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Screening of alkali assisted storage conditions to define the operational window of deacetylation within storage systems in the bioenergy supply chain

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Abstract

Overcoming biomass heterogeneity and associated recalcitrance to thermal, chemical, and enzymatic depolymerization is a necessary but challenging aspect of valorizing lignocellulosic biomass to fuels and chemicals. This study explores how this recalcitrance can be reduced during the supply chain unit operation of storage, which is required for seasonally harvested agricultural residues to maintain constant throughput at a biorefinery. In this work partial alkali pretreatment was performed just prior to corn stover entering storage, which had the benefit of providing a high pH environment entering storage such that soluble sugars were preserved as well as saponifying acetyl groups in hemicellulose. This work investigated a range of viable conditions where saponification and preservation occur simultaneously by varying the moisture content (40% and 60%) and concentrations of sodium hydroxide (low and high) during aerobic and anaerobic storage. Anaerobic conditions preserved overall dry matter below 5% in three scenarios evaluated, and the highest alkali loading solubilized up to 15% lignin, 18% xylan, and 50% of acetate meanwhile doubling the extractable components. Scanning electron microscopy images highlighted potential physical impacts including cell wall disruption near vascular bundles, pitting within parenchyma cells and cell wall distortion. Techno-economic assessment indicated that this storage approach and associated logistics system is economically competitive with a conventional approach using low-moisture bales.

1.0 Introduction

Corn stover has the unique advantage over other biomass crops of being a widely produced, commercially available feedstock for bioenergy conversion, and yet it and other lignocellulosic crops are inherently a challenging feedstock for conversion due to the molecular and physical complexity of the lignocellulosic matrix. Catalysts for depolymerization can include heat, caustic chemicals, and enzymes, and a combination of these approaches is generally used in low-temperature conversion approaches that utilize fermentation to produce fuels or chemicals. The residence time of these treatments is generally on the order of hours in order to minimize capital equipment costs at a biorefinery. However, additional opportunities for residence times become an opportunity for investigation when the entire feedstock logistics supply chain for agricultural residues, such as corn stover, are considered. For example, storage can be on the order of weeks to months. Corn stover is harvested within a seasonal window, and yet a biorefinery must have a consistent feedstock supply to maximize use of capital investment and ensure consistent fuel production. Thus, storage of biomass feedstocks must be accounted for to reduce the risk of biorefinery down time due to lack of feedstock. The focus of this study is to investigate approaches to reduce recalcitrance to conversion within storage operations in the supply chain.

Long term storage operations for herbaceous biomass typically are either performed in aerobic conditions using stacked bales or in the anaerobic approach of silage. Field-side storage of bale stacks is commonly utilized in feedstock logistics supply designs due to its low cost and to facilitate transportation to the biorefinery[1, 2]. Moisture content of less than 15% wet basis (w.b.) is required to reduce the risk of loss to microbial degradation[3]. However, significant degradation has been documented due to a number of factors including entering storage at high moisture contents[4, 5], wicking moisture from the ground[6], or from moisture condensation under tarps[6]. The alternative approach of using wet, anaerobic storage has been documented for bioenergy systems[7, 8]. These systems leverage forage chopping harvest and collection approaches to reduce particle size and facilitate increased packing density in compacted storage. High moisture contents (40-70%, w.b.) facilitate both mechanical oxygen removal by occupying void space in biomass pores and enable fermentation of soluble carbohydrates to organic acids. The resulting low pH environment has a stabilizing effect on biomass and has also shown promise to reduce biomass recalcitrance[9, 10]. However, designs using ensiled storage for agricultural residues have been shown to be 10% more costly than their baled counterparts primarily due to low density of chopped biomass in transportation[11]. However, storage and transportation in silage tubes has been documented to improve the economics by 24% compared to a baled scenario[12]. Therefore, anaerobic storage can be an economically viable approach to consider for opportunities to reduce biomass recalcitrance to downstream preprocessing.

Deacetylation is a frequently used pretreatment method for biochemical conversion of lignocellulosic fuels[13, 14]. This pretreatment chemistry has a dual purpose in saponifying acetyl and glycosidic bonds in hemicellulose and saponifying ester linkages between lignin and hemicellulose. Alkali extraction is followed by mechanical milling to improve surface area for enzymatic hydrolysis to monomerize carbohydrates[14]. This method allows conversion of both a carbohydrate stream as well as the lignin stream, resulting in multiple product streams and additional co-products beyond just fuels. Current challenges in this approach include problems with alkali impregnation due to the short residence time, alkali neutralization due to saponification of ferulic acid and acetyl groups, and additional alkali requirements for more recalcitrant biomass. 4.8-7 wt% sodium hydroxide is currently added to the biomass during deacetylation to accomplish all desired impacts within just a 2-hour window[13, 14]. Long term storage has the potential to address these challenges with the range of residence times that are possible in this unit operation. Sodium hydroxide addition to straws has been shown to increase digestibility for rumen[15, 16]. Others have shown that sodium hydroxide loading combined with anaerobic storage increased glucose and xylose yields after 5 days of storage, yet high dry matter loss after 10 days due to unstable storage conditions eliminated any further gains in digestibility[17]. However, no published studies exist to our knowledge that explore how treatment conditions in mechanical preprocessing and deacetylation could be reduced as a result of longer durations associated with anaerobic storage. The aim of this work was to assess if alkali could be added to corn stover prior to storage for the dual purpose of preserving biomass from unwanted microbial degradation along with providing a longer reaction time that can aid in depolymerization to reduce biomass recalcitrance. This approach is a process intensification strategy that has significant promise to impact how biorefineries manage their feedstock supply chain.

This work focused on designing a supply system that can facilitate sodium hydroxide treatment during storage to increase alkali impregnation prior to deacetylation at the biorefinery. Storage performance results are also reported for two concentrations of alkali-based treatment for 4 weeks at varied moisture content (40 and 60%, w.b.) in aerobic and anaerobic conditions. Characterization of dry matter preservation and extractable material was performed on all samples in order to select samples for full compositional analysis. Full compositional characterization of the anaerobic conditions enabled the assessment of changes in extractives, carbohydrates, lignin, and acetate. Integration of this approach into the feedstock logistics supply chain was explored to understand the potential for cost savings with this approach. A logistics system was designed that included partial alkali pretreatment prior to corn stover entering storage providing a high pH environment entering storage to (1) preserve soluble sugars, (2) saponify the ester linkages between lignin and hemicellulose and (3) to weaken the hydrogen bonding network between cellulose and hemicellulose.

2.0 Methods and Materials

2.1 Corn Stover Source and Storage Procedures

Corn stover was sourced from Boone, IA using a two-pass harvest and collection configuration following grain harvest; this biomass is available as reference material through Biomass Feedstock National User Facility Library at Idaho National Laboratory. Corn stover was knife milled using a Wiley Mill Model 4 (Thomas Scientific, Swedesboro, NJ) to pass through a 6 mm screen to prepare it for storage experimentation. Four moisture and alkali concentrations were utilized as described in Table 1 along with controls for 10 experimental conditions each performed in triplicate.

Concentrated NaOH (50 w/w%, Sigma Aldrich) was added to water for dilution, and then the mixture was applied to the corn stover such that a final moisture content of 40% or 60% w.b. was achieved alongside an alkali loading of either 0.5 % or 2.4% (w/w dry basis [d.b.] biomass). Concentrations were chosen to reflect overall alkali reduction of one tenth and one half of what has been reported previously[14, 18]. Aerobic storage was conducted in triplicate 250 ml flasks containing 20 g biomass d.b. with a loose fitted cap to prevent excessive moisture loss.

Anaerobic storage conditions were formed using 125 mL glass reactors based on a configuration reported previously using 0.1M NaOH loading at 8% solids content[19]. Alkali-treated corn stover was manually compacted in jars and sealed with airtight lids fitted with an S-shaped fermentation airlock to limit exchange with the atmosphere. Jars were purged with nitrogen immediately after sealing to rapidly establish an anaerobic atmosphere that would be likely observed in a large-scale silage pile that was rapidly compacted and sealed[20]. All samples were stored at room temperature in the dark. After four weeks of storage the corn stover was mixed thoroughly to create representative subsamples and assessed for moisture and mass changes. Dry matter loss was calculated gravimetrically:

Equation 1

Replicates for each storage condition (treatment, moisture content, alkali loading) were combined into a single composite sample for follow-on analysis, and a subsample was size reduced to pass through a 2 mm screen using a Thomas Model 4 Wiley® Mill (Thomas Scientific, Swedesboro, NJ) to prepare for compositional analysis.

2.2 Compositional Analysis

Corn stover samples were assessed for gross compositional changes using methods establish by the National Renewable Energy Laboratory (NREL) according to Laboratory Analysis Procedures (LAPs)[21, 22]. Total extractives were quantified with a 100°C water and subsequent ethanol extraction accomplished using an automated solvent extractor ASE 350 (Dionex, Sunnyvale, CA)[23]. Further analysis of select samples involved a two-stage acid hydrolysis to solubilize structural carbohydrates from the lignin and ash stream[24]. Carbohydrate monomers glucose, xylose, arabinan, and galactan were quantified using high performance liquid chromatography (HPLC) with a refractive index (RI) detector (Agilent, Santa Clara, CA) and

Aminex HPX 87P column (Bio-Rad, 300 x 7.8 mm, Hercules, CA)[25]. Acetate was also analyzed with HPLC equipped with an RI detector (Waters, Milford, MA) and an Aminex HPX 87H ion exclusion column (Bio-Rad, 300 × 7.8 mm, Hercules, CA). Acid insoluble lignin[24] and ash[26] were determined based on gravimetric difference, and acid soluble lignin was quantified using a Varian Cary 50 ultraviolet-visible spectrophotometer (Agilent, Santa Clara, CA)[24].

2.3 Scanning Electron Microscopy

Dried corn stover samples were sectioned using a protocol adapted for confocal imaging[27]. The corn stover pieces were rehydrated and slowly embedded in polyethylene glycol (PEG) 2000 (Sigma Aldrich, St. Louis, MO) at 60°C. The rehydrated samples were submerged in 50% PEG solution at 60°C in a closed container until completely permeated. The lids were removed from the sample containers to allow water to evaporate from the solution until the volume was reduced by half. The samples were then submerged in 100% PEG at 60°C overnight. A humid environment was created by placing a pan of water with the samples at 60°C to prevent the PEG from becoming too dry upon hardening. The samples were removed from the PEG and placed directly on a microscope slide in the desired orientation and allowed to harden to the microscope slide overnight at room temperature. The samples were hand sectioned with a scalpel, rinsed twice with water to remove PEG, and placed on a new microscope slide to dry overnight at room temperature. Sections were removed from the slide with a scalpel and mounted to SEM pin stub mounts with double sided copper tape. The sections were sputter coated with gold and imaged using a JEOL JSM-6610LV (Peabody, MA) scanning electron microscope.

2.4 Techno-economic assumptions

2.4.1 Chopped, Silage Tube Logistics Design

A logistics system compatible with alkali addition in an anaerobic environment was designed that included forage chopping, storage in silage tubes stored fieldside, and transportation to a depot co-located with a biorefinery. This case was designed around the 40% moisture anaerobic conditions explored experimentally in this study and is consistent with previous field results for corn stover[8]. An overview of the equipment list enabling the logistics design is shown in Table 2. Grain harvest was assumed a separate operation, consistent with previous designs[11, 28, 29]. Corn stover harvest was accomplished using a self-propelled forage harvester that pneumatically delivered chopped stover into a high dump wagon pulled by a tractor. Forage chopping of the corn stover has been shown to achieve a 11-17 mm particle size[30], which met the 18 mm size requirement entering deacetylation at the pretreatment reactor[18]. The high dump wagon transported corn stover to the designated field edge for silage tube formation. A Kelly Ryan Centerline bagger was used to form the silage tubes, and 40 ft lengths were used such that single units could be loaded onto a trailer for transportation. Sodium hydroxide was assumed to be sprayed on the stover during silage tube filling with a John Deere 110-gallon sprayer. Storage density in the silage tubes was assumed to be 8.7 lbs/ft^3 (dry weight basis), which has been previously reported for forage chopped, 40% moisture corn stover stored in silage tubes[7]. The overarching premise of this research is that alkali incorporated during pretreatment at a biorefinery can be partially integrated within the window of storage occurring in the supply chain. As such, alkali costs accounted for in biochemical biofuel conversion designs[13] were assumed to be costed downstream of logistics. This would result in no net increase of alkali in the supply system and a net zero impact on final fuel production costs.

The transportation design was modeled after what was reported previously for chopped corn stover stored in silage tubes[12]. Each 40 ft silage tube was recovered from storage by manually loading with a 45 ft long self-loading/unloading trailer with a walking floor bottom at a rate of 5.1 dry tons/hr. This was pulled by a conventional semi-truck day cab and transported 36 miles to a biorefinery gate. The transportation distance assumed was similar to what was used in a two-pass harvest baled logistics system[28]. On-site preprocessing at the biorefinery involved unloading the silage tube using the walking floor trailer, and plastic wrap removal that was facilitated by a high tonnage knuckle boom. The used wrap was assumed to be collected and disposed of in a local landfill. The receiving system for chopped corn stover described previously was used to provide a 24-hour supply to the biorefinery[11]. Corn stover was fed through a magnetic separator conveyance system to remove any rocks. Then a day pile was created using a stacking reclaimer and associated conveyance system, and the final conveyor delivered stover to the biorefinery throat as reported in a previously modeled logistics case that delivered ensiled biomass to a biorefinery reactor throat[11].

2.4.2 Cost basis

The cost-year of 2016 was chosen to be consistent with current feedstock logistics supply chain[28] and conversion models[13] to facilitate comparison. Capital costs provided for other years were adjusted to the basis year of 2016 using Consumer Price Index (CPI) from the U.S. Bureau of Labor Statistics CPI Databases[31]. The equation for year-dollar back-casting is shown below:

Equation 2

Grower payment for corn stover residues assumed was based on 2-pass corn stover harvest and collection approach representing the state of technology within the context of bioenergy production[28]. Fixed costs or all unit operations included capital recovery, insurance, and taxes, and were estimated following the guideline published by American Society of Agricultural and Biological Engineers (ASABE). A list of all equipment used in this scenario is presented in Table 2, along with machine purchase price, machine life, and salvage value. The equipment prices used were either obtained from local dealerships or online webpages and were used to estimate discounted salvage value and capital recovery based on machine lifespan. Annual discounted salvage value was calculated as:

Equation 3

Capital recovery was calculated as:

Equation 4

The ownership costs included interest and depreciation, insurance, and taxes. This scenario assumed an annual interest rate of 8% and insurance and tax rate of 2%, similar to previous analysis of a chopped logistics system for corn stover[11]. For the equipment in the receiving site such as magnetic separator, conveyor, and hopper, an installation factor of 0.5 was included to estimate additional installation-related costs including electrical connections, instrumentation, and safety control.

Operating costs (2016 US$ h^{-1}) accounted in this scenario included the costs of repair and maintenance, fuel, labor, and material and land for storing silage tubes. Repair and maintenance costs were calculated as 1% of capital recovery, which referred to the value of initial capital investment over the equipment lifespan. Fuel cost was estimated based on hourly energy usage of each equipment, and energy unit cost. Cost for off-road diesel and electricity were assumed at 2.13 US$/gal[32] and 0.065 $/kWh[33]. The assumed labor rate in this scenario was US$33 h^{-1} consistent with previous designs[11]. Material cost included cost of silage tube bags, which was assumed to be about 106.4 2016 US$ for each 40 ft silage tube used. Land cost for storing silage tubes was estimated based on assumed land cost of 105.0 2016 US$/acre[28].

3.0 Results and Discussion

3.1 Storage Performance of Alkali-Treated Corn Stover

Ten experimental conditions were screened as a function of both dry matter loss and the ability to shift structural components into soluble forms after 4 weeks of aerobic or anaerobic storage. The results in Figure 1 represent dry matter loss experienced over 4 weeks along with trends in the changes of extractives (1.8-2.2%), where water extractable and ethanol extractable components were assessed for their ability to suggest reduced downstream recalcitrance. No differences in ethanol extractives were observed across the ten treatments of corn stover, but significant changes in water extractives were present. Retention of water extractable components was observed in experimental controls stored aerobically; however, corn stover stored for 4 weeks at 40% and 60% moisture w.b. under aerobic conditions exhibited 8.1% and 10.6% total dry matter loss, respectively. Additionally, the water extractable component of the 60% moisture experimental control decreased by a relative 11%, likely the result of microbial respiration of soluble carbohydrates. This result is consistent with previous studies that correlated aerobic microbial degradation with moisture contents over 20% w.b.[34]. A full characterization of water extractable components in native corn stover has shown that monomeric carbohydrates are primary constituents in the extractable fraction (ranging from 14-27% on a dry weight basis) along with alditols, aliphatic acids, inorganic ions, and other soluble oligomers[35]. Monomeric carbohydrates provide the energy source for microbial respiration and are well-known to be consumed during aerobic storage[4, 36].

Corn stover stored under aerobic conditions at both low and high alkali loadings exhibited varied losses of dry matter. Both Low NaOH, aerobic corn stover samples stored at 40% and 60% moisture exhibited approximately 8% dry matter loss, consistent with the control samples that received no alkali addition. Of note, water extractives in the Low NaOH aerobic, 40% moisture stover were elevated (10.6%, dw basis) over the corresponding moisture control sample, signaling the impact of alkali addition on solubilization of structural components. Following the Aerobic, High NaOH loading and storage, approximately 20% and 18% of components were extractable in water after 40% and 60% moisture storage, respectively. However, losses over the 4-week period resulted in nearly 13% of total mass loss; solubilization of structural components that were microbial accessible are likely the cause of such substantial dry matter losses over the control samples.

Anaerobically stored, High NaOH 60% moisture stover and both Low NaOH samples exhibited nearly equivalent changes in water extractable components compared to the corresponding treatment in aerobically stored corn stover. A slight difference in extractives was present (16.4% vs 19.7%) between the High NaOH, 40% moisture stored corn stover, but the trend of elevated extractives after alkali loading was consistent in both aerobic and anaerobically stored samples. However, dry matter losses over the 4-week storage scenario were dramatically different in three of the four anaerobically stored samples. Dry matter losses were reduced from the 8-13% exhibited in the aerobic samples to less than 4%, apart from the Low NaOH, 60% moisture sample where equivalent losses of 7.3% were experienced in aerobic and anaerobic storage. This result can be understood by assessing the molar concentration of NaOH in the different treatments at the time of storage. Molar equivalents reported in Table 1 demonstrate that the Low NaOH, 60% moisture corn stover alkali loading was the lowest (0.08 M), suggesting that minimal alkali-induced effects and that higher alkali conditions (0.18-0.92 M) were required for preservation during anaerobic storage. While anaerobic conditions can preserve corn stover in storage, silage inoculants containing lactic acid bacteria are commonly applied to forage crops prior to entering long term storage[37, 38]. This controls against proliferation of microorganisms associated with silage spoilage including *Clostridia* species[39] that produce butyric and acetic acid, resulting in greater dry matter losses. In summary, the combined effect of alkali-treatments >0.18M and anaerobic storage were able to preserve corn stover over 4 weeks.

Further investigation of the structural composition was undertaken to probe for further impacts to the cellulose, hemicellulose, and lignin due to combined alkali treatment and anaerobic storage (Table 3). In comparison to the native corn stover, Low NaOH treatment had minimal impacts on composition after 4 weeks of storage. Slight lignin loss from 17.69% to 17.11% was observed in the Low NaOH, 40% moisture stover; likely the higher molar concentration of the alkali encouraged additional saponification of ester linkages in lignin and hemicellulose. No lignin changes were observed in the Low NaOH, 60% moisture stover. However, xylan was reduced in both Low NaOH samples (22.3%) compared to the native sample (23.58%). Previous results assessing anaerobic storage of corn stover showed that no xylan reduction occurred[8], and it is hypothesized that the alkali addition prior to storage in the present study destabilized hemicellulose sufficiently that a fraction was solubilized. However, no changes in acetate were observed highlighting that the alkali concentration was not sufficient to promote deacetylation. Additionally, the glucan and arabinan content were increased as a function of Low NaOH storage, likely a proportional enhancement due to loss of other components. Overall, these results show minimal compositional impacts as a function of the Low NaOH storage.

Table 3. Composition of native and alkali-treated corn stover after anaerobic storage for 4 weeks.

% Component (d.b.)	Native	Low NaOH, 40% moisture	Low NaOH, 60% moisture	High NaOH, 40% moisture	High NaOH, 60% moisture
Lignin	17.69	17.11	17.83	15.59	14.96
Glucan	35.61	37.17	38.52	35.84	35.07
Xylan	23.58	22.26	22.30	21.32	19.41
Galactan	1.14	1.18	1.18	1.12	1.09
Arabinan	2.55	2.96	2.98	2.77	2.61
Acetate	1.77	1.76	1.68	0.89	0.87
Protein	3.17	1.99	1.51	1.72	1.98
Structural Ash	2.66	2.43	2.38	1.91	2.39
Extractable Inorganics	2.60	2.91	3.06	5.48	4.84
Unquantified Extractives	5.48	7.90	5.88	10.93	13.27
Ethanol Extractives	2.60	2.91	3.06	5.48	4.84
Total	98.50	99.91	99.36	99.56	98.61

Differences in compositional components were observed in the High NaOH stored corn stover compared to the native corn stover as well as a function of moisture content. In general, the 60% moisture storage environment resulted in higher solubilization of structural components. Lignin was reduced from 17.7% in the native sample to 15.6% and 14.9%; xylan was reduced from 23.6% in the native to 21.3% and 19.4% in 40% and 60% moisture samples, respectively. Modest glucan changes were observed from 35.6% in the native to 35.1% in the 60% moisture sample. Acetate was reduced by half in both alkali treatments, highlighting the deacetylation occurred due to alkali treatment. These changes corresponded to extractable component increases highlighted in Figure 1 and designated in Table 3 as Unquantified Extractives. In summary, these changes show that initial saponification of acetyl bonds was accomplished with alkali treatment but that the moisture content during storage a greater impact on depolymerization of structural components than did alkali alone. Despite the 40% moisture conditions having twice the molarity of the alkali solution, the increased moisture content of 60% promoted additional depolymerization.

The one notable exception to moisture influenced structural components being released at 60% compared to 40% moisture is in the case of structural ash content, where a reduction from 2.6% in the native stover to 1.9% in the High NaOH, 40% moisture sample was observed, and little difference was seen in other samples. Alkali can solubilize some ash components such as silica at high pH (>10.5)[40], and it is possible that the 0.92 M NaOH concentration enabled that whereas the 0.4M NaOH concentration of the 60% moisture sample did not. This more than an issue of just pH shift in lignocellulosic but also of competing mechanisms of acetyl groups in hemicellulose being released and neutralizing the alkali as well as the overall buffering capacity of inorganics contained in lignocellulosic biomass. Regardless, the impact of silica on wear and abrasion as well as slagging in reactors has been characterized elsewhere[41, 42]. Further analysis of ash speciation would provide additional insights into how this approach may be leveraged in the future, perhaps to reduce the abrasiveness of specific biomass fractions.

In summary, low dry matter losses in both anaerobic High NaOH treatments suggest either approaches could be viable depending on factors such as moisture content at the time of harvest, moisture specification at the pretreatment reactor, and logistical concerns such as transportation of high-moisture material. While the Low NaOH treatment at 40% also preserved dry matter in anaerobic conditions, the Low NaOH 60% moisture treatment showed little utility.

An additional characterization approach, SEM, was used to assess for structural changes as a function of treatment and storage. Native corn stover pith cells at 50 and 200X magnification (Figure 2, A and B) with parenchyma and vascular bundles are visibly bound. SEM images of High NaOH, 40% moisture scenario pith at 50 and 200X magnification (Figure 2, C and D) show that parenchyma cells are visually similar in the two samples. However, there appears to be rupture of cells on the outside of the vascular bundle (depicted by red arrow) in the alkali treated stover. While this observation requires additional exploration, it does suggest the potential for the vascular bundle to be isolated from the remaining pith section. Separation and fractionation of distinct anatomical and histological tissues has been proposed as a means to manage variability in bioenergy conversion designs[43]. Vascular bundles are documented to provide strength to biomass stalks due to their fibrous nature[44], and an increase in vascular bundles has been shown to correlate with enhanced compressive strength[45].

3.2 Techno-economic Assessment of an Alkali-assisted anaerobic storage method

Experimental results highlight how anaerobic storage conditions can be utilized to preserve corn stover total dry matter in combination with alkali-assisted treatments. Techno-economic analysis was utilized to compare this approach with current designs that utilize baled biomass as the common format to facilitate storage, transportation, and handling. A chopped logistics system was designed that encompassed corn stover stored and transported in a silage tube at 40% moisture, similar to a design reported previously for transportable silage tubes[12]. This process uses forage chopping of corn stover to meet biorefinery size specifications and increase the packing density in anaerobic, long term storage and subsequent transportation to the biorefinery gate. The design also leveraged receiving and handling unit operations that had been designed for a logistics system that transported chopped corn stover in bulk form to a biorefinery gate for storage in 50,000 ton piles[11].

The costs of the chopped silage tube logistics system were compared to the bale-based logistics system using two-pass harvest and collection, storage of four bale high stacks, and transportation to a depot co-located with a biorefinery (Table 3). Grower payment was costed equally for both approaches at $20.13/ton. The anaerobic silage tube approach incurred $17.28/ton cost for harvest and collection; however, efficiencies were experienced in this system since size reduction occurred during the one-pass forage chopping operation. Harvest and collection in the baled logistics system include two-pass harvest and collection into square bales, and hence costs were slightly higher ($18.79/ton) compared to the chopped system. Storage costs were increased three-fold in the silage tube scenario ($21.70/ton) compared to the baled approach ($6.53/ton) due to cost of the silage tube bagging operation, which included costs for plastic utilization as well as the increased land use requirement compared to stacked bales. Likewise, transportation costs were higher in the silage tube scenario ($17.65/ton vs. $14.98/ton) because of the reduced total mass and increased moisture in each truckload delivered. In the baled logistics system, preprocessing at the depot required two-stage grinding operations to achieve biorefinery particle size targets and cost ($20.84/ton). However, in-plant preprocessing costs dropped dramatically for the silage tube scenario ($1.10/ton) because size reduction was incorporated during harvest. A dockage of $0.89/ton was also applied to the Bale Logistics Scenario to account for soil incorporated during the baling process, whereas corn stover harvested during the forage chopping process does not come in contact with the ground. The resulting total cost of the silage tube approach were calculated to be $77.86/ton compared to $82.37/ton baled logistics system.

In the silage tube logistics system, storage and queuing, transportation and handling, and harvest and collection each contributed about 25% to the total cost. To understand the sensitivity of the total cost of the silage tube logistics system to important factors such as harvesting productivity, silage tube density, and transportation distance, a sensitivity analysis was carried out and presented in Figure 3. This shows that the impacts of the three evaluated factors on the total system cost were nonlinear. Decreases in silage tube density and harvesting productivity and increase in transportation distances caused increases in the total logistics cost. Harvest productivity and bulk density in transportation have been identified as the major cost drivers for chopped corn stover logistics systems[11]. Among the three factors, decrease in silage tube density increased the total cost the most. This is attributed to the fact that silage tube density directly impacted both the number of silage tube units used and also the transportation weight per truckload. This result implies that to avoid system cost increase, it is most important to control the silage tube density. Bulk density in transportation also was identified as a key cost driver in previous chopped corn stover logistics designs[11].

The sensitivity analysis results also suggested further cost reductions should reduce the transportation distance, which is directly related to harvest yield and biorefinery size. This may not be possible with a crop such as corn stover that is limited to 1-2 ton/acre harvest yields. However, other energy crops such as switchgrass, miscanthus, or biomass sorghum[46-49] produce higher harvest yields and could benefit from the approach described in this study.

Overall, the hypothesis of this work is that the storage operation allows for potential reduction of total caustic loading. It was assumed no change in caustic usage or cost as a conservative approach, and additional research is warranted to verify this. Future work should explore the opportunity to further reduce the alkali loading and associated cost implications as well as the energy intensity of the entire pathway.

In conclusion, the technoeconomic analysis results showed that the designed silage tube logistics system incurred lower costs than a conventional two-pass baled logistic system, mainly due to moving biomass comminution upstream in the feedstock logistics supply chain and using an innovative approach to increase bulk density during transportation of silage. Future efforts should be focused on improving silage tube density, reducing silage tube costs, and alternate approaches to compact forage chopped corn stover.

4.0 Conclusion

The primary goal of this study was to explore the potential for partial deacetylation and saponification of intermolecular bonds between lignin and hemicellulose prior to the storage operation to reduce recalcitrance in corn stover. This study explored the working envelope of this approach to explore the compatibility of varying storage conditions in the supply chain, such as moisture content, oxygen availability, and alkali loading. Extractives were monitored as an indicator for effectiveness and results indicate that there is no difference in extractives between aerobic and anaerobic storage after four weeks of storage. However, significant dry matter loss occurred in aerobic storage (7.5-13%) compared to anaerobic storage (3-7%). Gross compositional changes in the anaerobically stored corn stover verify lignin, xylan, and acetate reduction consistent with low-severity structural sugar and lignin depolymerization. Three anaerobic storage scenarios were recommended for future investigation. A logistics supply chain configuration was designed around the anaerobic storage unit operation, and the modeled approach was found to be cost competitive to a bale logistics system traditionally used for corn stover. Additional research should investigate the opportunity that storage pretreatment has for reducing the total alkali loading in deacetylation. In summary, this work provides foundational data for the scientific community such that further optimization and understanding of the underlying physiochemical impacts can be explored.

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6.0 References

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Table 1. Sample nomenclature and corresponding experimental treatment for this study.

Sample ID	**Experimental Treatment**	**Alkali concentration (%, d.b.)**	**Alkali concentration (Molar, w.b.)**
Native	As-received corn stover	NA	NA
Control, 40% Moisture	Aerobic	NA	NA
Control, 60% Moisture	Aerobic	NA	NA
Low NaOH, 40% Moisture	Aerobic, Anaerobic	0.5	0.18 M
Low NaOH, 60% Moisture	Aerobic, Anaerobic	2.4	0.08 M
High NaOH, 40% Moisture	Aerobic, Anaerobic	0.5	0.92 M
High NaOH, 60% Moisture	Aerobic, Anaerobic	2.4	0.40 M

Table 2. Equipment list for chopped, silage tube logistics systems including quantity, capacity, purchase price and installation factor. All costs are shown in 2016 US dollars.

Operation	Description	Quantity	Design capacity	Purchase price	Installation Factor
Harvesting and collection	New Holland FR9060	7	40 tons/hr	$366,433	0
	Case IH Puma 180 HP Tractor	7	40 tons/hr	$129,090	0
	High Dump Wagon	7	40 tons/hr	$45,789	0
Field storage	John Deere 110 Gallon Standard Sprayer w/ 18' Boom, LP40782	53	-	$2,595	0
	Kelly Ryan Centerline silage tube bagger 5X12	53	8 tons/hr	$12,524	0
Transportation	Peterbilt 367 Conventional-Day Cab	37	11.27 tons/hr	$131,640	0
	IMCO 45' 2 axle aluminum loader	37	11.27 tons/hr	$57,966	0
Receiving site/Depot	JCB Wheel Loader, 457ZX	3	126 tons/hr	$179,990	0
	Magnetic Separator Conveyor	1	2577 m^3/hr	$30,000	0.5
	Magnetic Separator	1	-	$117,000	0.5
	30,000 BPH Pit Hopper	2	37333 m^3/hr	$16,473	0.5

Table 3. Cost comparison of a baled system using two-pass harvest compared to the chopped harvest utilizing silage tube storage. All costs are in US 2016 dollars per ton deliver corn stover.

Unit Operation	**Baled Logistics System ($/ton)**	**Chopped, Silage Tube Logistics System ($/ton)**
Grower payment	$20.13	$20.13
Harvest and collection	$18.79	$17.28
Storage and queuing	$6.53	$21.70
Transportation and handling	$14.97	$17.65
In-plant receiving and preprocessing	$19.43	$1.10
Dockage	$0.89	-
Total Feedstock Cost	**$79.92**	**$77.89**

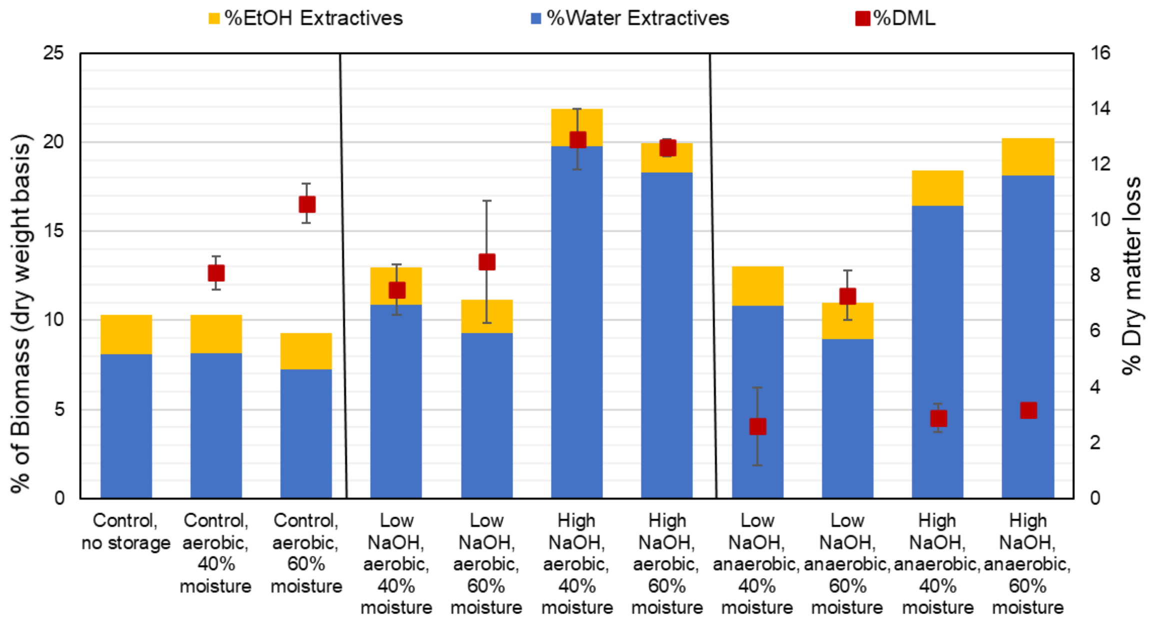

Figure 1. Changes in extractable component and associated dry matter loss (%DML) in alkali treated corn stover over 4 weeks of storage.

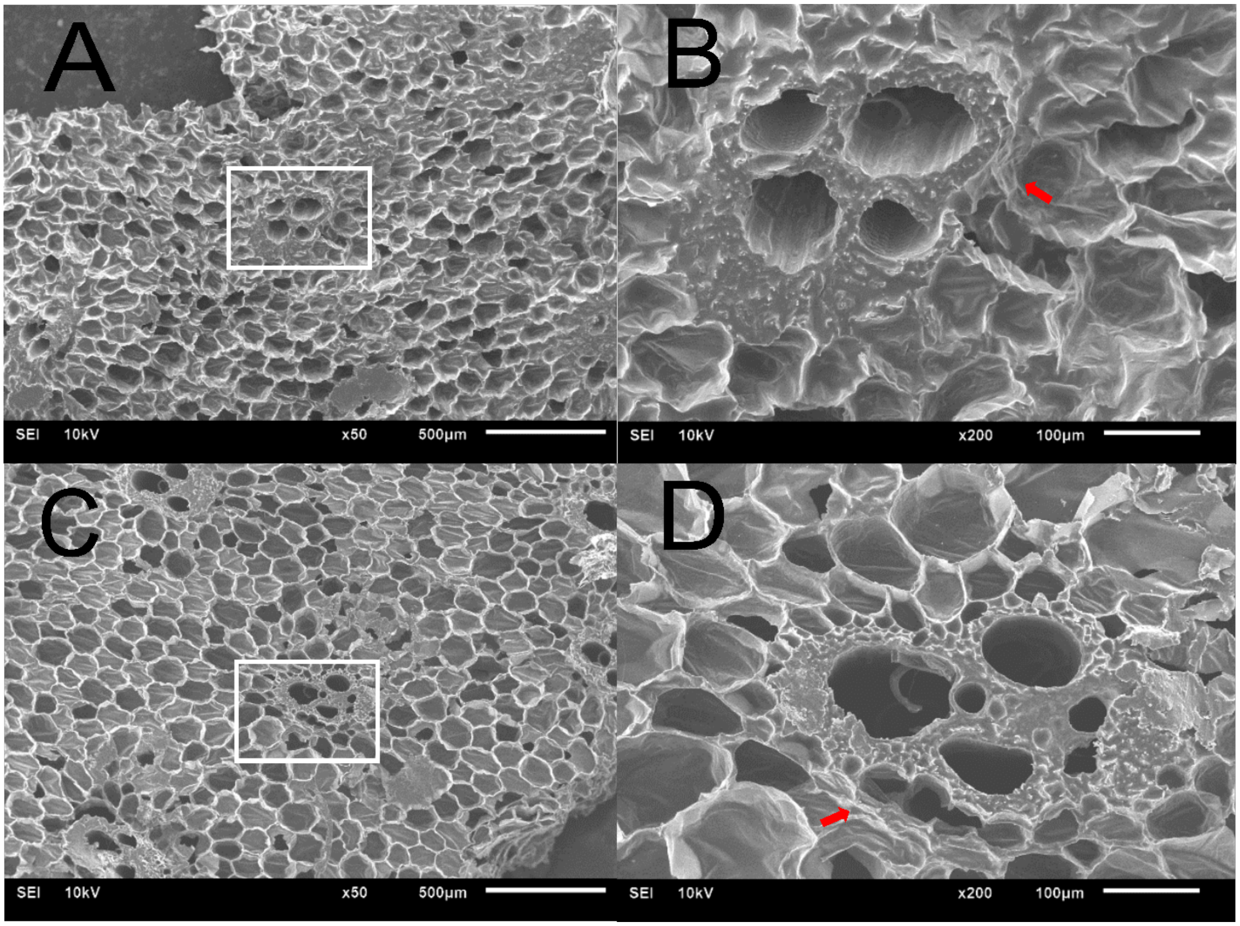

Figure 2. SEM micrographs at 50X (left) and 200X (right) of corn stover A, B: native; C, D: High NaOH, 40% moisture stored anaerobically for 4 weeks. Red arrows indicate linkages near vascular bundle.

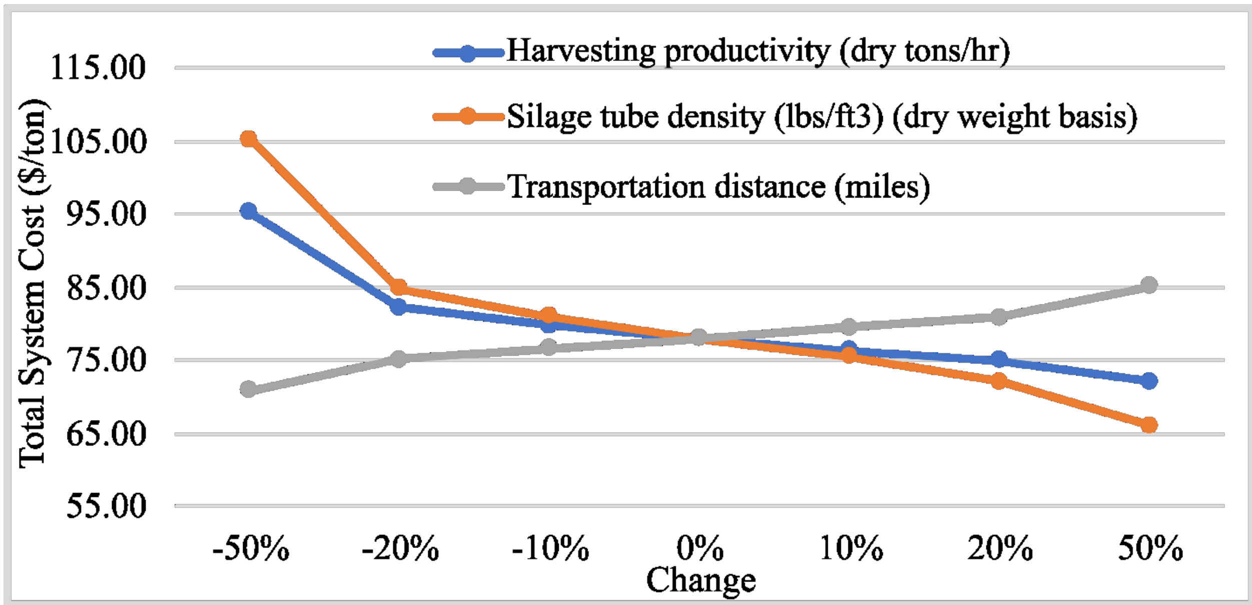

Figure 3. Changes in the total system cost for the silage tube logistics system corresponding to changes in harvesting productivity, silage tube density, and transportation distance.