Environ. Sci. Technol. **2010,** *44,* 5289–5297

Life Cycle Environmental Impacts of Selected U.S. Ethanol Production and Use Pathways in 2022

DAVID D. HSU,* DANIEL INMAN, GARVIN A. HEATH, EDWARD J. WOLFRUM, MARGARET K. MANN, AND ANDY ADEN

National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401-3393

Received January 18, 2010. Revised manuscript received May 10, 2010. Accepted May 25, 2010.

Projected life cycle greenhouse gas (GHG) emissions and net energy value (NEV) of high-ethanol blend fuel (E85) used to propel a passenger car in the United States are evaluated using attributional life cycle assessment. Input data represent national-average conditions projected to 2022 for ethanol produced from corn grain, corn stover, wheat straw, switchgrass, and forest residues. Three conversion technologies are assessed: advanced dry mill (corn grain), biochemical (switchgrass, corn stover, wheat straw), and thermochemical (forest residues). A reference case is compared against results from Monte Carlo uncertainty analysis. For this case, one kilometer traveled on E85 from the feedstock-to-ethanol pathways evaluated has 43%−57% lower GHG emissions than a car operated on conventional U.S. gasoline (base year 2005). Differences in NEV cluster by conversion technology rather than by feedstock. The reference case estimates of GHG and NEV skew to the tails of the estimated frequency distributions. Though not as optimistic as the reference case, the projected median GHG and NEV for all feedstock-to-E85 pathways evaluated offer significant improvement over conventional U.S. gasoline. Sensitivity analysis suggests that inputs to the feedstock production phase are the most influential parameters for GHG and NEV. Results from this study can be used to help focus research and development efforts.

Introduction

Forty-one billion liters of ethanol were produced in the United States in 2009, mostly from corn grain (*Zea mays* L.) (*1*). As part of a strategy to address national security, greenhouse gas (GHG) emissions, and rural economic development, the Energy Independence and Security Act of 2007 (EISA) (*2*) amended the 2005 renewable fuel standard (RFS) to mandate that approximately 136 billion liters per year (bLy) be produced by 2022. Under the 2007 RFS, a maximum of 56.6 bLy of ethanol derived from conventional sources (e.g., corn grain) may qualify as a renewable fuel (*2*); the remainder must be met by biofuel derived from second-generation feedstocks, such as agricultural residues, forest residues, and perennial grasses.

Life cycle net energy value (NEV) and GHG emissions have been used as metrics to compare different feedstock-to-ethanol production systems and gasoline. With a few exceptions (*3*, *4*), most studies conclude that corn ethanol has NEV and GHG advantages compared to gasoline (*5*−*9*). After harmonizing the methods of six previous life cycle assessments (LCA), Farrell and colleagues (*10*) found that current corn ethanol production yields an NEV of approximately 5 MJ L^{-1} and a GHG intensity of −18% (uncertainty range: −36% to +29%) compared with that of conventional gasoline. Similarly, ethanol derived from both switchgrass and corn stover has been shown to have higher NEV and lower GHG emissions when compared to gasoline (*11*, *12*). An LCA consistently comparing multiple feedstocks in the same production year would contribute to current research.

This study uses attributional LCA to compare projected GHG emissions and NEV of ethanol-based transportation fuel derived from five feedstocks grown and used in the conterminous United States in 2022 to that of conventional gasoline in 2005. Advanced designs for all life cycle stages of a first-generation feedstock (corn grain) and four next-generation feedstocks (corn stover, wheat straw, switchgrass, and forest residues) are considered. Life cycle GHG and NEV of gasoline are considered for the base year of 2005, similar to the mandates in EISA. Because EISA and other environmental mandates demand performance often far beyond current practice, this analysis aims to inform industrial and governmental research and development decisions by (1) determining the key input parameters that impact life cycle GHG emissions and NEV, and (2) quantifying the distribution of two environmental performance metrics. To do so, sensitivity and uncertainty analysis methods are applied.

Methods

SimaPro v.7.1 life cycle assessment modeling software (*13*) is used to develop and link unit processes. Most processes are custom created using primary, publicly available data. In the absence of such data, we use the Ecoinvent v.2.0 (*14*) and, to a lesser extent, the U.S. Life Cycle Inventory (U.S. LCI) (*15*) processes. For some processes that are developed from Ecoinvent and the U.S. LCI, we modify the former to be reflective of U.S. conditions and the latter to account for embodied emissions and energy flows. This study follows International Organization for Standardization standards for LCA, including stakeholder and external reviews (*16*, *17*); all processes underwent external review by experts from industry, academia, and government.

Modeling Approach and Assumptions. The modeling boundary for this study is from field to wheels including embodied energy and material flows. The functional unit is 1 km traveled by a light-duty passenger car operated on E85 in the year 2022. The ethanol is assumed to be produced in the conterminous United States (*18*). For our reference case, E85 is assumed to be 78 v% ethanol and 22 v% conventional unleaded gasoline, which includes gasoline denaturant (2 v% of ethanol). (This composition is based on an average of regional and seasonal blends (*19*)). The reference case evaluated in this study is based on extrapolation of national average data and anticipated industry learning and improvement. Therefore, the reference case is not necessarily indicative of any region of the country. Sensitivity and uncertainty analyses explore the impact of variability (considered on a national average basis) of a large set of input parameters on projected GHG and NEV results.

Avoided impacts are accounted for using product displacement (boundary expansion) (*16*, *17*). For products that

* Corresponding author e-mail: david.hsu@nrel.gov; phone: 303-384-6887; fax: 303-384-7449.

10.1021/es100186h
Published on Web 06/07/2010

share inputs (e.g., corn grain and corn stover), burdens are allocated between products based on a "product–purpose" approach (*20*). For example, irrigation used in corn production is driven by the purpose of growing grain, not stover; consequently all irrigation inputs are allocated to the corn grain. Other allocation approaches (mass-based, energy content-based) were investigated, and the effect that these had on GHG and NEV metrics does not change our overall conclusions. Impacts from infrastructure attributable to EISA are amortized over the lifetime of the infrastructure element. Inputs to multiyear cropping systems (i.e., switchgrass and forests) are likewise annualized by the length of the cropping rotation. Impacts from direct and indirect land use change (LUC) are not considered in this study. These impacts are potentially large (e.g., *21, 22)* and currently highly uncertain, but as will be shown from the results of this study, considerable uncertainty surrounds the direct emissions from the system as well. We focus on establishing the uncertainty of direct emissions, which is foundational to understanding the full consequences of ethanol production systems.

The sections below summarize the data sources, methods, and assumptions employed in the modeling of each life cycle stage. Additional information can be found in the Supporting Information.

Feedstock Production. Feedstock production includes all processes from field preparation and planting through harvest. Corn, corn stover, and wheat straw production are based on projections of historical U.S. national average data (*23*) to the year 2022. Switchgrass production is based on published research from large-scale, long-term, on-farm studies and reflects projected improvements in feedstock yield and management (*24, 25*) and an annual yield improvement of 2%, which is well in line with the annual increase expected from intensification (*26*). Forest residue production is based on modifications made to LCI data collected from whole-tree timber harvesting operations (*15*). The reference case removal rate for both the corn stover and wheat straw is assumed to be 30 wt% of total residue (*27*). In the reference case, loss of stover as a livestock feed supplement is modeled as being replaced by hay at a rate of 0.174 kg hay per kg stover removed for ethanol production (*28*).

Corn and wheat are assumed to be harvested using a single-pass harvest system (*29*). Switchgrass is assumed to be harvested using an advanced, one-step process (*29*). Forest residues, as modeled in this study, are assumed to be the nonmerchantable portions of the harvested tree that are brought to the landing, typically discarded, and in many cases burned. Forest residue harvesting is modeled based on U.S. whole-tree logging operations (*15*). Four logging regions are considered: the Pacific Northwest, the Intermountain West, the Southeast, and the Northeast–North Central regions (*15*); only private and state-owned forests are considered. Forest residues are assumed to be approximately 30% of the total cut volume; of this volume, it is further assumed that 30% is lost during skidding operations. The four regions are used to produce a weighted average, based on the regions' long-term, average annual production (*30*). The accumulated forest residues are assumed to be chipped at the landing using standard industrial chipping equipment.

Feedstock Preprocessing. Feedstock preprocessing is modeled to reflect an "Advanced Uniform-Format Feedstock Supply System" as described in the Idaho National Laboratory feedstock delivery design report (*29*). This feedstock supply system is modeled to provide a physically uniform feedstock to the biorefinery conversion facility, thereby minimizing feedstock preprocessing at the biorefinery. The biomass is separated from any grain, baled, and transported to a preprocessing facility where the biomass is dried, ground, and stored. The mass fractions of corn stover, switchgrass, and wheat straw that need to be actively dried instead of field dried are set at 0.85, 0.15, and 0.1, respectively (*31*).

Forest residue harvest already includes a chipping operation, therefore preprocessing only includes transport to a storage facility. Likewise, corn grain harvest includes separation of the grain, so preprocessing only includes transport to a storage facility based on distances from Yu and Hart (*32*).

Feedstock Transport. This stage models the transport of feedstock from the preprocessing/storage facility to the biorefinery. Distances are disaggregated by feedstock where possible (*29, 33–35*), otherwise recent corn grain logistics are assumed (*36–38*). Allocation to truck, rail, or barge transportation is based on previous experience assuming that a future system will be largely similar (*36–38*).

Conversion. While no commercial-scale cellulosic ethanol facilities exist today, conceptual designs, as documented in NREL reports, define the 2022 reference case cellulosic ethanol conversion processes. Biochemical production of ethanol, applied to corn stover, switchgrass, and wheat straw, is through dilute acid pretreatment, enzymatic hydrolysis, and fermentation (*39*); thermochemical production of ethanol, applied to forest residues, is via indirect gasification and mixed alcohol synthesis (*40*). Herbaceous feedstock compositions are based on distributional information from Lee et al. (*41*).

Corn dry mill mass balances are based on a 151 million liter ethanol per year version of a corn dry mill Aspen Plus model (*42*). The 2022 version of the corn dry mill is based on projected process heat and electricity mix, along with increased plant efficiencies, from a study by Mueller (*43*). The primary energy source for heat and power for corn dry mills is expected to shift from 97% fossil fuels (93% natural gas and 4% coal) in 2005 to 64% (60% natural gas and 4% coal) in 2022, with the remainder coming from renewable biomass and biogas power sources. In addition, the advanced corn grain case included increased ethanol yields based on Argonne National Laboratory's GREET model (*38*).

Enzymes used in the corn dry mill plant and the biochemical conversion process are based on information from Novozymes (*44, 45*). The biochemical conversion process exports electricity, which is assumed to displace U.S. grid electricity (*46*). The thermochemical conversion process produces mixed alcohols as a coproduct, which could be used in the chemical or fuel market; the LCI for the thermochemical conversion process is allocated between ethanol and mixed alcohols on an energy content basis. Corn dry mill plants produce distillers dried grains with solubles (DDGS). In this study, DDGS is assumed to be a marketable animal feed replacement. To account for this, the system boundaries are expanded to include displaced soy, corn, and urea production, as well as reduced methane emissions resulting from an assumed enteric fermentation credit. (Beef cattle fed DDGS reach their desired weight sooner than those fed a traditional feed ration, and are therefore slaughtered earlier, thus resulting in less methane released through enteric fermentation.) Feed displacement ratios and the enteric fermentation credit reported in Arora et al. (*47*) are used. LCIs for soybean meal and urea are based on Ecoinvent (*48*). Emissions from equipment such as heaters and dryers, which are not captured in Aspen Plus models, are taken from the Environmental Protection Agency's AP 42 emissions factor database (*49*). For NEV, a DDGS credit for the input energy avoided in production of the displaced soy, corn, and urea is assigned.

For the purposes of this LCA, the NREL Aspen Plus models (*50*) associated with these design reports are run for different parameter values, and linear regressions are developed for inputs and outputs of the processes. For the biochemical design, feedstock composition (cellulose, xylan, and lignin fractions), turbine efficiency, boiler efficiency, and ethanol yield (through pretreatment, hydrolysis, and fermentation conversions) are varied. For the thermochemical design, feedstock composition (ash, carbon, and oxygen content), feedstock moisture, and ethanol yield (through changing tar reforming and alcohol synthesis conversions) are varied. For the corn dry mill, the model is run for different corn ethanol yields by changing key parameters that influence saccharification and fermentation. As a result, the LCI for the biochemical, thermochemical, and corn dry mill conversion facilities can be calculated for a range of parameter values.

Ethanol Distribution. Ethanol distribution is modeled to include transport from the biorefinery to the point of refueling the consumer's vehicle, including blending with gasoline to produce E85. Distances and transport modal allocations are based on Reynolds (*51*), with expert judgment (*52*) and other sources (*35, 53*) used to fill gaps or, where possible, to make the modeled scenario feedstock-specific. Additional infrastructure required to distribute the volumes of ethanol mandated for 2022 under EISA is amortized over its useful lifetime and includes items such as blending tanks, new refueling dispensers, and retail storage tanks capable of holding E85.

Vehicle Operation. A flex-fuel passenger car (FFV) using E85 is modeled, with average on-road fuel economy and GHG emissions as projected for 2022 (incorporating EISA-mandated Corporate Average Fuel Economy standard improvements) by Argonne National Laboratory (*2, 38*). Other life cycle impacts associated with the vehicle (manufacture, servicing, end-of-life) are excluded; impacts associated with the manufacture of additional FFVs required to utilize the EISA-mandated ethanol volumes are negligible (*54*). The fuel economy and GHG emissions from an average U.S. passenger car consuming conventional gasoline in 2005 are also modeled based on GREET.

Gasoline. Gasoline used as denaturant and blendstock in E85 as well as gasoline consumed in various stages of the production of ethanol are modeled for 2022. Gasoline used as the point of comparison with the E85 system is modeled for 2005 for its relevance to current biofuels policy. Data to evaluate GHG emissions and NEV are based on the U.S. LCI (*15*). While unconventional crude sources, such as tar sands, are expected to increase in production by 2022, the impact of these changes on the factors addressed in this study is assumed to be small compared with the overall crude supply (e.g., *55*). The process of producing gasoline is far more mature than the process for producing ethanol; improvements from 2005 to 2022 in the efficiency of the gasoline life cycle are assumed negligible. Therefore, we model gasoline in 2022 with 2005 data.

Analytical Methods. The combined impact of emissions of GHGs is calculated using 100-year global warming potentials for all gases (*56*), though the focus of our assessment is in tracking the three dominant GHGs of bioenergy systems: carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). Net energy value (NEV) is calculated as output energy minus input energy, where output energy includes the energy content of coproducts that are not displacing other products and hence are already accounted for in decreased input energy (*57*). In this study, the coproduct energies are implicitly accounted for, so the output energy includes only that of ethanol and gasoline.

Sensitivity Analysis. We use the multivariate analysis technique of partial least-squares (PLS) regression modeling (*58*) to identify which input variables are most influential. PLS regression models are developed to predict each output metric using all model input variables, and the algorithm of Martens (*59, 60*) is used to select important variables. All input and output variables are mean-centered and standardized to unit variance prior to regression modeling. All modeling is performed using Unscrambler 9.8 (*61*).

The Martens algorithm calculates the distribution of each input variable's regression coefficient during full "leave-one-out" cross-validation of the calibration model. Any one input variable whose regression coefficient has a mean value that is not statistically significantly different from zero ($p = 0.05$) is removed from the population as unimportant, and the PLS model development is repeated. Additional unimportant variables are identified and removed from the population after the next cycle of model development. Typically, two to four cycles are necessary to reach a stable input variable population. The relative importance of these remaining variables is determined from the absolute value of their regression coefficients; the larger the magnitude of the regression coefficient, the more important the variable is deemed to be. We include several random input variables to help guide the identification of important variables. These are kept in the input variable population for all model development cycles even though they are flagged as unimportant. The magnitude of the regression coefficients of the random input variables serves as a lower bound with which to compare the regression coefficients of the "real" input variables; those variables with magnitudes double those of the random variables are deemed important.

PLS is a linear modeling technique, and most of the models we developed show significant curvature, indicating the presence of nonlinear relationships between the input and output variables and limiting the use of such models for quantitative prediction of the output variables. However, the purpose of these models is not quantitative prediction, but rather simply to identify important variables for the subsequent Monte Carlo simulations, and the curvature in the models does not prevent this identification.

Uncertainty Analysis. Fuel and feedstock comparisons made in this study are based on projected advances in agricultural, logistical, and conversion systems. As such, our reference case models and results do not reflect the only possible state of technology in 2022. Alternative scenarios are investigated through uncertainty analyses. Results from these analyses should capture much of the variability, on a national-average basis, that is foreseeable or expected from progressive biorefinery technologies (e.g., varying ethanol yields), agronomic advances (e.g., yield improvement), and feedstock production practices (e.g., irrigation, nutrient application, tillage practices). The reference case does, however, reflect the scenario commonly evaluated in previously published LCAs (*3, 12, 62*) in that each input parameter is set to its most frequent value.

Monte Carlo uncertainty analysis is focused on those parameters determined as most influential by the aforementioned procedure. An $N \times 1000$ matrix is established for input to the model, where N is the number of most influential parameters. Probability distribution functions (PDFs) are then assigned for each influential parameter. In the absence of empirical evidence, triangular distributions are assumed because sufficient data are lacking to define any other distribution. Distributional characteristics (mode and range for triangularly distributed parameters, mean and standard deviation for normally distributed parameters) are set to reflect reasonable bounds of national average conditions in 2022 (see Table S2). Standard descriptive statistics are used to evaluate the results from the 1000 trials.

Results and Discussion

Reference Case Results. Figure 1 presents the reference case and the projected range in values from the uncertainty analysis for both GHG and NEV. Projected GHG emissions and NEV attributable to E85 distribution and vehicle operation are constant across all feedstock-to-ethanol

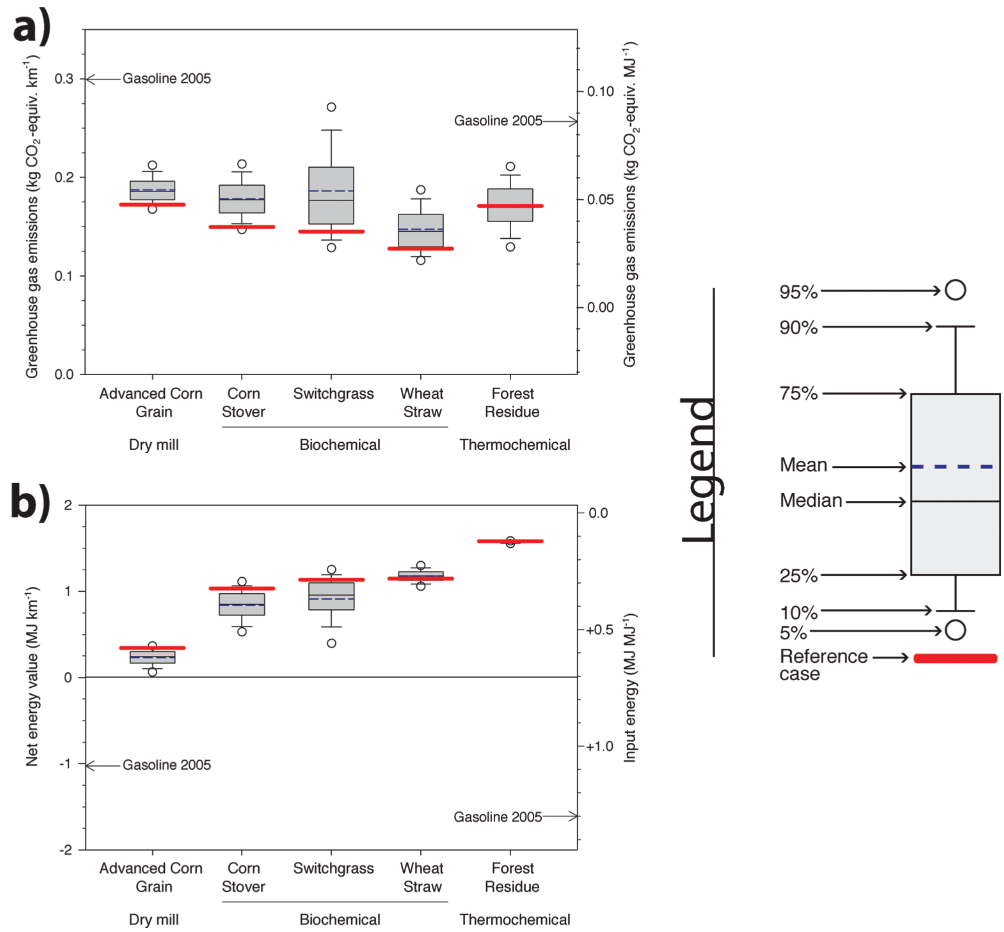

FIGURE 1. Boxplots of the Monte Carlo uncertainty analysis results for field-to-wheels, projected (a) greenhouse gas emissions and (b) net energy value and input energy for a U.S. passenger car in 2022 using E85 produced in 2022 from corn grain via corn dry milling; corn stover, switchgrass, and wheat straw via a biochemical pathway; and forest residues via a thermochemical pathway. The secondary *y*-axis, added to facilitate comparison with previous studies, is based on 1 MJ of ethanol used in a vehicle rather than the 1 km driven on E85 as shown on the primary *y*-axis. The secondary axis values in (a) are calculated starting from denatured ethanol after the conversion stage and thereafter summing only the ethanol-related emissions in the distribution and vehicle operation stages. In (b), the secondary *y*-axis is the sum of all process input energies (both fossil and nonfossil) needed to produce 1 MJ of ethanol and deliver to a vehicle. The reference case scenario (red line) is computed based on the mode of the distribution for each input parameter. In many cases, the reference case results lie outside of the edges of the boxes (the 25th and 75th percentiles of the distribution). The whiskers represent the 10th and 90th percentiles. The circles represent the 5th and 95th percentiles. The mean of the output distribution is represented by a blue dashed line and the median is represented by a solid line within the box. An estimate for conventional gasoline (base year 2005) is provided for reference.

pathways evaluated, therefore, differences in GHG emissions among feedstocks are caused by the upstream life cycle stages.

Results from the reference case indicate that, excluding impacts from LUC, E85 used in 2022 offers GHG and NEV benefits compared to conventional U.S. gasoline (base year 2005) (Figure 1). Compared to a gasoline-powered passenger car, an E85-powered car has 43%−57% lower GHG emissions per kilometer traveled. Also, net GHG emissions, on a per kilometer traveled basis, are similar for all evaluated feedstocks. The NEV of 2022 E85 is projected to be as much as 2.6 MJ km^{-1} higher than that of average 2005 U.S. gasoline.

Wheat straw-based E85 has the lowest reference case GHG emissions when compared to the other evaluated pathways. Because wheat straw is a residue, it has fewer production-related inputs than switchgrass and corn grain (Figure 2a). As compared to corn stover, wheat straw is not assumed to be a significant livestock feed supplement and thus does not require a product to displace the loss of wheat straw residue removed.

In contrast to studies that focus on current state-of-technology corn dry mills (*57*), our results suggest that advanced corn grain-based E85 has GHG emissions per kilometer traveled comparable to that of cellulosic feedstock-based E85. Improvements in GHG emissions attributed to advanced corn grain-based E85 are a result of changes in primary energy source and increases in energy efficiency at the refinery.

Collection and preprocessing is less GHG-emission intensive for forest residue than for the farm-based feedstocks because we assume forest residue is a waste product. However, the thermochemical conversion process is more GHG-emission intensive than biochemical conversion. Therefore, the GHG emissions are similar across all cellulosic pathways evaluated. The NEV for the thermochemical conversion of forest residues remains high since the conversion process is energy self-sufficient and forest residue production, harvest, and preprocessing are low in energy intensity.

As results reported by Liska et al. and Plevin (*6*, *63*) illustrate, progressive dry mill technology and corn production can render greater environmental benefits than current industry-average technology and production practices. Although our NEV results for advanced corn grain-based ethanol are about 30% higher than the NEV reported in an

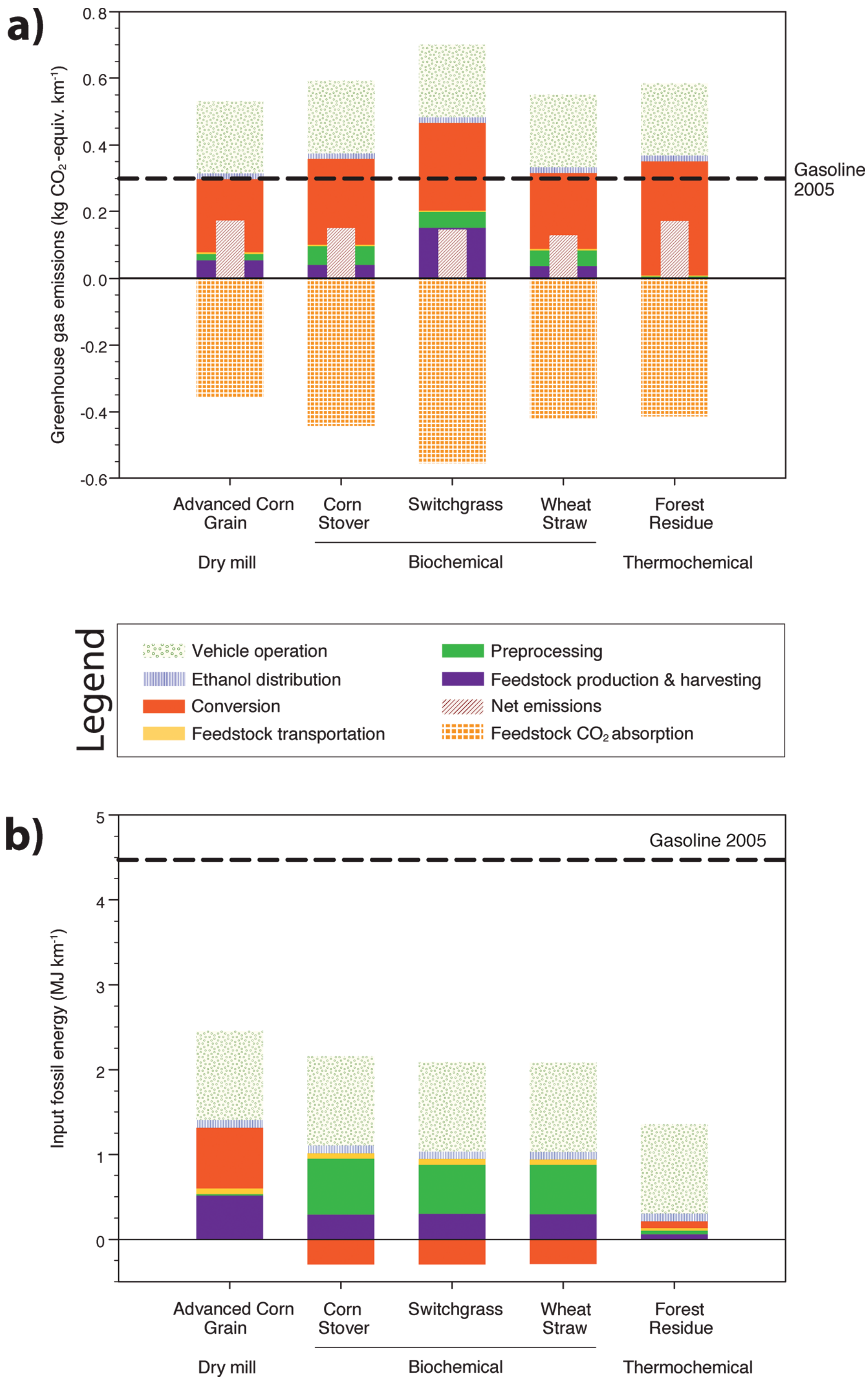

FIGURE 2. Field-to-wheels, projected (a) GHG emissions and (b) input fossil energy for a U.S. passenger car propelled 1 km using E85 in 2022 produced from corn grain via corn dry milling; corn stover, wheat straw, and switchgrass via a biochemical pathway; and forest residues via a thermochemical pathway. The stacked bar depicts the contribution from each life cycle stage, each of which is itself net of positive and negative contributions within the stage. In (a), the bar inset in the stacked bar represents net life cycle GHG emissions (the result after summing the absorption of CO_2 with the process stages). The dashed lines represent 1 km traveled by a U.S. passenger car using conventional gasoline in 2005.

analysis on conventional corn grain-based ethanol (*10*), advanced corn grain-based ethanol nevertheless is projected to have the lowest NEV and the second highest GHG emissions of the feedstock-to-ethanol pathways examined (Figure 2).

E85 produced from corn grain via dry milling is projected to require nearly 40% and 80% more fossil energy than production via the biochemical and thermochemical pathways require, respectively (Figure 2b). This disparity in energy requirements among the conversion technologies can be attributed, in part, to both biochemical and thermochemical process models being optimized with regard to process heat and power. Lignin, extracted during pretreatment, and residual syngas with heat recovery provide all heat and power demands of the biochemical and thermochemical processes, respectively (*39*, *40*). Projected NEVs for ethanol produced via biochemical conversion are similar among feedstocks and range from

TABLE 1. Most Influential Parameters[a] as Determined by Partial Least Squares Regression Analysis

input parameter	greenhouse gas emissions					net energy value					
	feedstock[b]										
	advanced corn[c]	corn stover	switchgrass	wheat straw	forest residue	advanced corn	corn stover	switchgrass	wheat straw	forest residue	total count
yield[d]	X	X	X	X		X	X	X	X		8
irrigation[e]		X		X		X	X	X	X		6
N[f]	X	X	X			X	X	X			6
removal[g]		X		X			X		X		4
moisture[h]		X			X		X			X	4
C[i]		X		X	X					X	4
DDGS[j]	X					X					2
N_2O[k]	X	X	X								3
harvest[l]			X					X			2
EtOH[m]					X					X	2
turbine[n]		X					X				2
boiler[o]		X					X				2
O[p]										X	1
ash[q]										X	1
hay[r]		X									1
H&P[s]						X					1

[a] Only input parameters found to be influential through partial least-squares regression are included. [b] Feedstocks are converted to ethanol via advanced corn dry milling (advanced corn); NREL's n^{th} plant, dilute-acid simultaneous saccharification and fermentation process (i.e., biochemical conversion) (corn stover, wheat straw, switchgrass); and NREL's n^{th} plant, indirect gasification and mixed alcohol synthesis process (i.e., thermochemical conversion) (forest residue). [c] "Advanced corn" represents improvements in the production of corn grain and corn dry milling facilities projected to the year 2022. [d] Harvested biomass yield. [e] Irrigation rate was allocated to residues for dedicated herbaceous crops for PLS analysis purposes only. [f] Nitrogen fertilizer application rate. [g] Residue removal rate. [h] Harvested feedstock moisture. [i] Carbon content in biomass. [j] DDGS substitution ratio for corn, soybeans, and urea. [k] N_2O emission factor assumptions. [l] Harvest efficiency (i.e., harvested biomass lost through machinery inefficiency). [m] Ethanol yield at the biorefinery. [n] Efficiency of the biorefinery turbine. [o] Efficiency of the biorefinery boiler. [p] Oxygen content of biomass. [q] Ash content in biomass. [r] Substitution of alternative animal fodder (hay) to replace the energy content of stover used for ethanol. [s] Proportion of national conversion facilities using certain fuel for heat and power (i.e., coal, natural gas, biomass).

1.0 to 1.1 MJ km^{-1} (Figures 1b and 2b). For those three feedstocks, the majority of the fossil energy demand is attributed to the feedstock production and preprocessing stages (Figure 2b). Notably, preprocessing accounts for nearly 50% of the field-to-refinery gate fossil energy attributed to switchgrass-based ethanol (see Table S5). Preprocessing (e.g., drying and grinding) is energy intensive yet necessary to ensure an efficient feedstock supply system. Improvements to energy efficiency of preprocessing are important to reducing the net GHG emissions and fossil energy demand attributed to ethanol produced via the biochemical feedstock-to-ethanol pathways evaluated.

Fertilizer use dominates the GHG emissions from the feedstock production phase for most evaluated feedstock-to-ethanol pathways (see Tables S4 and S5 for process contribution details). Fertilization accounts for 13%−43% of the net fossil energy demand and 32%−56% of the net GHG emissions from the starch and herbaceous feedstocks. Much of the GHG emissions and fossil energy demand of fertilizer is attributed to the production of inorganic nitrogen fertilizers. In contrast to dedicated crops, nitrogen fertilization for the agricultural residues is assumed to be applied at the rate needed to replace nitrogen removed in the biomass. Switchgrass is assumed to be produced to maximize biomass yields; therefore, a nitrogen application rate of 10 kg N per Mg of desired biomass yield is assumed (*24, 62*). Considering that nitrogen use efficiency for cereal crops is estimated to be 33% (*64*) and that the application of nitrogen fertilizer has a strong influence on the life cycle fossil energy input and GHG emissions, reduced fertilizer use and improved management may offer viable and substantial GHG benefits to both starch- and cellulosic-based ethanol.

E85 produced via thermochemical conversion of forest residues is projected to have the highest NEV compared to all other E85 pathways evaluated. Because forest residues are assumed to be a waste product, only chipping and loading are attributed to forest residue-based E85 in the feedstock production and preprocessing stages. The allocation method and type of timber harvesting operation assumed could both have significant implications for the overall life cycle impacts of E85 derived from forest residues. For instance, timber harvesting operations such as bole-only and cut-to-length result in residues being left in dispersed piles throughout the forest (*33*), which would necessitate a separate harvesting operation to collect said residues.

The corn dry mill and biochemical conversion processes have significant GHG and NEV credits associated with the production of coproducts, which are assumed to displace functionally equivalent products in the marketplace. If these coproducts were to provide no value, then the GHG emissions would be 20%−30% higher.

PLS and Uncertainty Analysis. Parameters that exert a statistically significant influence on projected GHG and NEV are reported in Table 1. Input parameters that display multiple entries for feedstocks across metrics are interpreted as most influential to the evaluated environmental performance metrics of the feedstock-to-ethanol system. Of the 86 input parameters evaluated, 30 significantly drive GHG and NEV. We observe commonalities in the important parameters for corn dry mill and biochemical conversion of cellulosic material. The thermochemical process is fundamentally different from both corn dry mill and biochemical conversion. The remainder of this paragraph will focus on dry mill and biochemical conversion. Biomass yield, nitrogen fertilizer rate, and biogenic carbon content are the most common influential parameters affecting GHG emissions from the evaluated pathways. For NEV, irrigation and biomass yield are the most common influential parameters. Considering both metrics simultaneously, biomass yield, irrigation rate, and nitrogen fertilizer application rate are the most common influential parameters. This sensitivity analysis highlights the importance of the feedstock production phase to the GHG emissions and NEV of the evaluated ethanol production systems.

Results of the Monte Carlo uncertainty analysis are presented in Figure 1. Despite any statistically significant differences in the mean values, given the large interquartile ranges for most feedstocks, these differences (at most 0.04 kg km^{-1} for GHG and 1.3 MJ km^{-1} for NEV) may not manifest themselves in practice. Differences in NEV appear to cluster by conversion technology rather than by feedstocks. The wide range of projected GHG emissions and NEV suggests that even within a limited analytic scope (i.e., using attributional instead of consequential LCA), there is significant uncertainty in the estimates. For instance, switchgrass displays the widest variability in projected GHG emissions and NEV among the evaluated feedstocks. Unlike the other feedstocks, switchgrass is not currently produced at a large scale and thus has more uncertainty related to its production and harvest.

In this study, the reference case estimates tend to skew to one end of the projected frequency distribution (Figure 1). Monte Carlo uncertainty analyses are sensitive to the PDF assumed. Scenarios that have GHG emissions the same as or lower than the reference case often occur in the 25th percentile of the distribution of results, and sometimes in the 10th percentile. NEV results are similarly skewed. These results are typically driven by skewed PDFs assumed for one or two of the most influential input parameters, which are mostly assumed to be triangular. For example, the reference case switchgrass-E85 GHG emissions occurring below the 25th percentile of the projected range of GHG emissions is strongly influenced by the assumed values and PDF for the N_2O emission factor, the biomass yield, and the application rate of nitrogen fertilizer. The IPCC N_2O emission factor of 1.325% of all nitrogen-based fertilizer applied is assumed for the reference case estimate, which is the mode of an assumed triangular distribution (*65*). A maximum of 4.00% (*66*) and a minimum of 0.40% is selected based on GREET (*38*). Holding all other parameters constant, N_2O alone accounts for 19% of the deviation between the reference-case estimate of life cycle GHG emissions and the median of the frequency distribution. An additional 53% of the deviation in GHG emissions is accounted for by the biomass yield and the nitrogen fertilizer applied. As with the N_2O emission factor, the yield and nitrogen fertilizer inputs are assumed to have skewed triangular distributions based on expert interpretation (*25, 67*). Analogous to the value from the sensitivity analysis, identifying the parameters that largely explain those cases where the reference case scenario is found to be extremely unlikely can help focus research and development of biofuel systems to (1) reduce uncertainty in the knowledge of and variability in key input parameter probability distributions, and (2) improve key parameters to enhance the GHG emissions and NEV of the system.

Forest residue-based E85, in contrast to the other evaluated feedstock-to-ethanol pathways, has a median result close to the reference case. This could be an artifact of modeling limitations and assumptions. Although the projection that future practice will resemble the present, with little improvement, is based on expert elicitation, it is subject to considerable uncertainty, as commercial-scale collection and use of forest residues does not currently exist. Furthermore, use of the product−purpose allocation method limits the number of input parameters tested in the uncertainty analysis. Finally, few influential input parameters to this pathway exhibit skewed PFDs.

Although results from the uncertainty analysis suggest the reference case is, in many instances, outside the middle 50%−80% of the distribution, the median outcome for both GHG emissions (not considering LUC) and NEV across all feedstock-to-ethanol pathways evaluated is still an improvement over conventional U.S. gasoline in 2005. In the context of the reference case and uncertainty results presented in this study, the reference case scenario appears to represent an optimistic case in which most key parameters are optimized in concert. In reality, however, all key parameters may not be optimized at any one time. This insight underscores the need to ensure the achievement of optimal performance for key parameters involved in feedstock production, harvest, and conversion to ethanol through targeted research and industrial experience.

Acknowledgments

Authors D.D.H. and D.I. contributed equally to this work. Funding for this project was provided by the U.S. Department of Energy's Office of the Biomass Program (DE-AC36-08-GO28308). Feedback and contributions from the following people are greatly appreciated: Brian Bush, Helena Chum, Joyce Cooper, Nathan Fields, Thomas Foust, Alison Goss Eng, Zia Haq, Sara Havig, Jacob Jacobson, Leonard Johnson, Lise Laurin, Andy McAloon, Laurel McEwen, Leslie Miller, Elaine Oneil, Bob Reynolds, Robert Rummer, Heather Wakeley, Bob Wallace, Michael Wang, Dwayne Westfall, Christopher Wright, May Wu, Winnie Yee, and Yimin Zhang.

Supporting Information Available

Detailed information describing the construction of the life cycle assessment models for each feedstock-to-ethanol pathway, as well as additional results. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Renewable Fuels Association Statistics: Historic U.S. Fuel Ethanol Production. www.ethanolrfa.org/pages/statistics/ (accessed April 12, 2010).

(2) Energy Independence and Security Act of 2007. Public Law 110-140, 2007; Vol. 121.

(3) Pimentel, D.; Patzek, T. Ethanol Production Using Corn, Switchgrass, and Wood; Biodiesel Production Using Soybean and Sunflower. *Nat. Resour. Res.* **2005**, *14* (1), 65–76.

(4) Patzek, T. W.; Pimentel, D. Thermodynamics of energy production from biomass. *Crit. Rev. Plant Sci.* **2005**, *24* (5−6), 327–364.

(5) Wang, M.; Wu, M.; Hong, H. Life-cycle energy and greenhouse gas emission impacts of different corn ethanol plant types. *Environ. Res. Lett.* **2007**, *2*, 024001.

(6) Liska, A. J.; Yang, H. S.; Bremer, V. R.; Klopfenstein, T. J.; Walters, D. T.; Erickson, G. E.; Cassman, K. G. Improvements in Life Cycle Energy Efficiency and Greenhouse Gas Emissions of Corn-Ethanol. *J. Ind. Ecol.* **2009**, *13* (1), 58–74.

(7) Shapouri, H.; Duffield, J. A.; Wang, M. The energy balance of corn ethanol revisited. *Trans. ASAE* **2003**, *46* (4), 959–968.

(8) Graboski, M. S. *Fossil Energy Use in the Manufacture of Corn Ethanol*; Colorado School of Mines: Golden, CO, 2002.

(9) De Oliveira, M. E. D.; Vaughan, B. E.; Rykiel, E. J., Jr. Ethanol as fuels: Energy, carbon dioxide balances, and ecological footprint. *Bioscience* **2005**, *55* (7), 593–602.

(10) Farrell, A. E.; Plevin, R. J.; Turner, B. T.; Jones, A. D.; O'Hare, M.; Kammen, D. M. Energy returns on ethanol production - Response. *Science* **2006**, *312* (5781), 1747–1748.

(11) Schmer, M. R.; Vogel, K. P.; Mitchell, R. B.; Perrin, R. K. Net Energy of Cellulosic Ethanol from Switchgrass. *Proc. Nat. Acad. Sci., U.S.A.* **2008**, *105* (2), 464–469.

(12) Sheehan, J.; Aden, A.; Paustian, K.; Killian, K.; Brenner, J.; Walsh, M.; Nelson, R. Energy and Environmental Aspects of Using Corn Stover for Fuel Ethanol. *J. Ind. Ecol.* **2004**, *7* (3−4), 117–146.

(13) SimaPro, v.7.1; Product Ecology Consultants: Amersfoort, the Netherlands, 2008.

(14) Ecoinvent, v.2.0; Swiss Center for Life Cycle Inventories: Duebendorf, Switzerland, 2007.

(15) U.S. Life-Cycle Inventory, v. 1.6.0; National Renewable Energy Laboratory: Golden, CO, 2008.

(16) International Organization for Standardization. *Environmental management -- Life Cycle Assessment -- Principles and Framework*; ISO 14040:2006; International Organization for Standardization: Geneva, Switzerland, 2006.
(17) International Organization for Standardization. *Environmental management -- Life Cycle Assessment -- Requirements and Guidelines*; ISO 14044:2006; International Organization for Standardization: Geneva, Switzerland, 2006.
(18) Perlack, R. D.; Wright, L. L.; Turhollow, A. F.; Graham, R. L.; Stokes, B. J.; Erbach, D. C. *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply*; DOE/GO-102005-2135, ORNL/TM-2005/66; United States Department of Energy, Oak Ridge National Laboratory: Oak Ridge, TN, 2005.
(19) EERE. *Handbook for Handling, Storing, and Dispensing E85*; DOE: Washington, DC, 2008; p 54.
(20) Wang, M.; Huo, H.; Arora, S. Methods of dealing with co-products of biofuels in life-cycle analysis and consequent results within the U.S. context. *Energy Policy* **2010**; doi:10.1016/j.enpol.2010.03.052.
(21) Searchinger, T.; Heimlich, R.; Houghton, R. A.; Dong, F.; Elobeid, A.; Fabiosa, J.; Tokgoz, S.; Hayes, D.; Yu, T.-H. Use of U.S. Croplands for Biofuels Increases Greenhouse Gases Through Emissions From Land-Use Change. *Science* **2008**, *319* (5867), 1238–1240.
(22) Fargione, J.; Hill, J.; Tilman, D.; Polasky, S.; Hawthorne, P. Land Clearing and Biofuel Carbon Debt. *Science* **2008**, *319* (5867), 1235–1238.
(23) USDA-NASS National Agricultural Statistics Service Quick Stats. http://www.nass.usda.gov/QuickStats (December 15, 2008).
(24) Perrin, R. K.; Vogel, K. P.; Schmer, M. R.; Mitchell, R. B. Farm-Scale Production Cost of Switchgrass for Biomass. *BioEnergy Res.* **2008**, *1* (1), 91–97.
(25) Sokhansanj, S.; Mani, S.; Turhollow, A.; Kumar, A.; Bransby, D.; Lynd, L.; Laser, M. Large-scale production, harvest and logistics of switchgrass (*Panicum virgatum* L.) -current technology and envisioning a mature technology. *Biofuels Bioprod. Biorefin.* **2009**, *3* (2), 124–141.
(26) Southgate, D.; Graham, D. H.; Tweeten, L. *The World Food Economy.*, 1st ed.; Blackwell: Malden, MA, 2007; p 401.
(27) Graham, R. L.; Nelson, R.; Sheehan, J.; Perlack, R. D.; Wright, L. L. Current and potential US corn stover supplies. *Agron. J.* **2007**, *99* (1), 1–11.
(28) Edwards, W. *Estimating a Value for Corn Stover*; File A1-70; Iowa State University- Extension: Ames, IA, December 2007.
(29) Hess, J. R.; Kenny, K. L.; Ovard, L. P.; Searcy, E. M.; Wright, C. T. *Uniform-format solid feedstock supply system*; INL/EXT-08-14752; Idaho National Laboratory: Idaho Falls, ID, April 2009.
(30) Smith, W. B.; Miles, P. D.; Vissage, J. S.; Pugh, S. A. *Forest Resources of the United States, 2002*; NC-241; USFS: St. Paul, MN, 2004; p 146.
(31) Jacobson, J. J. Personal communication. Idaho National Laboratory: 2008.
(32) Yu, T.-H.; Hart, C. E. *The 2006/07 Iowa Grain and Biofuel Flow Study: A Survey Report*; 08-SR 102; Center for Agricultural and Rural Development, Iowa State University: Ames, Iowa, October 2008.
(33) Leinonen, A. *Harvesting technology of forest residues for fuel in the USA and Finland*; Espoo 2004 VTT Tiedotteita-Research Notes 2229; VTT Processes: Finland, 2004.
(34) Pan, F.; Han, H.-S.; Johnson, L. R.; Elliot, W. J. Net energy output from harvesting small-diameter trees using a mechanized system. *Forest Prod. J.* **2008**, *58* (1/2), 25–30.
(35) Wakeley, H. L.; Hendrickson, C. T.; Griffin, W. M.; Matthews, H. S. Economic and Environmental Transporation Effects of Large-Scale Ethanol Production and Distribution in the United States. *Environ. Sci. Technol.* **2009**, *43* (7), 2228–2233.
(36) Denicoff, M. R. *Ethanol Transportation Backgrounder: Expansion of U.S. Corn-based Ethanol from the Agricultural Transportation Perspective*; United States Department of Agriculture: Washington, DC, September 2007; pp 1−29.
(37) Shapouri, H.; Duffield, J. A.; Wang, M. *The Energy Balance of Corn Ethanol: An Update*; Agricultural Economic Report No. 814; United States Department of Agriculture, Office of the Chief Economist, Office of Energy Policy and New Uses: Washington, DC, July 2002.
(38) *The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model*, v1.8c; Argonne National Laboratory: Argonne, IL, 2008.
(39) Aden, A.; Ruth, M.; Ibsen, K.; Jechura, J.; Neeves, K.; Sheehan, J.; Wallace, B. *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover*; TP-510-32438; National Renewable Energy Laboratory: Golden, CO, June 2002.
(40) Phillips, S.; Aden, A.; Jechura, J.; Dayton, D.; Eggeman, T. *Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass*; TP-510-41168; National Renewable Energy Laboratory: Golden, CO, April 2007.
(41) Lee, D.; Owens, V. N.; Boe, A.; Jeranyama, P. *Composition of Herbaceous Biomass Feedstocks*; South Dakota State University: Brookings, SD, June 2007.
(42) McAloon, A.; Taylor, F.; Yee, W.; Ibsen, K.; Wooley, R. *Determining the Cost of Producing Ethanol from Corn Starch and Lignocellulosic Feedstocks*; NREL/TP-580-28893; National Renewable Energy Laboratory: Golden, CO, October 2000.
(43) Mueller, S. *An analysis of the projected energy use of future dry mill corn ethanol plants (2010−2030)*; Energy Resources Center Report; University of Illinois at Chicago: Chicago, IL, October 10, 2007.
(44) Nielsen, P. H.; Oxenboll, K. M.; Wenzel, H. Cradle-to-gate environmental assessment of enzyme products produced industrially in Denmark by Novozymes A/S. *Int. J. Life Cycle Assess.* **2007**, *12* (6), 432–438.
(45) Oxenboll, K. M., Personal communication. Novozymes, 2008.
(46) Jungbluth, N.; Dinkel, F.; Doka, G.; Chudacoft, M.; Dauriat, A.; Gnansounou, E.; Sutter, J.; Speilmann, M.; Kljun, N.; Keller, M.; Schleiss, K. *Life Cycle Inventories of Bioenergy: Data v2.0*; ecoinvent report No. 17; Swiss Centre for Life Cycle Inventories: Dübendorf, Switzerland, December 2007.
(47) Arora, S.; Wu, M.; Wang, M. *Update of Distillers Grains Displacement Ratios for Corn Ethanol Life-Cycle Analysis*; Argonne National Laboratory: Argonne, IL, 2008; pp 1−15.
(48) Nemecek, T.; Kägi, T. *Life Cycle Inventories of Agricultural Production Systems Data 2.0*; Swiss Centre for Life Cycle Inventories: Zürich and Dübendorf, Switzerland, December, 2007.
(49) EPA. *AP-42 Compilation of Air Pollutant Emissions Factors*; U.S. Environmental Protection Agency: Washington, DC, August 2007.
(50) National Renewable Energy Laboratory Biorefinery Analysis Process Models. http://www.nrel.gov/extranet/biorefinery/aspen_models/ (accessed April 23, 2010).
(51) Reynolds, R. E. *Ethanol's Potential Contribution to U.S. Transportation Fuel Pool*; Downstream Alternatives Inc.: South Bend, IN, December 31, 2006.
(52) Reynolds, R. *Personal Communication.* Downstream Alternatives Inc.: South Bend, IN, 2008.
(53) Morrow, W. R.; Griffin, W. M.; Matthews, H. S. Modeling switchgrass derived cellulosic ethanol distribution in the United States. *Environ. Sci. Technol.* **2006**, *40* (9), 2877–2886.
(54) Farrington, R. Invited Testimony for the U.S. Senate Committee on Finance, Prepared Statement of Dr. Robert Farrington, Manager & Principal Researcher, Advanced Vehicle Systems Group, National Renewable Energy Laboratory, Golden, CO, April 19, 2007. In Committee, U. S. S. F., Ed. Washington, DC, 2007.
(55) Charpentier, A. D.; Bergerson, J. A.; MacLean, H. Understanding the Canadian oil sands industry's greenhouse gas emissions. *Env. Res. Lett.* **2009**, *4*, 014005.
(56) Forster, P.; Ramaswamy, V.; Artaxo, P.; Berntsen, T.; Betts, R.; Fahey, D. W.; Haywood, J.; Lean, J.; Lowe, D. C.; Myhre, G.; Nganga, J.; Prinn, R.; Raga, G.; Schulz, M.; Van Dorland, R., Changes in Atmospheric Constituents and in Radiative Forcing. In *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Solomon, S.; Qin, D.; Manning, M.; Chen, Z.; Marquis, M.; Averyt, K. B.; Tignor, M.; Miller, H. L., Eds.; Cambridge University Press: Cambridge, UK and New York, 2007; pp 129−234.
(57) Farrell, A. E.; Plevin, R. J.; Turner, B. T.; Jones, A. D.; O'Hare, M.; Kammen, D. M. Ethanol can contribute to energy and environmental goals. *Science* **2006**, *311* (5760), 506–508.
(58) Brereton, R. *Applied Chemometrics for Scientists*; John Wiley & Sons, Ltd.: Chichester, West Sussex, UK, 2007.
(59) Martens, H.; Martens, M. Analysis of designed experiments by stabilised PLS Regression and jack-knifing. *Food Qual. Pref.* **2000**, *11* (1−2), 5–16.
(60) Esbensen, K. H. *Multivariate Data Analysis in Practice*, 5th ed.; Camo Process AS: Oslo, Norway, 2002.
(61) *The Unscrambler 9.8*; CAMO Software AS: Oslo, Norway, 2008.

(62) Vogel, K. P.; Brejda, J. J.; Walters, D. T.; Buxton, D. R. Switchgrass Biomass Production in the Midwest USA: Harvest and Nitrogen Management. *Agron. J.* **2002**, *94*, 413–420.
(63) Plevin, R. J. Modeling Corn Ethanol and Climate. A Critical Comparison of the BESS and GREET Models. *J. Ind. Ecol.* **2009**, *13* (4), 495–507.
(64) Raun, W. R.; Johnson, G. V. Improving Nitrogen Use Efficiency for Cereal Production. *Agron. J.* **1999**, *91*, 357–363.
(65) Klein, C. D.; Novoa, R. S. A.; Ogle, S.; Smith, K. A.; Rochette, P.; Wirth, T. C.; McConkey, B. G.; Mosier, A.; Rypdal, K.; Walsh, M.; Williams, S. A., Chapter 11: N_2O Emissions from Managed Soils, and CO_2 Emissions from Lime and Urea Application. In *2006 IPCC Guidelines for National Greenhouse Gas Inventories, Vol. 4: Agriculture, Forestry, and Other Land Use*; Eggleston, S.; Buendia, L.; Miwa, K.; Ngara, T.; Tanabe, K., Eds.; IGES: Japan, 2006.
(66) Crutzen, P. J.; Mosier, A. R.; Smith, K. A.; Winiwarter, W. N_2O release from agro-biofuel production negates global warming reduction by replacing fossil fuels. *Atmos. Chem. Phys.* **2008**, *8* (2), 389–395.
(67) Perrin, R. K.; Williams, B. The Outlook for Switchgrass as an Energy Crop. *Cornhusker Economics* 2008, 2 pp.

ES100186H