

## Corn stover as a biofuel

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### **Abstract:**

Corn stover is one of several feedstocks being considered as a biofuel. Although corn stalks currently are not harvested routinely, the huge amount of biomass produced annually makes corn a potential commercial biofuel. Removal of crop residue from the field needs to balance against preventing soil erosion, maintaining soil organic matter levels, and preserving or enhancing productivity. After corn stover is fermented to produce ethanol, the remaining residue is about 70% lignin. Lignin decomposes slowly, which can help stabilize soil structure. One use of fermentation by-product would be as a soil amendment, thereby minimizing some of the negative impacts of stover removal on soil structure. Laboratory studies show that by-product of stover fermentation increased microbial biomass and soluble C by 20% compared to soil without amendment. In the Langhei soil, humic acid concentration ( $r^2=0.84$ ,  $p<0.0001$ ) and aggregate stability ( $r^2= 0.35$ ,  $p< 0.001$ ) increased linearly with increased fermentation by-product concentration. Thus, laboratory results suggest that this fermentation by-product has potential as a soil amendment. Returning by-product to the field may slow the loss of soil organic matter caused by removing corn stover. Careful management of stover removal (avoiding eroded or erosion prone areas) and selective placement of the by-product could contribute to a sustainable use of corn stover for ethanol production.

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## **Introduction:**

Burning non-renewable fossil fuels is a major contributor to the measured increase in greenhouse gas emissions (IPCC, 1990). One strategy for reducing rate of fossil fuel consumption is to increase the use of renewable biofuels. Biofuels cycle newly trapped carbon dioxide (CO<sub>2</sub>) rather than release CO<sub>2</sub>, which had been stored for millions of years. Use of biofuel can delay the depletion of non-renewable fossil fuels.

The product of ethanol typically has been from starchy material such as corn (*Zea mays* L.) grain. The production of ethanol from material, which has a large concentration of cellulose rather than starch, requires a development of new organisms or enzymes to convert the cellulose to simple sugars available for fermentation. The United States Department of Energy (DOE) and private enterprise are developing a fermentation process for producing ethanol from high-cellulose biomass (DiPardo, 2000; Hettenhaus et al., 2000).

It has been estimated that it will take about 1800 Mg dry matter d<sup>-1</sup> (4 million lbs d<sup>-1</sup>) to support an economically sized, processing facility (Hettenhaus et al., 2000). There are many potential sources of cellulose materials (e.g. woody biomass crops and lumber industry wastes, forage crops, industrial and municipal wastes, animal manure, and crop residues). Of these materials, crop residues are viewed as available in sufficient quantity and quality to support fermentation at an industrial scale (DiPardo, 2000; Hettenhaus et al., 2000).

It was estimated that there is about 137 Tg (10<sup>12</sup> g) of corn stover (the material remaining after grain yield) produced in Iowa, Illinois, Nebraska, and Minnesota, the states with the largest corn production (Wilhelm et al., 2003). If all of this material could be used for ethanol production it would supply 60 industrial size plants. It was estimated only 20 to 30% of the residue could be removed from the field for use as biofuel (McAloon et al., 2000; Nelson, 2002).

Using an estimate of 30% of the stover produced in Iowa alone could provide enough ethanol to meet current ethanol use for motor fuels, although it is small compared to the total gasoline consumption (Wilhelm et al., 2003). Iowa represents about 20% of the United States corn production and there are additional sources of biomass (e.g. wheat straw, rice straw and the residue remaining after sap extraction from sugarcane (*Saccharum officinarum* L.). Ethanol production from agricultural residues has potential to be a viable component in reducing US reliance on imported nonrenewable fossil fuels (Wilhelm et al., 2003).

Crop residues are a valuable resource both in the field and as a potential biofuel. Crop residues are critical in protecting and maintaining our nation's valuable natural resource (soil and clean water). Crop residues are used for erosion control (Gilley et al., 1986; Gregorich et al., 1998; Soil Conservation Society of America, 1979). Erosion removes the surface soil, which is rich in soil organic matter (SOM). Residues influence soil temperature, rate of evaporation and provide the raw material for the formation of SOM (Wilhelm et al., 2003). Loss of SOM can decrease soil productivity. It is critical to limit the removal of residue such that soil erosion is limited. The tolerable limits (T-values) were established by USDA-Natural Resource Conservation Service (Larson, 1979; Nelson, 2002), however there is debate if these values provide adequate protection to prevent environmental degradation and yield loss (Mann et al., 2002).

Removal of corn stover from the field can increase the risk of soil erosion and reduces the amount of raw material available to form new SOM. Maintenance of SOM requires that removal of SOM by decomposition or erosion does not exceed the formation of SOM. The vast majority (>80) of plant residues are decomposed and cycled back into the atmosphere within two years (Buyanovsky and Wagner, 1997), so only a small portion of the residue is converted into recalcitrant SOM (Barber, 1979).

It is important to understand all aspects of this new budding industry from residue harvest to disposal of fermentation by-products. After the fermentation process the remaining material is 60 to 70% lignin on a dry weight basis. Lignin decomposes slower than many other plant

components and is thought to play a role in stabilizing soil structure (Martens, 2000; Martens, 2002; Stevenson, 1994). The fermentation by-product after ethanol production from cellulose biomass could be used in producing electricity (Sheehan et al., 2002). Alternatively, the fermentation by-product could be used as a soil amendment.

It was hypothesized that since the by-product of stover fermentation is high in lignin, which is thought to play a role in stabilizing soil, incorporation in soils of the by-product may help maintain or improve soil structure and stability. This may reduce some of the negative effects of harvesting corn stover. The fermentation of corn stover for ethanol is still an experimental process, limiting the availability of the by-product. Soil biological, chemical and physical properties were compared among control (no amendment), corn stover or by-product amended soil, 120 days after application.

### **Material and Methods:**

Initial characteristics of the Svea and Langhei soils are summarized in Table 1. The soils were collected from the surface 15 cm (6"). All soil was air-dried and passed through a 3-mm sieve. The soil and amendments were incubated in PVC cylinders (10 cm x 20 cm) with sealed bottoms as described by Johnson et al. (2003). Columns were filled with soil and amendment mixture and packed to achieve an initial  $D_b$  of  $1.3 \text{ Mg m}^{-3}$ . The experiment was initiated by wetting the columns to  $0.306 \text{ cm}^3 \text{ cm}^{-3}$  volumetric water, which is 60% water-filled pore space (WFPS). Water content was checked weekly and if the soil had dried to  $0.178 \text{ cm}^3 \text{ cm}^{-3}$  ( $\leq 35\%$  WFPS), water was added to return the soil to 60% WFPS. The columns were incubated at ambient air temperature for 123 d.

The study had five treatments: no amendment (control), 2.4 g corn stover  $\text{kg}^{-1}$  soil, 0.75, 3.0 and 6.1 g by-product  $\text{kg}^{-1}$  soil. The corn stover application rate is comparable to returning 4.6  $\text{Mg ha}^{-1}$  (68 bushel  $\text{acre}^{-1}$ ) dry stover after grain harvest. The 0.75 g by-product  $\text{kg}^{-1}$  soil had

about the same amount of lignin as the corn stover treatment, while the 6.1 g by-product kg<sup>-1</sup> soil had comparable amounts of cellulose as found in the corn stover treatment (Table 2). By-product material and characteristics were provided courtesy of Jim McMillan at the National Renewable Energy Laboratory, Golden, CO (NREL). Dried and ground (4 mm) corn stover and by-product were added to air-dried, sieved (3 mm) soil, and then mixed thoroughly.

Measuring CO<sub>2</sub> flux monitored decomposition (Johnson et al., 2003). The cumulative flux as a function of time was calculated by assuming linearity between sampling points. Soluble C was extracted with 0.5 M K<sub>2</sub>SO<sub>4</sub> and microbial biomass C estimated by chloroform fumigation (Vance et al., 1987). The soil concentration of total N, total C and inorganic C (Wagner et al., 1998) were measured using a LECO CN-2000 (LECO Corporation, St. Joseph, MI). pH<sub>(H2O)</sub> and pH<sub>(CaCl2)</sub> were measured using 2:1 ratio (Thomas, 1996). The soil was fractionated into humin and humic acid fractions according to (Stevenson, 1994) and C and N of the humin and humic fractions measured. Aggregate stability of the 1 to 2 mm aggregates was determined both on moist soil (moisture content at the time of sampling) and on soil material that had been air-dried and then remoistened to near field capacity before wet-sieving (Kemper and Rosenau, 1986).

Each replication had four identical columns of each soil by treatment combination. The columns were set up as a two by five factorial arrangement randomized within each replication. Statistical differences were determined using generalized linear model,  $P \leq 0.05$  (Proc GLM; SAS version 8, SAS Institute Inc. Cary, NC). Linear regression analysis (Proc REG; SAS) was used to investigate the relationships between by-product added and humic acid concentration, and between by-product added and aggregate stability on Langhei soil.

## Results and Discussion:

Carbon dioxide flux is an indicator of decomposition and microbial activity. Amending with by-product or corn stover increased the flux and cumulative CO<sub>2</sub> released compared to the control by providing a C source on both soils (Table 3). The corn stover amended soil released 1.8 times as much total CO<sub>2</sub> compared to the control. Compared to the control, the amount of CO<sub>2</sub> released from soil amended with by-product level ranged from 1.1 times (0.75 g by-product kg<sup>-1</sup>) to 1.7 times (6.1 g by-product kg<sup>-1</sup>). Even with the 6.1 g by-product kg<sup>-1</sup> treatment, the by-product amended soil did not release as much CO<sub>2</sub> as the corn stover treatment. The amount of C released that originated from the newly added C compared to C previously in the soil was estimated based on net CO<sub>2</sub> flux (Table 3). The net CO<sub>2</sub> flux from a treatment was calculated by subtracting the amount of C released from the control treatment. This calculation neglects potential priming effects. Corn stover decomposed more quickly and showed up to 3.8 times more amendment C released than from the by-product treatments (Table 3).

The observed increases in CO<sub>2</sub> fluxes (Table 3) after amending the soil with by-product or corn stover were due to increased soluble C and the increased microbial biomass C (Table 4). Amending the soil increased both soluble C and microbial biomass C. The differences in soluble C and microbial biomass C were still measurable for the 6.1 g by-product kg<sup>-1</sup> soil and corn stover treatment at the 123 d sampling date.

At the end of the by-product study, 0.50 g C kg<sup>-1</sup> soil from corn stover remained in the soil, given that corn stover had 466 g C kg<sup>-1</sup> (Table 3). The by-product had 486 g C kg<sup>-1</sup>; at the 6.1 g by-product kg<sup>-1</sup> soil application rate, there would be 2.4 g C kg<sup>-1</sup> soil remaining after 123 d (Table 2). The initial organic C concentration was 3 g C kg<sup>-1</sup> in the Langhei soil and about 20 g

C kg<sup>-1</sup> in the Svea soil (Table 1). The C remaining in Svea soil from 2.4 g corn stover kg<sup>-1</sup> treatment represents only 2.5% of the initial soil organic C. In contrast, C from 2.4 g corn stover kg<sup>-1</sup> represents 17% of the organic C on Langhe soil. The C remaining after adding 6.1 g by-product kg<sup>-1</sup> to the soil represents 12% of the soil organic C on the Svea soil and 80% of initial soil organic C on the Langhe soil. Thus, it is reasonable to assume that added C impacted soil properties of the Langhe soil more than those of the Svea soil.

Humic acid concentration at 123 d increased on a Langhe soil with addition of by-product ( $r^2 = 0.84$ ,  $P < 0.0001$ ; Fig. 1.). This relationship between humic acids and by-product was not apparent on a Svea soil ( $r^2 < 0.1$ ;  $P > 0.05$ ). These results suggest that at least some of the amendment fractionated into the humic fraction, and as the amendments decomposed, their contribution to the humic fraction decreased. The fermentation by-product and corn stover were subjected to the humic acid extraction procedure. After the procedure, at least 0.3 g g<sup>-1</sup> of the fermentation by-product was recovered in the humic fraction but only a trace of the corn stover was recovered in the humic fraction.

A soil and amendment interaction was observed for aggregate stability measured on air-dried samples. Aggregate stability of a Langhe soil increased with additions of by-product ( $r^2 = 0.35$ ;  $p < 0.0001$ ; Fig. 2). The corn stover amended soil had 830 g water stable aggregates kg<sup>-1</sup>, which was fewer water stable aggregates compared to the 6.1 g by-product kg<sup>-1</sup> treatment. There were no measurable changes on water stable aggregates on a Svea due to the fermentation by-product compared to the control or corn stover treatments.

Amending soil with the fermentation by-product of ethanol production from corn stover can improve soil properties (Fig. 1 and 2), However, returning by-product to the field may not negate all potential problems of removing corn stover, as it provides little ground cover.

Amending the soil with by-product adds slowly decomposing C to the soil (Table 3). The addition of new C may have a larger impact on soil properties of severely eroded soil with low organic C compared to non-eroded soil with a large pool of organic C. The slow decomposition and long residence time of the by-product in the soil may allow the by-product to make a large and long-term contribution to SOM, which could be especially beneficial in low organic matter soils.

Corn stover is not a waste product. Corn stover provides a food source for soil fauna, surface residue to minimize erosion, and contributes to nutrient cycling (for example, C, N, P). Thus, only with prudent management of stover removal (avoiding highly eroded areas) and selective placement of the by-product (spreading it on eroded knolls), may a sustainable use of corn stover for ethanol production be developed.

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Table 1. Initial soil characteristics of Svea and Langhei soil.

Characteristic		Svea	Langhei
Sand	%	42.8	47.8
Silt	%	37.9	26.9
Clay	%	19.3	25.3
Total C	g kg <sup>-1</sup>	21.8	31.8
Organic C	g kg <sup>-1</sup>	20.4	3.0
pH(H <sub>2</sub> O)		7.9	8.3
pH(CaCl <sub>2</sub> )		7.4	7.8

Table 2. Constituents and their concentration (g kg<sup>-1</sup>) in materials used to amend soil.

Constituent	By-product <sup>†</sup>	Corn stover <sup>‡</sup>
Lignin	624	200
Cellulose	125	355
Hemicellulose	28	230
Ash	168	116
Total C	486	466
N	20	7

<sup>†</sup>Composition of by-product provided courtesy of J. McMillian at NREL.  
<sup>‡</sup>(NREL, 2002)

Table 3. Total CO<sub>2</sub> released from soil columns and the relative amount of C that originated from the amendment after incubating for 118 days.

Soil	Amendment	Rate	Total	Amendment C
			Accumulated CO <sub>2</sub>	release <sup>†</sup>
		-g kg <sup>-1</sup> -	g CO <sub>2</sub> m <sup>-2</sup>	%
Svea	Control	0.0	580 e <sup>‡</sup>	NA <sup>§</sup>
	By-product	0.75 <sup>¶</sup>	620 e	17 b
	By-product	3.0	790 d	15 b
	By-product	6.1	930 c	14 b
	Corn Stover	2.4 <sup>#</sup>	1030 ab	45 a
Langhei	Control	0.0	590 e	NA
	By-product	0.75	720 d	46 a
	By-product	3.0	790 d	17 b
	By-product	6.1	1010 b	17 b
	Corn Stover	2.4	1080 a	51 a
Source of variance	df			
Soil (S)	1		**	**
Amendment (A)	4		****	****
S x A	4		NS <sup>††</sup>	**

\*\* , \*\*\* , \*\*\*\* Significant at 0.05, 0.01, 0.001 and 0.0001 respectively.

<sup>†</sup> Net C flux = (treatment flux – control flux); relative C = net C flux/g C in amendment \*100.

<sup>‡</sup> Lower case letters in a column indicate significant differences at least p=0.05 using least squares means an

<sup>§</sup> NA, Not appropriate.

<sup>¶</sup> 0.75 g of the by-product per kg soil has lignin equivalent to 2.4 g of corn stover.

<sup>#</sup> 2.4 g corn stover added per kg soil is equivalent to the amount of stover that would be returned in 4.3 Mg l<sup>-1</sup> stover after grain harvest.

<sup>††</sup> NS, not significant at the 0.05 level.

Table 4. Amendment treatment means, average across soils for soluble C and microbial biomass C sampled at several times after incubating the soil with different levels of by-product or corn stover. Soil by amendment interaction was not detected at  $p \leq 0.05$ .

	Amendment				
	Control	0.75 <sup>†</sup>	3.0	6.1	2.4 <sup>‡</sup>
	-----g kg <sup>-1</sup> soil-----				
Day	0.0	0.75 <sup>†</sup>	3.0	6.1	2.4 <sup>‡</sup>
	-----µg C g <sup>-1</sup> Soil-----				
	<i>Soluble C</i>				
1	65 d	67 cd	72 ab	76 a	71 bc
3	62 b	63 b	66 b	73 a	74a
7	62 b	61 b	68 a	70a	69a
60	56 c	56 c	61 bc	67 a	64 ab
123	45 c	47 bc	52 ab	54 a	49 ab
	-----µg C g <sup>-1</sup> Soil-----				
	<i>Microbial Biomass C</i>				
1	310	306	331	338	324
3	334 c	354 c	384 b	411 a	398 ab
7	296 c	316 c	336 b	383 a	380 a
60	313 b	348 ab	368 a	377 a	367 a
123	260 c	284 bc	287 bc	329 a	301 ab

\*, \*\*, \*\*\*, \*\*\*\* Significant at 0.05, 0.01, 0.001 and 0.0001 respectively.

<sup>†</sup> 0.75 g of the by-product per kg soil has lignin equivalent to 2.4 g of corn stover.

<sup>‡</sup> 2.4 g corn stover added per kg soil is equivalent to 4.3 Mg ha<sup>-1</sup> dry stover after grain harvest.

<sup>§</sup> Significant differences determined by least squares means T-difference analyses ( $p \leq 0.05$ ) within general linearized model are indicated by different lower case letters among amendment treatments in a row.

<sup>¶</sup> NS, not significant at the 0.05 level.

Fig. 1. The concentration of humic acid as a linear function of by-product concentration 123 d after amending a Langhei soil with the by-product of corn stover fermentation. Each point is a single observation and the line is the best-fit linear regression.

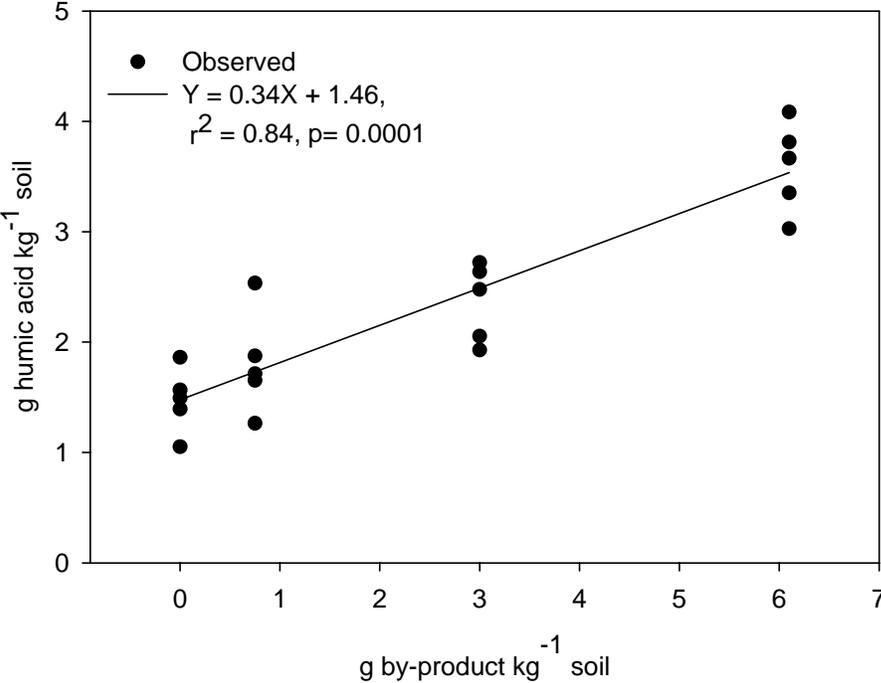


Fig. 2. Linear regression of water stable aggregates from a Langhei soil measured 123 d after application of amendment as a function of by-product added. Each point is a single observation, and the line is the best-fit linear regression.

