INL/RPT-23-71750-Revision-0

Fractionation of Lignocellulosic Biomass into High-Value Products - CRADA Report

May 2023

Changing the World's Energy Future

Carl Fredrik Mikael Karlsson, Troy A. Clark

Idaho National Laboratory

INL/RPT-23-71750-Revision-0

Fractionation of Lignocellulosic Biomass into High-Value Products - CRADA Report

Carl Fredrik Mikael Karlsson, Troy A. Clark

May 2023

Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517, DE-AC07-05ID14517

Final CRADA Report

Fractionation of Lignocellulosic Biomass into High-Value Products

PROJECT INFORMATION

CRADA No.: 21TCF1 Completion Date: 05/31/2023

Participant(s) and Point of Contact(s):

Battelle Energy Alliance, LCC	Carl Fredrik Mikael Karlsson	carlfredrikmikael.karlsson@inl.gov
Golden Leaf Energy, Inc.	Troy A. Clark	troyclark@goldenleafenergy.com

INL Point of Contact: Carl Fredrik Mikael Karlsson carlfredrikmikael.karlsson@inl.gov

Scope and Objective

Idaho National Laboratory (INL) has developed a process for adding value to the biomass feedstock supply chain. The key aspects of this process include: (1) anaerobic and chemical treatment of biomass during storage, (2) fractionation of biomass into conversion-ready feedstock and high-value coproducts, and (3) high-moisture pelleting to increase the bulk density and stabilize the feedstock. The purpose of the chemical treatment is to overcome the recalcitrant nature of the feedstock to improve the biochemical conversion process of breaking down the biomass into sugars. To maximize the utilization of the biomass, the feedstock can be fractionated into hemicellulose and lignin rich fractions. Finally, to increase the materials overall energy density, produce a shelf-stable material, and to facilitate transport, the feedstock is densified in a pelleting process. The first two steps of the processes have been verified at bench scale showing an improvement in theoretical glucose yield from 23.1% to 44.5% and an improvement in theoretical xylose yield from 8.9% to 23.1% from ground corn stover. It is hypothesized that densification will further increase the carbohydrate yield in the sample.

The goal of this project was to evaluate the technical feasibility and process economics of the above process and to provide preliminary data to Golden Leaf Energy, Inc to assess its potential commercialization for converting biomass to ethanol and renewable chemicals. Corn stover (CS), the largest available agricultural residue, and Chinese tallow (CT), an invasive wood species with no current commercial value, were chosen as feedstocks for this project.

Project Accomplishments

Fiscal year (FY) 22 Quarter (Q) 1
No activities were planned.

FY22 Q2
Washing is an indispensable step to improve sugar extraction from alkali stored biomass. In the washing step, solubilized lignin is removed, and the feedstock is neutralized. However, biomass with high moisture content (>40%, wet basis) cannot be efficiently pelleted. Thus, an initial washing, dewatering and densification process was evaluated on in-storage alkali-treated CS. After water washing the biomass, the moisture content was about 85%. A Vincent screw press was used to dewater the material to achieve a moisture content of less than 60%. Since this moisture content was relatively high (a commercial pellet plant operates at ~15% moisture content), a pellet mill with a pre-heater (160 °C) was utilized to densify the material. However, the final moisture content was found to be too high to form durable pellets. It was deemed that an improved washing, dewatering and pelleting process was needed.

FY22 Q3
Two batches of NaOH impregnated corn stover were prepared for later process evaluation. CS was impregnated with 4 wt% and 6 wt% NaOH on dry weight basis, respectively. This represents a reduced total alkali content compared to the pretreatment conditions associated with the deacetylation and mechanical refining process, which is 7-8 wt% After mixing, the material was stored at ambient temperature under anaerobic conditions for two weeks. Minimal reduction in pH (roughly 0.5 pH unit) and dry matter content (<0.1 wt.%) during storage were observed. Therefore, the corn stover material was considered stable under storage conditions with minimum degradation or fermentation.

After storage, the samples were washed with 40°C water at a mass-ratio of 1 to 8 biomass to water and filtered using cheesecloth. As in FY22 Q2, the samples had a moisture content of about 85% after the washing process. The samples were first dewatered with a Vincent screw press to a moisture content of about 50-55%. The samples were further dried with a No. 66 Laboratory Seed & Grain Dryer from Grainman for 1 hour with air at room temperature to a moisture content of 30-35%.

Chemical composition and enzymatic hydrolysis were performed on the washed and dewatered samples according to modified methods from (Sluiter, Ruiz, Scarlata, Sluiter, & Templeton, 2010) and (M. G. Resch, 2015), respectively. Untreated CS was used as reference sample.

Results from the compositional analysis are show in Table 1 and sugar yields from the enzymatic hydrolysis in Figure 1. The main trend seen in Table 1 is that with increasing alkaline concentration, the lignin and acetate concentration decreases while the glucan and xylan concentration increases. The alkaline treatment had a significant effect on the sugar yields, from 16.4 ± 1.0 % for the reference material to 55.0 ± 1.1% for CS impregnated with 6 wt.% NaOH. Although, the alkaline treatment showed a significant increase on the glucose yield it did not reach the target of 60%. Mechanical treatment that increases surface area (Rohrbach & Luterbacher, 2021; Yang et al., 2022) has been shown to have a positive effect on sugar yields. It was hypothesized that the samples analyzed in the quarter would be sufficiently size reduced in the dewatering step. This hypothesis was proven wrong. A densification process followed by disintegration of the pellets might further reduce of the size of individual fibers, thus increase the sugar yields. This was explored in FY22 Q4.

Table 1. Ash, lignin, acetate and sugar content in weight precent for impregnated and reference corn stover samples.

	%Whole Ash	%Lignin	%Glucan	%Xylan	%Galactan	%Arabinan	%Mannan	%Acetate
Reference sample	5.2	20.1	39.6	21.0	1.5	2.8	0.5	3.5
4% NaOH impregnated	6.8	18.8	42.1	22.1	1.5	3.3	1.5	0.6
6% NaOH impregnated	6.4	17.2	46.3	23.6	1.6	3.5	1.5	0.3

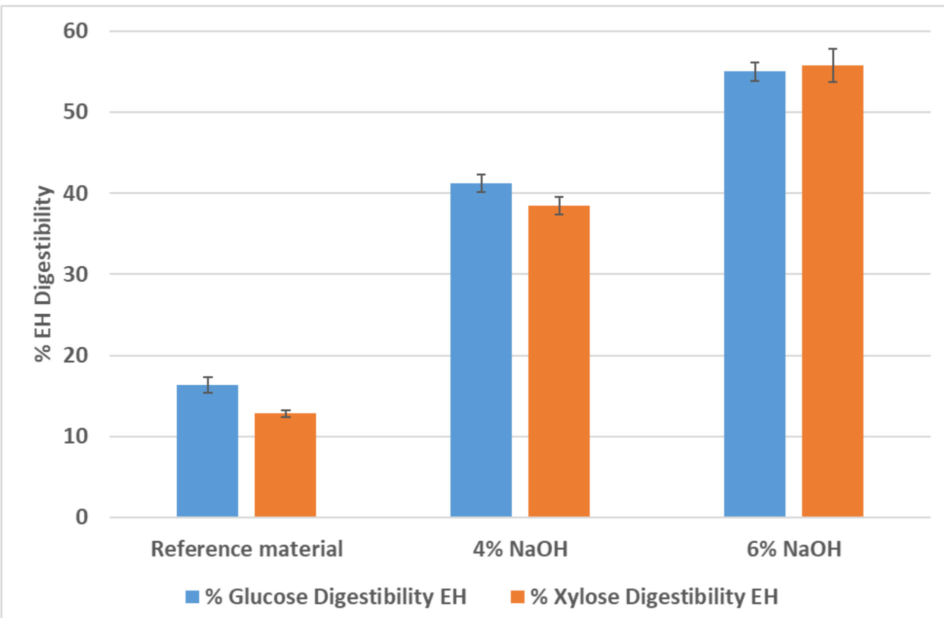

Figure 1. Glucose and Xylose yields from enzymatic hydrolysis from impregnated and reference corn stover samples. Error bars represent on standard deviation of triplicates.

FY22 Q4

Acid impregnation has the potential of reducing the inorganic content of biomass feedstock, so a chemical impregnation of corn stover with 1% H_2SO_4 on dry basis was made with the same procedure as described in section FY22 Q3. In the same way, Chinese Tallow that has been stored frozen at INL was impregnated with 6% NaOH and 1% H_2SO_4, respectively. The dry matter loss for all samples was less than 4% during the storage period of 2 weeks and the pH values did not change dramatically during the storage period. It was therefore deemed that the biomass was stable during the storage period.

Samples were washed and dried according to the procedure described under FY22 Q3. In addition, the material was pelletized to investigate the effect of densification of biomass on sugar yields. Two different pelleting processes were performed in this study. The first was targeted towards commercial scale and the second was laboratory scale for better comparison and reduced contamination risk among the samples. Commercial scale pelleting data was later used for the technoeconomic evaluation in FY23 Q1. Analytical laboratory scale pelleting was done according to the procedure described by Zettl et. al. with biomass containing 25 ± 5 wt.% moisture (Zettl et al., 2019) under 2 kN. The durability of the pellets was evaluated by dropping each pellet from 185 cm height onto a metal plate 4 times. The final weight of the remaining largest piece was then compared to the initial weight as a percentage. Durability tests were done in triplicates. Chemical composition and enzymatic hydrolysis were performed on disintegrated pellets according to the same methods as FY22 Q3. CS and CT fibers impregnated with 6% NaOH were collected after the enzymatic hydrolysis for evaluation as feedstock for the black pellet market. This material was also pelleted, and durability of the pellets was evaluated according to method described above.

Results from pellet durability tests are summarized in Figure 2. There was no significant difference in durability between the different pellets except for the pellets made of CS post enzymatic hydrolysis. This indicates that the impregnation and washing process has no negative impact on the durability of the resulting pellets and that production of black pellets from biomass residues after sugar hydrolysis should be possible.

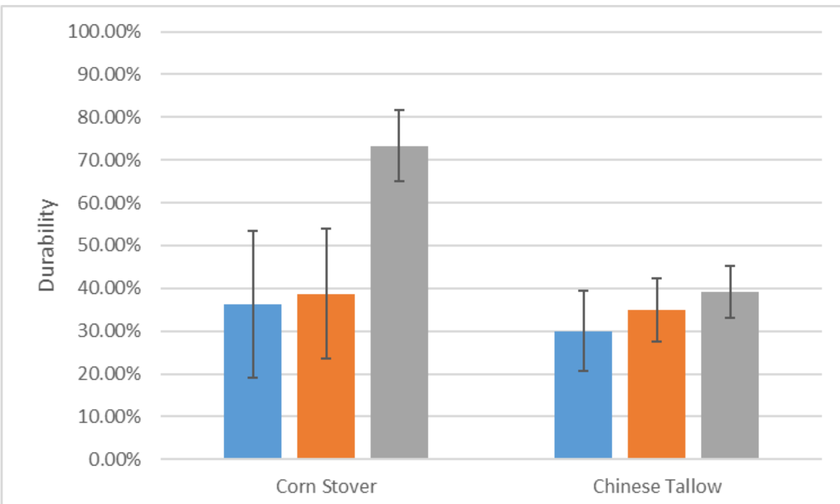

Figure 2: Durability of pellets. Pellets made from untreated biomass (in blue), biomass impregnated with 6% NaOH (in orange) and biomass impregnated with 6% NaOH after enzymatic hydrolysis (in gray). Error bars are one standard deviation from measurements in triplicates.

Results from the compositional measurements can be found in Table 2. The acid treatment is expected to reduce the overall ash content, targeting alkaline and alkali earth elements. However, the effect of the acid impregnation on the bulk ash content appears to be minimal. The alkaline treatment on CS reduced the lignin and acetyl content, as expected. Neither alkaline nor acid treatment seems to have reduced the ash or the lignin content in CT. Elevated temperatures and pressures and/or an increased chemical concentration in the impregnating process might be necessary for CT (Kim, Lee, & Kim, 2016). The limited effect of the pre-treatment on the CT also corresponds to the relatively low sugar yields in the enzymatic hydrolysis (Figure 3). The acid treatment had no measurable effect on the sugar yields and the alkaline treatment only had a limited effect on the glucose yield. However, xylose yield increased from non-measurable levels to about 15 % with the alkaline treatment, which must be seen as promising. Note that the CT used in this study was in-storage material which showed relatively low pre-storage pH (4.9 ± 0.2) when dispersed with water. This may indicate fermentation of easily hydrolysable sugars during storage resulting in a more recalcitrant feedstock. This recalcitrance of the biomass would result in lower yields in the enzymatic hydrolysis experiment. The acid treatment on the CS showed a marginal increase on the glucose yield while the alkaline treatment increased the glucose yield from about 15% for untreated CS to over 60% for alkaline impregnated and pelleted CS. When comparing alkaline treated non-pelleted CS from FY22 Q3 (marked with an asterisk in Figure 3) to alkaline treated and pelleted CS, the pelleted feedstock showed an increase of 10 percentage points in yield. This increase is most likely due to the size reduction of the individual fibers of the material during the densification process. With the subsequent disintegration of the pellet prior to the enzymatic hydrolysis process, the overall increase in surface area has been shown to have a positive effect on the sugar yields from enzymatic processes (Rohrbach & Luterbacher, 2021).

Table 2: Ash, lignin, acetate and sugar content in weight precent biomass for impregnated and untreated reference samples. Samples marked with an asterisk are from Q3, thus not pelleted before compositional measurement.

	%Whole Ash	%Lignin	%Glucan	%Xylan	%Galactan	%Arabinan	%Acetate
Chinese Tallow - Untreated	1.3	29.7	35.5	13.2	1.7	0.8	4.9
Chinese Tallow Water	1.1	30.7	38.4	14.2	1.3	0.7	5.2
Chinese Tallow NaOH 6%	3.2	31.4	36.8	13.9	1.4	0.9	1.4
Chinese Tallow H2SO4 1%	1.2	32.2	37.2	14.0	1.4	0.8	4.9
Corn Stover - Untreated*	5.2	20.1	39.6	21.0	1.5	2.8	3.5
Corn Stover NaOH 6%*	6.4	17.2	46.3	23.6	1.6	3.5	0.3
Corn Stover NaOH 6%	4.7	12.7	42.7	22.7	1.8	3.4	0.1
Corn Stover H2SO4 1%	4.0	17.4	37.0	22.2	1.2	3.2	2.9

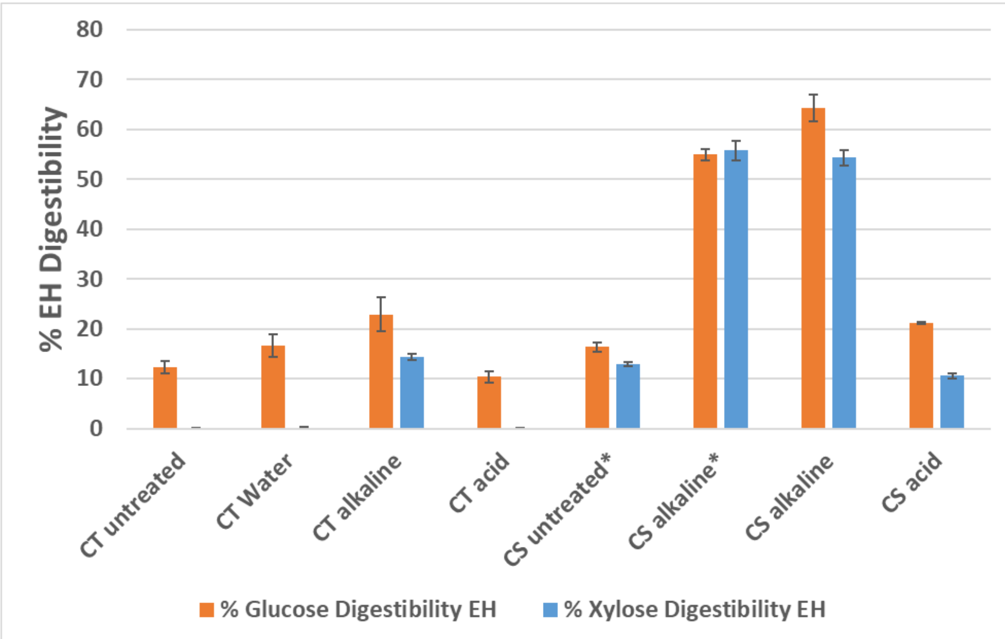

Figure 3: Glucose and xylose yields from enzymatic hydrolysis (EH) of impregnated and untreated reference samples. CT stands for Chinese tallow and CS for corn stover. Alkaline samples were impregnated with 6 % NaOH and acid samples with 1% H2SO4 on dry solids basis, respectively. Error bars represent one standard deviation of measurements in triplicates. Samples marked with an asterisk are un-pelleted feedstock measured in Q3.

FY23 Q1

A technical economic assessment (TEA) of the fractionation was performed. In the TEA, three different scenarios were evaluated: 1) the process described above with a water wash temperature of 40 °C; 2) a scenario where the water wash temperature was increased to 80 °C; 3) a more traditional steam explosion processes developed by Kazi, F et al (Kazi et al., 2010). Flowcharts for scenario 1) and 2) are presented in Figure 4. The total cost includes all steps presented in Figure 4, except the final enzymatic hydrolysis step. Aspen Plus software was used to model each route to estimate the mass and energy balance of each scenario. The capital expenditure calculation follows the procedure proposed by Southard and Green (Green & Southard, 2019). Operational cost includes the purchase of raw material, utilities, maintenance, insurance, and labor cost. General assumptions are summarized in Table 3.

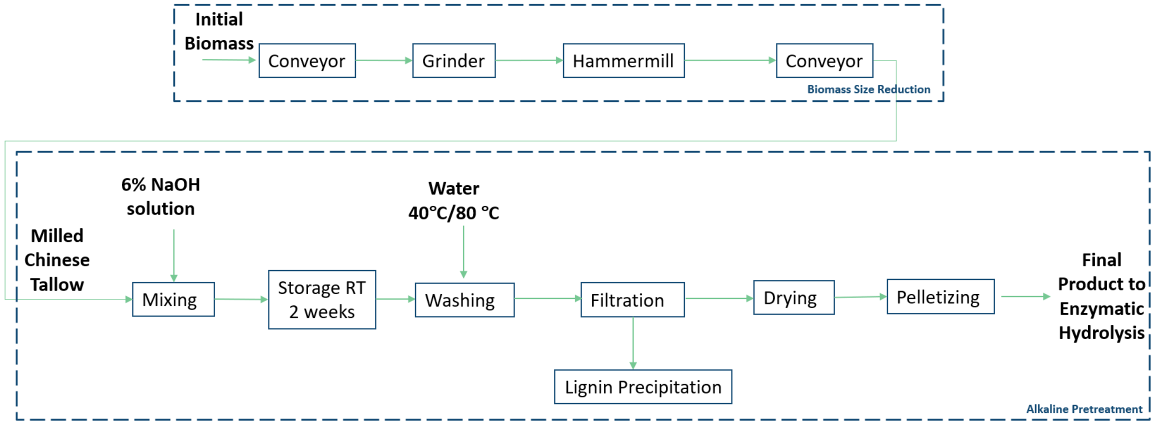

Figure 4: Flow diagram for alkaline wash pre-treatment process. Acronym RT stands for room temperature.

Table 3: General assumptions for the TEA analysis.

Assumptions	Unit	Value
Interest Rate	%	8
Maintenance for Equipment	%	1
Insurance	%	1
Salvage Rate	%	30
Equipment Life	years	30
Annual Operation Days	days/year	200
Operating hours	hrs./day	10
Natural Gas Cost	$/MMBtu	7.55
Diesel Cost	$/gal	2.55

It was concluded that for a process designed to for 10,000 Mt feedstock/year, the total cost was modelled to $25/ton (2022$) for scenario 1) and $34/ton (2022$) for scenario 2). For both scenarios, the combination of drying and pelletizer unit operation was the largest contributor to the capital expenditure cost. In terms of variable operating costs, energy consumption had by far the greatest impact, with about 94% for scenario 1) and 99% for scenario 2) of the total operational expenditure. Figure 5 shows a comparison between the three scenarios. Alkaline impregnated CT washed with water at 80°C results in the highest total cost. However, the overall cost of scenario 2) is almost the same as the steam explosion scenario in scenario 3).

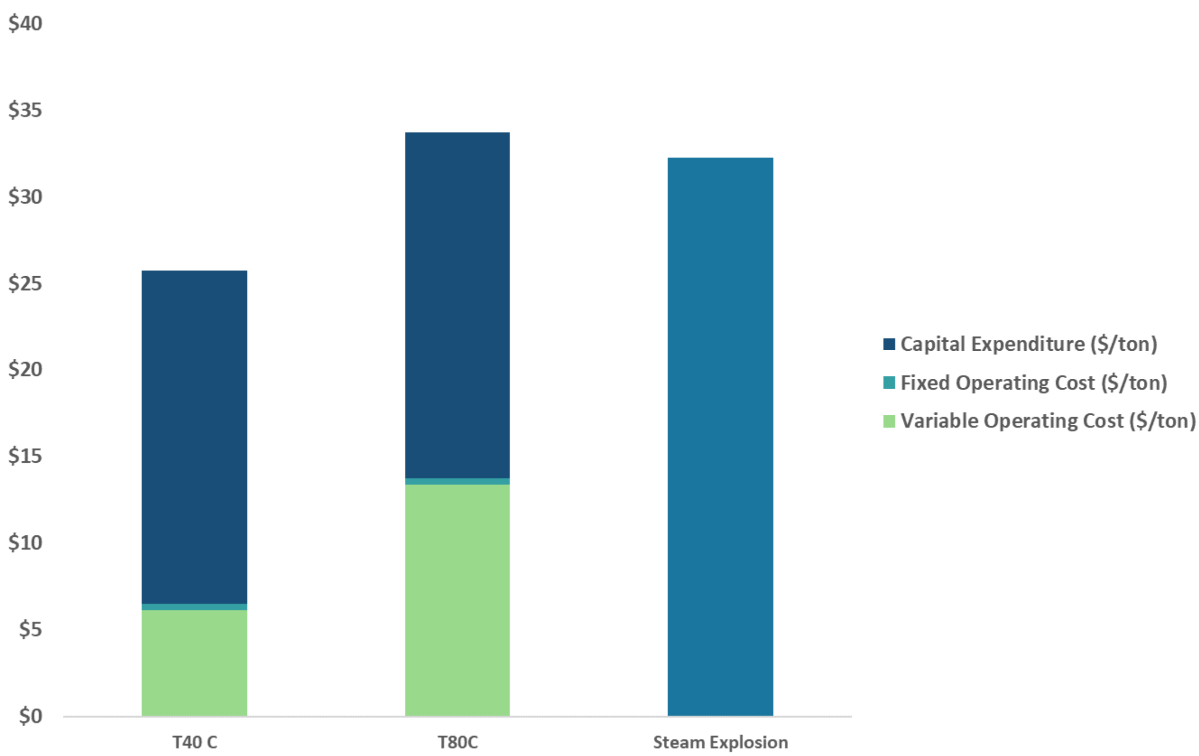

Figure 5: Comparison between the two case studies and a steam explosion scenario.

Benefit to DOE
The data presented in this report expands the knowledge of pre-processing and densification of biomass feedstock and the challenges of scale-up. Chemical pre-treatment, especially with alkaline, seems to be a potential path forward for increasing sugar yields compared to a more conventional steam explosion process. However, the efficiency of the chemical pre-processing step varies from feedstock to feedstock. It is therefore important to optimize process parameters such as alkaline or acid concentrations, chemical treatment time and rinse water temperature. Furthermore, in the TEA the capital cost of drying and pelletizer unit operation and of energy was identified as the major source of cost. Further development of a high moisture and a more energy efficient densification process would benefit the overall biomass feedstock program.

Economic Viability
The TEA results presented in section FY23 Q1 suggest that the low temperature (40C) wash is cost competitive compared to typical steam explosion, however, steam explosion likely carries a higher efficiency in recalcitrant reduction compared to hot water wastes. Future work should investigate chemical impregnating during anaerobic storage with steam explosion, dewatering, and pelleting to fully understand the benefit of such as method.

Generated Data and Reports
No outside publications or reports related to this project.

Project Status and Summary

Current project status is complete. INL's biomass fractionation process can produce multiple products that are suitable in several markets. However, directly applying processes developed for corn stover, an herbaceous agricultural residue, to Chinese tallow has proven to be a challenge. As reported in section FY2022 Q4, a 6% NaOH pretreatment of CT (TEA Scenario 1) had a limited effect on the resulting sugar yields in enzymatic hydrolysis. Compared to untreated CT, glucose yields increased from about 10 % to over 20% and xylose yield increased from non-measurable levels to about 15 % for the alkaline treated material. These sugar yields are relatively low, so the results from the TEA can be used to identify process steps which could be modified to give higher sugar yields. Sugar yields from steam exploded CT feedstock has not been found in literature, but a steam explosion process is still used as a benchmark for cost comparison. If further experiments are to be carried out in the future, it is recommended that the temperature of the washing water after the alkaline storage step is increased to 80 °C. Previous results from the team had tested 80 °C heat treatment prior to washing, and this resulted in reduced glucan and xylan yield in subsequent hydrolysis likely because solubilized lignin condensed and blocked enzyme access on the biomass. Hence the 40 °C washing was assessed in this project. It is hypothesized that a higher temperature at low solids would reduce this effect and still help solubilize the lignin for fractionation and improve enzymatic saccharification of the lignocellulose (Kim et al., 2016). The TEA shows that increasing the washing temperature from 40 °C to 80 °C still puts the pre-treatment process in the same cost range as a steam explosion process. Although not included in the TEA, an optimized enzymatic hydrolysis process, which would include an enzymatic mixture more suitable to woody biomass and close pH monitoring, has the potential to further increase the sugar yields, at a negligible cost increase. It has previously been shown that different enzymatic cocktails are necessary for CS compared to woody feedstock (Álvarez et al., 2016). The TEA also concludes that energy is the major operational cost. Focusing on the development of a more energy efficient drying and pelletizing steps would be greatly beneficial. This would apply to all types of biomass feedstocks, not just CT, which has been the focus of this project. The high energy consumption in the drying and pelletizing process also indicates that increased storage time and/or alkaline strength, which might be options to increase sugar yields, can be implemented without significant additional cost. However, a sensitivity analysis must be done to fully conclude this. Finally, the option of adding an alkaline and lignin recovery at the post-storage washing step should be investigated as potential value-added process steps.

References

Green, D. W., & Southard, M. Z. (2019). *Perry's chemical engineers' handbook*. New York, NY: McGraw-Hill Education.

Kazi, F. K., Fortman, J. A., Anex, R. P., Hsu, D. D., Aden, A., Dutta, A., & Kothandaraman, G. (2010). Techno-economic comparison of process technologies for biochemical ethanol production from corn stover. *Fuel, 89*, S20-S28. doi:https://doi.org/10.1016/j.fuel.2010.01.001

Kim, J. S., Lee, Y. Y., & Kim, T. H. (2016). A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass. *Bioresource Technology, 199*, 42-48. doi:https://doi.org/10.1016/j.biortech.2015.08.085

M. G. Resch, J. O. B., S. R. Decker. (2015). *Low Solids Enzymatic Saccharification of Lignocellulosic Biomass*. National Renewable Energy Laboratory (NREL)

Rohrbach, J. C., & Luterbacher, J. S. (2021). Investigating the effects of substrate morphology and experimental conditions on the enzymatic hydrolysis of lignocellulosic biomass through modeling. *Biotechnology for Biofuels, 14*(1), 103. doi:10.1186/s13068-021-01920-2

Sluiter, J. B., Ruiz, R. O., Scarlata, C. J., Sluiter, A. D., & Templeton, D. W. (2010). Compositional Analysis of Lignocellulosic Feedstocks. 1. Review and Description of Methods. *Journal of Agricultural and Food Chemistry, 58*(16), 9043-9053. doi:10.1021/jf1008023

Yang, J., Gao, C., Yang, X., Su, Y., Shi, S., & Han, L. (2022). Effect of combined wet alkaline mechanical pretreatment on enzymatic hydrolysis of corn stover and its mechanism. *Biotechnol Biofuels Bioprod, 15*(1), 31. doi:10.1186/s13068-022-02130-0