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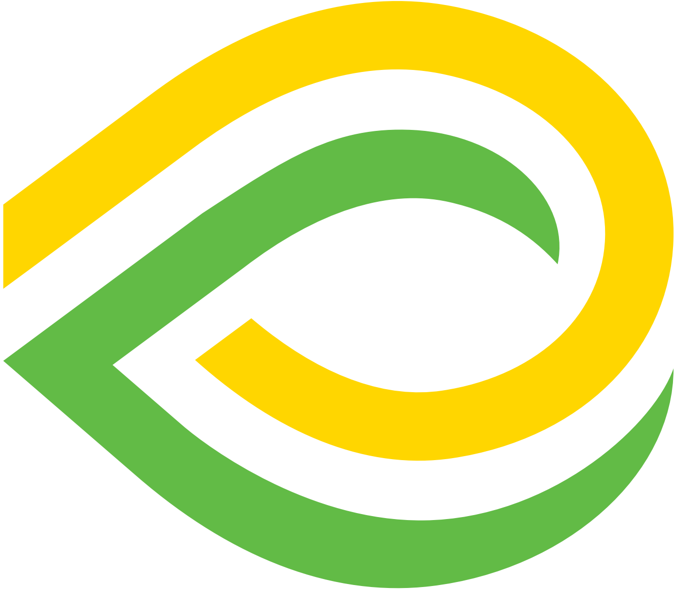
FEEDSTOCK-CONVERSION INTERFACE CONSORTIUM

Techno-Economic Case Study: Low-Temperature Conversion Performance Based on Isolated Anatomical Fractions of Corn Stover



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Disclaimer

About the Feedstock-Conversion Interface Consortium

The Feedstock-Conversion Interface Consortium (FCIC) develops first-principles-based knowledge and tools to understand, quantify, and mitigate the effects of feedstock and process variability across the bioenergy value chain, from the field and forest through downstream conversion. The FCIC is a collaborative and coordinated effort involving researchers in many different disciplines. It is led by the U.S. Department of Energy's Bioenergy Technologies Office (BETO) and includes researchers from nine national laboratories: Argonne National Laboratory, Idaho National Laboratory, Lawrence Berkeley National Laboratory, Los Alamos National Laboratory, National Energy Technology Laboratory, National Renewable Energy Laboratory, Oak Ridge National Laboratory, Pacific Northwest National Laboratory, and Sandia National Laboratories.

Research within the FCIC focuses on two complementary conversion pathways: (1) the low-temperature conversion of corn stover to fuels and chemicals using deacetylation and mechanical refining, enzymatic hydrolysis, and biological upgrading of the sugar- and lignin-rich streams; and (2) the high-temperature conversion of pine residues to fuels using catalytic fast pyrolysis and hydrotreating. Each pathway covers three sequential process areas—biomass harvest and storage, preprocessing, and conversion.

The FCIC is organized into eight collaborative tasks working in each of these process areas. The Feedstock Variability task investigates biomass attribute variations that originate in the harvest and storage process area; the Preprocessing, Materials Handling, and Materials of Construction tasks investigate the effects of biomass variability in the preprocessing area; and the High-Temperature Conversion and Low-Temperature Conversion tasks investigate the effects of biomass variability in the conversion process area. Two supporting tasks (Crosscutting Analyses and Scientific Data Management) support all FCIC research.

The Feedstock-Conversion Interface Consortium uses first-principles-based science to de-risk biorefinery scale-up and deployment by understanding and mitigating the impacts of feedstock variability on bioenergy conversion processes.

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Availability

This report is available electronically at no cost from http://www.osti.gov.

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List of Acronyms

DMR	Deacetylation and mechanical refining
FCIC	Feedstock-Conversion Interface Consortium
GGE	Gallons of gasoline equivalent
LT	Low temperature
MFSP	Minimum fuel selling price
NREL	National Renewable Energy Laboratory
SOT	State of technology
TEA	Techno-economic analysis

Executive Summary

This report summarizes analysis conducted to support a case study under the Feedstock-Conversion Interface Consortium (FCIC) focused on techno-economic analysis (TEA) modeling to quantify the process yield and resulting process cost impacts for processing isolated anatomical fractions of corn stover through a low-temperature conversion (biochemical) pathway. It is hypothesized that different individual anatomical fractions of corn stover vary in both composition and recalcitrance, giving biorefineries options in whether and how to deal with fractionated or whole biomass feedstock. By quantifying the techno-economic impacts of this variability, we provide actionable information for end users to understand tradeoffs in conversion system yields and economics in considering feedstock processing decisions at the biorefinery gate.

For this study, we worked with FCIC researchers to obtain data on the compositional analysis and conversion performance of whole corn stover alongside three individual anatomical fractions (cobs, husks, and stalks) across key steps of the biorefinery conversion process within FCIC's research scope—pretreatment and enzymatic hydrolysis. This TEA screening assessment highlighted biorefinery economic trade-offs observed through this approach. Namely, relative to processing whole stover biomass, two of the three anatomical fractions for which composition/conversion data were available (cobs and husks) demonstrated the ability to achieve higher fuel yields and lower minimum fuel selling prices (MFSPs), while the third fraction (stalks) led to the opposite result, as a composite reflection of compositional differences and process convertibility.

TEA results indicated fuel yields of 44 and 41 gallons of gasoline equivalent (GGE) per dry ton of biomass for the cob and husk fractions, respectively, decreasing to 29 GGE/ton for stalks, compared to whole stover at 34 GGE/ton. This equated to MFSPs of \$6.37/GGE for cobs, \$7.07/GGE for husks, and \$10.18/GGE for stalks, compared to \$8.76/GGE for whole stover when fixing all cases to a delivered biomass cost of \$80.10 per dry ton. Viewed differently, the biorefinery would be able to pay roughly \$70–\$100 per ton more for husks or cobs (valued at \$149/ton and \$185/ton, respectively) relative to the whole stover basis at \$80/ton in order to achieve equivalent economics measured as MFSP, but must pay \$40/ton less for fractionated stalks (\$39/ton equivalent biomass purchase price) than whole stover to maintain equivalent fuel selling prices.

The most direct takeaway from this assessment is that a biorefinery would stand to benefit economically from maximizing the use of cob and husk fractions while avoiding or minimizing the use of stalks, though recognizing practical constraints with this approach in maintaining an equivalent processing capacity (fixed at 2,000 dry metric tonnes per day in all cases). Future experimental work would benefit to investigate additional fractions (i.e. leaves) as well as downstream unit operations (i.e. fermentation and lignin upgrading to higher-value coproducts) beyond the details reported here.

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Introduction

A key area of interest under the Feedstock-Conversion Interface Consortium's (FCIC's) Low-Temperature (LT) Conversion pathway has been centered around understanding impacts and potential benefits of isolating and processing separate anatomical fractions of corn stover, relative to performance of whole stover biomass. Work on this topic seeks to understand the cost-benefit trade-offs of adding more preprocessing logistics steps to fractionate corn stover into its constituent anatomical fractions (e.g., cobs, husks, stalks, leaves) versus downstream benefits on conversion recalcitrance, yields, and ultimately biorefinery economics, which can be quantified utilizing techno-economic analysis (TEA) modeling. The hypothesis is that such biomass anatomical fractions vary in composition and recalcitrance. These compositional and recalcitrance impacts will cascade through the conversion pathway, impacting pretreatment conditions and titer/rates/yields of enzymatic hydrolysis and fermentation. This case study seeks to quantify impacts to biorefinery economics for the conversion of each isolated anatomical fraction as measured by the minimum fuel selling price (MFSP) at a fixed feedstock cost. The analysis also solves for variances in delivered feedstock cost that the biorefinery may be willing to pay across the individual anatomical fractions in order to maintain a fixed MFSP, in order to valorize the anatomical fractions for future feedstock optimization.

A simplified diagram of the LT conversion process is depicted in Figure 1, highlighting the key operations within the scope of experimental focus and thus data inputs furnished for TEA modeling. In brief, the National Renewable Energy Laboratory's (NREL's) 2018 biochemical design report forms the general basis for the integrated biorefinery process as leveraged for the present modeling efforts (Davis et al. 2018), consisting of deacetylation and mechanical refining (DMR) pretreatment, batch enzymatic hydrolysis, hydrolysate clarification/solids removal, fermentation of clarified sugars to intermediates, and catalytic upgrading of those intermediates to final hydrocarbon fuels. Of those operations, the steps within the scope of FCIC's experimental focus include DMR pretreatment, enzymatic hydrolysis, and sugar fermentation, and accordingly these steps are of primary attention in the process/TEA models exercised for this case study analysis, as summarized below. Additionally, the aforementioned design report included consideration for lignin valorization via deconstruction and bioconversion of lignin to value-added coproducts (adipic acid), for which experimental data were also collected in this FCIC effort. However, to simplify this case study (and because the economics for lignin deconstruction/upgrading do not yet break even with lignin combustion), the TEA presented herein does not include this lignin valorization route and instead simply routes lignin and other waste biomass to the boiler for heat and power generation.

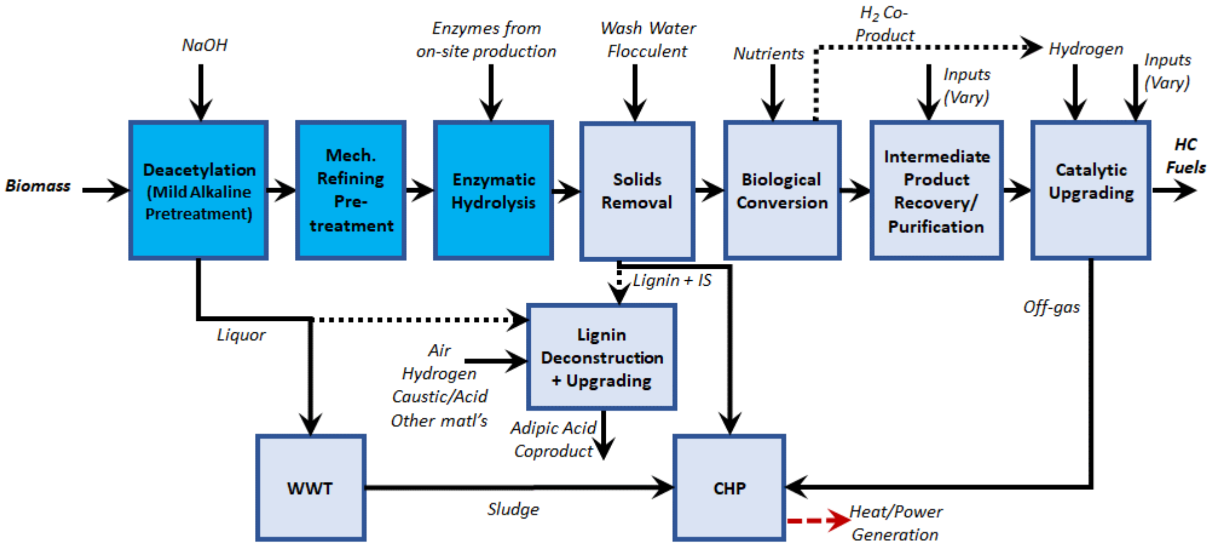

Figure 1. Block diagram schematic of framework LT conversion biorefinery process as modeled. Blue highlighted boxes represent the primary scope of FCIC's experimental focus for this study. To simplify the analysis, this assessment assumes routing all lignin and residual solids/off-gases to combustion for combined heat and power (CHP) rather than upgrading of lignin and deacetylation liquor (solubilized lignin) to coproducts.

Methods

As noted above, NREL's 2018 biochemical design case was utilized as the starting framework for TEA modeling conducted here (Davis et al. 2018). However, as highlighted in Figure 2, some details of that framework were modified to reflect the operations as performed experimentally, as well as the sequence of the operations. In summary, the key modifications incorporated into the models relative to the projected design case details (future 2030 targets) include:

- Deacetylation: Replaced continuous counter-current deacetylation operation (design case target approach) with standard batch deacetylation (FCIC experimental basis).
- Hydrolysis/hydrolysate clarification: FCIC model only reflects standard batch enzymatic hydrolysis (no continuous enzymatic hydrolysis [CEH] employed), followed by the addition of hydrolysate solids removal (not used in either design case pathway). For the latter step, the TEA model assumes the use of a vacuum belt filter with wash water and flocculant, following parameters as utilized in NREL's 2019 state of technology (SOT) benchmarks for this operation (Davis et al. 2020).
- Sugar fermentation: TEA models are based only on the acids fermentation pathway (the second design case pathway via 2,3-butanediol [BDO] upgrading to fuels is not included in this study). We note that this is not a reflection of a broader preference for one pathway over another in the LT Conversion platform, but strictly a decision to focus limited resources. Based on data availability, the TEA models maintain the use of fed-batch fermentations coupled with *in situ* acid removal via pertractive membranes reflecting 2019 SOT parameters for pertraction and downstream catalytic upgrading (outside of FCIC's scope).

- Lignin upgrading: To simplify this assessment, lignin valorization via deconstruction and upgrading to coproducts is not included in this report. Rather, solid residual lignin is routed to combustion for combined heat and power generation, while DMR liquor is routed to wastewater treatment.

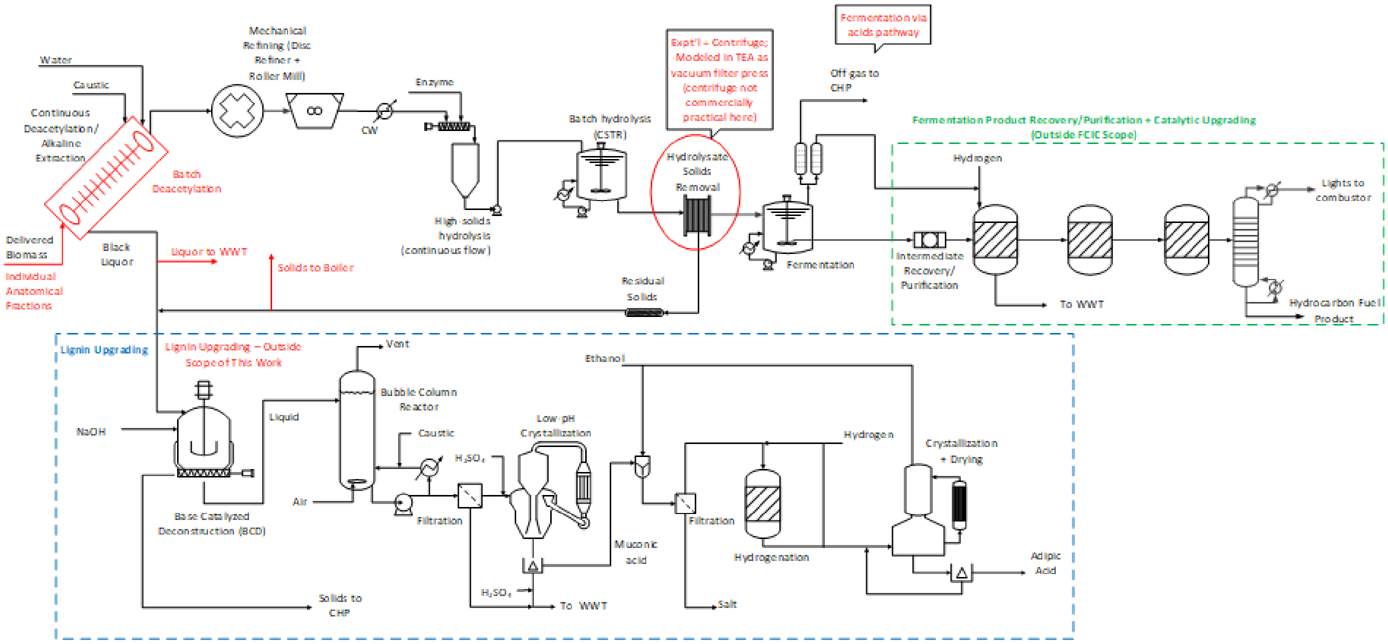

Figure 2. Process flow diagram of 2018 NREL design report framework for the LT conversion process. Modifications from design case models reflecting FCIC operational details are highlighted in red.

Whole corn stover as well as the anatomical fractions of cobs, husks, and stalks were provided to NREL by researchers at Idaho National Laboratory (a fourth anatomical fraction, leaves, was not available). Compositional analysis of the feedstocks and LT deconstruction experiments (using DMR and enzymatic hydrolysis) were performed by NREL researchers on the whole corn stover as well as the anatomical fractions. The conversion experiments correspond to the highlighted unit operations in Figure 1.

DMR pretreatment conditions were fixed across all feedstock cases, based on deacetylation at 70 kg sodium hydroxide loading per dry tonne biomass and 90°C. Biomass deconstruction through DMR pretreatment and hydrolysis was conducted under FCIC Task 5, evaluating two separate enzyme loading cases at approximately 12 and 20 mg total enzyme (cellulase plus hemicellulase) per gram of cellulose at 20% total solids; exact loadings varied slightly across each fraction. However, hydrolysate generation for purposes of providing material to downstream fermentation experiments was conducted separately under Task 7.1, using an enzyme loading of approximately 15 mg/g cellulose. This incurs an obvious disconnect in the continuity for a single data set across integrated conversion operations, but between the two loadings used for deconstruction, the 12-mg/g case was selected as the basis in the integrated model, given that the deconstruction data (as the primary focus of this assessment) were based on this loading.

Feedstock costs were set consistent with the latest 2020 SOT benchmarks furnished from Idaho National Laboratory, at $80.10/dry ton (Davis et al. 2021). This was initially fixed for all feedstock fractions in solving for MFSP, but then were allowed to vary in order to find the "value" for each fraction that would maintain a set MFSP associated with the whole stover case.

Results and Discussion

The delivered feedstock compositions representing the whole stover and three anatomical fractions (after adjusting to 100% mass closures) are summarized in Table 1.

Table 1. Delivered biomass feedstock composition for whole stover and anatomical fractions (input to TEA models after adjusting to 100% mass closures)

Component	Whole Stover	Cobs	Husks	Stalks
Glucan	37.61	34.67	39.65	36.26
Xylan	20.30	29.89	22.41	18.03
Lignin	15.79	16.91	14.55	16.95
Ash	6.82	1.55	3.60	4.00
Acetate [a]	2.21	2.88	2.58	2.35
Protein [b]	3.10	3.10	3.10	3.10
Extractives [c]	8.65	5.59	8.53	14.73
Arabinan	3.24	3.18	3.30	2.53
Galactan	1.58	1.59	1.57	1.28
Mannan [b]	0.60	0.60	0.60	0.60
Sucrose	0.10	0.04	0.11	0.17
Total structural carbohydrate	*63.33*	*69.93*	*67.53*	*58.70*
Total structural carbohydrate + sucrose	*63.43*	*69.97*	*67.64*	*58.87*
Moisture (bulk wt %)	*20.0*	*20.0*	*20.0*	*20.0*

[a] Represents acetyl groups present in the hemicellulose polymer, converted to acetic acid under low-pH conditions.

[b] Protein and mannan were not available in compositions provided; set here based on 2018 design report (Davis et al. 2018).

[c] Biomass extractives were approximately 2 percentage points lower based on data provided, but were further adjusted here to achieve 100% mass closures.

Tables 2 and 3 summarize the resulting quality attributes measured experimentally for the product streams exiting deacetylation (mass balances for component solubilizations to black liquor) and enzymatic hydrolysis (sugar yields), respectively. For deacetylation mass balances (Table 2), the original lignin solubilization yields to black liquor were not considered reliable on an absolute basis given the uncertainty in the underlying measurement method employed, although they were deemed appropriate on a relative basis to each other. Therefore, those values were readjusted by scaling relative to the 2019 SOT benchmark (Davis et al. 2020), which utilized similar deacetylation conditions and was felt to yield a more reliable 50% lignin solubilization fraction to black liquor, set accordingly here for the "whole stover" case and then scaled by ratio to the other anatomical fractions relative to originally measured values. Additionally, solubilizations of ash and extractives were not reported for this data set, and thus were fixed constant at 11% and 100%, respectively, based on the 2019 SOT.

After discussing the context for the data originally collected on the fermentation step with FCIC researchers, it was decided that this data set would not be included in the TEA models for the various biomass cases. The FCIC fermentations for carboxylic acid production were performed in small-scale batch operations with pH control, which is not optimal or practical for the way this fermentation would be run at scale (fed-batch with continuous pertractive acid removal). Among other issues, both the kinetics for sugar consumption (primarily seen to be problematic for xylose) and the biological cell response to the batch fermentation conditions (decreasing the ratio of butyrate versus byproduct acetate yields, the latter being less preferable for recovery and upgrading) would incur artificial impacts on fermentation performance and resultant quality attributes that wouldn't likely be expected under fed-batch fermentation with *in situ* acid product removal. Under more optimal conditions, sugar feed rates could be better controlled to ultimately support higher xylose consumption and lower acetate by-production. Thus, to avoid introducing such artificial impacts, which could risk conflating the results in the wrong direction, for this exercise the acid fermentation parameters were maintained consistent with NREL's 2019 SOT benchmark (95% conversion of glucose and xylose to product, 20% of arabinose to product, 50:1 mass ratio of butyrate vs. acetate production, 0.62-g/L-h productivity) (Davis et al. 2020).

Likewise, although additional data were collected for fermentation of lignin monomers to muconic acid (as can subsequently be upgraded to adipic acid, a value-added coproduct), the inclusion of lignin conversion to coproducts has been shown in prior NREL SOT reports to incur more processing costs than the resulting amount of coproduct revenue generated, based on *current* performance for lignin deconstruction and bioconversion (though this is projected to improve in the future) (Davis et al. 2021). As this can conflate the overall TEA results for the integrated biorefinery and alter the trends for MFSP attributed to carbohydrate conversion to fuels, to simplify the results for this report, all solid lignin and other residual materials are routed to combustion for heat and power generation, while the DMR liquor stream (containing solubilized lignin and other organics) is routed to wastewater treatment.

Table 2. Deacetylation mass balances reflecting solubilizations to black liquor

Solubilization to Black Liquor	Whole Stover	Cobs	Husks	Stalks
Glucan	1.5%	2.1%	1.3%	2.0%
Xylan	13.2%	14.6%	10.9%	24.3%
Arabinan	43.0%	65.0%	38.1%	81.9%
Lignin [a]	50.0%	64.3%	48.3%	40.0%
Acetate	100%	100%	100%	100%
Ash [b]	11%	11%	11%	11%
Extractives [b]	100%	100%	100%	100%

[a] Lignin solubilizations shown here reflect adjustments from originally reported data, which were not felt to be accurate on an absolute basis—scaled based on 2019 SOT benchmark relative to 50% as the basis for whole stover (Davis et al. 2020).

[b] Ash and extractives were not reported for this data set—fixed constant at 11% and 100%, respectively, per 2019 SOT.

Table 3. Enzymatic hydrolysis yields and enzyme loadings

Hydrolysis Sugar Yields	Whole Stover	Cobs	Husks	Stalks
Enzyme loading (mg/g cellulose)	12.5	13.4	11.2	13.2
Glucose monomer yield	70.9%	89.1%	80.2%	70.3%
Xylose monomer yield	83.2%	89.0%	87.9%	74.8%
Arabinose monomer yield	63.7%	56.8%	69.3%	65.9%
Glucan oligomer yield	6.0%	6.5%	7.1%	5.3%
Xylan oligomer yield	9.9%	12.4%	12.2%	5.8%

After running the above data for each biomass case, the resulting model outputs are presented in Figure 3 and Table 4. The results are presented two ways: one solving for variable MFSP at a fixed biomass feedstock cost of $80.10/dry ton (consistent with the 2020 *n^th^*-plant SOT basis for whole stover [Davis et al. 2021]), and a second solving for variable biomass feedstock costs that the biorefinery would be able to pay in order to maintain the same fuel selling price as the "whole stover" basis for all anatomical fraction cases. As shown here, the "whole stover" biomass is shown to exhibit a higher MFSP and lower fuel yield (gallons of gasoline equivalent [GGE] per ton) relative to two of the three anatomical fractions (cobs and husks), translating to the ability for the biorefinery to accommodate higher delivered biomass feedstock costs for those fractions while maintaining the same output fuel selling price, with the stalks fraction faring worse than whole stover.

The trends in MFSPs are correlated with fuel yields, with the cob fraction achieving the highest fuel yields and lowest MFSPs, followed closely by husks, and lastly by stalks with the lowest fuel yields and highest MFSPs of the individual fractions (and also worse than whole stover, while cobs and husks fared better than the whole material). This reflects overall combinations of biomass fraction compositions and yields across the various steps to fuel outputs, with both cobs and husks exhibiting higher conversions of more carbohydrates, but stalks suffering from higher recalcitrance leading to lower conversions of less starting carbohydrates, coupled with higher losses to deacetylation liquor—particularly for xylan and arabinan.

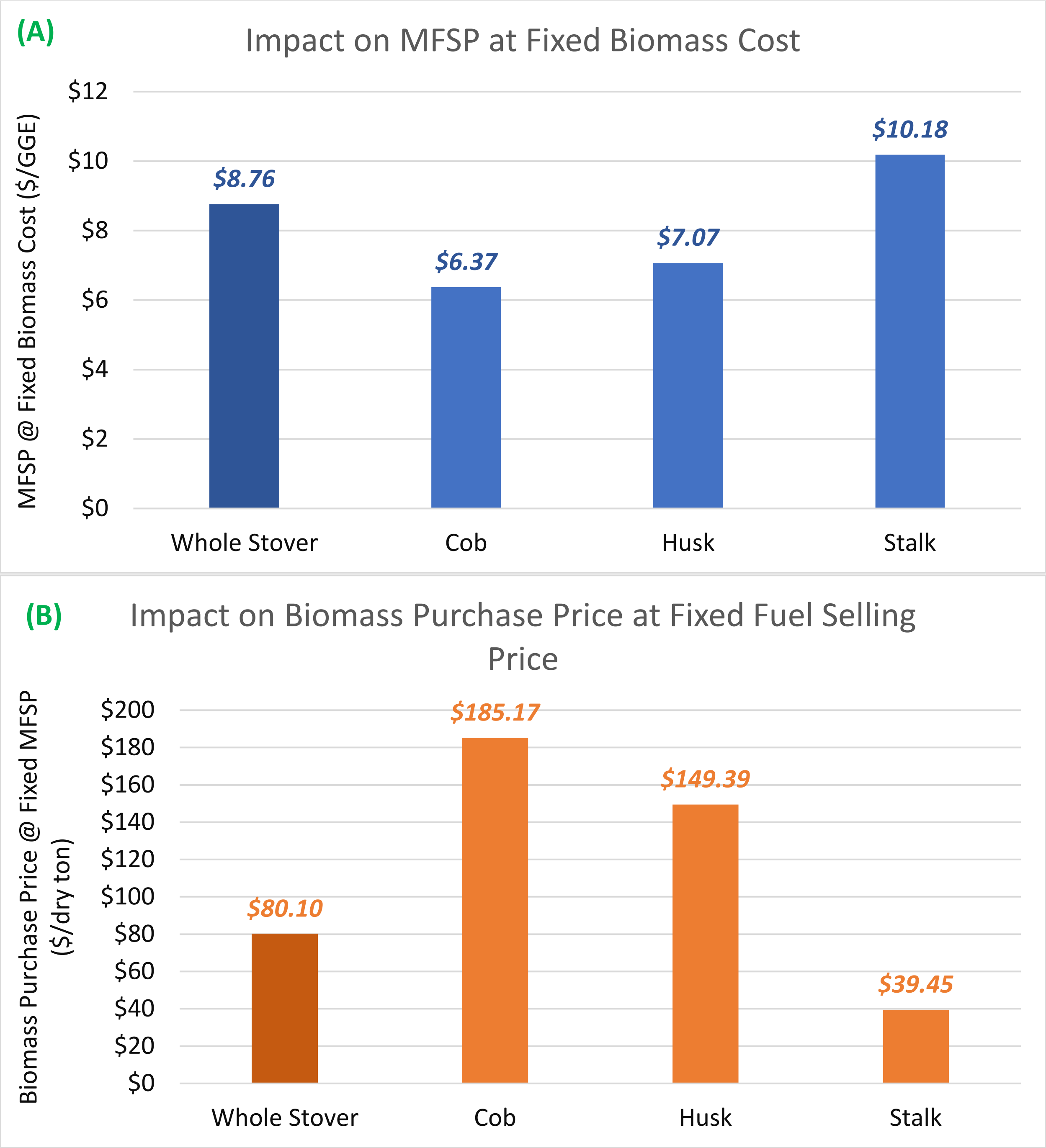

Figure 3. TEA results for (A) MFSP at fixed biomass feedstock cost ($80.10/dry ton) and (B) biomass feedstock price that can be accommodated at fixed fuel selling price (matching whole stover basis = $8.76/GGE)

The most direct takeaway from these results is that a biorefinery could greatly benefit from preferentially processing cob and husk tissue fractions, while avoiding or minimizing the use of stalks, relative to processing whole stover. However, as the stalk material constitutes a considerable fraction of the total stover biomass (representing 48% of the total share of corn stover amongst these three fractions evaluated, versus 16% for cobs and 36% for husks), it may not be economically practical to avoid the stalk fraction entirely, as this would increase the necessary biomass collection radius and transportation distance to a biorefinery to maintain the target 2,000-tonne/day processing capacity. Alternatively, further analysis may be warranted to evaluate economic tradeoffs between reducing the share of stalk material processed through the biorefinery versus economy of scale penalties as would be incurred at smaller biorefinery processing scales through the avoidance of a portion of the stalk fraction. Further experimental work could also investigate alternative technologies or processing conditions as may achieve more favorable results for conversion of the stalk fraction.

Table 4. Key TEA results for whole stover and anatomical fractions evaluated

Anatomical Fraction	MFSP ($/GGE, $80/ton biomass)	Fuel Yield (GGE/ton)	Biomass Cost Allowance to Maintain Whole Stover MFSP ($/ton)
Whole stover	$8.76	34.3	$80.10
Cob	$6.37	44.0	$185.17
Husk	$7.07	40.9	$149.39
Stalk	$10.18	28.7	$39.45

Conclusion and Next Steps

The work conducted here demonstrates promising potential for an alternative approach to biorefinery feedstock preprocessing through separation of the individual anatomical fractions of corn stover before being sent through biorefinery conversion operations. Relative to whole stover biomass, the combination of compositions and conversion performance translates to higher fuel yields and lower biorefinery MFSPs for two of the three individual anatomical fractions evaluated (cobs and husks), though with stalks suffering from lower compositional quality and higher recalcitrance, and ultimately higher MFSPs. Moving forward, further research is warranted to obtain and evaluate process convertibility for additional fractions (primarily leaves) to understand how these trends extend accordingly to those materials, as well as to investigate downstream impacts on hydrolysate fermentation under commercially relevant conditions. Additional work could also be done to identify alternative technologies or processing conditions to achieve improved conversion of the stalk fraction, or otherwise to evaluate TEA implications of reducing the use of stalks at smaller associated biorefinery processing scales.

In light of focus being paid to this topic of biomass anatomical fractionation across multiple FCIC tasks spanning the field-to-fuel supply chain, the outcomes of this TEA assessment may ultimately allow for tie-ins with other TEA case studies being pursued in upstream feedstock collection and preprocessing logistics focused on this topic. For example, if economic analysis work in those tasks can be linked to establish an overall cost premium for delivering fractionated biomass to the biorefinery relative to whole corn stover, those findings may be integrated with analysis such as this from the conversion step in quantifying the additional premium that a biorefinery may be able to pay for such material while maintaining, or ideally improving, overall economics relative to whole stover processing.

Citations and References

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