Impacts of Pre-treatment Technologies and Co-products on Greenhouse Gas Emissions and Energy Use of Lignocellulosic Ethanol Production

Mohammad Pourbafrani[1], Jon McKechnie[2], Timothy Shen[1], Bradley A. Saville[1], Heather L. MacLean[1,3]

[1] Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, ON, M5S 3E5, Canada
[2] Division of Energy and Sustainability, University of Nottingham, University Park, Nottingham, NG7 2RD, UK
[3] Department of Civil Engineering, University of Toronto, 35 St George Street, Toronto, ON, M5S 1A4, Canada

Corresponding author: Mohammad Pourbafrani

Email: mohammad.pourbafrani@utoronto.ca

Tel: +1 647 223 7442

Abstract

Life cycle environmental performance of lignocellulosic ethanol produced through different production pathways and having different co-products has rarely been reported in the literature, with most studies focusing on a single pre-treatment and single co-product (electricity). The aim of this paper is to understand the life cycle energy use and greenhouse gas (GHG) emissions implications of alternative pre-treatment technologies (dilute acid hydrolysis, ammonia fiber expansion and autohydrolysis) and co-products (electricity, pellet, protein and xylitol) through developing a consistent life cycle framework for ethanol production from corn stover. Results show that the choices of pre-treatment technology and co-product(s) can impact ethanol yield, life cycle energy use and GHG emissions. Dilute acid pathways generally exhibit higher ethanol yields (20 to 25%) and lower net total energy use (15 to 25%) than the autohydrolysis and ammonia fiber expansion pathways. Similar GHG emissions are found for the pre-treatment technologies when producing the same co-product. Xylitol co-production diverts xylose from ethanol production and results in the lowest ethanol yield (200 litres per dry t of stover). Compared to producing only electricity as a co-product, the co-production of pellets and xylitol decreases life cycle GHG emissions associated with the ethanol, while protein production increases emissions. The life cycle GHG emissions of blended ethanol fuel (85% denatured ethanol by volume) range from -38.5 to 37.2 g CO_2eq/MJ of fuel produced, reducing emissions by 61% to 141% relative to gasoline. All ethanol pathways result in major reductions of fossil and petroleum energy use relative to gasoline, at least 47% and 67%, respectively. Pathways with electricity as the sole co-product use the least fossil energy All ethanol pathways studied meet the USA Energy Information and Security Act requirement of a 60% reduction in GHG emissions compared to gasoline for classification as a cellulosic biofuel; however, greater reductions are achievable through strategic selection of co-products.

Keyword: bioethanol, corn stover, life cycle assessment, biorefinery, co-products, pre-treatment

1. Introduction

Interest in alternatives to fossil fuels for the transportation sector has motivated research, development and deployment of biofuels. In particular, ethanol produced from lignocellulosic feedstock has seen increasing attention as a light-duty vehicle fuel, giving rise to a large number of production pathways that have been examined in technological reviews (Chen and Qui 2010; Mabee and Saddler 2010). While there are "semi-mature" technologies that produce ethanol from corn and sugarcane, ethanol produced from lignocellulosic feedstock remains on the verge of commercialization due to higher capital and operating costs (Stephen et al. 2011).

The potential contributions of lignocellulosic ethanol to reducing petroleum energy use and greenhouse gas (GHG) emissions have been identified in numerous life cycle studies (e.g., von Blottnitz and Curran 2007) and are sensitive to impacts of different life cycle stages (Mullins et al. 2011; Spatari et al., 2010). However, most LCA studies examine a single biomass pre-treatment process and a single co-product. A broader approach utilizing a consistent analysis framework capable of considering co-product compatibility with a range of pre-treatment processes or comparing the relative benefits and disadvantages of potential pre-treatment technologies and co-product opportunities provides additional valuable insights.

Due to the relatively low market value of ethanol as a fuel, financially-viable ethanol production pathways are expected to involve co-product production following a biorefinery concept (FitzPatrick et al. 2010). The co-production of value-added products with lignocellulosic ethanol is an emerging opportunity, due to the wide variety of possible products and their potential environmental and economic benefits. Biorefinery concepts in the literature have considered various biomass feedstocks and evaluated a variety of co-products, including electricity (e.g., Delivand et al. 2012), isolated lignin (Pan et al. 2006), acetic acid and hydrogen (Zhang, 2008), protein (Laser et al. 2009a), and antioxidants (Ekman et al. 2013). However, life cycle environmental impacts have only been quantified in a subset of the studies.

A smaller set of studies compared the environmental implications of multiple co-products. Uihlein and Schebek (2009) examined the life cycle of ethanol from wheat straw using dilute acid pre-treatment, with electricity, isolated lignin and xylitol as potential co-products. The study reported results in terms of human health, resource use and eco-system quality, and showed beneficial impacts for lignocellulosic biorefineries. Laser et al. (2009a) studied the environmental impact of the ammonia fiber expansion (AFEX) process considering various co-products (protein, electricity, Fischer-Tropsch liquids and hydrogen). Laser et al. (2009a) found that the choice of co-product has a significant impact on the environmental performance of the AFEX process. Cherubini and Ulgiati (2010) studied ethanol from corn stover and wheat straw using an autohydrolysis pre-treatment with electricity and lignin-derived phenols as co-products. Ethanol production from both feedstock was reported to have lower life cycle GHG emissions than gasoline; however, corn stover showed better performance than wheat straw in terms of GHG savings, ozone depletion, photochemical oxidation and human toxicity. McKechnie et al. (2011) studied steam explosion (autohydrolysis) with different co-products (steam, electricity and pellet). Pelletizing lignin remaining following fermentation was found to have clear environmental advantage over using lignin for electricity generation. The scope of the above studies, however, is limited to evaluating a single pre-treatment process.

Biomass pre-treatment processes differ in terms of chemical and energy inputs, as well as effectiveness in liberating cellulosic material for subsequent hydrolysis to sugars. These factors impact the life cycle GHG emissions and energy use of lignocellulosic ethanol. As some co-products may be incompatible with some pre-treatment processes (Chiesa and Gnansounou, 2011), pre-treatment technology selection may affect co-product options, with potential consequences for life cycle GHG emissions and energy use. Among the most promising pre-treatments under development are dilute acid hydrolysis, AFEX and autohydrolysis (steam explosion) (Cherubini and Stromman 2011). Prior studies have typically considered a single pre-treatment technology when assessing lignocellulosic ethanol production, including: rice straw ethanol production via dilute acid pre-treatment (Delivand et al. 2012); switchgrass ethanol production via AFEX pre-treatment (Bai et al. 2010); poplar ethanol production via autohydrolysis (McKechnie et al. 2011). Based on our knowledge, there are also a limited number of studies (Spatari et al., 2010; Wang et al. 2013) that considered different pre-treatments and a single co-product (electricity). Wang et al. (2013) found ethanol production using steam explosion (autohydrolysis) to provide greater reductions in GHG emissions compared to ethanol production employing dilute acid as a pre-treatment process. Spatari et al. (2010) concluded that AFEX pre-treatment showed more promise than dilute acid for reducing life cycle GHG emissions. Our literature survey was unable to locate a published study that considered both a range of pre-treatment technologies and a range of different co-products within a consistent life cycle framework.

Understanding the energy use and GHG emissions implications of lignocellulosic ethanol requires evaluation of alternative pre-treatment technologies and co-products within a consistent life cycle framework. In this study, we compare three conversion pathways that are strong candidates for commercialization (dilute acid, AFEX and autohydrolysis) and four potential co-products (electricity, lignin pellets, xylitol and protein). A single lignocellulosic feedstock, corn stover, is considered to facilitate comparison of the pre-treatment technologies and potential co-products. We evaluate the energy and environmental consequences of these production decisions using a consistent life cycle-based ("well-to-wheel") framework. Results of the evaluations can inform energy sector stakeholders and government as to how cellulosic ethanol production decisions may impact eligibility under relevant renewable energy policies (e.g., Energy Independence and Security Act (2007)).

2. Methods

2.1 Life Cycle Assessment

Life cycle inventory analysis models are developed for the set of ethanol pathways described in Table 1. In each pathway, ethanol is the primary product and potential co-products include electricity, lignin pellets, protein, and xylitol. The ethanol product of each pathway is blended with gasoline to produce E85 (83%v/v of ethanol). The E85 pathways include activities associated with corn stover collection and transportation to a biorefinery, conversion of corn stover to ethanol in the biorefinery, blending of the ethanol with gasoline and its distribution, combustion of E85 in a flexible fuel light-duty vehicle and finally, utilizing biorefinery co-products (Figure 1). Cradle-to-gate modules for energy and material inputs into the main life cycle stages are included in the boundaries (e.g., recovery and processing of petroleum, generation of regional electricity, production of process chemicals). The E85 pathways are compared with those of the gasoline vehicle reference pathway. The life cycle inventory of the reference pathway includes oil recovery, refining, transportation of gasoline and the combustion of gasoline in a light-duty vehicle.

Energy use in terms of total, fossil, and petroleum, as well as GHG emissions are examined. Total energy use includes energy from both renewable (e.g., solar, wind, hydro) and non-renewable (e.g., coal, petroleum, nuclear) sources in addition to the renewable energy in the corn stover feedstock itself. For GHG emissions, CO_2, CH_4 and N_2O emissions are reported as well as CO_2 equivalent (CO_2eq) emissions based on Intergovernmental Panel on Climate Change 100-year global warming potentials (IPCC, 2006). The functional unit is 1 MJ of fuel produced (E85 or gasoline) and used in a light-duty vehicle. The biorefinery is assumed to be located in the Midwest USA, due to the large amount of corn stover potentially available in the region.

The system expansion approach for dealing with co-products of the biorefinery is utilized due to its recommendation by ISO 14044 (2006) as well as its adoption as a standard method by the US Environmental Protection Agency for the Renewable Fuel Standard (Environmental Protection Agency, 2007). Considering system expansion, E85 is selected as the primary product and all other products (electricity, pellets, protein and xylitol) are treated as co-products. GHG emissions associated with feedstock transportation, the biorefinery processes, blended gasoline, E85 distribution and use are attributed entirely to the E85, and emissions credits from co-products (electricity, lignin, protein and xylitol) displacing reference products (electricity from Midwest U.S.A. grid, coal, soymeal and sugar from sugar beet, respectively) are assigned to the E85. See Section 2.4 for additional detail on co-product displacement.

2.2 Feedstock Production and Transportation

Corn stover is selected as the feedstock due to its commercial interest in the USA and the development of near term ethanol production processes using this feedstock (Aden et al. 2002). A common biorefinery capacity (2,000 t/day dry corn stover) is assumed for all ethanol production pathways. Energy and emissions associated with corn stover collection, fertilizer supplementation due to residue removal, and transportation activities are obtained from GREET 1.8d.1 (Argonne National Laboratory, 2011). In line with prior life cycle studies (e.g., Hsu et al., 2010), in our base case analysis corn stover is considered a by-product of corn production, and therefore impacts associated with corn farming are not attributed to the stover. In sensitivity scenario analysis (Section 3.3), we consider implications of allocating, on a mass basis, a portion of the GHG emissions associated with corn cultivation to stover. Land use change (direct and indirect) GHG emissions are assumed to be negligible due to selection of corn stover as feedstock (Dunn et al. 2013).

Corn stover removal has been found in prior studies to reduce soil organic carbon (SOC) (e.g., Koschsiek and Knops, 2012); however, stover removal also has a counteracting effect of reducing field N_2O emissions (Kim and Dale, 2009). SOC and N_2O impacts of stover removal are location-specific and their detailed quantification falls outside the scope of the present study. The base case analysis assumes that the removal of corn stover from fields avoids any net field GHG emission (balance of SOC and N_2O emissions). To examine the potential impact of field emissions on life cycle results, we develop a scenario where an emission factor of 35 kg CO_2eq/dry t stover, based on relevant literature (Kim and Dale 2009; Cherubini and Ulgiati 2010), is applied to all pathways to account for SOC and N_2O emissions (Section 3.3).

2.3 Biorefinery

Three pre-treatment methods, dilute acid (DA), ammonia fiber expansion (AFEX) and autohydrolysis (AH), are selected due to their compatibility with selected co-product production and data availability. Aspen Plus® models from NREL (Aden et al. 2002) (dilute acid-electricity (DAEL)-pathway) and Laser et al. (2009a) (ammonia fiber expansion-electricity (AFEL) pathway) and a proprietary model adapted from SunOpta Bioprocess Inc. (auto hydrolysis-electricity (AHEL)-pathway) are used to model the gate-to-gate (conversion facility) stage of the corn stover-to-ethanol pathways. Since these models only consider electricity as a co-product, they are modified to incorporate production of other co-products, including protein, pellets and xylitol. Technical data for the modeling of protein concentrate extraction and pelletization are sourced from Laser at al. (2009b) and Thek and Obernberger (2004), respectively. Based on mass and energy balances from the Aspen Plus® models, the energy requirement (steam and electricity) of each pathway and the co-product and ethanol production capacities are calculated. Life cycle inventory data for process chemicals and enzyme required for each pathway are obtained from MacLean and Spatari (2009) and Hsu et al. (2010), respectively. A detailed description of pre-treatment technologies and downstream process stages including hydrolysis, fermentation, purification, lignin pellet production, xylitol production, electricity generation and protein extraction can be found in the Supplementary Information (SI).

Three pre-treatment technologies and four co-products are combined to create nine pathways (Table 1); separate Aspen Plus® models were developed and optimized for each pathway. Co-product and pre-treatment combinations are selected due to their compatibility. Electricity and lignin pellet co-product production are investigated for all three pre-treatment technologies. Protein concentrate co-production is only investigated for AFEX pre-treatment. Combining AFEX pre-treatment with a high pH protein extraction process has the beneficial effect of allowing ammonia to be recycled. Dilute acid pre-treatment would degrade proteins while the milder conditions of AFEX are able to preserve them (Dale et al. 2009; Chiesa and Gnansounou 2011). Autohydrolysis pre-treatment conditions may also be able to preserve protein; however, recovery of protein would require ammonia. Due to the high GHG emissions and petroleum energy use associated with ammonia production, we do not consider protein extraction as a viable option for autohydrolysis pre-treatment pathways. Xylitol production is likewise only investigated in the autohydrolysis pathways, where xylose can be separated from glucose using proprietary technology, such as that employed by Xylitol Canada Inc.

Table 1 presents energy sources used in each pathway. For pathways with electricity as a co-product, the biorefinery energy requirement (steam and electricity) is provided by utilizing lignin residues in an on-site combined heat and power plant. For pathways with pellets as a co-product, the electricity required by the biorefinery is imported from the grid and the steam is provided by utilizing natural gas.

2.4 Product transportation, distribution and use

Ethanol is assumed to be blended with gasoline to produce E85 (83% (v/v) ethanol), which is consumed in a flexible-fuel light-duty vehicle. The E85 and baseline gasoline (35% conventional and 65% reformulated gasoline) vehicles have fuel economies of 10.1 L gasoline equivalent/100 km (Argonne National Laboratory 2011). For the system expansion approach, the products assumed to be displaced by the co-products are as follows:

- Co-produced electricity displaces electricity generated by the average USA Midwest grid mix
- Lignin pellets displace coal in biomass co-fired power plants on an energy equivalent basis
- Corn stover-derived protein concentrate displaces soy meal on an equivalent mass basis, and,
- Xylitol replaces sugar derived from sugar beet on an equivalent mass basis.

Fuel cycle energy use and emissions associated with electricity generation for the Midwest grid mix are obtained from GREET 1.8d.1 (Argonne National Laboratory 2011). Lignin pellets are assumed to displace coal in biomass co-fired power plants as in prior work (McKechnie et al. 2011) and as is common practice; credits associated with replacing coal with lignin pellets are likewise sourced from GREET 1.8d.1. The substitution of soymeal with co-produced protein is assessed based on previous studies (Tzeng et al.1990; Dalgaard et al. 2008). For the xylitol credit calculation, life cycle information for the displacement of sugar beet-derived sugar is sourced from Renouf et al. (2008).

3. Results and Discussion

Ethanol and co-product outputs produced from corn stover via each of the pathways are quantified in Table 2. Ethanol yield differs among the pre-treatment technologies due to differences in C6/C5 sugar conversion. The highest ethanol yield is achieved with pathways involving dilute acid (DA) pre-treatment, producing approximately 23% more ethanol than the AFEX pathways (374 L per dry t corn stover vs. 304 L/dry t corn stover) and 21% more ethanol than the autohydrolysis (AH) pathways (308 L per dry t corn stover) when C6 and C5 sugars are utilized for ethanol fermentation.

The process ethanol yield is determined by the efficiency by which each technology converts cellulose and hemicellulose into glucose and xylose, and the efficiency of the corresponding fermentation process that converts these monomers into ethanol. Certain co-products may reduce the amount of sugars available for fermentation, and lead to a corresponding reduction in ethanol yield. The only co-product in this study that considerably affects ethanol yield is xylitol, as C5 sugars recovered for xylitol production are no longer available for ethanol production. Autohydrolysis pathways with xylitol co-production produced the least ethanol (140 million L/y), reducing ethanol yield by approximately 35% relative to co-production of electricity and pellets.

Electricity, lignin pellets, and protein are produced from non-fermentable components of lignocellulosic biomass. Protein is extracted in sufficient purity to be used as animal feed, whereas unconverted cellulose, hemicellulose and carbohydrates may supplement the lignin used to generate electricity or "lignin" pellets.

Electricity and pellet production are thus generally dependent on ethanol yield. Lower ethanol yield corresponds to a greater amount of "residual" biomass being available for on-site electricity generation or pellet production. The amount of net electricity co-product is reduced as the biorefinery's electricity requirements increase. In other words, if the biorefinery process is more energy intensive, it will consume a higher proportion of the electricity (or thermal energy) that is generated from the biomass residues. Among the cases studied, the biorefinery consumes 37% to 56% of the total electricity generated. The co-product electricity is assumed to be exported to the local grid. The largest amount of net electricity co-product output (218 GWh/y) is produced via the AFEX pathway with electricity as its sole co-product (AXEL), due to the relatively low ethanol yield of the AFEX process, the absence of any other co-production processes, and lower energy demands for pre-treatment compared to autohydrolysis and dilute acid pathways. In contrast, the smallest amount of net electricity co-product is produced by the AFEX-protein and electricity (AXPR) pathway (53 GWh/y), due primarily to additional electricity/energy requirements of protein co-production. Yields of lignin pellets in general are inversely correlated with ethanol yield: AFEX-pellet AXPE pathway produces 4% more lignin pellet than dilute acid-pellet (DAPE) pathway. The autohydrolysis-pellet (AHPE) pathway has the lowest pellet yield since stillage is not recovered from the distillation column for pellet production. Pellet co-product yields are similar between the AHPE and autohydrolysis-xylitol and pellet (AHXP) pathways (although ethanol production is considerably different), mainly because use of xylose, whether for producing xylitol or ethanol, has little effect on the amount of leftover residues available for pellets. Protein concentrate is only produced via the AFEX process (AXPR), whereas xylitol is only a co-product from authohydrolysis pre-treatment (AHXE, AHXP), and so, for these co-products, comparisons between technologies are not possible. Protein recovery (34 kg/dry t corn stover) sacrifices electricity co-product output (75% reduction in electricity export) but does not impact ethanol yield. The autohydrolysis pathways with xylitol as a co-product (AHXE, AHXP) produce 0.77 kg xylitol per kg isolated xylose at 96% purity.

3.1 Greenhouse Gas Emissions Results

Figure 2 illustrates well-to-wheel GHG emissions for E85 and gasoline vehicle pathways. Net GHG emissions range from -38.5 to 37.2 g CO_2eq/MJ for the E85 pathways, a reduction of 61 to 141% relative to the reference gasoline vehicle pathway, which has emissions of 95.4 g CO_2eq/MJ. Negative net values indicate that overall, GHGs are sequestered rather than emitted, and implies that the co-product credit is larger in magnitude than the sum of the well-to-pump and pump-to-wheel emissions. All E85 pathways meet the eligibility requirement for cellulosic biofuels under the 2007 Energy Independence and Security Act (EISA) (60% reduction in GHG emissions compared to gasoline).

A comparison of pathways with different pre-treatment technologies reveals similar GHG emissions when producing the same set of co-products (e.g., electricity or pellets as the sole co-product). These results are highly dependent on chemical use in the dilute acid process, ammonia recovery in the AFEX process, and ethanol yields in each pathway, parameters that still have some uncertainty and need to be validated at commercial scale. As variations in these parameters may impact any 'ranking' of pre-treatment technologies, it is not possible to identify a particular technology as preferred in terms of minimizing well-to-wheel GHG emissions or energy use.

A comparison of pathways with common co-products provides some valuable insights. Pathways with pellet co-production have lower GHG emissions than pathways with only electricity co-production. This results from the assumption that pellets specifically displace GHG-intensive coal use in electricity generation, leading to a large co-product credit. Co-product electricity is assumed to displace the US Midwest grid-average mix, consisting of coal, natural gas, nuclear, and other generation sources, and providing a relatively smaller co-product credit. Alternate displacement scenarios (e.g., alternate uses of pellets, displaced electricity sources) would impact GHG results for pathways producing these co-products, but these pathways would still be expected to result in substantial GHG emissions reductions relative to the gasoline pathway.

Based on well-to-wheel results for the six pathways with either only electricity or only pellet as a co-product, it is found that pathways with lower ethanol yields have lower GHG emissions. A similar result was reported in our prior work (McKechnie et al. 2011). A lower ethanol yield results in more residual biomass for co-product production, thereby providing a larger co-product GHG credit when these co-products are used in place of alternatives (electricity co-product displacing grid electricity; pellet co-product displacing coal).

The AFEX-protein pathway (AXPR) has higher GHG emissions compared to the other AFEX pathways, although it still reduces GHG emissions relative to gasoline by 61% as required under EISA for classification as a cellulosic biofuel. Protein co-production reduces N_2O emissions associated with soybean production. However, protein co-production substantially reduces the electricity co-product. Higher life cycle GHG emissions for ethanol produced through the AXPR pathway (37.2 g CO_2eq/MJ) compared to the AFEX pathway with electricity co-product (AXEL) (16.9 g CO_2eq/MJ) result from the relatively larger co-product credit for electricity compared to that for biomass-based protein.

Among the studied pathways, the autohydrolysis-xylitol-pellet (AHXP) pathway is associated with the lowest GHG emissions (141% reduction compared to gasoline), due to the large total GHG credit received for lignin pellets displacing coal and and xylitol displacing sugar beet. The autohydrolysis pathway with xylitol and electricity as co-products (AHXE) has lower GHG emissions (83% reduction in emissions relative to gasoline) compared to the autohydrolysis pathway with solely electricity as the co-product (AHEL) (66% reduction in emissions relative to gasoline). Xylitol co-production alongside electricity or pellets increases the GHG emissions co-product credit, and reduces the overall GHG emissions. The co-product credit is allocated over a relatively smaller output of ethanol, due to the diversion of xylose to xylitol co-production. This result, however, does not indicate a GHG advantage to producing xylitol as a co-product at the expense of ethanol yield. Taking into account both the well-to-wheel GHG emissions intensity of E85 relative to gasoline (g/MJ) and the total E85 output (MJ E85/y) reveals that the autohydrolysis pathway with co-product electricity (AHEL) reduces total GHG emissions by 0.30 million t CO_2eq/y, compared to 0.24 million t CO_2eq/y for the same amount of biomass processed using the autohydrolysis pathway with xylitol and electricity as co-products (AHXE).

3.2 Energy Use Results

Figure 3 illustrates the well-to-wheel total, petroleum and fossil energy use. Co-product credits are also shown in the figure. Net total energy use (per MJ of E85) for the dilute acid pathways is generally 15-25% lower than for the autohydrolysis and AFEX pathways producing similar co-products, due to the dilute acid pathways producing more ethanol than the other pathways. Net total energy use in the dilute acid and AFEX pathways differs by only 8-10%.

Pathways co-producing lignin pellets have the largest net total energy use of all E85 pathways, due to considerable energy (natural gas) required to dry and pelletize lignin residues. The autohydrolysis pathway with xylose and pellet co-products (AHXP) have the highest net total energy use, due to considerable energy required for xylose purification and xylose hydrogenation to xylitol, and energy required to dry and pelletize lignin residues.

Production of xylitol demands more input energy to the process than production of protein (Figure 3). To produce xylitol and electricity as co-products of the autohydrolysis pathway (AHXE), a 22% increase in net total energy is required compared to autohydrolysis with electricity as the sole co-product (AHEL). In contrast, to produce protein and electricity as co-products of the AFEX pathway (AXPR), only a 9% increase in net total energy is required compared to that required for AFEX with electricity as the sole co-product (AXEL).

All E85 pathways have higher well-to-wheel net total energy use when compared to the reference gasoline pathway. However, a large portion of well-to-wheel total energy is renewable (biomass-based), and therefore net fossil energy use is much lower for E85 pathways compared to the gasoline pathway. All E85 pathways have at least a 47% lower net fossil energy requirement relative to the gasoline reference pathway. The AFEX pathway with electricity (AXEL) has the lowest net fossil energy use (approximately 80% lower than gasoline). Net petroleum energy use for all E85 pathways is at least 67% lower than net petroleum use for the gasoline pathway, as petroleum energy use associated with these biofuel pathways is mainly attributable to energy for feedstock and E85 transport, and the gasoline blended with ethanol to produce E85. Net petroleum energy use associated with the E85 production pathways is essentially the same despite variations in pre-treatment technology and co-production scenarios because the same volume of gasoline (17% v/v) is blended with the ethanol produced in each pathway to make E85.

Differences among fossil energy inputs for the E85 pathways are due primarily to process energy sources assumed to be utilized at the biorefinery. All biorefinery scenarios with electricity as a co-product are energy self-sufficient due to the electricity and steam generated from combustion of lignin residues (Table 2). In contrast, pathways with pellet production utilize natural gas for heating purposes and import electricity from the USA Midwest grid mix, which is dominated by fossil fuel generation sources. Therefore, pathways with pellet co-production have higher fossil energy inputs compared to pathways with electricity co-production. However, pellet co-production is also associated with a large fossil energy credit related to the substitution of coal (1:1 displacement ratio on an energy basis). As a result, net fossil energy use of pathways with a pellet co-product is only slightly higher than that of pathways with electricity as a co-product (Figure 3).

The value-added co-products considered in this study (pellets, protein, xylitol) typically require additional energy “investment”. Both pellets and protein production result in an increase in net fossil energy use. However, the autohydrolysis pathway with xylitol and electricity as co-products (AHXE) has 14% lower fossil energy use than the authohydrolysis pathway solely producing electricity (AHEL), despite a higher plant energy demand. This outcome arises from the fossil energy credit from displacement of sugar beet-derived sugar by xylitol. This credit is larger than the additional energy required for xylitol production, compared to a process with only electricity co-production. In addition, less ethanol production in the xylitol co-production pathways reduces the distillation energy demand.

3.3 Scenario Analysis

Scenarios were developed to examine the impact on the life cycle results of two parameters related to the corn stover feedstock: 1) allocation of a portion of corn cultivation GHG emissions to stover; and 2) field emissions (SOC, N_2O) implications of stover removal. Allocating a portion of emissions associated with corn cultivation based on relative mass of corn grain and stover (mass allocation) increases stover-related emissions to 218 kg CO_2eq/dry t stover, compared to 54 kg CO_2eq/dry t stover when only stover collection and fertilizer replacement for stover removal are included (the base case). Under the mass allocation scenario, the GHG emissions of all pathways increase, with the increase depending on ethanol yield. The increase in GHG emission ranges from 15 to 30 g CO_2eq/MJ E85. While most pathways still qualify as a cellulosic biofuel under EISA rules, the AHXE pathway would reduce emissions by 58% relative to gasoline and thereby qualify only as an advanced biofuel (minimum 50% GHG emission reduction compared to gasoline). The AXPR pathway achieves a GHG emission reduction of 45% relative to gasoline and so would no longer qualify as a cellulosic or advanced biofuel.

Compared to the base case, applying a field emission factor of 35 kg CO_2eq/dry t stover increases stover-related emissions to 89 kg CO_2eq/dry t stover. GHG emissions for the dilute acid pathways increase by 3 g CO_2eq/MJ E85; for the AFEX ,AHEL and AHPE pathways increase by 4 g CO_2eq/MJ E85; and for the AHXE and AHXP pathways increase by 6 g CO_2eq/MJ E85. The inclusion of field emissions alone, at the level investigated, does not prevent any pathway from meeting the EISA GHG reduction requirement.

Conclusion

Potential future USA Midwest lignocellulosic corn stover-to-ethanol systems, employing three different pre-treatment technologies (dilute acid, ammonia fiber expansion and autohydrolysis), with four different co-product options (electricity, lignin pellets, protein concentrate, xylitol) are examined using well-to-wheel analyses. Different combinations of the various technologies and products are assessed. Based on the data currently available, there is little difference in GHG emissions of the processes using the three pre-treatments. As these technologies are developed and optimized, differences in chemical, energy and enzyme use may ultimately lead to a differentiation among these technology pathways. However, it is likely that the primary differentiation will be based on process performance metrics, and additionally financial performance, given the comparable level of GHG reduction observed for all of the pre-treatments.

All of the E85 pathways examined meet EISA's GHG reduction requirement for categorization as a cellulosic biofuel in our base case. The sensitivity analysis is meant to represent a first step in exploring the potential impacts of the corn stover-related parameters on the life cycle results. The primary message from the simplified analysis undertaken is that these parameters are potentially important and additional detailed analysis of these issues should be undertaken in future studies.

The fossil energy use and GHG emissions reductions possible with each pathway are dependent on co-product choice. The pathways with electricity as a co-product have lower fossil energy use compared to the other pathways, whereas pathways with pellets generally provide the greatest GHG emissions reductions. Greater emissions reductions were found for pathways with xylitol and pellet production compared with other E85 pathways. It should be noted that the ranking of co-products in term of GHG implications is dependent on assumed reference (displaced) products, and changing these products (or their sources) may alter this ranking. The choice of a co-product can also affect the yield of the primary product (ethanol) or other co-products in some situations. Therefore, an analysis of financial-environmental trade-offs is required to inform decisions about co-product production.

5. Acknowledgments

We thank Genome Canada and the Ontario Genomics Institute (2009-OGI-ABC-1405) and the Government of Ontario through the ORF-GL2 program, the Natural Sciences and Engineering Research Council, AUTO21 Network Centre of Excellence, BioFuelNet Network Centre of Excellence, as well as Mark Laser, SunOpta Bioprocess Inc. and Xylitol Canada Inc. for providing initial models used as the basis for this work.

6. References

Aden A., Ruth M., Ibsen K., Jechura J., Neeves K., Sheehan J., Wallace B., 2002. Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover. National Renewable Energy Laboratory, Golden, CO, Tech. Rep. TP-510-32438.

Argonne National Laboratory, 2011. The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model Version 1.8d, Argonne, IL.

Bai Y., Luo L., Ester van der V., 2010. Life cycle assessment of switchgrass-derived ethanol as transport fuel. Int. J. Life Cycle Assess., 15, 468-477.

Chen W., Qui W., 2010. Key technologies for bioethanol production from lignocellulose. Biotechnol. Adv.*,* 28, 556-562.

Cherubini F., Stromman A.H., 2011. Life cycle assessment of bioenergy systems: state of the art and future challenges. Bioresour. Technol., 102, 437-451.

Cherubini F., Ulgiati S., 2010. Crop residues as raw materials for biorefinery systems. Appl. Energy, 87, 47-57.

Chiesa S., Gnansounou E., 2011. Protein extraction from biomass in a bioethanol refinery – possible dietary applications: use as animal feed and potential extension to human consumption. Bioresour. Technol., 102, 427-436.

Curran M. A., 2010. Life cycle assessment principles and practice. Scientific Applications International Corporation (SAIC), Cincinnati, OH, EPA/600/R-06/060.

Dale B.E., Allen M., Laser M., Lynd L., 2009. Protein feeds co-production in biomass conversion to fuels and chemicals. Biofuels Bioprod. Biorefin., 3, 219-230.

Dalgaard R., Schmidt J., Halberg N., Christensen P., Thrane M., Pengue W.A., 2008. LCA of soybean meal. Int. J. Life Cycle Assess.*,* 13, 240-254.

Delivand K.M., Barz M., Gheewala H.G., Sajjakulnukit B., 2012.Environmental and socio-economic feasibility assessment of rice straw conversion to power and ethanol in Thailand. J. Clean. Prod., 37, 29-41.

Dunn B.J., Mueller S., Kwon H., Wang Q.M., 2013. Land use change and greenhouse gas emissions from corn and cellulosic ethanol. Biotechnol. Biofuels, 6, 51.

Ekman A., Campos M., Lindahl S., Co M., Börjesson P., Karlsson N.E., Turner C., 2013. Bioresource utilization by sustainable technologies in new value added biorefinery concepts - two case studies from food and forest industry. J. Clean. Prod., 57, 46-58.

Energy Independence and Security Act of 2007. Public Law 110-140. http://www.gpo.gov/fdsys/pkg/PLAW-110publ140/html/PLAW-110publ140.htm (Accessed 16 July 2013).

Environmental Protection Agency, 2007. Regulation of fuels and fuel additives: renewable fuel standard program: final rule part II. Federal Register, 72, 23900-24014.

FitzPatrick M., Champagne P., Cunningham M.F., Whitney R.A., 2010. A biorefinery processing perspective: Treatment of lignocellulosic materials for the production of value-added products. Bioresour. Technol., 101, 8915-8922.

Guinée J.B., 2002. Handbook on life cycle assessment: operational guide to the ISO standards. Kluwer Academic Publisher. Dordrecht.

Hsu D.D., Inman D., Heath G.A., Wolfrum E., Mann M., Aden A., 2010. Life cycle environmental impacts of selected us ethanol production and use pathways in 2022. Environ. Sci. Technol., 44, 5289–5297.

Kochsiek A.E., Knops M.H., 2012. Maize cellulosic biofuels: Soil carbon loss can be a hidden cost of residue removal. GCB Bioenergy, 4, 229-233.

Laser M., Larsen E., Dale B.E., Wang M., Greene N., Lynd R.L., 2009a. Comparative analysis of efficiency, environmental impact and process economics for mature biomass refining scenarios. Biofuels, Bioprod. Biorefin., 3, 247-270.

Laser M., Jin H., Jayawardhana K., Lynd L.R., 2009b. Coproduction of ethanol and power from switchgrass. Biofuels Bioprod. Biorefin., 3, 195-218.

Mabee W.E., Saddler J.N., 2010. Bioethanol from lignocellulosics: status and perspectives in Canada. Bioresour. Technol., 101, 4806-4813.

MacLean H.L., Spatari S., 2009. The contribution of enzymes and process chemicals to the life cycle of ethanol. Environ. Res. Lett., 4, 014001.

McKechnie J., Zhang Y., Akifumi O., Saville B., Sleep S., Turner M., Pontius R. and MacLean H.L., 2011. Impacts of co-location, co-production and process energy source on life cycle energy use and greenhouse gas emissions of lignocellulosic ethanol, Biofuels Bioprod. Biorefin., 5, 279-292.

Mullins K. A., Griffin, W. M., Matthews H. S., 2011.Policy Implications of Uncertainty in Modeled Life-Cycle Greenhouse Gas Emissions of Biofuels. Environ. Sci. Technol., 45, 132-138.

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

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

Pan X., Gilkes N., Kadla J., Pye K., Saka S., Gregg D., Ehara K., Xie D., Lam D., Saddler J., 2006. Bioconversion of hybrid poplar to ethanol and co-products using an organosolv fractionation process: Optimization of process yields. Biotechnol. Bioeng., 94, 851-861.

Renouf M.A., Wegener M.K., Nielsen L.K., 2008. An environmental life cycle assessment comparing Australian sugarcane with US corn and UK sugar beet as producers of sugars for fermentation. Biomass Bioenergy, 32, 1144-1155.

Spatari S., Bagley D.M., MacLean H.L., 2010. Life cycle evaluation of emerging lignocellulosic ethanol conversion technologies. Bioresour. Technol., 101, 654-667.

Stephen D.J., Mabee E.W., Saddler N.J., 2011. Will second-generation ethanol be able to compete with first-generation ethanol? Opportunities for cost reduction. Biofuels Bioprod. Biorefin., 6, 159-176.

Thek G., Obernberger I., 2004. Wood pellet production costs under Austrian and in comparison to Swedish framework conditions. Biomass Bioenergy, 27, 671-693.

Tzeng Y.M., Diosady L.L., Rubin L.J., 1990. Production of canola protein materials by alkaline extraction, precipitation, and membrane processing. J. Food Sci., 55, 1147-1156.

Uihlein A., Schebek L., 2009. Environmental impacts of a lignocellulosic feedstock biorefinery system: An assessment. Biomass Bioenergy, 33, 793-802.

von Blottnitz H., Curran A.M., 2007. A review of assessment conduced on bioethanol as a transportation fuel from a net energy, greenhouse gas, and environmental life cycle perspective. J. Clean. Prod., 15, 607-619.

Wang L., Littlewood J., Murphy J.R., 2013. Environmental sustainability of bioethanol production from wheat straw in the UK. Renew. Sust. Energ. Rev., 28, 715-725.

Zhang Y.H., 2008. Reviving the carbohydrate economy via multi-product lignocellulose biorefineries. J. Ind. Microbiol. Biotechnol., 35, 367-375.

Table 1

Corn Stover-to-Ethanol Pathway Designations, Characteristics, and Energy Sources

Pathway Name	Pretreatment Technology	Co-Product(s)	Electricity	Steam
DAEL	Dilute Acid (DA)	Electricity (EL)	Onsite	Onsite
DAPE	Dilute Acid (DA)	Lignin Pellets (PE)	US Midwest Average Mix	Natural Gas
AXEL	Ammonia Fiber Expansion (AFEX)	Electricity (EL)	Onsite	Onsite
AXPE	AFEX	Lignin Pellets (PE)	US Midwest Average Mix	Natural Gas
AXPR	AFEX	Electricity, Protein concentrate (PR)	Onsite	Onsite
AHEL	Autohydrolysis(AH)	Electricity (EL)	Onsite	Onsite
AHPE	Autohydrolysis(AH)	Lignin Pellets (PE)	US Midwest Average Mix	Natural Gas
AHXE	Autohydrolysis(AH)	Xylitol and Electricity (XE)	Onsite	Onsite
AHXP	Autohydrolysis(AH)	Xylitol and Lignin Pellets (XP)	US Midwest Average Mix	Natural Gas

Table 2. Annual Ethanol Production, Ethanol Yield and Co-product Production for each Pathway

Product	Unit	DAEL	DAPE	AXEL	AXPE	AXPR	AHEL	AHPE	AHXE	AHXP
Ethanol	10^6 L	273	273	220	220	220	225	225	146	146
Ethanol Yield	L per dry t	374	374	304	304	304	308	308	200	200
Electricity	GWh	181		218		53	186		151	
Lignin Pellets	TJ[a]		5711		5965			5258		5241
Xylitol	10^3 t								111	111
Protein Concentrate	10^3 t					25				

[a] TJ: terajoule

Figure Captions

Figure 1. Production of E85, Lignin Pellets, Electricity, Protein and Xylitol from Corn Stover

Figure 2.Well-to-Wheel GHG Emissions of Gasoline and Corn Stover-to-E85 Pathways

DAEL = DA + Electricity, DAPE = DA + Pellets, AXEL = AFEX + Electricity, AXPE = AFEX + Pellets, AXPR = AFEX + protein & electricity, AHEL = AH + Electricity, AHPE = AH + Pellets, AHXE = AH + Xylitol & Electricity, AHXP = AH + Xylitol & Pellets.

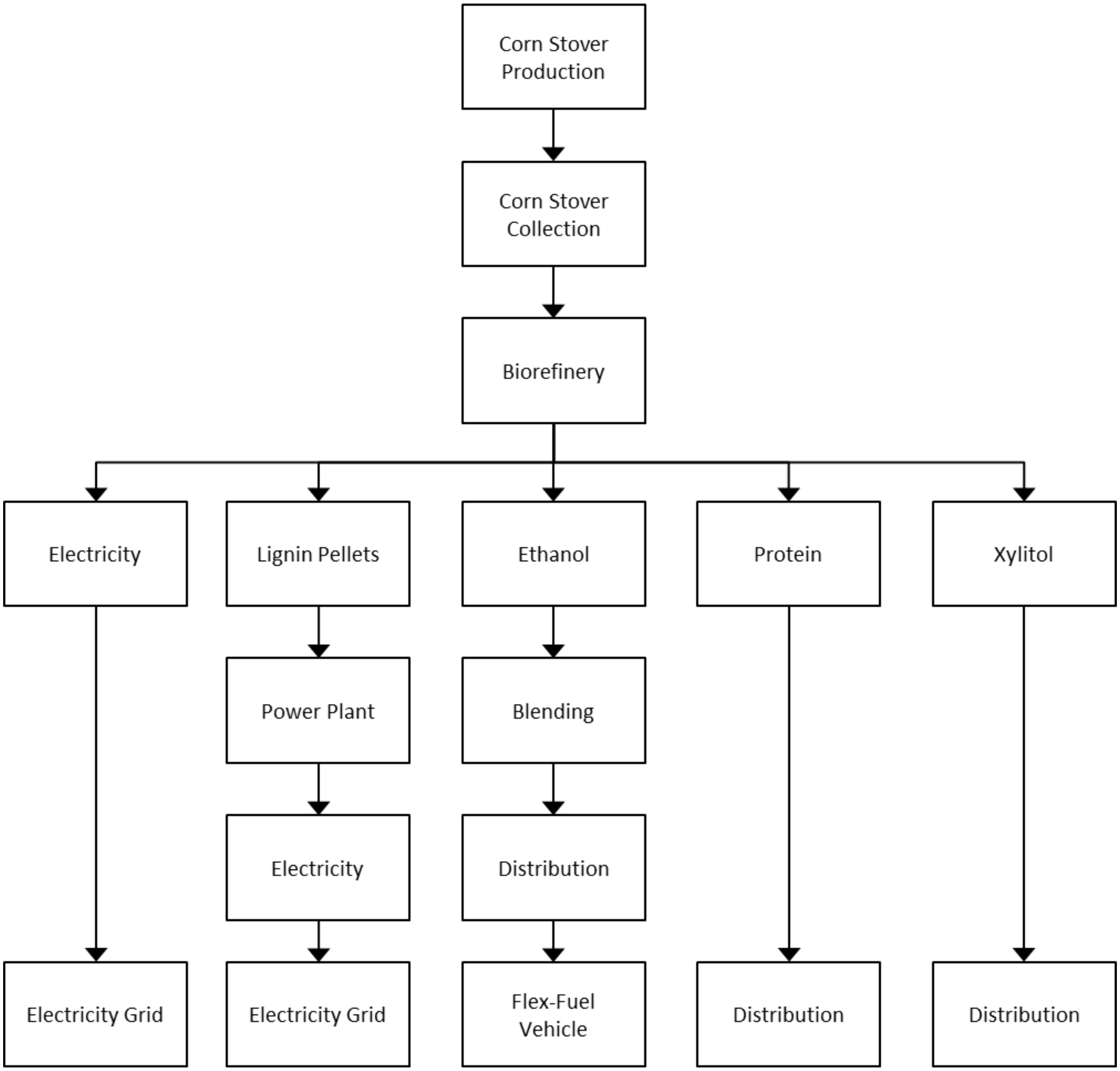
[1] Pump-to-wheel (PTW) emissions are those associated with combustion of fuel during vehicle operation.

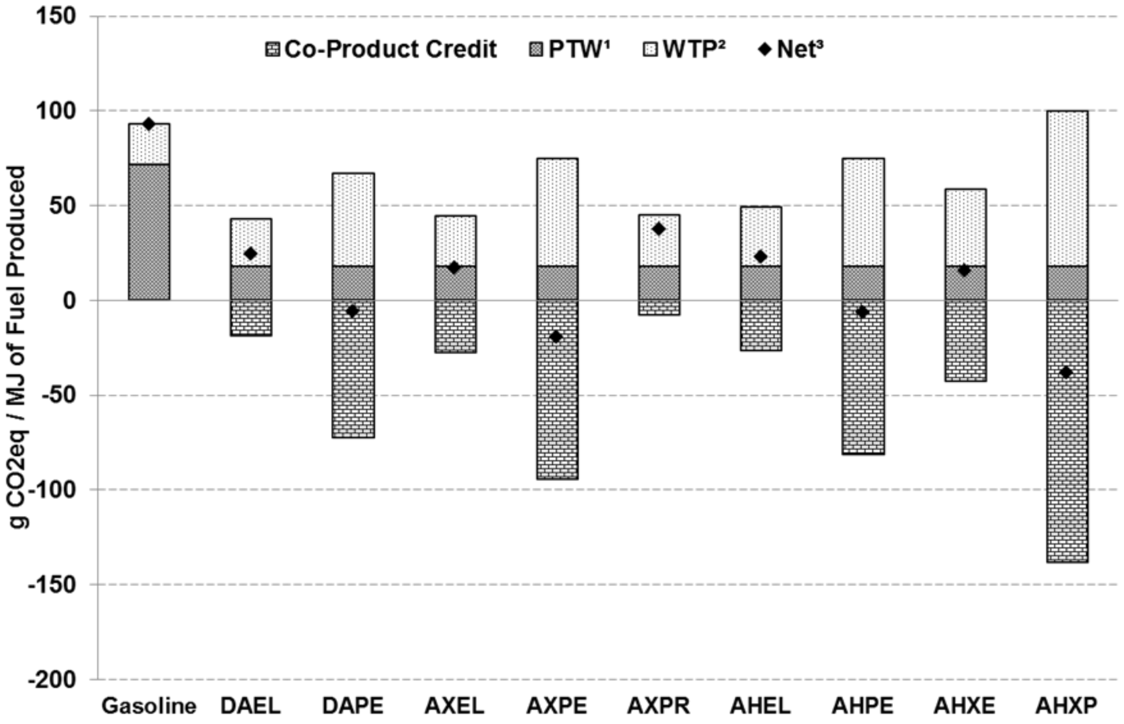
[2] Well-to-pump (WTP) emissions.

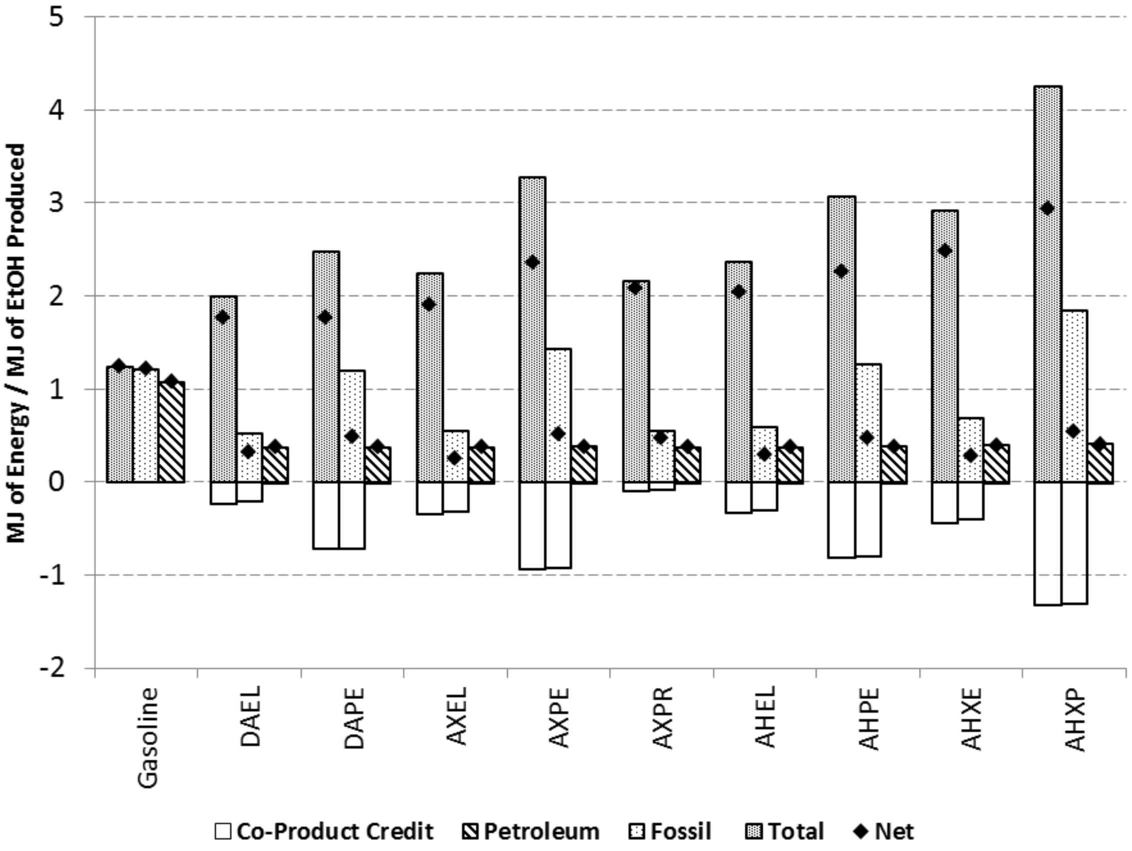
[3] Net refers to the net WTW emissions with the co-product emissions credit included in each pathway

Figure 3. Well-to-Wheel Energy Use of Gasoline and Corn Stover-to-E85 Pathways

DAEL = DA + Electricity, DAPE = DA + Pellets, AXEL = AFEX + Electricity, AXPE = AFEX + Pellets, AXPR = AFEX + protein & electricity, AHEL = AH + Electricity, AHPE = AH + Pellets, AHXE = AH +Xylitol & Electricity, AHXP = AH + Xylitol & Pellets.


Corn Stover Production
Corn Stover Collection
Biorefinery
Electricity
Lignin Pellets
Ethanol
Protein
Xylitol
Power Plant
Blending
Electricity
Distribution
Electricity Grid
Electricity Grid
Flex-Fuel Vehicle
Distribution
Distribution


Co-Product Credit
PTW¹
WTP²
Net³
g CO2eq / MJ of Fuel Produced
150
100
50
0
-50
-100
-150
-200
Gasoline
DAEL
DAPE
AXEL
AXPE
AXPR
AHEL
AHPE
AHXE
AHXP



5
4
3
2
1
0
-1
-2
MJ of Energy / MJ of EtOH Produced
Gasoline
DAEL
DAPE
AXEL
AXPE
AXPR
AHEL
AHPE
AHXE
AHXP
☐ Co-Product Credit
▧ Petroleum
▨ Fossil
▩ Total
◆ Net

1