

# Engineering, nutrient removal, and feedstock conversion evaluations of four corn stover harvest scenarios

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## Abstract

Crop residue has been identified as a near-term source of biomass for renewable fuel, heat, power, chemicals and other bio-materials. A prototype one-pass harvest system was used to collect residue samples from a corn (*Zea mays* L.) field near Ames, IA. Four harvest scenarios (low cut, high-cut top, high-cut bottom, and normal cut) were evaluated and are expressed as collected stover harvest indices (CSHI). High-cut top and high-cut bottom samples were obtained from the same plot in separate operations. Chemical composition, dilute acid pretreatment response, ethanol conversion yield and efficiency, and thermochemical conversion for each scenario were determined. Mean grain yield in this study ( $10.1 \text{ Mg ha}^{-1}$  dry weight) was representative of the average yield ( $10.0 \text{ Mg ha}^{-1}$ ) for the area (Story County, IA) and year (2005). The four harvest scenarios removed 6.7, 4.9, 1.7, and  $5.1 \text{ Mg ha}^{-1}$  of dry matter, respectively, or 0.60 for low cut, 0.66 for normal cut, and 0.61 for the total high-cut (top + bottom) scenarios when expressed as CSHI values. The macro-nutrient replacement value for the normal harvest scenario was  $\$57.36 \text{ ha}^{-1}$  or  $\$11.27 \text{ Mg}^{-1}$ . Harvesting stalk bottoms increased stover water content, risk of combine damage, estimated transportation costs, and left insufficient soil cover, while also producing a problematic feedstock. These preliminary results indicate harvesting stover (including the cobs) at a height of approximately 40 cm would be best for farmers and ethanol producers because of faster harvest speed and higher quality ethanol feedstock.

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## 1. Introduction

The US Department of Energy (DOE), Office of Biomass Program (OBP) plans to accelerate the use of agricultural residue as a near-term source of biomass for renewable fuel, heat, power, chemicals and other bio-materials. To implement this vision [1], the OBP is supporting development of science and technologies that

will help establish biomass as a significant source of environmentally sound, sustainable and renewable fuels, heat, power, chemicals and materials [2]. These efforts will complement commercial ventures [3] and are expected to make important contributions to US energy security while supporting and enhancing rural economic development and environmental quality [4]. The OBP plan is to work through existing and new partnerships toward a major solicitation for a biomass-based ethanol plant in 2008 [5].

Graham et al. [6] estimated the total corn stover production in the Northern Iowa/Southern Minnesota region at  $7.61 \text{ Mg ha}^{-1}$  and that about two-thirds ( $5.16 \text{ Mg ha}^{-1}$ ) could be collected in a sustainable manner.

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Though Graham et al. [6] suggest a portion of the stover produced should be left in these Corn Belt fields, they give no information on what portion of the plant would be most advantageous for biomass ethanol production or which part or parts of the plant would be best to leave in the field. An additional question of how to most efficiently collect stover has not been addressed.

Stover is composed of several identifiable components, all with different functions in the plant and different characteristics. Hanway [7] reported that cobs represented about 9% of the above ground biomass at physiological maturity. Overall, husks, shanks, silks and cobs account for 30% of the stover mass, while stalks, tassels, leaf blades and leaf sheaths account for the remaining 70%. Pordesimo et al. [8] reported 15% of the stover dry mass is cob and that stalks (plus leaf sheaths and tassel), leaf blades, and husks (plus shank) accounted for 51%, 21%, and 13% of the stover, respectively. These differences may reflect harvest method and/or cultivar, but including cobs as part of the collected stover fraction is important and would partially address transportation and storage concerns because cobs are the most dense stover component. Crofcheck and Montross [9] reported greater conversion efficiency, release of glucose, from both native (untreated) and NaOH-pretreated cobs than other stover components (leaves, stalks, and husks).

With regard to sustainability of the soil resources, removing stalks very close to the soil surface will result in less surface residue cover, exacerbate the potential wind and water erosion [10–12], accelerate the decline in soil organic carbon levels [13,14], and potentially reduce future crop yields [15]. More detailed discussions of potential impacts of stover removal on future productivity and soil quality are presented by Wilhelm et al. [16], Wilts et al. [17], and Kim and Dale [18]. Understanding this component of biomass removal, including the additional plant nutrients that will be removed and have to be replaced, is very important for the long-term success of the bio-energy system.

To minimize the effect of residue removal on soil resources, Crofcheck and Montross [9] suggested collecting only the fraction of corn stover with the greatest glucose potential (i.e. cobs, leaves, and husks) and leaving the remaining stover in the field for soil erosion control and to help sustain soil organic carbon reserves. Currently, that fraction (~30% of stover mass) passes through the combine and falls to the ground. Development of a harvest system to capture this material is thus an engineering challenge that will make biomass recovery from corn more efficient and profitable.

Our assessment based on 2005 field-plot data examines (i) the engineering challenges associated with harvesting corn stover, (ii) the amount of plant nutrients removed with the stover and the potential impact of stover removal on future crop production and soil quality indicators, and (iii) the potential ethanol production from the various stover fractions.

## 2. Materials and methods

### 2.1. Stover collection and analyses

Corn stover samples were collected from plots established within a general production site at the ISU Agronomy and Agricultural Engineering Farm near Ames, IA (42° 2' N 93° 48' W). The corn hybrid was 'Fontenell 5393', grown following a 2004 soybean [*Glycine max* (L.) Merr.] crop and fertilized with ~170 kg N ha<sup>-1</sup>. Four stover harvest scenarios (low cut, high-cut top, high-cut bottom, and normal cut) were evaluated approximately 30 days after physiologic maturity (growth stage R6) using an experimental harvesting system that consisted of a John Deere 9750 STS combine, a 6-row John Deere 653A row crop header with a prototype corn reel, and a standard John Deere rear chopper (Deere & Co, Moline, IL<sup>1</sup>) (Fig. 1).

The four harvest scenarios were achieved by varying the cutting height of the combine head. The low cut left approximately 10 cm of stubble and a minimum amount of leaf tissue in the field (Fig. 2). All other material passed through the combine with the grain being separated from the stover and cobs. For the normal cut, the header was positioned about midway between the base of the ears and the soil surface. This left approximately 40 cm of stubble plus the leaves that had been attached below the cutting height (Fig. 2). High-cut top samples were obtained by cutting the plants just below the ears so that only the ears and plant parts above them entered the combine. This resulted in a stubble height of approximately 75 cm (Fig. 3). The high-cut bottom samples were collected in a subsequent operation by making a second pass across the high-cut top transects with the header set as it had been for the low cut treatment (i.e. stubble height of ~10 cm).

All cobs and stover material above the header's rotary knives were conveyed into the combine threshing system through the feederhouse. Stover discharged from the rear chopper was directed into a Gehl forage blower (Model FB85, Gehl, West Bend, WI) driven by a 48 kW, Wisconsin V-4 air-cooled engine (Model V465D, Wisconsin Motors, LLC, Memphis, TN) attached to the rear of the combine. Stover passing through the forage blower was collected in a forage wagon equipped with a Weigh-Tronix weight measurement system (Model 1000R, Weigh-Tronix, Fairmont, MN) to record the mass of stover collected for each harvest transect. In addition, the mass of grain for each harvest transect was recorded using a Parker 500 Grain wagon equipped with a similar Weigh-Tronix measurement system (Model 1015, Weigh-Tronix, Fairmont, MN).

<sup>1</sup>References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government, any agency thereof, or any company affiliated with the Idaho National Laboratory or Iowa State University.



Fig. 1. The low cut stover collection.

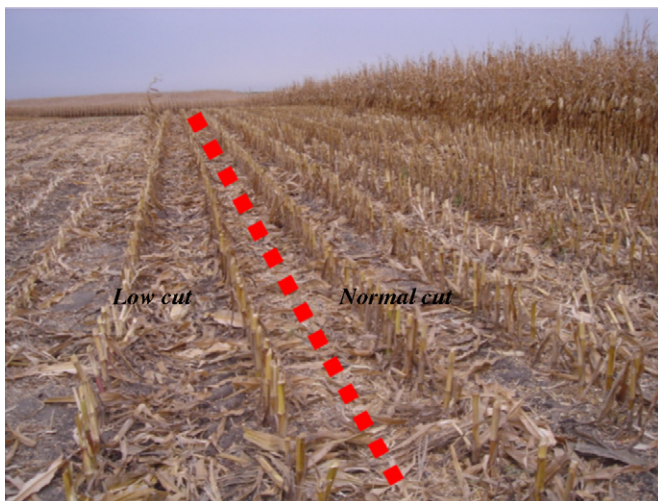


Fig. 2. Showing the low cut area (left side) and the normal cut area (right side).



Fig. 3. Reference height of stubble remaining after high-cut top stover collection.

The stover samples from all four harvest scenarios were analyzed for water content, macro- and micro-nutrient concentrations, chemical composition influencing ethanol production, dilute acid pretreatment response, and ethanol conversion efficiency. Subsamples were also sent to a commercial laboratory to determine several thermochemical conversion parameters: ultimate, proximate, chlorine, ash, chlorine and carbon dioxide in ash, as well as oxidizing and reducing fusion temperatures.

## 2.2. Stover nutrient removal

Plant nutrient removal and water content were determined on stover samples dried for 48 h in a forced-draft oven at 60 °C. Dried samples were ground to pass a 0.5 mm stainless-steel screen and a subsample was digested in sulfuric acid and 30% hydrogen peroxide [19]. Digests were analyzed for total P, K, Ca, Mg, Cu, Fe, Mn, and Zn content via inductively coupled plasma (ICP) spectroscopy. Another subsample of the dried, ground stover was analyzed for total C and N via dry combustion. Macro- and micro-nutrient removal was calculated using the measured nutrient concentrations and the amount of biomass corrected for water content to a dry-weight basis. A third set of stover samples were analyzed for their chemical constituents for relevance as a feedstock for biochemical conversion to ethanol. A Foss 6500 NIR instrument, calibrated using the NREL corn stover calibration model [20], was used to estimate the compositional characteristics.

## 2.3. Stover conversion

A reduced-severity dilute sulfuric acid pretreatment screening method was used to estimate the potential for using cheaper industrial ethanol production methods. The samples were ground to pass a 2-mm stainless-steel screen with a knife mill, dried overnight at 80 °C, allowed to cool, and digested with 0.8% sulfuric acid (w/w). A 2.5 g biomass subsample was added to 75 mL of acid, allowed to incubate at room temperature for about 2 h to enable the acid to permeate the biomass, and then autoclaved at 121 °C, 145 kPa for 30 min. After cooling, the wet biomass was vacuum filtered through Gooch crucibles with glass filters, rinsing with a minimal amount of deionized water to recover all the biomass. Liquid recovered from the wet biomass and the rinsate were combined and brought to 100 mL with deionized water (this liquid is called the pretreatment liquid in the remainder of the paper). The biomass was washed with deionized water for 3–4 min to remove residual H<sub>2</sub>SO<sub>4</sub>, which can inhibit fermentation, weighed and stored for later use in simultaneous saccharification and fermentation (SSF) reactions.

Oligomers in a 2.95 mL aliquot of the pretreatment liquid were hydrolyzed with 0.05 mL of concentrated sulfuric acid. This mixture was autoclaved at 121 °C, 145 kPa for 20 min. The hydrolyzed pretreatment liquid

(2 ml) was then neutralized with 1–3 g of lead carbonate, by intermittent vortexing, until the pH was 4.5 or above. Samples were then diluted 10× with deionized water, filtered, and analyzed on an HPLC for lignocellulosic sugars as previously described [21].

The SSF analysis was conducted aseptically in 60 mL serum vials as previously described [22,23]. All solutions were sterilized by autoclaving for 30 min at 121 °C and 145 kPa, and/or by filter sterilization (0.2 µm) prior to use. The samples plus a series of controls without corn stover were analyzed in quadruplicate. Each vial received 1.0 g of dry biomass sample or an equivalent of pretreated sample (corrected for water content to provide 1 g of dry material). Water was added to achieve a final volume of 30 mL. The vial headspace was purged for 2 min with oxygen-scrubbed ultra high purity nitrogen, and sealed with butyl stoppers and aluminum closures. Vials were autoclaved at 121 °C and 145 kPa for 30 min. Once cooled to room temperature, 5 mL of enzyme cocktail was added. The cocktail contained 1.36 mL of 1 M citric acid buffer, pH 4.4; 2.7 mL of 10× yeast-peptone stock solution (100 g/L yeast extract, 200 g/L peptone); and 1 mL of diluted Spezyme CP (Genencor; Palo Alto, CA) diluted to a final concentration of 0.03 mL/30 mL reaction vial, in phosphate buffered saline (PBS, 11.8 mM phosphate buffer, pH 7; 200 mM NaCl, 27 mM KCl) solution. Finally, 1.0 mL of yeast preparation was aseptically added to each vial. This gave a final OD600 of 0.5 for each experimental vial. The yeast was prepared by inoculating one colony forming unit (CFU) of *Saccharomyces cerevisiae* NRRL Y-2034 in a 300 mL liquid yeast peptone glucose solution (YPG; 10 g/L yeast extract, 20 g/L peptone, 50 g/L glucose). The culture incubated aerobically overnight (19–22 h) at 30 °C rotating at 175 rpm. It was then pelleted by centrifugation and washed once with PBS buffer. The washed yeast pellet was resuspended in PBS to an OD600 of 15. Ethanol production was quantified on days 1, 3, 5, and 7 by injecting 200 µL of the headspace gas into a gas chromatograph with a flame ionization detector (GC-FID). Standards were prepared using aqueous concentrations of ethanol. Ethanol concentrations were normalized to the theoretical production of 0.51 g ethanol per 1.0 g of C6 sugars for graphical presentation and statistical analyses [23].

#### 2.4. Thermochemical conversion of stover

A third set of stover samples was tested for thermochemical conversion parameters by Hazen Research, Inc. in Golden, CO where they used American Society for Testing and Materials (ASTM) Standards. The analyses included proximate analyses; ash by ASTM D3174 modified (600 °C), volatiles using ASTM D3175; ultimate analyses using ASTM D5373, sulfur by ASTM D4239, and chlorine by ASTM D2361; and heating values using ASTM D5865, from which other parameters were calculated. Ash chemical composition was determined using ASTM D2795 modified (600 °C), and ash fusion temperatures were estimated using ASTM D1857.

### 3. Results and discussion

#### 3.1. Grain yield

Corn grain yield (Table 1) compared favorably with the 11.7 Mg ha<sup>-1</sup> average (150 g kg<sup>-1</sup> water content) reported for 2005 in Story County, IA by the National Agricultural Statistics Service (NASS) [24]. Having a geographically representative grain yield was important because the NASS does not report stover yields. Consequently, many investigators have estimated crop residue production based on harvest indices [HI = grain mass/(grain mass + stover mass)] and grain yield. Use of HI and grain yield to compute potential stover yield is bolstered by the fact that for corn, HI varies over a relatively narrow range (0.48–0.53) [25]. Linden et al. [26] reported that their HI (0.56) did not vary with time (13 yr) or among treatments (including tillage intensity, N application rate, and stover removal). Tollenaar [27] reported that harvest index differed very little among several era hybrids when grown at their optimum plant population in Ontario. Harvest index and other ratios of grain and stover have been employed to estimate source carbon from corn residues, roots, and rhizodeposits as well as stover yield [28,29].

It should be noted, however, that HI is a precise term used by plant scientists to describe the partitioning of dry matter. To be calculated accurately and conform to the definition, all above ground mass must be included in the

Table 1  
Grain and stover yields for the four harvest scenarios

Harvest scenario	Grain			Stover		
	Water (mg g <sup>-1</sup> )	Wet <sup>b</sup> (Mg ha <sup>-1</sup> )	Dry	Water (mg g <sup>-1</sup> )	Wet (Mg ha <sup>-1</sup> )	Dry
High-cut top	112	11.83	10.47	196	6.05	4.86
High-cut bottom <sup>a</sup>	—	—	—	639	4.75	1.71
Low cut	121	11.41	10.03	338	10.10	6.68
Normal cut	118	11.04	9.74	237	6.67	5.09

<sup>a</sup>This stover fraction comes from the same transect as high-cut top so there is no grain.

<sup>b</sup>Wet corn grain is the harvest weight adjusted for a water content of 150 g kg<sup>-1</sup>.

denominator. Therefore, to avoid confusion with other references to HI, we defined an alternative parameter, *collected stover harvest index* (CSHI) where:  $CSHI = \text{grain mass} / (\text{grain} + \text{collected stover})$ . This was done because even for the low cut harvest scenario, a portion of the corn stover was left in the field. The CSHI is a more accurate representation of the amount of *collectable* stover produced by crops with specific grain yield. The CSHI values were 0.60, 0.66, and 0.61 for the low, normal, and total high-cut (top + bottom), respectively. Though these values were greater than the 0.5 HI widely used in the literature [25,26,29], we suggest they are more realistic for computing the amount of stover (including cobs) that can be collected with a one pass mechanical harvesting system.

### 3.2. Stover collection

Stover yield, as expected, was greatest for the low-cut scenario ( $\sim 6.7 \text{ Mg ha}^{-1}$ ) and for the total high-cut (top + bottom) ( $\sim 6.6 \text{ Mg ha}^{-1}$ ). We anticipated the lower stalk (i.e. high-cut bottom) would contribute a substantial amount of dry matter because of greater stalk thickness at the base of the plant. However, the high-cut top fraction produced more stover because cobs, the most dry matter dense component of stover, were part of that fraction.

The normal cut scenario provided about 76% of the stover achieved by the low cut, with far less risk of combine damage and much greater field efficiency because the ground speed was greater [30]. This scenario also collected about 5% more stover than the high-cut top, with less risk of leaving grain in the field. In comparison to estimates by Graham et al. [6], our normal cut scenario collected only  $0.07 \text{ Mg ha}^{-1}$  less than their estimate, but the amount of residue left on the soil in our study ( $\sim 24\%$ ) was less than their prediction ( $\sim 32\%$ ). This may appear to be sufficient residue for surface cover, but the amount of C returned to the soil was only 25–30% of that suggested by Johnson et al. [28] as being needed to maintain soil organic matter.

The high-cut bottom fraction also had a very high water content ( $\sim 64\%$ ) which would significantly increase transportation costs and require either extensive drying or storage under anaerobic (wet) conditions [31]. Biomass that needs to be collected with greater water content is generally more expensive to harvest, store, and transport than dry

biomass. Mixing the very wet stover with the drier upper plant parts and cobs (i.e. low-cut scenario) resulted in intermediate water content for the low-cut scenario (Table 1). The relatively small mass and very high water content make the base of the stalk less desirable as an ethanol feedstock. This fraction would also likely incur dockage at a dilute acid biorefinery, because 60% water content is the cutoff point beyond which those operations will become more expensive due to dilution of the pretreatment catalytic agents such as sulfuric acid. The base of the stalk is also the stover fraction that has greatest potential for soil contamination due to raindrop splash and field operations during harvest. Our preliminary results suggest that leaving the stalk base in the field would be a wise choice from several perspectives.

### 3.3. Stover nutrient removal

Macro-(N, P, K, Ca, and Mg) and micro-nutrient (Cu, Fe, Mn, and Zn) concentrations in the stover for the various harvest scenarios are presented in Table 2. The concentrations were consistent with other corn hybrids [29,32] and when multiplied by the dry biomass revealed an additional N-removal in the stover of 34 and  $42 \text{ kg ha}^{-1}$  for the high-cut top and normal cut harvest scenarios, respectively (Table 3). Phosphorus and K removed in the stover averaged 3.9 and  $34 \text{ kg ha}^{-1}$ , respectively. The increased nutrient removal associated with harvesting crop residues for biofuels or other bio-products is a consideration that has a short-term economic impact and a potential long-term sustainability impact. For soils such as the Clarion–Nicollet–Webster association where this field study was conducted, one long-term effect could be an increased potassium deficiency [33], especially if no-till or other reduced tillage practices are used to minimize soil erosion because harvest of crop residue has reduced surface cover. The short-term impact is the additional fertilizer cost that may be incurred to replace the N, P, and K removed with the stover. Recent increases in the cost of natural gas used for fertilizer N production and increases in general transportation costs for all fertilizer materials have substantially increased the value of recycling plant nutrients from one crop to the next. For example, total replacement cost for the three macronutrients averaged

Table 2  
Nutrient concentrations in corn stover collected using different harvest scenarios

Harvest scenario	C	N	P	K	Ca	Mg	Cu	Fe	Mn	Zn
	$\text{mg g}^{-1}$				$\mu\text{g g}^{-1}$					
High-cut top	444	7.0	0.79	7.05	3.95	3.07	1.4	42	7	6
High-cut bottom	440	8.1	0.57	19.62	4.05	3.83	0.8	86	8	4
Low cut	444	7.0	0.62	6.52	3.70	3.74	1.1	63	6	4
Normal cut	440	8.0	0.79	6.74	5.40	4.04	1.2	51	13	9
LSD (0.05)	ns	0.6	Ns	5.58	0.87	0.25	0.2	12	ns	ns

\$54.41 ha<sup>-1</sup> for the high-cut top and normal cut harvest strategies. Collecting the bottom portion of the corn plant increased replacement cost to \$67 and \$84 ha<sup>-1</sup> for the low cut and high-cut total (top plus bottom) scenarios, respectively. When calculated per metric ton (Mg) of corn stover, the average nutrient replacement cost for the high-cut top and normal cut scenarios was \$10.93 Mg<sup>-1</sup>. Including compensation for Ca, Mg, and four micronu-

trients (Cu, Fe, Mn, and Zn) would increase these costs even further.

### 3.4. Stover conversion

The high-cut bottom scenario resulted in the greatest glucan concentration while the normal cut scenario produced the most xylans (Table 4). When converted to

Table 3  
Nutrient removal associated with four corn stover harvest scenarios

Harvest scenario	C	N	P	K	Ca	Mg	Cu	Fe	Mn	Zn
	Mg ha <sup>-1</sup>	kg ha <sup>-1</sup>	g ha <sup>-1</sup>							
High-cut top	2.16	34.3	3.8	34.2	19.2	14.9	7	202	35	28
High-cut bottom	0.75	13.8	1.0	33.5	6.9	6.6	1	148	14	6
Low cut	2.97	47.1	4.1	43.6	24.7	25.0	8	419	40	25
Normal cut	2.24	42.0	4.0	34.3	27.5	20.6	6	258	64	46
LSD (0.05)	0.07	2.9	1.8	ns	4.6	0.9	1	26	ns	ns

Table 4  
Chemical characterization of corn stover collected using four different harvest scenarios

Harvest scenario	EtOH solubles	Water ext								Structural inorganics	
		Sucrose	Others	Glucan	Xylan	Galactan	Arabinan	Mannan	Lignin	GH <sup>a</sup>	NH <sup>b</sup>
mg g <sup>-1</sup>											
High-cut top	46	13	42	337	212	15	29	10	134	0	
High-cut bottom	39	0	73	376	189	11	21	10	164	0	
Low cut	42	6	59	359	207	15	27	8	155	11	
Normal cut	45	0	24	339	215	14	30	11	127	0	
Harvest scenario	Extractable inorganics	Protein	Acetyl	Uronic acid	Total solubles	Total structurals	Total				
mg g <sup>-1</sup>											
High-cut top	21	36	29	36	129	883	1010	0.711	0.207		
High-cut bottom	25	52	35	38	89	838	930	3.58	1.48		
Low cut	27	45	34	38	127	844	970	1.83	0.560		
Normal cut	25	41	25	33	128	865	990	1.61	0.392		

<sup>a</sup>Global H (GH) is a measure of the probability that a sample belongs to the calibration population set [X].

<sup>b</sup>Neighborhood H (NH) is a measure of how far the nearest calibration sample is from the measured sample. NH values over 0.6 will have higher error bars than the traditional error bars [X].

Table 5  
Theoretical ethanol yields from corn stover collected using four different harvest scenarios

Harvest scenario	Theoretical C6 yield	Theoretical C5 yield	Theoretical total yield	C6 EtOH	C5 EtOH	Total EtOH
	L Mg <sup>-1</sup> dry basis			L ha <sup>-1</sup>		
High-cut top	261	178	439	1270	865	2135
High-cut bottom	287	154	441	492	265	757
Low cut	276	173	449	1846	1156	3002
Normal cut	262	181	443	1338	921	2258

theoretical ethanol using the NREL calibration model for C6 fermentation [34] yields ranged from 492 to 1846 L ha<sup>-1</sup> (Table 5).

Stover samples from the four harvest scenarios were also compared using a reduced-severity dilute acid pretreatment followed by C6 SSF conversion to ethanol. This process showed significant differences in the polymer yields, particularly in the high-cut top stover samples (Table 6). Arabinan removal was also most complete in the high-cut top and normal cut samples.

Pretreated and native stover samples were also compared using the SSF procedure (Fig. 4). None of the native samples showed statistically different ethanol conversion

after 7 days of SSF processing (Figs. 4 and 5) but with pretreatment, the high-cut top fraction produced significantly more ethanol than the high-cut bottom fraction. This outcome agrees with pretreatment results suggesting that the high-cut top stover harvest scenario may also result in lower biorefinery processing costs. These results also correlate well with other INL and University of Kentucky (UK) studies (unpublished data), and work at NREL [35].

The intensity of what is an “adequate” dilute-acid pretreatment varies significantly among the various anatomical fractions of corn stover. In the NREL study [35], it was found that the optimum pretreatment severity for cobs

Table 6  
Sugars analyzed in the hydrolysate wash water from the reduced severity, dilute-acid pretreatment screening assay

Harvest scenario		Glucan	Xylan	Galactan	Arabinan	Mannan
High-cut top	Hydrolysate sugars <sup>a</sup>	4.0 A	17.5 A	0.4	3.0 A	0.1
	Sd	0.90	3.47	0.05	0.68	0.02
	Polymer removal <sup>b</sup>	12.0	82.8	27.7	101.0	15.0
High-cut bottom	Hydrolysate sugars	1.8 C	10.8 B	0.3	1.4 B	0.1
	Sd	0.17	1.02	0.02	0.11	0.01
	Polymer removal	4.9	57.3	22.5	65.8	10.8
Low cut	Hydrolysate sugars	2.6 BC	13.9 AB	0.4	2.2 A	0.1
	Sd	0.17	1.02	0.02	0.11	0.01
	Polymer removal	7.1	67.3	27.5	81.3	12.3
Normal cut	Hydrolysate sugars	3.0 B	14.3 AB	0.4	2.3 A	0.1
	Sd	0.23	1.22	0.05	0.19	0.00
	Polymer removal	8.8	66.4	27.1	77.7	9.6
NREL 34M95 (control biomass)	Hydrolysate sugars	4.0 A	14.6 AB	0.5	2.6 A	0.2
	Sd	0.34	1.47	0.04	0.23	0.02
	Polymer removal	11.9	64.4	41.8	99.5	28.9

Data are means of quadruplicate samples; identical letters within a column denote no significance was found using a one-way ANOVA followed by Tukey–Kramer HSD at an alpha of 0.05 using JMP statistical software (SAS Institute Inc., Cary, NC).

<sup>a</sup>Hydrolysate sugars units: (polymer wt/total wt) × 100–% total wt.

<sup>b</sup>Polymer removal units: (wt polymer removed/wt original polymer) × 100–% original polymer wt.

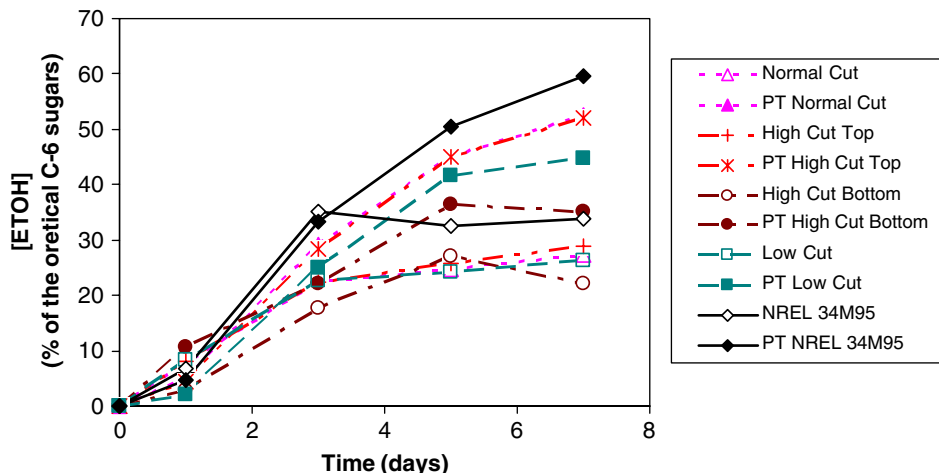


Fig. 4. Time courses of the means of quadruplicate samples processed with and without a reduced severity dilute acid pretreatment then run for ethanol SSF.

and husks was much less than for the stalk fractions (node, internode, and rind). Those results may be relevant to this study because the proportion of cobs and husks was greater in the high-cut top stover fraction and lowest (i.e. none) in the high-cut bottom fraction of stover. This suggests that the high-cut top fraction in our study may have more efficient processing due to the partial anatomical fractionation. Normal cut theoretical ethanol yield from C6 sugars was not different from that of the high-cut top, supporting the proposal that the normal cut scenario may optimize harvest convenience and speed, soil erosion and quality protection, and ethanol yield.

Correlations between theoretical ethanol yield and several ethanol and dry matter yield characteristics are presented in Table 7. We found no relationship between total and theoretical ethanol yield per unit of dry mass ( $r < 0.950$ , the critical  $r$ ). However, when the correlation between ethanol yield per unit land area was computed, a strong correlation was found between total ethanol yield and amount of ethanol from both the C6 ( $r = 0.9986$ ) and C5 ( $r = 0.9964$ ) sugars. The strongest correlation was found between total ethanol yield and stover yield ( $r = 0.9997$ ), suggesting that among the harvest scenarios, stover yield plays a greater role in determining ethanol

yield than the amount of ethanol produced per unit dry matter.

### 3.5. Thermochemical conversion of stover

A thermochemical conversion study of the residue collected by the different harvest scenarios showed that percent moisture (Table 1) had the largest effect on gasification parameters and was the major discriminator among the four harvest scenarios when evaluated as a potential feedstock. Beyond moisture, the most notable result was that the ash fusion temperature of the high-cut top stover was markedly lower than for stover from the other harvest scenarios (Table 8). This difference would probably not require major gasification system design changes other than perhaps the use of a fluidized bed reactor to avoid hot pockets, as optimal temperatures for gasification of this material reportedly fall between 900 and 1000 °C [36]. Other differences and trends in the gasification parameters are likely not significant, and several observations violate rules of mixtures. For example, constituent concentrations found in the ultimate analysis of low cut stover should fall within the range between the high-cut top and the high-cut bottom stover. In practice several of the constituent concentrations of the low cut material fell outside of this range, including SiO<sub>2</sub>, CaO, K<sub>2</sub>O, and Cl. However, those differences were typically quite small and point to feedstock variability more than operational errors.

Comparable thermochemical conversion (Table 8) and nutrient concentration (Table 2) data showed a low but positive correlation confirming similar trends in residue samples from the four harvest scenarios. For example, total C concentrations ranged from 440 to 444 mg g<sup>-1</sup> when measured by dry combustion (Table 2), while the ultimate analysis showed a range of 469–472 mg g<sup>-1</sup> (Table 9). This small difference (2.6–3.2%) provides confidence in the estimates of carbon concentrations in the four corn stover samples. Many of the other elements showed similar trends for both methods. The most likely cause for the differences was volatilization due to the high temperature during the ashing process.

## 4. Conclusions

To be acceptable to producers, the harvest scenario for stover collection must not adversely affect grain harvest.

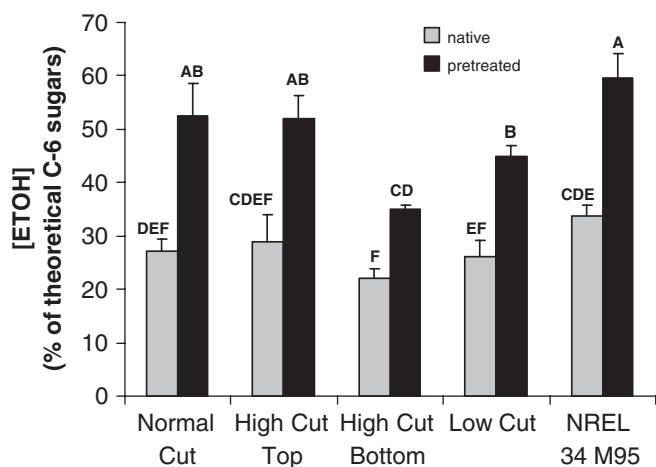


Fig. 5. Day 7 statistics for ethanol-SSF of pretreated and native corn stover. Data are means of quadruplicate samples and error bars represent one standard deviation; identical letters within a column denote no significance was found using a one-way ANOVA followed by Tukey–Kramer HSD at an alpha of 0.05 using JMP statistical software (SAS Institute Inc., Cary, NC).

Table 7

Simple correlation ( $r$ ) between theoretical total ethanol yield and several theoretical ethanol and stover yield characteristics across harvest scenarios

	Stover yield	Theoretical C6 yield	Theoretical C5 yield	Theoretical total yield	C6 EtOH	C5 EtOH
Total EtOH	0.9997	-0.5332	0.7758	0.6245	0.9986	0.9964
Significance <sup>a</sup>	**	ns	ns	ns	**	**

\*\*, significant at  $\alpha = 0.01$ .

<sup>a</sup>ns, not significant.



Table 8  
Thermochemical conversion data for corn stover from the four harvest scenarios

	High-cut top	High-cut bottom	Low cut	Normal cut
Proximate	mg g <sup>-1</sup>			
Ash	46	57	47	57
volatile	781	766	789	779
fixed C	173	177	164	164
Total	1000	1000	1000	1000
Ultimate	mg g <sup>-1</sup>			
Carbon	472	469	472	470
Hydrogen	57	56	57	58
Nitrogen	6	6	5	6
Sulfur	1	0	1	1
Ash	46	57	47	57
Oxygen	420	412	418	409
Chlorine <sup>a</sup>	2	3	2	3
Total	1000	1000	1000	1000
C/H ratio	8.3	8.4	8.3	8.2
Elements in Ash	mg g <sup>-1</sup>			
SiO <sub>2</sub>	448	404	522	513
Al <sub>2</sub> O <sub>3</sub>	1	21	1	1
TiO <sub>2</sub>	1	1	1	1
Fe <sub>3</sub> O <sub>3</sub>	5	7	6	6
CaO	93	110	112	99
MgO	65	126	97	84
Na <sub>2</sub> O	24	10	12	9
K <sub>2</sub> O	193	198	138	138
P <sub>2</sub> O <sub>5</sub>	69	28	54	55
SO <sub>3</sub>	15	12	13	12
Cl	31	36	26	27
CO <sub>2</sub>	5	12	6	7
SiO <sub>2</sub> /K <sub>2</sub> O ratio	2.3	2.0	3.8	3.7
Ash fusion temp	°C			
Oxidizing atm				
Initial	984	1166	1140	1141
Softening	1032	1173	1168	1175
Hemispherical	1108	1178	1188	1192
Fluid	1142	1184	1192	1204
Reducing atm	°C			
Initial	998	1038	1070	1090
Softening	1021	1118	1189	1176
Hemispherical	1092	1132	1201	1186
Fluid	1117	1149	1226	1193
Energy parameters (dry basis)				
HHV (kJ g <sup>-1</sup> )	18.3	18.3	18.2	18.3
MMF (kJ g <sup>-1</sup> )	19.2	19.5	19.2	19.4
MAF (kJ g <sup>-1</sup> )	19.2	19.4	19.1	19.4
kg alkali (GJ <sup>-1</sup> )	0.6	0.7	0.4	0.5
kg ash (GJ <sup>-1</sup> )	2.8	3.5	2.9	3.5
kg SO <sub>2</sub> (GJ <sup>-1</sup> )	0.1	0.1	0.1	0.1
DSCF (GJ <sup>-1</sup> )	9959	9899	10040	10041

<sup>a</sup>Chlorine is not usually reported as part of the ultimate analysis.

Our one-pass harvest system is a prototype and does not exist in the marketplace. Therefore, it must be assumed that the normal cut scenario would be most acceptable because the others would slow ground speed and harvest efficiency. The preliminary results reported here indicate harvesting at the normal height would probably provide

the amount of crop residue projected from long-term yield records and typical harvest indices, although the amount of residue left on the soil surface may be less than expected. The macro-nutrient replacement value for the normal harvest scenario under our conditions was \$57.36 ha<sup>-1</sup> or \$11.27 Mg<sup>-1</sup>. Harvesting the lower portion of the stalk

would add very little dry matter, slow harvest efficiency, increase nutrient replacement costs, and decrease surface cover and protection from wind and water erosion. Harvesting the bottom portion of the stalks would also produce a feedstock with excessive water content that would increase transportation and storage costs, result in minimal improvement on theoretical ethanol yield, and may create contamination problems in the biorefinery.

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