Throughput, Reliability, and Yields of a Pilot-Scale Conversion Process for Production of Fermentable Sugars from Lignocellulosic Biomass: A Study on Feedstock Ash and Moisture

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ABSTRACT

Early lignocellulosic biorefineries have been plagued with numerous issues that involve feedstock handling problems and variations in conversion efficacy that stem from feedstock variability and complexity in dimensional, physical, chemical, and mechanical attributes. Feedstock ash and moisture content vary considerably in corn stover harvested from farms for bioconversion, and their effects on preprocessing (grinding/milling) and subsequent chemical and enzymatic conversion to fermentable sugars is systematically explored here using pilot-scale hammer mill grinders and chemical hydrolysis reactor. Corn stover with high ash content due to contamination from soil was found to (1) consume higher power during grinding and resulted in reductions of processing rates, and (2) produce a larger fraction of fines in the feedstock that were lost to dust mitigation systems and caused higher mechanical wear rates. Corn stover feedstock coming from fields with a high residual moisture content resulting in bale degradation due to self-heating caused a more pronounced drop in preprocessing throughput due to grinder overloads and process upsets leading to equipment downtime. Conversion yield to sugars was not affected, although differences in fermentation performance on these sugar streams was not examined. The overall process throughput was only 40–70% of nameplate capacity due to preprocessing problems.

KEYWORDS: biomass milling; pretreatment; chemical hydrolysis; enzymatic hydrolysis; corn stover.

Introduction

Many of the process bottlenecks and difficulties experienced in the nascent bioenergy industry are centered on feedstock handling and preprocessing operations. These operations, while broadly defined, focus on the process of converting biomass resources such as baled corn stover into a material suitable for chemical conversion (typically called a biomass feedstock), and then conveying the biomass feedstock into the conversion process. Biomass resources and feedstocks are complex and variable in dimensional, physical, chemical and mechanical attributes, and differ dramatically from other natural products such as grains, which have been successfully conveyed and converted into value-added products for decades.

Historically, biorefineries were designed and built based on equipment used in the agricultural and pulp & paper industry. Engineering approaches were embodied in proprietary design handbooks which are based mainly on experience and empiricism with model biomass feedstocks. This approach is adequate for mature industries where equipment is improved and scaled-up incrementally but is not suitable for new industries like biomass conversion, where the feed handling characteristics, the impact of feedstock variability, and scaleup rules are not yet well-understood. The feedstock-conversion interface is where problematic operations have plagued pioneer biorefineries.[1]

Pilot plants are used in order to bridge the R&D gap between lab and industrial scale processes. The purpose of a pilot plant is to produce process engineering data necessary for scale-up and assess process behavior changes (conversion yields, flow rates, reliability, etc.) from batch processes developed at laboratory scales to continuous equipment and reactors representative of full-scale production. This allows the assessment of technical and process feasibility to mitigate the risk of failure at commercial scale. Two bioprocess pilot plants involved in this work include the Idaho National Laboratory Biomass (INL) Biomass Feedstock National Users Facility (BFNUF)[2] and the National Renewable Energy Laboratory (NREL) Integrated Biorefinery Facility (IBRF).[3]

The main goal of the work presented here was to generate well-curated and publicly-available experimental data using industrially relevant pilot-scale equipment to demonstrate, document, and begin to quantify the effects of biomass resource and feedstock variability on throughput and conversion performance in preprocessing and conversion. Because of this goal, the experiments reported here are qualitatively different than previous work performed. Typically, experiments performed at the pilot scale focused on reproducing results from a laboratory-scale system operated in batch mode to pilot-scale equipment performed in continuous mode. Feedstock variability is usually seen as a known issue to be managed, but not a main focus; however, we focus on understanding process throughput and conversion yield variability due specifically to feedstock variability. The commercial success of next-generation biorefineries lies on the ability to maintain high levels of equipment up-time and conversion efficacy. As-received feedstock was characterized by ash and moisture content, which can serve as proxies for material quality, and the resulting throughput and conversion yields in continuous pilot-plant equipment are analyzed and discussed.

Materials & Methods

A two-factor two-level factorial matrix of conditions (2x2) was designed to probe feedstock moisture content and ash content effects on the process. It was assumed that moisture content at harvest could be used as a proxy for the potential for degradation during storage as moisture often results in microbial self-heating.[4] Ash content was considered a proxy for harvest method and conditions since ash over 5% is generally attributable to contamination with soil.[5] Corn stover (maize plant minus corn kernels) bales were selected with moisture content of 10–20% (low, LM) and 25–40% (high, HM) and ash content of 5–10% (low, LA) and 10–20% (high, HA). In all cases, corn was harvested at 4” cut height and the stover was windrowed and baled in a 3x4x8 ft (0.9x1.2x2.4 m) format and stored in the field without coverings. Sourcing occurred in autumn

2017 within Hamilton, Hardin, Poweshiek, and Story Counties, IA, USA, and all bales were transported to the Iowa State University BioCentury Research Farm (BCRF) and subsequently Idaho National Laboratory (INL). Six bales representing each moisture and ash combination were selected based on bale screening for moisture and ash content using three 51–64 mm diameter cores per bale. For a more thorough characterization, nine 51 mm diameter cores were taken from these six bales using a previously published coring strategy[4,5] and were analyzed for moisture (40ºC for 72 h followed by 107°C) and ash (750°C) according to ASTM D3174-04.

Preprocessing

The INL BFNUF has the ability to store and process 4x4x8 ft (1.2x1.2x2.4 m) bales of biomass through a multi-stage grinding process while collecting online data and samples at different points in the process. Bales were processed at the BFNUF through (1) a Vermeer BG480 bale processer ("grinder 1") using a 3 in (75 mm) screen and then (2) up a drag-chain conveyor to a Bliss hammermill ("grinder 2") ground to pass a 1 in (25 mm) screen, as depicted in Figure 1. After grinder 2, material was transported by screw conveyor into 1 m^3 flexible intermediate bulk containers (FIBC). Samples were collected after first and second stage grinding and analyzed for moisture, ash, carbohydrate composition, particle size distribution, and bulk density. Bale mass, online process time, and motor load/power were recorded for all equipment during processing. Stoppage events were also logged and the root cause(s) evaluated. FIBCs for each moisture/ash conditions were shipped to NREL for pilot-scale conversion testing at the IBRF.

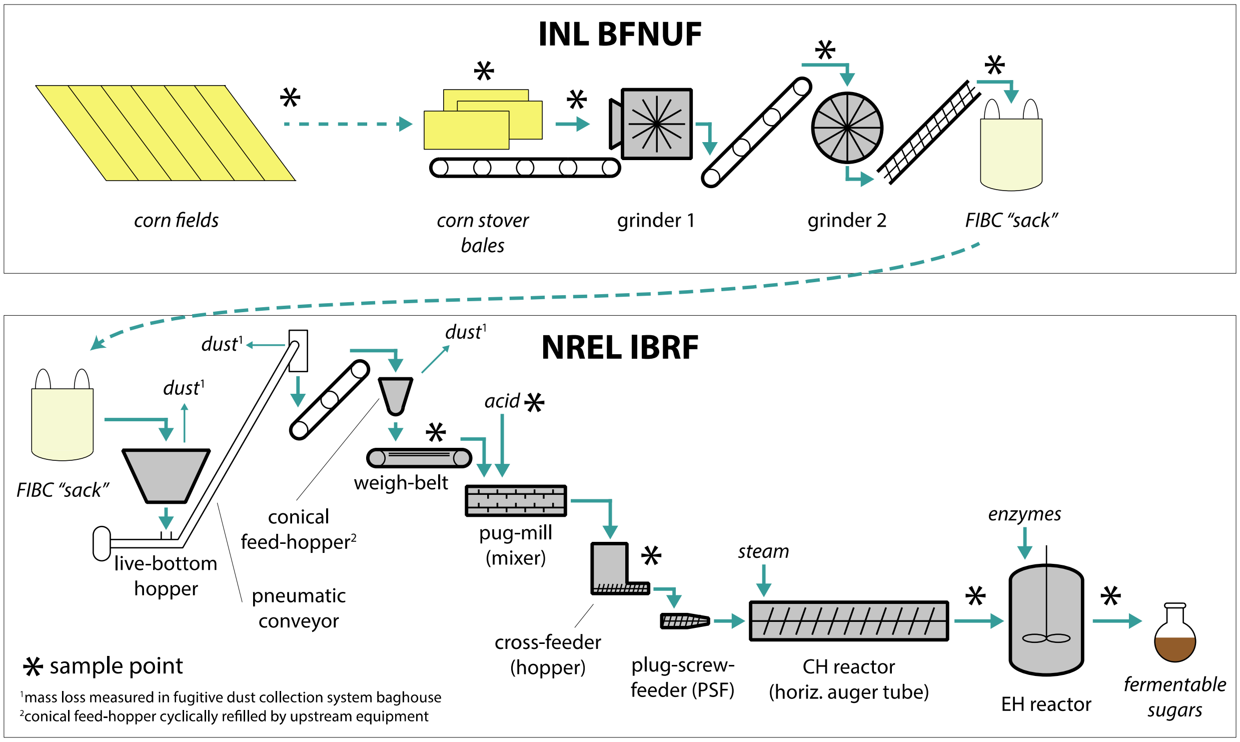

Figure 1. Flow diagram of the preprocessing and conversion process at the INL Biomass Feedstock National Users Facility and the NREL Integrated Bioenergy Research Facility. FIBCs were used to transport feedstock between facilities.

Preprocessing throughput for the two-stage grinding was calculated by dividing the cumulative material processed (dry mass) by the processing time (including downtime); throughput fraction was calculated using this value divided by the equipment nameplate capacity: 5 ton/h (metric tonnes: 4.5 MT/h). Grinder energy was calculated as net real electrical energy consumed per unit feedstock mass (kWh/MT).

Conversion

The four different preprocessed corn stover lots were processed in the NREL IBRF that is designed to convert raw biomass into sugar intermediates that can be further upgraded via fermentation at the 9000-L scale in the facility. The IBRF is depicted in Figure 1, with downstream fermentation and other unit operations omitted here. Dilute-acid chemical hydrolysis (CH, also known as *pretreatment*) was performed on the preprocessed feedstock in a 500 kg/d continuous, horizontal, direct steam injected reactor as previously described.[6] Corn stover was transferred through a pneumatic conveying system to a tubular drag conveyor that served a conical, live-bottom volumetric feed-hopper. The conical feeder and weigh-belt were automated to maintain a constant feedstock mass flow rate, and the volumetric feed-hopper was batch-refilled by upstream equipment approximately every 30 min. A camera was placed over the weigh-belt and JPEG images of feedstock were captured every 30 s by a GoPro HERO 6 camera modified with a rectilinear lens. Subsequently, metered feedstock and diluted sulfuric acid were mixed in a pug-mill (paddled continuous-flow mixer) to achieve 50% w/w total moisture and 33 mg acid/g of bone-dry corn stover—conditions previously identified as generally optimal.[7] A cross-feeder/hopper running at 100% speed (to serve only as a conveyor with no holdup of material) moved wetted feedstock from the pug-mill to a tapered-screw plug-screw-feeder (PSF) that continuously fed into the CH reactor steam pressure zone.

Abrasive wear of the type 316L stainless steel PSF was quantified by the difference in mass of the screw before and after each run. A freshly rebuilt screw was used for each experiment to ensure the flight geometry was consistent at the start of each run. All process data associated with the reactor was collected via an online data acquisition system, including motor loads, flow rates, temperatures, pressures, etc. In order to prevent hazardous steam "blowback" events at the PSF that occur due to failure of the continuously moving biomass plug pressure seal when starved of fresh feedstock, equipment operators manually intervened periodically to clear bridged material there, and these events were documented.

For each of the four runs, the CH reactor was operated for ~48 h continuously. Samples were taken hourly and analyzed as 8 h composites (equally weighted mixes of samples taken at run hours 1–8, 9–16, etc.). Enzymatic hydrolysis of the composite CH reactor product slurries was performed at 60 g working mass in a 125 mL roller bottle apparatus using an 80/20 mixture of Cellic CTEC 3 and HTEC 3 at 20 mg/g total protein loading, pH 5, 50°C, and for 72 h. Sample analyses and yield calculations were performed as previously described.[8–11]

Throughput fraction of the conversion process was calculated by taking the product of the time-series weigh-belt mass flow rate (automation records) and feedstock total solids fractions (8-h composites) and dividing by the bone-dry nameplate capacity of 500 kg/d. The EH process was assumed negligible in this study in terms of reliability since it is a batch process even at production-scale and is operating at mild conditions.[12]

Results & Discussion

Preprocessing Performance

The average moisture and ash mass fractions for each six-bale run are shown in Figure 2. The moisture content for the two low-moisture conditions was in the desired range of 10–20% but the high-moisture conditions were much lower in moisture than indicated by the initial screening performed at the BCRF prior to shipping the bales from Iowa to Idaho. Nonetheless, the bales from the HA-HM condition showed evidence of degradation due to self-heating on the bale exterior. In addition, browning as a result of self-heating was visible on the bale exterior for bales screened from all four fields in this study. This is caused when high moisture stimulates microbial activity within the bales that then generates heat and causes both loss of moisture and physical and chemical alteration of the biomass materials.[13] Interestingly, some of the high-ash but *low-moisture* bales selected also showed evidence of self-heating—autumn 2017 had wetter-than-usual weather in the source counties and is indicative of how wet conditions during the harvest can impact bale properties. The two sets of high-moisture bales likely had higher moisture content when harvested but lost moisture during the 6-month storage time between harvest and processing. The low ash and high ash levels met the criteria that had been set of 5–10% for low ash and 10–15% for high ash.

System throughput was highest for the LA-LM material at 72% of the nominal 5 ton/h capacity. Throughput dropped for the remaining three conditions with the HA-LM at 59%, HA-HM at 40% and LA-HM at 44% of nominal capacity. At first glance, this seems to demonstrate that lower moisture bales are more easily processed than bales with higher moisture. Given that the LA-HM bales had an average moisture of 16% when processed compared to 13% and 18% for the low moisture conditions; it might be expected to have a similar throughput. However, LA-HM throughput was the same as for the HA-HM bales. As mentioned above, the LA-HM bales showed evidence of self-heating after harvest and the measured moisture before being transported from Iowa to Idaho was much higher. Thus, it appears that *moisture history* is an important parameter to consider in addition to *moisture at the time of processing*.

For the first stage bale grinding, the LA-LM material had a considerably lower grinder energy requirement than the other three conditions indicating that this material was easier to process. LA-LM was also the only condition that did not have any stoppages due to plugging or overheating (Table S1). Interestingly for the second stage grinder, these differences appear to have disappeared with the grinder energies not statistically significantly different for each condition ($p \leq 0.05$). This is likely due to the homogenizing effect of reducing corn stover from baled stalks to ~75 mm (nominal) particles.

Finally, the D10 calculated from the particle size distribution appear different between the two HA and two LA materials. The D10 metric is the value for which 10% (w/w) of the sample has a particle size less than or equal to the value reported and is representative of the fines present. The two HA conditions had statistically lower D10 values ($p \leq 0.05$) than the LA conditions and is likely because small ash particles are enriched in the fines.

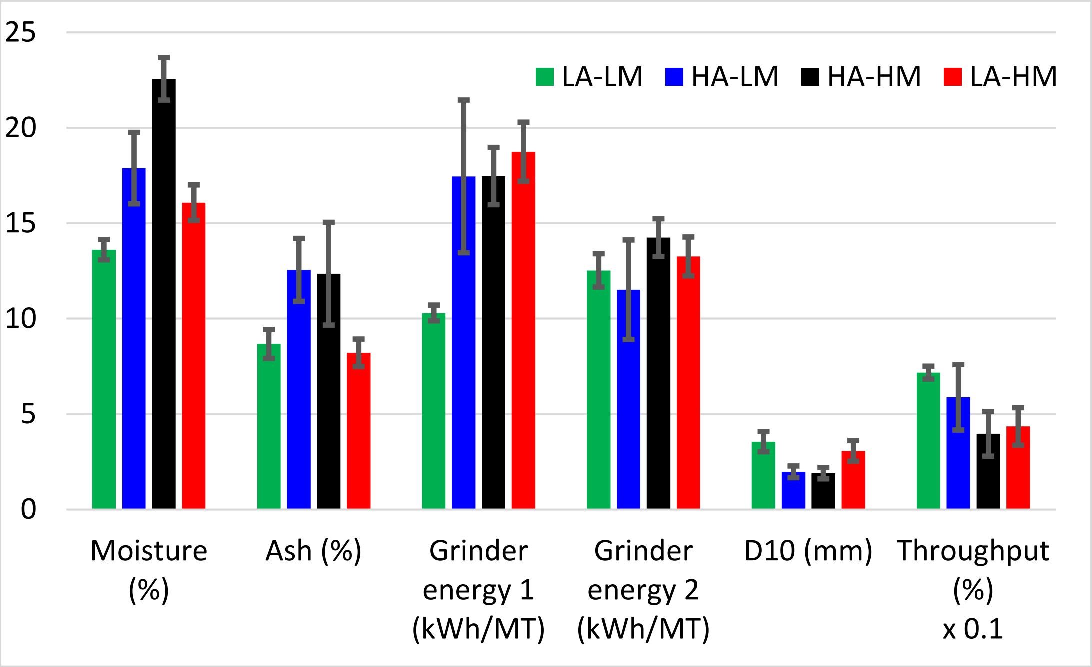

Figure 2. Run average moisture, ash, grinder energies, D10 particle size, and throughput for the four corn stover materials processed at the INL BFNUF. Grinder energy and throughput are on a dry-mass basis. Error bars represent 95% confidence intervals.

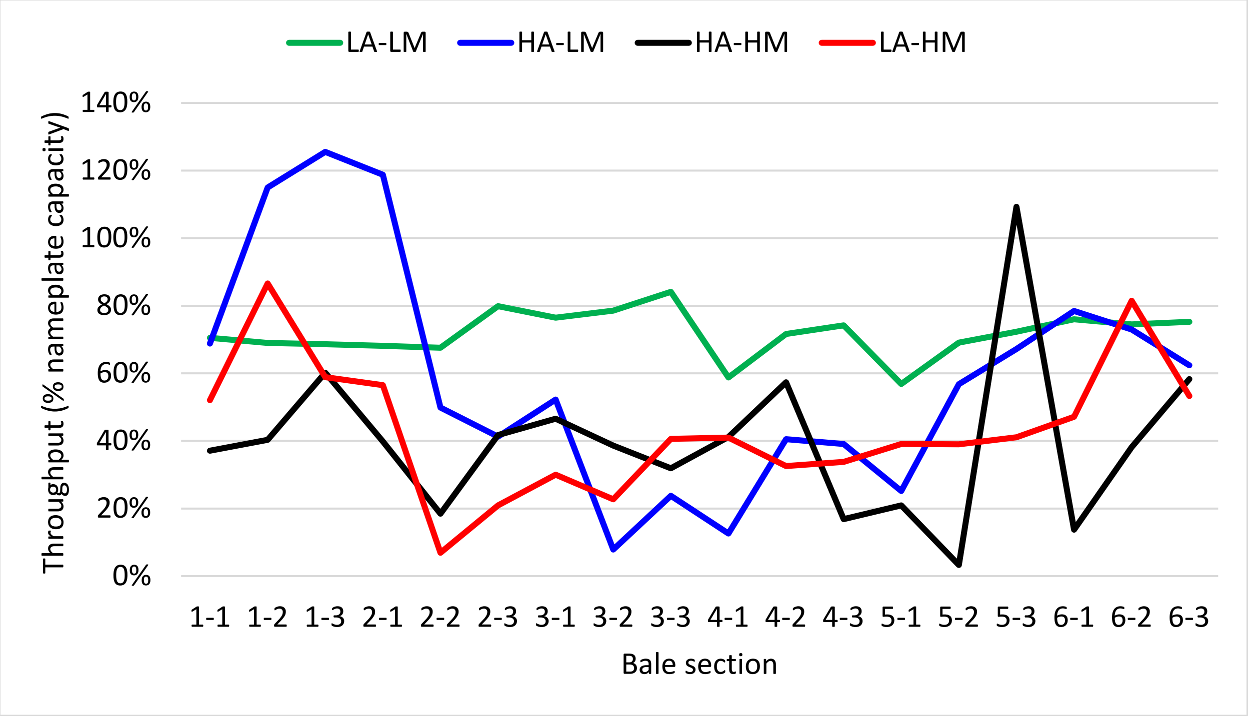

Figure 3. System throughput for each set of bale conditions. Each of six bales is broken up into three sections, and the throughput and moisture were calculated for each section. Throughput is on a dry-mass basis.

In Figure 3, the temporal throughput of the LA-LM material was very steady throughout the entire six-bale run, implying that these bales were fairly consistent in their properties. The other three runs were much more variable across bale sections. Throughput appears to be inversely proportional to moisture, particularly in the HA-LM case (see Figure S1 for moisture plotted vs. bale section). The dramatic increase and then decrease in throughput observed during the HA-HM case for bale 5 (almost a 10x difference) is an artifact of a plugging event. The large increase in throughput occurred right after the screw conveyor plugged and was subsequently cleared. The throughput increased momentarily but then was slowed almost immediately as the screw conveyor plugged again (6-1).

Hydrolysis Conversion Performance

The dilute-acid chemical hydrolysis reactor has two duties: (1) hydrolyze hemicellulose to fermentable sugars, and (2) prepare material for effective enzymatic hydrolysis of remaining structural carbohydrates into fermentable sugars. We used two different metrics to assess the results of the chemical hydrolysis runs. First, we calculated the carbohydrate component molar yields following CH, as plotted in Figure 4. Second, we performed EH on the same samples and calculated the overall monomeric sugar yield, which includes total monomeric sugar production over CH and EH, which represents the overall sugar production process. Average absolute yields (kg total sugar produced vs kg dry feedstock—coupling molar yield with feedstock carbohydrate content) of CH and CH+EH for the four feedstock types are plotted in Figure 6a.

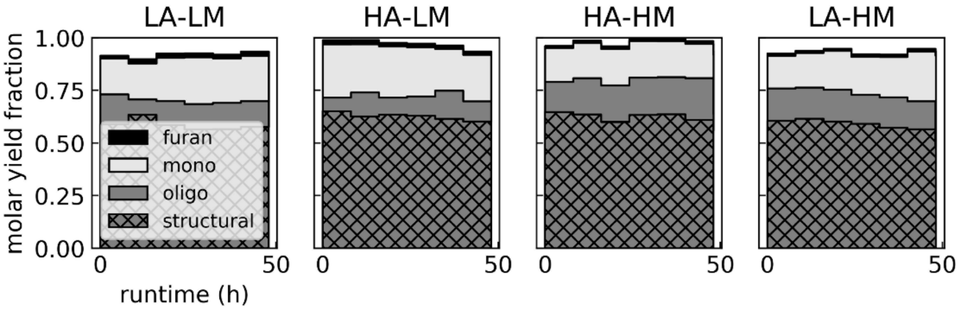

Figure 4. Chemical hydrolysis yields (molar fractions of original structural carbohydrate) versus time for the four feedstocks, assessed as 8-h composites of 1-h samples. Species are broken out into four categories: furans (furfural and HMF), monomeric sugars, oligomeric sugars, and remaining structural carbohydrates. The sum of individual glucan-, xylan-, arabinan-, and galactan-based species is reported.

The overall mole-closures for structural carbohydrate species was >90%, and systematic losses are attributed to further degradation of the furans, and also some of the monomeric sugars directly, into other condensation products that are not readily quantified.[14] We did not see any significant differences ($p \leq 0.05$) between absolute conversion yields with the exception of the HA-HM material that appears to have a slightly reduced chemical hydrolysis yield. Overall, there was no statistical difference between the four feedstock types in terms of overall feedstock-to-sugar conversion performance (CH+EH). However, we did not examine the fermentation performance of the four different materials and therefore we are hesitant to draw any firm conclusions about differences among the four materials in the absence of fermentation data; there have been multiple reports where non-sugar constituents in enzymatic hydrolysates affect fermentation performance.[15,16]

To probe possible causes of the small yield variability within the distinct runs as observed in Figure 4, the monomeric sugar yields were compared with both feedstock ash content and moisture content, as measured just prior to wetting with acid and entering the CH reactor; however, no connection was observed (data not shown). Investigating further, there was a significant correlation ($p=2\times10^{-5}$) between chemical hydrolysis yield and the measured biomass slurry liquor pH exiting the CH reactor, with a variation of 8% molar monomer yield between the measured extremes. The measured slurry pH varied between 1.7 and 2.3, and this change in aqueous acid concentration on the order of ~4x likely impacted the conversion yields by altering the hydrolysis kinetics rates.[17] Feedstock and acid flow rates were steady, and the source of pH variation is uncertain. A possible explanation may lie within a combination of effects including variations in (1) feedstock moisture at the CH reactor, (2) other feedstock properties—such as organic acid content—altered by moisture-induced degradation during storage, and (3) reactor steam injection rate and subsequent water condensation and dilution of acid. Advanced process control strategies, such as online moisture sensors providing closed-loop feedback, could allow for tighter pH control and thus reduce yield variation in the small ranges observed here.

Hydrolysis Equipment Wear

Long-term observations of the chemical hydrolysis reactor used in this study have revealed that mechanical wear of the PSF's screw flights is a major issue requiring periodic overhaul/replacement of the screw. However, until now, we have not systematically examined this issue. The PSF experiences high mechanical force and wear since it is compressing the feedstock to form a pressure-tight plug that continuously extrudes into the reactor space. Historic (but anecdotal) experience at this pilot-plant indicates screw replacement or overhaul is necessary approximately every 150–400 h of runtime and is influenced by the feedstock ash content. The tapered screw begins wearing at the tip (outlet end) and as metal is removed, the wear advances backwards along the screw axis while feeding capacity can become erratic and motor load slowly increases—this effect is observed in Figure 7. It should be noted that no measured mechanical wear has been observed on any other parts of the reactor system.

Figure 5 compares screw wear rates with feedstock ash content and amount of fines lost to dust mitigation during pneumatic conveyance. In general, the high-ash feedstocks did accelerate wear compared to the low-ash feedstocks as expected, and higher feedstock loss rates as dust also correlated with ash content. The HA-HM feedstock appeared to accelerate wear compared with the HA-LM feedstock, which is possibly due to other feedstock characteristics that are altered when stored wet.

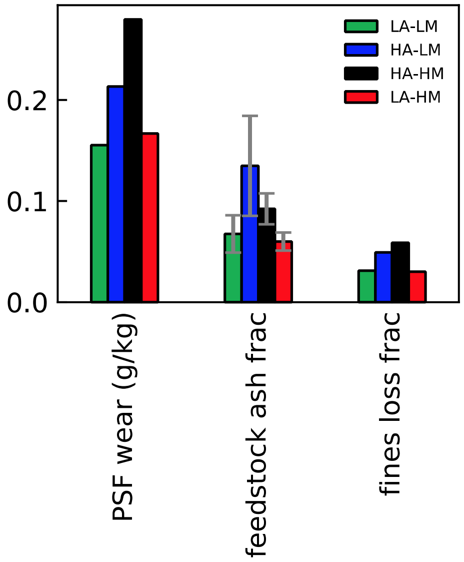

Figure 5. Plug-screw-feeder (PSF) wear rates (g metal lost per bone-dry kg of corn stover fed) versus feedstock ash mass-fraction and mass-fraction of total feedstock lost as fines to dust collection, sampled just prior to mixing with acid at chemical hydrolysis reactor inlet.

Hydrolysis System Reliability and Throughput

The equipment associated with the hydrolysis reactor was assessed for reliability and feeding performance, both quantified by fraction of actual throughput versus nameplate capacity, operator manual intervention frequency, and motor loads while targeting a 500 bone-dry kg/d production rate. Five key pieces of equipment were observed: (1) conical feed-hopper, (2) weigh-belt, (3) pug-mill, (4) cross-feeder, and (5) PSF. Other motor loads and equipment function, such as upstream bulk hoppers/conveyors and horizontal auger conveyor screws within the reactor, were also monitored, but variation was not observed.

Operator interventions were necessary to avoid reactor shutdowns caused by feedstock starvation at the PSF and subsequent hazardous escape of steam. Interventions were almost exclusively necessary for clearing bridged feedstock at the PSF inlet. We were hopeful that logging these events would provide meaningful information to compare throughput performance among the different runs but after close inspection of these data we determined they were too subjective (e.g., some operators were much more inclined to intervene than others regardless of the issue) and also may not represent larger scale performance. However, some qualitative observations were striking. Although supposedly the “cleanest” feedstock and with most favorable preprocessing behavior, CH reactor operators described the LA-LM material as very stringy compared with the other three feedstocks and occasionally was composed of large-dimension “birds nest” assemblies that were difficult to feed.

Though the LA-LM material had the highest throughput during preprocessing, it was the most difficult to process during conversion, and ultimately required reducing the mass flowrate of the biomass feedstocks to approximately 90% capacity to operate (graphically presented in Figure S2). Figure 7 presents relative comparison of feed handling equipment motor loads, which also indicates the LA-LM material was not the easiest to use—instead, the HA-LM material exhibited the smoothest operation. We hypothesize that the LA-LM material was composed of a higher fraction of light and stringy fibers (difficult to quantify with sieving-type particle size measurement) that were unaffected by the hammers in grinder 2 and also passed through the grinder rejection screen without further size-reduction. Frequent trouble automatically maintaining the weigh-belt mass rate at the setpoint was also observed—results of this behavior are quantified as the mean throughput fractions of nameplate in Figure 6(b).

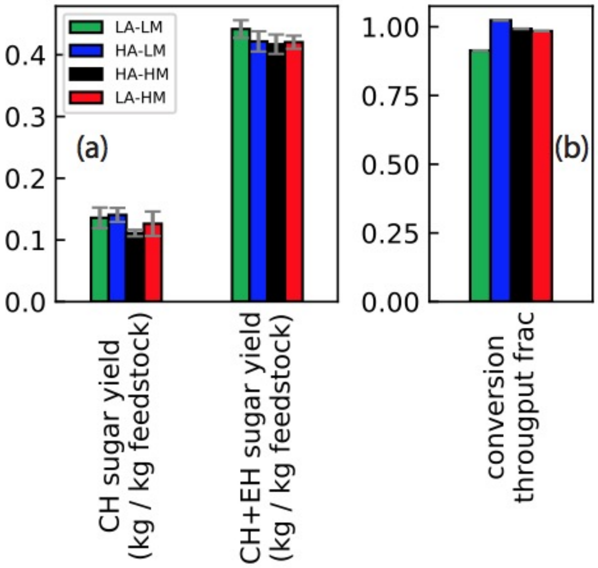

Figure 6. (a) Monomeric sugar yields (kg total of xylose, glucose, arabinose, and galactose per kg dry feedstock) plotted for both chemical hydrolysis alone and combination with subsequent enzymatic hydrolysis. 95% confidence intervals reported. (b) Mean throughput fraction of CH conversion reactor nameplate capacity.

The HA-LM material offered the most favorable operational stability at the weigh-belt. Analysis of the cross-feeder motor loads (percent max. available torque) shown in Fig. 7 indicates the HA-LM feedstock also resulted in the lowest motor load standard deviation at 0.9 versus 2.0, 2,7, and 2.0 respectively for the LA-LM, HA-HM, and LA-HM feedstocks—this indicates a smoother load experienced at the hopper by this material. A possible explanation is that high-ash material with greater content of fines results in a lower *volumetric* rate for the constant mass-rate and less difficulties in both conveyance and gravity-assisted hopper flow. Material with low moisture resulted in smoother operation of CH reactor conveyors/hoppers than high-moisture and is likely caused by difficulties milling the HM material during preprocessing.

While operating the five feed handling units described above, a regular, cyclic phenomenon was observed in weigh-belt speed and downstream conveyor motor loads. We observed motor loads correlated with the conical feed-hopper refill events that occurred approximately every 30 min and the low-frequency speed and load spikes seen in Figure 7 are centered on feed-hopper refill events (not shown for clarity).

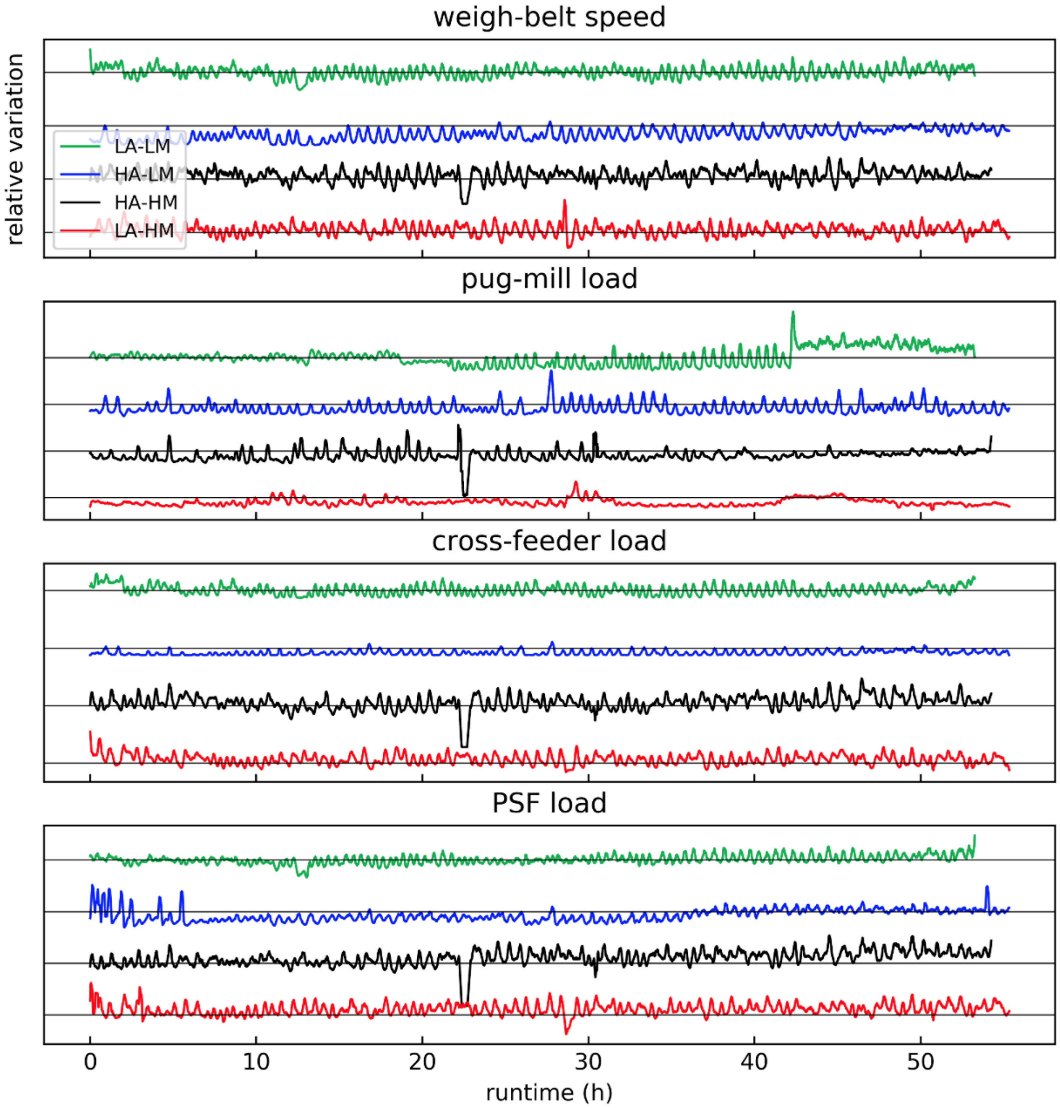

Figure 7. Conversion reactor upstream feeding equipment speeds and motor loads. Plotted offset for each feedstock for clarity. Horizontal black lines are the median values for the LA-LM feedstock for direct comparison between feedstocks.

Interviews with reactor operators indicate that “fluffier”, “stringier” dry feedstock was metered out onto the weigh-belt as the upstream conical hopper level approached the empty level and refill was initiated. We hypothesize that the feed-hopper was artificially classifying particle size during dispensing operations between refills, assisted by the bridge-breaker agitator slowly rotating within. Lower-density feedstock floated to the top of the feed-hopper and only emerged when the level was sufficiently low—indeed, motor load upsets began just before the feed-hopper was refilled and were reduced when fresh feedstock began flowing again.

The cyclic phenomenon demonstrated in Fig. 7 and described above may be considered simply as an artifact of pilot-scale equipment, and theoretically not a problem for deployment. Caution must be exercised here, as although an ideal plant would have truly continuous feeding from the front-end to reactor and avoid cyclic operation/refills of hoppers, our observations indicate that (1) potential for feedstock classification/segregation exists in hoppers, especially with bridge-breakers, and (2) feedstock particle size, density, and other qualities significantly affect conveyor and hopper performance and required motor load/torque in a manner that we cannot fully explain or predict. The pilot-plant’s CH reactor motor *headspace*—or additional available torque—is high compared to the typical load requirements to accommodate extremes; however, at demonstration-scale and beyond where tighter tolerances are required for efficiency, the fraction of available headspace will be smaller and may not allow sufficient available torque to continue operation if large variations in feedstock quality are encountered.

High-frequency feedstock sampling and subsequent particle size measurement would quantify this cyclic behavior described above but is prohibitively laborious. Instead, a visual record could be used to quantify feedstock and make decisions. Image analysis using machine vision is a popular growing practice both in commerce and industry,[18] and we believe there is the potential to measure feedstock particle quality in real-time and make automatic adjustments to the process to avoid upsets. Indeed, comparing images at the weigh-belt when motor loads are *normal* and when loads are spiking results in qualitative differences, as compared in Figure 8: on average, coarser and longer-aspect ratio material is seen during feed-hopper refills, and these images also show more shadows and texture. While these results are encouraging, we recognize that further development is required to objectively characterize feedstock quality attributes using on-line techniques, such as with cameras and machine-vision models.

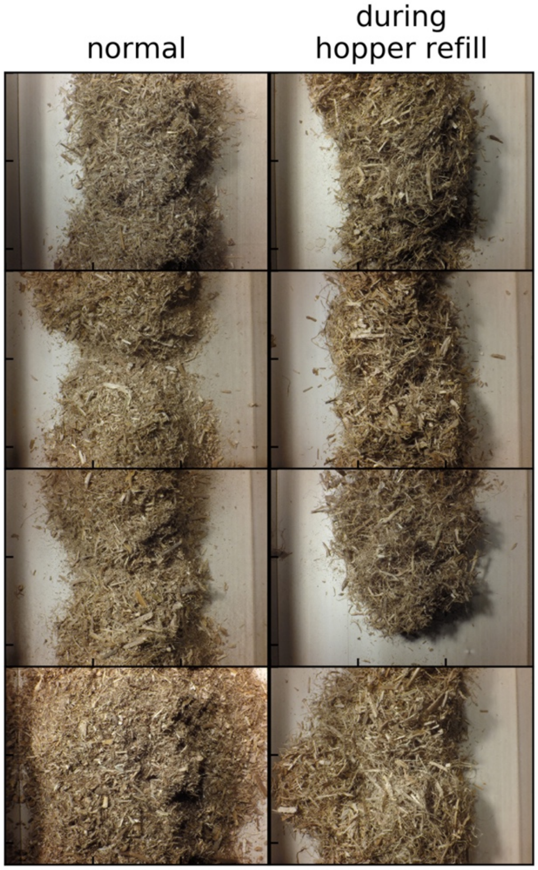

Figure 8. Comparison of feedstock images taken on the weigh-belt during normal operation and during conical-feeder refill events when downstream equipment motor loads spiked.

Overall System Throughput

Results have been discussed for the two separate operations at the BFNUF and IBRF on the same feedstock due to the special nature of equipment available at these facilities. In a scaled-up production biorefinery, the preprocessing and conversion operations would take place at the same facility. Industrially, these operations would have equipment of same/similar nameplate capacities for continuous, coupled operation, and comparison of the preprocessing throughput and conversion throughput on fractions of nameplate capacities (Figures 2 and 6b) allows assessment of theoretical *overall* system throughput. Here, the minimum value in the entire processing train represents the true theoretical coupled throughput that results due to a bottleneck at that lowest-throughput step. In all studied cases here, the preprocessing constrained the throughput due to difficulties with the raw feedstock, and the projected overall throughput of a field-to-sugar process are those illustrated by Figure 2.

Conclusions

In previous work, pilot-plant research has been primarily focused on optimizing yield—that is maximizing process performance without considering the operability of equipment and the implications on scale-up. Here, data is presented for a more realistic operating mode where processing is attempted at the set nameplate capacity of equipment over a long period of time at pilot-scale. Significant reductions in overall throughput were observed with reductions in feed rate necessary to keep preprocessing equipment running, and several instances of downtime occurred, nonetheless. Conversion yields to soluble sugars were not significantly affected by feedstock variation.

Although we could offer recommendations on alternative milling methods and conversion methods/chemistries that would possibly increase plant throughput, we cannot do so in a quantitative manner here that could be scaled and applied broadly in industry. Instead, we recommend further study on the intrinsic material properties of feedstocks and their causal effects on equipment performance using a first-principles-based approach. Although ash and moisture content of feedstock upon arrival at the processing plant gate serve as good proxies, measured material attributes and models that predict the behavior of those materials will likely yield better equipment design and at the very least, a means to grade the monetary value of feedstock based on its processability and its ultimate economic value.

ASSOCIATED CONTENT

Supporting Information. The supporting Information is available free of charge http://pubs.acs.org/XXXXXX

Supplemental preprocessing results and conversion results (PDF)

Corn stover preprocessing and characterization data is publicly available at the Bioenergy Feedstock Library (http://bioenergylibrary.inl.gov)

AUTHOR INFORMATION

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

CH, chemical hydrolysis; EH, enzymatic hydrolysis; LA, low-ash; HA, high-ash; LM, low-moisture; HM, high-moisture; MT, metric tonne.

REFERENCES

1 Biorefinery Optimization Workshop Summary Report. U.S. Department of Energy Report: DOE/EE-1514, 2016; pp 1–66. https://www.energy.gov/sites/prod/files/2017/02/f34/biorefinery_optimization_workshop_summary_report.pdf (accessed Nov 12, 2017).

2 Biomass Feedstock National User Facility Process Development Unit. https://bfnuf.inl.gov/SitePages/Process%20Development%20Unit.aspx (accessed Oct 15, 2019).

3 Integrated Biorefinery Research Facility. https://www.nrel.gov/bioenergy/ibrf.html (accessed Oct 15, 2019).

4 Smith, W. A., Bonner, I. J., Kenney, K. L., & Wendt, L. M. Practical considerations of moisture in baled biomass feedstocks. *Biofuels.* **2013**, *4*, 95–110. DOI:10.4155/bfs.12.74

5 Shinners, K. J., Bennett, R. G., & Hoffman, D. S. Single-and two-pass corn grain and stover harvesting. *Trans. ASABE.* **2012**, *55*(2), 341–350. DOI:10.13031/2013.41372

6 Sievers, D. A. & Stickel, J. J. Modeling residence-time distribution in horizontal screw hydrolysis reactors. *Chem. Eng. Sci.* **2018**, *175*, 396–404. DOI:10.1016/j.ces.2017.10.012

7 Shekiro III, J., Kuhn, E. M., Nagle, N. J., Tucker, M. P., Elander, R. T., & Schell, D. J. Characterization of pilot-scale dilute acid pretreatment performance using deacetylated corn stover. *Biotechnol. Biofuels*. **2014**, *7*, 23, 1–10. DOI:10.1186/1754-6834-7-23

8 Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D. Determination of Sugars, Byproducts, and Degradation Products in Liquid Fraction Process Samples. National Renewable Energy Laboratory Analytical Procedure: NREL/TP-510-42623, 2006. https://www.nrel.gov/docs/gen/fy08/42623.pdf (accessed Apr 20, 2018).

9 Sluiter, A.; Hyman, D.; Payne, C.; Wolfe, J. Determination of Insoluble Solids in Pretreated Biomass Material. National Renewable Energy Laboratory Analytical Procedure: NREL/TP-510-42627, 2008. https://www.nrel.gov/docs/gen/fy08/42627.pdf (accessed Apr 20, 2018).

10 McMillan, J. D.; Jennings, E. W.; Mohagheghi, A.; Zuccarello, M. Comparative performance of precommercial cellulases hydrolyzing pretreated corn stover. *Biotechnol. Biofuels,* **2011**, *4*, 29, 1–17. DOI :10.1186/1754-6834-4-29

11 Chen, X.; Tao, L.; Shekiro, J.; Mohaghaghi, A.; Decker, S.; Wang, W.; Smith, H.; Park, S.; Himmel, M. E.; Tucker, M. Improved ethanol yield and reduced Minimum Ethanol Selling Price (MESP) by modifying low severity dilute acid pretreatment with deacetylation and mechanical refining. *Biotechnol. Biofuels.* **2012**, *5*, 60, 1–10. DOI:10.1186/1754-6834-5-60

12 Davis, R., Tao, L., Scarlata, C., Tan, E.C.D., Ross, J., Lukas, J., & Sexton, D. Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbons: Dilute-Acid and Enzymatic Deconstruction of Biomass to Sugars and Catalytic

Conversion of Sugars to Hydrocarbons. National Renewable Energy Laboratory: NREL/TP-5100-62498, 2015. DOI:10.2172/1107470

13 Wendt, L. M., Bonner, I. J., Hoover, A. N., Emerson, R. M., & Smith, W. A. Influence of airflow on laboratory storage of high moisture corn stover. *Bioenergy Res*. **2014**, *7*(4), 1212–1222. DOI:10.1007/s12155-014-9455-3

14 Schell, D. J., Farmer, J., Newman, M., McMillan, J. D. Dilute-sulfuric acid pretreatment of corn stover in pilot-scale reactor. *Appl. Biochem. Biotechnol.* **2003**, *105*(1-3), 69–85. DOI:10.1385/ABAB:105:1-3:69

15 Pienkos, P. T., & Zhang, M. Role of pretreatment and conditioning processes on toxicity of lignocellulosic biomass hydrolysates. *Cellulose.* **2009**, 16(4), 743–762. DOI:10.1007/s10570-009-9309-x

16 Chen, X., Shekiro, J., Franden, M. A., Wang, W., Zhang, M., Kuhn, E., Johnson, D. K., & Tucker, M. P. The impacts of deacetylation prior to dilute acid pretreatment on the bioethanol process. *Biotechnol. Biofuels.* **2012**, *5*, 8, 1–14. DOI:10.1186/1754-6834-5-8

17 Esteghlalian, A., Hashimoto, A. G., Fenske, J. J., Penner, M. H. Modeling and optimization of the dilute-sulfuric-acid pretreatment of corn stover, poplar and switchgrass. *Bioresour. Technol.* **1997**, *59*(2-3), 129–136. DOI:10.1016/S0960-8524(97)81606-9

18 Yin, S., Ding, S. X., Xie, X., & Luo, H. A review on basic data-driven approaches for industrial process monitoring. *IEEE Trans. Ind. Electron.* **2014**, *61*(11), 6418-6428. DOI:10.1109/TIE.2014.2301773

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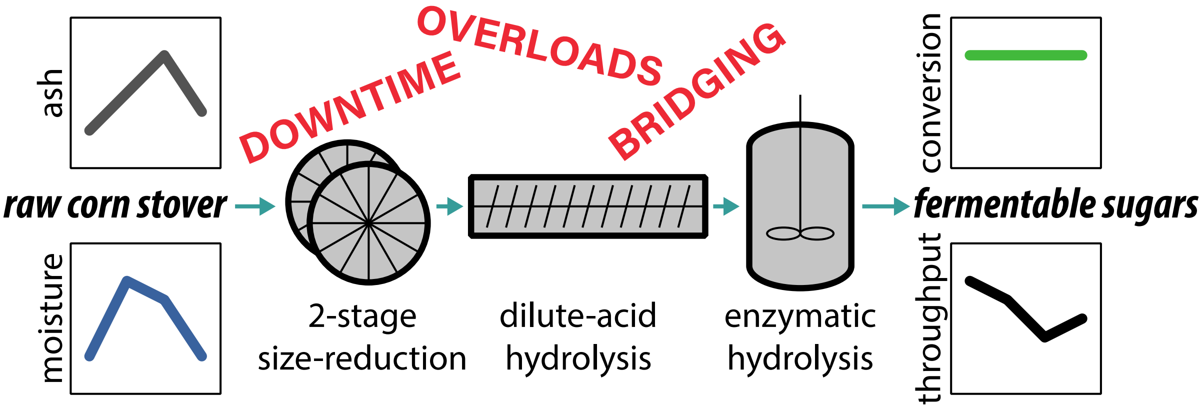

SYNOPSIS: We explore effects of feedstock variability on reliable operation and consistent conversion yield, which are essential for successful deployment of next-generation biorefineries.