site.

Table 1.1 summarizes the possible toll processers identified for each of the processing steps. Feedstock procurement and processing are each a separate large task within NARA. They took on the task of supplying feedstock to the pretreatment facility per specification developed with the selected toll processer (see Section 2).

Two of the unit operations have several potential toll processers. A two-step review was conducted: first, examining the suitability of available equipment and comparing to the size and needs of the NARA process; second, conducting site visits of the short list to better understand process equipment available, operating characteristics, cost, and availability of the unit to meet project needs.

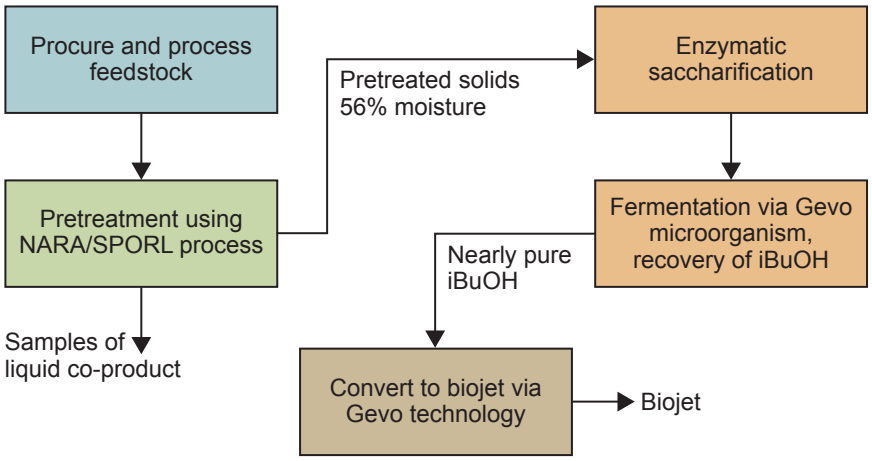

Figure 1.1—General process flow for production of 1,000 gal of NARA biojet fuel.

Table 1.1—Potential process tollers

Pretreatment	Andritz, Inc., Pilot Facility, Springfield, OH
	American Process International (API) Development Plant, Thomaston, GA
	ZeaChem Development Plant, Boardman, OR
	Cosmo Specialty Fiber, Cosmopolis, WA
	Forest Products Lab (FPL), Madison, WI
	ICM Biofuels, Inc., St. Joseph, MO
	University of Florida Pilot Plant, Perry, FL
Enzymatic saccharification and fermentation	ICM Biofuels, Inc., St. Joseph, MO
	American Process International (API) Development Plant, Thomaston, GA
	NREL Biomass Pilot Plant, Golden, CO
Isobutanol conversion to jet	South Hampton Resources (SHR), Silsbee, TX

1.1 Pretreatment Toll Processers

Several possible pretreatment toll processers were quickly eliminated. The main factor in eliminating the FPL was that it was too small to process the volume needed. The National Renewable Energy Laboratory (NREL) pilot plant was almost too small, but they and the University of Florida pilot plant had not used SO_2 (a key reactant in the SPORL process), and both informed us that obtaining approval to use SO_2 would be a long process with an unknown outcome. The ICM facility in St. Joseph was also eliminated due to concerns about using SO_2 in their facility.

This left Cosmo, American Process, Inc. (API, Atlanta, Georgia, USA), Andritz, and ZeaChem. Cosmo and API routinely handled SO_2, whereas Andritz had used SO_2 and was confident that they could do so. The Andritz facility, although essentially the same size as ZeaChem, was limited to operating only 8 h per day, 5 days per week. This led to their elimination because it would take too long to process enough feedstock to meet the requirement of the project.

It should be pointed out that most of these facilities charge by time, so the smaller the throughput the more difficult it is for them to be price competitive. Cosmo is a production facility, and although they are interested in the possibility of someday running a sulfite-based process like SPORL commercially, the logistics of separating out one of their digesters to use a different feedstock (NARA's slash grade) without risk of contaminating their expensive commercial pulp products was too great. In addition, Cosmo was probably too large because it would have taken only about two digester batches to process all the NARA feedstock. If something went wrong with one of these batches, it would be a major problem.

The two remaining facilities were visited, and "fitting" the NARA process into their equipment was considered. API had the advantage of operating with SO_2, with the facilities and procedures already in place to accommodate this. Regarding through-put, they were bigger than Andritz but smaller than ZeaChem, and the process could have

been accomplished in a reasonable amount of time. They were more expensive per operating day than ZeaChem and did not have the liquid–solid separation system that would make moving the product solids to the next location easier. There was the option of doing an enzymatic saccharification on their site and concentrating the resulting sugars for shipment; however, their saccharification reactor was poorly agitated and would have required many dilute runs and a considerable concentration of the resulting sugars afterword. ZeaChem could handle a higher through-put and could separate the resulting solids for a wet-cake only product to ship to the next step. They did not have prior experience in handling SO_2, but they were willing to consider design modifications to their system for that purpose.

It will be covered in more detail in the section on ZeaChem, but the issues of handling and feeding SO_2 at ZeaChem were eliminated to a large extent by utilizing $Mg(HSO_3)_2$ and H_2SO_4, as demonstrated in initial practice of SPORL at FPL (Zhu et al. 2009; Wang et al. 2015), such that SO_2 would be generated only within the digester and would not need to be purchased and handled on site as a feed chemical. The vent of the digester would contain SO_2, and that was accommodated by converting a vent clean in place (CIP) system to a scrubber using a dilute caustic solution.

1.2 Enzymatic Saccharification and Fermentation

Several locations could have accomplished these tasks if it were not for the need to recover isobutanol from the fermentation broth while the fermentation was in process to avoid the toxicity of isobutanol to the GEVO microorganism. In addition, enzymatic saccharification, which produces sugars at conditions nearly optimal for fermentation but also avoids contamination (depending on the microorganism), should be done only on site with fermentation. This minimizes the risk of contamination in shipping sugar solution a long distance or storing for any length of time. Only the NREL and ICM locations had suitable enzyme saccharification and fermentation facilities at the same site (API's enzymatic saccharification capabilities were limited). The NREL facility was much smaller (2,500-gal saccharification tanks) than ICM (35,000-gal saccharification tanks) and did not have any way to effectively recover the isobutanol from the fermentation broth. ICM houses the Gevo pilot GIFT (Gevo Integrated Fermentation Technology) system for isobutanol recovery, which could easily be connected to the ICM pilot fermentation tanks. For these reasons ICM was the only viable option for these steps.

1.3 Conversion of Isobutanol to Biojet

Gevo built a demonstration facility at South Hampton Resources in Silsbee, Texas, USA, to convert isobutanol to jet fuel in 2011. This process has the capacity to produce 1,000 gal in a short time and so is the appropriate size for this project. Gevo continues to utilize this facility for jet fuel and other operations (through contract to South Hampton Resources (SHR)). In addition, Gevo is a partner in the NARA project and has a vested interest in seeing the success of NARA producing biojet fuel from forest residue. Therefore, this was a logical choice and maybe the only choice to make the final jet fuel. Gevo was willing to work with NARA to allow this project time in the facility, which would otherwise be used by Gevo. Before Gevo built the SHR facility, they looked for other locations that might have all the equipment available as a tolling operation. Although the unit operations are common in the hydrocarbon processing industry, no one had all the units available for use together and certainly not in a size appropriate for Gevo's need then or NARA's now. Most combined units are lab or small pilot plant size for feasibility or proof of concept testing. That drove Gevo's initial decision to build. NARA was then in a position to capitalize on Gevo's investment.

The geographical locations of all considered toll processers are shown in Figure 1.2.

2. Feedstock Procurement and Processing

2.1 Feedstock

The feedstock utilized in the NARA project was softwood residue material left in the forest after logging operations in the Pacific Northwest region of the United States. A separate task within the NARA project, managed by Gevan Marrs and John Sessions, was responsibility for researching what feedstock would be used and where it would be sourced for the entire NARA project and specifically for the 1,000 gal biojet fuel production. The quantity of material needed for this operation was vastly larger than that of the rest of the NARA project.

Various mixtures of feedstock had been collected and tested in the labs associated with NARA (Weyerhaeuser, Catchlight Energy, Washington State University, USDA Forest Products Laboratory, Gevo). In the end the feedstock mixture FS-10 was chosen as a typical and suitable reference feedstock. Therefore, it was determined that a "FS-10 like" feedstock would be used for this project. As explained below, materials from three locations (designated as FS-17, FS-18 and FS-19) were blended into FS-20, which was used in the 1,000-gal biojet fuel task through SPORL pretreatment. The individual and combined materials are compared to FS-10 in Table 2.1.

2.2 Feedstock Sourcing

The largest source of feed material (FS-17) was from Weyerhaeuser's western Oregon Siuslaw 900 site (Lat 43 50 46 N x Long 123 22 14 W). Forest residues were from a 45-year-old Douglas-fir stand that had been shovel logged. Lane Forest Products used a Peterson 4710B horizontal

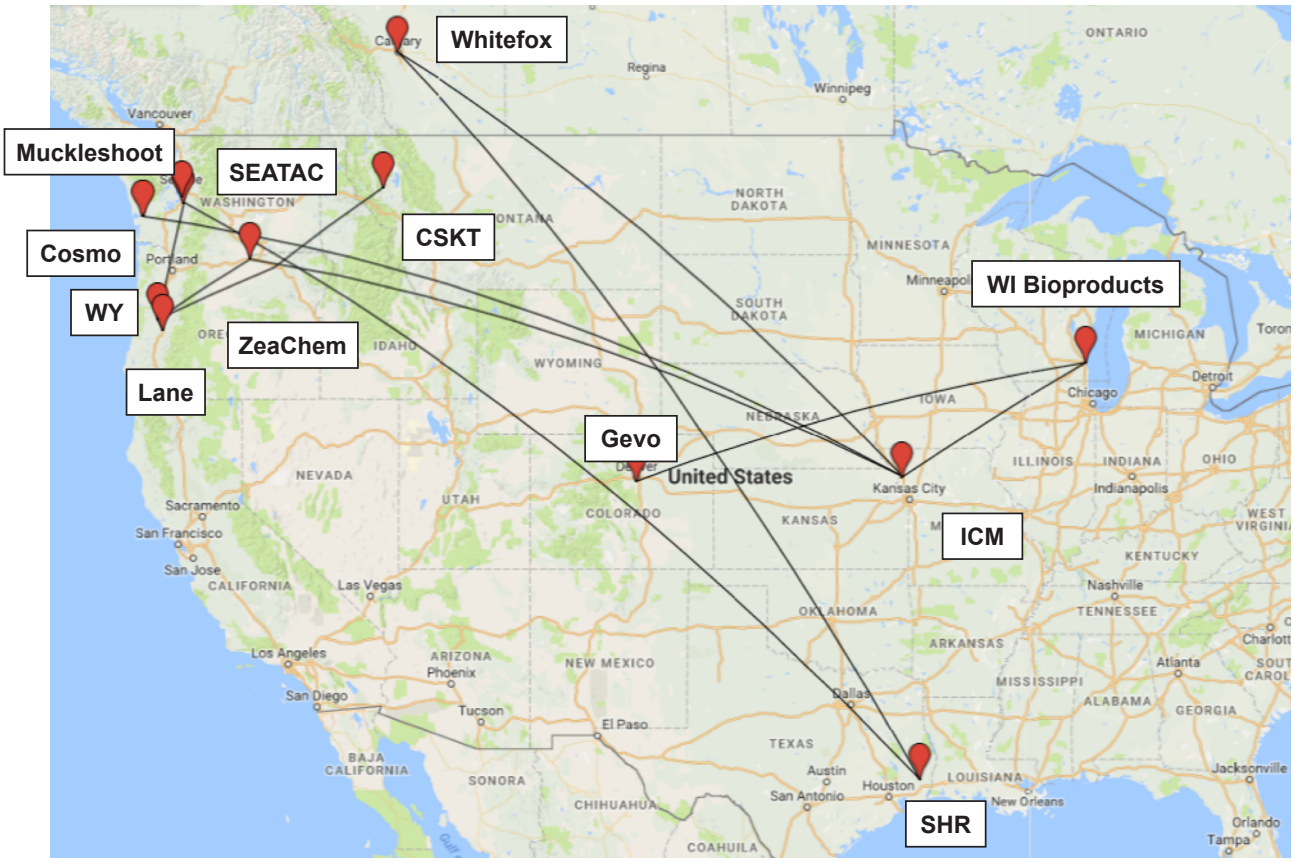

Figure 1.2—Various processing sites involved with the NARA 1,000 gal biojet production.

grinder with 3-in./4-in. grates to grind (Fig. 2.1) 317 GT (2,000 lb) (approximately 180 BDT, 13 truckloads) of Douglas-fir forest residuals in the woods to roughly 1.5- to 2-in average particle size with 6- to 8-in. maximum particles. This material was hauled to the Lane Forest Products Yard in Junction City, Oregon, USA.

Two Native American tribes also supplied feedstock. The Muckleshoot Tribe, from their lands east of Auburn, Washington, USA, supplied material from their Tee-Off timber sale (FS-19). The Tee-Off Unit is a 45-year-old Douglas-fir stand at about 1,400 ft elevation (Lat 47 11 21 N, Long 121 56 40 W). Species mix was Douglas-fir 95%, western hemlock 2%, red alder 2%, and other hardwoods (such as cottonwood) 1%. It was shovel logged. Piles (Figs. 2.2, 2.3) were prepared by the logger as part of logging operations using the same shovel. The unit was logged and piled from January through April 2014. Approximately 23 GT of feedstock was collected from the Tee-Off site for NARA. Material was ground by Rainier Wood Recyclers using a horizontal grinder with 3-in./4-in. grates and hauled to Lane Forest Products in Junction City, Oregon, USA.

The second tribal source of material (FS-18) was from the Confederated Salish and Kootenai Tribes (CSKT) Flathead Indian Reservation, near Lone Pine, Montana (T23N R23W, sections 14-15-16-23). Their slash piles were primarily Douglas-fir tops and residues from log manufacturing (Fig. 2.4). The majority of the residues are large diameter (Fig. 2.5). CSKT sorted out the larger diameter residues from the branches with green needles, which were the upper part of the piles (Fig. 2.6) and sides of some piles (Fig. 2.7). Grinding was done by John Jump Trucking using a Peterson HC 2410 horizontal grinder with 5-in. grates. Two truckloads (approximately 38 GT) were hauled to Lane Forest Products in Junction City, Oregon, USA.

2.3 Tribal Land Material

The Muckleshoot Tribe material, from their lands east of Auburn, Washington, USA, was 5% of the total FS-20 blend. A similar amount was supplied by the Confederated Salish and Kootenai Tribes from the Flathead reservation, near Lone Pine, Montana. This was approximately 13.6 tons from each site, or 27.2 GT, added to Siuslaw 900 feedstock, for a total of approximately 272 GT. Total original Siuslaw 900 was approximately 317 GT, but some of this was lost in pile storage and yard movements.

2.4 Feedstock Processing

Feedstock processing is depicted in Figures 2.8–2.10. The material was reground at Lane Forest Products, put through a 1.5-in. grate, and then screened with 1-in. top, 1/8-in.

Table 2.1—Characteristics of NARA feedstocks[a]

	FS-10	FS-20	FS-17	FS-18	FS-19
Chemical composition (wt %)					
Total polysaccharides	57.9	59.7	60.4	60.6	64.2
C6 polysaccharides	52.8	52.2	52.0	54.4	59.8
C5 polysaccharides	5.1	7.5	8.3	6.2	4.4
Ash-free lignin, acid insoluble (Klason)	27.0	30.2	29.3	31.2	29.6
Acid-soluble lignin	2.0	3.0	2.95	2.0	1.7
Hot water extractives	6.1	2.43	3.47	6.14	4.57
Ethanol extractives	0.6	0.94	0.74	1.93	1.21
Ash	0.1	0.60	0.47	0.48	0.06
Acetyl	1.8	—[b]	—	—	—
Total	95.5	96.9	97.3	102.4	101.3
Polysaccharides detail (wt % of total wood)					
Glucan (C6)	40.30	39.8	40.67	40.0	45.3
Mannan (C6)	2.39	9.14	8.48	11.2	12.3
Galactan (C6)	0.49	3.22	2.88	3.19	2.23
Xylan (C5)	4.61	6.55	7.49	4.94	3.7
Arabinan (C5)	10.10	0.98	0.84	1.28	0.65
Total	57.89	59.69	60.35	60.61	64.18
Species composition (wt %)					
Douglas-fir	64	68	64	97	97
Hemlock	15	5	9	1	1
Cedar	1	1	1	0	0
Pine	1	3	3	0	1
Spruce	3	4	3	1	1
True fir	1	0	1	0	0
Hardwood	15	19	19	1	0
Total	100	100	100	100	100

[a]NARA FS-10, Douglas-fir forest residual accepts.
NARA FS-20, 1,000-gallon biojet feedstock blend accepts.
NARA FS-17, Siuslaw 900 Douglas-fir residuals accepts.
NARA FS-18, CSKT Montana Int Douglas-fir and pine FHR accepts.
NARA FS-19, Muckleshoot Enumclaw WA FHR accepts.
[b]Not measured.

Figure 2.1—Grinding feedstock at the Weyerhaeuser Siuslaw site.

Figure 2.2—Lower pile on Tee-Off site.

Figure 2.3—Larger residues above road on Tee-Off site.

Figure 2.4—Piles of feedstock at CSKT.

Figure 2.5—Forest residue from log manufacturing.

Figure 2.6—Slash piles of branches and needles.

Figure 2.7—Other side of pile of branches and needles.

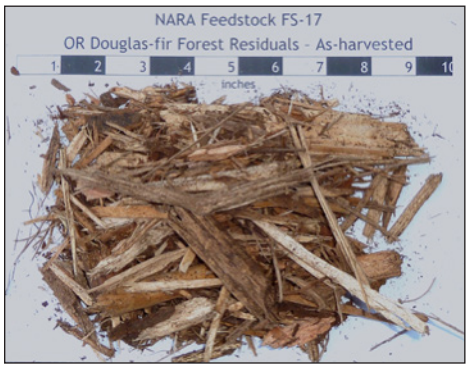

Figure 2.8—FS-17 Weyerhaeuser Siuslaw 900 site.

Figure 2.9—FS-18 CSKT site.

Figure 2.10—FS-19 Muckleshoot Tribal site.

Figure 2.12—NARA FS-20 at Lane Forest Products before resizing.

Figure 2.11—FS-20 blended and screened.

Figure 2.13—"Crumbled" FS-20 from Forest Concepts.

bottom screen. Oversized materials were reground with a 1.5-in. screen, and fines were disposed of. This allowed stringers as long as 2 in. and some fines greater than 1/8 in. to stay in the accepted mix (Figs. 2.11, 2.12).

This was unacceptable for use at ZeaChem, and size specification was changed to a 1/4 in. Several different top screen sizes (1, 3/4, and 5/8 in.) were tried. All the material was ground through a 1.5-in. grate, and part of it was screened, but there was still too much oversized material, so it was ground through a 1-in. grate. A sample was screened, but it did not meet the specification. All fines were disposed of.

To produce material for the Andritz trial (using the same particle size specification as for ZeaChem), approximately 7 GT was sent to Forest Concepts (Auburn, Washington, USA) to be screened and crumbled to get approximately 1 BDT to Andritz. Forest Concepts used a "muncher" to give a first shot and keep rocks out of the Crumbler (Forest Concepts). Next the Crumbler was set at 3/16 in. followed finally by the oribital screen with a 3/8-in. round hole punched plate top deck and a very small bottom screen (about 16 mesh, or approximately 1.5 mm clear opening) (Fig. 2.13). The screen oversized materials were batch recycled into the feed material, so that >3/8-in. oversized particles got many passes through the Crumbler and a chance to be sized as accepts.

This process made an acceptable product to feed to the Pressafiner and digester at Andritz or to the digester at ZeaChem. However, the size of equipment available at Forest Concepts was so small that processing the entire FS-20 blend would have been time and cost prohibitive.

An alternative to the Forest Concepts Crumbler process was found in a full-scale portable Peterson microchipper at Lane Forest Products that could produce an acceptable size material. All FS-20 material was run through the microchipper and rescreened 3/8-in. top, 3/16-in. bottom. This gave approximately 40 BDT of accepts, 40 BDT of oversized, and 40 BDT of fines. Because our target was to have at least 60 BDT, we microchipped the overs and screened using one section of 1/2-in. top and 3/16-in bottom, which gave approximately 20 BDT of accepts and approximately 15 BDT of overs. Because this would be our last opportunity with the microchipper (Lane Forest Products had other projects needing the microchipper), the 15 BDT of oversized material was run through the microchipper again and screened, giving us 65–66 BDT of

sized FS-20 accepts. The 1/2-in. top was chosen to make sure we had enough accepts. Only one (the middle) 3/8-in. top screen section was replaced with a 1/2-in. screen (3/8 to 1/2 to 3/8 in.).

Thus, starting with approximately 272 GT, we ended with approximately 108 GT of accepts, or approximately 66 BDT plus a small pile of oversized material (15 GT).

3. SPORL Pretreatment

3.1 Overview

The NARA team decided to use SPORL pretreatment (Zhu et al. 2009) at the ZeaChem Boardman, Oregon, USA, facility. As explained earlier, this facility had a large enough throughput, a reasonable tolling cost, and limited residence time in the reactor to no greater than 45 min. The SPORL process is versatile, operating over a range of residence time. The resident time and temperature can be scaled using a CHF (Zhu et al. 2012; Zhou et al. 2013); for example, a short residence time can be compensated by a higher temperature, although a higher temperature might cause more degradation of the solubilized sugars. For this work, the decision was made to forego use of the majority of the pretreatment liquid hydrolyzate for at least three reasons: (1) the pretreatment liquid hydrolyzate would be low pH and therefore a hazard and cost prohibitive for shipping half way across the country; (2) the liquid hydrolyzate could potentially be high in fermentation inhibitors for pretreatment at high temperatures; and (3) the sugar yield loss could be made up for with additional pretreated solids. Because the solids were not washed but only filter pressed, only the portion of hydrolyzate squeezable from the solids was lost with some of the liquid retained in the solids.

To be able to use the ZeaChem facility, we had to come up with an alternative method of making the pretreatment liquor. Normally in a commercial sulfite pulping process, SO_2 is mixed with water slurry of CaO (or MgO). These will react to form Ca^{++} (or Mg^{++}) and HSO_3^-, and/or SO_3^{2-} depending on pH. An excess of SO_2 is added so that there will be free SO_2 in solution. At ZeaChem, this would require the purchase and handling of SO_2. Because ZeaChem was not already set up to handle and purchase SO_2, it would be complicated and expensive. The alternative was to purchase a solution of $Mg(HSO_3)_2$, mix that with the wood and then add H_2SO_4 in the reactor to adjust the pH of the sulfite solution (Zhu et al. 2009; Wang et al. 2015). This resulted in a solution containing Mg^{++}, SO_2, and HSO_3^- at pH of approximately 2. When the pH is finally adjusted to the targeted pH of 2.0 with H_2SO_4 the proper amount of free SO_2 will be present in solution. SO_2 concentration in a bisulfite (HSO_3^-) solution is an equilibrium reaction driven by pH (Fig. 3.1). The SO_2 is formed only in the digester, so none had to be purchased. However, there would be SO_2 in the vent. ZeaChem added a caustic scrubber to accommodate removing SO_2.

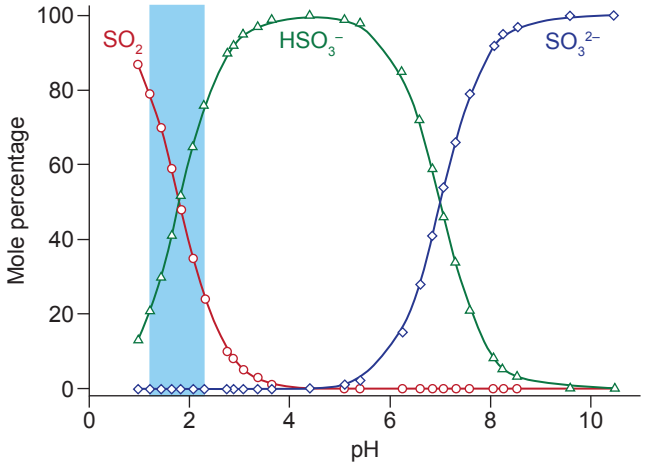

Figure 3.1—Calculated equilibrium concentration of SO_2 at 25 °C as a function of pH in a bisulfite/sulfite solution for scale-up SPORL using the equipment at ZeaChem. Although using a mixture of $Mg(HSO_3)_2$ and H_2SO_4 had been practiced at FPL extensively (Zhu et al. 2009; Wang et al. 2015) and proven robust for pretreating softwood forest residue, these SPORL experiments had been run only at lab scale at batch mode. Because ZeaChem's facility is continuous, with fixed residence time of 45 min, a higher temperature had to be used. A combined hydrolysis factor (CHF), a kinetic-based reaction severity factor developed by FPL (Zhu et al. 2012; Zhou et al. 2013, 2014; Zhang et al. 2014), was used to design the desired reaction temperature to achieve good pretreatment. The design conditions had been tested at pilot scale (Zhu et al. 2015).

One of the benefits of selecting ZeaChem was that the manufacturer of their equipment, Andritz, had a large-scale demonstration unit with which we could conduct a short test. This is the Andritz Springfield, Ohio, USA, test facility that we initially considered as the location for our whole production. They were too small for our 1,000-gal biojet production, but were an excellent place to do a short test to determine if the continuous, shorter time would work the same as the longer batch times typically conducted in the lab.

3.2 Andritz Piloting

The digester unit available at Andritz was exactly the same design as that at ZeaChem, but there were some differences in the impregnation system and the maximum pressure at which it can operate (Andritz was lower). ZeaChem had a lock hopper plus an inclined steam mixing conveyor to mix the chemicals and the heating steam with the wood. The Andritz unit had a screw press feeder to push the feedstock into the digester "T" mixing section, where chemicals and steam are added. To simulate the ZeaChem's steam mixing conveyer, Andritz suggested that we use their 560 Pressafiner (Fig. 3.2) to mix $Mg(HSO_3)_2$ solution with the wood before feeding to the digester (Fig. 3.3). This was a separate unit and open to the room. If we mixed only the $Mg(HSO_3)_2$, there would be no SO_2 formation. We then used the digester's screw feeder to feed the

Figure 3.2—560 Pressafiner at Andritz.

Figure 3.4—Crumbler feedstock at Andritz.

Figure 3.3—Continuous digester at Andritz.

Figure 3.5—Feedstock prepared with Forest Concepts Crumbler.

wood/$Mg(HSO_3)_2$ mixture to the "T" piece contained H_2SO_4 to make SO_2, along with the addition of steam for heating.

Another difference between the pilot operations at Andritz and a full-scale operation at ZeaChem was the size and character of the wood chips. Large digesters that can accommodate hundreds of tons per day of feedstock can be designed to handle larger chips than a 10-BDT/day unit. ZeaChem wanted a "chip" that was approximately 1/4 by 1/4 by 1.5 in., so the feedstock processing group ground the forest residue material collected to the desired specification (see Section 2, Feedstock Procurement and Processing). Two alternatives were used to produce properly sized material. One was to use a Forest Concepts Crumbler, which resulted in the desired material for the run at Andritz (Fig. 3.4). However, the lab or pilot unit at Forest Concepts was too small to accommodate the large quantity of material that would be needed for the run at ZeaChem. Another process called a microchipper was developed at Lane Forest Products, Junction City, Oregon, USA. Lane Forest Products was handling the sorting and screening of the material as received from the forest, so they were a logical location to process it further to small chips. The final feedstock was designated as FS-20 (Figs. 3.4, 3.5).

An experimental plan was worked out among the Andritz engineers, FPL scientists (FPL being the inventor of the SPORL process), and other NARA team members. The tests needed to be conducted within two days so as to make optimal use of resources. The first day focused on processing the wood through the Pressafiner to mix in the $Mg(HSO_3)_2$ solution: the second day focused on processing that material through the digester while adding H_2SO_4 and steam. The desired SPORL reaction temperature and time were calculated based on the scaling-up CHF of approximately 22.5, or lab-optimal condition of T_{op} = 165 °C for t_{op} = 75 min for similar feedstock (Leu et al. 2013) using the following equation (Zhu et al. 2015) with activation energy E = 100,000 (J/mole). This resulted in a residence time of 45 min for reaction pressure of 130 psig (pounds per square inch gauge) or temperature 173 °C. $Mg(HSO_3)_2$ and H_2SO_4 loadings on wood were 12 and 2.2 wt%, respectively (Leu et al. 2013).

$$\mathrm{CHF} = e^{\left(\alpha - E/RT + \beta C_A + \gamma C_B\right)}\left(C_A + C_B\right)t \qquad (3.1)$$

$$t^{T_{\mathrm{up}}} = e^{\left(E/R\right)\left(1/T_{\mathrm{up}} - 1/T_{\mathrm{op}}\right)} t^{T_{\mathrm{op}}} \qquad (3.2)$$

where α, β, γ are the adjustable parameters; C_A, C_B are the molar concentration of the reaction chemicals (i.e., H_2SO_4, and $Mg(HSO_3)_2$), T_{op} and t_{op} are optimal temperature and time based on laboratory study, and T_{up} and t_{up} are desired temperature and time for the scale-up run.

The Andritz unit was limited to a maximum pressure of approximately 125 psig. The pressure limits the maximum temperature at which that the reactor could be run. So, the experimental conditions listed in Table 3.1 were design for the trial runs at Andritz.

Each test was designed to be about 1.5 h, which was at least two residence times. The lower residence time was included because the ZeaChem unit has a higher throughput with shorter residence time. The tolling fees at ZeaChem were based on the length of running time, so a shorter residence time could reduce tolling fee charge.

Highlights of the Andritz runs included the following:

1. The pressure in the digester was limited to 113–115 psig, even though they thought they could hold a higher pressure and their steam supply was 150 psig. This limited the temperature at which the digester could be operated. There was no temperature gauge in the digester because normally the Andritz facility was operated with mainly steam, so the temperature could be determined from the pressure of the digester. Back calculating the pressure contribution of the SO_2 in the system, 115 psig would be 170 °C, so runs at the higher temperature of 173 °C were not possible.
2. It was not possible to make three runs in an 8-h day as planned. Because we were limited in temperature, only two runs at the residence times of 35 and 45 min were carried out.
3. The material from the 45-min run had the appearance (dark color) of being considerably more digested than that from the 35-min run. Saccharification and fermentation testing (below) at Gevo would confirm the digestion.
4. There was also a desire to evaluate how easily the pretreated material could be dewatered. Although ZeaChem had a filter press, Andritz had only the Pressafiner; but Andritz thought the Pressafiner would give an indication of the ease of filtration. The 45-min material was too fine to attempt in the Pressafiner. The feeding of the 35-min material failed. Therefore, no information was obtained regarding filtering the pretreated material at Andritz.

Table 3.1—Designed test conditions at Andritz

SPORL	45 min	40 min	35 min
170 °C (~115 psig)	x	x	x
173 °C (~130 psig)[a]	x	x	x

[a]Or maximum pressure, e.g., 173 °C is ~125 psig.
psig, lb/in^2 (gauge).

Andritz supplied a supplemental report (Codner and Joshua 2015) providing the detailed material balance for the 560 Pressafiner operations. They briefly mentioned the second day operation through the 418 System (their digester).

Gevo conducted enzymatic hydrolysis and fermentation tests on the two sets of materials that we produced at Andritz. The material from the run with 45-min residence time gave results similar to those obtained earlier from pretreated material made at FPL in a batch system. The 35-min material appeared to be under-pretreated, as expected.

3.3 ZeaChem Runs

A demonstration plant built by ZeaChem to process plantation-grown and harvested hardwood using a dilute acid technology was used to conduct the SPORL pretreatment of the NARA-collected softwood forest residuals. The plant has a nominal capacity of approximately 10 BDT/day at the maximum digester residence time of 45 min.

To produce 1,000 gal of biojet fuel, it was estimated that approximately 75 BDT of forest residuals would need to be processed, given the designed inefficiencies inherent in using equipment not optimized for this process and in using toll processers that are located at multiple sites. To that end, approximately 71.6 BDT of feedstock (Table 3.2) was processed at ZeaChem, producing approximately 52 BDT of processed solids that were sent to ICM. Section 2, Feedstock Procurement and Processing, indicated that approximately 66 BDT of process material meeting the specifications of ZeaChem were prepared. It also mentioned that an additional 15 BDT of oversized materials were available. Approximately 7 BDT of those oversized materials were utilized as the last material used at ZeaChem, without issue. Five different “runs” were made at ZeaChem (Table 3.3). Based on original material balance estimates, this amount of feedstock would produce 1,000 gal or more of biojet fuel.

The ZeaChem process (Fig. 3.6) was slightly modified. An additional line was added to feed $Mg(HSO_3)_2$ solution along with a dilute solution of H_2SO_4 to the digester just about where the solids were fed. The $Mg(HSO_3)_2$ feed tank was one of their existing large liquid hydrolyzate tanks. A 30% $Mg(HSO_3)_2$ solution was purchased in 300-gal totes and loaded into the storage tank with an appropriate amount of dilution water before starting up. The second modification to the ZeaChem process was to scrub the

Table 3.2—NARA feedstock received at ZeaChem, Boardman Demonstration Plant

Date	Weight delivered (lb)	Weight delivered (ton)	Moisture (%)	Weight (BDT)[a]
8/14/2015	49,040	24.5	26.7	18.0
8/17/2015	51,300	25.6	31.9	17.5
8/24/2015	50,520	25.3	26.6	18.5
8/31/2015	16,200	8.1	28.2	5.8
8/31/2015	26,960	13.5	12.5	11.8
Total	194,020	97.0		71.6

[a]BDT, bone dry ton.

Table 3.3—Hydrolysis cake generated at ZeaChem, Boardman Demonstration Plant

Run	No. sacks	Weight (wet) (lb)	Weight (dry) (BDT)[a]
NR01	27	12,860	2.5
NR03	68	57,340	11.2
NR04	96	76,720	17.0
NR05	35	29,900	7.2
NR06	44	40,150	9.6
Total	270	216,970	47.5

[a]Based on an average 39% for NR01 and about half of NR03; the rest averaged 48% solids content.

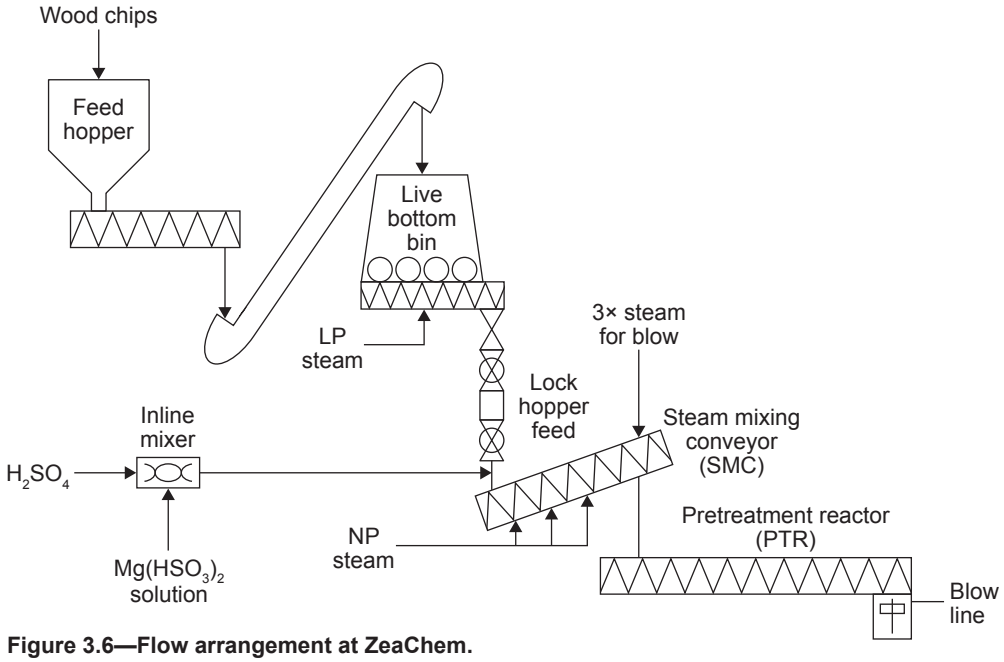

Figure 3.6—Flow arrangement at ZeaChem.

blow tank vent of SO_2 gas that evolved when the digester pressure was reduced through the blow tank. To accomplish this, a continuously recirculating stream of dilute caustic was added through the CIP system of the vent condenser. This spray of caustic into the vent stream was effective in reacting with and removing the venting SO_2.

Laboratory SPORL runs with batch digestions (Zhu et al. 2009; Wang et al. 2015) had no "blow" or rapid reduction in reactor pressure that tends to explode the pretreated solid material. Therefore, it was necessary to run the pretreated material through a disk refiner to further reduce the particle size in lab batch operation. Initially the disk refiner was used at ZeaChem to further reduce the size of the material as carried out at the Andritz trial. Because the ZeaChem system was equipped with a significant "blow" or rapid pressure reduction that the pretreated material is subjected to, it was concluded that disk refining might not be necessary.

The NARA-prepared forest residual feedstock, designated as FS-20 (Fig. 3.7), was delivered by a self-unloading tractor–trailer from Junction City, Oregon, USA (Fig. 3.8).

The NARA team had prepared the feedstock at Lane Forest Products using a microchipper, which produced material with essentially the same size characteristics as the Crumbled-produced chips used at Andritz.

Two quick tests ultimately determined whether the pretreatment was being conducted properly. First was the compositional analysis showing unsolubilized cellulose. It is desirable to preserve as much of the starting cellulose as possible because the majority of the glucose solubilized in pretreatment is lost when the liquid is removed. Second was the digestibility of the pretreated solids, that is, the amount of unsolubilized cellulose that could be converted into fermentable glucose through enzymatic saccharification. Both tests were difficult and require several days to complete. However, the FPL developed a "quick saccharification" test that gave a relative indication of the digestibility of solids within a few hours. With the reference materials of the two runs at Andritz, we would be able to determine if the ZeaChem material was more similar to the good run (45-min run) at Andritz or to the poor run (35-min run) at Andritz (Table 3.1).

Figure 3.7—ZeaChem-accepted feedstock.

Figure 3.8—NARA feedstock at ZeaChem.

Based on the Andritz trial runs, the initial conditions for $Mg(HSO_3)_2$ loading were 12% bisulfite to wood, H_2SO_4 was 0.35% v/v, L:S was 4.0 (including all liquid with feedstock and condensed steam), temperature was set to 175 °C, and an expected pressure of 132 psig (steam pressure alone at 175 °C is 114.7 psig, overpressure is due to dissolved SO_2).

3.3.1 Operation at ZeaChem

After various initial delays (such as $Mg(HSO_3)_2$ not delivered on time, issues with three pumps, agitator "key" found in flushing out blow tank), the process was started very early in the morning of August 19, 2015. The running temperature was 175 °C, but the pressure was at only 119–120 psig, which was below the expected pressure of 130 psig, accounting for the partial pressure of the SO_2 generated from the levels of $Mg(HSO_3)_2$ and H_2SO_4 added. The pretreated material was lighter in color than either of the runs at Andritz. Furthermore, the quick saccharification test resulted in a concentration of only 4.13 g/L glucose after 6-h saccharification, or approximately 45% glucan conversion in enzymatic hydrolysis, compared with the result from the 45-min run at Andritz (Table 3.4). The system was not pretreating the feedstock properly. The

Table 3.4—Results of FPL "quick" saccharification test on Andritz trial material (as reference)

Enzymatic hydrolysis time (h)	Glucose by YSI analyzer[a] at two digester residence times (g/L)	
	35 min	45 min
0	0.06	0.06
1	2.43	3.06
2	3.66	4.95
4	5.41	7.51
6	6.31	8.73
8	6.96	9.58

[a]YSI 2700 Biochemistry Analyzer, YSI Inc., Yellow Springs, OH.

results were also poorer than the 35-min run (6.31 g/L) at Andritz (Table 3.4), even though the amount of sulfur making its way to the vent condenser was about what would have been expected for the design amount of SO_2 in the vent. We quickly identified that the most probable cause of poor pretreatment was loss of SO_2 throughout the continuous reactor, especially at the discharge.

At this point we encountered more operational difficulties, such as hot slurry being fed to the filter press even though interlocks should have prevented this. As a result, one of the filter frames was destroyed, as was part of the filter cloth; this allowed solids to enter the liquid filtrate tank, where they had to be laboriously cleaned.

H_2SO_4 loading was increased to increase SO_2 concentration. Additional acid lowered the pH and increased the amount of SO_2 (Fig. 3.1), which was verified by the pressure in the system. Pressure was approximately 15 lb/in^2 higher than just pure steam at process temperature. We also increased the amount of liquid being added. The feedstock was only about 27% water, compared with an estimated value of 50%, so the resulting L:W in the digester was very low. Increasing the system temperature should also help the digestion as expected based on the scale-up design CHF (Eq. (3.1)) (Zhu et al. 2012), so temperature was increased to 180 °C and then 185 °C from the initial 175 °C.

With temperature increased to 185 °C, the SO_2 overpressure was slightly increased. We also achieved a L:W ratio of about 5 by increasing the water flowing in with the chemicals (diluted the $Mg(HSO_3)_2$). However, the system was shut down on August 20 due to a blow line plug.

The system down time provided the opportunity to determine the cause of SO_2 loss, which had been identified as the cause of poor pretreatment. We began investigating how the steam was entering the system. Because of the small size of the ZeaChem unit (smaller than a production unit), the blow line was designed based more on being large enough to avoid plugging and availability of standard pipe sizes than on desired pressure drop for the designed flows. A higher steam flow than required for the thermal heating

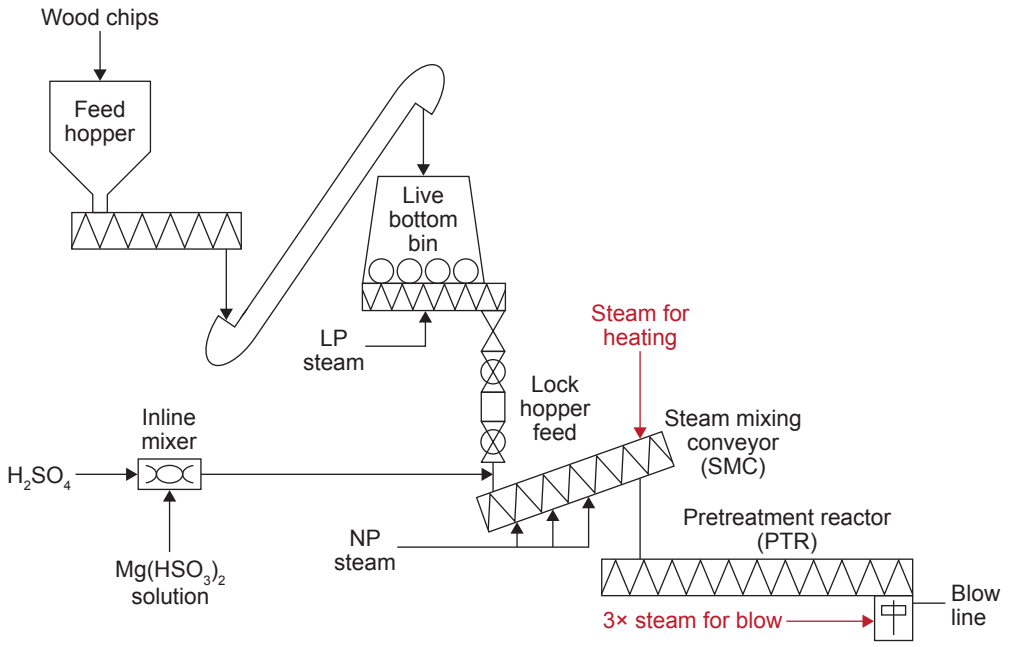

Figure 3.9—Modified steam flow arrangement.

of the system was needed to avoid frequent plugging. As much as 1,500 lb/h of excess steam was swept through the reactor to maintain the pressure drop through the exit blow line, compared with less than 500 lb/h needed to maintain the temperature of the system. We calculated that as much as 150 lb/h of SO_2 could be removed from the system with that much steam sweeping through the digester. The required flow of SO_2 through the system was only about 20 lb/h. Consequently, most of the SO_2 being generated was not remaining in the solution but was being stripped out by the excess steam. This large steam flow through the blow line is needed to operate the ZeaChem reactor. However, this steam flow does not need to sweep through the entire reactor and can be added just before the discharge. One of the lead operators conveyed that they had operated this way at various times (Fig. 3.9).

The change was made to have the excess "blow" steam for blow (Fig. 3.9) added at the digester discharge. We were able to maintain 158 psig at 185 °C. This is about a 10 lb/in^2 over the pure steam pressure but was still lower than we would expect due to SO_2 loss by the steam for heating the reactor (Fig. 3.9). After these changes, the enzymatic test results for the pretreated solid was now similar to those between the 35-min and 45-min runs at Andritz, a definite improvement.

From this point forward, various stops and starts occurred due to mechanical and other issues (for example, Fig. 3.10 shows material that collected in a progressive cavity pump and in the blow-line). However, in general, the system continued to run fine and produce material that was digestible (Table 3.5). The historical summary of the run is provided in Appendix A. When the process was running or shut down can be ascertained from Figure 3.11. When

Figure 3.10—Material from pump and blow line.

the line was flat, the process was shut down; when it was increasing, the process was running. The slope of feedstock usage was the feed rate of the system. From about 9/4/2015 until 9/15/2015, the plant was shut down for repairs; from 9/18/2015 to 9/21/2015, the plant was again experiencing mechanical issues but finally came up on the 9/21/2015 and ran the rest of the feed material, completing the run on 9/24/2015.

3.3.2 Run Designations

During the course of the ZeaChem operation, different "runs" were identified. Generally, each time a major process change was made, the run designation was changed. The bags of product solids were marked as to the run number, the sequential filter press dump (the filter press is a batch process and a single discharge cycle would be several bags full), and the sequential bag within that dump. Such as NR01-2C would be run 01, filter press dump 2, and bag C, or the third bag filled from that dump. The runs are

Table 3.5—ZeaChem run designations

Run	Start time	Stop time	Description
NR01	8/18/2015 3:30 AM	8/21/2015 7:40 PM	Steam feeding to inlet of digester stripping SO_2
NR03	8/22/2015 3:00 AM	8/24/2015 11:59 PM	Excess steam moved to discharge of digester
NR04	8/25/2015 00:01AM	9/3/2015 10:15 PM	Refiner off (off for remaining two "runs" as well)
NR05	9/3/2015 10:27 PM	9/17/2015 8:10 PM	Lower $Mg(HSO_3)_2$ to match unexpected lower wood flow
NR06	9/21/2015 1:30 PM	9/23/2015 5:40 PM	Switched to a coarser wood chip

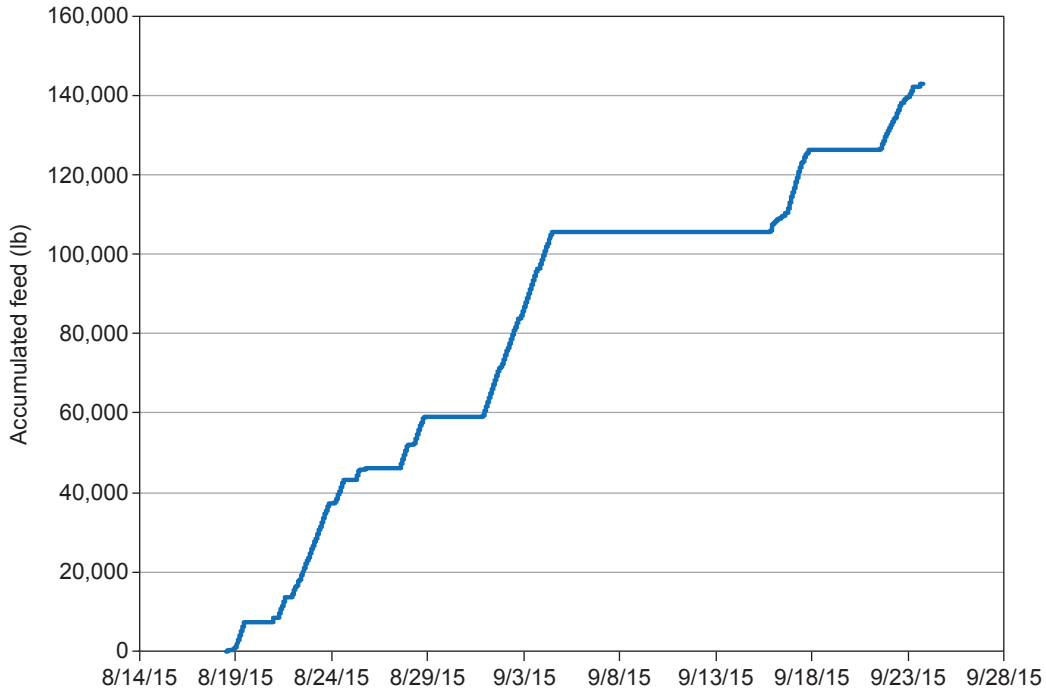

Figure 3.11—ZeaChem accumulated wood feed.

as shown in Table 3.6 (there was never a NR02 run, we skipped from 01 to 03).

3.3.3 Pretreatment Yields

ZeaChem conducted an 8-h material balance study on liquid accumulating in the blow tank. This gave a reasonable accounting for the yield of glucose and xylose in the pretreatment hydrolyzate stream (Table 3.7). ZeaChem did not analyze mannose for this analysis, so we have no accounting of how much mannose was solubilized. By ZeaChem analysis, 8% of the feedstock glucose and greater than 100% of all the xylose was solubilized. It was not possible to utilize the pretreatment hydrolyzate that was pressed out of the pretreated solids through dewatering due to hazardous shipping required with the multiple tolling sites for the present project. The sugar stream in the pressed-out portion of pretreatment hydrolyzate was lost to the production of isobutanol but will be reclaimed in a commercial operation.

3.3.4. Solids Yields

The overall solids yield from the run can be determined from the total amount of feed and total amount of water-insoluble solids. A few bags were analyzed at ZeaChem for moisture (Fig. 3.12). Many bags were analyzed for solids composition by NARA partner Weyerhaeuser. Those analyses are presented in Appendix B. The most difficult aspect of assessing yield was accurate determination of moisture content of both feedstock and pressed product. The feedstock was held in a pile in the open air in the very dry climate of eastern Oregon and was continuously losing moisture, so we added water by running a hose into the feed drag line. This moisturized material was weighed.

In general, early bags averaged about 39% consistency, or 61% moisture of filter-pressed product, whereas later bags were about 48% consistency, or 52% moisture.

Using the moisture data from analyses and interpolating for the bags that were not analyzed, we estimated the overall yield. In summary, 47.5 BDT of solids were produced from 71.6 BDT of feedstock, or an overall solids yield of 66%. This solids yield is higher than typical laboratory washed solids yield of 62.6% from equivalent feedstock (Leu et al. 2013). These were not quite washed solids, but rather were pressed solids with a substantial amount of the dissolved solids gone with the filtrate, so a significant

Table 3.6—Summary of enzymatic saccharification quick assay[a]

	YSI glucose (g/L)													
Sample	0 h	1 h	2 h	4 h	6 h	6.5 h	8 h	16.5 h	17 h	24 h	48 h	72 h	94 h	115 h
Andritz 35 min	0.06	2.43	3.66	5.41	6.31		6.96			9.46	10.10	10.40		
Andritz 45 min	0.06	3.06	4.95	7.51	8.73		9.58			12.80	13.30	13.50		
NR01-FP1	0.12	1.65	2.52	3.53	4.13					6.24	6.68	6.92		
NR01-FP3	0.09	1.73	2.65					5.79		6.26	6.64	7.11		
NR01-FP3 2X enzy		2.70		4.40	4.66					7.32	7.91			
NR03-FP1	0.16	2.59	4.30	6.48	7.67					10.90	11.80			
NR03 FP2	0.21	2.52	4.25	6.52						11.60	12.40			
NR03 FP5	0.29	2.38	4.17	6.59	8.13					13.20				
NR03 FP6	0.30	2.47	4.20	6.45	8.19					13.50				
NR03 FP6 2X enzy		4.39	7.49	10.60	12.00					14.10				
NR03 FP8	0.51	2.66	4.52						11.30	14.10	16.20			
NR03 FP9		2.43	4.76	6.99										
NR04 FP4	0.20	2.61	4.51						11.70	13.50	15.40			
NR04 FP6	0.23	2.68	4.71						12.50	14.80	15.60			
NR04 FP8	0.29	2.58	4.69						12.10	14.30	15.30			
NR04 FP10	0.24	2.29	4.18						11.50	13.70	15.00			
NR04 FP12	0.28	2.66	5.15							13.50				14.20
NR04 FP14	0.32	2.22	4.53							13.60				14.70
NR04 FP16	0.25	2.40	4.59							13.60				14.80
NR04 FP18	0.21	2.51	4.57	7.23		9.35				13.10	14.00	14.20		
NR04 FP20	0.24	2.35	4.40	6.71		9.58				13.40	14.40	14.60		
NR04 FP22	0.23	2.25	4.11	7.17		8.89				12.90	14.00	14.20		
NR04 FP24	0.33	2.25	4.23					12.70		12.40	14.30	14.60		
NR04 FP25	0.27	2.14	4.03					12.60		13.50	14.50	14.50		
NR05 FP1	0.30	2.31	4.21					12.30		13.20	14.30	14.00		
NR05 FP2	0.25	2.41	4.31					12.10		12.90	14.20	14.20		
NR05 FP3	0.39	3.02								12.95				
NR05 FP4	0.36	2.57								13.45				
NR05 FP4 (duplicate)	0.21	2.29	4.08							13.10			14.60	
NR05 FP5	0.30	2.51	4.38							12.60			14.10	

[a]3% solids loading, 5% Ctec3 loading, pH 5.5, 50 °C.

amount of solublized sugars was retained, and therefore a slightly higher solids yield was reasonable. This solids yield was lower than pilot scale unwashed solids yield of 88.8% (Zhu et al. 2015) from equivalent feedstock FS10 using a much lower pretreatment temperature of 145 °C for 240 min at equivalent severity CHF. The solids yield from the ZeaChem runs being lower than that from the pilot-scale run could be due to the higher temperature (185 °C) used at ZeaChem than the substantially lower temperature (145 °C) at pilot scale, in addition to the improved filter press at ZeaChem.

We also calculated solids yield from the rate of feed addition and product solids collection during periods of constant operation. Figure 3.13 shows two periods of consistent continuous operation, the first from about 8/21/2015 to 8/23/2015. There was a lag between counting feedstock and product. The calculated dry solids yield for that period was 64% (Table 3.8). A second period from about 8/31/2015 to 9/4/2015 gave the result of 67%.

Full solids composition measurement was time consuming and can be costly. Weyerhaeuser measured the compositions of samples from 39 product bags (from a total of 270). The results of selected samples are summarized in Table 3.9; glucan and total carbohydrate analyses are given in Figure 3.14. Additional data are included in Appendix B.

Solids composition measurements were not made for Run NR01 (Fig. 3.14) because Run NR01 was sub-optimal in terms of pretreatment. Average glucan composition of

Table 3.7—ZeaChem 8-hour mass balance experiment[a]

	Initial value	Final value
Blowtank level	11,855.0 L	24,297.0 L
Blowtank fill rate		1,493.0 L/h
Total condensate		1,213.8 L/h
Hybrid poplar chips fed to system		2,137 BDkg
Hydrolyzate glucose concentration	5.08 g/L	5.66 g/L
Hydrolyzate xylose concentration	12.31 g/L	13.15 g/L
Hydrolyzate formic acid concentration	0.00 g/L	0.00 g/L
Hydrolyzate acetic acid concentration	1.34 g/L	2.16 g/L
Hydrolyzate levulinic acid concentration	0.00 g/L	0.54 g/L
Hydrolyzate HMF concentration	1.49 g/L	1.80 g/L
Hydrolyzate furfural concentration	0.16 g/L	0.44 g/L
Condensate glucose concentration		0 g/L
Condensate formic acid concentration		0 g/L
Condensate acetic acid concentration		1.29 g/L
Condensate furfural concentration		0.06 g/L
Blowtank glucose produced		72.2 kg
Glucose yield		8.0%
Blowtank xylose produced		162.1 kg
Xylose yield		102.2%

[a]Run NR03 single fill mass balance, 9/2/2015 from 6:00 to 14:20. Hydrolyzate refers to the liquid portion of the pretreated slurry.

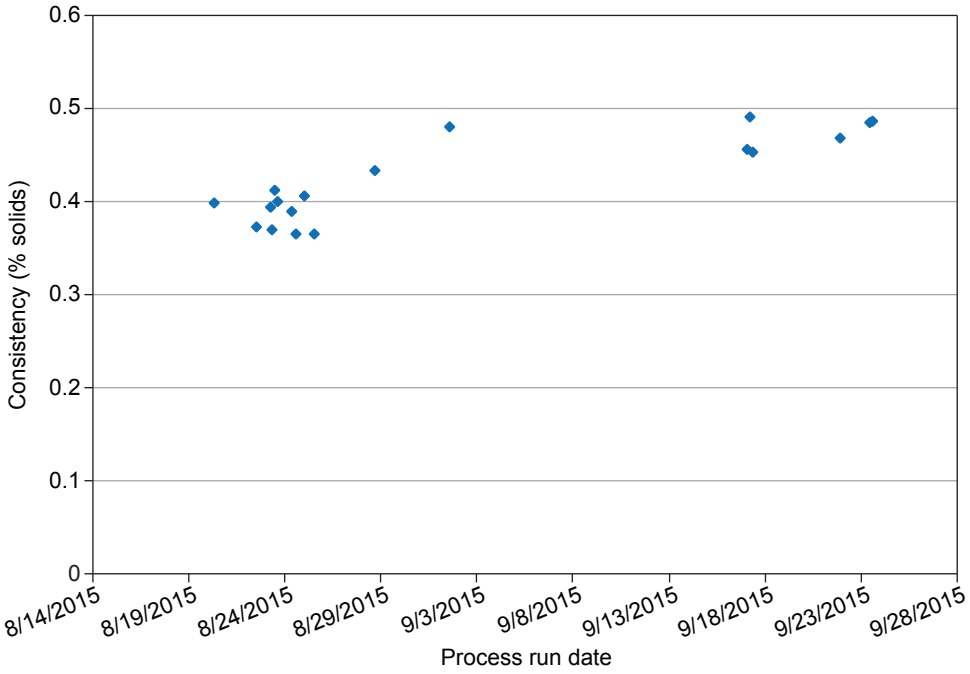

Figure 3.12—Moisture analyses of filter press cakes.

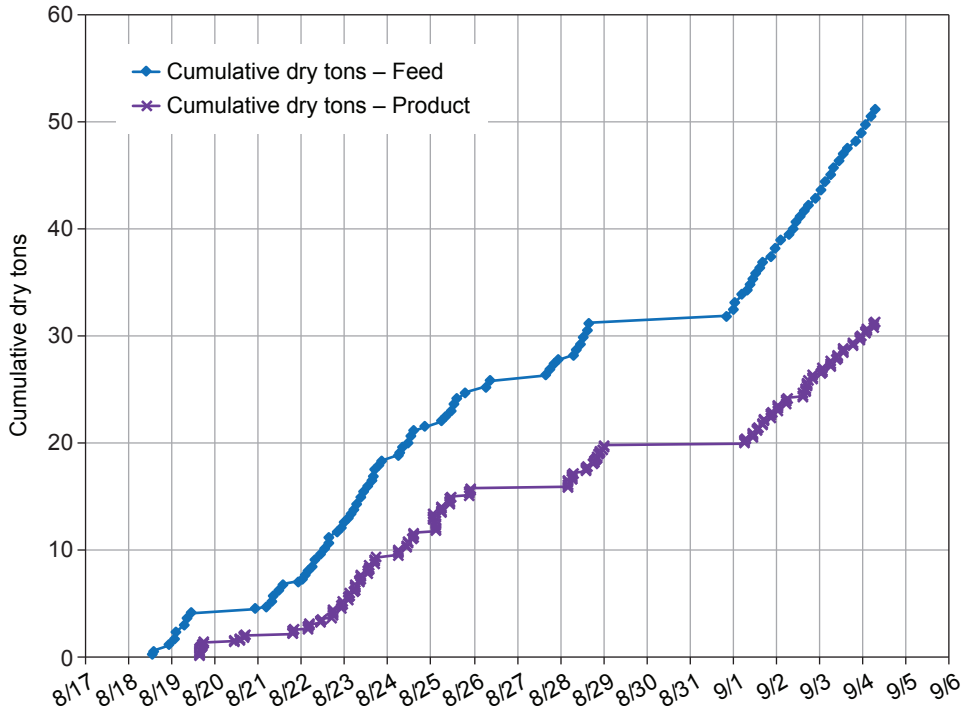

Figure 3.13—Accumulated feedstock and product at ZeaChem.

Table 3.8—Solids yield calculated from continuous operation[a]

Product start	8/22/2015 3:30 AM	2.62 BDT
Product finish	8/24/2015 6:05 AM	9.82 BDT
Feed start	8/21/2015 10:12 PM	7.07 BDT
Feed finish	8/23/2015 8:48 PM	18.38 BDT
Total feed		11.3 BDT
Total product		7.2 BDT
Average solids yield		64%

[a]Feed moisture ~30%, product moisture ~60%.

Table 3.9—Summary of Weyerhaeuser solids composition measurements

Run	Total bags	Bags samples	Solids content (weight % ± standard deviation)				
			Glucan	Mannan	Galactan	Xylan	Total
NR01	27	0					
NR03	68	2	48.47 ± 1.6	1.54 ± 0.22	0.35 ± 0.07	1.54 ± 0.22	51.28 ± 1.91
NR04	96	16	50.87 ± 1.37	1.46 ± 0.1	0.23 ± 0.04	1.46 ± 0.1	53.55 ± 1.33
NR05	35	9	46.47 ± 1.78	1.22 ± 0.04	0.24 ± 0.04	1.22 ± 0.04	48.7 ± 1.82
NR06	44	12	47.82 ± 1.23	1.23 ± 0.21	0.29 ± 0.07	1.23 ± 0.21	50.07 ± 1.14
Total	270	39	48.79 ± 2.22	1.34 ± 0.19	0.26 ± 0.06	1.34 ± 2.22	51.24 ± 0.14

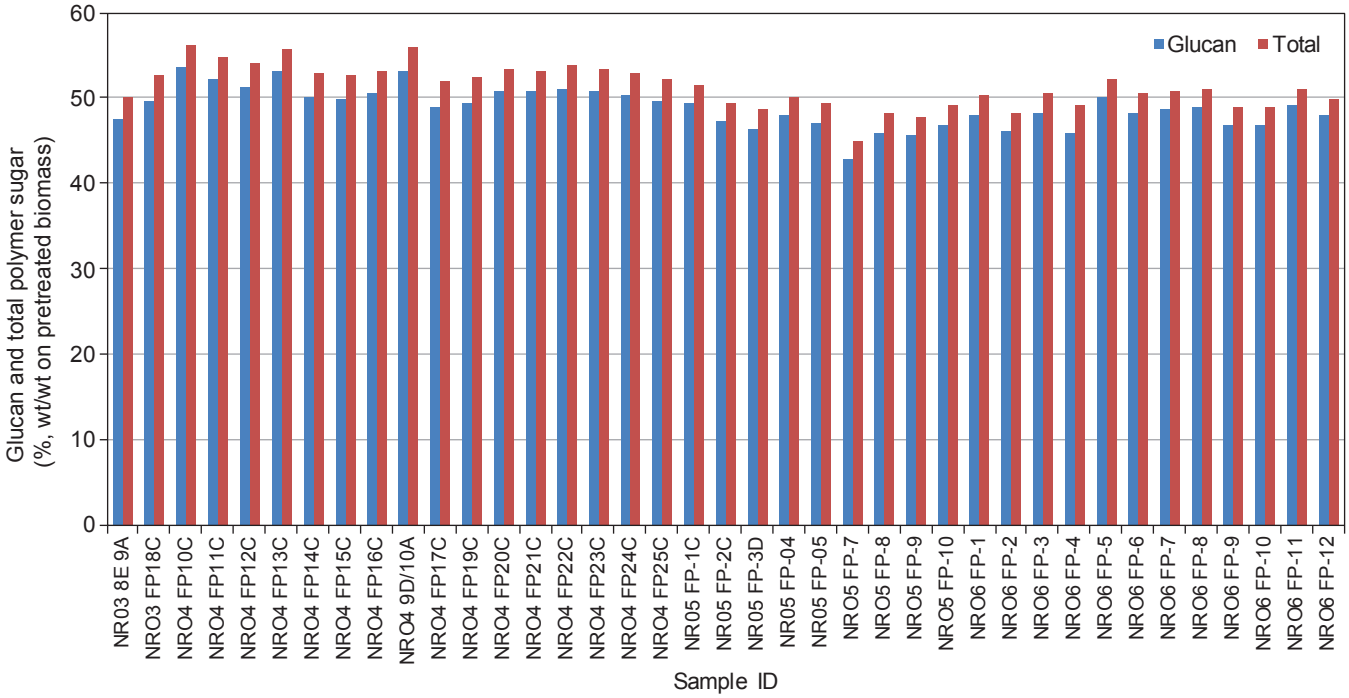

Figure 3.14 —Carbohydrate composition of selected filter cake samples analyzed by Weyerhaeuser.

Table 3.10—ZeaChem run solids and glucan yield from 8/31/15 to 9/4/15

Product start	9/1/2015 6:10 AM	19.94 BDT
Product finish	9/4/2015 6:34 AM	31.34 BDT
Feed start	8/31/2015 8:32 PM	31.81 BDT
Feed finish	9/3/2015 11:01 PM	48.90 BDT
	Solids	Glucan
Feed	17.1 BDT	7.0 BDT
Product	11.4 BDT	6.8 BDT
Yield	67%	97%

48.8% compares with 57.3% in the washed pretreated solids or 44.1% in the unwashed pretreated solids from a pilot-scale experiment using similar feedstock and $Ca(HSO_3)_2$ (Zhu et al. 2015).

Total glucan recovery from 8/31/2015 to 9/3/2015 is 97% (Table 3.10); Zhu et al. (2015) showed a glucan recovery of 95.5%. This does align with the 8% glucose that the 8-h ZeaChem liquid material balance showed as being solubilized (Table 3.7). Suffice it to say the recovery of glucan was very good.

3.3.5 Saccharification Yields

In addition to the "quick" saccharification test that FPL developed and conducted, Weyerhaeuser ran several saccharification tests using conditions more reflective of the large-scale enzymatic saccharification (that is, 15% solids, no buffer solution, and relevant enzyme loadings). The elevated pH 6.5 can reduce nonproductive cellulase binding to lignin, as discovered by Lou et al. (2013) and Lan et al. (2013), which was especially important for the present study using unwashed solids. The glucose yields of three typical samples from the ZeaChem runs are given in Table 3.11.

All the saccharification yields after 72 h were excellent, greater than 88%. The primary difference between the three ZeaChem runs was that NR03 was disk milled, whereas the other two, NR04 and NR05, were not. Furthermore, NR05 had a lower $Mg(HSO_3)_2$ dosage than NR03 and NR04. The differences in yields seem to be contrary to what might be expected, that is, highest yield with high $Mg(HSO_3)_2$ and disk refiner (Table 3.11). Disk milling apparently did not result in enhanced saccharification as expected, because the materials were well pretreated and the hot blow was able to substantially reduce the size of the pretreated material (Zhu et al. 2010). A higher $Mg(HSO_3)_2$ loading might have increased the pH of the pretreatment liquor, which reduced hemicellulose removal even though it increased lignin dissolution, which can reduce saccharification (Zhu et al. 2009).

In total, 270 supersacks of pretreated solids, pressed to 40% to 50% solids were produced (Fig. 3.15). Given the composition (moisture and glucan) and enzymatic saccharification test results, we could predict how much biojet fuel can be produced from this material. An expected amount of biojet fuel that could be produced was calculated from the amount of filter cake produced (Table 3.3), the average amount of glucan in that material (Table 3.9), a conservative saccharification yield based on Table 3.11, but reduced by 5% to account for processing loss, and some reasonable yield expectations for fermentation and jet production. That amount of jet fuel expected was over 1,250 gal (Table 3.12). The goal was at least 1,000 gal.

Table 3.11—Weyerhaeuser saccharification results

Sample ID	Refiner	MgBS on wood (%)	Glucan in solid (%)	Enzyme dose	24-h hydrolysis Glucan titer (%)	24-h hydrolysis Glucan yield (%)	48-h hydrolysis Glucan titer (%)	48-h hydrolysis Glucan yield (%)	72-h hydrolysis Glucan titer (%)	72-h hydrolysis Glucan yield (%)	HMF titer (%)
Sugar yields by high enzyme dosage for solid hydrolysis from three pretreated conditions[a,b]											
NR03 8E/9A	Yes	17	47.33	High	6.90	87.80	7.60	96	7.50	95	0.07
NR04 9D/10A	No	17	53.00	High	7.40	84.30	8.10	91	8.30	94	0.04
NR05 FP3D	No	15	46.27	High	6.80	88.70	7.60	98	7.60	98	0.05
Sugar yields by low enzyme dosage for solid hydrolysis from three pretreated conditions[a,c]											
NR03 8E/9A	Yes	17	47.33	Low	5.80	73.00	7.00	73.00	7.10	90	0.07
NR04 9D/10A	No	17	53.00	Low	6.30	70.80	7.30	70.80	7.80	88	0.04
NR05 FP3D	No	15	46.27	Low	6.10	79.20	7.20	79.20	7.40	96	0.05

[a]Solids concentration: 15%; initial pH 6.5, ending pH ~5.0 without base addition during hydrolysis. Glucan yield is based on glucan in pretreated solids.
[b]High enzyme dose: 10% Cellic Ctec3 and 1% HTec3 on solid.
[c]Low enzyme dose: 5% Cellic Ctec3 and 0.5% HTec3 on solid.

Figure 3.15—Supersacks of pretreated forest residues produced at ZeaChem.

Table 3.12—Expected jet production from the pretreated forest residue material produced at ZeaChem

Parameter	Value
Filter cake, NR03–NR06[a]	45 BDT
Average glucan[b]	49% wt
Glucan	44,100 lb
Saccharification yield[c]	85%
Glucose	41,608 lb
Processing losses[d]	5%
Glucose to fermentation	39,528 lb
Isobutanol yield[e]	0.32 lb/lb glucose
Isobutanol produced	12,649 lb
Isobutanol produced	1,879 gal
Isobutanol losses[d]	5%
Biojet carbon yield[f]	86%
Max theoretical jet yield	0.766 lb jet/lb iBuOH
Actual jet yield	0.659 lb jet/lb iBuOH
Jet density	6.31 lb/gal
Final jet	7,916 lb
Final jet	1,255 gal

[a]Table 3.3.
[b]Table 3.9.
[c]Table 3.11 (less 5%).
[d]Estimated losses.
[e]Typical Gevo yield.
[f]Gevo yield (this is with C_8 production minimized).

4. Enzymatic Hydrolysis

4.1 ICM Run C0290

Two campaigns were executed at ICM's Facility in St. Joseph, Missouri, USA, to produce isobutanol from pretreated solids. The first in November and December 2015 was referred to by ICM's run number C0290. A second campaign (C0310) was conducted in March through May 2016. ICM operates multiple pilot plants at this location in addition to a corn-ethanol production facility. The pilot plants include a cellulosic pretreatment and enzymatic saccharification facility and a fermentation facility. In addition, they house the Gevo GIFT pilot plant for recovering isobutanol from fermentation and purifying it.

The overall plan for enzymatic saccharification in run C0290 at ICM was to utilize the best or prime ZeaChem-produced solids of approximately 45 BDT and saccharify in two batches in the 35,000-gal saccharification tanks available in ICM's cellulosic biomass pilot plant. In addition, some reject pulp from the Cosmo Specialty Fiber mill in Cosmopolis, Washington, USA, was also used in C0290 to evaluate the suitability of commercial sulfite pulp mill rejects for biofuel production. The Cosmo mill is a magnesium bisulfite pulping process that uses hemlock wood to produce a high-quality dissolving pulp. The process is similar to the SPORL process used at ZeaChem, at a much higher SO_2 dosage (three to four times) and longer cooking time of 4 to 6 h but at a much lower temperature of 140 °C (Gu et al. 2016). Cosmo was interested in exploring the opportunities to produce sugars from their rejected pulp stream, which was burned at the mill only for its heating value. It was planned that the Cosmo material would be hydrolyzed in a small third hydrolysis batch.

As described in Section 3, Pretreatment, pretreated solids from ZeaChem were delivered to ICM in supersacks (Fig. 4.1). The supersacks were stored in the feedstock tent, and as needed, they were dumped onto the relatively clean concrete floor of the feedstock tent. A front-end loader was used to fill the feed hopper (Figs. 4.2, 4.3) that conveyed them into a slurrying tank. From the slurrying tank, the material was pumped to the saccharification tanks located across the street in the cellulose pilot plant area. This is a distance of about 280 ft plus the vertical runs to get up to the second floor (Fig. 4.4).

Pumping a slurry of targeted concentration of 15% solids had not been done at ICM. ICM's usual feed to their cellulose pilot plant was a dry untreated material, like chopped or ground corn stover or switchgrass. Their normal conveying system over this distance is pneumatic, which works well for dry solids. There were difficulties in pumping this slurry, but generally it was accomplish by going into a second slurry tank (Fig. 4.5) at about half the distance and using a second pump (large diaphragm pump) to get the slurry from the second tank to the hydrolysis tank.

4.2 C0290 Saccharification

With ICM's four 35,000-gal saccharification tanks, it was possible to fill two and even three tanks in sequence and start the saccharification by adding enzyme as each tank was full. (The alternative would be filling one tank, running the saccharification to make sure it worked properly, and then filling the second.) ICM wanted to push through all the solids transfer as quickly as possible to get that problematic operation completed and not have to start and stop the solids transfer. As we saw in C0310, starting and stopping the solids transfer a few times was not an issue.

As each tank was nearly filled, Cellic CTec3 cellulase enzyme cocktail (complimentarily provided by Novozymes) was added, and saccharification was started. All the prime ZeaChem material (ZeaChem batches NR03, NR04, NR05, and NR06) was not able to fit into two saccharification tanks, because maintaining the targeted 15% solids in the feed slurry was not possible due to difficulties in pumping slurry at high solids. Therefore, the third tank, rather than being exclusively for saccharifying the Cosmo material, would be a mixture of prime ZeaChem material and Cosmo rejected pulp. All the ZeaChem sub-prime material (NR01) was also added to the third tank because there was spare volume in the third tank and the saccharification run in third tank was already a mixture. This would produce some additional sugar overall.

Figure 4.1—CM facility in St. Joseph, Missouri, USA.

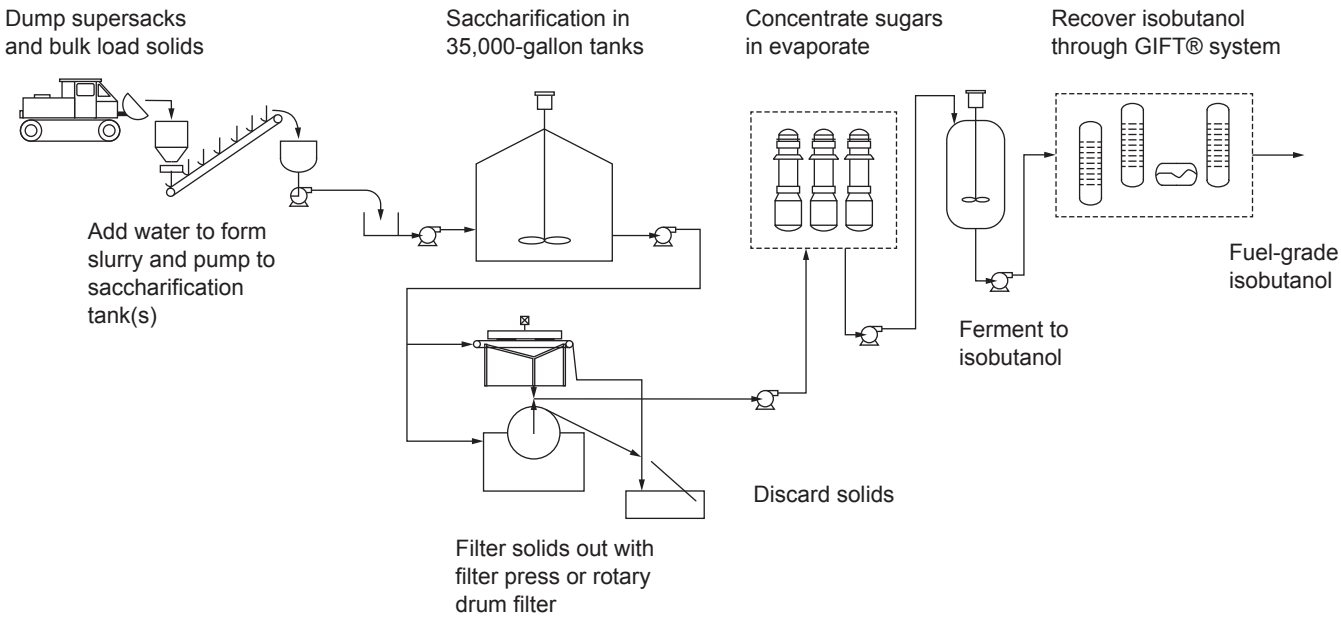

Figure 4.2—Overall process at ICM.

Figure 4.3—Loading of dumped supersacks into feed hopper.

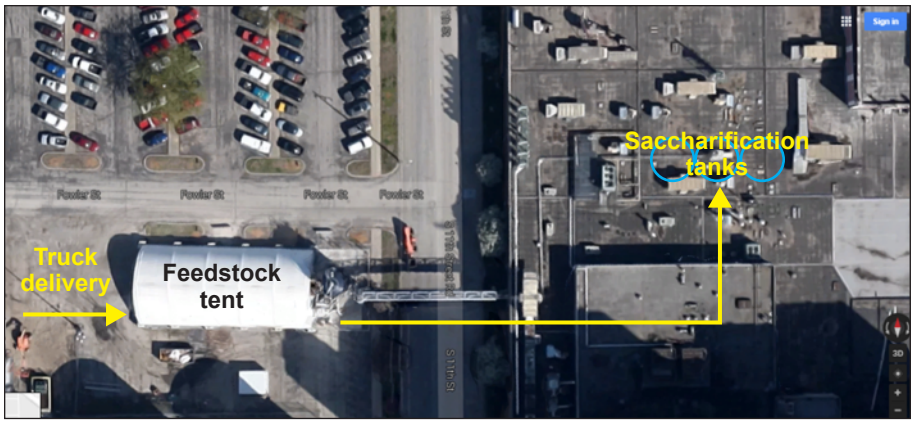

Figure 4.4—Location of feedstock and enzymatic digestion tanks at ICM.

Figure 4.5—Intermediate slurry pumping tank.

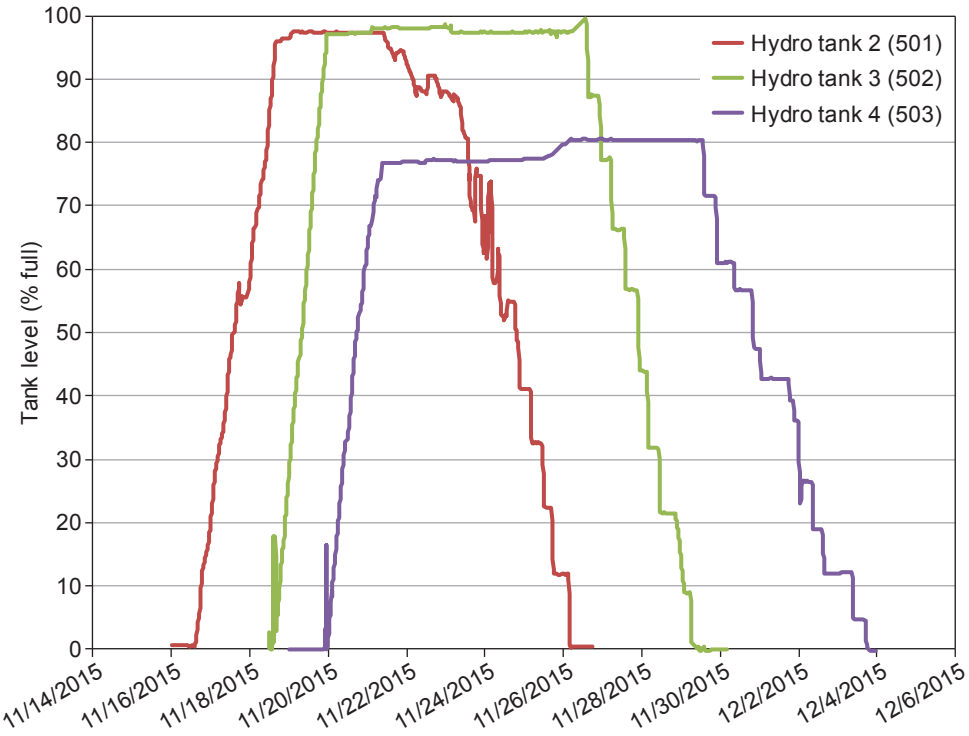

Figure 4.6—Filling and emptying the enzyme saccharification tanks with slurry.

Figure 4.6 and Tables 4.1 and 4.2 indicate the time required to fill and empty the saccharification tanks. It took between 30 and 50 h to fill each tank. The filling process was plagued with various line plugging issues due to the high solids concentration, but there were also problems in the centrifugal pumps with small rocks that seemed to have carried through with the feedstock. These could have come from the dumping of the supersacks on the floor of the feedstock tent, but that was cleaned. These were more likely from the original feedstock, as was experienced at ZeaChem. A very small amount of enzyme, approximately 5 gal, was added during the fill of tanks 2 and 3 to help reduce viscosity and improve mixing for pH adjustment through neutralization. The pH of the tanks was low, about 3.5 to 4, before being neutralized with KOH, so it was expected that all the initial enzyme applied for initial reduction of viscosity may had been lost.

Batch 601 began on 11/16/2015. Filling the saccharification tank took 50 h. After filling, the pH (target 5 to 5.5) and temperature (target 122 °F, 50 °C) were adjusted. The CTec3 enzyme was added on 11/18/2015 at the dosage of 7% based on the biomass solids. This was significantly higher than generally used in the laboratory (4%), but the objective here was to maximize yield of sugar. This enzyme loading equates to approximately 250 gal of enzyme cocktail based on the solids in the tank. Lactrol (~400 g) was added at the same time to control any possible contamination. The bulk of the saccharification was completed within 24 h and

Table 4.1—Hydrolysis composition, volume and fill times

Batch	Glucose (g/L)	Total solids (%)	Volume (gal)	Project time (h)				Hours		
				Start	Full	Drop	End	Fill	Filter	Duration
601	67.2	14.2	32,718	6	56	97	236	50	139	230
602	69.7	15.2	32,751	53	88	245	310	35	65	257
603	61.9	13.1	27,137	88	121	316	418	33	102	330

Table 4.2—Enzyme addition timed for saccharification tanks

Batch	Enzyme added	Saccharification time (h)	Heat-up for pasteurization	Start drain to filter	Finish drain	Drain time (h)
601	11/18/2015 20:00	60–121	11/24/2015 1:00	11/21/2015 11:00	11/26/2015 4:00	113
602	11/21/2015 02:30	91	11/24/2015 22:00	11/26/2015 14:00	11/29/2015 7:00	65
603	11/22/2015 12:00	72	11/25/2015 12:30	11/29/2015 11:50	12/3/2015 5:30	90

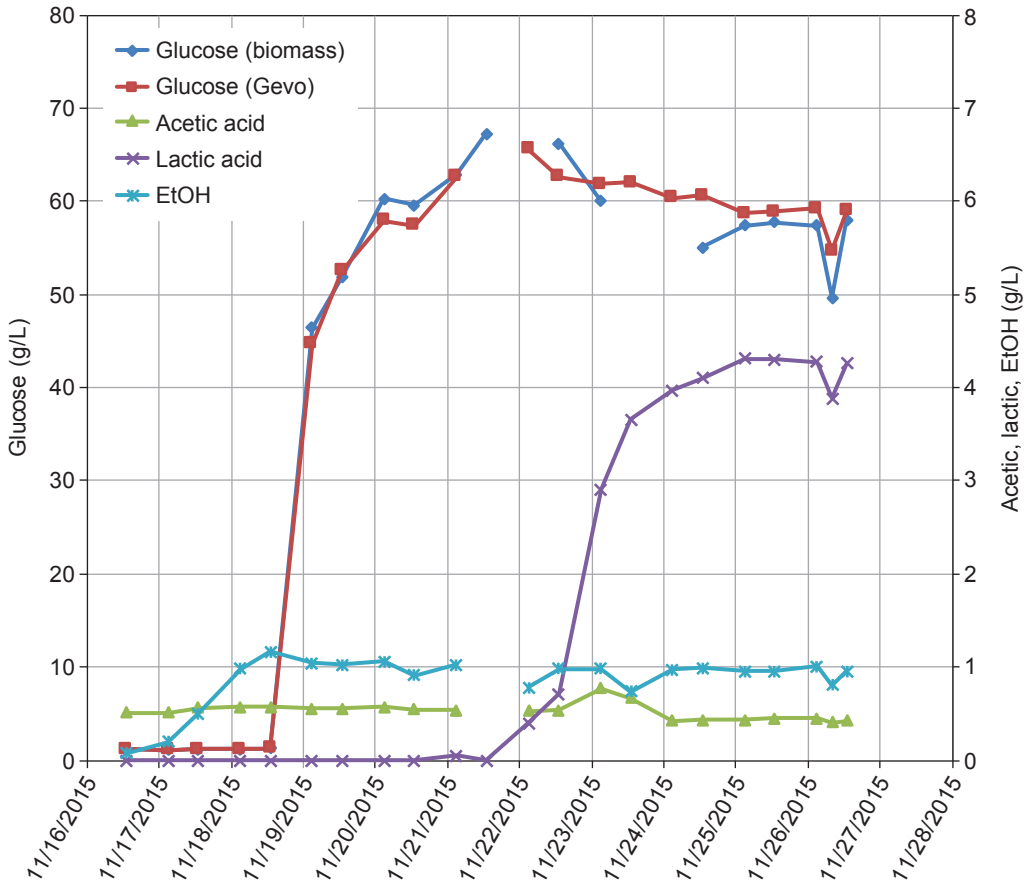

Figure 4.7—Batch 601 tank compositions.

peaked with peak glucose concentration of 67.2 g/L. The slurry was mixed thoroughly after the enzyme was added. Shortly after the filtering process began for batch 601, lactic acid began to accumulate in the tank (Fig. 4.7). The cause of the contamination was the techniques used during the filtering process (see Section 5, Filtration, Concentration, and Storage).

Batch 602 began on 11/18/2015, shortly after the filling of batch 601 was completed. It took hours to fill the saccharification tank. Again, a small amount of enzyme was added to the tank during filling to reduce slurry viscosity. The enzyme addition improved mixing and created a small amount of glucose. The full dose of enzyme, 250 gal, was added at 2:30 AM on 11/21/2015. Batch 602 produced a peak glucose concentration of at 69.7 g/L. Lactic acid

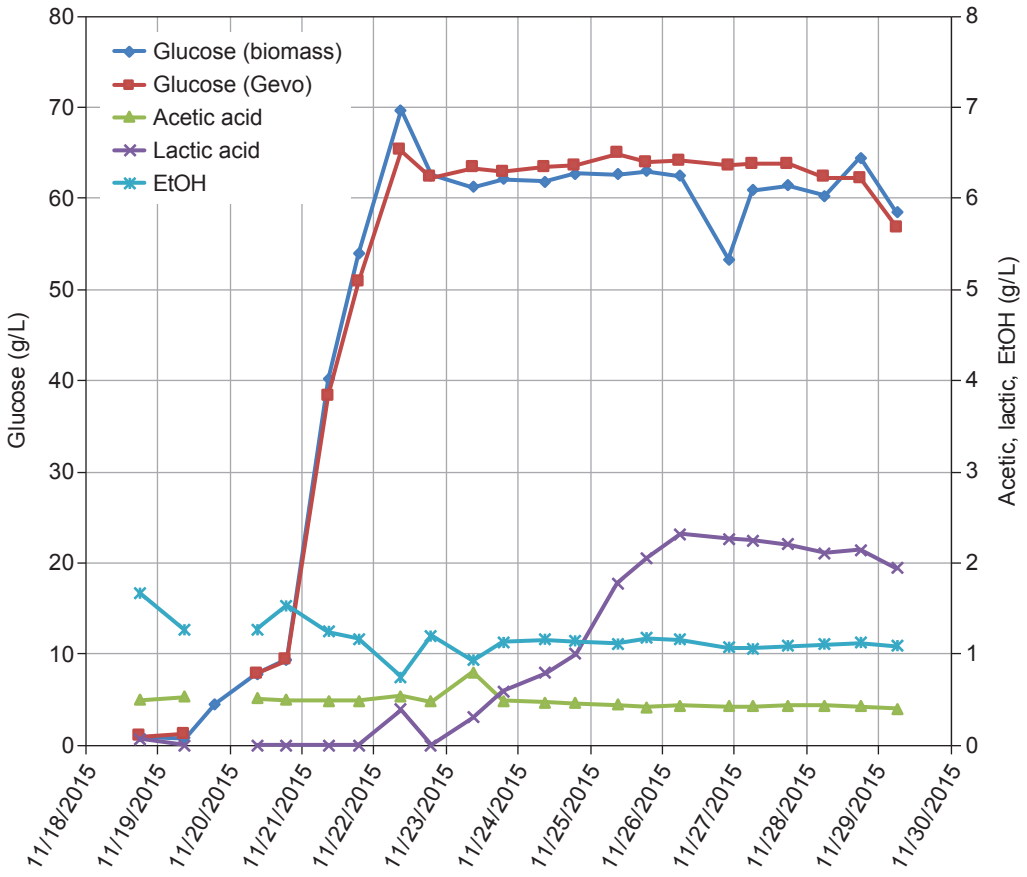

Figure 4.8—Batch 602 tank compositions.

began to appear at about 96 h after filling began, or about 48 h after the application of the main enzyme dose when saccharification was completed (Fig. 4.8). After additional antibiotics were added and the temperature was raised to approximately 160 °F, the contamination seemed to be controlled. There was no obvious cause for the contamination.

Batch 603 began on 11/19/2015, shortly after the filling of batch 602 was completed. Batch 603 was a composite of ZeaChem material and Cosmo pulp rejects. ZeaChem fiber was pumped in with the same hydroconveyor system that was used to fill 601 and 602. Cosmo fiber was slurried in a cut off tote with hot city water and pumped a few feet into the side of the hydrolysis tank. Solids content in batch 603 was slightly lower than 601 and 602, largely due to difficulties in pumping the Cosmo fiber slurry, which was nearly impossible to pump at about 10% solids. At about noon on 11/22/2015, 190 gal of enzyme was added. The tank started showing some contamination shortly after the addition of enzyme. Antibiotics did not stop the contamination. Increasing the temperature of the tank to 160 °F (71 °C) during 11/25/2015 stopped the contamination. However, approximately 7 g/L lactic acid had been produced (Fig. 4.9). The high temperature also denatured the enzyme. Fortunately, the system had completed 72 h of saccharificationand the glucose concentration had been leveled off.

4.3 Saccharification Yield

The yield of enzymatic saccharification is dependent on the solids concentration in the tank, which was difficult to measure accurately due to the poor mixing in the tank at the beginning of saccharification. Table 4.3 shows a yield calculation based on the final (peak) concentration of glucose in the tank and the solids concentration. The composition of the starting solids (see Section 3) was determined. The maximum theoretical glucose is the amount of glucose that would be generated at 100% yield from the feed solids loaded. The final glucose concentration of the liquid in the saccharification tank was adjusted for the amount of insoluble solids remaining at the end. Batch 602 appears to have a lower insoluble solids concentration (10.9%) than does batch 601 (12.7%) (Table 4.3; Fig. 4.10). This is puzzling because batch 602 has higher total solids, and these are essentially the same prime ZeaChem material. The yield for batch 602 appears unrealistically high. However, if the percentage insoluble solid is adjusted to be a similar ratio to total solids as that of batch 601, the yield is more in line with that of the other two batches (see modified line in Table 4.3). With the adjustment to batch 602, the yields for all three batches range from 84% to 87%.

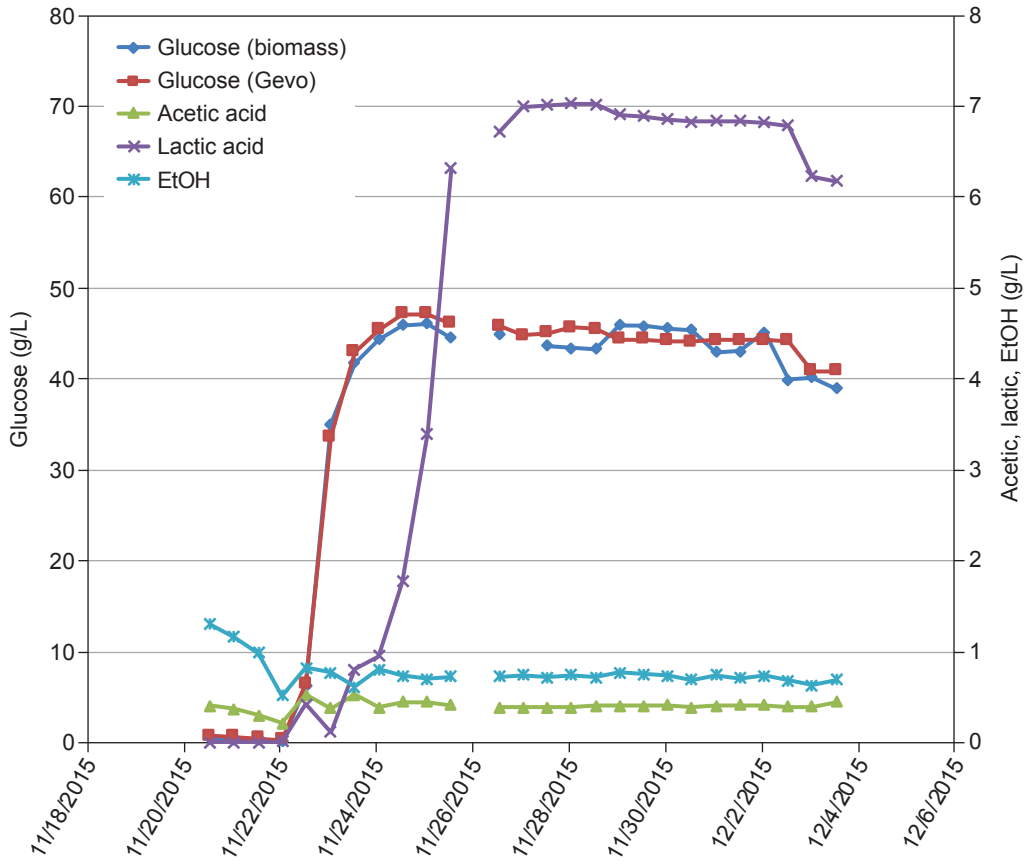

Figure 4.9—Batch 603 tank compositions.

Table 4.3—Saccharification batch yields

Batch	Final glucose (g/l)	Total solids (%)	Starting insoluble solids (%)	Ending insoluble solids (%)	Soluble solids (%)	Tank volume (gal)	Final glucose (lb)	Initial glucose in solids[a] (lb)	Max theoretical glucose[b,c] (lb)	Yield (%)
601	67.2	14.2	12.7	5.50	7.90	32,717	17,360	126	19,686	87.5
602	69.7	15.2	10.9	6.00	8.20	32,740	17,923	138	16,908	105.2
602[d]	69.7	15.2	13.6	6.00	8.20	32,740	17,923	138	21,087	84.3
603	61.9	13.1	12.2	5.00	7.30	25,859	12,706	91	14,947	84.4

[a]Glucose dissolved in liquor coming in with the solids. 7% glucose in ZeaChem liquor.
[b]Batch 601 and 602 have a solids glucan composition of 48.8%, Prime ZeaChem material.
[c]Batch 603 is a mix of Prime and sub-Prime ZeaChem and Comos. Glucan assumed to be same at 48.8%.
[d]Insoluble solids concentration for batch 602 adjusted to be more like batch 601—result is a more realistic yield.

4.4 Potential for Biojet Production

It is worth noting how much isobutanol could be produced if the rest of the process went as planned. Table 4.3 illustrates the production of 47,989 lb of glucose based on the volumes of the hydrolysis tanks and their respective glucose concentrations. This was more than expected because more solids (that is, the sub-prime ZeaChem and Cosmo solids) were processed; furthermore, the actual yields appeared to be slightly better than expected. At this point we would have expected to have enough sugar to produce 1,450 gal of biojet (Table 4.4).

5. Filtration, Concentration, and Storage

Fermentation can be accomplished with much higher sugar concentrations that are realized from enzymatic saccharification. By fermenting at high sugar concentrations, the total number of fermentation runs (or full tanks) is minimized, which also minimizes the amount of yeast and nutrients required overall. The isobutanol was continuously removed by the GIFT system, so its concentration was maintained at a low level in the fermenter, regardless of sugar concentration. Before concentrating the sugars by

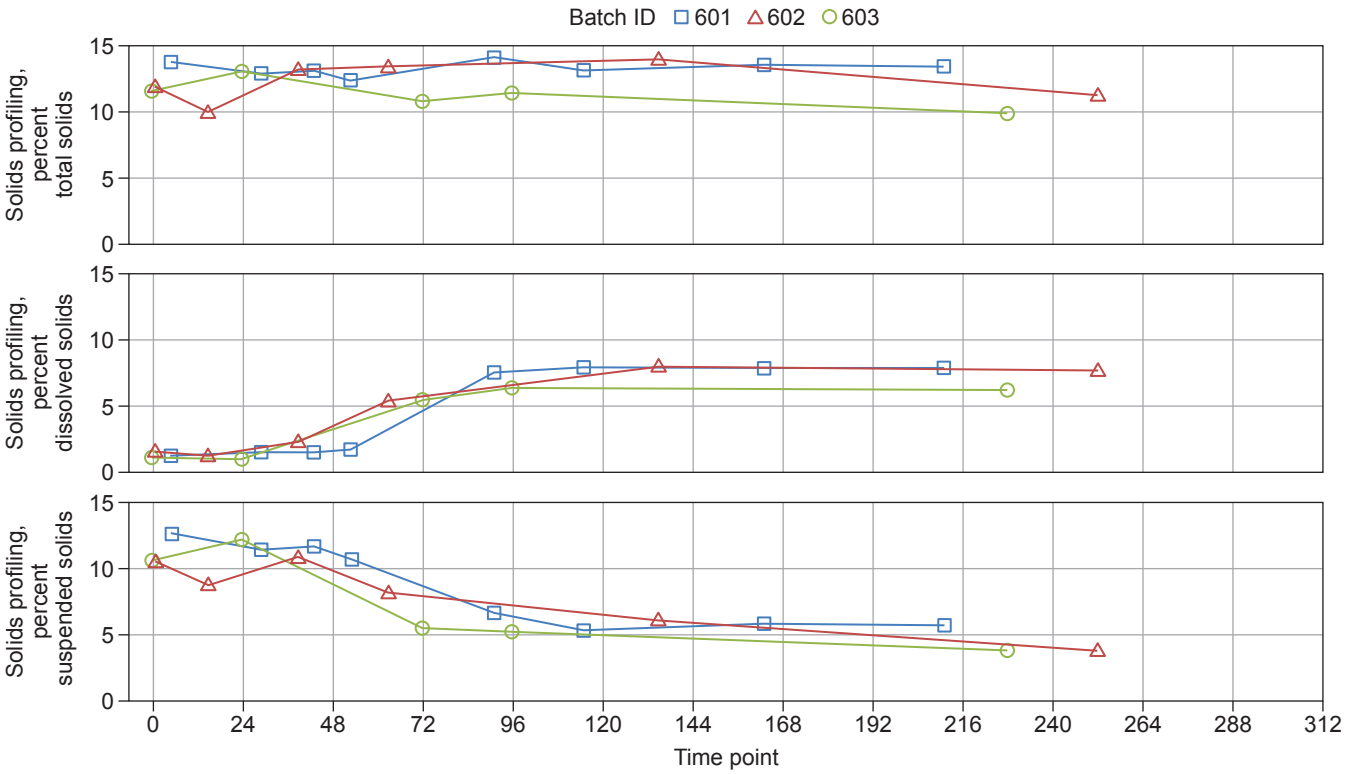

Figure 4.10—Solids concentration in the saccharification tanks.

Table 4.4—Project biojet production amount given the sugar produced in saccharification

Parameter	Value
Glucose from saccharification[a]	47,989 lb
Processing losses[b]	5%
Glucose to fermentation	45,590 lb
Isobutanol yield[c]	0.32 lb/lb glucose
Isobutanol produced	14,589 lb
Isobutanol produced	2,167 gal
Isobutanol losses[d]	5%
Biojet carbon yield[b]	86%
Max theoretical jet yield	0.766 lb jet/lb iBuOH
Actual jet yield	0.659 lb jet/lb iBuOH
Jet density	6.31 lb/gal
Final jet	9,130 lb
Final jet	1,448 gal

[a]See Table 4.3, amount of glucose produced in saccharification.
[b]Gevo yield (this is with C_8 production minimized).
[c]Typical Gevo yield.
[d]Estimated losses.

evaporation, the insoluble solids must be removed by filtration. ICM has two filtration systems that could be used. The first, a plate and frame pressure filter, is preferred because it is more automated and does not usually introduce a foreign filtering aid. The plate and frame filter has the ability to wash the solids to maximize sugar recovery. The second unit operation available is a rotary drum vacuum filter (RDVF). This system uses diatomaceous earth as a coating on the drum, which should act to trap fine particle and prevent the filter from plugging. It has the ability to rinse the solids and therefore should result in high sugar recovery. Its primary drawback is that the solids become mixed with the diatomaceous earth and are no longer useable. For this project, that was not an issue, because we were not going to further process lignin solids. For a production process, this would be a problem because the lignin has value, which is significantly diminished by mixing it with foreign material.

A test was conducted during the filling of batch 601. Approximately 1,800 gal of slurry was diverted to a smaller tank (yeast conditioning tank) and dosed with enzyme. Once saccharification was completed, it was filtered using the filter press. The results were not promising. The loss of sugar was substantial. The resulting cake was higher in moisture than other hydrolyzed materials, and the filter cloth plugged quickly. One cycle of 1,200 gal took 3 h, which would calculate to 80 h for the full batch 601. A choice was made to start batch 601 filtering with the RDVF.

Filtering of batch 601 began on 11/21/2015 with the RDVF. The RDVF operates by drawing liquid through a thick layer of a diatomaceous-earth- (DE-) coated drum by vacuum. The drum rotates through a pool of slurry, picking up hydrolyzate solids on the drum. Liquids pass through the DE. Solids (biomass and some portion of the DE) are scraped off one side of the drum.

The RDVF turned out to be very slow for filtering the hydrolyzate. Filtering began at 11:00 AM 11/21/2015 with 32,729 gal in batch 601. At 08:00 AM 11/23/2015, after 45 h of filtering, the tank level was 18,975 gal; 13,750 gal had been filtered in 45 h, for a filtering rate of 5.1 gal/min. This ultimately diminished to an average of 2 gal/min.

In the course of filtering with the RDFV, saccharification slurry was drained from the open pool in the filter back to the saccharification tank each time the filter needed to be recoated with DE. This introduced contamination to batch 601, which was controlled by adding more antibiotics and raising the temperature to 160 °F. The operation of returning hydrolyzate from the open filter to the main tank was stopped, and a small tank was used to store the recycle.

After two days of filtering with the RDVF, we considered the possibility that if the DE were premixed as a filter aid with the slurry, it might filter better in the filter press. So we moved the hydrolyzate from the hydrolysis tank to a 6,000-gal tank, where it was mixed with DE. Hydrolyzate with DE filtered more quickly than hydrolyzate without DE on the filter press. Over a 21-h period of filter pressing, 9,800 gal of hydrolyzate was filtered, yielding approximately 7.8 gal/min; 51,300 gal of hydrolyzate was filtered in five days, averaging approximately 7.1 gal/min.

On 11/21/2015, evaporation of the filtered sugar solution began. There was some initial foaming in the evaporators, but it was controlled with a small amount of antifoam. The evaporators generally ran without issue and at a much faster rate than the filters.

The original intent was to concentrate the filtered hydrolyzate to >150 g/L sugar and store it in one of the unused ethanol fermenters at a reduced temperature of 40 °F. By 11/24/2015, it was evident that the cooling system was not adequate to reduce the temperature of the sugar to 40 °F; it had only cooled to 56 °F. After consulting with Gevo, we decided to store the sugar hot, so the temperature of the storage tank was raised to 140–160 °F. The hydrolyzate was ultimately concentrated to 191 g/L, with measurement of 174 g/L in the two storage tanks (ethanol fermenters EF3 and EF4).

Because sugar loss in the filter press was excessive (as much as 25%), batch 602 was filtered using the RDVF again. The RDFV initially ran at approximately 11 gal/min, dropping off to approximately 7 gal/min and then approximately 4 gal/min with batch 603. Filtering was finished on 12/4/2015.

6. Fermentation

Fermentation of the concentrated sugars using a Gevo proprietary organism was conducted at the ICM site using three 6,000-gal aerobic fermenters connected together in series to act as a single fermenter. Some years before, Gevo had installed a pilot GIFT isobutanol recovery and purification system in the ICM pilot facility. The GIFT unit was piped up to the three aerobic fermenters and used to remove isobutanol during the course of fermentation and to strip residual isobutanol remaining in the fermentation broth after the fermentation finished (Fig. 6.1).

6.1 Fermentation 501

The aerobic fermentation tanks were emptied and prepared for steam-in-place cleaning (SIP) on 12/2/2015. SIP was conducted and the tanks cooled (Fig. 6.2).

After SIP of the tanks was completed, the concentrated sugar was added (Fig. 6.3). In the course of adding the concentrated sugar, it was discovered (twice) that there was a leak on the dissolved oxygen (DO) probe port in tank 2. To fix it, the tank was emptied back to the storage tank. Finally, once the tanks were full of about 15,000 gal, fermentation nutrient was added, and SIP was started at 3:00 AM on 12/3/2015.

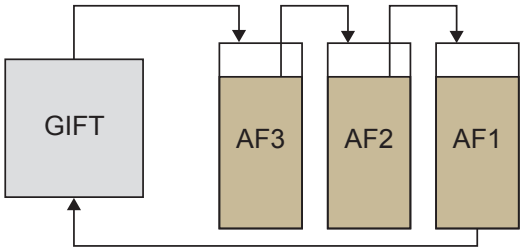

Figure 6.1—Aerobic fermenters and GIFT recovery system arrangement.

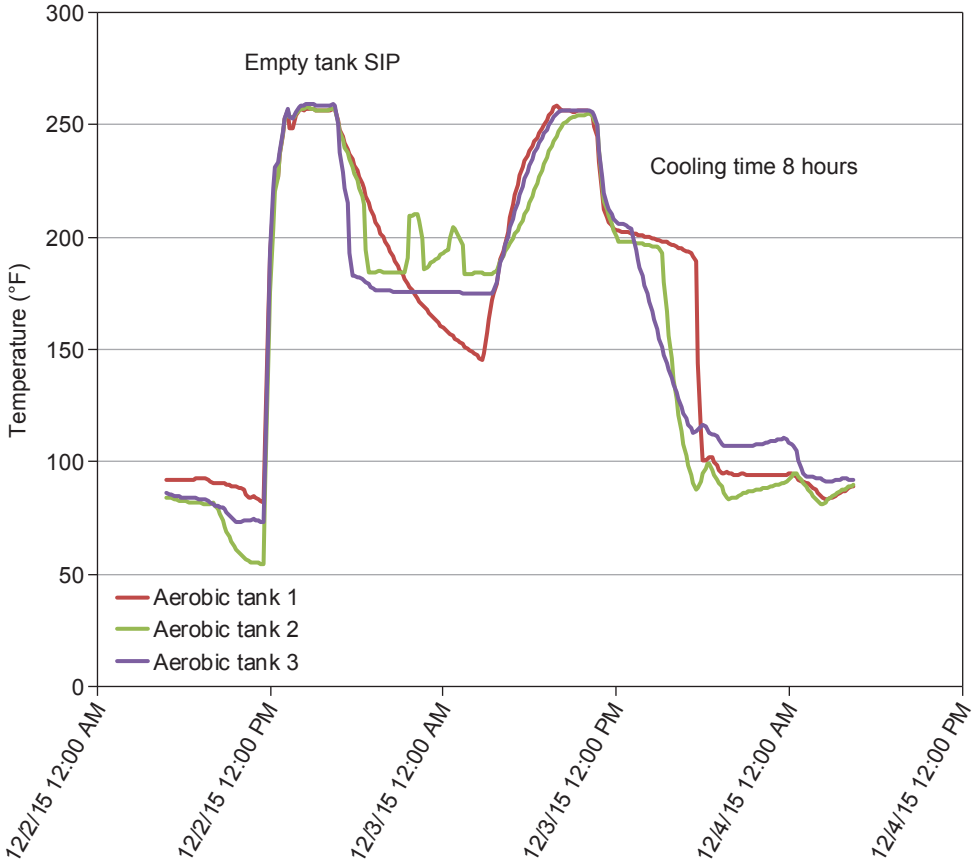

Figure 6.2—Fermentation 501 sterilization temperature profile.

The temperature in the fermenters was raised to 250 °F, held for 60 min, then cooled. Fermentation temperature was reached about 6:00 PM on 12/3/2015, and additional fermentation nutrients were added.

The next step was to add the yeast. The original plan was to use an IKA blender-pump that could be completely steam sterilized. However, during SIP, the seal was blown, which resulted in seal water (nonsterile) being pushed backed into the yeast tote when pumping was started. In addition, the yeast tote had been sitting without mixing for about 3 weeks, which caused substantially more settling of solids than expected. The material seemed to be not pumpable. We decided to use a large diaphragm pump. The pump was sanitized with 4-Quat and a recycle loop set up. This was able to pump the yeast. All the yeast was unintentionally sent to one tank rather than distributing it among the three tanks. The yeast would be distributed over time due to the normal circulation between the individual tanks and the GIFT system. Yeast addition was completed at 4:30 AM 12/4/2015.

The target isobutanol broth concentration was higher than planned because the GIFT system was not able to maintain the design pressure. All efforts were made to determine if there was a leak, and none could be found. There could have been an issue with too much dissolved CO_2 and an inability of the vacuum jets to remove all the noncondensables. No resolution was found. Because the G-Column was operating at a higher pressure than design, the boiling point was also higher, which lowered the temperature differential on the

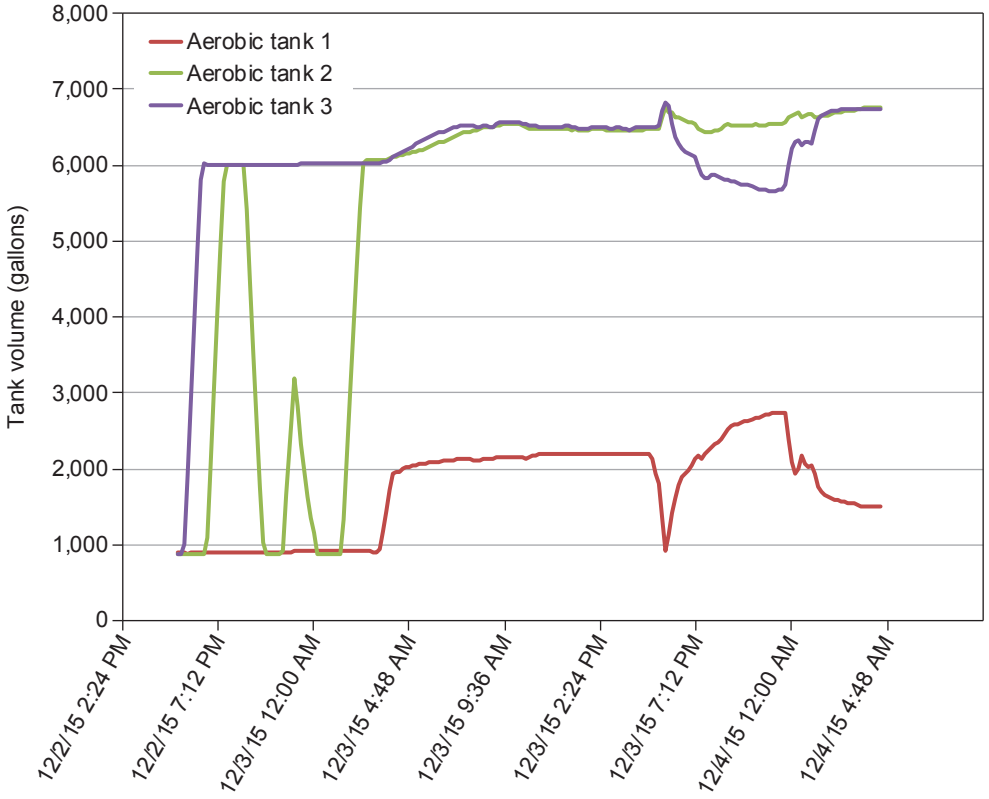

Figure 6.3—Batch 501 aerobic tank volume during fermentation.

reboiler and reduced the amount of isobutanol that could be removed. The isobutanol titer peaked at about twice the intended level. As an aside, without fermentation operating, the G-Column was able to hold the design pressure.

In this first batch, the sugar was consumed slowly and the fermentation was continued for over 100 h (Figs. 6.4, 6.5). It was hypothesized that the extremely long storage of the concentrated sugar at high temperature (to avoid contamination) created inhibitors and retarded the fermentation. This was confirmed later when fermentations performed well using sugars that did not have long heat histories (see Section 7.1).

No contamination was seen in the fermentation until about 94 h into the run. At that time, the concentration of both acetic acid and lactic acid (typical products of contaminating bacteria) started to increase (Fig. 6.6). We decided about 8 h later to end the fermentation.

The amount of isobutanol produced was calculated using the flow of broth through the GIFT and the concentration differential (amount removed). Figure 6.7 shows the profile of isobutanol production during the run.

The yield of isobutanol from the first run was lower than expected, given the planned starting sugar concentration. This can be attributed to the high temperature and long duration that the sugar was stored due to issues with filtration. There were certainly various toxic compounds during this storage that resulted in yields lower than measured in the lab with the same saccharified biomass but without a storage history.

6.2 Fermentation 502

At the end of the first fermentation the aerobic fermenters were emptied to a storage tank to wait on determining their final disposition. The aerobic tanks were rinsed and sterilized by SIP (Figs. 6.8, 6.9). Upon finishing the tank SIP, the tanks were partially cooled and the stored sugar and fermentation nutrient were added. The volume of remaining sugar was less than needed to fill the fermenters so it was decided to add dilution water to help dilute out the inhibitor concentrations that built up during the >250-h at >140 °F sugar storage. All the contents were then sterilized by SIP. The cooling was improved and accomplished in 10 h in this second batch.

The pressures in the GIFT and G-Column were no better during this run, hovering higher than the design pressure.

The isobutanol titer actually peaked a little higher in this run compared to run 501. This was primarily due to a faster production rate in the fermenter coupled with the reduced ability (due to pressure) of the GIFT to remove isobutanol.

Sugar concentration was significantly lower in this batch than the previous one, 63 g/L compared with 126 g/L, but the consumption rate was much higher. The fermentation was completed in 40 h and consumed all the sugar (Fig. 6.10).

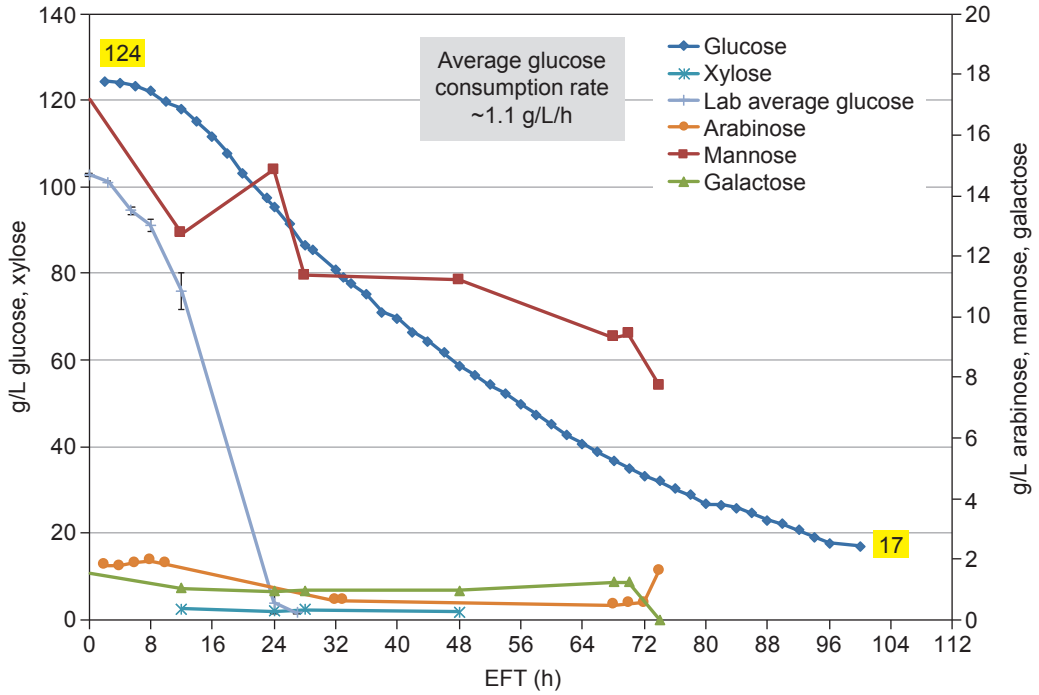

Figure 6.4—Fermentation 501 sugar profile.

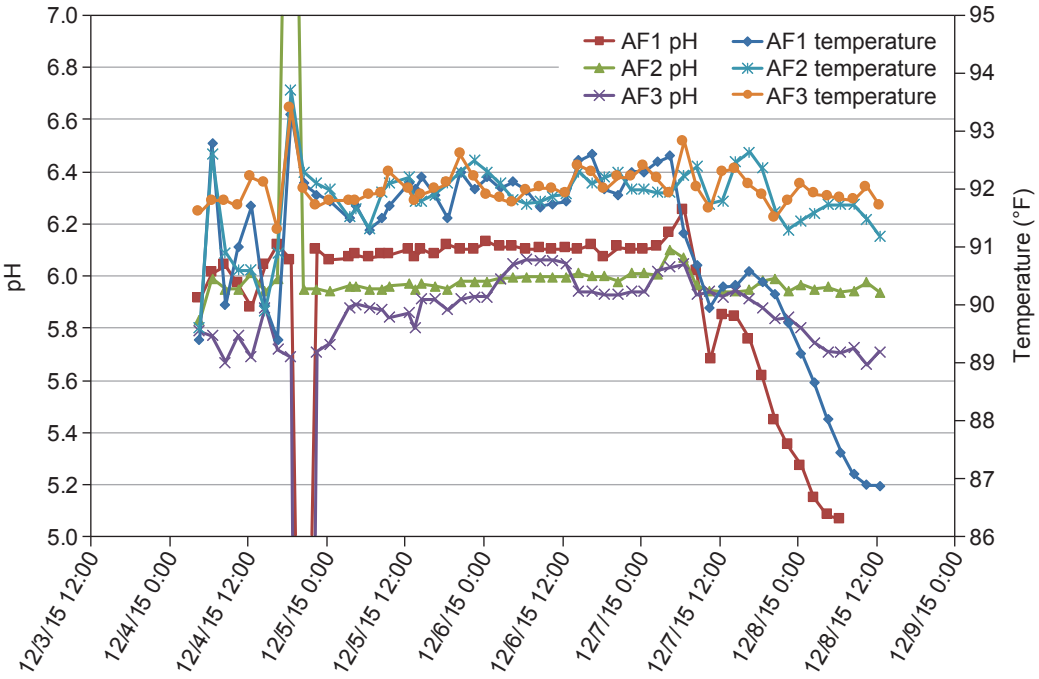

Figure 6.5—Fermentation 501 pH and temperature profiles.

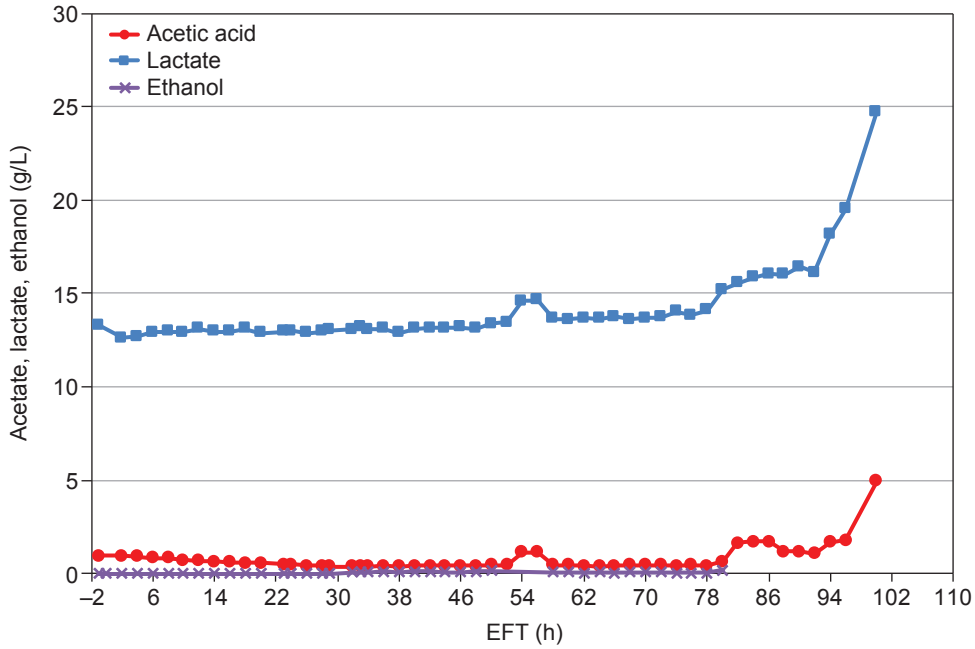

Figure 6.6—Fermentation 501 contamination profile.

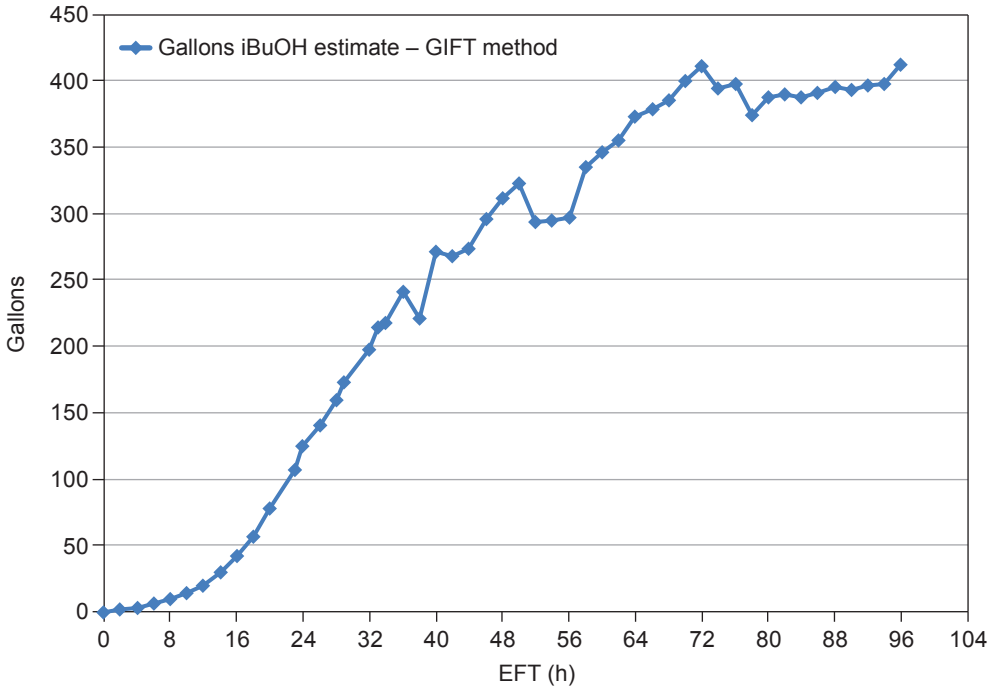

Figure 6.7—Fermentation 501 isobutanol production profile.

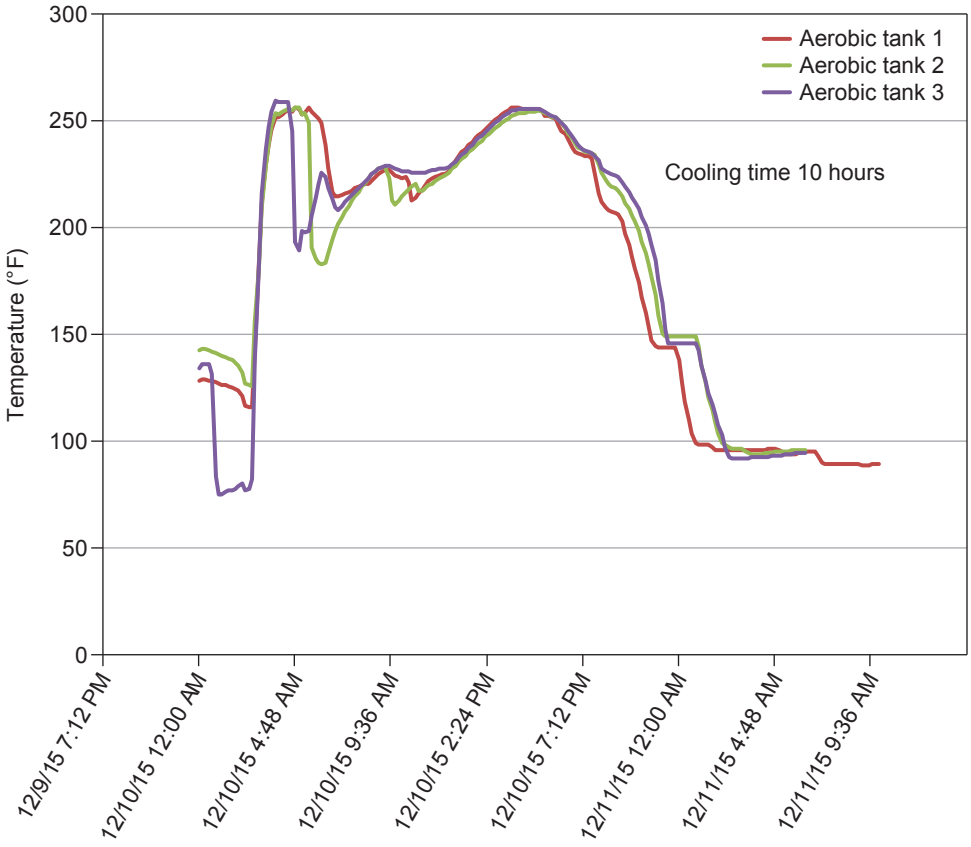

Figure 6.8—Fermentation 502 sterilization temperature profile.

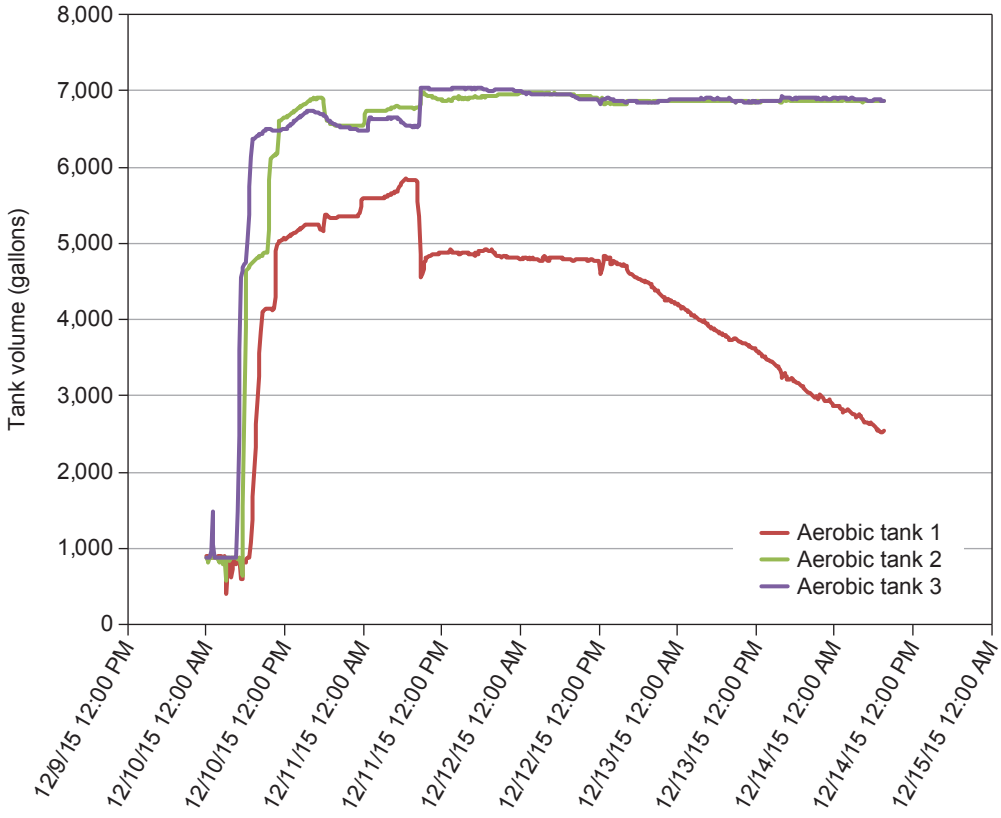

Figure 6.9—Batch 502 aerobic tank volume during fermentation.

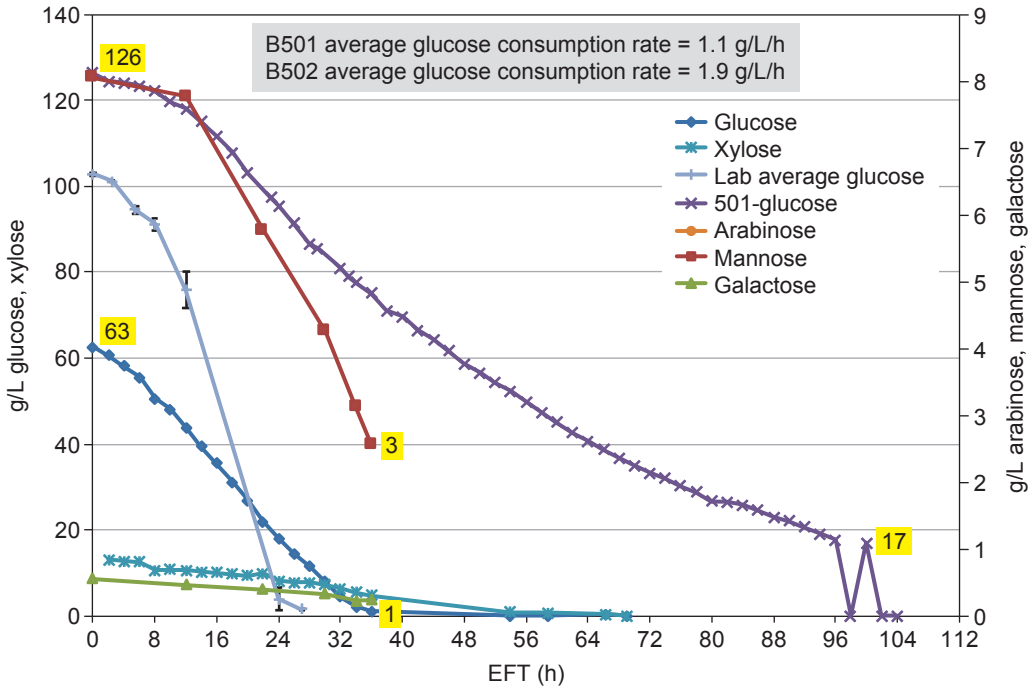

Figure 6.10—Fermentation sugar profile, runs 501 and 502.

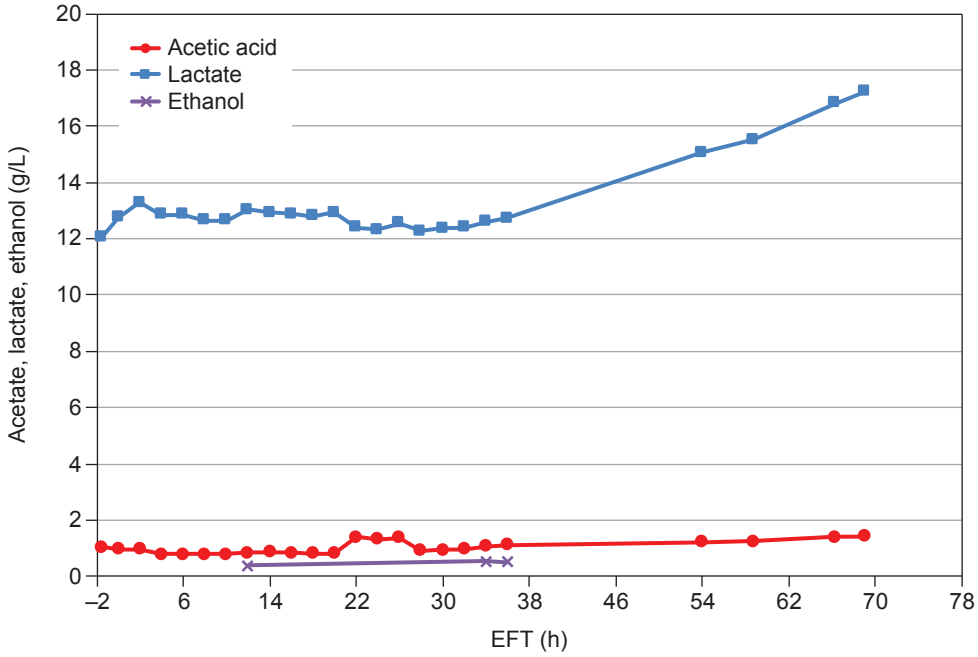

Figure 6.11—Fermentation 502 contamination profile.

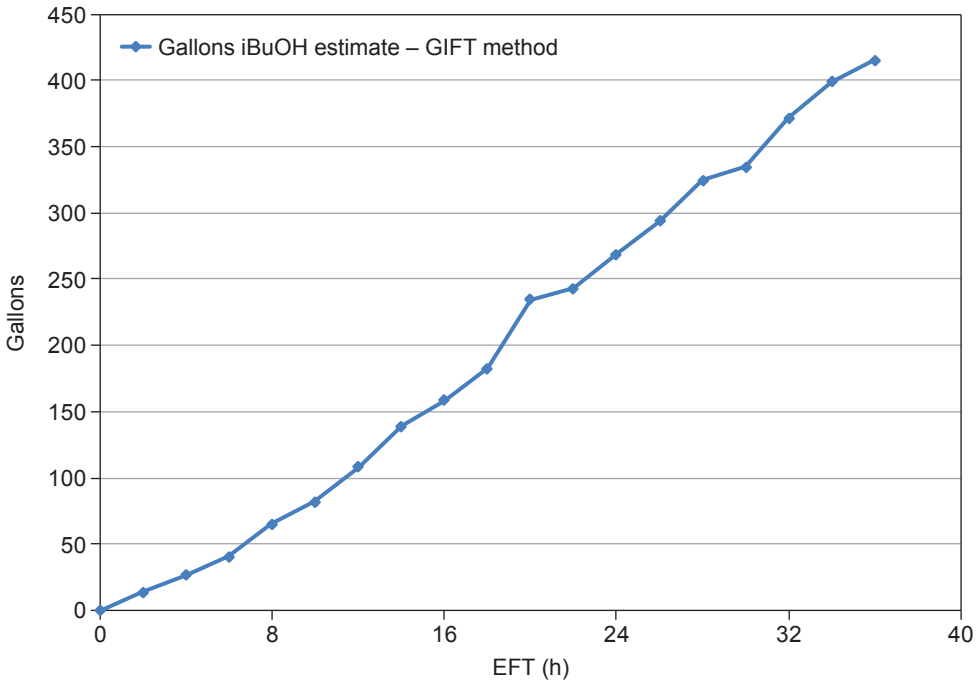

Figure 6.12—Fermentation 502 isobutanol production profile.

Contamination was also low in this run. Lactic acid increased slightly toward the end of the run (Fig. 6.11). Considerable background of lactic acid was noticed in the sugar from saccharification and storage. It is well known in the fuel ethanol industry that 0.8% w/v or 8 g/L lactate can lead to yeast inhibition or even death. The tolerable level of acetate is even lower, at 0.05% w/v or 0.5 g/L. Both of these byproducts were above this threshold in the first and second fermentations and likely led to lower than optimal performance.

Isobutanol production in this batch nearly matches the previous batch with only about half the sugar that was present in the first batch (501) (Fig. 6.12). A plausible explanation of the difference between these two batches is that the second batch of sugar was not held for hundreds of hours at elevated temperatures. Thus, the generation of inhibitors may have been lower in 502.

The yield of isobutanol from the run was encouraging. Overall, production of isobutanol was much better in this run and was not that far from results realized in the lab with these feedstocks that did not have the storage and heat history.

7. Product Isobutanol

Fermentation 502 fairly well completed all the sugars. However, run 501 left some sugars unconsumed, at approximately 17 g/L. ICM had transferred the contents to a storage tank. After run 502 was completed, they transferred it back to the aerobic tanks and attempted to complete the fermentation. Unfortunately, in the transfer process, the broth picked up an ethanol-producing organism. The ethanol contaminated some portion of the remaining isobutanol that had not been completely dehydrated yet.

At the end of operations, there were three partial totes that met water specifications and one tote that was contaminated with ethanol and could not be dehydrated by distillation. Table 7.1 summarizes the materials produced and their compositions. Samples from two of the totes were sent to Midwest Laboratories to test for acid. The isobutanol specification for acid was 70 ppm, or 0.007%. The results for the two totes tested were 0.529% and 0.165%, considerably over the specification.

In total, 627 gal of isobutanol met the specifications for water and isobutanol but failed in acid. In addition, 380 gal of isobutanol containied too much ethanol to be dehydrated by distillation. Roughly 296 gal of potentially recoverable isobutanol was in that high ethanol material. The total possible isobutanol would then be 923 gal if all could be recovered and finally purified.

In addition, the appearance of the product was not water-white; it looked more like “swamp water” (Fig. 7.1). Twice during the operation, operator error caused a considerable amount of isobutanol to be dumped on the floor: the first was a valve position error and the second caused a relief valve to open. This material was put back into the recovery system, but it contained dirt and contaminants from the floor and the floor trenches. The isobutanol was a bottoms product from the recovery system, so there was no way to remove heavy components (it would need to be sent through the entire GIFT to do that). This is probably where the adverse color came from. Fermentation broth was carried

Table 7.1—Isobutanol quantity and composition from Campaign 1

Tote	Volume (gal)	Water[a] (%)	Acid weight[b] (%)	Content (%)							
				EtOH	1-PrOH	iBuOH[c]	3M1BuOH	2M1BuOH	2PhEtOH	Unknown	Other
901	82	0.4939		0.084	0.027	95.677	3.338	0.764	0.055	0.032	0.023
902	274	0.4117	0.529	0.031	0.015	97.531	1.617	0.291	0.111	0.397	0.007
903	272	0.4017	0.165	0.072	0.026	97.046	2.209	0.446	0.074	0.12	0.007
Total iBuOH	627										
Hi ethanol totes											
Hi EtOH-1	170	29.6		2.4		67.3	0.5	0.1			0.1
Hi EtOH-2	210	9.5		3.6		86.4	0.3	0.1			0.1
Potential iBuOH	296										
Total potential iBuOH	923										

[a]Specification for water is <1.0%.
[b]Specification for acid (expressed as acetic) is <0.007% or 70 ppm.
[c]Specification for isobutanol is >97%.

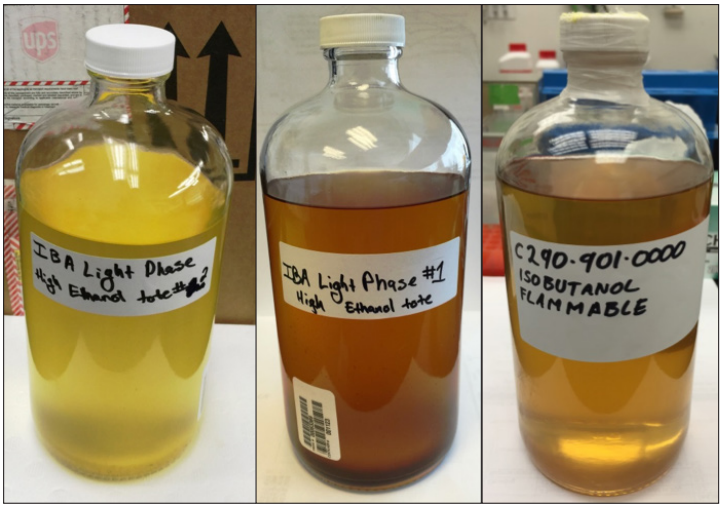

Figure 7.1—Product isobutanol samples.

overhead in the GIFT multiple times due to pressure upsets in the G-Column. This would cause organic acids that would otherwise be left in the fermenter to end up in the product. A daily historical summary of the first campaign at ICM to produce isobutanol is given in Appendix D.

The result of the first campaign was disappointing. The amount of isobutanol produced was only enough to potentially make 515 gal of jet fuel, whereas we had expected to have enough isobutanol to make well more than the goal of 1,000 gal of jet fuel.

Multiple processing issues occurred. Filtration to remove residual solids after saccharification was unsatisfactory. A very limited amount of preliminary testing indicated that there might be a problem with filtration, but it was not deemed to be as serious as it turned out.

For unexplained reasons, filtration rates through both the filter press and the rotary drum vacuum filter were extremely low. The excessive sugar loss in both units was alarming. Sugar losses through the filter press were estimated to be 25% at one point. We had expected about a 3% sugar loss through the filter press based on ICM's previous experience separating residual biomass solids after saccharification.

The very slow filtration led to very long storage times for the resulting sugar. To avoid contamination (which did occur during saccharification and initially in storage), the concentrated sugar (and impurities) were held at high temperatures, initially at 160 °F but then mostly at 140 °F. We believe that this long storage at high temperature created even more inhibitors for the yeast, leading to a low yield of isobutanol in the first fermentation. The second fermentation, which was diluted and not stored as long, performed much better.

Figure 7.2 illustrates the potential for production of jet fuel and where the "normal" flow of carbon would go. Figure 7.3 attempts to show where the carbon actually went and how

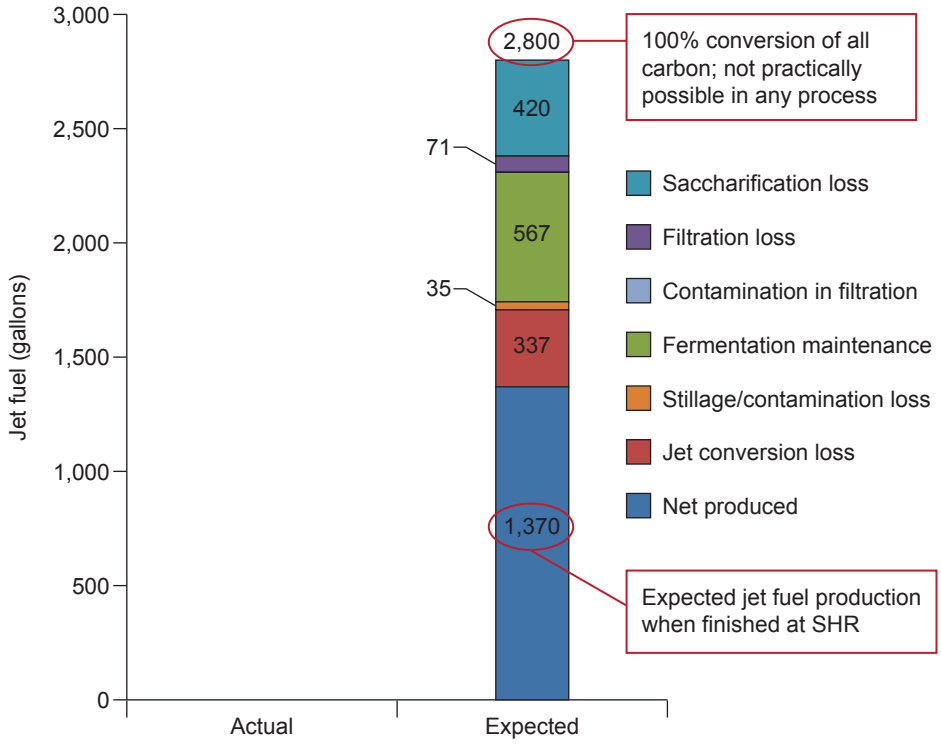

Figure 7.2—Potential for jet fuel production from material delivered to ICM.

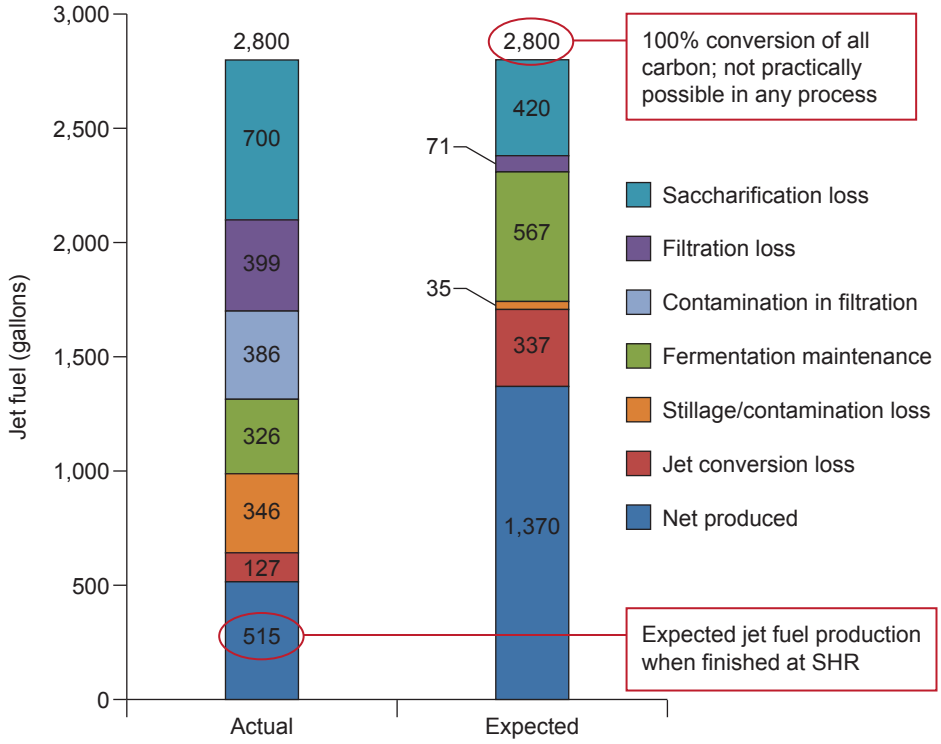

Figure 7.3—Losses during the processing at ICM.

we got from a potential of over 1,300 gal of jet fuel to about 500. These figures make reasonable assumptions about the conversion yields of isobutanol to biojet.

8. Saccharification of Cosmo Reject Pulp—Part 1

As described in Sections 5, 6, and 7, the processing of pretreated forest residue at ICM produced significantly less isobutanol than expected because of a variety of issues. The amount of isobutanol produced was less than 900 gal, which when processed to biojet, would result in only approximately 500 gal of finished biojet fuel. The goal of the project was to produce 1,000 gal of biojet fuel.

8.1 What Could Be Done?

When the second fermentation was completed at ICM in mid-December 2015, about 25% of a tote of Gevo proprietary yeast remained unused. The first thought was to quickly obtain some additional Cosmo reject pulp and run an additional enzymatic saccharification and fermentation to isobutanol before the holiday season. Cosmo was contacted and was willing to supply NARA with more reject material, but time ran out with respect to the availability of the ICM facility.

The next window of availability at the ICM facility was March 1, 2016. In the intervening time, the NARA team was able to assess some of the issues encountered in the first campaign and develop a new operating plan to improve the operation.

The Gevo organism had performed well. The yeast dosage could be less than what was used in the first campaign, in which two totes were used. We calculated that we could potentially do four fermentations with only one tote. NARA requested that Gevo sell the project one tote and keep one of the two totes usually produced in a batch at the vendor.

8.2 Pretreated Feedstock Material

As mentioned, Cosmo Specialty Fiber was willing to donate additional material to the project. Using material from Cosmo would be the only way a second campaign could be accomplished. The time and cost required to go back and procure additional wood slash and process it at ZeaChem were prohibitive. Cosmo was generous enough to contribute their rejected pulp material (which has a positive fuel value to them) to NARA for no cost. It was described earlier how the Cosmo process uses wood from the Pacific Northwest and a sulfite pulping process similar to the SPORL process. In addition, Cosmo is interested in the potential for producing fermentable sugars from this stream. About 15,000 lb of Cosmo material had been combined with ZeaChem pretreated material in the third saccharification batch of the campaign with no noticeable impact on results. Based on these positive factors, it was decided to use Cosmo reject pulp as the enzymatic saccharification substrate for the second campaign. A total of 319,000 lb wet or 121,000 lb dry of Cosmo material was shipped to ICM. A detailed chemical analysis for the Cosmo rejected fibers and the subsequent fermentation solids is provided in Appendix E.

8.3 Process Changes at ICM

The biggest issue in the first campaign at ICM was the liquid–solid separation after enzymatic saccharification. This separation was required to enable concentrating of the sugars by evaporation, thus allowing for fewer fermentation batches. There is no reason to expect that the fermentation would not perform well with the solids present. Processing with the solids is how cellulosic ethanol simultaneous saccharification and fermentations are run. Corn ethanol dry mills operate with the solids present as well, but corn solids are quite different. The primary issue of running these fermentations with solids might be the operation of GIFT. The GIFT loop includes a plate and frame heat exchanger through which the fermentation broth with solids must pass. That heat exchanger was reconfigured to a “wide gap” on the process side to help minimize plugging due to solids.

The basic concept for the start of Campaign 2 at ICM was as follows:

1. Procure rejected pulp from Cosmo in bulk. This required transporting about 23 wet tons per load using a moving bed truck that could self-unload at the ICM feedstocks tent.
2. Load the solids into a 32,000-gal saccharification tank at about 13% solids. In Campaign 1, Cosmo solids were loaded by dumping the cardboard boxes they arrived in into a plastic tote, adding water to make a slurry and pumping directly into the tank. This resulted in only about 10% solids, which was being mixed with higher concentration ZeaChem material. For this run, mixing the solids with partially saccharified slurry from the tank might enable pumping and increase the solids concentration.
3. Add enzyme and allow the saccharification to go to completion.
4. Transfer about half or 16,000–17,000 gal of slurry directly to the fermentation tanks, sterilize, and add yeast.
5. Run the fermentation and recover the isobutanol through the GIFT.
6. Clean the fermenters and transfer the remaining saccharified slurry, sterilize, and add yeast
7. Run the fermentation and recover the isobutanol through the GIFT.
8. Repeat for a second load in the enzymatic saccharification and subsequently two more fermentations.

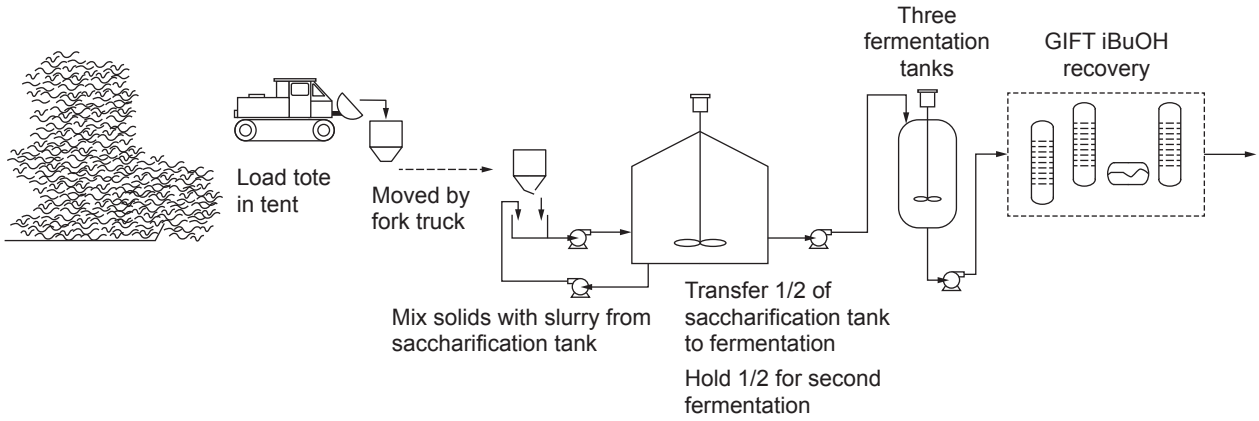

Figure 8.1—ICM campaign 2 initial flowsheet.

The general flowsheet for this scheme is illustrated in Figure 8.1.

8.4 Batch 605

The first saccharification batch was run using the procedure described above. Loading the saccharification tank began on March 3, 2016, at an initial rate of approximately 650 lb solids per hour.

The as-received Cosmo material (Fig. 8.2) was hammer milled in the feedstock tent at ICM. The material could not be air lifted from the mill, so it was allowed to drop on the floor (Fig. 8.3). This was particularly cumbersome for ICM because it could not be easily picked up by the front loader and mostly had to be shoveled into the front loader scoop by hand.

The material was loaded into a portable bin and shuttled from the feedstock tent to near the saccharification tank, where it was laboriously scraped out through a 12- by 12-in. hole in the bottom of the bin into an open tote. Initially they added water in the tote to slurry the solids and then pumped it into the 32,000-gal saccharification tank.

Novozymes Cellic CTec3 enzyme was added to the saccharification tank, first 10 gal and then 50 gal, while the tank was being filled to help reduce the viscosity of the slurry. Two bags of lactrol (antibiotic) were also added. At some point early in the filling, they switched from using only fresh water to using partially saccharified slurry (reduced viscosity) from the tank and some water to mix with the new solids, with the hope of increasing the solids content. An additional 40 gal of enzyme was added on the third day. The solids content was measured at 11.5%, with 26,000 gal in the tank. The tank was running a little hot, so 3,500 gal of water (at 45 °F) was added to cool.

While attempting to adjust the pH in the tank, they overshot to about 6.7. There was no capability to add acid to bring the pH down. They finally added some acid manually to bring the pH to 6.0. At that point the rest (250 gal) of enzyme was added. It was hoped that as the saccharification continued,

Figure 8.2—Cosmo feedstock as received at ICM.

Figure 8.3—Hammer mill discharge of Cosmo material.

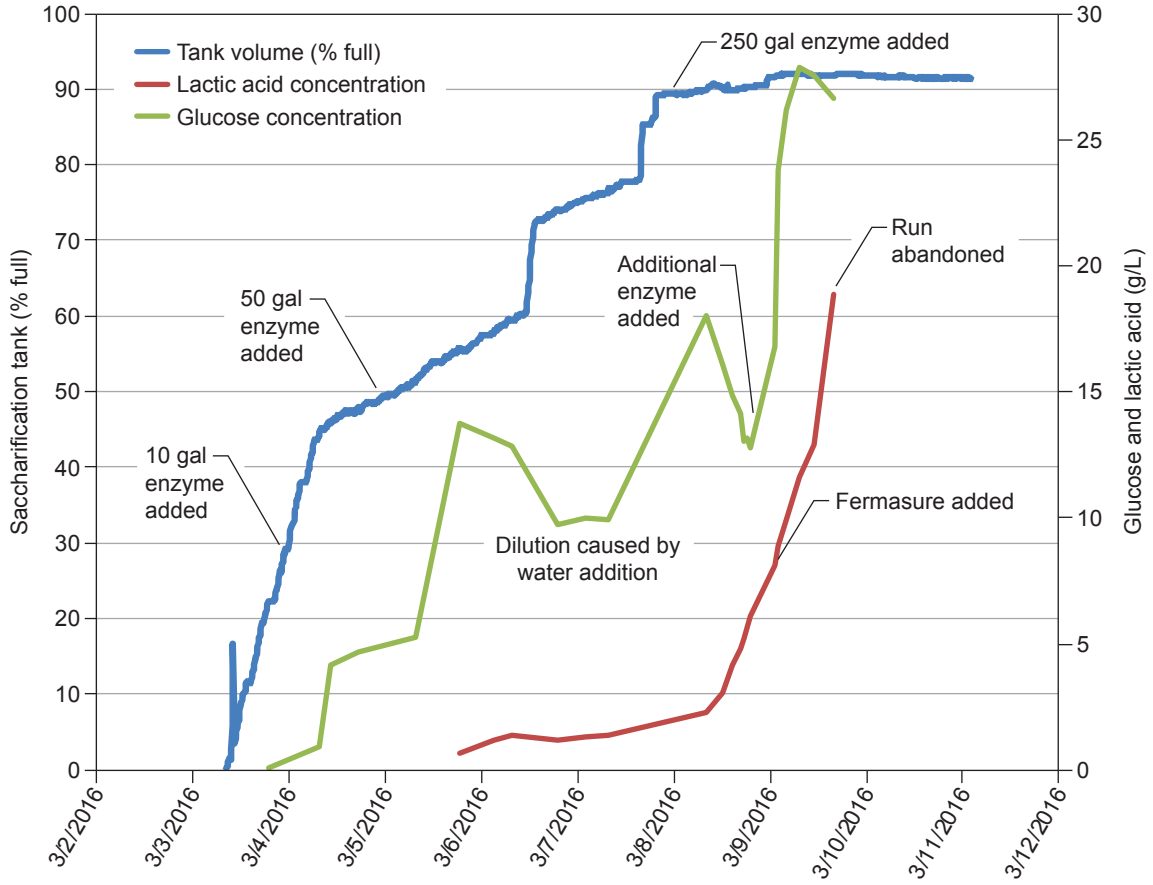

Figure 8.4—Batch 605 volume and production profile.

the solids at the bottom would break up and that the pH would come down naturally.

When the saccharification broke up the solids in the bottom of the tank, the pH shot up to 7. There must have been a pocket of KOH trapped in the solids. Generally, people with enzyme experience at ICM felt that the enzymes would recover after the pH had been adjusted back to 5.5.

Saccharification did not recover after the pH was lowered. Additional enzyme was added to a sample from the large tank in the lab and saccharification restarted, indicating that the enzymes in the large tank had been denatured. The lactic acid was also climbing even though a significant amount of lactrol had been added. A dose of chlorine-based disinfectant Fermasure was added, but it did not stop the lactic acid. Additional saccharification did occur after more enzyme was added.

The lactic-acid-producing contaminant seemed to have taken over the tank and all efforts to stop it did not work (Fig. 8.4). The decision was made to abandon the batch.

9. Saccharification of Cosmo Material—Part 2 and Fermentation

9.1 What Next?

The scheme described in Section 8 seemed to be unworkable due to contamination risk. It was not clear if the contamination was caused by recirculating partially saccharified slurry with free sugars outside the tank and into the open slurrying tank and back or if the contamination was inherently in the feedstock. During Campaign 1, the tank with Cosmo material did have an unexpected contamination event, which was controlled. Whether that came from the feedstock was undetermined.

ICM came up with a scheme to more easily transport the solids from the feedstock tent, get them into a slurry of high solids and get it pasteurized as soon as possible before fully saccharifying and fermenting (Fig. 9.1). That procedure is as follows:

1. Mix the Cosmo solids as received in the feedstock tent with water to make 2% to 5% solids slurry. (This is the approximate solids concentration that Cosmo uses when pumping this material in their plant.)

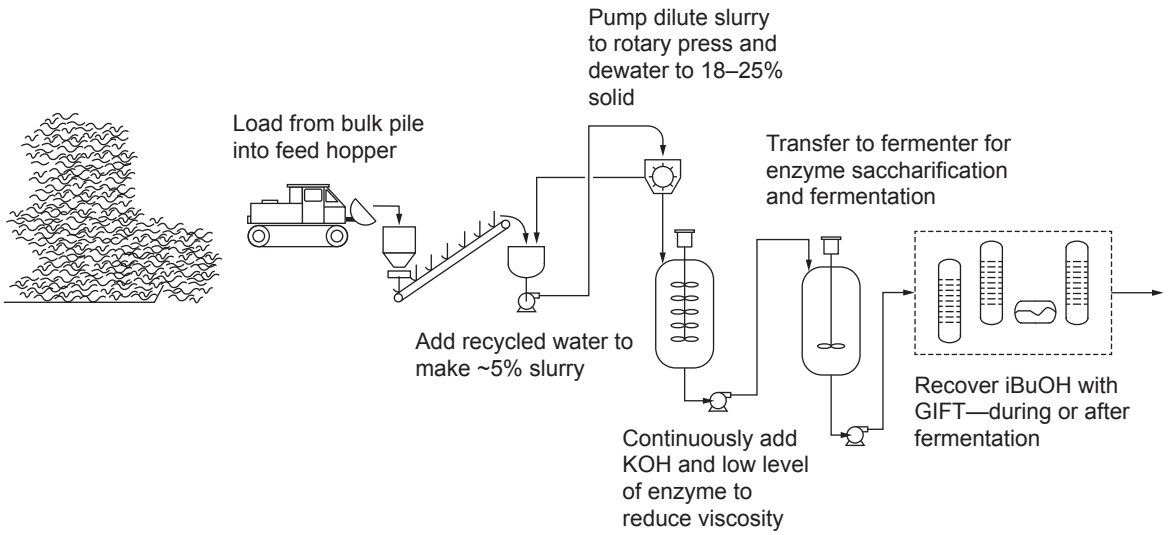

Figure 9.1—ICM campaign 2 final flowsheet.

2. Pump this dilute slurry (as a hydro conveyor) to a rotary press mounted on top of a 3,000-gal "viscosity break tank" (VB1). The press produced a solids cake of 18% to 25%, which fell into the tank with high agitation. Enzyme was continuously added to help reduce the viscosity. A second tank (YC1) of approximately 6,000 gal was added in series to allow a longer residence time for viscosity reduction. The water removed with the press was recycled to mix with fresh solids.
3. Pump the high solids, but lower viscosity, to the aerobic fermenter and heat to pasteurization (190 °F). The original plan was to pump through the ICM pretreatment reactor to heat pasteurize, but this proved to be unwieldy. The enzymes added earlier would be denatured. More would be added after cool down.
4. Cool the aerobic fermenters, and add the appropriate level of enzyme to saccharify.
5. Run a saccharification at 55 °C for 2–3 days.
6. Add nutrients and sterilize the sugar and nutrients.
7. Cool the fermenter; add yeast and ferment, recovering the isobutanol through the GIFT. The recovery of isobutanol was later changed to be after the fermentation was completed because of plugging issues with the GIFT.
8. Repeat for four fermentations.

This procedure was intended to minimize the possibility of contamination because there were only a few hours before the partially saccharified material was pasteurized. Because the solids were being dewatered to a cake at the slurry tank and enzyme was being added to break the viscosity, higher solids slurry should be possible.

9.2 Operation of the Solids Transfer and Rotary Press

The hydro conveyor (pump) used large volumes of water to move the solids from the feedstocks tent, across the street to a rotary press on the viscosity break tank (VB1). The rotary press removed the water, making a wet cake that dropped into the tank. Warm water (140 °F) was pumped from a holding tank to a slurry tank in the feedstocks tent. In this tank, solids were added at a rate that would result in slurry of about 5% solids. That slurry was pumped to the rotary press, where the solid was dewatered. The solids fell into the VB1 tank. Water pressed out was returned to the water holding tank.

The rotary press for dewatering the hydroconveyor slurry used a restriction gate to maintain a condensed fiber plug, which prevented water from passing with solids into the tank. Water was forced through screens by the compression of the fibers. In the hydroconveyor system, the water was recycled and pumped back to the hydroconveyor slurry tank. Compressed fibers were slowly ejected from the press and fell into the VB1 tank.

The mechanism for adding solid fibers to the slurry was not optimal. Sometimes large amounts and sometimes very small amounts of fiber would be added to the slurry. The hydroconveyor slurry solids content would swing between about 2% and 7% because of the rate at which the fibers were entering the slurry tank. High solids in the hydroconveyor would tend to form plugs in the line. Low solids in the hydroconveyor would tend to allow water to pass through the rotary press into the VB1 tank. The rotary press was configured so that fiber cake exiting the press was damp at around 18% total solids. Damp fiber cake, 15% to 18% total solids, would sink into the slurry. With the settings to provide 15% to 18% solids, the condensed fiber plug in the rotary press occasionally would be pushed

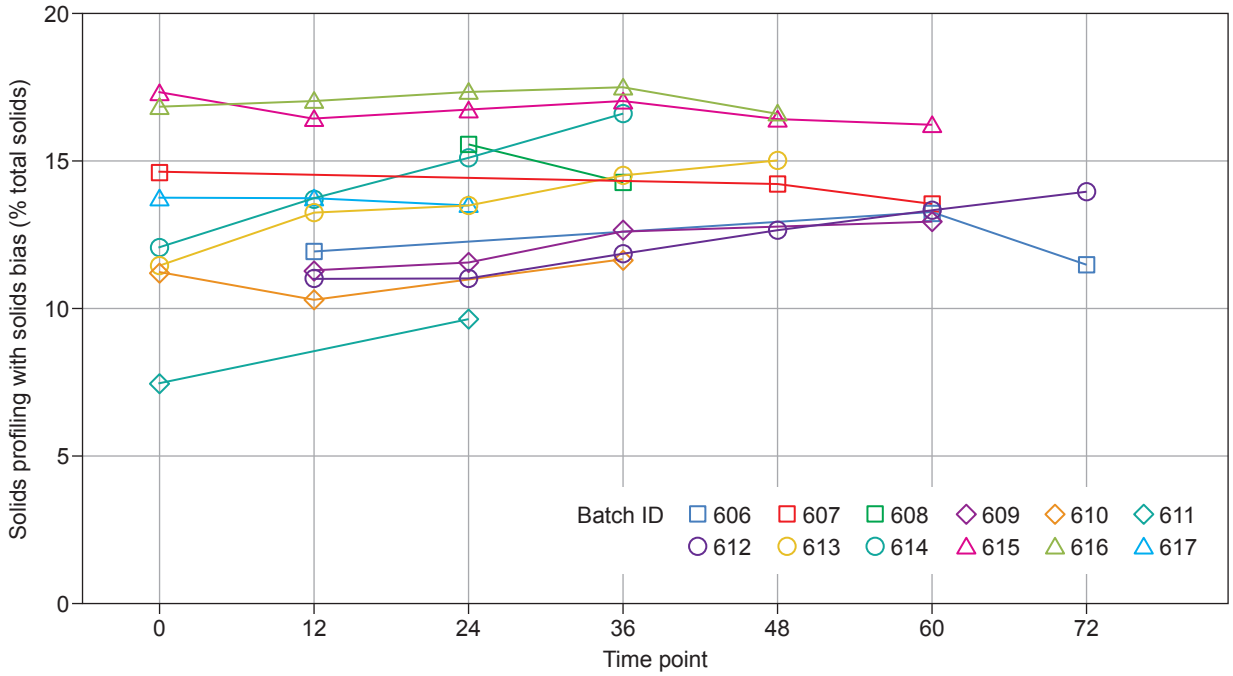

Figure 9.2—Solids profiles during different runs of enzymatic hydrolysis.

through, allowing copious amounts of water to enter the VB1 tank. The resulting slurry in VB1 rarely contained more than 15% solids.

Conversely, drier fiber cake, 20% to 25% total solids, tended to float on top of the slurry in VB1. If the liquid level in VB1 was above the top agitator, dry fiber cake would pile up and form a raft. When this happened, the hydroconveyor would need to be stopped until the fiber raft was incorporated into the slurry.

In the 3,000-gal VB1 Tank, solids were combined with water and enzyme. The pH was maintained by metering in potassium hydroxide (KOH). Temperature was maintained at 130 °F in VB1 by adjusting the temperature of the water in the hydroconveyor. Enzyme was added to the slurry to begin the liquefaction process. Residence time in the tank allowed the material to liquefy enough to make the slurry pumpable for a short distance.

One goal of the VB1 tank was to increase slurry solids content to about 15%. Due to the varying concentration of solids in the hydroconveyor slurry, there were periodic failures of the solid fiber plug at the outlet of the filter, allowing copious amounts of water to enter the tank. The resulting slurry typically averaged 10% to 13% (Fig. 9.2).

From the viscosity break tank, fiber slurry was pumped with a diaphragm pump to a 6,000-gal liquefaction tank, which provided longer residence time. In the liquefaction tank known as “yeast conditioning tank 1” (YC1), the slurry continued to liquefy for several hours. Continuous pumping from the liquefaction tank to the hydrolysis tank did not provide the velocity through the pipe needed to prevent settling of solids, which would allow clogs to form. Periodically, the liquefaction tank was pumped to a 6,000-gal aerobic fermenter. Higher velocity in the line between the tanks reduced plugging.

Liquefaction of the fibers resulted in the release of glucose from the fibers. Typically, slurry leaving the liquefaction tank contained 20 to 40 g/L glucose. This is the initial point on Figure 9.3. Only one hydrolysis batch, batch 608, developed more than 2 g/L lactic acid during liquefaction. This is the initial point on Figure 9.4.

During run 7, batches 615, 616, and 617 had the rotary press set so that the cakes were dry enough to float. The liquid level in the secondary slurry tank was maintained just below the top agitator, which allowed cakes to be hit with agitator blades and not form a raft of dry fibers. Relatively dry fiber cake allowed the rotary press to maintain the solid fiber plug needed to force the water through the rotary press screens instead of allowing the water to pass through the rotary press and into the secondary slurry tank. This allowed the slurry to contain higher solids in run 7 than in previous runs.

9.3 Enzymatic Saccharifications

Hydrolysis was conducted in the same tanks as fermentation. The 6,000-gal aerobic fermenters provided temperature control, mixing, pH control, and a sterile environment. The tanks were first sterilized. The tanks were heated to 190 °F as fiber slurry was pumped into the tanks. Fiber slurry was pasteurized to 190 °F to eliminate contamination as was seen in batch 605 (run 3). After pasteurization, enzyme was added to complete hydrolysis of the fibers. Aerobic fermenters were filled sequentially.

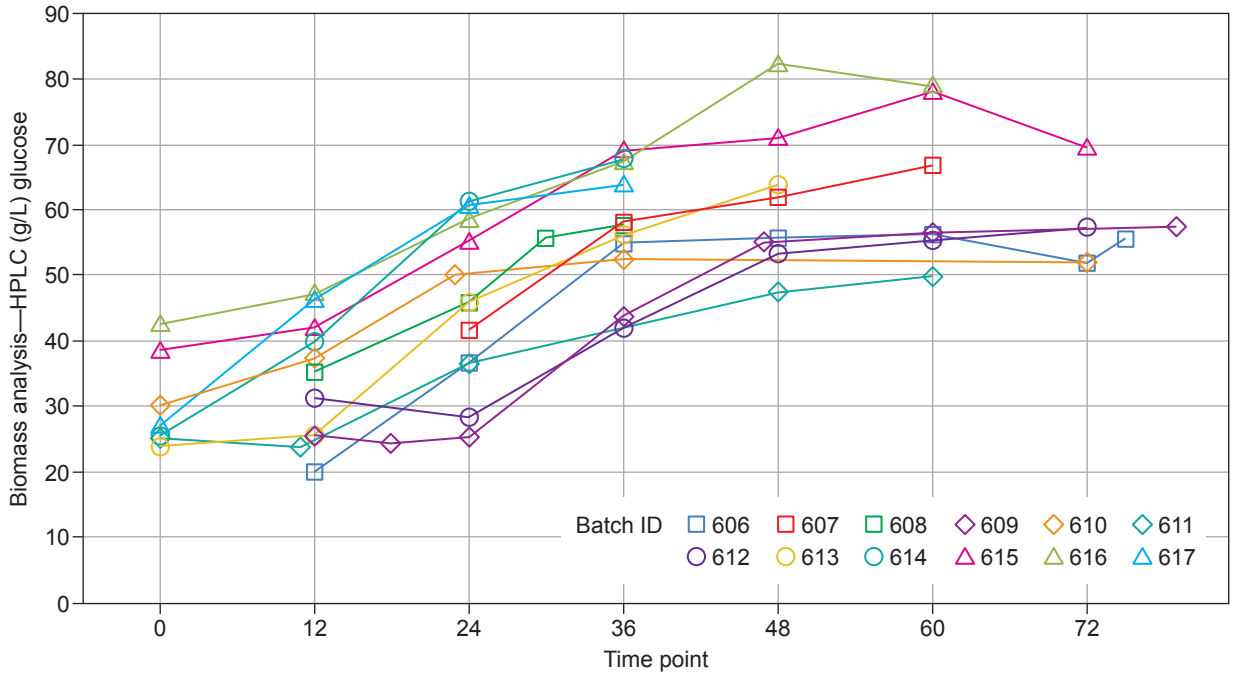

Figure 9.3—Glucose profile during enzymatic saccharification.

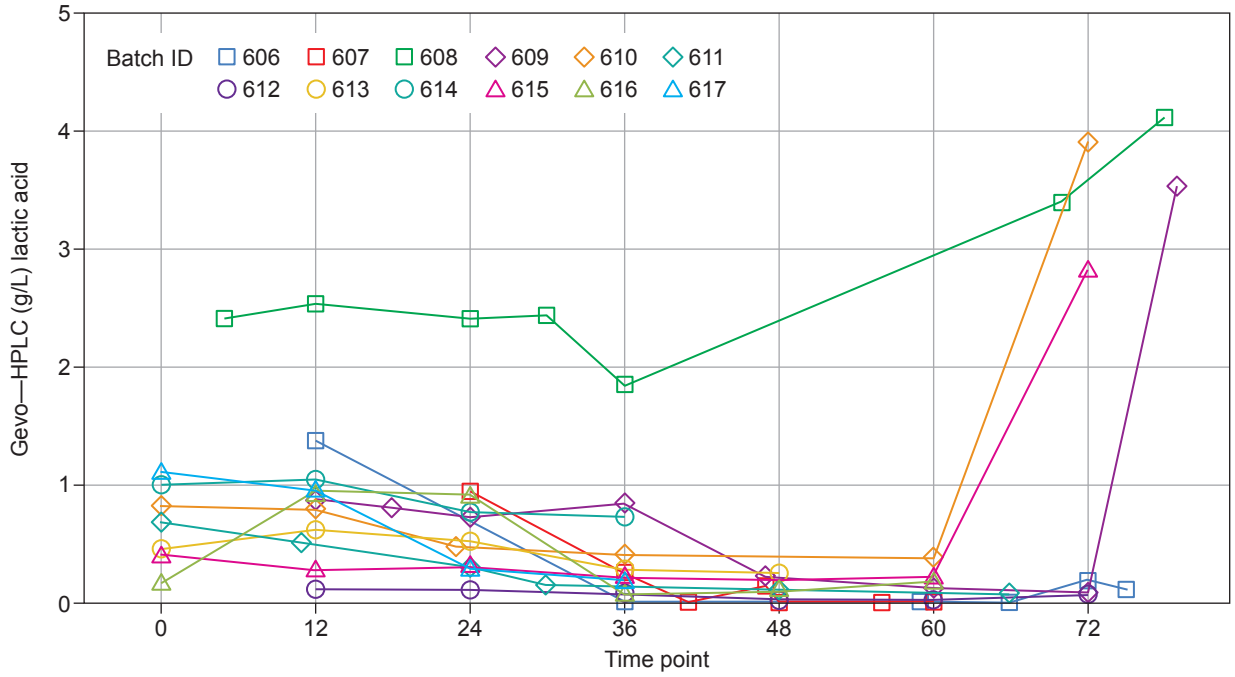

Figure 9.4—Lactic acid profile during enzymatic saccharification.

Slurry in aerobic fermenter 1 (AF1) typically hydrolyzed for 24 h longer than slurry in aerobic fermenter 3 (AF3).

Because the fiber slurry was pumpable through a 2-in. pipe for several hundred feet, the fiber slurry was at a viscosity that would allow for thorough mixing. Fiber slurry had hydrolyzed and liquefied in VB1 and YC1 for several hours before it was pumped to the aerobic fermenters. However, controlling pH was problematic. The particulate nature of the slurry tended to blind over the pH probe, separating the probe from the majority of the volume. Because the pH probe reading was unreliable, the tanks were checked periodically through sampling and measurement with a lab pH probe.

Sampling was problematic in run 4. The sample ports on the aerobic fermenters were designed for liquids that were largely free from suspended solids. The suspended solids in the hydrolyzate would quickly blind over the sample port opening. As a result, new sample ports were fabricated. During run 4, AF1 and AF2 had sample ports installed on the top of the fermenter. Because AF3 had not been filled when this problem was discovered, AF3 had a 1-in. sample port installed where the pH probe opening was. After run 4, similar sample ports were fabricated and installed on AF1 and AF2. All ports were equipped with steam to allow sterile sampling.

Solids profiling of the hydrolyzate was especially difficult. Obtaining a representative sample was problematic. The hydrolyzate contained a wide array of particle sizes, some larger than 1 mm, some smaller than 10 µm. Passing hydrolyzate through a 0.22-µm filter was nearly impossible. One syringe filter would allow approximately 200 µL to pass through the filter before it clogged. During this project, dissolved solids measurements was performed by centrifuging 15 ml of hydrolyzate, and then pouring the centrate into a solids weighing pan. Total solids testing was performed by using a cut off 10-mL transfer pipette, stirring the hydrolyzate with the transfer pipette, and sampling while the sample was being stirred. Typically, the difference between sample A and B was much larger than seen with other liquids tested this way.

Obtaining enough liquid for high-pressure liquid chromatography (HPLC) was challenging. A standard 0.22-µm syringe filer would clog after a few drops, perhaps 200 µL. Centrifuging the sample at 5100 rpm for 5 min did not improve the filterability of the centrate. To filter enough liquid for an HPLC vial, three to four syringe filters were required. We purchased filtering centrifuges. Typically, the 15-mL sample yielded approximately 2 mL after 5 min of centrifuging at 5100 rpm. Because a syringe filter absorbs approximately 1 mL of liquid, we centrifuged the samples for 10 min to obtain enough liquid for the two HPLC vials—one vial for the acid column, which provides good data on substances like ethanol and isobutanol and one vial for the lead column, which provides good data on sugars such as glucose and mannose.

Table 9.1—Amount of enzyme (CTec3) applied

		Enzyme added (gal)	
	Batch	In AF[a]	In VB[b]
Run 4	606	23.4	65.2
	607	17.1	33.2
	608	26.3	18.0
Run 5	609	15.1	60.0
	610	11.7	0.9
	611	9.4	18.2
Run 6	612	14.4	41.0
	613	15.2	15.4
	614	20.2	11.1
Run 7	615	17.5	56.0
	616	20.5	18.8
	617	16.7	3.3
Average		17.3	28.4

[a]Amount added to aerobic fermenter after pasteurization.
[b]Amount added continuously to VB tank for liquefaction; demarcation between batches is difficult, so overall average is more accurate.

The amount of Novozymes Cellic CTec3 enzyme added is given in Table 9.1. In general, the VB1 tank was being filled continuously. Certain amounts were periodically transferred to the AF tanks. Therefore, exactly how much enzyme went into each batch prior to pasteurization is difficult to know. Unfortunately, the entire initial enzyme application was denatured during the heat-up. Only the amount actually added to the AF would have acted in the final complete saccharification.

9.4 Fermentation

After the completion of hydrolysis, the aerobic fermenters were sterilized and then dosed with 100 gal of nutrients. During fermentation run 4, comprising hydrolysis batches 606, 607, and 608, the tanks were sterilized simultaneously, which took a total of 37 h of heating and cooling. During fermentation run 5, comprising hydrolysis batches 609, 610, and 611, the tanks were sterilized sequentially, which took 34 h of heating and cooling. Runs 6 and 7 each took 40 h to complete sterilization (Table 9.2).

Following sterilization, the tanks were cooled to the fermentation temperature, and then a nutrient solution was pumped into the fermenters through a sterile filter.

After the first nutrient addition, a mixture of additives was added to the tanks by filter sterilizing through a 0.2-µm filter. The additives were combined in a sterile add bottle and pumped into the aerobic fermenters through a steam sterilized port.

Table 9.2—Fermentation sterilization time

	Run 4			Run 5			Run 6			Run 7		
Batch	505	506	507	509	510	511	512	513	514	515	516	517
Heat time (h)	24	24	24	8	13	11	13	17	22	15	18	28
Cool time (h)	13	13	13	13	3	5	4	8	4	6	3	4
Total time (h)	37	37	37	21	16	16	17	25	26	21	21	32
Run total time (h)		37			34			40			40	

Table 9.3—Fermenter volume

	Fermenter volume (gal)			
	Run 4	Run 5	Run 6	Run 7
End of hydrolysis	18,111	17,103	18,740	17,111
Start of fermentation	20,292	18,149	20,113	18,740
Difference	2,181	1,046	1,373	1,629

During sterilization, the tanks were diluted as a result of the introduction of condensing steam into the tanks. The simultaneous sterilization strategy used in run 4 resulted in an additional 2,181 gal of condensate from steam. The sequential sterilization strategy used in runs 5, 6, and 7 resulted in an additional 1,046 gal, 1,373 gal, and 1,629 gal of water from steam, respectively (Table 9.3).

After run 1, the standard inoculation procedure was to pump the yeast using a 4-Quat sanitized diaphragm pump. A 2-in. diaphragm pump was used in run 4, which resulted in the loss of many gallons of yeast cream. A 1-in. diaphragm pump and 1-in. hoses were used in run 5, which limited the loss during inoculation. The inoculation dosage in run 4 was about 150 lb per tank. The dosage in runs 5 and 6 was reduced to approximately 100 lb per tank. For inoculation in run 7, sterile water was added to the yeast cream tote to facilitate mixing prior to pumping yeast cream for inoculation.

The fermentation plan for run 4 included running the broth through GIFT during fermentation. When the GIFT recirculation was engaged, the flow blocked nearly immediately in the beer flash preheater (ET-4701). A few attempts were made to clear the line but were unsuccessful. Removing isobutanol during fermentation became untenable, and a recovery step was added to the process. One batch in three tanks became three one-tank batches. The new batches were designated 505, 506, and 507 (but should have been 506, 507, and 508 to coincide with the hydrolysis batches). The fermentation scheme remained the same for follow-on batches.

Glucose consumption rates and isobutanol production rates were similar among all batches. The lag phase for run 4 fermentations was not very long; within the first 3 h, glucose consumption began to steadily increase (Fig. 9.5). During runs 5, 6, and 7 fermentations, however, there was a pronounced lag phase; 6 h into runs 5 and 6, glucose began to be consumed (Figs. 9.5, 9.6).

Glucose consumption and isobutanol production were slow in batch 514 of run 6, largely as a result of the low yeast population. At inoculation, average population in runs 4 and 5 were 3 and 1.4 times higher than batch 514, respectively. The populations in the other batches of run 6, batches 512 and 513, were also higher.

9.5 Fermentation Details

A run consisted of the following steps:

1. Sterilize each of the 3,000–6,000-gal aerobic fermenters.
2. Cool and fill each tank sequentially with partially liquefied slurry from the VB1 and YC1 tanks, where a small amount of enzyme had been added.
3. As each tank was filled, the partially liquefied slurry was pasteurized by heating to 190 °F. Volume and temperature profiles are provided in Figures 9.7–9.10.
4. After pasteurization (which also denatured the applied enzymes), the tank was cooled and a new dose of enzymes was added to complete saccharification. Saccharification yields are presented in Table 9.4 (with key times for the saccharification and fermentation runs given in Table 9.5).
5. Upon completion of saccharification, nutrients were added, and the tank was sterilized.
6. After cooling, the tanks were inoculated and fermentation started.
7. GIFT recovery of isobutanol was attempted during the fermentation in run 4, but plugging due to solids was too severe, so in the other runs GIFT was delayed until the fermentation was completed.
8. At the end of run 4, the fermenter was pasteurized after fermentation to kill the yeast and avoid any conversion of isobutanol to isobutyric acid.
9. After the completion of fermentation, GIFT was run until all isobutanol was recovered.

9.6 GIFT Operation

During run 4, a considerable amount of isobutyrate was produced between the end of fermentation and the end of isobutanol recovery (Fig. 9.11). We hypothesized that the yeast was consuming isobutanol and converting it to

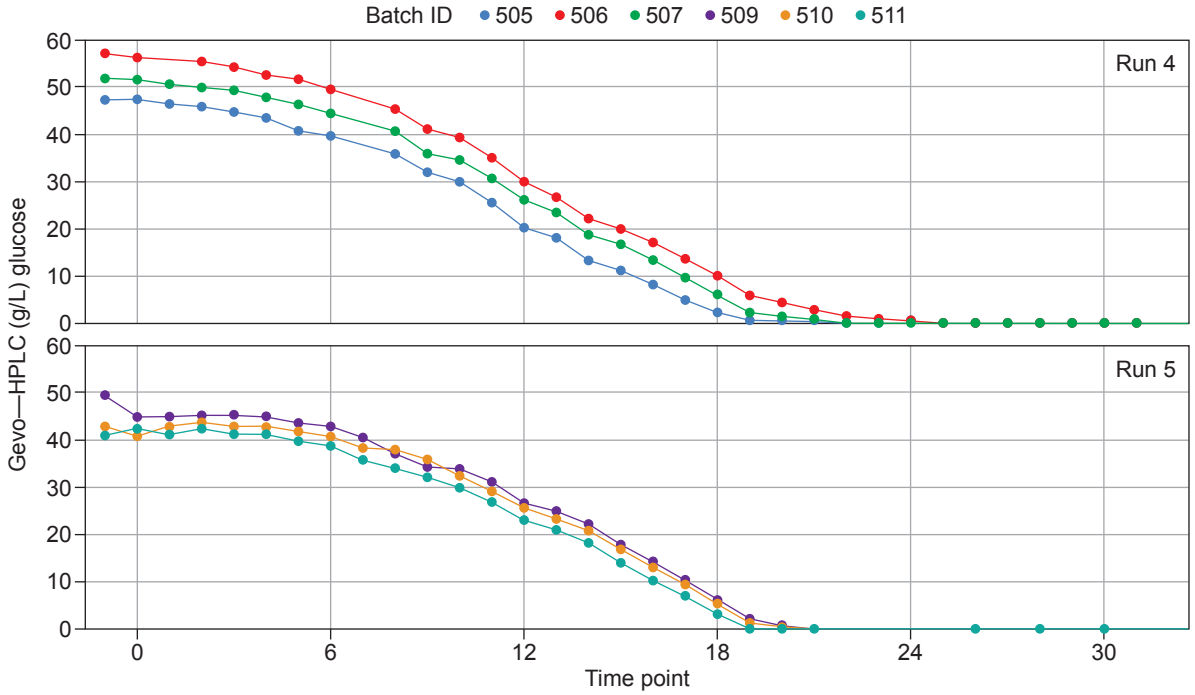

Figure 9.5—Run 4 (505, 506, 507) and run 5 (509, 510, 511) glucose consumption profiles.

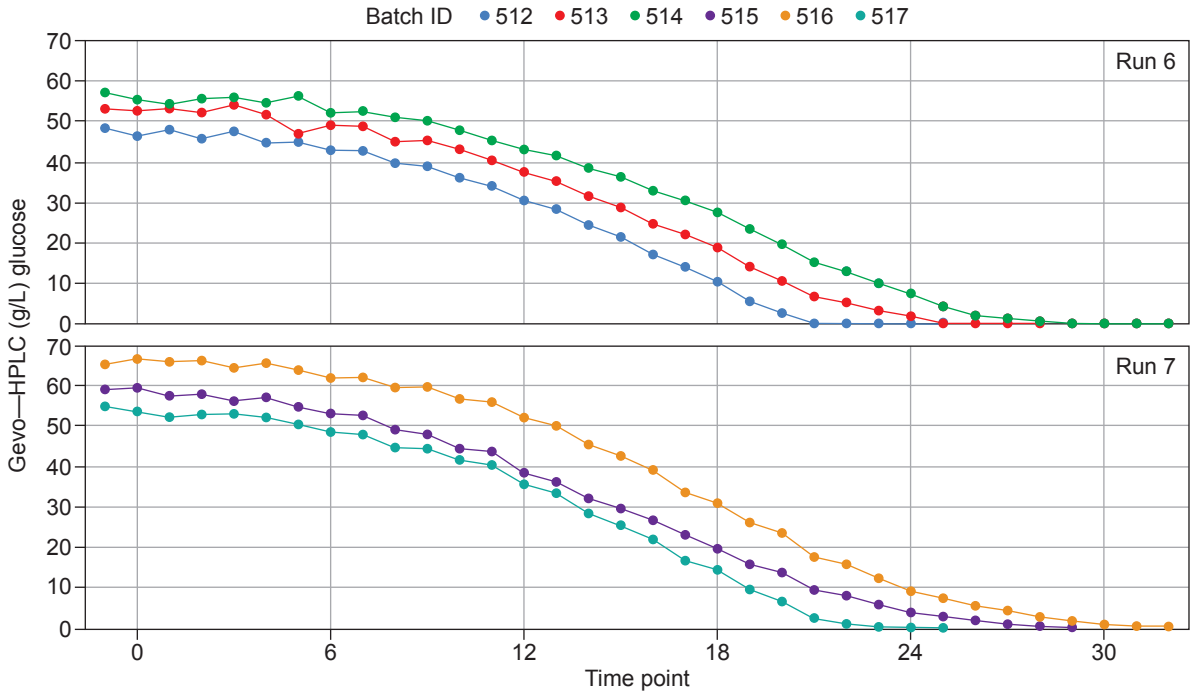

Figure 9.6—Run 6 (512, 513, 514) and run 7 (515, 516, 517) glucose consumption profiles.

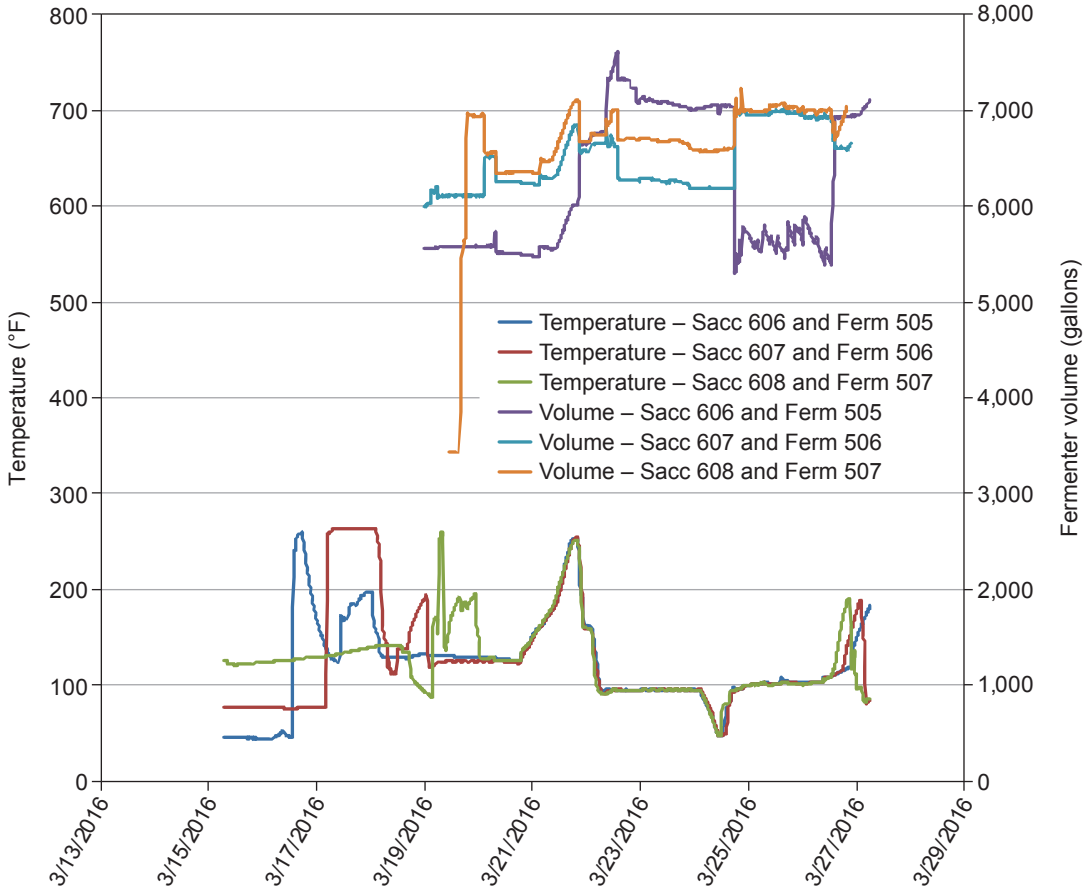

Figure 9.7—Run 4 saccharification and fermentation temperature and volume profiles.

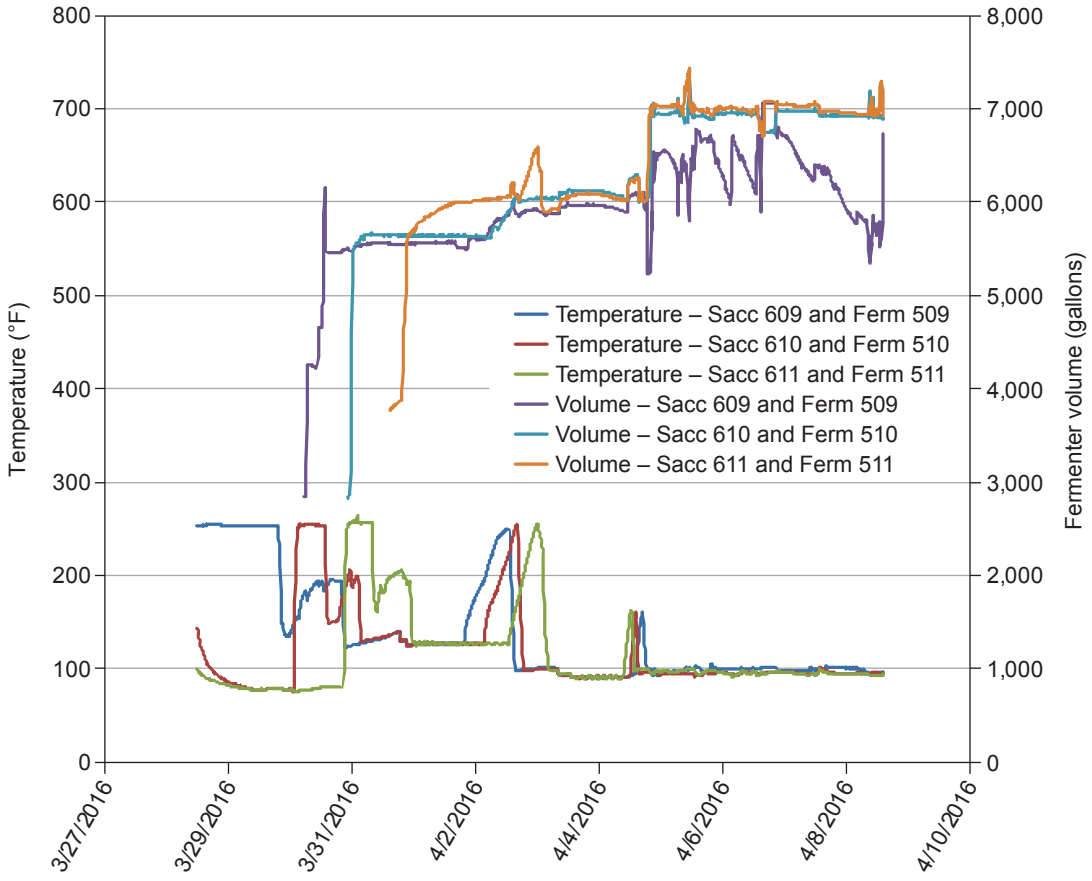

Figure 9.8—Run 5 saccharification and fermentation temperature and volume profiles.

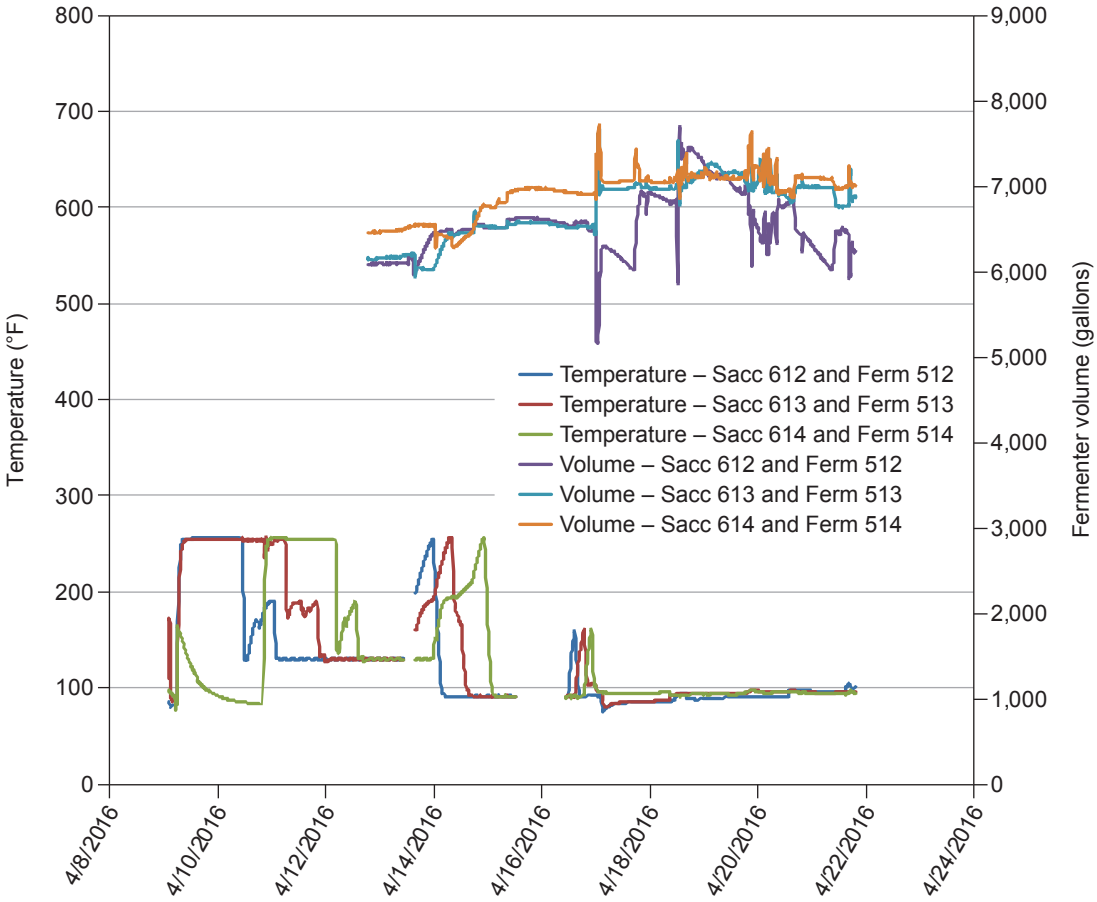

Figure 9.9—Run 6 saccharification and fermentation temperature and volume profiles.

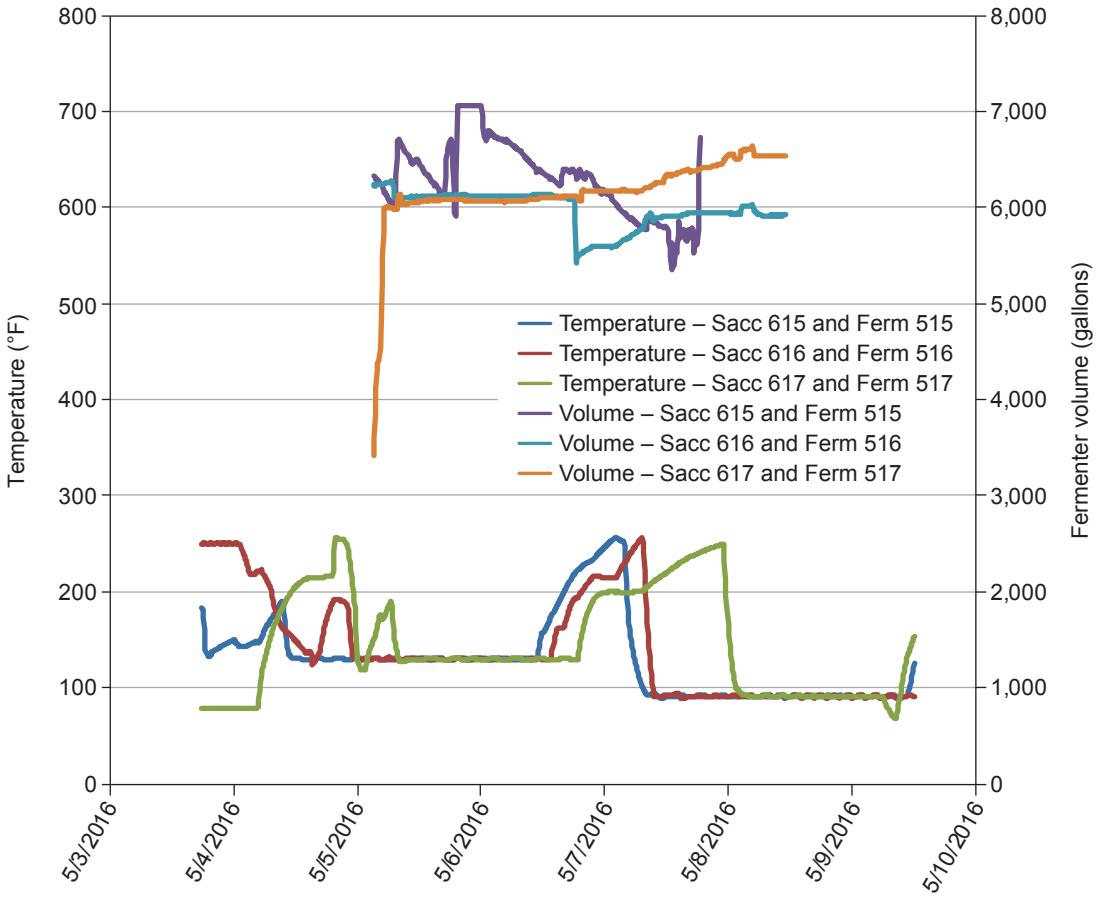

Figure 9.10—Run 7 saccharification and fermentation temperature and volume profiles.

Table 9.4—Campaign 2 saccharification yield (key times for the saccharification and fermentation runs are given in Table 9.5)

	Batch	Final glucose (g/L)	Total solids (%)	Suspend solids (%)	Tank volume (gal)	Total solids (lb)	Volume liquid (gal)	Total glucose (lb)	Theoretical glucose (lb)	Glucose yield (%)
Run 4	606	56.3	11.5	4.0	5,514	5,532	5,292	2,486	3,414	73
	607	66.7	13.5	5.0	6,251	7,398	5,940	3,307	4,565	72
	608	57.6	14.3	6.3	6,353	7,923	5,952	2,863	4,889	59
Run 5	609	57.4	12.9	5.0	5,561	6,266	5,286	2,531	3,867	65
	610	52.4	11.6	4.9	5,636	5,726	5,362	2,345	3,534	66
	611	49.8	9.6	5.7	5,907	4,975	5,567	2,314	3,070	75
Run 6	612	57.2	13.9	5.6	5,980	7,294	5,643	2,695	4,501	60
	613	63.7	15.0	6.7	6,116	8,005	5,705	3,031	4,940	61
	614	67.5	16.6	7.2	6,439	9,331	5,973	3,366	5,758	58
Run 7	615	78.0	16.2	6.2	6,016	8,523	5,643	3,675	5,260	70
	616	82.4	16.6	5.8	6,152	8,929	5,792	3,982	5,510	72
	617	63.8	13.5	4.9	6,031	7,107	5,737	3,054	4,386	70
Overall C0310		59.4	13.8	5.6	71,957	87,008	67,893	35,650	53,693	66

Table 9.5—Key times for each saccharification and fermentation batch

	Batch	Tank	Fill start	Enzyme addition	Inoculation	Start of GIFT	End of run
Run 3	C0310-605	H4	3/3/2016 8:00	3/7/2016 21:00			4/14/2016 0:00
Run 4	C0310-606	AF1	3/17/2016 9:00	3/18/2016 9:00	3/23/2016 0:00	3/23/2016 22:00	3/27/2016 6:00
	C0310-607	AF2	3/18/2016 5:00	3/19/2016 5:00	3/23/2016 0:00	3/24/2016 1:00	3/27/2016 1:00
	C0310-608	AF3	3/19/2016 4:00	3/20/2016 4:00	3/23/2016 0:00	3/23/2016 23:00	3/26/2016 20:00
Run 5	C0310-609	AF1	3/29/2016 16:00	3/31/2016 16:00	4/3/2016 12:00	4/4/2016 9:00	4/8/2016 15:00
	C0310-610	AF2	3/30/2016 13:00	3/31/2016 13:00	4/3/2016 12:00	4/4/2016 8:00	4/8/2016 21:00
	C0310-611	AF3	3/31/2016 10:00	4/1/2016 10:00	4/3/2016 12:00	4/4/2016 8:00	4/8/2016 23:00
Run 6	C0310-612	AF1	4/10/2016 11:00	4/11/2016 10:00	4/15/2016 13:00	4/16/2016 10:00	4/22/2016 1:00
	C0310-613	AF2	4/11/2016 8:00	4/11/2016 23:00	4/15/2016 13:00	4/16/2016 14:00	4/22/2016 2:00
	C0310-614	AF3	4/12/2016 5:00	4/12/2016 16:00	4/15/2016 13:00	4/16/2016 19:00	4/22/2016 3:00
Run 7	C0310-615	AF1	5/3/2016 18:00	5/4/2016 18:00	5/8/2016 5:00	5/9/2016 4:00	5/14/2016 0:00
	C0310-616	AF2	5/4/2016 15:00	5/5/2016 5:00	5/8/2016 5:00	5/9/2016 8:00	5/14/2016 0:00
	C0310-617	AF3	5/5/2016 0:00	5/5/2016 9:00	5/8/2016 5:00	5/9/16 11:00	5/14/2016 0:00

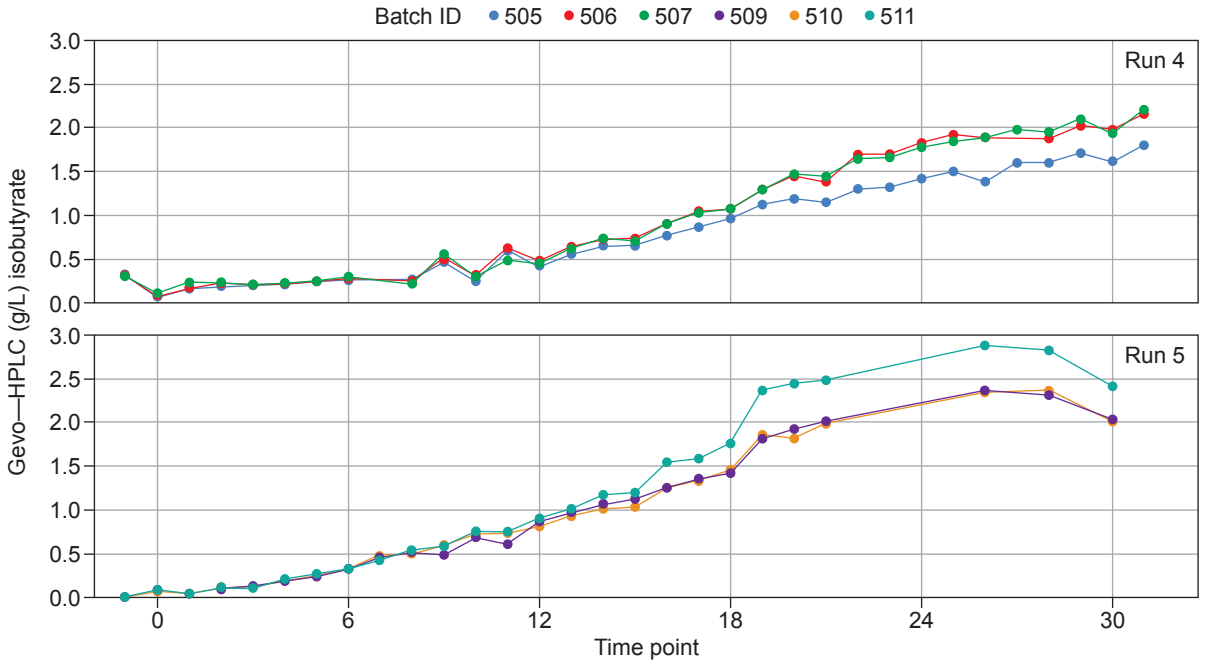

Figure 9.11—Run 4 (505, 506, 507) and run 5 (509, 510, 511) isobutyrate generation profiles.

isobutyrate under carbon starvation conditions. Glucose was completely consumed after 24 h. Between the end of fermentation and the end of GIFT, an additional 2.54 g/L isobutyrate was produced, equivalent to a loss of 2.54 g/L isobutanol.

To limit the loss of isobutanol to isobutyrate, a pasteurization step was implemented in run 5 (Fig. 9.11). At the conclusion of fermentation, the temperature was increased in the fermenters to 160 °F to kill the yeast. Thermodynamics of the system limited how quickly the yeast could be killed. On average, heating the tank to 160 °F took 2 h. To prevent loss of isobutanol, the tank was sealed during heating and cooling.

During run 4, recovery was about 44 h. During run 5, recovery was about 72 h. One of the biggest challenges in using GIFT for isobutanol recovery was limited flow through the GIFT reboiler. Flow steadily declined during run 4 from 350 to 100 gal/min. In the first 16 h of recovery for run 5, reboiler flow declined from 350 to 0 gal/min. Reboiler recirculation was stopped twice during run 5 to flush the heat exchanger; however, the best flow rate of post-cleaning was approximately 200 gal/min. In the last 18 h of run 5, reboiler flow averaged 50 gal/min. The residual solids fibers from the unmilled Cosmo material were simply too large for this particular reboiler design.

Data for runs 6 and 7 are shown in Figure 9.12.

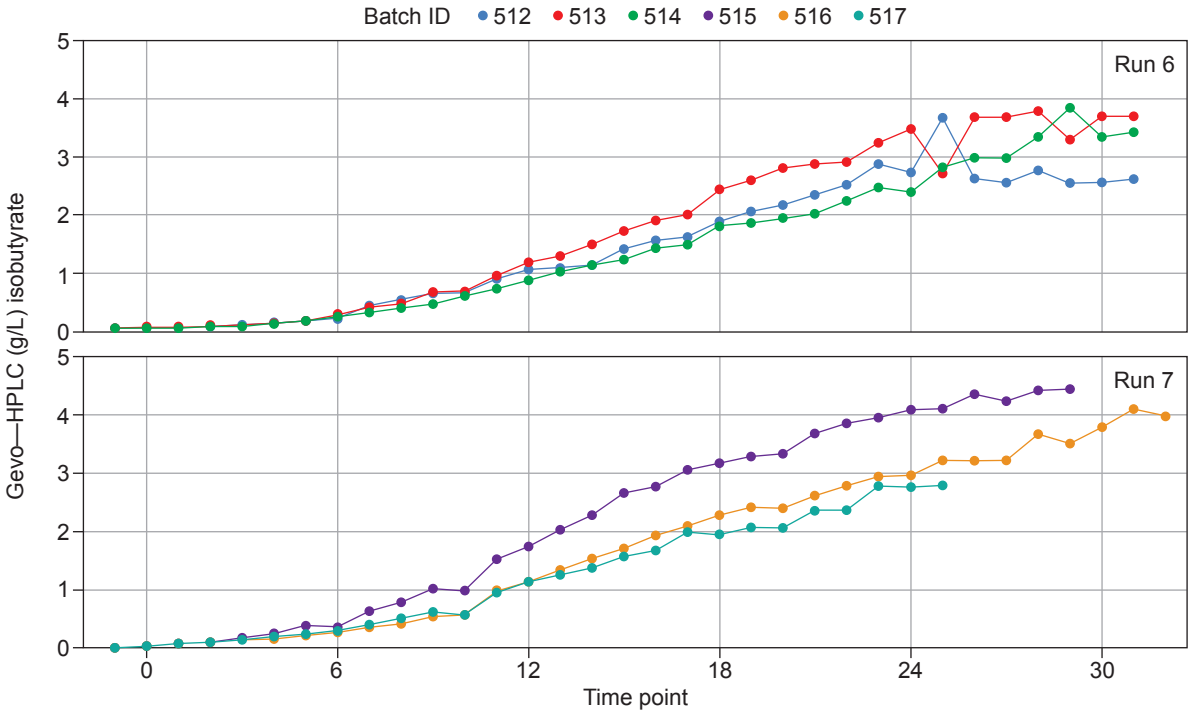

Figure 9.12—Run 6 (512, 513, 514) and run 7 (515, 516, 517) isobutyrate generation profiles.

9.7 Post-Fermentation Processing

GIFT recovery successfully removed isobutanol from the fermentation broth, typically down to <1 g/L remaining in the fermenter. Condensation following the GIFT column results in two liquid phases. These are separated in a liquid/liquid (L/L) separator. The heavy phase (about 90% water) is stripped of isobutanol in a steam stripper. The overheads of the stripper, when condensed, are again two phases and are recycled to the L/L separator. This process effectively recovers all the isobutanol from the heavy phase. The light phase (about 80% isobutanol) is usually recovered in a second stripper (generally called the "rectifier," a legacy name from the ethanol process). The rectifier for isobutanol recovery in the ICM pilot plant is too large to easily run continuously, so it is operated in a batch mode after the GIFT column operation is completed. Dehydration of the isobutanol light phase in campaign 1 (November–December 2015) was generally accomplished in the rectifier column (see totes 901, 902, and 903 in Table 9.6). Two of the totes (801 and 802) became contaminated with ethanol at the end of campaign 1 and could no longer be dehydrated with the simple distillation method. These two partial totes were 2.7% and 3.7% ethanol. The light phase from campaign 2 was all relatively low in ethanol (totes 905, 906, 907 in Table 9.6).

Importantly, all the totes (Table 9.6) were out of specification with respect to acid number (as acetic acid, ASTM D1613). The specification is <70 ppm. It was deemed that the easiest way to remove this acid would be to return all the isobutanol to the fermenter and rerun through GIFT under different conditions.

ICM did not have the capability to measure acid number (as acetic acid, ASTM D1613) during the fermentation runs, and the acid number results obtained were from either Mid-West Laboratory or Gevo (Table 9.7). The off-site analysis required many days to complete. ICM assured us that they had a reliable method on-site.

Putting the light phase back into the fermenter has limitations. Due to flammability issues, we were limited to a maximum isobutanol concentration of 50 g/L in the fermenter. This required that isobutanol be added to the fermenters multiple times because we had approximately 1,700 gal of isobutanol and added only 6,000 gal of fermenter volume. Isobutanol had to be adding within the GIFT room because this was the only area electrically classified to allow high concentrations of isobutanol, such as was in the totes. Adding the isobutanol into the bottom of the GIFT column was difficult, and more than once the vacuum was upset in the column. Each time one of these upsets happened, multiple analyses were conducted of the GIFT overhead; each time, acid concentration was found to be only approximately 35 ppm, well within the specification of 70 ppm. It is unclear why initial analyses indicated that reprocessed isobutanol was out of specification, even though all on-site analyses indicated otherwise. The resulting isobutanol was crystal clear (Fig. 9.13).

After removing the acid (or most of it) from the isobutanol, the next step was to remove the water using the batch

Table 9.6—Isobutanol material available after initial GIFT® recovery (analyses by Gevo)

Tote	Total weight (lb)	Specific gravity	Water (%)	Acid no. (ppm)	iBuOH (%)	EtOH (%)	1-PrOH (%)	3M-1BuOH (%)	2M-1BuOH (%)	2PhEtOH (%)	Unknown (%)	Other (%)	Comments
901	599	0.8041	0.53	900	94.65	0.13	0.03	3.63	0.80	0.11	0.05		Dehydrated in Dec–Nov
902	1,834	0.8050	0.52	5,800	96.62	0.04	0.02	1.72	0.29	0.13	0.27	0.06	Dehydrated in Dec–Nov
903	2,087	0.8036	0.50	1,900	96.35	0.12	0.03	2.26	0.43	0.08	0.09	0.02	Dehydrated in Dec–Nov
801	762	0.8436	16.55	19,200	76.20	2.69	0.70	0.76	0.15	0.23	1.03	0.77	Hi-EtOH partly dehydrated Dec
802	1,870	0.8402	17.44	4,900	76.86	3.73	0.34	0.27	0.06	0.04	0.37	0.75	Hi-EtOH partly dehydrated Dec
905	1,870	0.8366	16.07	1,200	79.13	0.76	0.09	1.74	0.30	0.02	0.30	0.34	Light phase Mar–April
906	1,868	0.8376	16.46	1,500	79.98	0.60	0.22	1.78	0.27	0.02	0.03	0.50	Light phase Mar–April
907	2,199	0.8370	16.48	400	80.07	0.50	0.22	1.78	0.27	0.02	0.03	0.60	Light phase Mar–April

Table 9.7—Light phase available after acid removal by GIFT® (analyses by Gevo)[a]

Tote	Gross weight (lb)	Tare weight (lb)	Net weight (lb)	Water weight (%)	iBuOH weight (%)	EtOH weight (%)	Acid no. (ppm)	Density (kg/L)	Estimated iBuOH weight (lb)	Estimated iBuOH volume (gal)
C0310-820	2,790	573	2,217	16.03	81.25	0.26	71	0.827	1,806	262
C0310-821	2,843	578	2,265	16.99	79.88	0.31	97	0.830	1,824	264
C0310-822	2,846	582	2,264	14.86	81.50	0.49	120	0.827	1,870	271
C0310-823	2,867	565	2,302	16.85	79.88	0.47	102	0.830	1,857	269
C0310-824	2,873	578	2,295	14.93	82.98	0.40	88	0.826	1,894	275
C0310-825	2,244	576	1,668	14.52	82.62	1.32	189	0.824	1,383	201
C0310-827	2,384	576	1,808	13.16	83.64	0.32	65	82.5%	1,523	222
Total									12,156	1,764

[a]Compositions and density were measured by Gevo. Data are from 160628 Gevo-GC13_NARA samples_160621.xls.

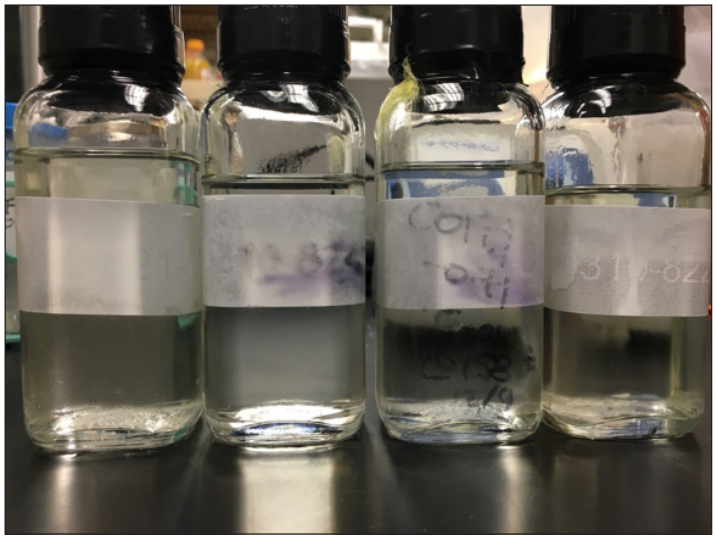

Figure 9.13—Tote samples of completed material from ICM.

rectifier column. Unfortunately, this did not work. Apparently there was enough ethanol in this material (0.6–0.76%) to hold down the separation of water and isobutanol.

An alternative method of removing water from alcohol is by membrane separation. ICM had been discussing this possibility with Whitefox as a means to recover isobutanol from the two high ethanol totes from campaign 1. Now it would be necessary to process all the light phase through their process. A detailed daily historical summary of the ICM second campaign can be found in Appendix F.

9.8 Whitefox Dehydration of Isobutanol

Whitefox has a technology for removing water from alcohols using membrane systems. A vapor permeation hollow fiber membrane (HFM) module was used by Whitefox to remove water from the isobutanol to the required specification (<1%). The tests were completed with a 92% recovery of isobutanol; an optimized membrane dehydration process is expected to deliver yields higher than 99% (Table 9.8).

Two totes were analyzed for composition beyond water content to get an idea of what, if anything, changed during membrane dehydration. Table 9.9 shows that there were no changes other than the removal of the water.

The isobutanol was shipped from Whitefox to South Hampton Resources to conduct the final step, conversion of isobutanol to biojet fuel.

Table 9.8—Material returned from Whitefox

Tote	Water concentration (w%)	Liquid weight (kg)
823	1.43	249
821	0.82	255
827	0.77	299
820	0.48	319
907	0.79	304
822	0.76	258
Total		1,683
Overall isobutanol yield		92%
Water content (wt%)		0.82%

Table 9.9—Comparison of isobutanol composition before and after membrane processing

	iBuOH (%)			Water (%)		Acid no. (ppm)	
Original tote	Before	After calc[a]	After actual	Before	After	Before	After
820	81.3	96.0	96.7	16.0	0.55	70.5	76
824	79.9	95.6	96.1	14.9	0.42	88.0	52

[a]This is the concentration of isobutanol expected (calculated) if the water is removed.

Figure 10.1—Gevo-designed isobutanol to biojet process.

Figure 10.2—South Hampton Resources facility.

10. Production of Biojet from Isobutanol

10.1 Overview

The production of biojet from isobutanol was done using technology that Gevo put together, and for which they built a demonstration process (Fig. 10.1) at South Hampton Resources (SHR) in Silsbee, Texas, USA (Fig. 10.2). SHR now owns and operates the process on a contract basis for Gevo.

The process consists of three main reactions: (1) dehydration of isobutanol to isobutylene, (2) oligomerization of isobutylene to branched C12 and C16 olefins, and (3) hydrogenation of the olefins to paraffins. The process is shown in Figure 10.3. Usual operation of the process includes the production of C8 olefin or paraffin. This is a useful product for applications other than jet fuel. To maximize the amount of jet fuel produced, the C8 olefin was recycled to the oligomerization reaction rather than segregating it as a separate product.

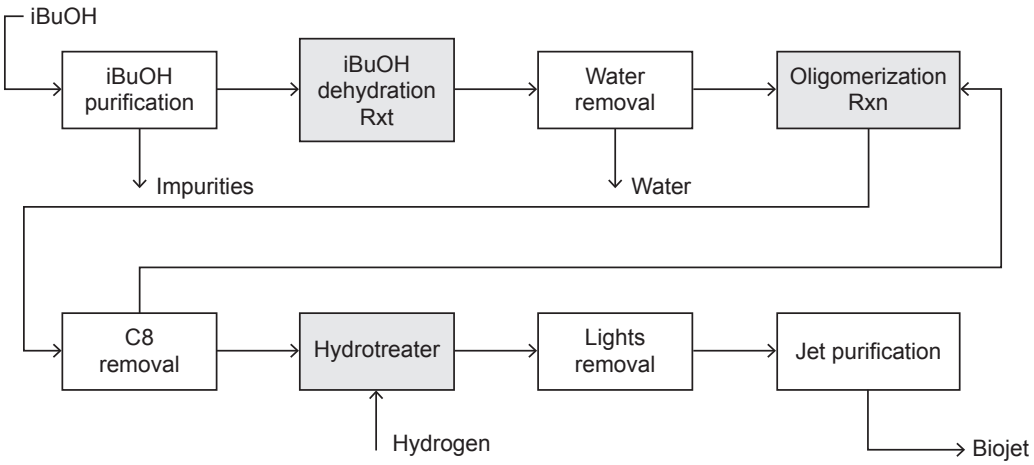

Figure 10.3—Gevo isobutanol to biojet process at SHR.

10.2 Isobutanol Preparation

Approximately 1,680 gal of purified isobutanol was received by SHR from Whitefox after removal of water. As noted earlier, all totes of isobutanol were tested for water and met the water specification of <1 %. Only two samples were analyzed for isobutanol after dewatering (Table 9.9). In one sample (tote 820), the acid number actually increased from 70.5 to 76 ppm, but in the other sample (tote 824), the acid number decreased from 88 to 52 ppm, a significant reduction. The results were inconclusive as to whether the membrane process reduced the acid aumber. Gevo installed a distillation at the beginning of the process at SHR (before the dehydration reactor) to purify isobutanol by removing heavy components that may result in gums (solvent washed gum is one of the isobutanol specification items) and salts of organic acids. A small amount of caustic was added to each isobutanol feed tote received by SHR to ensure that any organic acids contributing to the acid number were converted to salt. The amount of caustic added was 10% excess of the amount required to neutralize 150 ppm acid. Analysis of the isobutanol after distillation indicated acid number below the specification of <70 ppm (Fig. 10.4).

10.3 Process Operation

The process was started on August 29, 2016, by first building up some inventory of C8 olefin to ensure a smooth recycle. After a day of operating in this mode, the feed was shifted to NARA-produced isobutanol. For the next 10 days, NARA isobutanol was fed, making a steady amount of jet fuel. No unexpected issues came up using the NARA isobutanol. There had been some concern that this feed contained a little more ethanol, which does not dehydrate to the olefin at the same rate as isobutanol and might make water removal more difficult. Figure 10.5 shows that water content in the oligomerization reactor ranged from approximately 30 to 100 ppm, which is about normal for the process.

Further, the product distributions were typical for this process and generally 80% to 90% C12, 8% to 10% C16, and ~1% C20 (Fig. 10.6).

Olefin content was initially very high. There is no specification on olefin content. The mass percentage of paraffin is reported in the Certificate of Analyses, but there is no specification on paraffin either. It is generally held that the product should be <2% olefin to make sure that other analyses are passed. Figure 10.6 shows that the initial olefin content was about 7%. This could have been due to an upset in the oligomerization system the week before the NARA project that might have sent sulfur through the system, reducing the capacity of the hydrogenation reactor. Operations supervisor at SHR raised the temperature of the feed to hydrogenation and that increased the reaction, bringing the product back down to a <2% value. A composite sample of the final product tank showed <2% (Table 10.1)

When the NARA isobutanol was exhausted, there was still a considerable amount of C8 olefin in the recycle tank. It was decided to just run this through the system. Laboratory experiments with pure C8 olefin at Gevo indicated that product was nearly all C16 at a low temperature of approximately 140 °F and a mixture of C12 and C16 at the normal operating temperature. There seemed to be no reaction. Nothing but C8 left the reactor. Figure 10.7 shows that C12 and C16 concentrations in the effluent of the oligomerization reactor dropped considerably.

The run was finished by running with Gevo isobutanol to flush out all o the NARA isobutanol. Approximately 1,060 gal jet fuel were produced. Due to starting and stopping of NARA feed into a continuous process that already contained Gevo product (which Gevo needed to retain), it is estimated that between 25% and 30% of the final jet fuel is from Gevo isobutanol.

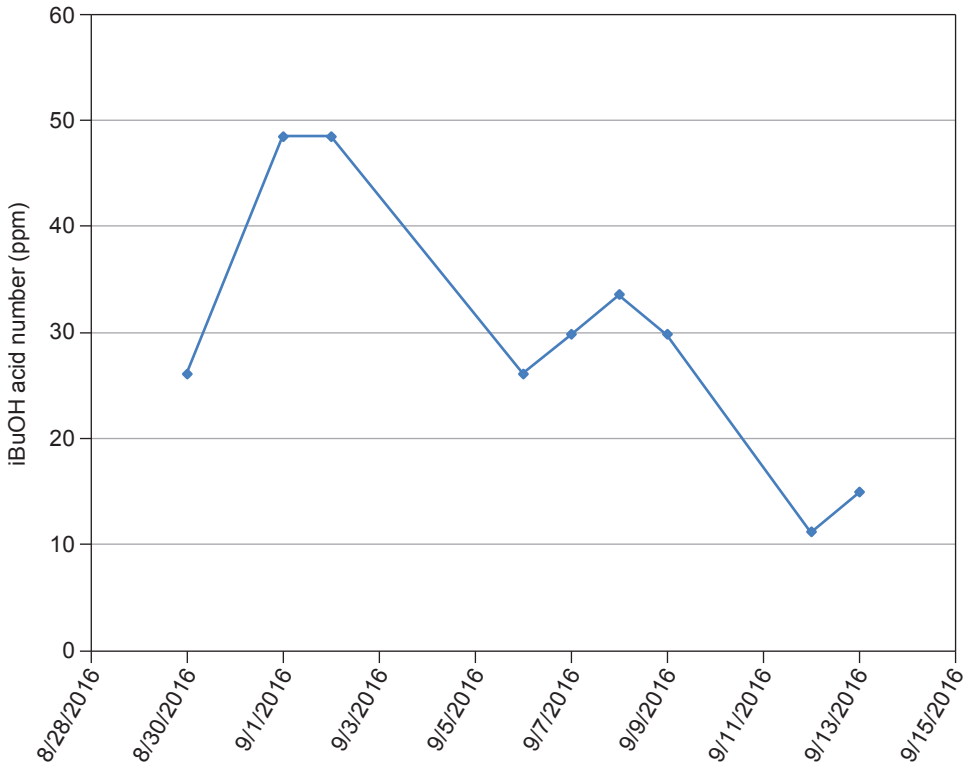

Figure 10.4—Acid concentration in isobutanol after distillation.

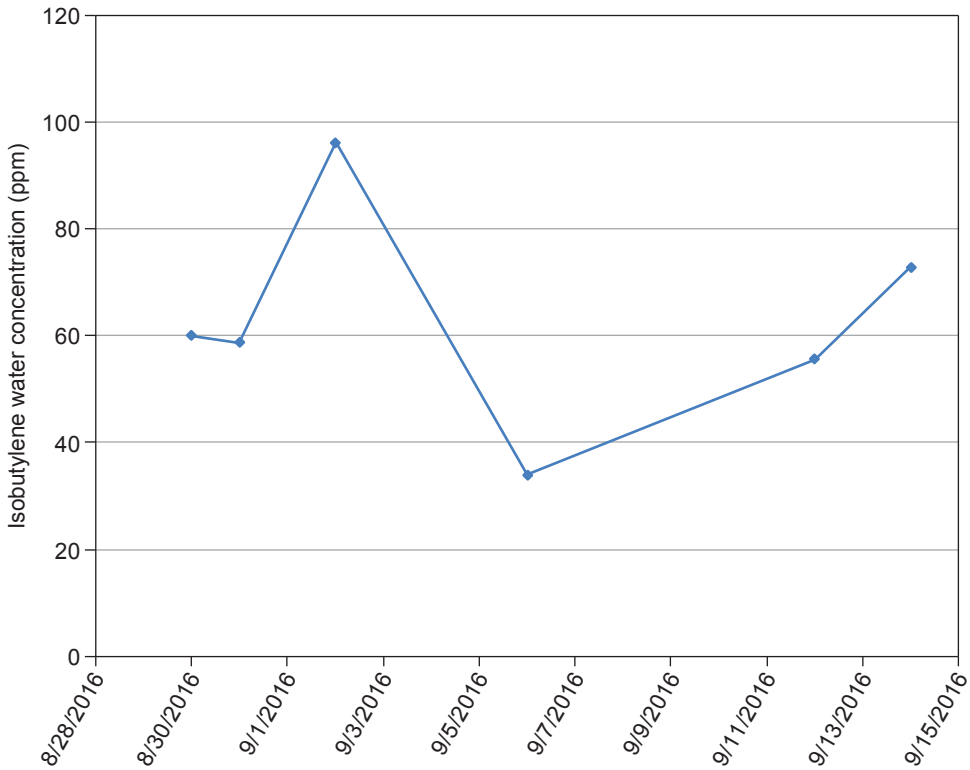

Figure 10.5—Water content of isobutylene feed to oligomerization reactor.

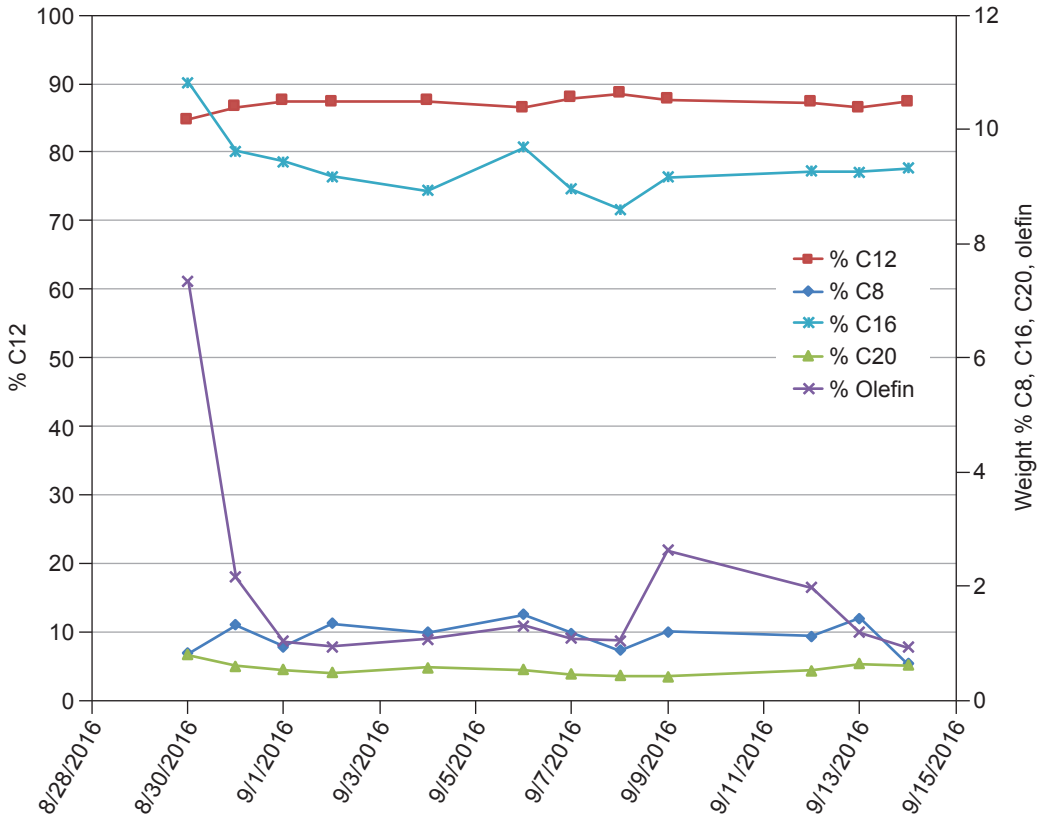

Figure 10.6—Composition of biojet product while being produced.

Table 10.1—Final biojet composite analysis

Component	Mass (%)
C_4	0
C_5–C_7	0.01
C_8	1.25
C_9–C_{11}	0.41
C_{12}	87.05
C_{13}–C_{15}	1.15
C_{16}	9.28
C_{17}–C_{19}	0.25
C_{20}	0.55
C_{24}	0.05
Olefin	1.93

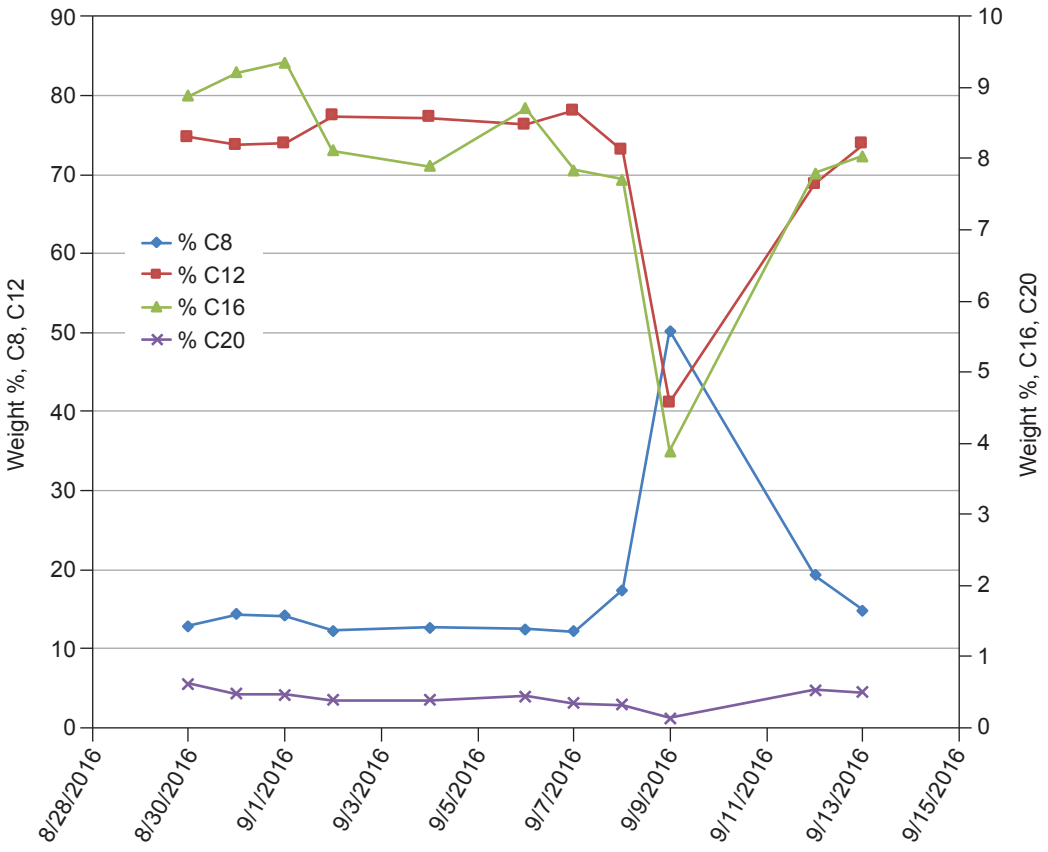

Figure 10.7—Bottoms of oligomerization column.

A final product sample was sent to Inspectorate in Beaumont, Texas, USA, for an independent Certificate of Analysis confirming that the jet fuel produced conforms to the specifications of ASTM D7566 Annex 5 (Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons). The final fuel passed all tests and a Certificate of Analysis was issued (App. G).

10.4 Final Accounting

The jet fuel was loaded into three totes for transportation to Seattle to be used in a commercial flight by Alaskan Airlines. The actual commercial flight, flight number AS04 from Seattle (SEA) to Washington, DC (DCA), took place on November 14, 2016.

Table 10.2 summarizes the total weight and volume of the jet fuel produced. The fuel was visually exceptionally clear, as shown in Figure 10.8.

Table 10.2—Final biojet production weight and volume

Tote serial number	Net weight of fuel (lb)	Volume[a] (gal)
244582	1,380	218.5
244601	2,540	402.2
244614	2,740	433.9
Total	6,660	1,054.6

[a]Specific gravity = 0.7581.

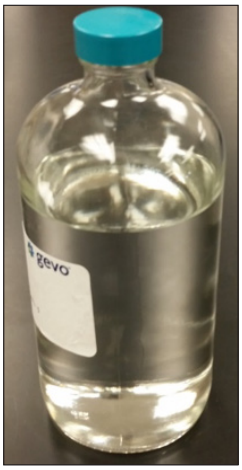

Figure 10.8—Sample of final biojet.

11. Conclusions

11.1 NARA Outputs

As a result of this work, a little more than 1,000 gal of biojet fuel was produced utilizing softwood forest residue that was processed using the SPORL process and GEVO microorganism by NARA, with additional feedstocks provided by an industrial partner.

A presentation of results was given at the 38th Symposium on Biotechnology for Fuels and Chemicals, held in Baltimore, Maryland, USA, April 25–28, 2016.

11.2 NARA Outcomes

This project constituted the first ever production and use of commercial jet fuel from softwood wood wastes from the U.S. Pacific Northwest.

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Appendix A—Daily Historical Summary of the ZeaChem Run

Wednesday 8/19/2015 1:00 AM – 10:00 AM

- Ran consistently until needed to filter then shutdown due to problems in filtration system.
- *T* = 175 °C, *P* = 119–120 psig (about 4 psi over saturated steam pressure); expected ~15 psi over sat steam or 130 psi.
- Feedrate ~7–7.8 BDT/day.
- Feed moisture ~28%.
- Feed moisture after pre-steaming bin ~27–28%.
- Material pre-refiner still "felt" hard, not mushy, material after refining looks fairly fine.
- Lighter in color than 35 or 45 min runs at Andritz.
- Produced ~3,500 lb pressed pulp (~40% solids).
- Conducted enzymatic hydrolysis resulting in about 40% yield to glucose.
- L:W ratio in chemical feed zone was extremely low (<2) due to under estimation of feed moisture out of steamer bin (estimated 50% moisture in chips was actually 27%).
- SO2 measured in vent condensate (after neutralization with NaOH) is about what we expected to make in the reactor.
- Measured SO2/HSO3 in blow tank and found none.
- Plan at restart
  - Increase acid to increase delta P closer to 15 psi.
  - Follow with increase of temperature to 180 °C and finally 185 °C.
  - Increase liquid to initial feed chemical zone (lower conc H2SO4 and Mg(HSO3)2 feeds), target L:W in feed "zone" at 3 (before steam addition).
  - Resulting also in increased overall L:W to ~5.

Thursday 8/20/2015 10:00 PM – 12:30 PM

- Looked like it was coming up, delta P was increasing to about 10 psi.
- Then discovered discharge blow-line was plugged — Shutdown.
- Observations
  - If desired partial pressure of SO2 is about 15 psi in system that is 145 psi, then concentration of SO2 is ~10%.
  - If we "sweep" ~1500 lb/h of steam through reactor without condensation, then we are removing 150 lb/h of SO2.
  - We only generate about 18 lb/h!

Friday 8/21/2015 5:00 AM – 10:00 AM

- Tom discovered that steam is superheated going into steam bin (corrected, but still some level of superheat).
- Discovered way to perhaps by by-pass steam from main digester body and feed just to discharger chamber.
- Work has been underway since about 10:30, not accomplished yet (problems with block valves).
- Tried to open the steam by-pass to the discharger chute, but found it was plugged — shutdown to clear.
- Current plan
  - Took sample and are starting a hydrolysis test.
  - Resolve steam by-pass issues — Done.
  - Add acid to increase delta P — Done.
  - Investigate adding water to feedstock — Done.
  - Investigate addition of bisulfite to feedstock — Decided not to do.
  - Increase *T* to 185 °C — Done.

Friday 8/21/2015 10:00 PM — Still Running

- Have been running pretty much smoothly since 10:00 PM last night.
- Minor shutdown (~1/2 h) when water addition to feed drag chain caused plug. Remedy was to better regulate water to flow only when biomass is flowing. This is a manual system, so we'll see if they can keep-up with it.
- Minor upset (~1 h, about 8:00 AM) when acid tank went empty.
- Took filter press sample at 6:00 AM — Enzymatic hydrolysis results at 6 h are 7.67 vs Andritz 35 min Run: 6.31, Andritz 45 min Run: 8.71 (don't worry about units they are relative).
- Feedstock moisture after steaming bin @ 1:00 PM was 44.6% (could still be higher).

- Temperature is 185 °C, pressure is about 158 psig or about 10 psi over pressure due to SO2, still lower than expected.
- Steam flow certainly appears to be 2/3 to 3/4 by-passing digester straight to discharger chute and blow line. There have been no issues with blow-line (so the amount of steam to that location must be sufficient). Also we are maintaining temperature in digester, so maybe enough steam is going there. Digester steam valve is nearly closed.
- Blow-tank pH is about 2.4 to 2.8.
- Current plan
  - Investigate increasing water to feedstock — Look at getting 50–55% moisture in discharge of steamer bin — Decided not to do this as amps on drag line are up and don't want to trip out, also pump is maxed, also L:W was increased due to increase in Mg(HSO3)2, see below.
  - Review current acid and bisulfite concentrations and decide whether to increase, increased Mg(HSO3)2 by about 15%.
  - Review inventory of Mg(HSO3)2 Inventory and use rate to determine probable shutdown Date/Time (we expect to run out before we get the new shipment) — will do a more detailed accounting today.
  - Continue enzyme hydrolysis runs of each filter dump — continuing, results about the same.
  - Investigate getting data for temperature in chemical mixing area of Inclined Screw (there is a probe and transmitter, just need range to interpret data in DCS) — Got data, temperature is holding steady at about 248 °F (reasonable temperature for mixing chemicals).
  - Investigate steam control valves to determine if we can deduce flow to each — Not done.

Sunday 8/23/2015 10:00 AM — Continues running smoothly since 10:00 PM Friday 8/21 (36 h)

- No known issues in last 24 h.
- Rates are steady as are *T & P*.
- Current plan
  - Inventory feedstock fed — 20 BDT as of 12 NOON Sunday.
  - Inventory filter cake produced —13 BDT as of 6 AM Monday.
  - Identify if moisture has been run on each filter press drop and get done if not already — Remains about 44%.
  - Determine general solids material balance — TBD.
  - Photograph each filter press material since start-up for visual comparison — TBD.
  - Continue hydrolysis testing for each filter pressing — Material is improving and is about equivalent with best 45 min run at Andritz.
  - Continue conditions as they are now.
  - Inventory Mg(HSO3)2 — Should last until Thursday, new shipment is due on Thursday.

Monday 8/25/2015 9:00 AM

- Running smoothly since 10:00 PM Friday 8/21 until about 6:00 PM last night (with a short shutdown for rock plugged blow line), restart 6:00 AM today.
- Small pebbles plugged the blow line on Saturday night. They had to shut-down and clear them out, which took a few hours after which they returned to normal operation.
- Ran smoothly until about 7 PM Sunday when they had to shutdown till 2:00 AM Monday to refill the Mg(HSO3)2 tank.
- That was followed by an issue with the refiner and the boiler. They lost the back pressure regulator on the boiler and have to manually regulate the pressure. Refiner is down and probably needs a rebuild so it won't be available for us on the remainder of the run.
- Restarted about 6:00 AM and seems to be running fine. We will see the first filter dump about 10–11:00 without the refiner.
- We also discovered that the unit was only feeding 6 BDT/day rather than 7, so the decision was made to increase the rate of biomass and ratio up the chemicals as well. This morning it doesn't appear that they have changed the feed rate.
- Enzymatic hydrolysis results have improved and are on par with the 45 min Andritz–Springfield results with a yield of glucose of about 75%.
- Have produced about 13 BDT of product.

- Current plan
  - Understand if feed rate change is going to be made — Yes it was.
  - Try to assess impact of no refiner — Appearance of the material was only slightly different. Rather than being all small particles about 1/16 x 1/16 x 1/16 in. in size, there are a few strings mixed in, still about 1/16 x 1/16 in. but maybe up to 3/8–1/2 in. in length. I did not see any large pieces. Sorry I didn't think to take a photo before I left.
  - Ship 2 pails of solids to Gevo — These have been received by Gevo.
  - Determine general solids material balance — This is very difficult from the "batch" feed weights into the feed bin and "batch" discharge of filter presses. Look like it is in the 50-55% range. I will try to work with Brian to do a material balance on one blow tanks fill. For that they will keep close track of the feed in and the cake out. He has done this on other runs and claims it gives him a good balance.

Wednesday 8/26/2015 11:00 AM

- Shutdown last night to repair boiler back-pressure regulator valve and discharger motor. They expect to restart by noon.
- Restarted about 6:00 AM Tuesday. Seems to have run fine without the refiner.
- Sent a sample to WSU about 1:00 PM for enzyme hydrolysis test. Initial (very preliminary results as this is a new lab and analytical) indicated the yield might be a little lower than it was, but this is early to make that conclusion.
- Back-pressure valve on boiler was replaced over night as was the discharger sweeper motor which was failing.
- 44 super sacks from NR03 have been loaded on the trailer to be transported to cold storage.
- Current plan
  - Plan is to continue to run through Friday, which should complete the initial 40 tons feedstock — Boiler issues caused down time thru the week.
  - Shutdown for the weekend and restart on Monday to run remaining 20 tons — Plan is to shut down for the weekend.
  - See if we can do a "material balance" around a single blow tanks fill. This is standard for ZeaChem and should give us a better understanding of yield. — Brian was about to do this and we started experiencing various issues with continuous operation.

Friday 8/28/2015 10:00 AM

- System experienced issues with the boiler through Wednesday and Thursday. Thursday 2:00 PM boiler was operating well and system was brought back-up and ran into the night until there were issues with the progressive cavity pump feeding the filter. That was repaired and system restarted this morning.
- We've received product solids analysis from WSU–Tricities.
- Current plan
  - Plan is to shut down tonight for the weekend and restart on Monday morning — Shutdown on Friday, restart delayed on Monday.
  - Will clean out the blow tank to make sure there is no debris that might foul the pump again — Done.
  - Fourth load of wood will be delivered from Lane on Tuesday — Was Delivered Monday.
  - They had scheduled a boiler manuf rep to come out on Tuesday, but the boiler is running so well they cancelled that.
  - Still want to do a "material balance" around a single blow tanks fill. This is standard for ZeaChem and should give us a better understanding of yield. Need to have the system running smoothly to perform this.
  - Review mass in/out of system and compositional data now on hand to get a better "feel" for probable yield — Done.

Monday 8/31/2015 6:00 PM

- System was shut down as scheduled last Friday night. Start-up was delayed on Monday waiting to replace the connector between the reactor and the blow-line. That was completed about 5:30 PM and the system is starting up.
- About 18 BDT of feedstock was received from Lane Products. This load consisted of about 8 BDT of material as we have received to date and some larger material. Pete feels this larger material would work without issue. I am trying to have them keep the material separate and only use the larger material if we need to.

- 29.5 BDT have been fed and 18.1 BDT of product has been bagged through the shutdown last Friday night (NR01: 2.6BDT, NR03: 10.1, NR04: 5.4).
- 88 supersacks have been delivered to the cold storage.
- Current plan
  - Six samples of solids are being sent to FPL for tests similar to what they were doing on-site at Boardman the first week of the run — Shipped today for delivery at FPL tomorrow morning.
  - Still want to do a "material balance" around a single blow tanks fill. This is standard for ZeaChem and should give us a better understanding of yield. Need to have the system running smoothly to perform this.
  - Concern continues regarding the rocks and stones that were cleaned out of the blow-tank pump, these can possibly destroy the pump. Replacement of the pump is a long delivery time (might not impact us, but would possibly impact their continued operation).
  - What to do about the refiner is still being discussed. There may not be room to get at it with the current operations on the pad (wood-chip pile and bags). Will continue to engage them in a discussion to determine the fate of the unit for this run.

Tuesday 9/1/2015 8:00 PM — System puffed along all day without issue.

- ~34 BDT have been fed and ~22 BDT of product has been bagged.
- Mg(HSO3)2 tank was nearing empty at the end of the day (the end of the initial 12 totes).
- There will probably be some length of shutdown as the Mg(HSO3)2 tank is recharged.
- Current plan
  - Sample of NR04 FP9 was sent to Weyerhaeuser (Johnway Gao), more will be sent as the week goes on.
  - Samples of each filter pressing will be sent to FPL as the week goes on.
  - Still want to do a "material balance" around a single blow tanks fill. This is standard for ZeaChem and should give us a better understanding of yield. Need to have the system running smoothly to perform this — Test was completed today, result to be available TBD.
  - No resolution on the refiner.

Wednesday 9/2/2015 5:00 PM — System puffed along all day without issue.

- ~39.5 BDT of chips have been fed.
- Mg(HSO3)2 tank was successfully replenished last night by feeding 2-Mg(HSO3)2 totes plus water measured in empty totes. This went faster and the concentration was right on. Before they had been adding water based on tank level, which is not very accurate. They will need to repeat this tonite and tomorrow nite and then mix the remainder on Friday and let it mix over the weekend.
- The 8 h material balance run was made today. We should see the data from this tomorrow.
- A new storage location was found for the remainder of the sacks. It is not refrigerated, but the hottest of temperatures might be over here. It will keep the bags out of the sun, wind and rain.
- Current plan
  - One sample bag of each filter press in the last 24 hours was sent to FPL and to Weyerhaeuser. This sampling will continue until I leave on Saturday.
  - They seem to be running just a little over 5 BDT/day. Therefore another 4–5 days of operation are needed to complete the 62 BDT. With 2 days left this week, and restarting on Tuesday after Labor Day, I project they will finish next Wednesday or Thursday.
  - Repair of the refiner seems to be a moot point now.
  - Plan is to fill 6, 5-gallon Jerri cans with liquid hydrolyzate, 5 for freezing and 1 for shipping as is. Four cans will be taken back to WSU next week and the others will be sent from here. — Cans have been filled and 5 are in the freezer.
  - Additional pails of solids will be sent to Gevo on Friday. — Material has been packaged and will be shipped on Friday.

Thursday 9/3/2015 5:00 PM — System puffed along all day without issue.

- ~45 BDT of chips have been fed, completion of 63 BDT might be late Wednesday 9/9/2015, another day if we run extra or have issues.
- Mg(HSO3)2 tank was replenished last night by feeding 2-Mg(HSO3)2 totes plus water measured in empty totes. Concentration was high ~ 8.1% rather than 7.5%.
- The 8 h material balance run was made yesterday. We should see the data from this Monday.

- Mg(HSO3)2 is higher than expected, conference call was held and decision was made to reduce concentration by 15%.
- Current plan
  - Reduce Mg(HSO3)2 concentration from target 7.5% to 6.6% concentration and monitor performance over tomorrow. A sample of filter cake will be sent to JY at 3:00 on Friday for Saturday delivery and analysis over the weekend. Based on those results we will restart on Monday with low concentration (good results) or back at the high concentration (bad results).
  - The supply of Mg(HSO3)2 is running low, so reduction of use is necessary to insure we can run 63 or possibly more BDT.

Friday 9/4/2015 3:00 PM — System puffed along all day without issue until about 2:00. Plan was to shutdown tonight for the weekend anyway.

- ~50 BDT of chips have been fed, completion of 63 BDT might be early Thursday 9/10/2015, another day if we run extra feedstock or have issues.
- Mg(HSO3)2 tank was replenished last night by feeding 2-Mg(HSO3)2 totes plus water measured in empty totes. Concentration was lowered to ~6.3% so as to lower the use of Mg(HSO3)2. We've been running about 1.5x what we originally intended, so a reduction should not interfere with the results.
- *P & T* were unaffected by the reduction of Mg(HSO3)2, indicating that the SO2 concentration was not impacted. The material looked the same as it has been (color and texture).
- Current plan
  - Samples were sent to JY for analysis over the weekend. — Analysis completed.
  - Start-up is not scheduled until Tuesday (taking the holiday weekend off). Based on the results of JY's analysis we'll either keep the Mg(HSO3)2 in the lowered condition or raise it back to where it was. — Analysis was the same as previous samples.

Tuesday 9/8/2015 7:00 PM — System is down for repairs.

- Repairs are still in progress for the blow tank agitator bearings and seal issues. The discharger was also being repaired. We should know more tomorrow about when we'll start-up.
- Samples from NR05 with a 15% reduction in Mg(HSO3)2 were sent to JY and an enzymatic hydrolysis test performed. The results were the same as for all of the recent samples from ZeaChem. A decision was made to continue at the reduced Mg(HSO3)2 level.
- Contract was signed with Cascade warehouse who is just down the street from ZeaChem. They have lots of space (not refrigerated) so we'll start sending our super sacks there probably tomorrow.
- Current plan
  - Start-up when repairs are completed.

Wednesday 9/9/2015 7:00 PM — System is down for repairs.

- Repairs are still in progress for the blow tank agitator bearings and seal issues. Turns out they need to get a new shaft for the blow tank agitator, so that might not arrive till Monday. So start-up will be sometime after that.
- Super sacks are being taken to the warehouse, 3 or 4 loads today and the rest tomorrow.
- Current plan
  - Start-up when repairs are completed. — Repairs completed Tuesday 9/15.
  - I won't plan to update you all, until I know more definitely the start-up date, so probably next Monday.
  - This delay does not impact our schedule as we are not planning on starting at ICM until November 1.

Tuesday 9/15/2015 5:00 PM — System is being restarted.

- Repairs to blow tank agitator bearings and seal have been completed.
- Remaining 4 totes of Mg(HSO3)2 have been diluted with water in the feed tank.
- System is being restarted tonight.
- All super sacks on site have been taken to the Cascade warehouse down the road.
- Current plan
  - Continue to run until Mg(HSO3)2 supply is exhausted.
  - We will inventory where we are tomorrow to make sure we want to run all of Mg(HSO3)2 or not.

Wednesday 9/16/2015 11:00 PM — System is being restarted, again.

- They restarted last night and ran for about 2 h before finding that the Mg(HSO3)2 pump was not working. Took quite some time to figure out why the pump was not pumping. A check valve in the pump had cracked, not completely failed so it was leaking back and not going forward.
- They had the parts so they were able to fix the pump.
- Restarting this evening.
- Current plan
  - Continue to run until Mg(HSO3)2 supply is exhausted.

Friday 9/18/2015 5:00 PM — System ran into the night of Thursday, 8/17, when they experienced a valve positioner failure. Without mechanical help to fix, they shutdown. Plan was to shut down for the weekend anyway.

- The finer feedstock (Accepts) has been completely fed to the system. By the incoming truck weights, that is about 60 BDT.
- They started into the Overs pile. They will restart on Monday and Pete estimates that they will run out of Mg(HSO3)2 solution late Monday or early Tuesday.
- Current estimate is that the total feed will be about 68 BDT when complete.
- ZeaChem will be having visitors on the site on Monday and Tuesday so they need to hold off on any videotaping until Wednesday. Pete assured me that they will be running on Wednesday, so we'll be able to tape material being loaded into the sacks (just not ours, but it all looks the same).
- Current plan
  - Continue to run until Mg(HSO3)2 supply is exhausted. As of Monday night there is about 24 h of material left.
  - We'll inventory the warehouse when completed and get an exact accounting of the sacks and weights.

Monday 9/21/2015 5:00 PM — When they started up on Monday there was a problem with the discharger, some foreign material in it. They shutdown to clear it. About 2:00 PM PDT when I talked to Brian, they had just gotten going.

- Current plan
  - Continue to run until Mg(HSO3)2 supply is exhausted.
  - We'll inventory the warehouse when completed and get an exact accounting of the sacks and weights.

Thursday 9/24/2015 2:00 PM —The run is completed.

- No data or accounting yet of feed amount and product super sacks.
- Current plan
  - Obtain data, weights and inventory of filter press super sacks.
  - Obtain samples of final filter pressings.
  - On to St. Joseph.

Appendix B—Chemical Analyses Performed at Weyerhaeuser for Magnesium-Bisulfite-Pretreated Douglas-fir Forest Residuals

Table B.1—Polymer sugar composition in magnesium-bisulfite-pretreated forestry residuals (Douglas-fir)

	Composition (%, wt/wt)					
Sample ID	Arabinan	Galactan	Glucan	Xylan	Mannan	Total
NR03 8E 9A	<0.09	0.40	47.3	0.80	1.38	49.93
NR03 FP18C	<0.09	0.30	49.6	1.04	1.69	52.63
NR04 FP10C	<0.09	0.16	53.4	1.04	1.35	56.05
NR04 FP11C	<0.09	0.21	52.1	1.01	1.43	54.75
NR04 FP12C	<0.09	0.25	51.2	1.00	1.49	53.94
NR04 FP13C	<0.09	0.23	53.0	0.96	1.47	55.66
NR04 FP14C	<0.09	0.23	50.1	0.97	1.50	52.85
NR04 FP15C	<0.09	0.25	49.8	1.00	1.53	52.58
NR04 FP16C	<0.09	0.21	50.5	1.00	1.41	53.12
NR04 9D/10A	<0.09	0.17	53.0	1.05	1.43	55.75
NR04 FP17C	<0.09	0.30	48.8	1.07	1.68	51.85
NR04 FP19C	<0.09	0.30	49.3	1.02	1.68	52.30
NR04 FP20C	<0.09	0.24	50.8	0.94	1.45	53.43
NR04 FP21C	<0.09	0.22	50.6	0.89	1.38	53.09
NR04 FP22C	<0.09	0.23	51.0	0.96	1.44	53.63
NR04 FP23C	<0.09	0.24	50.6	0.94	1.48	53.26
NR04 FP24C	<0.09	0.22	50.2	0.94	1.38	52.82
NR04 FP25C	<0.09	0.19	49.6	0.96	1.29	52.04
NR05 FP-1C	<0.09	0.18	49.2	0.90	1.22	51.50
NR05 FP-2C	<0.09	0.21	47.1	0.84	1.19	49.34
NR05 FP-3D	<0.09	0.19	46.3	0.73	1.24	48.52
NR05 FP-04	<0.09	0.24	47.8	0.75	1.14	49.93
NR05 FP-05	<0.09	0.26	47.0	0.75	1.23	49.24
NR05 FP-7	<0.09	0.25	42.2	0.70	1.18	44.35
NR05 FP-8	<0.09	0.30	44.5	0.80	1.40	47.01
NR05 FP-9	<0.09	0.27	45.8	0.70	1.23	48.03
NR05 FP-10	<0.09	0.30	46.9	0.75	1.32	49.29
NR06 FP-1	<0.09	0.29	47.2	0.70	1.25	49.49
NR06 FP-2	<0.09	0.29	46.3	0.69	1.22	48.46
NR06 FP-3	<0.09	0.32	48.1	0.77	1.30	50.54
NR06 FP-4	<0.09	0.50	45.8	1.03	1.85	49.18
NR06 FP-5	<0.09	0.26	49.9	0.79	1.21	52.16
NR06 FP-6	<0.09	0.23	48.2	0.77	1.17	50.37
NR06 FP-7	<0.09	0.24	48.6	0.76	1.18	50.78
NR06 FP-8	<0.09	0.29	48.8	0.70	1.20	50.99
NR06 FP-9	<0.09	0.25	46.8	0.69	1.12	48.86
NR06 FP-10	<0.09	0.26	46.8	0.66	1.12	48.84
NR06 FP-11	<0.09	0.26	49.0	0.65	1.11	51.02
NR06 FP-12	<0.09	0.25	47.8	0.60	1.06	49.71

Table B.2—Lignin and acid-soluble lignin in magnesium-bisulfite-pretreated forestry residuals (Douglas-fir)

	Composition (%, wt/wt)		
Sample ID	Lignin	Acid-soluble lignin	Total lignin
NR03 8E 9A	32.0	0.28	32.3
NR04 FP 11C	27.6	0.38	28.0
NR04 FP 14C	28.2	0.35	28.6
NR04 9D/10A	27.5	0.35	27.9
NR04 FP-24C	29.7	0.30	30.0
NR05 FP-3D	32.0	0.26	32.2
NR05 FP-9	34.8	0.31	35.1
NR06 FP-1	33.7	0.31	34.0
NR06 FP-3	33.6	0.26	33.9
NR06 FP-7	32.8	0.26	33.1
NR06 FP-11	34.4	0.24	34.6

Table B.3—Extractives in magnesium-bisulfite-pretreated forestry residuals (Douglas-fir)

Sample ID	Extractives (%, wt/wt)
NR03 8E 9A	12.5
NR04 FP 11C	9.4
NR04 FP 14C	10.0
NR04 9D/10A	8.5
NR04 FP-24C	9.9
NR05 FP-3D	10.0
NR05 FP-9	10.6
NR06 FP-1	11.4
NR06 FP-3	11.4
NR06 FP-7	NA
NR06 FP-11	10.5

Table B.4—Ash in magnesium-bisulfite-pretreated forestry residuals (Douglas-fir)

Sample ID	Ash (%, wt/wt)
NR03 8E 9A	2.43
NR04 FP 11C	2.89
NR04 FP 14C	2.97
NR04 9D/10A	2.54
NR04 FP-24C	2.60
NR05 FP-3D	2.28
NR05 FP-9	2.23
NR06 FP-1	2.17
NR06 FP-3	2.13
NR06 FP-7	1.81
NR06 FP-11	2.02

Table B.5—Sulfur content in magnesium-bisulfite-pretreated forestry residuals (Douglas-fir)

Sample ID	Sulfur (%, wt/wt)
NR03 8E 9A	1.45
NR04 FP 11C	1.76
NR04 FP 14C	1.98
NR04 9D/10A	1.73
NR04 FP-24C	1.57
NR05 FP-3D	1.35
NR05 FP-9	1.38
NR06 FP-1	1.40
NR06 FP-3	1.37
NR06 FP-7	1.25
NR06 FP-11	1.28

Table B.6—Total composition balance of magnesium-bisulfite-pretreated forestry residuals (Douglas-fir)

	Composition (%, wt/wt)					
Sample ID	Total lignin	Extractives	Ash	Sulfur	Polymer sugar	Total
NR03 8E 9A	32.3	12.5	2.43	1.45	49.93	98.6
NR04 FP 11C	28.0	9.4	2.89	1.76	54.75	96.8
NR04 FP 14C	28.6	10.0	2.97	1.98	52.85	96.3
NR04 9D/10A	27.9	8.5	2.54	1.73	55.75	96.4
NR04 FP-24C	30.0	9.9	2.60	1.57	52.82	96.9
NR05 FP-3D	32.2	10.0	2.28	1.35	48.52	94.4
NR05 FP-9	35.1	10.6	2.23	1.38	48.03	97.3
NR06 FP-1	34.0	11.4	2.17	1.40	49.49	98.5
NR06 FP-3	33.9	11.4	2.13	1.37	50.54	99.3
NR06 FP-11	34.6	10.5	2.02	1.28	51.02	99.5

Table B.7—Metal content in magnesium bisulfite pretreated forestry residuals (Douglas-fir)

	Metal content (mg/kg, ovendried basis) by sample ID										
Metal	NR03 8E 9A	NR04 FP11C	NR04 FP14C	NR04 9D/10A	NR04 FP-24C	NR05 FP-3D	NR05 FP-9	NR05 FP-1	NR06 FP-3	NR06 FP-7	NR06 FP-11
Ag	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Al	225	320	270	280	250	240	250	180	190	150	170
As	0.1	0.1	0.2	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
B	2	3	3	2	2	2	2	2	2	2	2
Ba	29.95	30.1	30.8	30.5	28.5	28.5	30.6	27.7	28.2	24.1	24.2
Be	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bi	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Ca	695	970	920	860	810	780	820	720	520	640	590
Cd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Co	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.2	0.2	0.2	0.2
Cr	29.15	7.9	8.2	8.9	6.1	9.6	19.4	14.5	15.4	24.2	33
Cu	3.65	4.1	4	4.4	3.3	3.9	4.8	4.4	4.5	3.9	5.1
Fe	230	200	190	180	140	170	170	140	150	130	170
K	195	170	190	160	160	150	180	170	170	160	150
Li	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mg	4,810	5,830	6,680	5,620	5,540	4,620	4,670	4,650	4,860	4,480	4,420
Mn	20.7	19	20.7	17.8	16.7	15.6	18.5	17	17.1	14.5	14.6
Mo	4.15	3.1	3.6	3.7	2.9	2.8	7.2	4.9	5.2	3.6	6.2
Na	50	40	40	40	40	30	40	40	40	40	40
Ni	8.35	20.5	15.6	14.2	13.2	15.4	15.3	11.7	11.3	9.8	23.4
P	30	30	30	20	20	20	20	20	20	20	20
Pb	0.3	21.6	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1
Sb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Se	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sn	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Sr	4.8	6.1	6	5.7	5.2	5.2	5.6	5.1	4	4.6	4.8
Tl	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
V	0.4	1.5	1.6	1.4	1.6	1.3	0.8	0.7	0.5	0.4	0.2
Zn	3	3	4	3	2	2	3	2	2	2	2
Total	6,341.8	7,680.3	8,418.2	7,252.1	7,041.9	6,096.7	6,257.6	6,010.4	6,040.6	5,709.4	5,675.8

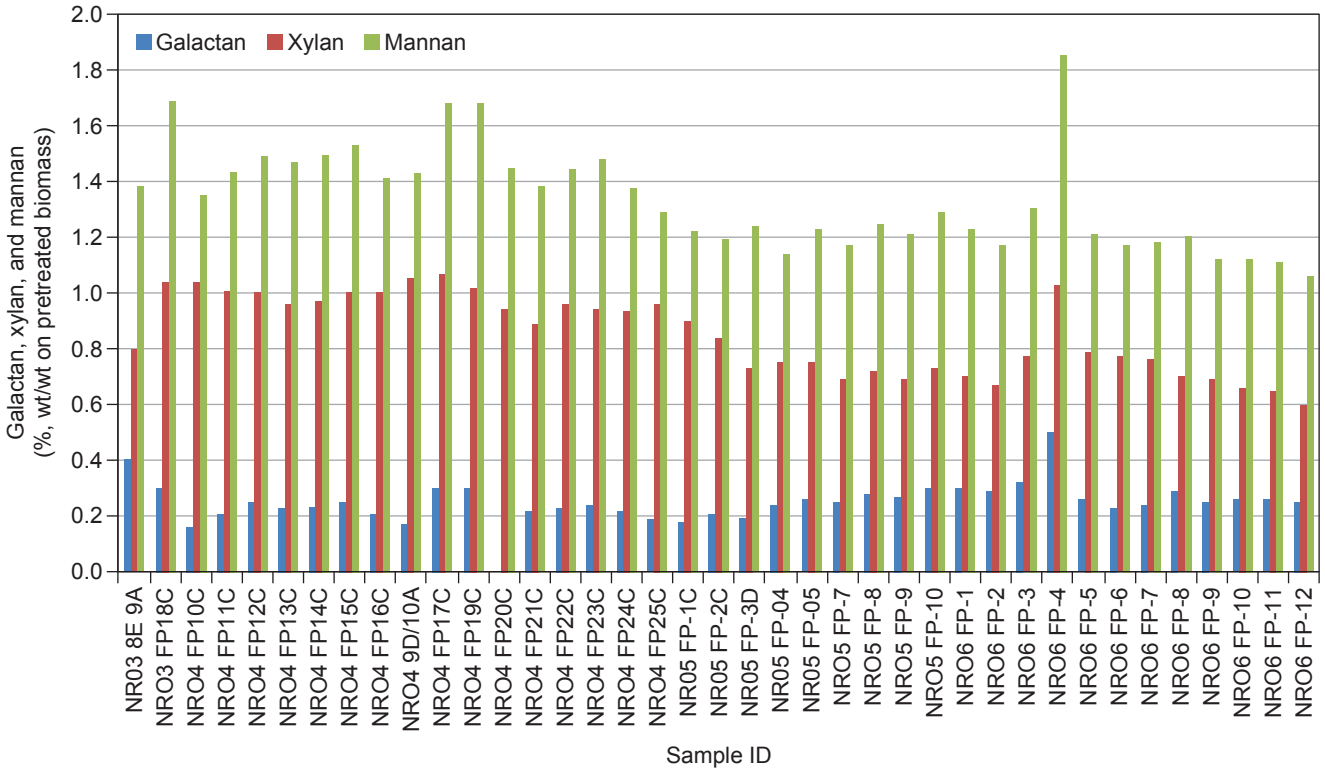


Figure B.1—Galactan, mannan, and xylan in pretreated forestry residuals (Douglas-fir).

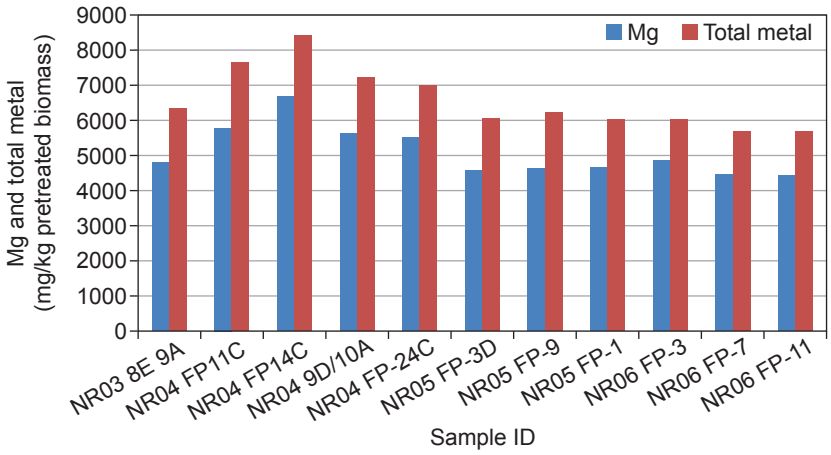


Figure B.2—Magnesium and total metal (mg/kg) in magnesium bisulfite pretreated forestry residuals (Douglas-fir).

Appendix C—Stream Ladder

In an effort to determine how much wood would be required to produce 1,000 gal of biojet fuel, given the various processing steps and inherent inefficiencies in the multiple site tolling operation, a material balance was developed. A complete stream ladder with a breakdown of compositional flows was developed based on a known feed composition and anticipated yields. Yields for the SPORL pretreatment were derived from Zhu et al. (2015).

The detailed stream ladder was documented in multiple spreadsheets (150319 ICM Mat Balance.xls).

Table C.1—Material balance and yield calculations to determine how much wood would be required to produce 1,000 gallons of biojet fuel

Process step	Proposed yields	Yield by step (%)
Feedstock		90
Starting feedstock	74 BDT	
Feedstock to Rxt	66.60 BDT	
Poly carb out of Rxt		4.3
Glucan	21.97 BDT	
Mannan	0.48 BDT	
Xylan	0.31 BDT	
Poly carb ship to ICM		95
Glucan	20.87 BDT	
Mannan	0.46 BDT	
Xylan	0.29 BDT	
After saccharification		77.2
Glucose	18.55 BDT	
Mannose	—	
Xylose	—	
Feed to fermentation		90
Glucose	16.69 BDT	
Arabinose	—	
Xylose	—	
iBuOH produced	5.63 BDT	82
iBuOH produced	1,700.9 gal	
iBuOH/feed ratio	22.99 gal/BDT	
iBuOH shipped to SHR	5.07 BDT	90
iBuOH after distillation	4.82 BDT	95
Jet produced and recovered	3.17 BDT	86
Jet produced and recovered	1,005.4 gal	
Product/feed ratio	13.6 gal/BDT	
Overall yield	21%	

Appendix D—Daily Historical Summary of the ICM First Campaign—0290

Monday 11/16/2015 6:35 PM

- ICM spent most of the morning doing some final preps on the solids feeding system. Turns out that the only way to practically feed the solids is to dump the bags on the floor and scoop up with a Bobcat into a feed hopper. This operation is working well and we're trying to collect the printed sheets that we had on each sack as a form of inventory control.
- The solids are then augered into a small tank and mixed with hot water and pumped out. They have a capability to flow control the water and the solids are volumetrically metered in together.
- Pumping of the 14+% solids seems to be going well now, we'll see if they can keep it up overnight.

Tuesday 11/17/2015 7:57 PM

- Continued dumping supersacks, slurrying them up and pumping to hydrolysis tank and adjusting pH. Hydrolysis tank is now over 50% full.
- Charles and Kevin from WSU visited and completed the videotaping with great cooperation from ICM folks.
- We decided late in the day to transfer about 2,000 gal of slurry to a smaller tank, adjust final pH, T and add full enzyme. This 2,000 gal will on be complete on Friday and give us a good read on the rate and yield of saccharification and allow us to start the filter press to see how it will work. This will save time at the end of the full hydrolysis tank completion, we'll know what filtering option we're going to use.
- Also started adding enzyme to the large tank as it fills to get a jump start on that saccharification.
- Additional heat exchanger plates arrived and a team will show up tomorrow to install, greatly increasing the GIFT reboiler capacity. We plan to do a test of the GIFT system with isobutanol and water on Friday.
- Last of the sacks from Oregon arrive this morning.

Wednesday 11/18/2015 9:43 PM

- A small 2,000 gal tank was initiated with enzyme at about 1:00 AM this morning. Sugar concentration when sampled this morning was about 30 g/L, on track with lab runs at this time.
- Tomorrow this tank will be used to test filtration when completed late tomorrow.
- The expansion HX plates for the GIFT reboiler were received yesterday and installed today.
- GIFT is being pressure tested. We expect to add the isobutanol tomorrow or Friday to test the capacity.
- The first large saccharification tank was filled today and is currently being pH adjusted and will have enzyme added tonight.
- The second large saccharification tank is now filling. The scheme of dumping sacks and scooping into a small slurry tank and pumping over to the saccharification is working, but it is slower than had been expected (by ICM, not by me). There has been some minor plugging, but they have been generally able to continue.
- Schedule is about a day behind, but the first fermentation is expected to be completed before Thanksgiving.
- At 13% solids in the saccharification reactor is lower than anticipated. To make up for this, more ZeaChem material will be co-hydrolyzed with the third saccharification with Cosmo material. This is not expected to increase our cost.

Thursday 11/19/2015 6:53 PM

- A small 2,000 gal tank was initiated with enzyme at about 1:00 AM this morning. Sugar concentration when sampled this morning was about 30 g/L, on track with lab runs at this time.
- Tomorrow this tank will be used to test filtration when completed late tomorrow.
- The expansion HX plates for the GIFT reboiler were received yesterday and installed today.
- GIFT is being pressure tested. We expect to add the isobutanol tomorrow or Friday to test the capacity.
- The first large saccharification tank was filled today and is currently being pH adjusted and will have enzyme added tonight.
- The second large saccharification tank is now filling. The scheme of dumping sacks and scooping into a small slurry tank and pumping over to the saccharification is working, but it is slower than had been expected (by ICM, not by me). There has been some minor plugging, but they have been generally able to continue.
- Schedule is about a day behind, but the first fermentation is expected to be completed before Thanksgiving.

- At 13% solids in the saccharification reactor is lower than anticipated. To make up for this, more ZeaChem material will be co-hydrolyzed with the third saccharification with Cosmo material. This is not expected to increase our cost.

Friday 11/20/2015 8:30 PM

- First 33,000 gal enzyme saccharification batch will be completed tomorrow by morning. This morning after 36 h of saccharification the conversion had reached about 85%. This is very good for that point in the reaction. This batch is all ZeaChem best material.
- Second 33,000 gal tank finished filling last night. It will be *T* and pH adjusted and the enzyme added tonight. This batch is all ZeaChem best material.
- Third saccharification tank will finish accepting the last of the ZeaChem and the Cosmo material. This batch is a combination of the last of the ZeaChem best material, the ZeaChem NR01 material and the Cosmo.
- Feeding the Cosmo solids to the top of the saccharification tank was attempted with one box, but was deemed too dangerous for the operator. An alternative approach of dumping Cosmo solids into an open tote located on the floor next to the large tank, adding a random amount of water and using a diaphragm pump to pump it directly into the large tank. This is working and will be finished tonight.
- GIFT system was tested out re: vacuum pressure and recirculating water. Testing with iBuOH will happen tomorrow.
- The filter press trial was analyzed today and the rate was slow but reasonable. The sugar recovery was close to being not acceptable. The rotary drum filter will be tested in the morning as the first 33,000 gal batch is completed.
- We continue to examine and optimize the schedule with Gevo. We are trying to balance the duration of filtration with the optimum schedule for fermentation and sugar storage.
- When sugar storage is necessary, ICM experience suggests that storing concentrated (150 g/L) cold (40 °F) will be best.

Saturday 11/21/2015 10:02 PM

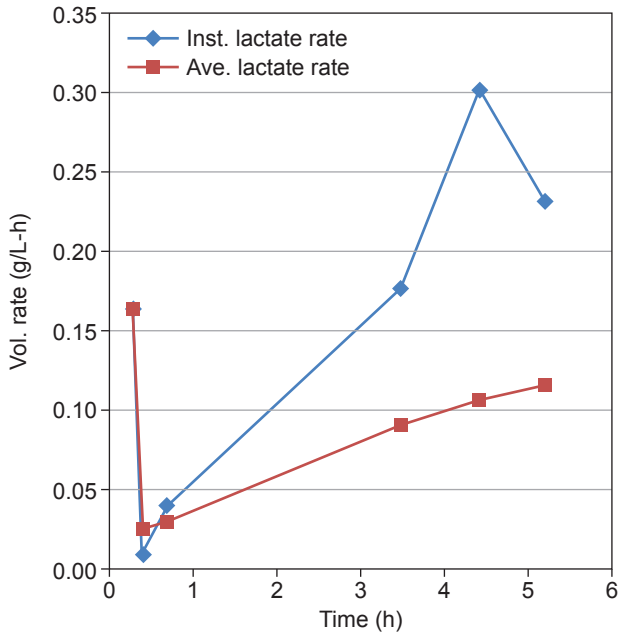
- Started filtering first 33,000 gal enzyme saccharification batch through rotary drum filter. Apparently it is going well, but overnight will tell for sure.
- Evaporation of the filtered material was started late today. Sugars will be stored in clean ethanol fermenters until the aerobic fermenters are emptied after GIFT testing.
- Enzyme was added to the second 33,000 gal tank finished filling last night.
- Third saccharification tank has completed filling and is waiting for pH to stabilize before enzyme is added. It is about 26,000 gal and about 12.5% solids. It contains a mix of ZeaChem good material, NR01 and Cosmo solids. A total of about 15,000 lb of Cosmo wet solids were added.
- No contamination has been detected in any of the saccharification tanks.
- Final flow meter was replaced in GIFT system and it appears ready to go. It was decided to wait until Monday to test GIFT system with iBuOH when Jon Licklider is available.

Sunday 11/22/2015 7:11 PM

- Filtering of first 33,000 gal enzyme saccharification batch through rotary drum filter continues to be slow. We will be meeting with engineers Jon and Jesse and lead operator Kelly tomorrow to improve the filter operation. None of these guys was in today.
- Filtration remains the main issue and is currently delaying the schedule.
- Evaporation of the filtered material seems to be going well. Sugars are being stored cold (40 °F) in clean ethanol fermenters until the aerobic fermenters are emptied after GIFT testing.
- Second 33,000 gal saccharification batch has been underway for a little over 24 h. We will report on yield progress tomorrow.
- Third saccharification batch is about 26,000 gal and is made up of 57% “good” ZeaChem solids (NR03, 04, 05, 06), 16% NR01 ZeaChem material and 27% Cosmo solids. Enzyme was added this afternoon and is reacting. I will report on its progress tomorrow.
- No contamination has been detected in any of the saccharification tanks.
- GIFT system is ready to go. It will be tested with isobutanol from Gevo tomorrow.

Monday 11/23/2015 10:02 PM

- After two days of rotary drum filter with an average rate of 2 gal/min we have gone back to filter pressing. Filter press is averaging 10 gal/min over the last 10 h. Filtering at this rate will enable fermentations to begin back to back starting Monday 11/30/2015.
- The first saccharification batch has some contamination.
- This morning's HPLC analysis from the first enzyme hydrolysis tank showed increasing levels of lactic acid indicating the presence of bacterial contamination in the tank. It is suspected that material returned from the rotary drum filter to the hydrolysis tank (during recoating with DE) contributed to introducing bacteria into the tank. When the lactate level was observed Monday morning, ICM took steps to mitigate the situation by increasing the dosage of virginiamycin and introduced erythromycin and penicillin, increased the temperature from 122 °F to eventually 150 °F, and stopped adjusting pH allowing it to drop naturally.
- Since these steps were taken, the rate of lactate production has slowed. ICM staff will continue to monitor the glucose and lactate in the tank.
- Kent and Andrew from Gevo are both in St. Joseph. Contamination prevention and control is Kent's specialty.
- See graph below.
- The second saccharification batch is essentially complete (it has been going for 67 h; it is not contaminated). It will be held at a higher (pasteurization) temperature and has had antibiotic added all to ward off contamination until it can be filtered and evaporated. It will be continued to be monitored for hints of contamination.
- The third saccharification batch is still going (it has been 34 h since enzyme was added); it was at 45 g/L glucose this afternoon.
- GIFT testing began this morning at 10. We injected about 500 gal of isobutanol into the system. During GIFT startup the vacuum pump became problematic and GIFT was shut down. During start up, the vacuum pump seal water began to leak (it had been working fine as it is used for the evaporator also). The testing was stopped to repair the pump. Repair parts are on order and should arrive about 1200 tomorrow.



Tuesday 11/24/2015 9:31 PM

- The first saccharification batch contamination appears to be under control, the rate of lactic acid formation has dropped to zero.
- Filtration through the filter press is continuing for the first saccharification batch. Average rate is about 6–7 gal/min, including the whole cycle.
- Adding DE as a precoat to the filter press did not help, nor did adding DE to the hydrolyzate before filtering.
- The second saccharification batch has completed reacting. The temperature was raised to pasteurization temperature to ward off contamination as the batch waits to be filtered.
- The third saccharification batch is essentially complete (it has been 58 h since enzyme was added); it was at 62 g/L glucose this afternoon.
- We will test a centrifuge tomorrow. This method could possibly operate at 20–25 gal/min and recover 80% of the sugar. The solids would be re-slurried and returned to an empty reactor to be filtered through the filter press (or possibly Fournier Press) to recover the remainder of the sugar. If the centrifuge proves out to be useful this could be started as soon as Saturday after the first saccharification batch is emptied through the filter press so that it can be used to receive the solids from the second and third batches as they are processed through the centrifuge.
- Parts to repair the vacuum pump in GIFT will not be received until Friday. GIFT testing to be done Sunday afternoon or Monday.
- First fermentation should be able to start Monday or Tuesday, depending on timing and success of GIFT testing.

Thursday 11/26/2015 9:08 AM (Thanksgiving Day)

- Filtering, evaporation and contamination battling continue on through Thanksgiving.
- Adding more DE to the slurry before going to the filter press has improve the filtration rate significantly (the first attempt didn't add enough and so it looked like this scheme wouldn't help, but with more addition it has helped). We are now at a rate of close to 10 gal/min.
- Filtration of the first saccharification batch is just about complete ~4,000 gal to go.
- The sesond saccharification batch has not shown any signs of contamination and is being held hot waiting to be filtered.
- The third saccharification batch was declared complete yesterday morning and the temperature was raised 160 °F to ward off contamination. There still appears to be contamination. Final concentration of sugar was lower than reported yesterday, more like 48 g/L, which is about 70% yield for that batch.
- Concentrated sugars are being held in EF1. Kent detected contamination in that tank yesterday and because we couldn't cool it fast enough (intent was to cool to 40 °F and store) it was decided to keep it hot. It is now 160 °F. There is 6700 gal of 150 g/L sugar there.
- With the improved filtration performance, we have put off testing the centrifuge as we probably won't need it.
- Parts to repair the vacuum pump in GIFT will not be received until Friday. GIFT testing to be done Sunday afternoon or Monday.
- First fermentation should be able to start Monday or Tuesday, depending on timing and success of GIFT testing.

Friday 11/27/2015 11:23 PM

- Filtering, evaporation continue. Contamination seems to be under control for now.
- Filtration rate appears to have leveled out at about 7.5 gal/min, ~70 h for the whole saccharification batch.
- The second saccharification batch is currently being filtered.
- The third saccharification batch is holding at 140 °F after an extended time at 160 °F to pasteurize, contamination seems to be stopped.
- Concentrated sugars are being held in EF1. This is also at 140 °F.
- Parts to repair the vacuum pump in GIFT should arrive about noon today. GIFT testing will be done Sunday afternoon most likely.
- First fermentation should be able to start Monday or Tuesday, depending on timing and success of GIFT testing.

Saturday 11/28/2015 9:19 PM

- Filtering of 602 (second saccharification batch) seemed to go at a record pace, completing 24,000 gal in 24 h. However, the amount of concentrated sugar collected in the storage tank waiting to feed fermentation seemed to be a little short.

- Filtration was stopped while various aspects could be sorted out, like sugar analysis of tanks and what was being lost in filtration.
- Jeremy and Rick calculate that we have enough sugar for 1,500 gal of isobutanol (this would be just 1,000 jet fuel). I have yet to verify.
- The third saccharification batch is holding at 140 °F after an extended time at 160 °F to pasteurize, contamination seems to be stopped.
- Concentrated sugars are being held in EF1. This is also at 140 °F.
- Vacuum pump in GIFT has been repaired successfully. GIFT testing will be done Sunday afternoon most likely.
- First fermentation should be able to start Monday or Tuesday, depending on timing and success of GIFT testing.
- No shift reports today.
- I will verify where I think we are with respect to amount of sugar, and predicted amounts of isobutanol and jet fuel as soon as I arrive in St. Joseph tomorrow.

Sunday 11/29/2015 10:01 PM

- Filtering of 602 (second saccharification batch) is complete.
- After switching back to the rotary drum filter, they are running at a rate of about 10+ gal/min. It is unclear what is different from the original attempt on the rotary drum, which only got about 3 gal/min. Sugar recovery should certainly be much better as there is positive washing.
- The third saccharification batch is bring filtered.
- EF1 is now full of concentrated sugar and a second tank is being filled.
- GIFT testing was started tonight. The desired pressure of 0.6 psia was reached in the vacuum condenser, but we could not get that in the GIFT column due to a leak somewhere. They will be tracking down leaks tonight. We expect that to be successful.
- First fermentation should be able to start Tuesday or Wednesday as it will take at least 24 h after the GIFT test is completed.
- There are no shift reports today.
- I will verify where I think we are with respect to amount of sugar, and predicted amounts of isobutanol and jet fuel tomorrow.

Monday 11/30/2015 10:03 PM

- Filtering of 603 (third saccharification batch) is about 25% complete going through the rotary drum filter at a good pace. The first and second saccharification batches have completed filtering and evaporating.
- An inventory of glucose shows 25,500 lb of glucose “in the bank”, i.e., filtered, evaporated and stored at pasteurization temperature. Another 10,000 lb of glucose is either in the process of filtering and evaporating or still in the third saccharification tank. This is enough sugar to make about 1,080 gal of biojet, assuming conservative yields in fermentation and conversion to biojet. In addition, there is some amount of mannose and galactose, probably about 5% additional fermentable sugars.
- The GIFT was successfully started up. After some difficulty in finding the last leak in the G-Column the pressure was reached in the barometric condenser and just a little higher pressure in the G-Column is holding. The system was run for about 8 h and was shutdown until morning so that the key people could complete the start-up and testing.
- First fermentation should be able to start Wednesday or Thursday as it will take at least 24 h after the GIFT test is completed.
- Andrew compiled all of the data thus far from the three hydrolysis batches as well as the concentrated/filtered sugar storage tanks. This required opening each PDF file, copy-pasting the date & time of injection, method name, and any analytical results into a tab for each tank, e.g. T601, T397, etc. Tank names are not the same as the DCS codes. There are several different “methods” labeled on the HPLC printouts that needed to be sorted out
- There was no filtering, everything was imported. If an analyte was reported on multiple methods, I copied it all in. This can explain some of the saw-toothed charts.

Wednesday 12/2/2015 5:53 AM

- Filtering of 603 (third saccharification batch) is about 50% complete going through the rotary drum filter. The first and second saccharification batches have completed filtering and evaporating.

- The GIFT was successfully started up. Testing through the day yesterday confirmed the operation of the system. A range of feed iBuOH compositions and reboiler heat was tested as well as completely purifying iBuOH to <1% water. All systems are ready to go. A relatively easy restart after 4.5 years of abandonment.
- GIFT was shut down about 7:00 PM last night and the fermenters are being prepared for fermentation. Filling and sterilization will continue through today.
- First fermentation will start early tomorrow morning.

Wednesday 12/2/2015 8:37 PM

- Filtering of 603 (third saccharification batch) continues, there are about 5,000 gal remaining. No additional contamination has been detected in 603 or the sugar storage tanks.
- The fermenters were steam sterilized as was the GIFT loop today.
- Sugar and a portion of the nutrients were being added tonight. The tanks of sugar and nutrient will be sterilized (heating to 121 °C and holding) in place tonight.
- After cooling the fermenter to operating temperature the remaining nutrients will be added through sterile filters.
- Inoculum will be added tomorrow morning and we'll be off to the races with the first fermentation. The first fermentation is expected to be completed in 48 h.
- Recirculation through GIFT will occur immediately. Heat and vacuum being added to GIFT once isobutanol reaches a threshold value and isobutanol will begin.
- Once 603 has completed filtering and evaporating, there is a tank of additional low concentration sugars (evaporator carry-over) that will be re-evaporated and the sugars recovered to supplement the second fermentation.

Friday 12/4/2015 11:28 AM

- We have started making isobutanol! After a much longer time to cool and pH adjust we were ready to add yeast last night about 2:00 AM and the pump we had chosen would not pump the yeast. The yeast had settled after setting in the tote for several weeks and without a sterile way of mixing we planned to use a blender pump that could be sterilized to recirculate the tote, thus mixing it up. Well, the yeast was so thick on the bottom (kind of a light colored peanut butter). They then switched to a large diaphragm pump (these pumps had saved us twice already in saccharification), sanitized it with chemicals (it's plastic and can't take steam) and Andrew and company were able to get the yeast in about 4:30 AM (I had left at 3:00 AM). By early morning we were detecting isobutanol and the GIFT was started about 10:30 AM.
- Filtering of 603 (third saccharification batch) is complete. There is still some evaporation continuing to finish up some rinse water that has sugar. We'll take an accounting of remaining sugar this afternoon.
- This first fermentation is expected to be completed in 48 h, by Sunday morning.

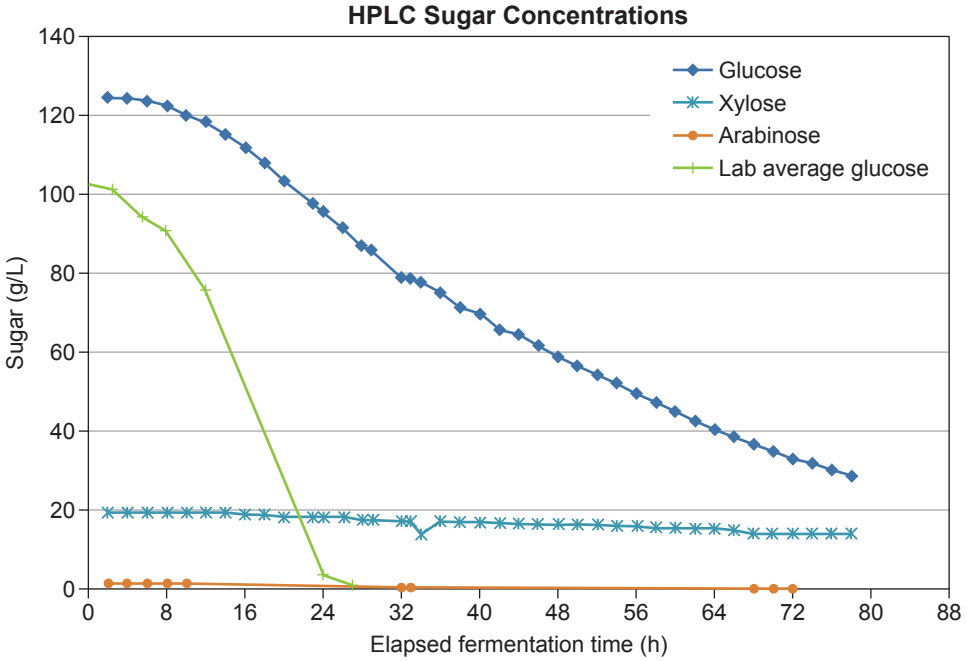
Saturday 12/5/2015 6:40 PM

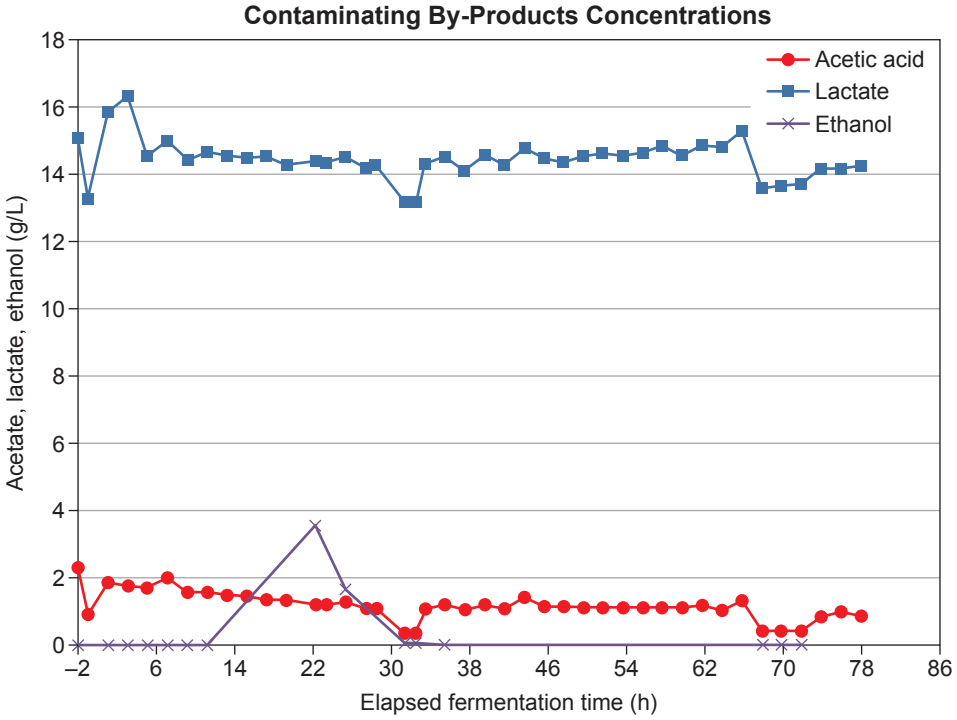
- We are making isobutanol. The fermentation is very slow, it appears that there was not any growth. At the same time we have struggled to keep the GIFT at a reasonable pressure, so removal of isobutanol is slow and the concentration appears to be drifting up, but our analytical is multiple hours behind. We will probably need to increase the reboiler temperature to try and get the isobutanol out and see what happens to the cells. The amount of lactic acid has not changed, but the levels of glycerol and isobutyric acid are slowly increasing.
- We have two tanks of sugars in waiting, 8,500 gal @ 162 g/L and 1,000 gal @ 54 g/L.
- At the current glucose consumption rate the fermentation will be another 24 h.

Monday 12/7/2015 9:10 PM

- We are nearly complete with the first fermentation. The fermentation was much slower than expected, there are multiple reasons for this, few if any are related to the NARA technologies, but are more the result of compromises that we had to make at ICM.
- One of the biggest issues has been the inability to get the same vacuum level in GIFT during fermentation that we had seen in testing. Even the slightest increase in pressure makes isobutanol recovery from the fermentation difficult.
- On the positive side, we have not seen any contamination during the long fermentation, see the nice charts below that Andrew prepared. The yield of isobutanol is still being determined as we finish processing the streams through distillation.

- We expect the fermentation to finish tomorrow. At that point we will investigate the GIFT to determine if the vacuum can be improved (ICM exhausted all efforts of fixing it that were possible while we kept it operating). Hopefully without trying to support a fermentation and diagnose the problem we'll be able to fix the vacuum. We also need to improve the cool-down time after sterilization to shorten the time the sugar and media are exposed to high temperature.
- After fixing GIFT and cleaning the system the remaining sugars will be loaded, sterilized and we'll start the second fermentation.





Saturday 12/12/2015 10:07 AM

- The first fermentation, B501, completed on Wed 12/9/2015. It was shut down due to contamination with little sugars remaining. We are still trying to determine if we can recover those sugars as a "feed" into the second batch, B502. It is currently in tank EF1, 10,100 gal, of unknown quality.
- The B501 broth was processed to remove iBuOH to <0.7 g/L.
- During that final processing, the iBuOH product was contaminated with fermentation broth because of several separate UPEs.
- ICM reprocessed the product and was able to recover several hundred gallons of iBuOH.
- We are in the process of analyzing this 'product' now to determine composition and best path forward.
- We are also further estimating and measuring gallons of product made in the first batch. This is not an easy task, as there is product in several totes, pipes, and tanks. We may not know total gallons until the end of the campaign and all equipment is drained.
- The second fermentation batch, B502, started on Friday 12/11/2015 at 10:00 AM Central time.
- Despite holding the concentrated hydrolyzate/sugars again for >250 h at >140 °F, contamination of the sugars with lactic and acetic acids, and likely contamination by other thermochemical products that act as inhibitors, the yeast is performing well.
- We had lower initial sugar concentration in B502 because we a) did not start with as much sugar mass as B501 and b) added some dilution water to dilute out the inhibitor concentrations that built up during the sugar hold. This seems to have worked.
- I'll share a couple charts below to show comparison between B501 and B502 (first and second batches) (Supplemental Material D.1).
- Attached are also recent shift reports from ICM that contain additional details (Supplemental Material D.2).

Sunday 12/13/2015 7:46 AM

- Bob arrived safely at ICM yesterday and Joe departed.
- Bob and I babysat B502 (second fermentation) until about 8:00 PM last night.
- By 10:00 PM, glucose was exhausted <1 g/L, galactose <1g/L and mannose was still being consumed, but <2.5 g/L.
- Therefore, we instructed ICM to raise the temp on GIFT and begin the iBuOH recovery phase.
- This batch went considerably better than the first. Rates were ~2-fold higher, there was no 12 h lag at the beginning, and the fermentation consumed all C6 sugars in <38 h.
- We used the same yeast and same amount as the first batch, but added ~9,000 gal dilution water to the ~9,000 gal sugar to reduce the high concentrations of inhibitors that had been created during the crazy long 1.5 week sugar hold at 140 °F.
- iBuOH recovery will continue today. We have now two totes of iBuOH product that are being analyzed.

Tuesday 12/15/2015 2:20 PM

- Fermentation 2 completed late Saturday night. Since Sunday has been spent recovering iBuOH from the fermentation broth and processing through distillation.
- As of yesterday we had 627 gal of iBuOH in product totes with another 100–150 gal in the process. The plant is stripping all of the fermentation broth (stripper is independent of GIFT) to wring out the last little bit of iBuOH.
- We have sent samples to Gevo and an outside laboratory for analysis. The physical appearance of some of the material is poor. Water analysis at ICM shows the product meeting the <1% and ranging about 0.5%. A mass spec analysis at Gevo of an initial sample showed some lignin degradation compounds, likely caused during various upsets in the GIFT operation. Composition in the standard Gevo gas chromatograph analysis showed ~96% iBuOH with several percent of pentanol and very little ethanol, all as we would expect. We have no analysis on the acid content, that is being done at the outside lab.
- The lignin derivative and poor color (indicating possible other unknown compounds) will probably require that the material be redistilled. Redistillation will remove the acid if it is present as well.
- This is well short of the amount necessary to produce 1,000 gal of biojet.
- We are in the process of analyzing the run, identifying where everything went and what our next options are.
- On a positive note we made about 44,000 lb of sugar, enough for >2,000 gal of iBuOH, we just didn't get it to the fermenter.

- Saccharification yields for tanks 1 & 2 were 77.6% and 78.7%, respectively, this is very good. The third tank, which was a mix of good ZeaChem material, poor ZeaChem material and Cosmo material, had a yield of 66.2%, also very good.
- Filtration of the solids after saccharification was the primary cause of our problems. This aggravated contamination issues and caused a long heat history for the sugars causing other losses and problems. Filtration of saccharification solids is not a step envisioned in the commercial process.

Appendix E—Composition of Cosmo Rejects and Fermentation Residuals

Table E.1—Polymer sugar composition in Cosmo rejects

	Composition (%, wt/wt)					
Sample ID	Arabinan	Galactan	Glucan	Xylan	Mannan	Total
Cosmo rejects	<0.09	<0.09	55.0	0.60	2.00	57.60
Cosmo rejects truck 4	<0.09	<0.09	55.9	0.60	2.04	58.54
Cosmo rejects truck 5	<0.09	<0.09	56.3	0.75	2.05	59.10
Cosmo rejects truck 6	<0.09	<0.09	55.4	0.72	2.00	58.12
Last Cosmo rejects	<0.01	0.05	57.8	0.63	1.99	60.47

Table E.2—Lignin in Cosmo rejects

	Composition (%, wt/wt)		
Sample ID	Lignin	Acid-soluble lignin	Total lignin
Cosmo rejects	29.4	0.57	29.97
Cosmo rejects truck 4	29.7	0.56	30.26
Cosmo rejects truck 5	29.2	0.51	29.71
Cosmo rejects truck 6	28.7	0.54	29.24

Table E.3—Solids, extractives, ash, and sulfur in Cosmo rejects

	Composition (%, wt/wt)			
Sample ID	Solids	Extractives	Ash	Sulfur
Cosmo rejects	NA	5.23	1.02	1.11
Cosmo rejects truck 4	36.4	5.71	1.05	1.25
Cosmo rejects truck 5	38.9	5.93	1.07	1.19
Cosmo rejects truck 6	39.5	5.47	1.11	1.21

Table E.4—Metal content in Cosmo rejects

	Metal content (mg/kg, ovendried basis) by sample ID			
Metal	Cosmo rejects	Cosmo rejects truck 4	Cosmo rejects truck 5	Cosmo rejects truck 6
Ag	<0.2	<0.1	<0.1	<0.1
Al	22.5	14	16	23
As	<0.2	<0.1	<0.1	<0.1
B	<2	<1	<1	<1
Ba	1.1	1.2	1.3	1.5
Be	<0.2	<0.1	<0.1	<0.1
Bi	<2	<1	<1	<1
Ca	485	360	360	490
Cd	<0.2	<0.1	<0.1	<0.1
Co	<0.2	<0.1	<0.1	<0.1
Cr	0.85	0.5	0.8	0.8
Cu	3.3	4	3.8	3.7
Fe	585	67	50	64
K	40	130	80	90
Li	<0.2	<0.1	<0.1	<0.1
Mg	3,165	3,410	3,350	3,250
Mn	55	60.4	48.9	47.6
Mo	0.5	0.3	0.1	0.1
Na	30	50	20	40
Ni	3.05	0.3	0.3	0.3
P	<20	20	20	20
Pb	<0.2	0.1	<0.1	<0.1
Sb	<0.2	<0.1	<0.1	<0.1
Se	<0.2	<0.1	<0.1	<0.1
Sn	<20	<10	<10	<10
Sr	2.15	2.1	1.8	2.4
Tl	<0.2	<0.1	<0.1	<0.1
V	<0.2	<0.1	<0.1	0.2
Zn	3	3	1	2
Total	4,396.5	4,122.9	3,954.0	4,035.6

Table E.5—Polymer sugar composition in fermentation residuals of Cosmo rejects

	Composition (%, wt/wt)					
Sample ID	Arabinan	Galactan	Glucan	Xylan	Mannan	Total
C310 515 9999	<0.01	0.05	19.1	0.20	1.35	20.70
C310 516 9999	<0.01	0.06	20.2	0.21	1.40	21.87
C310 517 9999	<0.01	0.05	21.7	0.22	1.33	23.30

Table E.6—Lignin in fermentation residuals of Cosmo rejects

	Composition (%, wt/wt)		
Sample ID	Klason lignin	Acid-soluble lignin	Total
C310 515 9999	58.3	3.6	61.9
C310 517 9999	57.5	3.3	60.8

Table E.7—Total solid, ash, and sulfur in fermentation residuals of Cosmo rejects[a]

	Composition (%, wt/wt)		
Sample ID	Total solid	Ash	Sulfur
C310 515 9999	8.41	11.4	1.66
C310 517 9999	8.44	10.9	1.60

[a]Extractives were not analyzed in the fermentation residual samples.

Table E.8—Metal content in fermentation residuals of Cosmo rejects

	Metal content (mg/kg, ovendried basis) by sample ID	
Metal	C310 515 9999	C310 517 9999
Ag	<0.1	<0.1
Al	30	30
As	<0.1	<0.1
B	2	2
Ba	2.9	2.8
Be	<0.1	<0.1
Bi	<1	<1
Ca	1,420	1,380
Cd	<0.1	<0.1
Co	<0.1	<0.1
Cr	1.8	1.9
Cu	4.8	4.6
Fe	180	180
K	86,600	85,200
Li	0.3	0.4
Mg	5,700	5,570
Mn	85	80
Mo	0.8	0.8
Na	15,600	15,100
Ni	1.6	1.7
P	3,200	3,030
Pb	0.2	0.2
Sb	<0.1	<0.1
Se	<0.2	<0.2
Sn	<10	<10
Sr	7.2	6.8
Tl	<0.1	<0.1
V	0.1	<0.1
Zn	30	20
Total	112,867	110,611

Appendix F—Daily Historical Summary of the ICM Second Campaign—0310

Thursday, March 3, 2016

- Loading of the first hydrolysis tank began today, current volume is about 18%.
- The material was being fed at a rate of about 650 lb/h, which will take a little over the budgeted 4 days to load, if the rate isn't increased (they should be able to increase the rate).
- As received Cosmo material is being hammer milled in the feedstock tent and then loaded into tote boxes and shuttled to the biomass building next to the hydrolysis tank. The tote is held over a "slurrying bin" (a liquid tote with the top cut out) and the solids are scrapped thru a hole in the bottom of the tote (hole is about 12 x 12 in. max) and they are not pushing it into the hole from the top, but trying to scrape it out through the hole from the bottom (very awkward). I suggested that they need to safely get on top of the tote to push it through. Not sure they will do that. They could also use a dumping tote, but were afraid it would all dump into the "slurry bin" too fast. I'll check in the morning to see if they have improved any and put more pressure on them if they haven't.
- The hammer mill bag house was giving them some plugging issues. They decided to go directly from the mill to the floor and not use the blower, that seems to be working much better, but maybe milling a little less.
- Need to monitor the solids level in the tank, they seemed to be adding a little too much water (more than I think might be needed) and therefore are probably low in total solids. We'll check that in the morning.

Friday, March 4, 2016

- Loading of the first hydrolysis tank continued today, at about 50% after about 30 h. We are still ahead of schedule.
- 10 gal of CTec added last night another 50 gal today, viscosity seems to be less. ~4 g/L of glucose on an analysis a little after noon. Don't expect much glucose (good) from initial viscosity reduction.
- Added 2 bags of lactrol (antibiotic) as a preventive measure.
- Recycling slurry from the hydrolysis tank to mix with the added solids with the intent to increase the solids concentration. Temperature has gone down to 140 °F and they are recirculation through HX, but that is only heated with hot water making for a slow heat up. Will check in morning for temperature and composition (glucose and contamination). Maybe steam sparging will be needed to get temp up.
- No reliable solids analysis yet.
- Milling went well. They were milling material from truck 3, so they have plenty for this tank load.
- Wet weight of solids received in first three trucks is 136,920 lb with fourth truck total should be 183,320 at a conservative moisture content of 45% that gives us 15% more than we planned for. With the viscosity reduction due to initial CTec addition we will try and get more solids in (and hopefully more iBuOH).
- Fourth truck load was picked up at Cosmo yesterday and is expected to arrive here over the weekend.

Saturday, March 5, 2016

- Loading of the first hydrolysis tank continued today, IR solids at 11% and pH 5.4, continuing to use recycled slurry to mix with added solids (thus continuing to increase solids).
- Continued milling throughout the day.
- Added two bags of Lactrol, "hint" of lactic acid, pH probe not working, monitoring by grab sample. Analysis from hour 60 (which is either 8:00 PM today according to the run clock or 6:00 PM per the HPLC time) shows 0.7 g/L lactic acid. Glucose is up to 13 g/L.
- Slurry being recycled appears reasonably "thin" and it is coming from the bottom of the tank. Rick says there is no movement in the bottom sight glass, but that there is a little higher. I'm not sure that is critical at this early stage.
- Added another 40 gal of CTec today (total expected quantity is about 350 gal of CTEC).
- As of 3:00 PM there was still 6–8 ft of head space to fill in the tank and they have not been adding any additional water today, so there is still flexibility there to get us to our ultimate solids volume.

Sunday, March 6, 2016

- Received fourth and final truck load of pulp rejects last night.
- Composition this morning was about the same as last night, a little higher in lactic acid, up to about 1.3 g/L from 0.7 g/L last night. There is enough lactrol in the vessel to take care of the contamination, but the bacteria

might be in some of the solids that might not be mixing at the bottom edges of the tank (Andrew is not concerned about this increase).
- Solids by oven test were 11% this morning, but level was only about 60% and below the top agitator blade. Water was added to get to the top agitator (~74% now) and solids went down as expected. Hopefully mixing is as good as it can be. Jesse thought it would be possible to increase the power to the agitator, but that would take DCS programming (we're at 100% on DCS, but amps are not excessive). Jon can probably do this in the morning.
- The material seems "thin" enough and pumps well. The only indication that there might not be perfect mixing is there appears to be no movement past a sight glass near the bottom of the tank. However, this sight glass is at the same height and within a few feet of the pump suction and the pump is pumping well and from that pump is where the solids samples are taken. They've added a second pump (large diaphragm) to recirc to the top of the tank (I don't think the flow is really high enough to make much difference, but it shouldn't hurt).
- Milling is going well. They will be done with it tomorrow if they continue. There is more than enough milled for the first tank full.
- About 100 gal of CTec has been added to this point (350 gal is what is planned for the whole tank). Temperature in the tank is around 67 °C out of the HX and probably >60 °C in the tank.
- Will assess where we are re: schedule, solids addition, possible contamination and next step tomorrow morning. We could decide that it is time to get to optimal *T* and add the rest of the enzyme or continue to add solids.

Monday, March 7, 2016

- This morning after examining the volume change due to solids addition it was estimated that we probably had enough solids in the tank, even though the solids measurement was only 11.5% and 26,000 total gallons (target is 13% and 32,000 gal), we stopped adding solids. It is anticipated that there is a ring of solids around the bottom. Further, due to the high temperature of the system, most enzyme that had been added (about 100 gal or 1/3 of the full dose) was probably denatured. Viscosity did not appear to be going down and the solids obviously present in the bottom sight glasses of the tank were not moving.
- We were behind schedule this morning, as temperature and pH would need to be adjusted before enzyme could be added, another reason to move on.
- To cool the tank about 3,500 gal of 45 °F water was added (this was superior to the method they had anticipated using to cool the tank).
- Then we found that they had overshot the pH, which was at about 6.5, too high to add enzyme.
- They had no procedure to add acid, so after spending too much time discussing how to add the acid we added a calculated dose that brought the pH down to about 6. (There were also problems with the pH meter in the tank and we finally moved it to the recirculation line.)
- With the pH and temperature finally adjusted (pH is still a little high at 6, but we expect it to drift down as saccharification starts), temperature is about 55–58 °C, also a little high, but still reasonable.
- About 250 gal of enzyme was added at about 10:00 tonight.
- It is expected that as the saccharification proceeds, the solids in the bottom will be broken-up and solubilized (like what happens in a shake flask).
- About half of the remaining feedstock has been milled, they might finish that tonight, if they don't have other issues.
- Given the delays today, we are currently about 12 h behind schedule. With the impact of the Lifeline fumigation happening on Wednesday, we will be about 24 h behind and it looks like we will inoculate early on Friday morning.

Wednesday, March 9, 2016

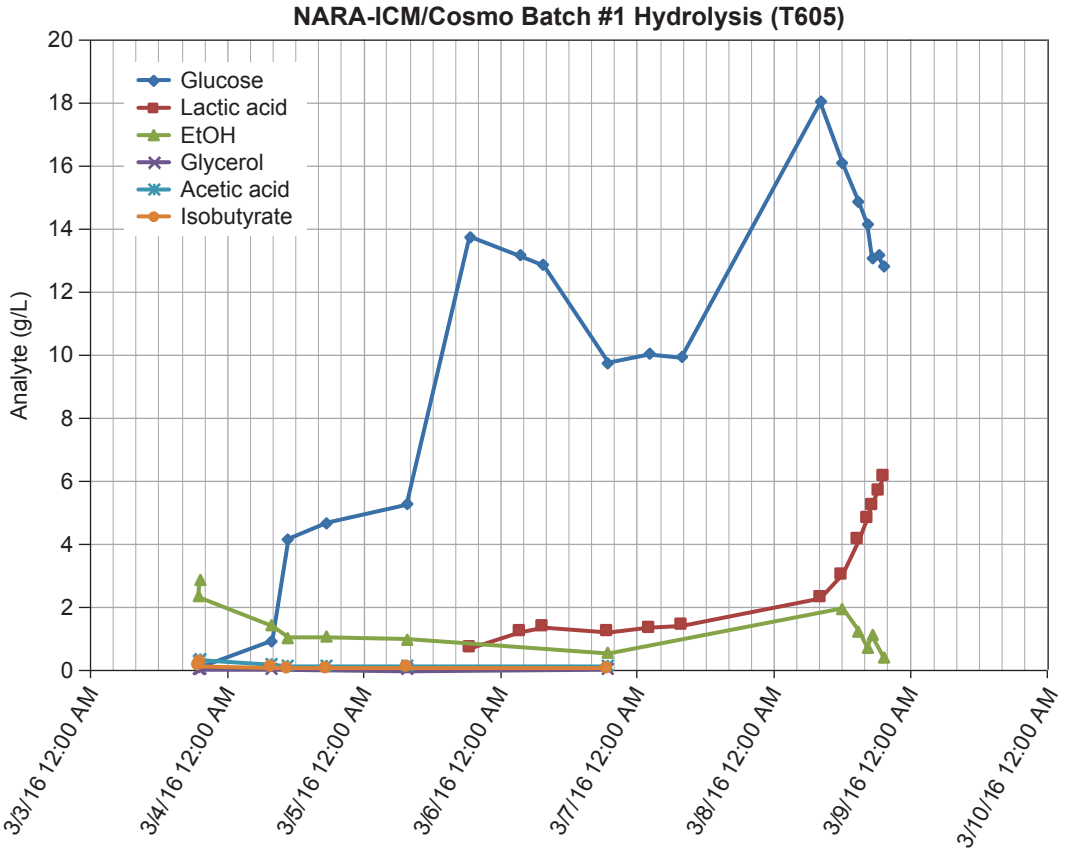
Good News
- After adding enzyme on Monday night saccharification got underway, the glucose shot up to 18 g/L, the solids at the bottom of the tank were freed up and the tank was fully mixing.
- Experimented with adding solids using an insulation blower showed very good promise, but a more industrial version would be needed to sustain an operation.

Bad News
- Saccharification broke up the solids in the tank and must have freed up a pocket of KOH, spiking the pH up over 7. Took most of the night to recover the pH.

- Everyone with experiences in enzymatic sacc at ICM thought that while high pH would reduce the activity of the enzymes, that they would return to normal when the pH was recovered.
- Saccharification did not return and lactic acid production picked up significantly. A second antibiotic was added to no avail.
- Once all of the solids were mobilized the concentration of solids did not increase. Result is that we are about 30% short of our targeted solids in the tank.

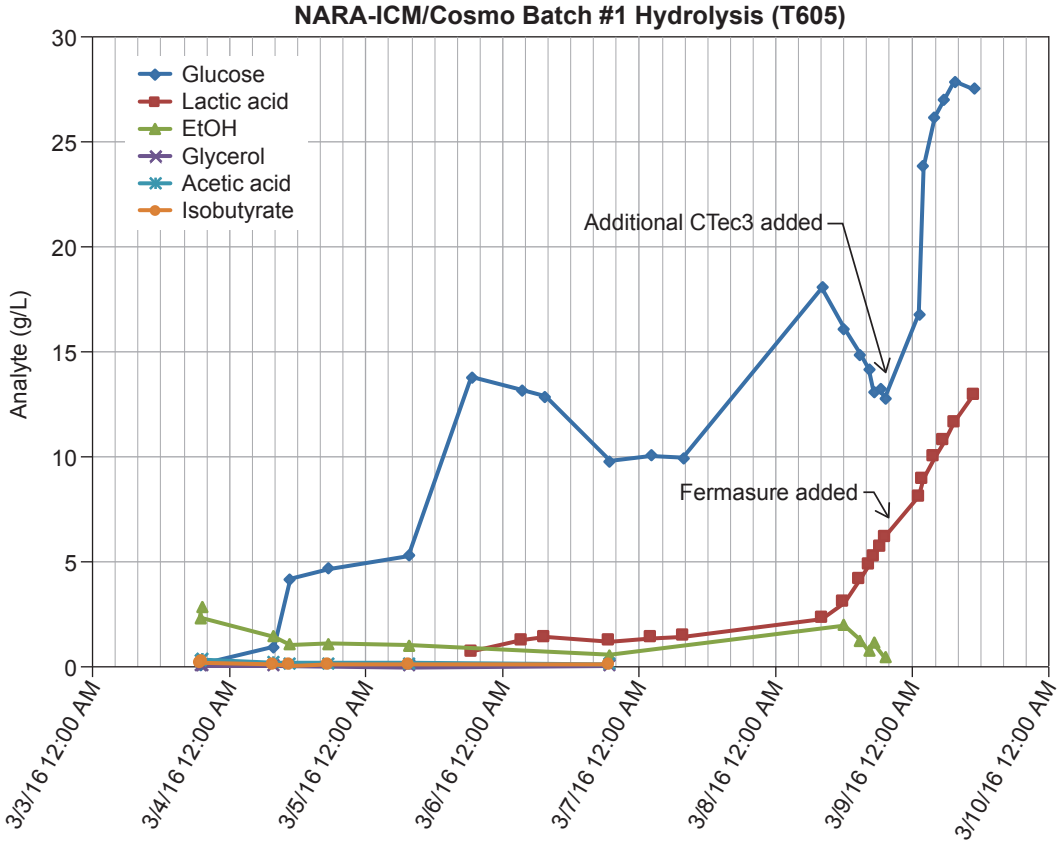
Next Steps

- Added additional enzyme to a sample from the large tank and saccharification began again, confirming that the enzymes in the large tank were probably irreversibly destroyed by the high pH.
- A chlorine based disinfectant Fermasure was added to try to stop the contamination. This has been used by ICM extensively and is usually more effective than antibiotics.
- Add another dose of enzyme to the tank.
- Continue to assess the value of continuing this tank.



Thursday, March 11, 2016

- The Fermasure did not stop or really even slow down the lactic acid production.
- Glucose production took off after addition of additional 5% CTec3.
- Combining the glucose and lactic acid results in a 70% saccharification in 12–20 h. That is above expectations.
- Other than trying to heat the tank, we know of no way to control the contamination and then that might not work either. Given that we were short of our target solids and with all of the sugar lost to lactic acid, it is really not good use of our limited supply of expensive yeast to attempt to ferment this batch.
- We (with the approval of Mike) have decided to scrap this batch.
- We have already started developing plans for another run. A key criterion is to learn from this run and make significant procedural changes to try and avoid the contamination (or reduce it to a tolerable amount).
- We are working through the costs to continue, this is a key point. We must see that we can produce the isobutanol needed to meet our goal, and do it with the funds available.



Friday, March 11, 2016 AM

- ICM (Jeremy) came up with a new scheme that should allow us to more easily load the system and sterilize the material.
- The idea is to pump a slurry of about 2% to a screw press immediately above a small tank capable of high viscosity mixing. Along with the pressed cake, water to dilute to 13% solids, KOH to adjust pH and a low dose of enzyme will be continuously added.
- With about a 3–5 h residence time in that tank the material will liquefy. It is next pumped through the ICM pretreatment reactor to sterilize and then directly to the aerobic fermenter where it will be cooled to saccharification temperature and the remainder of the enzyme added. When saccharification is complete, the fermenter will be sterilized and prepared for fermentation.
- On Thursday they tested the filter press, liquefaction rates at low enzyme loading and last night they were to test pumping the 2% solution.
- Today we will review costs, amount spent and a detailed estimate of conducting this scheme, if the tests are all satisfactory and the costs are reasonable, we will begin on Monday morning.

Friday, March 11, 2016 PM

- Some successful testing was completed last night and today.
- Filtering of a low concentration slurry of feedstock was successfully tested tin the Fornier screwpress.
- Pumping the low solids slurry from the feedstocks tent to the area of the hydrolysis reactor was successful. Liquefaction of 13% solids was easily accomplished with low level of enzymes.
- Setting up equipment modifications will be completed on Monday and start-up on Tuesday.

Monday, March 14, 2016

- Parts of the new processing scheme were tested, high flow rate of dilute solids were successfully run through the Fornier press.
- The press was relocated to the top of the “viscosity break tank” high mixing tank to be used for liquefaction.
- Pumping system was set up in the feedstocks tent.

- A flow test on the GIFT was conducted with hydrolyzate from the failed batch, the first valve encountered plugged quickly. While the particles are generally small, many are oblong, maybe 1/16 by 1/4 in., but there are also bits of rubber in the solids (perhaps from conveyor belts at Cosmo). Additional schemes and testing are being explored to overcome this problem.

Wednesday, March 16, 2016 AM

- Started the new system last night. Slurry feed to Fornier press worked reasonably well. Every so often the solids concentration in the slurry being pumped over from the feedstocks tent would drop off and cause the filter press to "blow through". This means that the filterpress stops working and the dilute slurry runs through. The operators were watching pretty close, so they were able to make adjustments and get the filter cake back. A little extra water would go into the tank, but the solids were generally coming out of the filter press at 23%, so there was a need to add water.
- The solids "metered feeder" is not so reliable, and there is no positive control of water to the dilute slurry (I'll check on that this morning and see what can be done to fix).
- The operators did not get the enzyme loaded last night due to a miscommunication, so the material in the "viscosity break tank" (our liquefaction tank) was extremely high, but it was still pumpable with the diaphragm pump and was generally mixing, but solids were accumulating at the bottom. Enzyme was added this morning, 10 gal to a mix of 2,500 gal of 12.5% slurry. That is 3.7%, I think too much, glucose level is already 20 g/L.
- They are working on getting pretreatment ready to start to sterilize the slurry and start filling the first aerobic fermenter to finish the enzymatic saccharification.

Wednesday, March 16, 2016 PM

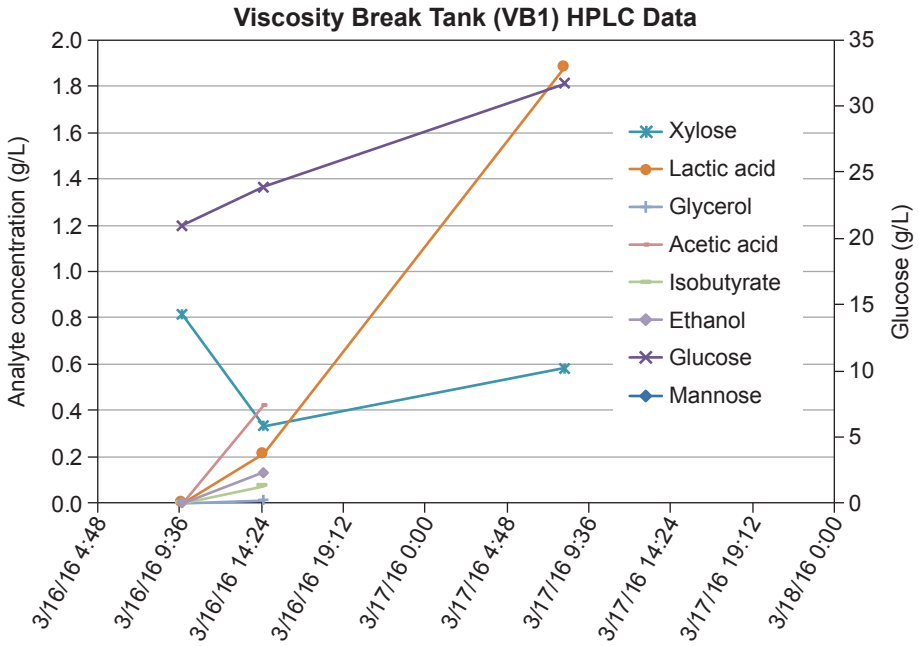
- ICM felt that they needed 5,000 gal inventory of liquefied material before attempting to start-up the pretreatment reactor (this will act as the HTST sterilizer) for the liquefied material. Unfortunately, this means a minimum of an additional 8 h that the first 2,500 gal will have to sit before sterilization. Also this is the first I heard of this requirement.
- The amount of enzyme initially added to the liquefaction tank was 10 gal (4.8% wt enz/wt biomass). An additional 10 gal was added to 2,500 gal of 13% solids, another 4%. Seems too high for liquefaction. Plan for tonight is to continuously add 3.1% wt enz/wt biomass.
- ICM spent all day shift not being able to run the liquefaction system. Seems they overflowed the slurry tank and that not only destroyed some feedstock, but took multiple hours to clean up before the liquefaction system could be restarted.
- Analysis of liquefaction tank at 10:00 AM was about 20 g/L (seems high for simple liquefaction), no contamination. At 3:00 PM glucose production had slowed and was 23 g/L. Lactic was at 0.2 g/L, I'm not sure if that is an indication of anything or not. So as of 5:00 PM they still wanted to make the extra 3,000 gal. Pretreatment hopefully starts tonight.
- As soon as pretreatment starts it will begin filling the aerobic fermenter for hydrolysis.
- Tomorrow will be a big day to see if the liquefaction and pretreatment (sterilization, HTST) can work continuously and fill the aerobic fermenters.

Thursday, March 17, 2016

High Level

- The Cosmo reject material is being liquefied and saccharified! Glucose levels are 30–35 g/L—just not yet in the tank where we planned hydrolysis (aerobic fermenter 1, AF1). Those sugar levels were measured this morning in the viscosity break tank and "surge tank" as I describe below and in the attached process flow sketch.
- Lactic acid increased from last night to this morning—from 0.2 g/L to about 1.8 g/L as of 8:00 AM today. This level may still be OK. I don't have more recent data yet. But ICM injected steam into the surge tank earlier today to try to stop the contaminants.
- There have been a few issues with plugging from larger feedstock particles and chunks of rubber (>1 in.) in the Cosmo feedstock. Bob's looking into the origin of the rubber. Current hypothesis is conveyor belts at Cosmo. I checked the tires on the ICM skid-loader in the feedstock tent, too, but that's not a probable match.
- New plan is to get the partially saccharified material from its current location in several tanks into the AF1 tank, pasteurize at 180–190 °F, adjust to hydrolysis pH and temperature as quickly as possible, and add more CTec3 to finish liberating sugar.

- The first fermentation will not begin until next Monday, 3/21/2016. I will provide continued tech support by phone and PC for the fermentation (Dad duty calls with my 6-year old starting this Sunday).



Details

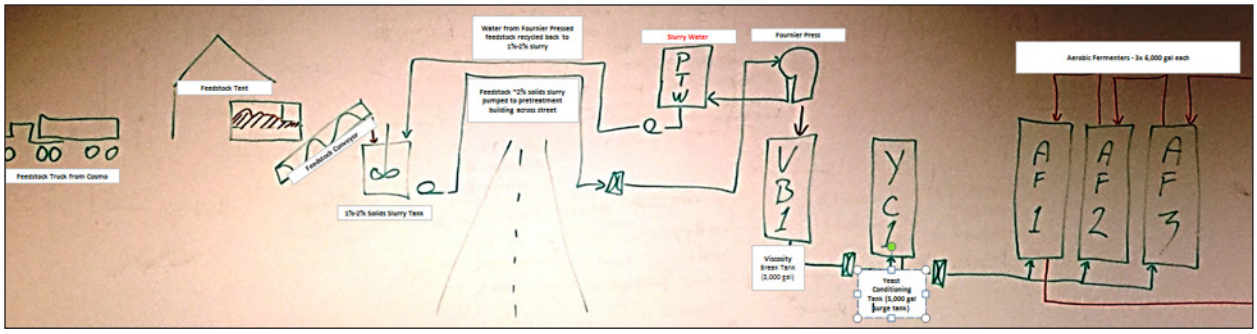
- The solids in the viscosity break tank are currently not pumpable. Rick indicated it was at ~14%, but they're not mixing well and keep plugging the lines out of that tank. This is despite adding a 0.1 g CTec3 per g glucan dose of enzyme to that tank. I don't know the temperature or pH of the tank…perhaps that's the issue. The Fournier press also expels "bricks" of solids that ICM hypothesized might settle to the bottom of the tank. Here's a photo.

- Rick also said that larger chunks of feedstock and bits of rubber in the feedstock are plugging the pretreatment reactor. The pretreatment reactor was intended to sterilize the feedstock at 300 °F for 10 min before hydrolysis. ICM now wants to bypass the pretreatment reactor. We agreed this could work, because Rick also has a plan to pasteurize in the aerobic fermenter. Again, I'm concerned that the "sugar dinner bell" rang with the first drop of enzyme was added yesterday or earlier…and the clock is ticking.

- A surge tank called YC1 was added in line after the viscosity break tank. See attached XLS for a process flow sketch. ICM made that decision sometime yesterday after Bob left because of struggling to keep the viscosity break tank flowing.
- Rick said they want to keep going from viscosity break tank (about 140 °F) into the surge tank to enable longer residence time to enhance liquefaction. The surge tank, aka tank YC1, is about 160 °F because they added steam directly injected, but Rick needs to laser this to know the actual temp because there is no control or gauge on it.
- Right now, ICM is planning to add hot water to the viscosity break tank to thin that out to become mixable and pumpable again. Then they will start the flow back to the surge tank.
- Rick thinks that there is now ~4,000 gal of partly saccharified material in the surge tank and about 1,000 gal in the aerobic fermenter 1. Goal would be to push that all over to AF1 as soon as possible (not sure when) and top it off to get hydrolysis really started with more enzyme.
- Rick also wants to keep AF1 hot at 180 °F or higher (by adding 210 °F water to the jacket and coils of that vessel) to fend off contamination prior to cooling, pH adjustment, then adding enzyme and starting the hydrolysis.
- Once hydrolysis reaches the estimated glucose concentration of 50 g/L or greater, hydrolysis would be considered complete (per expected hydrolysis yield and solids).
- Fermentation nutrients would be added, the entire vessel(s) SIPed, cooled, pH adjusted, then inoculated with Gevo yeast.

Friday, March 18, 2016

- Today was a good day at ICM.
  - Most of the feedstock for this batch (B606 hydrolysis, B505 fermentation) has been slurried and is pumping or hydrolyzing somewhere in the system.
  - ICM is continuing to feed the slurry tank (VB1) until level is ~2,200 gal, targeting 15% TS, currently ~1,500 gal in VB1. Should finish tonight.
  - The surge tank, YCT1, has 3,400 gal of product ready for transfer to AE3.
  - I have attached a process block flow sketch that I labeled (pardon the quality).
- AF1 is hydrolyzing!
  - A dose of CTec3 was added to the tank at about 1:00 PM today after the tank was pasteurized at 190 °F.
  - As of 6:00 PM tonight, pH = 5.13, 37 g/L glucose (sugar column), 1.2 g/L lactic, 0.75 g/L acetic, 1.4 g/L furfural (organic acid column).



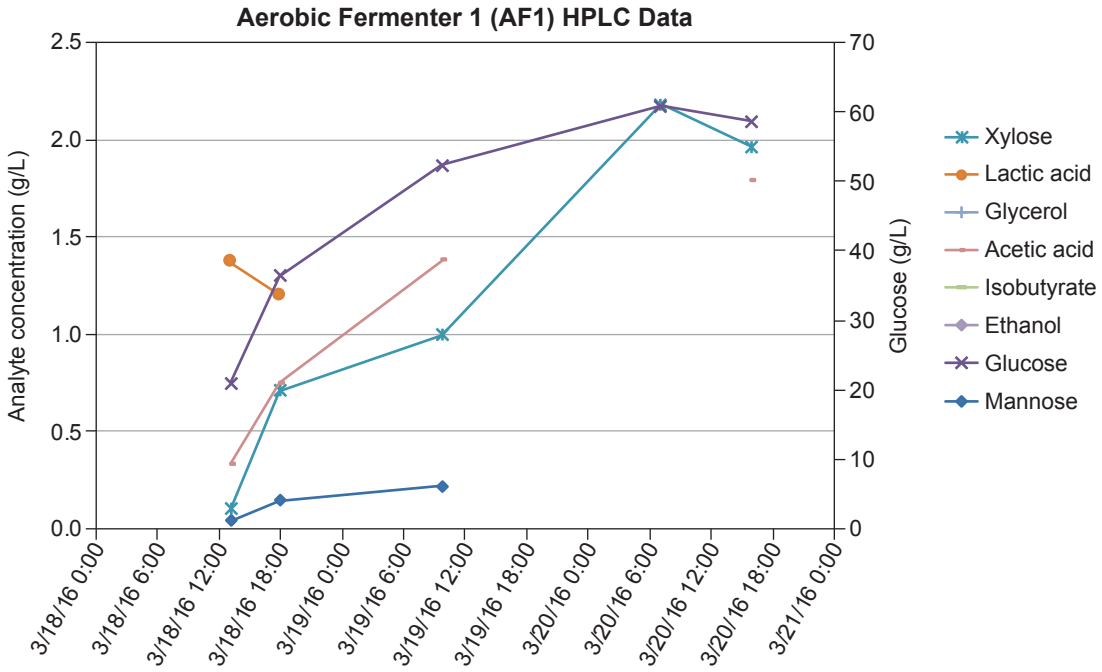
- AF2 is full and being pasteurized to 190 °F.
  - Heating now and at 170 °F on the way up to 190 °F.
  - Will be held for 1 h at 190 °F (long pasteurization).
  - ICM thought it would be at hydrolysis temp and have enzyme dosed sometime overnight.
- AF3 is now empty and will be cleaned and sterilized.
  - AF3 is the third and final fermenter that will pull double duty as a hydrolysis tank then fermenter.
  - Tank is empty and spray balls are being installed for CIP.
  - After CIP, empty SIP will take place.
  - After SIP, 5,500 gal of media from VB1/YCT1 will be transferred and pasteurized for 1 h.
- PROJECTIONS (these are my own estimates)
  - All three AFs should be in hydrolysis mode by the time I leave here at 11:00 AM-ish Saturday.
  - Hydrolysis should be complete in each tank by Sunday evening (AF3 might take until Monday AM).
  - Once hydrolysis is complete, all three AFs (aerobic fermenters) will have fermentation nutrients added and will be steam sterilized prior to inoculation.
  - Then fermentation should be inoculated sometime on Monday.

Saturday, March 19, 2016

- So far, so good today at ICM. I am headed back to sunny CO this afternoon, so this will be my final report. Bob will take the baton back tomorrow.
- Aerobic1 is hydrolyzing and is at close to 24 h of hydrolysis (enzyme added 3/18/2016 1:00 PM).
- Aerobic2 is hydrolyzing and is at close to 12 h of hydrolysis (enzyme added 3/18/2016 8:00 PM)? Need to verify time.
- Aerobic3 was still being SIPed in preparation to receive the last 5,500 gal of "pre-hydrolyzed" feedstock.
- AF3 will then be pasteurized, enzyme added when cooled and at pH, and enzyme added to start hydrolysis.
- GIFT testing was completed yesterday and went OK.
- While CIPing the GIFT unit, the valve between the GCOL and the CO2 scalper plugged (likely with feedstock). ICM is working to unplug this, then will finish CIPing and do SIP on the GIFT loop. Note: the test material used was NOT fully hydrolyzed. So it may be a worst-case scenario.
- Rick reported that there was a pH upset in the first slurry tank, VB1—and about 2,000 gal of feedstock destined for AF3 tank was overdosed with KOH to a pH of about 10. ICM is working to neutralize this before pumping into AF3. I'm told it's "kinda thick".
- Because all of the feedstock received a higher dose of CTec3 in the liquefaction process than planned (0.1 g enzyme/g glucan), the hydrolysis in each of the AF tanks is expected to take 24 h or less. ICM will monitor the hydrolysis reactions, but fermentation nutrient addition and SIP will not occur until the last tank filled (AF3) finished hydrolysis.
- Attached is the most updated data I have for the five tanks in the process (Supplemental Material F.1).
- Solids analysis has also been taken and is drying in the oven. Data are pending.
- Awaiting additional data from HPLC and solids analysis as hydrolysis continues.

Sunday, March 20, 2016

- All three aerobic fermenters have been loaded from the liquefaction system (consisting of viscosity brake tank and yeast conditioning tank). Enzyme was added to the third tank last night.
- The sugar concentrations in the three tanks are 59, 69, 58 g/L and lactic acid levels of ~0, ~0, 2.4 g/L. Our target concentrations of sugar was about 48 g/L, so we have exceeded that.
- Sterilization of the tanks has been started and with inoculation expect tomorrow afternoon.


Aerobic Fermenter 1 (AF1) HPLC Data
Analyte concentration (g/L)
Glucose (g/L)
2.5
2.0
1.5
1.0
0.5
0.0
70
60
50
40
30
20
10
0
3/18/16 0:00
3/18/16 6:00
3/18/16 12:00
3/18/16 18:00
3/19/16 0:00
3/19/16 6:00
3/19/16 12:00
3/19/16 18:00
3/20/16 0:00
3/20/16 6:00
3/20/16 12:00
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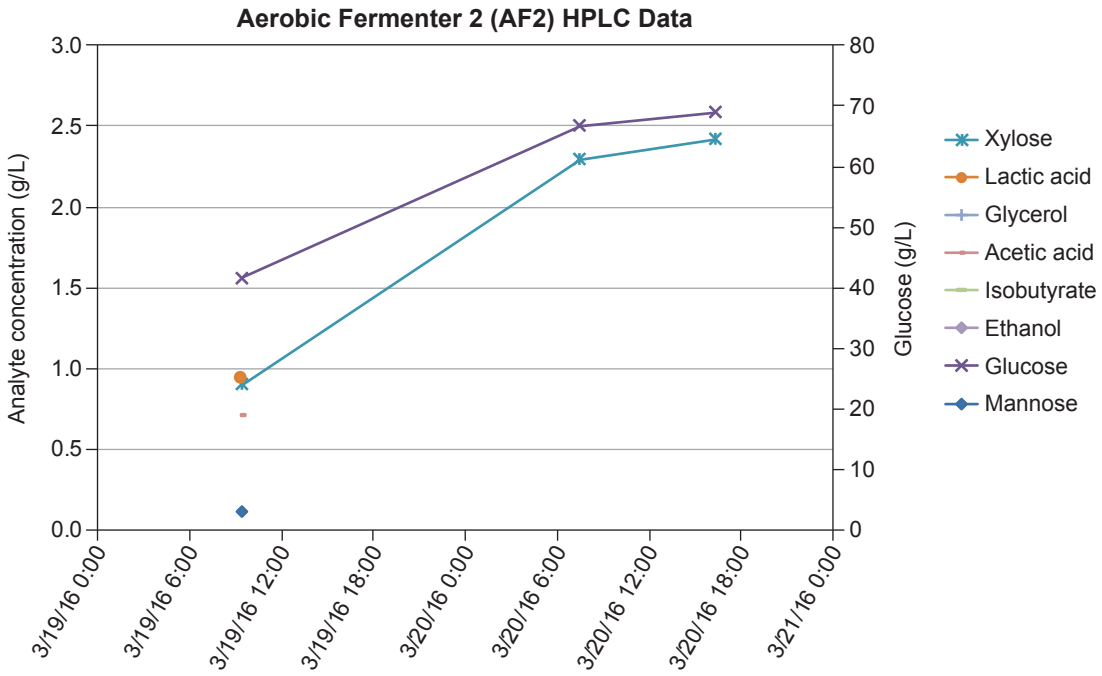
Glycerol
Acetic acid
Isobutyrate
Ethanol
Glucose
Mannose


Aerobic Fermenter 2 (AF2) HPLC Data
Analyte concentration (g/L)
Glucose (g/L)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
80
70
60
50
40
30
20
10
0
3/19/16 0:00
3/19/16 6:00
3/19/16 12:00
3/19/16 18:00
3/20/16 0:00
3/20/16 6:00
3/20/16 12:00
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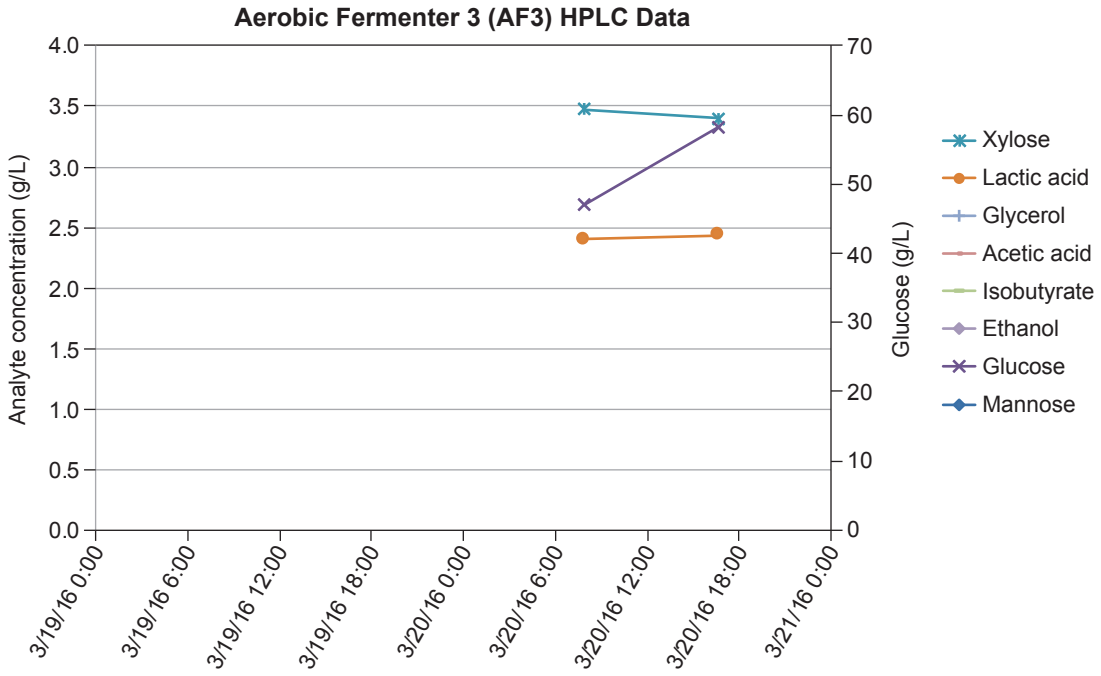
Isobutyrate
Ethanol
Glucose
Mannose



Tuesday, March 22, 2016

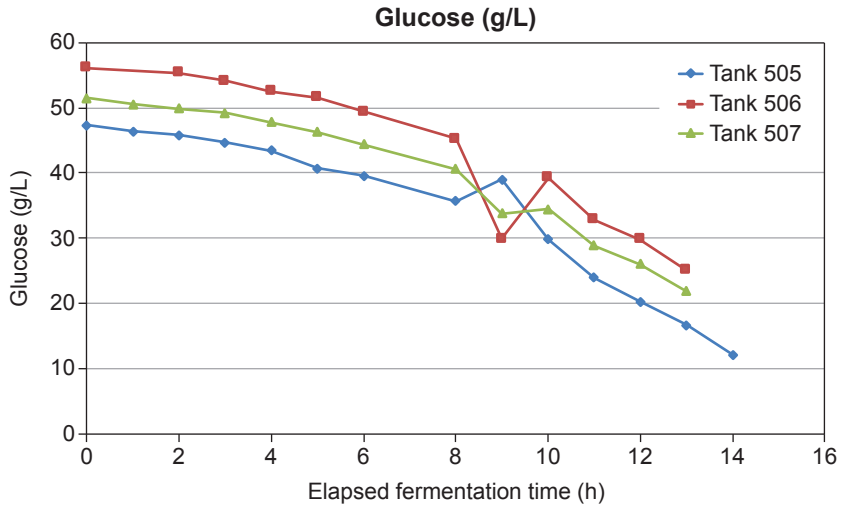
- SIP was completed on three aerobic fermenters with nutrients added.
- pH dropped with the introduction of nutrient.
- They have had trouble with adjusting pH, took considerable time, by 10:00 AM the next step was to try to run GIFT and then inoculate.
- There were issues with sterility of the GIFT loop and they SIPed the GIFT independently of the fermenters.
- Attempted to flow through GIFT and plugged around pre-heater.
- Plan is to inoculate without GIFT, continue to clean-out plug.
- I am concerned that they have a clear plan to vent the tanks. Operation without GIFT will be without vacuum and venting through the scalper. Jon Licklider needs to be consulted as to how this is to be operated, Rick was unclear. It is how they would normally operate fermentation when not making iBuOH.

Wednesday, March 23, 2016 AM

- All three fermenters were inoculated at 11:40 PM last night and are fermenting.
- All tanks seem to be running about the same (they are now independent because we are not running through GIFT).
- We will look at options for recovery of iBuOH when the batch is completed, we will not try to use GIFT while the fermentation is underway. We will not exceed a level of iBuOH that would be toxic.

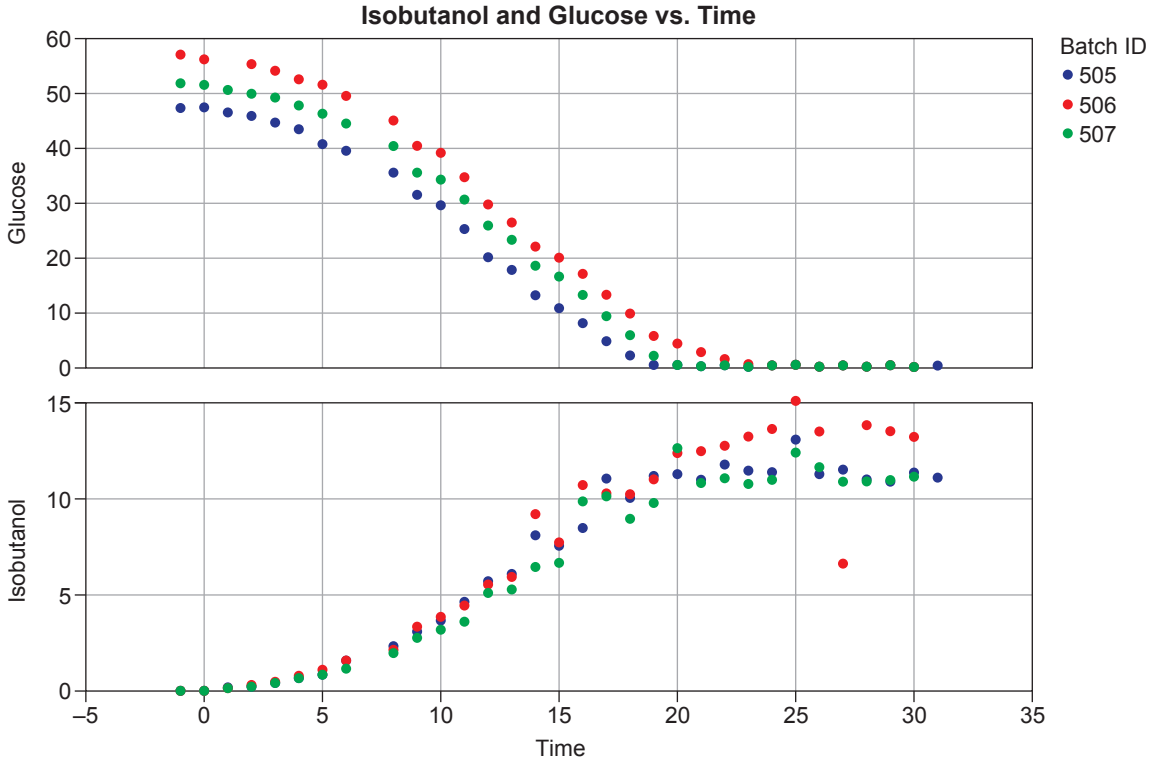
Wednesday, March 23, 2016 PM

- Fermentation continues, see charts below as of about noon today.
- Some of the level in the tanks had to be emptied because they were too full, (lost about 4%).
- As of 1:00 PM the amount of iBuOH produced was about 160 gal if the rest of the sugars are consumed at the yield so far there would be another 122 gal produced for a total of 280 gal. Our goal per fermentation was 285 gal, so at this point we are on target.
- They are having difficulty with the pH probes, they appear to be in the heavier solids, which are suspected of being at the bottom of the tank.
- There is concern as to how the recovery will go once the fermentation is complete.
- Below are graphs of the sugar consumption and iBuOH production through 1 or 2 PM, 0 time is midnight.
- Fermentation could be completed by early tomorrow.



Friday, March 25, 2016

- Fermentation was declared complete as of yesterday morning, see graph below.
- Given the volume of liquid in the fermenters, the final composition and discounting a little for a volume of solids in the fermenter, the total amount of iBuOH produced is about 275–280 gal, very close to our target of 285 gal.
- They installed a dip-pipe into the fermenter and slowed the agitator to 20% in a hope to pull liquid out with minimal solids to feed GIFT.
- GIFT was started last night.



Tuesday, March 29, 2016

- GIFT recovery of the fermenters was completed late Saturday.
- The fermenters were successfully washed out, the solids did not cause an issue. In addition, the GIFT system (reboiler & GCOL) were also flushed of solids with no issues.
- About 300 gal of "light phase" was recovered. This translates to about 240 gal of iBuOH. In addition, there is still some hold-up in the system as it was started after being cleaned out. Our target was 275 gal of iBuOH from one fermentation, so this should be about right.
- The distillation of light phase to iBuOH is a batch operation and will be started later.
- A fifth load of pulp rejects was received from Cosmo on Friday.
- The system was sterilized last night and solids addition should be starting today.

Wednesday, March 20, 2016

- Monday started out with considerable difficulty pumping the dilute slurry across from the feedstock tent to the screw press & viscosity break tank. They are not milling the Cosmo material, to save labor.
- In the afternoon they changed the slurry pump and that corrected their pumping issues. System is pumping well over to the tank to add enzyme (viscosity break tank).
- As of about 4:00 PM (CDT) they had about 5,000 gal in the two tanks being used for initial saccharification and liquefaction (viscosity break tank and yeast conditioning tank).
- Liquefaction showed 10 g/L glucose and 0 g/L lactic acid (i.e., no contamination).
- They will start transferring to one of the sterilized aerobic fermenters overnight.
- They are on target to complete hydrolysis and begin the second fermentation on Sunday.

Friday, April 1, 2016

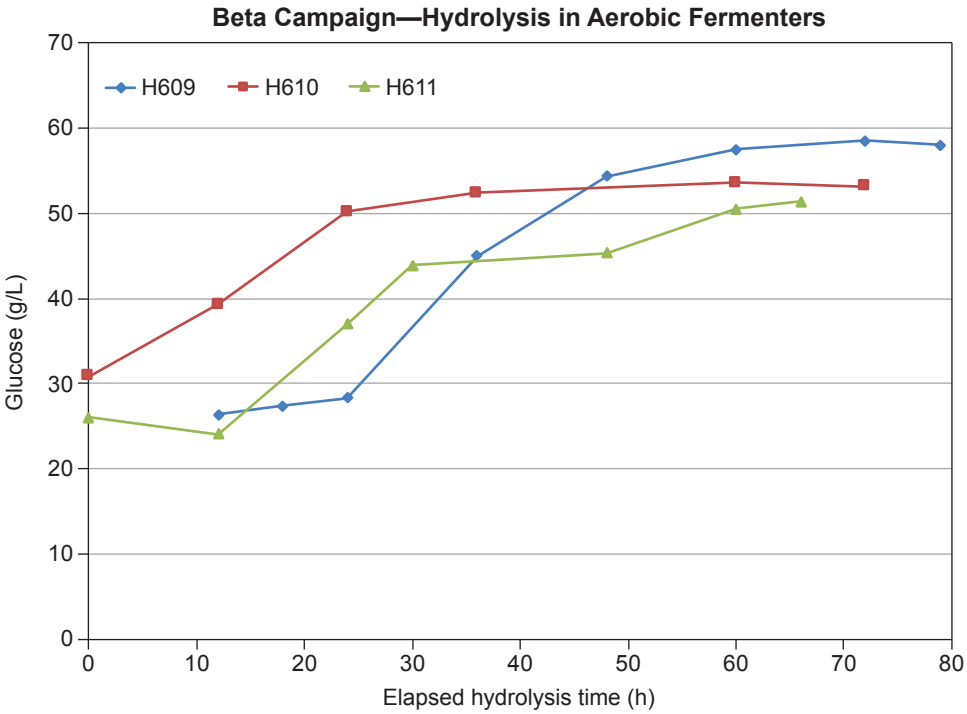
- Operations at ICM continue to be OK!
- Solids additions for liquefaction run #2 was completed yesterday and all three fermenter tanks are now full, have been pasteurized to 190 °F and have had enzyme added.
- Fermenter 1 is now at 58 g/L glucose, 1.9 g/L lactic. It has been about 32 h since enzyme was added (target is about 50 g/L).
- Fermenter 2 is now at 53 g/L glucose, 1.8 g/L lactic. It has been about 28 h since enzyme was added.
- Fermenter 3 is now at 37 g/L glucose, 1.3 g/L lactic. It has been about 12 h since enzyme was added.
- Plan is to continue fermenter 1 in hydrolysis mode until about 6:00 PM today and then start SIP, followed by fermenter 2 a few hours after that.
- Fermenter 3 will be allowed to continue hydrolyzing until sometime tomorrow, targeting 55+ g/L sugar in that tank as well before SIP is started. SIP takes about 24–30 h.
- As each fermenter is finished with SIP it will be held at fermentation temperature (it is sterilized) until all three tanks have been SIPed.
- It is expected that inoculation will take place on Sunday.

Sunday, April 3, 2016

- Hydrolysis was completed in all fermentation tanks.
- All tanks were sterilized followed by sterile addition of the urea, lactrol and vitamins.
- Yeast was added about 11:00 AM CDT Sunday.
- Andrew expects the fermentation to be complete in about 30 h, which would be late Monday.

Monday, April 4, 2016

- Round 2 fermentation was completed this morning.
- All tanks were then closed (to prevent loss of iBuOH and heated to 160 °F to kill the yeast.
- Once cooled again, the GIFT will be started.
- The yield was as expected by Andrew at about 0.23 to 0.26 g iBuOH/g glucose.
- The following graph shows the progress of enzymatic saccharification that occurred over the weekend. Sugar doesn't start at zero because of sugars liberated during liquefaction.



Tuesday, April 5, 2016

- Fermentation was finished Monday morning and was then pasteurized at 160 °F to kill the yeast and prevent the yeast from possibly consuming isobutanol and or making more isobutyric acid.
- GIFT was started Monday night, there were issues with foaming in the fermenters and GIFT column. Theory is that perhaps the yeast was lysed during the pasteurization and the protein was causing the foaming.
- Antifoam was added as well as the reboiler appeared to be plugging, reducing the flow through it (high flow through the reboiler is key to being able to get heat into the GIFT to effect the iBuOH stripping).
- The reboiler was flushed out and eventually the foaming subsided (it probably took some time to distribute the antifoam throughout the system).
- As of this evening the GIFT was running with good flow and heat input through the reboiler.
- Fermentation start time (0 on charts) was at 12:00 Noon on Sunday (4/3/2016) and was complete at 20 h, pasteurization was from 20–30 h and GIFT recovery has been since then.

Wednesday, April 6, 2016

- GIFT continued to go well overnight and until late afternoon. The iBuOH level was <3 g/L when the system foamed over into the GIFT condenser, contaminating the iBuOH in the system.
- Material in the downstream equipment was returned to the fermenters to be separated a second time.
- There was about 205 gal of light phase that had been taken out of the system and put in temporary tote storage; this was not contaminated.
- It is expected that it will take through the night to finish the iBuOH recovery.
- As soon as stripping of this batch through GIFT is completed the tanks will be emptied, cleaned and the next run started.
- We will reexamine the goals for the third run tomorrow.

Sunday, April 10, 2016

- The GIFT recovery of iBuOH from the second fermentation was completed on Friday.
- Tanks were cleaned out Saturday and the next enzymatic hydrolysis was started at 10:00 AM this morning.
- The first tank was filled at 6:00 PM this evening and was showing 27 g/L glucose and <0.1 g/L lactic.
- The other two of three tanks will fill in series as before.

Tuesday, April 12, 2016

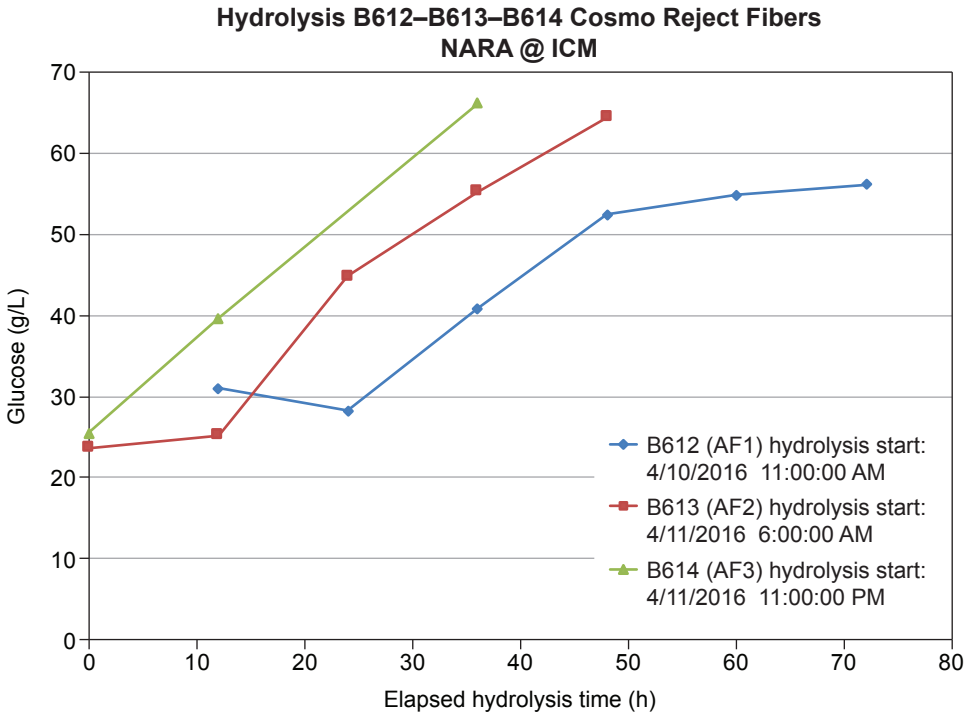
- One side of the Fournier press is a view window and it popped off—had to be re-seated over the weekend. The Fournier press is used to dewater the solids going into the liquefaction tank (initial enzymatic hydrolysis).
- Shutdown of the EtOH plant for annual maintenance will occur on 4/25/2016. This will force pilot plant to shut down by midnight on 4/24/2016. So NARA work will either need to be finished before this—or pause.
- Rick thinks that B611–613 will start fermentation on Thursday 4/14/2016 and the next fermentation will start Friday 4/22/2016 or 4/23/2016 Sat. So this will be tight. May need to delay fourth fermentation till after shutown.
- 38,000 lb of feedstock remaining as of the start of this batch—might not be enough for two batches, including the current one, so we're considering getting another load.
- GIFT reboiler HX was very clogged at the end of running on the last fermentation. ICM will try flushing out (which has worked to a reasonable extent after the last fermentation and once during this last GIFT run). An alternative would be to hire an outside firm to dismantle and clean (~$6–8K).
- Second fermenter started filling at 6:00 AM yesterday and should have been finished yesterday afternoon. Tank 3 is probably filled as well by now. Will update the status of the hydrolysis tanks this afternoon.

Wednesday, April 13, 2016

- All fermentation tanks have been filled and are being enzymatically saccharified.
- Sugar concentrations as of about 9:00 AM today are AF-1 57 g/L, AF-2 62 g/L, AF-3 59 g/L. AF-1 has been at this stage for 48 h and AF-3 about 24 h.
- Plan is to start SIP (sterilization) of AF-1 this afternoon, followed by the other two.
- Fermentation inoculation will either be late Thursday or early Friday.
- We have decided that we will wait until after the ICM Plant shutdown (4/25/2016 to 5/1/2016) before doing run 4. This takes the pressure off trying to get finished with 3 and complete fermentation and GIFT 4 by 4/24/2016.
- We will get one more load from Cosmo as the amount of solids remaining would either be extremely close or probably short of what we would like to run in the last run.
- They are still working on flushing out the GIFT reboiler in anticipation of completing this fermentation about Saturday or Sunday.

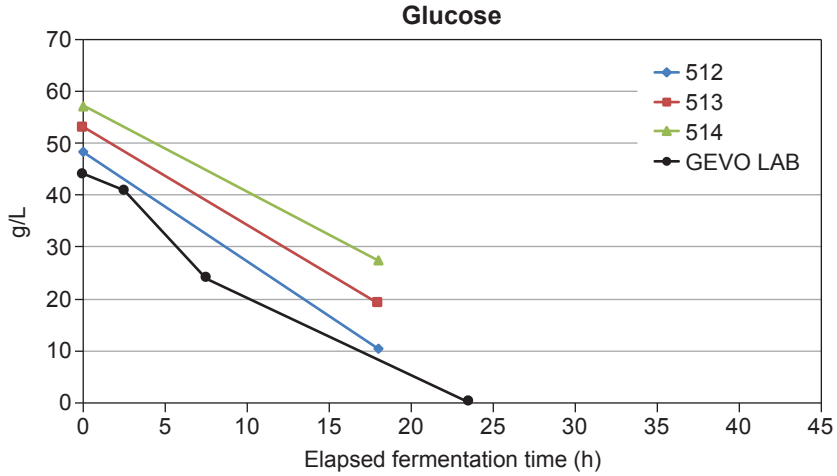
Friday, April 15, 2016

- All three fermentation tanks were finished with enzymatic saccharification yesterday. See the graph below to see the progress of sugar production. Sugar levels this time (56, 64, 66 g/L) were better than the previous run, which were 57, 53, 51 g/L. So here's hoping for a little more iBuOH.
- All tanks were steam sterilized overnight and inoculated with the Gevo yeast at 1:00 PM today. It is expected that the fermentation will be completed in about 24–30 h, or tomorrow afternoon.



Saturday, April 16, 2016

- Fermentation to isobutanol is progressing well in run 3 and after 18 h the glucose is down to 10.4, 19.1 and 27 g/L in the three tanks. See the charts below from Andrew regarding formation progress.

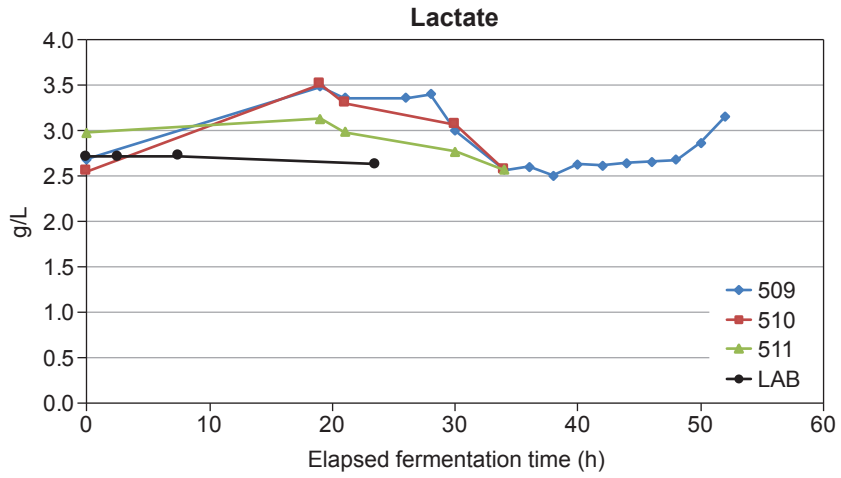


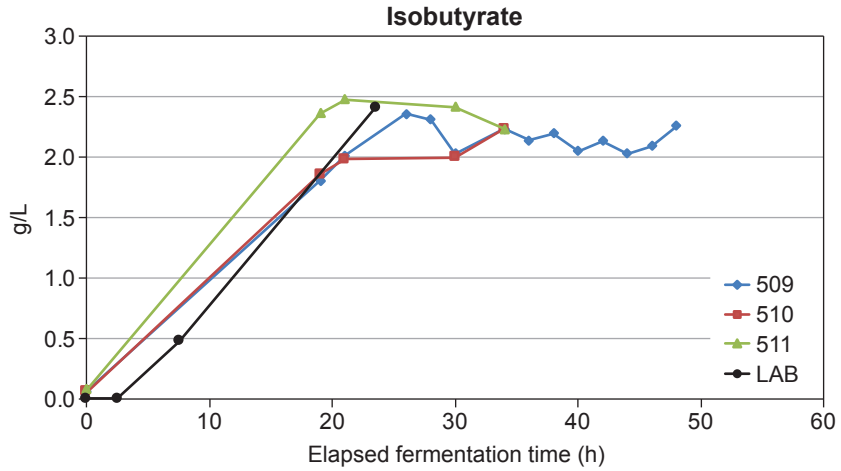
Sunday, April 17, 2016

- All three tanks were heated to kill the yeast and GIFT was started late last night.
- Recovery of isobutanol via GIFT has been taking about 36 to 48 h, so still a couple more days to complete the iBuOH recovery.
- There is not enough time to complete the fourth and final fermentation before the ICM plant shutdown a week from Monday, so it will be delayed and start two weeks from tomorrow, 5/2/2016.

Tuesday, April 19, 2016

- The GIFT operation ran well for about 30+ h until yesterday afternoon. See chart below from ICM regarding the concentration coming out of the GIFT. The chart is through about 8:00 AM yesterday.
- The concentration into the GIFT is not taken at a representative location. They remove the liquid from the fermenters through a dip-pipe to avoid solids and the sample is not taken from that line so disregard.
- The plan was to run with no agitation and avoid the solids for as long as possible, then agitate and mix in iBuOH that might be at the bottom. That was done yesterday at about 2:00 PM, which created a foaming event and plugging of the reboiler.
- The downstream system was contaminated (not the product tote, which has about 130 gal of light phase in it) with material from the fermenters, so it was sent back to the fermenters and the system cleaned. The reboiler was flushed out as well. Shouldn't have been much iBuOH actually lost.
- System was brought back and the reboiler is running at about 250 gal/min (max is probably 350 gal/min). For some reason the lactic acid is increasing, there is no glucose for it to consume, so it isn't clear what is happening. No one suspects that it is consuming iBuOH, so the decision is to just continue.
- There is at least another day's worth of recovery left.





Thursday, April 21, 2016

- Recovery of isobutanol from run 3 is just about complete. It is taking a while because of the solids and the fact that they had one of the agitators off to keep solids out and then when they turned it on, the iBuOH went back up high. The low concentrations take the longest time to get the iBuOH out because you're boiling mostly water.
- Run should be completed tonight.
- ICM Biofuels production plant is down next week, so we can't start another run. That will wait until May 2.
- I'll be in Europe for the next run, so I'll ask someone else to send out some updates.
- Another load of solids will be picked up and delivered from Cosmo next week, in time for the last run.
- After completion of the runs, two steps of purification will be performed on all material:
- First, removal of acid, this is done by putting the iBuOH back in a fermenter and running thru GIFT at hi pH, which holds all the acids as nonvolatile salts.
- Second, removal of water from light phase, batch distillation in the "rectifier" will accomplish this.

Wednesday, May 4, 2016

- The load of Cosmos material arrived. Rick noted that the % solids are 42% and higher than the last loads, which were in the 38% range. The material has a lighter appearance, probably due to the higher solids. No foreign matter has been detected in the Cosmos material so far.
- Filling of the fermenters started late Monday. AF1 is full at this time with an IR solids of 17%. The oven dried measurements will be completed this afternoon. There is only a trace of lactic acid detected. AF2 should be filled today.
- The solids in the fermenter are higher than the last runs due to operating the Fournier press at higher pressure. The operating staff is running the press at the fine line between a wet solids discharge and a discharge that is too dry to easily sink into the slurry.
- There was some concern at ICM that the glucose levels may be too high using a higher solids loading in enzymatic hydrolysis. It was felt that 17% solids was a good target. It was discussed that 17% solids was one of the original targets so this should not be an issue. If after enzymatic hydrolysis is complete, the slurry could always be diluted to lower the glucose levels.
- There was discussion on yeast viability. Andrew indicated the yeast typically have a shelf life of 10–12 weeks and since it was delivered in early March, it should be fine. ICM's plan is to dilute the remaining yeast with sterile water so the level is above the tote mixer and then mix for ~1 h. The yeast will then be evenly distributed between the three fermenters.
- Fermentation is expected to start Sunday, May 8.

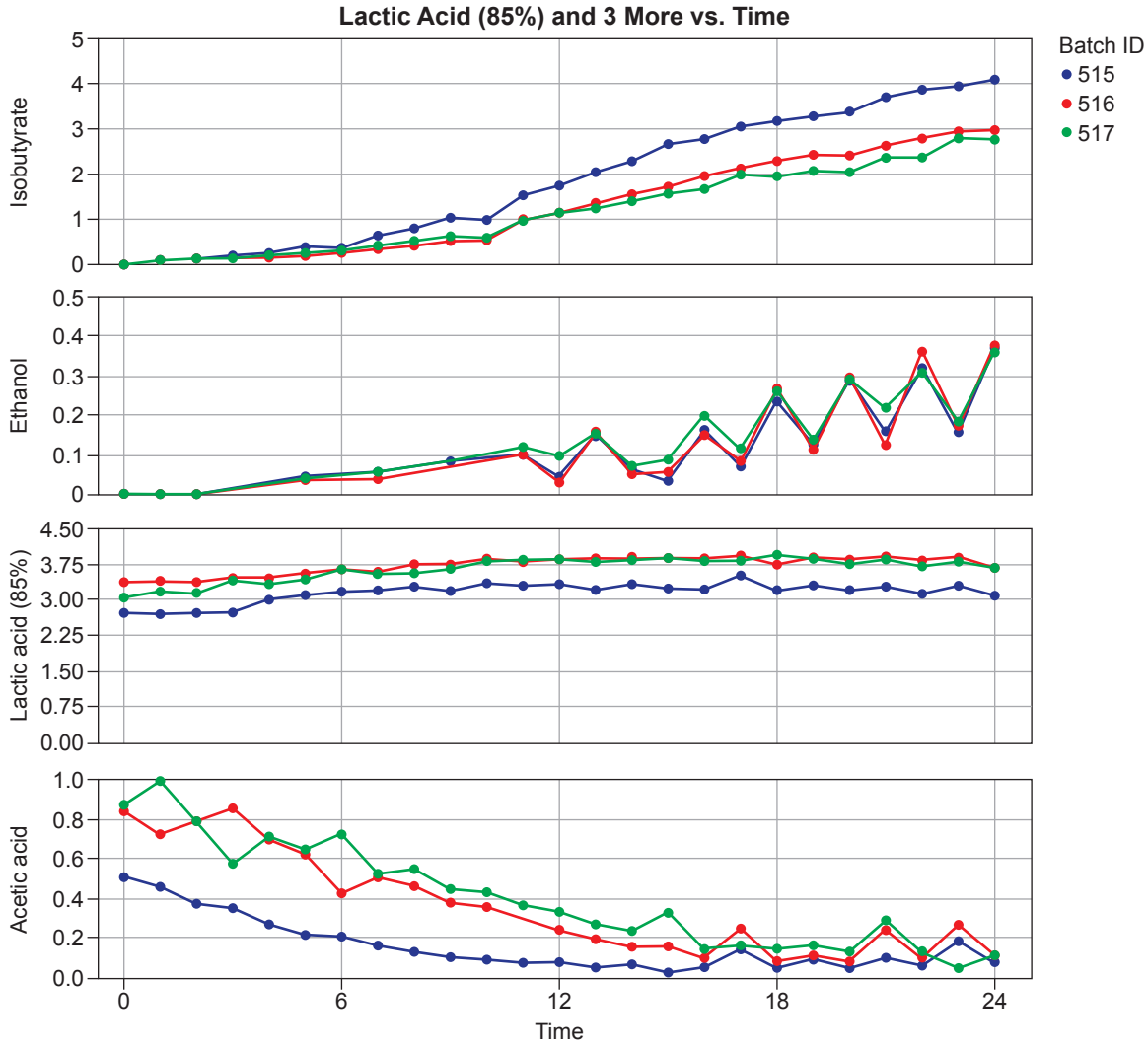
Friday, May 6, 2016

- AF1 hydrolysis is complete with 76 g/L glucose.
- AF2 hydrolysis is almost complete with 79 g/L glucose although it has not quite plateaued.
- AF3 hydrolysis still needs 12 h to finish and is at 59 g/L.
- There is concern that this is too much glucose. The worry is that using the previous yield of 0.28 g isobutanol/g glucose, the excess glucose could lead to ethanol production during the GIFT separation.
- The concentration of glucose will drop during SIP, but it is not known if the dilution will get into the 65 g/L glucose range. It will be close as it is estimated that ~500 gal of steam will condense in the fermentation tanks during SIP and there is only about 500 gal volume left in the tanks.
- ICM could drop some of the hydrolysis slurry before SIP, add sterile water and then SIP. This option would present the lowest chance of contamination in fermentation, since the transfers would occur before SIP. However, there is the risk of possibly ending up low on glucose.
- After much calculation and discussion, Andrew suggested that the option of SIP the slurry, measure the glucose and then dump slurry only if necessary was most prudent. It was felt that since flow would be out, and since ICM has been able to keep contamination issues under control, this option should give minimal risk. Rick was going to discuss with his team, gather any other concerns and verify this option is possible after SIP. He will contact Andrew directly to confirm today.
- If system configurations allow, AF3 may receive SIP first when its glucose level reaches ~70 g/L, stopping any further glucose production and thus avoid the need for dilution other than SIP.
- Inoculation is still expected to occur Saturday, May 7.

Saturday, May 7, 2016

- At current heating pace we will get to 250 °F in AF3 at about 4:00 PM. If we can cool as fast as we did with AF2, tanks will be at ferm temps around 7:00 PM. We will inoculate about an hour later after we add urea and pH adjust to 5.1.
- AF1 60 g/L glucose after SIP.
- AF2 67 g/L glucose after SIP.
- AF3 65 g/L glucose before SIP.

Monday, May 9, 2016



Tuesday, May 10, 2016

- Fermentation is complete in all vessels. There are only traces of glucose and no further increases in any contaminants.
- After pasteurization, the pH in the broth was raised to 8 to minimize any acid carryover during GIFT. Additional dilution water was also added to aid in GIFT recirculation. Additional broth samples were taken as a basis for monitoring the separation.
- The GIFT system is being started this morning. Agitation will be used in AF2 & AF3. AF1 agitation will be started later in the GIFT separation.
- The latest DCS and LIMS data were uploaded to the FTP site.
- Re-GIFTing of the isobutanol inventory is expected to start May 18 followed by rectification on the May 19 and 20.

Wednesday, May 11, 2016

- GIFT was started yesterday and the current isobutanol level is down to 4 g/L. Based on the previous runs, it is expected to take an additional 24–36 h to finish.
- AF2 and AF3 are being continuously agitated. AF1 was briefly agitated this morning to release any trapped isobutanol. With only intermittent agitation in AF1, ICM has not had any plugging problems in the GIFT system thus far.
- Lactic acid is slowly increasing in the broth. The source is not known as there are only traces of glucose and 0.5 g/L xylose left and the broth was pasteurized at the end of fermentation. It is not anticipated to be a problem.
- The pH of the broth had dropped to 7.5 by this morning. It will be brought back up to 8 for the remainder of GIFT.
- After GIFT is complete, the fermenters will be cleaned and AF3 filled with water waiting for the start of re-GIFTing the isobutanol inventory (May 18).
- ICM is working on the logistics and paperwork for sending the two high-ethanol totes to Whitefox in Canada for processing.
- Andrew will try to get ICM the full list of ASTM required tests to be conducted on the isobutanol after the inventory is reprocessed next week. It will be determined if ICM can conduct the tests themselves or if GEVO (or others) need to complete the tests.

Thursday, May 19, 2016 AM

- Re-GIFTing is going OK. The over-optimistic predictions of yours truly were squelched by the inability of the LL separator to handle the high flow of iBuOH, so it's running per the "ICM way", slower than expected. A method of adding the iBuOH to the system was worked out, it was not simple because the totes are flammable and must be kept in the electrically classified area when open and the fermenter is in the standard electrical area (which is ok once the iBuOH is diluted). Once this procedure for adding was worked out (took most of the morning) it seemed to purr along.
- Great progress was made till late into the night shift, when things slowed.
- Four totes have been filled with acid on-spec light phase. There are still two totes waiting to be added (maybe 1/3 of the total). They should complete the low ethanol totes today. Or at least they should be in the "draw down" mode (pulling the last iBuOH out after all totes have been added) by that.
- Acid spec is 70 ppm, all analyses that I've seen have been 30–50 ppm.

Thursday, May 19, 2016 PM

- All totes (hi acid, lo EtOH) have been fed into the GIFT with about 2/3 of the product having been recovered in totes and the rest still in the process as of this afternoon, yet to be recovered.

Appendix G—Final Fuel Certificate of Analysis

IAC Port Arthur
6175 Highway 347
Beaumont, Texas 77705-7657 United States of America
T: 409-212 9322
F: 409-212-9327

Certificate of Analysis

INSPECTORATE

Vessel / Shore Tank :	Submitted Sample	Sample Submitted By :	South Hampton Refining -- S
Product :	BioJet	Analysis Performed By :	IAC Port Arthur
Client Reference :		Date Sampled :	15-Sep-2016
Terminal / Port / Office:	South Hampton Refining -- Silsbee, TX	Date Reported :	04-Oct-2016
Job ID :	577508-16-0041472	Submission ID :	008-1603881
Comments :	Serial# 244686, 244814 ,& 244801 (Lot# F023F40001)		

		Submitted		
	Sample Number	008-1603881-01-005		
Method	Test	Result	Specification	Pass-Fail
ASTM D3242	Acid Number , mg KOH/g	0.000	0.015 Max.	Passed
ASTM D86	Observed Barometric Pressure , mm Hg / kPa	760 / 101.3		
	Initial Boiling Point , °C	163.2		
	5% Recovered , °C	175.8		
	10% Recovered , °C	176.4	205 Max.	Passed
	20% Recovered , °C	177.3		
	30% Recovered , °C	178.4		
	40% Recovered , °C	179.4		
	50% Recovered , °C	180.3		
	60% Recovered , °C	181.6		
	70% Recovered , °C	183.7		
	80% Recovered , °C	187.8		
	90% Recovered , °C	205.9		
	95% Recovered , °C	237.2		
	Endpoint , °C	258.8	300 Max.	Passed
	Recovery , %	98.1		
	Residue , %	1.1	1.5 Max.	Passed
	Loss , %	0.8	1.5 Max.	Passed
	T90-T10 , °C	29.5	21 Min.	Passed
ASTM D56	Manual / Automated	Automatic		
	Flash Point , ° C	46.0	38 Min.	Passed
ASTM D1298	API Gravity @ 60°F , ° API	55.2		
	Density , kg/m³	758.1	730 - 770	Passed
	Reference Temperature	15.0°C (59°F)		
ASTM D5972	Freezing Point , ° C	<-80	-40 Max.	Passed
ASTM D3241	Test Temperature	325°C	325 Min.	Passed
	Pressure Drop , mm Hg	0.0	25 Max.	Passed
	Heater Tube Deposit Rating	0	3 Max.	Passed
	Color	None	No peacock or abnormal color Max	Passed
IAC Lab ASTM D2425	Paraffins , % Mass	85.2		
	Aromatics , % Mass	0.2	0.5 Max.	
	Cycloparaffins , % Mass	Under 15%	15 Max.	
IAC ASTM D5291 Method A	Carbon and Hydrogen , % Mass	100.0	99.5 Min.	
	Hydrogen , % Mass	15.3		
	Carbon , % Mass	84.7		
	Nitrogen , % Mass	<0.8		
ASTM D4629	Nitrogen , ppm (mg/kg)	<0.3	2 Max.	Passed
ASTM D2622	Sulfur Content , ppm (mg/kg)	<3.0	15 Max.	Passed
UL ASTM D7111	Aluminum , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Calcium , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Phosphorous, ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Chromium , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Palladium , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Copper , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Iron , ppm (mg/kg)	0.03	0.1 Max.	Passed
	Strontium , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Potassium , ppm (mg/kg)	0.04	0.1 Max.	Passed
	Tin , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Lithium , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Cobalt , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Magnesium , ppm (mg/kg)	<0.01	0.1 Max.	Passed

ISO 9001 registered; BSI certificate # FS 566562

Page 1 of 2

IAC Port Arthur
6175 Highway 347
Beaumont, Texas 77705-7657 United States of America
T: 409-212 9322
F: 409-212-9327

Certificate of Analysis

INSPECTORATE

Vessel / Shore Tank :	**Submitted Sample**	**Sample Submitted By :**	**South Hampton Refining -- S**
Product :	**BioJet**	**Analysis Performed By :**	**IAC Port Arthur**
Client Reference :		**Date Sampled :**	**15-Sep-2016**
Terminal / Port / Office:	**South Hampton Refining -- Silsbee, TX**	**Date Reported :**	**04-Oct-2016**
Job ID :	**577508-16-0041472**	**Submission ID :**	**008-1603881**
Comments :	**Serial# 244585, 244614 ,& 244601 (Lot# F025F40001)**		

		Submitted		
	Sample Number	008-1603881-01-006		
Method	Test	Result	Specification	Pass-Fail
IAC ASTM D7111	Platinum , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Manganese , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Molybdenum , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Sodium , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Nickel , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Lead , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Titanium , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Vanadium , ppm (mg/kg)	<0.01	0.1 Max.	Passed
	Zinc , ppm (mg/kg)	<0.01	0.1 Max.	Passed
IAC ASTM D7359	Fluorine , ppm (mg/kg)	<1.0	1 Max.	Passed
	Chlorine , ppm (mg/kg)	<1.0	1 Max.	Passed
ASTM D6304 Proc. B	Water Content , ppm (mg/kg)	72	75 Max.	Passed

IAC **Analysis performed by alternative IAC laboratory.**
ext Lab **Analysis performed by External Laboratory**

For Inspectorate: _____
Vilas Dalal , Assistant Laboratory Manager