# Exploring Impacts of Process Technology Development and Regional Factors on Life Cycle Greenhouse Gas Emissions of Corn Stover Ethanol

Jon McKechnie<sup>1,\*</sup>, Mohammad Pourbafrani<sup>2</sup>, Bradley A. Saville<sup>2</sup> and Heather L. MacLean<sup>2,3</sup>

\*Corresponding Author: Jon McKechnie

Email: Jon.Mckechnie@nottingham.ac.uk

Tel: +44 (0) 115 74 84435

<sup>&</sup>lt;sup>1</sup> Division of Energy and Sustainability, University of Nottingham, University Park, Nottingham NG7 2RD, UK

<sup>&</sup>lt;sup>2</sup> Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, ON, M5S 3E5, Canada

<sup>&</sup>lt;sup>3</sup> Department of Civil Engineering, University of Toronto, 35 St George Street, Toronto, ON, M5S 1A4, Canada

#### **Abstract**

This paper examines impacts of regional factors affecting biomass and process input supply chains and ongoing technology development on the life cycle greenhouse gas (GHG) emissions of ethanol production from corn stover in the U.S. Corn stover supply results in GHG emissions from -6 gCO<sub>2</sub>eq./MJ ethanol (Macon County, Missouri) to 13 gCO<sub>2</sub>eq./MJ ethanol (Hardin County, Iowa), reflecting location-specific soil carbon and N2O emissions responses to stover removal. Biorefinery emissions based on the 2011 National Renewable Energy Laboratory (NREL) process model are the single greatest emissions source (18 gCO<sub>2</sub>eq./MJ ethanol) and are approximately double those assessed for the 2002 NREL design model, due primarily to the inclusion of GHG-intensive inputs (caustic, ammonia, glucose). Energy demands of on-site enzyme production included in the 2011 design contribute to reducing the electricity co-product and associated emissions credit, which is also dependent on the GHG-intensity of regional electricity supply. Life cycle emissions vary between 1.5 and 22 gCO<sub>2</sub>eq./MJ ethanol (2011 design) depending on production location (98% to 77% reduction vs. gasoline). Using system expansion for co-product allocation, ethanol production in studied locations meet the Energy Independence and Security Act emissions requirements for cellulosic biofuels; however, regional factors and on-going technology developments significantly influence these results.

Keywords: Life Cycle Assessment, Corn Stover, Ethanol

## Highlights:

- We evaluate the impacts of regional parameters and technology development on the life cycle greenhouse gas emissions of corn stover-derived ethanol
- The impacts of corn stover removal on soil carbon stocks and N<sub>2</sub>O emissions are the dominant regionally-dependent parameters
- Biorefinery emissions based on the 2011 NREL design model are approximately double that
  of the preceding 2002 NREL model due to inclusion of greenhouse gas-intensive inputs
  (caustic, ammonia, glucose)
- For all regions and process design models considered, corn-stover derived ethanol would meet the emissions reduction threshold of the US Energy Independence and Security Act when system expansion is used for co-product allocation.

## 1. Introduction

Sustainability-related concerns surrounding fossil fuel use, and improvements in biomass conversion technologies have increased interest in producing fuels from lignocellulosic feedstock. Considerable focus has been placed on the development of second generation biofuels from non-food biomass (e.g., Luo et al., 2009; Cherubini et al., 2010; Liao et al., 2011). With improvements in biomass pretreatment, reductions in enzyme loading and prices, and the production of valuable co-products such as pellets and electricity, the financial metrics of lignocellulosic biofuel production have improved (Humbird et al., 2011). Lignocellulosic biomass feedstock options include energy crops, forest and agricultural residues, and the organic fraction of municipal solid waste. These feedstocks do not directly compete with agricultural crops, and in the case of crop residues, are produced from biomass already grown on the same parcel of land.

Corn stover, an agricultural residue, is gaining interest as a feedstock because it is an abundant and inevitable co-product of corn grain production (Bhardwaj et al., 2011). Corn stover and grain are produced in approximately equal amounts. Graham et al. (2007) and Nelson et al. (2002) discuss that corn stover could be used for ethanol production in the U.S., provided it is removed from the field in a sustainable manner, e.g., with minimal soil erosion and preservation of soil carbon. In the U.S. most of the corn stover is left in the fields; Kim et al. (2009) reported that only 5% of the total corn stover is removed, and that it is used as animal feed and bedding. The amount of stover which could be removed without soil organic carbon loss is dependent upon geography and local/regional soil conditions (Luo et al., 2009). Kim et al. (2009) suggest that the stover removal rate ranges from 25% to 50% in the U.S.

Life cycle assessment (LCA) provides a transparent methodology that can be used to examine biofuel production. Life cycle studies have evaluated lignocellulosic ethanol production from a variety of feedstocks including: corn stover, switchgrass, hybrid poplar, alfalfa and reed canary grass (e.g., Sheehan et al. 2004; Spatari et al. 2005; Kim and Dale, 2005; Adler et al., 2007, Gonzalez-Garcia et al., 2010; Wang et al. 2012). The studies examined the production and use in road transportation vehicles of ethanol/gasoline blends in the forms of E10 (10 vol% ethanol), E85 (85 vol% ethanol), and E100 (100% ethanol). Each of these studies reported a reduction in GHG emissions for the ethanol compared with the reference fossil fuel(s). LCA studies are particularly

relevant in jurisdictions that use GHG metrics to accompany biofuel mandates, such as the Low Carbon Fuel Standard in California (California Air Resources Board, 2009), and the GHG reductions stipulated under the US Energy Independence and Security Act (EISA, 2007).

There are a number of LCAs of the corn stover to ethanol process (e.g., Sheehan et al., 2004, Luo et al., 2009, Hsu et al., 2010, Spatari and MacLean, 2010, Kaufman et al., 2010). These studies all reported that replacing gasoline with ethanol produced from corn stover would reduce GHG emissions; however, the percentage reductions (compared to gasoline) reported in the studies vary between 58% and 106%. Key factors impacting the study results include: agricultural activities associated with corn stover production; the design of the conversion process, which impacts electricity and thermal energy demands; the source of electricity; and assumptions regarding enzyme and process chemical inputs to the conversion process. According to EISA 2007, to meet the requirements for categorization as a cellulosic biofuel, ethanol should reduce GHG emissions by 60% compared to gasoline. Spatari and MacLean (2010) studied both National Renewable Energy Laboratory (NREL) (Aden et al, 2002) and Michigan State University conversion process design models, but most other studies relied only on technical process information for conversion of stover to ethanol reported by NREL (Aden et al., 2002). Hsu et al.(2010), Spatari and MacLean (2010) and Kaufman et al. (2010) used US-average data for corn yield, fertilizer application rate and electricity grid intensity. Sheehan et al. (2004) determined the aforelisted data based on a specific location in Iowa. These studies did not include the impact of geographical variation on their LCA results, and did not distinguish between different stover harvesting requirements and biorefinery locations. Furthermore, there have been significant changes in the NREL conversion process design since 2002, including a major update published in 2011 (Humbird et al., 2011). Changes in the NREL design model include a process for enzyme production, the introduction of new chemicals (ammonia and caustic) to the process, and significant changes in ethanol yield and electricity generation capacity.

The objective of this paper is to evaluate impacts of process technology development and regional aspects on life cycle GHG emissions associated with ethanol produced from corn stover in the U.S. In particular, we develop our life cycle models based on the updated process model published by NREL (Humbird et al. 2011). We additionally provide a comparison of NREL's 2011 and 2002

process designs, and compare our life cycle results with those of Hsu et al. (2010), a study based on NREL's 2002 design. To our knowledge this is the first life cycle study comparing the 2002 and 2011 NREL designs. The impacts on life cycle GHG emissions of site-dependent variations in agricultural practices and outcomes, regional variations in the electricity grid and different emissions allocation methods are examined. Resulting life cycle GHG emissions are compared with EISA's thresholds to assess the implications of ethanol conversion technology development and regional parameters on GHG emissions of corn stover ethanol.

# 2. Methodology

## 2.1. Life cycle assessment

Life cycle inventory analysis models are developed to quantify GHG emissions associated with ethanol production from corn stover. The life cycle system boundary includes activities associated with the corn stover-ethanol production process from field to ethanol use in a light duty vehicle as a blended fuel with gasoline. These include corn farming and stover harvesting, pre-processing of stover, transportation of stover and ethanol production in a biorefinery (Figure 1), transportation of ethanol and final combustion of ethanol. The functional unit is 1MJ of ethanol (E100) produced. Spreadsheet-based models are developed to quantify life cycle emissions of selected GHGs (CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O) which are reported as carbon dioxide equivalents (CO<sub>2</sub>eq.) based on 100-year global warming potentials (IPCC, 2006).

#### 2.2 Corn stover production

Corn stover produced in eight counties located in the U.S. corn belt is examined. These counties are: Hardin (IA), Fulton (IL), Tuscola (MI), Morrison (MN), Freeborn (MN), Macon (MO), Hamilton (NE), and Codington (SD). These counties are selected to correspond with counties evaluated previously by Kim et al. (2009) as there is now a body of relevant data for corn and corn stover production in these counties. It is assumed that a bioethanol plant (biorefinery) located in each county obtains and processes stover harvested in the same county. If the stover supply from one county is not sufficient for the NREL 2011 design (700,000 t/year), additional stover is assumed to be provided from neighbouring counties. Corn stover is assumed to be harvested in a second pass through the field (Sheehan et al., 2004). The corn stover is harvested, collected, preserved and stored

in square and round bales. The dry matter content of stover and ratio of stover to grain are 79% and 1:1, respectively (Kim and Dale, 2004).

## 2.3 Allocation of GHG emissions to stover production

Corn stover is a co-product of corn grain production; therefore, it is necessary to allocate emissions between these two products. There are different co-product treatment approaches utilized in LCA, including allocation and system expansion (ISO 14044, 2006). Two approaches, system expansion and mass allocation, are used in this study to distribute emissions from corn production and harvesting to stover and grain.

System expansion is the most common approach used in previous studies (e.g., Sheehan et al. 2004; Kim et al. 2009; Spatari and MacLean 2010; Hsu et al 2010). In the system expansion approach, only emissions related to the additional activities required to harvest stover are assigned to the stover. The environmental effects of harvesting stover include changes in nitrogen related emissions and soil organic carbon levels, phosphorous loss, additional nutrient requirements in the subsequent growing season, and fuel consumption for stover harvesting. For this approach, the GHG emissions assigned to stover presented in Kim et al. (2009), who used the DAYCENT model and system expansion to calculate the GHG emissions assigned to stover for the eight counties considered in this study, are utilized directly.

The mass allocation approach distributes the GHG emissions associated with corn cultivation and harvest between corn grain and harvested corn stover based on their respective masses. The mass allocation approach based on average 2006-2010 corn yield and fertilizer application rates for each specific county is applied. Fertilizer use and yield data are obtained from the Agricultural Statistics Service (NASS) survey of corn cultivation practices in the eight counties (see Table 1). The data for agronomical inputs (e.g., fertilizer use) and production yields are averages based on survey data from 2006-2010. Fertilizer application rates can vary by location due to soil characteristics, management practices, and other factors. In our study, we do not attempt to make a causal link between fertiliser application rates and yield. Data for stover removal rate, lime and fossil fuel usage are not available in NASS; these multi-year averages (2001-2004) were obtained from Kim et al. (2009). The data are summarized in Table 1.

#### 2.4. Pre-processing

There is a pre-processing facility for corn stover handling and processing prior to its arrival at the biorefinery (Humbird et al. 2011). This pre-processing concept is based on the pioneering implementation of the 'Uniform-Format' solid feedstock supply system described by Idaho National Laboratory (INL) (Hess et al., 2009) and used by NREL (Humbird et al., 2011) in their process design for biochemical conversion of lignocellulosic biomass to ethanol. This is an interim stage supply system design, where square and round bale technologies and co-handling technologies are used to model supply chain logistics. The pre-processing has two stages: (1) decomposition, which includes receiving operations such as weighing the biomass material, removal of covering and conveying to grinding stages, and (2) grinding, which includes a hammer mill and dust management equipment as well as associated conveyors. The electricity consumption of these two stages was reported in Hess et al. (2009).

## 2.5 Biorefinery

The corn stover-ethanol production process is modeled based on the process presented in the 2011 NREL report (Humbird et al., 2011). This biorefinery produces 230 million litres ethanol per year. Table 4 compares the ethanol yield, electricity production (surplus) and chemical consumption reported in Humbird et al. (2011) with those reported in the 2002 NREL process design (Aden et al., 2002). The main differences in the process designs include: lower ethanol yield and electricity credit in the 2011 design; introduction of new chemicals (ammonia, caustic and glucose) in the 2011 design; and onsite enzyme production in the 2011 design versus offsite enzyme production in the 2002 design. These factors are all expected to impact life cycle GHG emissions.

The production of ethanol involves pre-treatment of corn stover with dilute acid, followed by enzymatic hydrolysis of the cellulose and hemicellulose fractions. The resulting glucose and xylose are fermented to produce ethanol. Substrate management and storage, purification of the product, wastewater treatment, lignocellulose ignition, and product storage are all included in the process. The enzyme is produced on-site from *T. reesei*, with glucose (corn syrup) as the carbon source. Cellulase production occurs in two steps. An initial seed fermenter is fed with a portion of this

glucose, which is used to induce cellulase production. Then, a larger scale fermentor is used to produce cellulase. The whole cell broth, rich in cellulase, is then fed to the cellulosic ethanol process.

The pre-processed corn stover is fed to the biorefinery. The biomass is then sent to a pre-treatment reactor, which operates at high temperature for a few minutes. Dilute sulfuric acid is introduced in the pre-treatment and conditioning as a catalyst to release hemicellulosic sugars and to break down biomass for enzymatic hydrolysis. Prior to enzymatic hydrolysis, slurry is created from effluent biomass from the pre-treatment, which is then neutralized with ammonia to achieve a pH of  $\sim$ 5 - 6. Cellulase is added to a high-solids continuous enzymatic hydrolysis reactor, creating a partially hydrolyzed slurry. The slurry is then processed in parallel batch reactors to accomplish complete hydrolysis. The slurry is cooled and inoculated with a co-fermenting microorganism, which converts the glucose and xylose into ethanol after about five days of sequential fermentation and hydrolysis.

The ethanol, water and residual solids are separated by distillation followed by centrifugation of the distillation bottoms to "de-water" solids. The ethanol is further distilled and purified to 99.5%. The distillation bottoms (primarily lignin solids) are sent to a boiler, while the liquid is treated in a wastewater treatment plant. The combustor is supplemented with biogas generated by the wastewater treatment plant. Sludge from the digesters is burned and the treated water is recycled and used in the process. Plant wastewater streams are treated with both anaerobic and aerobic digestion. Methane-rich biogas from anaerobic digestion is sent to the same combustor where sludge from the digesters is also burned. Treated water is suitable for recycling and is returned to the process. Electricity and heat are cogenerated from the combustion of distillation solids and biogas. A portion of generated electricity and all of the produced heat are used to meet requirements of the biorefinery processes. It is assumed that the excess electricity generated in the biorefinery displaces grid-average electricity from the state grid in which the county is located. The sources of electricity generation in each state are presented in Table 3.

2.6. Allocation of GHG emissions to ethanol as the primary product of the biorefinery System expansion is employed to assess GHG emissions of the co-produced ethanol and excess electricity. In this approach, ethanol is treated as the primary product and all life cycle GHG emissions are attributed entirely to the ethanol. GHG emissions for corn stover-derived ethanol thus

include emissions associated with the feedstock (corn stover) production, stover pre-processing and transport, biorefinery emissions, distribution and use of ethanol, and emissions credits due to the electricity co-product. This approach is consistent with that employed to assess fuels under the EISA (2007).

## 3. Results and Discussion

### 3.1. Life cycle GHG emissions for E100 produced from corn stover

Life cycle GHG emissions, those associated with the activities from stover production through ethanol (E100) combustion are discussed in this section for each of the eight counties/locations considered. Emissions results are presented based on the system expansion method for the corn stover production (Fig. 2). Results based on the mass allocation method are presented in Section 3.2.

As presented in Figure 2, biorefinery-related GHG emissions are the highest contributor to life cycle emissions, with 17.7 g CO<sub>2</sub> eq./MJ of E100 produced. The emissions associated with the biorefinery are the same for each of the eight counties/locations because the NREL biorefinery model includes conversion of residues to supply all of the biorefinery's thermal and electrical energy needs. The GHG emissions for chemicals used in the process are assumed independent of location and are therefore the same for all biorefinery locations. The contribution of the chemicals to GHG emissions of the biorefinery is presented in Table 5. Caustic, ammonia and corn steep liquor are the largest sources of GHG emissions in the biorefinery. The sum of these three chemicals accounts for 74% of biorefinery-related GHG emissions. As mentioned earlier, caustic, ammonia and glucose were introduced in NREL's 2011 process, whereas these three chemicals were not used in their 2002 design.

The GHG emissions associated with stover harvesting and pre-processing can be significant contributors to the life cycle emissions of E100 (Fig. 2). These two emission sources are dependent on location. The GHG emissions associated with stover harvesting range from 12.7 (Hardin County, Iowa) to -5.7 (Macon County, Missouri) g CO<sub>2</sub> eq./MJ of E100. At all studied locations, stover removal reduces soil carbon sequestration (relative to not collecting stover) but also has a counteracting effect of reducing field N<sub>2</sub>O emissions. Stover production in Macon County has

negative GHG emissions as the associated reduction in N<sub>2</sub>O emissions exceeds emissions related to reduced soil carbon stocks; this results from a lower allowable stover removal rate in that county (Table 2)(Kim et al., 2009). Figure 3 presents GHG emissions of stover harvesting per kg of stover. The GHG emissions of stover harvesting range from 90 (Hardin) to -40 (Macon) g CO<sub>2</sub> eq./kg of stover. By comparison, GREET 2012 (Argonne National Laboratory, 2013) also uses a system expansion approach, but uses U.S. average data, and reports GHG emissions of 90 g CO<sub>2</sub>eq/kg of stover.

Emissions associated with corn stover pre-processing and the electricity co-product credit are dependent on the local grid mix. Electricity is the major form of energy used in pre-processing and it is provided by the local grid. The GHG emissions from pre-processing range from 2.8 g CO<sub>2</sub>eq/MJ of E100 in Codington County, SD, where hydro is the major generation source, to 5.8 g CO<sub>2</sub>eq/MJ of E100 in Macon County, MO, where coal is the main generation source (Table 3). Lignin-derived electricity exported to the grid by the biorefinery creates a GHG credit for ethanol. The electricity credit is higher for counties in states that use coal as a major source for electricity generation. Therefore, the biorefinery in Macon County is assigned the largest credit for lignin-derived electricity (19.9 g CO<sub>2</sub>eq/MJ of E100), while the biorefinery in Codington County is assigned the lowest credit (8.4 g CO<sub>2</sub>eq/MJ of E100) (Fig. 2). Greater emissions associated with pre-processing and greater credits for the electricity co-product are observed in states/counties with more GHG intensive grids. Since the co-product electricity output is greater than electricity consumption during preprocessing, biorefineries located in states with more GHG intensive electricity grids have lower net GHG emissions, once these two stages (pre-processing and electricity co-product) are considered. For example, the sum of the pre-processing emissions and the electricity credit for Codington County is 5.6 g CO<sub>2</sub>eq/MJ of E100, compared to -14.1 g CO<sub>2</sub>eq/MJ of E100 in Macon County.

Transportation-related emissions (transportation of stover to the biorefinery and transportation of ethanol to point of use) are the smallest contributor to life cycle GHG emissions (1.1 to 2.7 g CO<sub>2</sub>eq/MJ of E100) (Fig. 2).

The net life cycle GHG emissions of E100 range from 1.5 (Macon County) to 22 (Codington County) g CO<sub>2</sub>eq/MJ of E100 (Fig. 2), representing reductions relative to gasoline of 98% and 77%,

respectively. While the lowest GHG emissions for E100 production are achieved in Macon County, the ability to site a plant that could achieve these emissions might be hindered by the low corn (and stover) yield in Macon County compared to other counties. Macon County has the lowest corn yield (4790 kg/ha) (Table 1), and stover removal rate (25%) (Table 2). The low corn yield and low stover removal rate would increase the ethanol production cost by limiting the scale of the biorefinery and/or increasing the cost for stover collection/transportation. Therefore, from a financial perspective, Macon County may not be as attractive as other counties for locating a biorefinery.

The net life cycle GHG emissions of E100 for the three counties with the highest corn yields – Hamilton (9740 kg/ha), Hardin (9203 kg/ha) and Freeborn (9069 kg/ha) - are 18, 20 and 19 gCO<sub>2</sub>eq/MJ of E100. Although Freeborn and Morrison Counties are located in same state (MN), the life cycle GHG emissions of E100 produced in Morrison are 24% lower than those of E100 produced in Freeborn (Fig. 2). This is due primarily to greater soil carbon losses associated with stover removal in Freeborn County (Table 2), resulting in emissions for stover harvesting of 28 gCO<sub>2</sub>eq./kg and 58 gCO<sub>2</sub>eq./kg, respectively (Fig. 3).

## 3.1.1 Comparison of life cycle GHG results of NREL's 2011 and 2002 process designs

The life cycle GHG emissions in the current study, based on the 2011 NREL process design, are lower than those reported by Hsu et al. (2010) for the 2002 NREL process design (Table 6). One key process design difference arises with stover pre-processing: the current study does not include drying or densification, resulting in overall pre-processing electricity consumption of 42 kWh/tonne of feedstock. Hsu et al. (2010) included drying and densification, consuming a total of 100 kWh/tonne of feedstock, resulting in correspondingly higher GHG emissions. GHG emissions resulting from biorefinery operations, however, are greater for the 2011 than 2002 NREL process design. The 2011 design includes ammonia, caustic and glucose as inputs, whereas the 2002 design did not use these chemicals (Aden et al., 2002). Ammonia is used to raise the pH of hydrolyzate prior to enzymatic hydrolysis. Caustic is utilized in the anaerobic digestion process to control the pH. Glucose is used as a feedstock for cellulose enzyme production. Half of the 2011 design biorefinery related GHG emissions result from ammonia and caustic while 10% of biorefinery emissions relate to glucose, demonstrating the significance of these design changes. Ethanol yield is lower in the 2011 process design: 332 L/dry tonne compared to 374 L/dry tonne in the 2002 design.

A lower ethanol yield results in more residual biomass available for co-product electricity production, thereby providing a larger co-product GHG credit when displacing grid electricity. However, the electricity co-product credit is less in the 2011 NREL process design due to the additional electricity consumption associated with enzyme production.

Differences in GHG emissions results between the current study and Hsu et al. (2010) also arise due to use of different data and assumptions in the studies. The GHG emissions assigned to enzyme production in the current study are 11.5 g CO<sub>2</sub> eq./g of produced enzyme, based upon the onsite enzyme production process proposed by NREL 2011 (Hong et al., 2013) whereas Hsu et al. (2010) utilized 4.1 g CO<sub>2</sub> eq./g of cellulase consumed in the process. Differences also arise due to the current study's use of the state grid mix to calculate the electricity credit, while Hsu et al. (2010) used the U.S. average grid mix. The state based grid mix allows evaluation of site-dependent factors that influence overall GHG emissions for a biorefinery.

#### 3.2 Allocation of GHG emissions to corn stover

As described in Section 2, under system expansion, only the incremental GHG emissions associated with harvesting stover (fuel and nutrient replacement) are assigned to stover, while under mass allocation, GHG emissions from corn farming and stover harvesting are allocated to stover and corn grain based on their mass. Figure 3 presents the life cycle GHG emissions from stover production (gCO<sub>2</sub>eq/kg of stover), considering mass allocation and system expansion. GHG emissions for stover production under mass allocation range between 218 to 289 gCO<sub>2</sub>eq/kg of stover, while under system expansion, they range from -40 to 90 g CO<sub>2</sub>eq/kg of stover (Fig. 3). In all cases, GHG emissions from stover production under mass allocation are much higher than they are under system expansion.

The life cycle GHG emissions associated with E100, assuming mass allocation is used to calculate emissions from stover production, are presented in Figure 4. Stover production is the highest contributor to life cycle emissions, contributing 31 to 41 gCO<sub>2</sub>eq/MJ of E100, while the net life cycle GHG emissions range from 38 to 52 gCO<sub>2</sub>eq/MJ of E100.

#### 3.3 Eligibility of corn stover ethanol under the Energy Independence and Security Act

To meet the EISA GHG emissions threshold for cellulosic biofuels, emissions for corn stover-derived ethanol must be less than 38 gCO<sub>2</sub>eq./MJ (assuming gasoline emissions of 95 g CO<sub>2</sub>eq./MJ (GREET 2012)). When system expansion is employed to calculate GHG emissions from corn stover production and harvesting, ethanol production in all eight counties considered in the current study can meet the GHG reduction required under EISA for a cellulosic biofuel. In contrast, if mass allocation is used to calculate emissions from corn stover production and harvesting, only a cellulosic ethanol plant in Hardin County would meet the legislated GHG emissions reduction.

Most life cycle studies and the ISO standard for LCA (ISO 14044, 2006) recommend system expansion. Therefore, in this work, more emphasis is placed upon the system expansion results than the mass allocation results. Promising GHG reductions for ethanol produced from corn stover are reported when a system expansion approach is used. The different outcomes observed with the 2002 and 2011 NREL models highlight that future developments in pre-processing and bioconversion technologies may alter the life cycle GHG emissions of ethanol produced from corn stover. Furthermore, regional differences in soil carbon, corn stover production and removal, and the carbon intensity of the local grid can lead to different GHG emissions.

#### 4. Conclusions

GHG emissions for E100 from corn stover are strongly dependent upon regional factors. Emissions associated with biorefinery operation, corn stover production, and the electricity co-product credit dominate the overall life cycle GHG emissions for ethanol produced from corn stover. The latter two factors are strongly affected by the location of the biorefinery, which impacts the GHG emissions from stover production and the GHG emissions credit for co-product electricity that displaces emissions from the local grid. The magnitude of the GHG emissions for preprocessing is inversely related to the magnitude of the electricity co-product credit. The magnitude of the reduction due to co-product electricity always exceeds the magnitude of the emissions associated with pre-processing, leading to a net credit from these two factors that increases with the carbon intensity of the grid. Thus, the type of energy used for grid electricity influences two key components of the overall life cycle GHG emissions, and a larger credit (benefit) is obtained when more fossil fuel is utilized in the grid.

The GHG emissions from stover production and harvesting are higher when a mass allocation approach is used to assign GHG emissions of corn farming and stover production to stover. However, the standard approach for allocation of emissions to co-products is system expansion; when a system expansion is considered for stover GHG emissions, the ethanol produced from stover will reduce GHG emissions by at least 60% in all counties, and thus meet the EISA requirement.

GHG emissions associated with biorefinery operations are higher for the 2011 NREL process design compared to the 2002 NREL design. This difference in GHG emissions is due to inclusion of GHG intensive materials (caustic, ammonia, glucose) and the lower ethanol yield. In addition, less co-product electricity is exported to the grid under the 2011 design due to increased biorefinery electricity demands resulting largely from on-site enzyme production. However, life cycle GHG emissions in the current study, based on the 2011 NREL process design, are lower than those reported by Hsu et al. (2010), due primarily to less energy-intensive biomass pre-processing.

This study has evaluated impacts of technology development and regional aspects on the life cycle GHG emissions of ethanol production from corn stover. While all ethanol production scenarios were found to exceed the EISA emission reduction threshold of 60% (relative to gasoline), results are found to vary significantly due to both design changes between 2002 and 2011 NREL process models and key region-specific parameters (stover collection emissions; GHG-intensity of grid electricity).

## Acknowledgements

We thank the Government of Canada through AUTO21 Network Centre of Excellence, Genome Canada (2009-OGI-ABC-1405), the Natural Sciences and Engineering Research Council, as well as the Government of Ontario (ORF-GL2-01-004) and BioFuelNet Network of Centres of Excellence for financial support.

#### References

Aden A, Ruth M, Ibsen K, Jechura J, Neeves K, Sheehan J, Wallace B, Montague L, Slayton A, Lukas, J. 2002. Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover. NREL/TP-510-32438.

Adler PR, Grosso SJD and Parton WJ. 2007. Life-cycle assessment of net greenhouse-gas flux for bioenergy cropping systems. Ecol. Appl. 17: 675-691.

Argonne National Laboratory, Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET). 2013. Computer Model, GREET 2012 rev1 model. Available at:http://www.transportation.anl.gov/modeling\_simulation/GREET/index.html

Bhardwaj AK, Zenone T, Jasrotia P, Robertson GP, Chen J and Hamilton SK. 2011. Water and energy footprints of bioenergy crop production on marginal lands. GCB Bioenerg. 3: 208-222.

California Air Resources Board 2009.Proposed Regulation to Implement the Low Carbon Fuel Standard (Volume I). Sacramento, California.

Cherubini F, Ulgiati S. 2010. Crop residues as raw materials for biorefinery systems – A LCA case study. Applied Energy 87:47–57.

Energy Independence and Security Act of 2007. Public Law 110-140. Accessed 16/07/2013. Available at: <a href="http://www.gpo.gov/fdsys/pkg/PLAW-110publ140/html/PLAW-110publ140.htm">http://www.gpo.gov/fdsys/pkg/PLAW-110publ140/html/PLAW-110publ140.htm</a>

Gonzalez-Garcia S, Moreira MT and Feijoo G. 2010. Comparative environmental performance of lignocellulosic ethanol from different feedstocks. Renew. Sustain. Energy Rev. 14: 2077-2085.

Graham RL, Nelson R, Sheehan J, Perlack RD, Wright LL. 2007. Current and potential U.S. corn stover supplies. Agron. J. 99:1–11.

Hess JR, Kenney KL, Ovard LP, Searcy EM, Wright CT. 2009. Uniform-Format Solid Feedstock Supply System: A Commodity-Scale Design to Produce an Infrastructure-Compatible Bulk Solid from Lignocellulosic Biomass, Section 3: Pioneer Uniform Feedstock Supply System. Report No. INL/EXT-08-14752. Idaho Falls, ID: Idaho National Laboratory. http://www.inl.gov/bioenergy/uniform-feedstock.

Hong Y., Nizami A.S., Pourbafrani M., Saville B.A., MacLean H.L. 2013. Impact of cellulase production on environmental and financial metrics for lignocellulosic ethanol.Bifuels Bioprod. Biorefin. 7, 3, 303-313.

Hsu DD, Inman D, Heath GA, Wolfrum E, Mann M and Aden A. 2010. Life cycle environmental impacts of selected U.S. ethanol production and use pathways in 2022. Environ. Sci. Technol. 13: 5289–5297.

Humbird D, Davis R, Tao L, Kinchin C, Hsu D, Aden A. 2011.Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol. NREL/TP-5100-47764

ISO 14044 (International Organisation for Standardisation) 2006. Environmental Management—Life Cycle Assessment—Requirement and Guidelines.

IPCC (Intergovernmental Panel on Climate Change) 2006 Guidelines for National Greenhouse Gas Inventories ed S Egglestton et al (Hayama: Institute for Global Environmental Strategies)

Kaufman SA, Meier JP, Sinistore CJ, Reinemann JD. 2010. Applying life-cycle assessment to low carbon fuel standards-How allocation choices influence carbon intensity for renewable transportation fuels Energ. Policy.38:5229-5241.

Kim S, Dale BE. 2004. Global potential bioethanol production from wasted crops and crop residues. Biomass Bioenerg. 26:361–375.

Kim S, Dale BE. 2005. Life cycle assessment of various cropping systems utilized for producing biofuels: bioethanol and biodiesel. Biomass Bioenerg. 29:426–439.

Kim S, Dale BE and Jenkins R. 2009. Life cycle assessment of corn grain and corn stover in the United States. Int. J. Life Cycle Assess. 14:160-174.

Liao W, Heijungs R, Huppes G. 2011. Is bioethanol a sustainable energy source? An energy-, exergy-, and emergy-based thermodynamic system analysis. Renew. Energ. 36:3479-3487.

Luo L, van der Voet E, Huppes G, Udo de Haes HA. 2009. Allocation issues in LCA methodology: a case study of corn stover-based fuel ethanol. Int. J. Life Cycle Assess. 14:529–539.

National Agricultural Statistics Service (NASS) 2007. U.S. Department of Agriculture. Available at http://www.nass.usda.gov.

Nelson RG. 2002. Resource assessment and removal analysis for corn stover and wheat straw in the Eastern and Midwestern United States—rainfall and wind erosion methodology. Biomass Bioenerg. 22:349–363.

Spatari S and MacLean HL. 2010. Characterizing Model Uncertainties in the Life Cycle of Lignocellulose-Based Ethanol Fuels. Environ. Sci. Technol. 44:8773–8780.

Sheehan J, Aden A, Paustian K, Killian K, Brenner J, Walsh M and Nelson R. 2004. Energy and environmental aspects of using corn stover for fuel ethanol. J. Indust. Ecol. 7:117-146.

Spatari S, Zhang YM and MacLean HL. 2005. Life cycle assessment of switchgrass- and corn stover-derived ethanol-fueled automobiles. Environ. Sci. Technol. 39: 9750-9758.

Wang M, Han J, Dunn BJ, Cai H, Elgowainy A. 2012. Well-to-wheels energy use and greenhouse gas emissions of ethanol from corn, sugarcane and cellulosic biomass for US use. Environ. Res. Lett. 7 045905.

Table 1. Fertilizer input and yield for corn cultivation for counties studied

County	Yield dry	N fertilizer	P fertilizer	K fertilizer
	(kg ha <sup>-1</sup> )	(kg N ha-1)	(kg P <sub>2</sub> O <sub>5</sub> ha <sup>-1</sup> )	(kg K <sub>2</sub> O ha <sup>-1</sup> )
Hardin (IA)	9203	159	73	90
Fulton (IL)	6776	187	104	119
Tuscola (MI)	7350	137	36	105
Morrison (MN)	7880	140	56	71
Freeborn (MN)	9069	140	56	71
Macon (MO)	4790	141	71	64
Hamilton (NE)	9740	157	46	29
Codington (SD)	7157	145	57	33

Source: National Agricultural Statistics Service based on 5 year average from 2006-2010

Table 2. Inputs of lime and fossil fuel, stover removal rate and carbon sequestration in corn cultivation for counties studied (Source: Kim et al. 2009)

County	Lime	Fossil fuel use <sup>1</sup>	Stover removal	Carbon sequestration by
	(kg ha-1)	(MJ ha <sup>-1</sup> )	rate (%)	soil
				(kg CO <sub>2</sub> eq. ha <sup>-1</sup> year <sup>-1</sup> )
Hardin (IA)	23	1546	50	46
Fulton (IL)	23	1243	50	46
Tuscola (MI)	23	2420	50	0.8
Morrison (MN)	23	1815	50	-36
Freeborn (MN)	23	1815	50	-144
Macon (MO)	23	1680	25	-52
Hamilton (NE)	23	4167	50	153
Codington (SD)	23	1479	45	141

<sup>1.</sup> Fossil fuel use includes fuel use for both corn production and stover collection.

Table 3. Energy sources of state electricity in 2010 (Source: US State Electricity Profile 2010)

Energy Source (Percent of total)	Nebraska	Missouri	Minnesota	Michigan	Iowa	Illinois	South Dakota
Coal	63.8	81.3	52.3	58.8	71.8	46.5	32.8
Petroleum	0.1	0.1	0.1	0.3	0.3	0.1	0.1
Natural Gas	1.0	5.1	8.1	11.0	2.3	2.8	1.3
Other Gases 1	-	*	-	0.3	-	0.1	-
Nuclear	30.2	9.7	25.1	26.6	7.7	47.8	-
Hydroelectric	3.6	1.7	1.6	1.1	1.6	0.1	52.1
Other Renewables <sup>2</sup>	1.3	1.1	12.4	2.5	16.3	2.6	13.6
Pumped Storage	-	1.0	-	-0.9	-	-	-
Other <sup>3</sup>	-	*	0.5	0.3	-	0.1	-
GHG emissions (g CO <sub>2</sub> eq./kWh)	685.6	890.9	600.3	682.3	782.7	509.7	375.4

<sup>&</sup>lt;sup>1</sup>Other gases include; blast furnace gas, propane gas, and other manufactured and waste gases derived from fossil fuels.

<sup>&</sup>lt;sup>2</sup>Other renewables include; biogenic municipal solid waste, wood, black liquor, other wood waste, landfill gas, sludge waste, agriculture by-products, other biomass, geothermal, solar thermal, photovoltaic energy, and wind.

<sup>&</sup>lt;sup>3</sup>Other includes; non-biogenic municipal solid waste, batteries, chemicals, hydrogen, pitch, purchased steam, sulfur, tirederived fuels and miscellaneous technologies.

<sup>\*</sup> Value is less than half of the smallest unit of measure (e.g., for values with no decimals, the smallest unit is 1 and values under 0.5 are shown as \*)

<sup>-</sup> data not available

Table 4. Comparison of National Renewable Energy Laboratory (NREL) 2002 (Aden et al. 2002) and 2011 (Humbird et al. 2011) lignocellulosic ethanol design processes.

Design	Year (2002)	Year (2011)
Chemical Use		
(kg/dry tonne of feedstock)		
Sulfuric Acid	39.5	23.8
Ammonia	0	12.6
Caustic	0	27.0
Lime	28.7	10.7
Diammonium Phosphate	2.0	1.7
Sorbitol	0	0.5
Corn Steep Liquor	15.7	13.9
Nutrient	0	0.8
Sulfur Dioxide	0	0.2
Glucose	0	29.0
Purchased Cellulase	8.3	0
On site enzyme production	0	7.4
Ethanol Yield	374	332
(liter/dry tonne of feedstock)		
Excess Electricity	225	154
(kWh/dry tonne of feedstock)		

Table 5. GHG emissions of chemicals used in the process of NREL 2011  $\,$ 

Chemical	GHG emissions
	(g CO <sub>2</sub> .eq./MJ of E100)
Sulfuric Acid	0.43
Ammonia	3.44
Caustic	5.54
Lime	1.90
Diammonium Phosphate	0.15
Corn Steep Liquor	4.06
Nutrient	0.30
Sulfur Dioxide	0.02
Glucose	1.90
Total	17.74

Table 6. Comparison of greenhouse gas emissions results for E100 from current study with those of Hsu et al. (2010).

	g CO <sub>2</sub> eq./MJ of produced ethanol		
	This work	Hsu et al. (2010)	
Stover production <sup>1</sup>	-5.6 to 12.7 (Avg: 6.5)	18.0	
Pre-processing	3.8 to 6.7 (Avg: 4.8)	25.0	
Transportation	1.5	2.0	
Biorefinery	17.7	9.8	
Electricity Credit	-8.3 to -19.9 (Avg: -14.3)	-21.0	
Net	1.5 to 21.9 (Avg: 16.5)	34.8	

<sup>1.</sup> The system expansion approach is used to allocate GHG emissions from corn farming and stover harvesting to stover.

Figure legends:

Figure 1. System boundaries for life cycle assessment of E100 from corn stover

Figure 2. GHG emissions of E100 produced from corn stover based on system expansion approach (a) GHG emissions of stover production, (b) GHG emissions of transportation, which includes transportation of stover and also ethanol produced, (c) GHG emissions of pre-processing, (d) GHG emissions of biorefinery, (e) electricity credit, (f) Net GHG emissions. Note: the combustion of ethanol is considered as a carbon neutral process and the emissions assigned to ethanol combustion are zero.

Figure 3. Figure 3. GHG emissions associated with corn stover production in the counties studied utilizing system expansion and mass allocation. The system expansion results are taken from Kim et al., 2009.

Figure 4. Figure 4. GHG emissions of E100 produced from corn stover based on mass allocation (a) GHG emissions of stover production, (b) GHG emissions of transportation, which includes transportation of stover and also ethanol produced, (c) GHG emissions of pre-processing, (d) GHG emissions of biorefinery, (e) electricity credit, (f) Net GHG emissions. Note: the combustion of ethanol is considered as a carbon neutral process and the emissions assigned to ethanol combustion are zero.

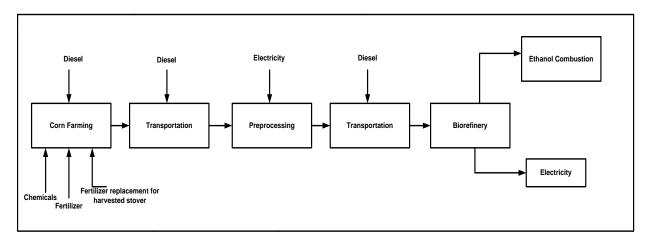


Figure 1. System boundaries for life cycle assessment of E100 from corn stover

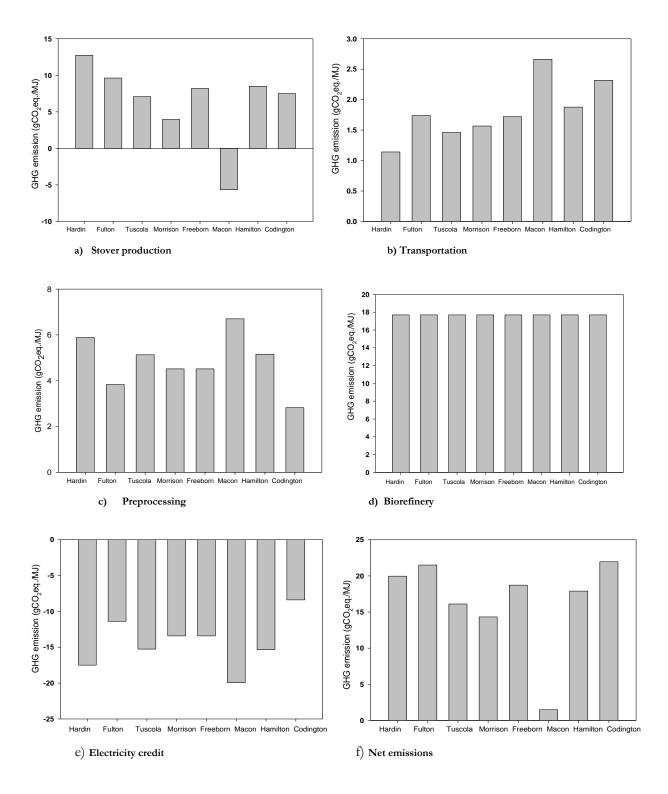


Figure 2. GHG emissions of E100 produced from corn stover based on system expansion approach (a) GHG emissions of stover production, (b) GHG emissions of transportation, which includes

transportation of stover and also ethanol produced, (c) GHG emissions of pre-processing, (d) GHG emissions of biorefinery, (e) electricity credit, (f) Net GHG emissions. Note: the combustion of ethanol is considered as a carbon neutral process and the emissions assigned to ethanol combustion are zero.

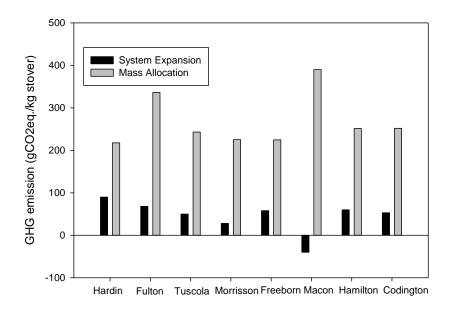
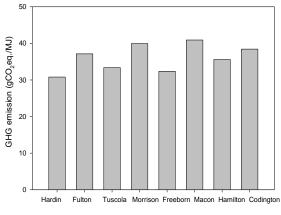
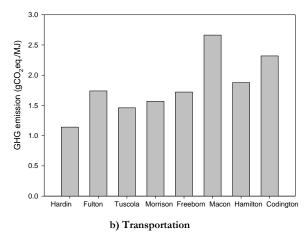
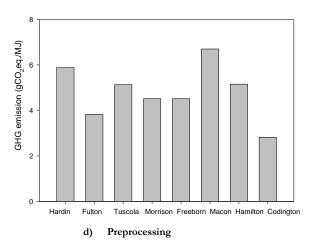


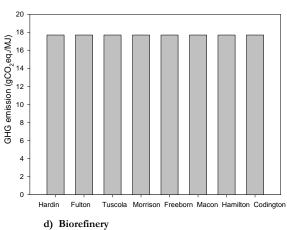
Figure 3. GHG emissions associated with corn stover production in the counties studied utilizing system expansion and mass allocation. The system expansion results are taken from Kim et al., 2009.

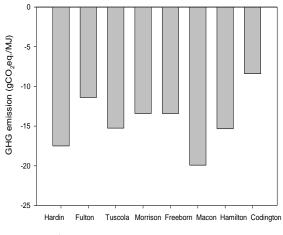


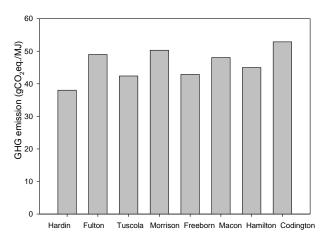


a) Stover production









e) Electricity credit

f) Net emissions

Figure 4. GHG emissions of E100 produced from corn stover based on mass allocation (a) GHG emissions of stover production, (b) GHG emissions of transportation, which includes transportation of stover and also ethanol produced, (c) GHG emissions of pre-processing, (d) GHG emissions of biorefinery, (e) electricity credit, (f) net life cycle GHG emissions. Note: the combustion of ethanol is considered as a carbon neutral process and the emissions assigned to ethanol combustion are zero.