The NREL Biochemical and Thermochemical Ethanol Conversion Processes: Financial and Environmental Analysis Comparison

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The financial and environmental performance of the National Renewable Energy Lab's (NREL) thermochemical and biochemical biofuel conversion processes are examined herein with pine, eucalyptus, unmanaged hardwood, switchgrass, and sweet sorghum. The environmental impacts of the process scenarios were determined by quantifying greenhouse gas (GHG) emissions and TRACI impacts. Integrated financial and environmental performance metrics were introduced and used to examine the biofuel production scenarios. The thermochemical and biochemical conversion processes produced the highest financial performance and lowest environmental impacts when paired with pine and sweet sorghum, respectively. The high ash content of switchgrass and high lignin content of loblolly pine lowered conversion yields, resulting in the highest environmental impacts and lowest financial performance for the thermochemical and biochemical conversion processes, respectively. Biofuel produced using the thermochemical conversion process resulted in lower TRACI single score impacts and somewhat lower GHG emissions per megajoule (MJ) of fuel than using the biochemical conversion pathway. The cost of carbon mitigation resulting from biofuel production and corresponding government subsidies was determined to be higher than the expected market carbon price. In some scenarios, the cost of carbon mitigation was several times higher than the market carbon price, indicating that there may be other more cost-effective methods of reducing carbon emissions.

Keywords: Biofuel; LCA; Environmental impacts; GHG; Conversion technology; Ethanol; Thermochemical; Biochemical

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INTRODUCTION

Conversion technologies for lignocellulosic biomass types are rapidly emerging to meet the government-mandated production levels for renewable fuels (Spath *et al.* 2005; Phillips *et al.* 2007; Sequeira *et al.* 2007; Bright and Strømman 2009; Consonni *et al.* 2009; Foust *et al.* 2009; He and Zhang 2011; Leibbrandt *et al.* 2011; Daystar *et al.* 2012; Dutta *et al.* 2012). The thermochemical and biochemical processes are two different fuel production routes widely proposed for biomass-to-biofuel scenarios. Previous studies have considered the thermochemical and biochemical conversion routes relative to their technical or economic feasibility (Hamelinck *et al.* 2005; Piccolo and Bezzo 2009; Anex *et al.* 2010; Cherubini and Jungmeier 2010; Kazi *et al.* 2010; Seabra *et al.* 2010; Swanson *et al.* 2010; González-García *et al.* 2012; Xue *et al.* 2012; Treasure *et al.* 2014). Few

studies have considered the environmental burdens of this pathway or compared life cycle emissions using various biofuel feedstocks to those of fossil fuels.

Biochemical conversion processes have been carefully analyzed for techno-economic feasibility, conversion efficiency of various biomass feedstocks, environmental impacts, chemical and enzyme use, and ways to optimize the bench-top, pilot-scale, and commercial-scale processes (Frings *et al.* 1992; Canakci and Van Gerpen 1999; Foust *et al.* 2009; Inman *et al.* 2010; Mu *et al.* 2010; Balat 2011; Balan *et al.* 2012). Biochemical conversion technologies use various pretreatment methods to increase enzymatic hydrolysis conversion yields and sometimes to extract valuable co-products. The product of enzymatic hydrolysis and sugars are often neutralized and fermented to produce ethanol at a low concentration. This low concentration ethanol, often referred to as beer, is then distilled and molecular-sieved to around 99.95% ethanol as the final product (Foust *et al.* 2009; Inman *et al.* 2010; Mu *et al.* 2010; Balat 2011; Balan *et al.* 2012; Romaní *et al.* 2012). Many studies have explored the biochemical conversion processes and determined them to be relatively inherently inflexible in terms of multiple feedstock operation, requiring a larger collection radius to provide the necessary biomass supply for full-scale fuel processing (Huang *et al.* 2009).

Indirect gasification, as modeled for this study, was explored previously by researchers at the U.S. Department of Energy (Phillips *et al.* 2007; Carpenter *et al.* 2010; Swanson *et al.* 2010; and Dutta *et al.* 2011; Jett 2011). Indirect gasification produces a mixture of carbon monoxide and hydrogen gas referred to as synthesis gas or syngas. Raw syngas contains catalyst-fouling contaminants that must be removed before alcohol synthesis. The clean syngas is then converted to mixed alcohols, mainly ethanol and propanol, using a molybdenum catalyst.

Thermochemical conversion can use a wider range of feedstocks than biochemical conversion and produces reasonably high alcohol yields (Dutta and Phillips 2009; Dutta *et al.* 2011; Dutta *et al.* 2012). Unlike the biochemical process, the thermochemical process is not adversely affected by lignin in the biomass; however, biomass feedstock moisture content heavily influences alcohol yields and emissions for the thermochemical process (Daystar *et al.* 2013). Power requirements for alcohol conversion processes are provided by combined heat and power facilities burning waste, biomass, char, or produced syngas (Balan *et al.* 2012).

This article presents both environmental (Daystar *et al.* 2015a,b) and financial (Gonzalez *et al.* 2011, 2012; Treasure *et al.* 2014) performance results for two of the biochemical and thermochemical conversion pathways, as well as a novel integrated financial and environmental performance metric. The National Renewable Energy Lab (NREL) biofuel pathway comparison has not been previously performed using both financial and environmental metrics for multiple feedstock scenarios. This research will provide additional information to allow for a more holistic view of conversion technology and biomass feedstock pairing decisions.

METHODS

System Boundaries

To determine the full lifecycle environmental impacts of cellulose-based transportation fuel production and use, environmental impacts from all process stages must be incorporated, including raw material production, fuel conversion, and fuel combustion.

The Clean Air Act (EPA 2009) defines this boundary and analysis approach for greenhouse gases (GHGs) as:

> "The term 'lifecycle greenhouse gas emissions' means the aggregate quantity of greenhouse gas emissions (including direct emissions and significant indirect emissions such as significant emissions from land use changes), as determined by the Administrator, related to the full fuel lifecycle, including all stages of fuel and feedstock production and distribution, from feedstock generation or extraction through the distribution and delivery and use of the finished fuel to the ultimate consumer, where the mass values for all greenhouse gases are adjusted to account for their relative global warming potential." (EPA 2009)

This definition was expanded here to include additional impact categories beyond global warming potential (GWP) including impact categories in the updated **T**ools for the **R**eduction and **A**ssessment of **C**hemical **I**mpacts (TRACI) 2 method. This system boundary is often referred to as cradle-to-grave or well-to-wheel analysis. Figure 1 displays process steps included within this study which include feedstock production, fuel production, fuel use, and direct land use change (LUC), as required by the Renewable Fuels Standard (RFS2) accounting method (US Legislature 2007).

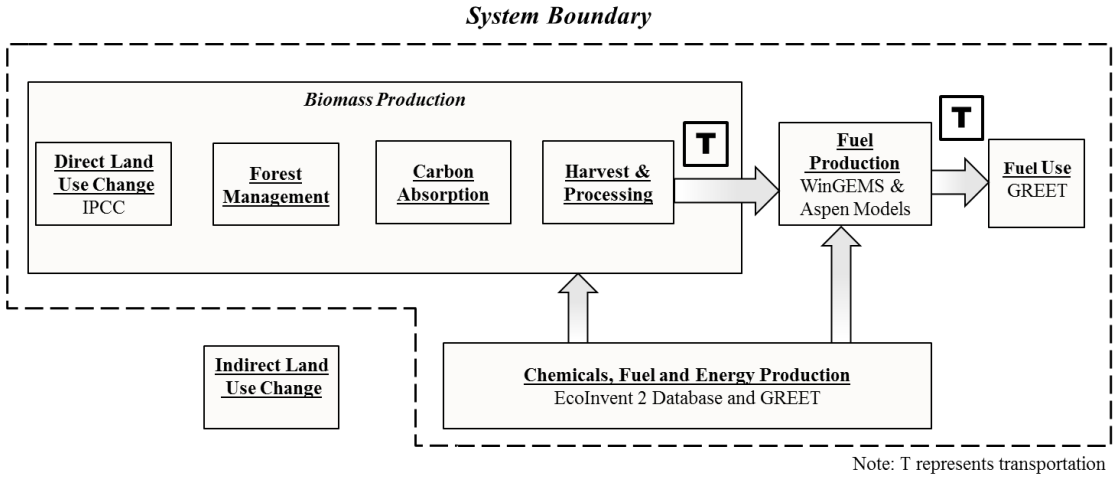

Fig. 1. Cradle-to-grave bioethanol life cycle assessment system boundary using the biochemical and thermochemical conversion processes

Life Cycle Inventory

This life cycle assessment of biofuel conversion processes integrates both biofuels production simulations and biofuels LCA models to determine the environmental impacts of transportation fuels. Methods used to develop a biofuel lifecycle impact (LCI) are discussed below to propose a method for biofuels LCA that expands the RFS2 guidelines. Additional LCI data are located in the appendix and in the cited publications.

Co-product Treatment Methods

GHG emissions and other environmental impacts are sensitive to co-product treatment methods. Both system expansion and energy allocation co-product treatment methods were used for ethanol produced from the biochemical conversion process.

Depending on the feedstock, the biochemical route produces excess electricity that must be accounted for using one of these methods.

The thermochemical conversion process was modeled to have an energy balance where no electricity needs to be purchased from or sold to the grid. The thermochemical process produces a distribution of alcohol products in addition to ethanol. Based on their respective embodied energy contents, these products were converted to ethanol equivalents for accounting purposes. Although fuel product specificity varied in accordance with the biomass feedstock modeled, higher alcohols represent approximately 15% of the total alcohol by mass. The system expansion method was not explored for the mixture of higher alcohols as the mixture does not represent an end product with an existing market, as in the case of electricity.

Ethanol Conversion Process

Biochemical conversion process model

A brief process flow diagram is presented here to give the reader a working understanding of the process under analysis. However, Treasure *et al.* (2014) and Humbird *et al.* (2011) both contain more detailed process overviews and technical specifications. The biochemical conversion process flow diagram as depicted by Treasure *et al.* (2014) is shown in Fig. 2.

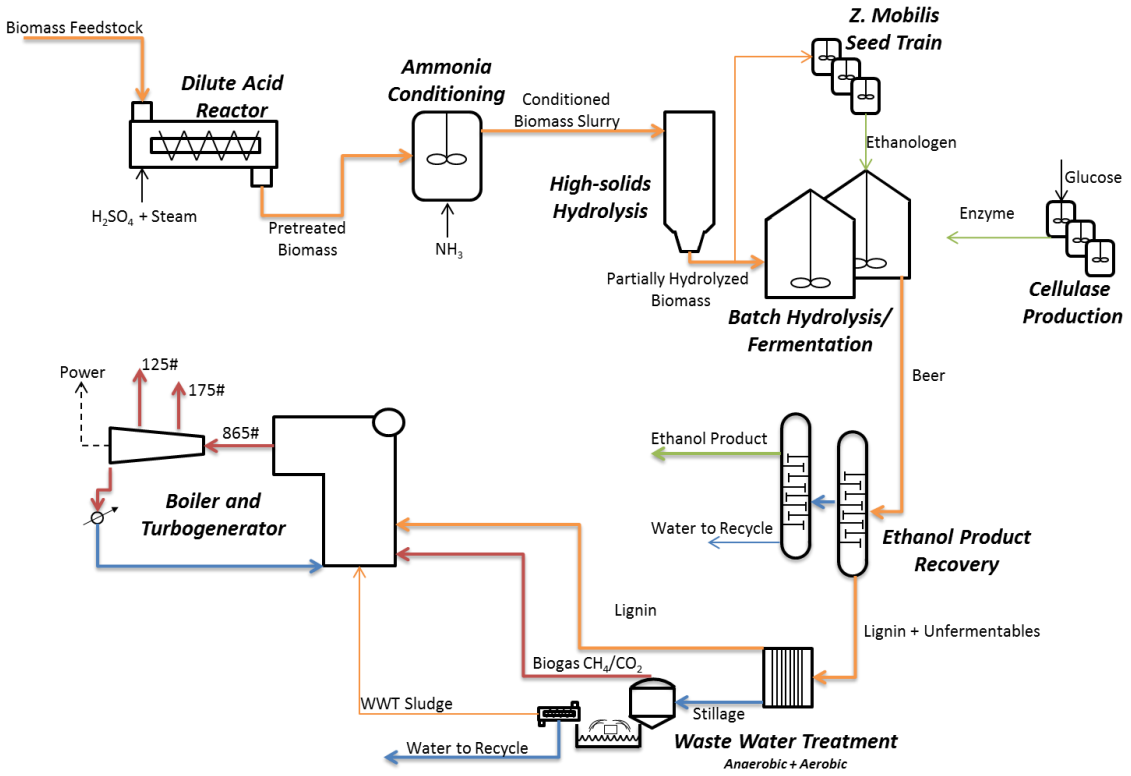

Fig. 2. NREL dilute acid pretreatment biochemical ethanol conversion process flow diagram (Treasure *et al.* 2014)

Thermochemical conversion process model

Aspen Plus was used to model NREL's thermochemical mixed alcohol production process and generate life cycle inventory data (Daystar *et al. 2015a;* Spath *et al.* 2005; Phillips *et al.* 2007; Jett 2011). Simulation modifications, described by Gonzalez *et al.* (2012), were made to the original model received from NREL in order to operate the process conversion model using feedstocks other than the hybrid poplar baseline. Figure 3 illustrates the major unit processes in the thermochemical conversion pathway. These unit processes are summarized in Daystar *et al.* (2015a) and detailed in Spath *et al.* (2005), Phillips *et al.* (2007), and Jett (2011).

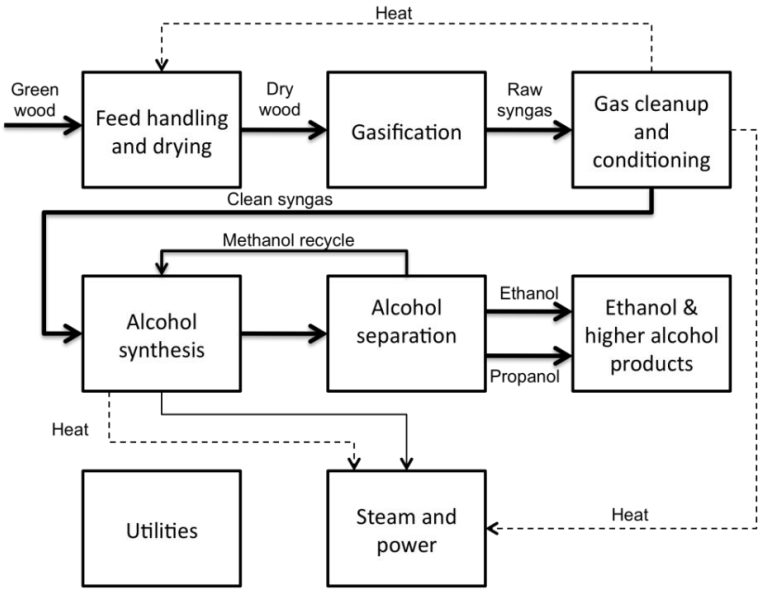

Fig. 3. The process flow diagram (gate-to-gate) for the thermochemical gasification of biomass to produce ethanol (Phillips *et al.* 2007)

Both conversion processes were simulated with a feedstock supply of 700,347 dry metric tons (tons from here forth refers to metric tons) per year (772,000 dry short tons per year) with moisture contents of 45% for forest based feedstocks and 16% for switchgrass (Filbakk *et al.* 2011; Patterson *et al.* 2011). For more detail on biomass characterization including the ultimate and proximate analyses, see Daystar *et al.* (2014).

Impact Assessment Methods

The Tool for the Reduction and Assessment of Chemical and other Environmental Impacts 2.0 (TRACI 2) impact assessment method was used to analyze global warming potential, acidification, eutrophication, carcinogens, non-carcinogens, respiratory effects, ozone depletion, eco-toxicity, and smog (Bare 2002; Jolliet *et al.* 2004; Plevin 2009; Bare 2011). The global warming equivalents for methane and dinitrogen oxide were updated to the most recent IPCC report values of 25 and 298 global warming equivalency to CO_2, respectively (IPCC 2007).

Life cycle impact assessment (LCIA) midpoint indicators were normalized using Bare and Gloria's normalization factors (Bare and Gloria 2006) and are listed in the appendix. The more recently updated normalization factors were not used here, as they are based on different midpoint indicators that are consistent with the Ecoinvent 3 database

and which are not compatible with SimaPro 7 (Shapouri *et al.* 2002; Frischknecht *et al.* 2005; Gloria *et al.* 2007; Bare 2011). These normalized values were then weighted using multiple weighting systems as described by Gloria *et al.* (2007) and Rogers and Seager (2009). To develop a weighting system, Gloria *et al.* (2007) surveyed product users, product producers, and LCA experts to determine the relative importance of each environmental midpoint indicator to each user group. In this survey, each group was asked to weight the mid-point indicators using three time perspectives: short-term (0 to 10 years), medium-term (10 to 100 years), and long-term (100+ years).

Minimum Carbon Price

The minimum ethanol revenue (MER) represents the revenue per gallon of ethanol that must be achieved for the operation to reach a net present value (NPV) of zero. Gasoline and commodity ethanol prices were compared to the MER to determine market competitiveness. A parameter integrating financial and environmental performance, referred to as the minimum carbon price (MCP), is defined as the lowest value of carbon for a biofuel operation to attain an NPV of zero if the facility were subsidized based on carbon offsets rather than gallons of fuel produced. MCP is calculated by the following two equations (Eq. 1 and 2), where the market price was listed as $2.42 per gallon of ethanol (NASDAQ 2014).

$$\Delta P = MER - Ethanol\ Market\ Price \quad (1)$$

The carbon emission savings component of the MCP is incorporated by dividing the difference between produced value and market value, ΔP, of ethanol by the tons of CO_2 avoided when a gallon of ethanol is used instead of gasoline on an equal energy basis. Ethanol market price herein is in US Dollars per gallon of ethanol, at present value.

$$Minimum\ Carbon\ Price = \frac{\Delta P\ (\$/\text{gal. ethanol})}{Tons\ CO_2\ avoided\ per\ gallon\ ethanol\ used} \quad (2)$$

This MCP will be at a minimum for the production facilities offering the most environmental GWP benefit for the lowest cost. The cost to avoid CO_2 was also calculated with a 1.00 USD subsidy and the observed biofuel scenario GHG reductions. The scenario carbon price was also compared to the RFS2 carbon price where a 1.00 USD subsidy was given and biofuel use on an equal energy basis reduces GHG emissions by the mandated 60% as compared to gasoline.

$$Scenario\ Carbon\ Price = \frac{1\$\ subsidy\ per\ gallon\ ethanol}{\begin{matrix}Tons\ CO_2\ avoided\ per\ gallon\ ethanol\ use \\ (Observed\ \%\ GHG\ emission\ reduction\ per\ MJ)\end{matrix}} \quad (3)$$

$$RFS2\ Carbon\ Price = \frac{1\$\ subsidy\ per\ gallon\ ethanol}{\begin{matrix}Tons\ CO_2\ avoided\ per\ gallon\ ethanol\ use \\ (60\%\ GHG\ emission\ reduction\ per\ MJ)\end{matrix}} \quad (4)$$

The application of these metrics was applied to the current analysis of cellulosic biofuels produced using the biochemical conversion route described by Humbird *et al.* (2011). Biofuel production scenarios utilizing six different biomass feedstocks are examined herein.

RESULTS AND DISCUSSION

Financial Analysis

The financial performance of both the biochemical (Treasure *et al.* 2014) and thermochemical (Gonzalez *et al.* 2012) conversion processes are shown in Fig. 4. Process conversion models linked to CAPEX models were used to calculate capital investment for a 15-year evaluation horizon using a 12% discount rate. Process model data was used to calculate operational costs, and average market costs were used for direct costs and revenue. The financial analysis was not done within this study; however, data from the two previous studies are compared alongside LCA data in the present study. Both financial analyses used similar methods that are described in full in Gonzalez *et al.* (2012) and Treasure *et al.* (2014).

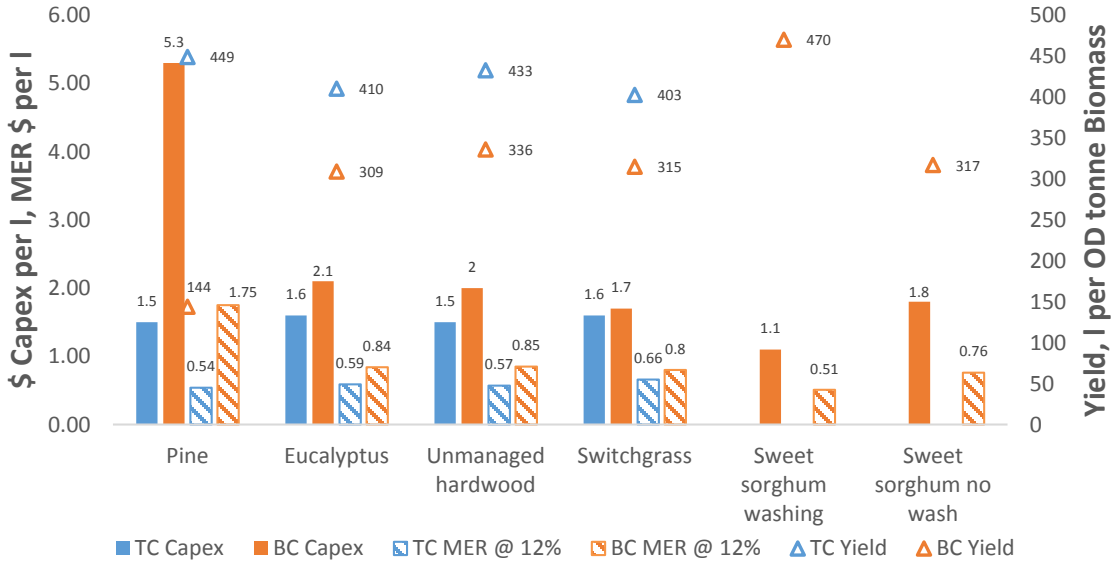

Fig. 4. Capex, MER, and alcohol yields for different biomass types using the thermochemical and biochemical ethanol conversion processes (TC=thermochemical ethanol conversion, BC= biochemical ethanol conversion)

Greenhouse Gas Emissions

Greenhouse gas (GHG) emissions associated with 1 MJ of ethanol from different feedstocks and using different conversion pathways are shown in Fig. 5. Ethanol produced using the thermochemical process resulted in lower GHG emissions per MJ of fuel than ethanol produced using the biochemical conversion process when the energy allocation method was applied to the biochemical conversion scenarios. This can be attributed in part to the higher carbon efficiency of the thermochemical conversion process, which results in more carbon remaining in the products and less CO_2 being emitted during fuel production. Additionally, the thermochemical process requires less process chemicals than the biochemical conversion process.

When comparing ethanol made from the thermochemical process to that made with the biochemical process using the system expansion method for electricity (average US grid), biochemical ethanol was determined to result in lower GHG emissions for the pine, eucalyptus, and switchgrass fuel scenarios (Fig. 5). Avoided GHG emissions associated

with offset average US grid electricity use are the primary driver behind this reduction when using the system expansion method for handling co-product accounting as also determined by Mu *et al.* 2010. When biomass based electricity and the system expansion method was used for the biochemical process, ethanol scenarios resulted in bioethanol with higher GHG emissions than the equivalent thermochemical fuel scenarios. This showed that the market product that the ethanol co-product displaces can highly impact the net GHG emissions of biofuel.

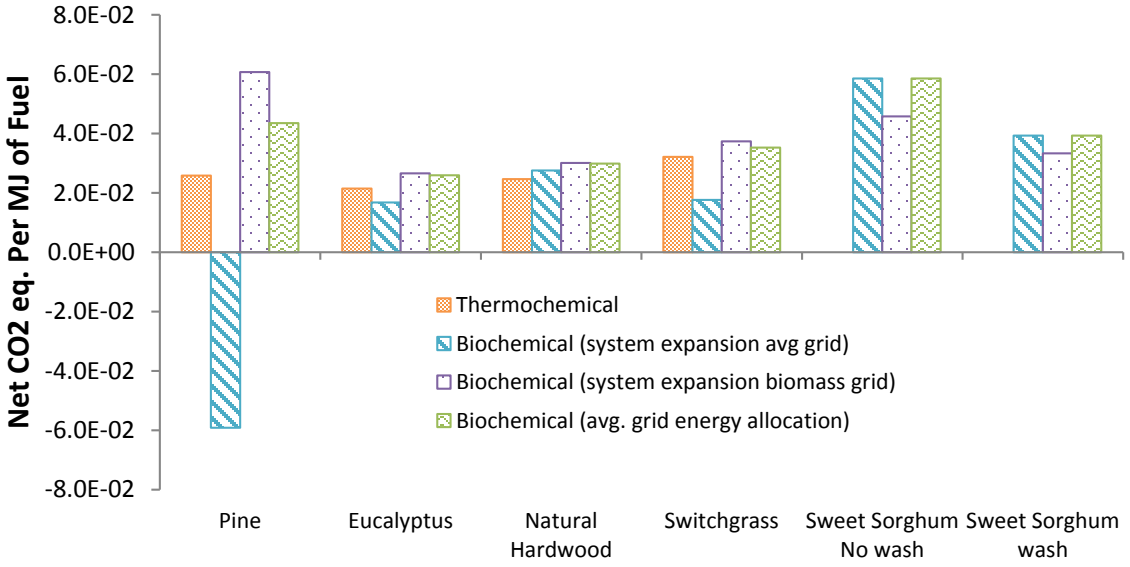

Fig. 5. Greenhouse gas emissions per MJ of ethanol from different feedstocks and conversion technologies

Examining both financial and environmental performance of the biofuel conversion processes together with different biomass types can inform technology developers and policy makers. For GHG emission criteria, pine based ethanol from the thermochemical process would result in lower GHG emissions as compared to pine based ethanol from the biochemical conversion process, except for when electricity from the average US grid is displaced. The same is true for eucalyptus-based ethanol. When examining ethanol made from natural hardwoods, the biochemical conversion process resulted in higher GHG emissions in all examined scenarios as compared to the thermochemical conversion scenario.

Biomass composition also influenced the GHG emission of switchgrass-based ethanol. The high ash content reduces the alcohol yields and lowers the heating value, making switchgrass more suited for a biochemical conversion process. Williams *et al.* (2009) similarly determined that switchgrass-based ethanol produced from the biochemical conversion process resulted in lower GHG emissions per MJ compared to conversion using the thermochemical conversion pathway. Hsu *et al.* (2010) also supports that switchgrass based ethanol from the biochemical conversion process results in higher GHG emissions per MJ of fuel compared to ethanol from the thermochemical conversion of forest based feedstocks.

The conversion of sweet sorghum to ethanol was not modeled for the thermochemical conversion process as the high moisture content and high soluble sugar

content make it more suited for the biochemical conversion process. The Aspen Plus process simulation did not reach model convergence for biomasses with a moisture content over approximately 60%, as the energy required to dry the incoming biomass to 5% was too high. However, the sweet sorghum scenarios resulted in higher GHG emissions per MJ of fuel than all other scenarios except the biochemical pine conversion using the system expansion with biomass grid electricity and energy allocation co-product treatment methods and the switchgrass scenario using system expansion and biomass based energy co-product treatment methods.

Single Environmental Score

The single environmental score is a method used to identify scenario options with the lowest environmental impacts when tradeoffs exist between different impact categories. This metric is sensitive to normalization factors and weighting methods. Previously, the choice of weighting method was shown not to change the biofuel scenario ranking (Daystar *et al.* 2015b). For this reason, only one weighting method was explored when comparing the two conversion technology options.

Ethanol produced from the biochemical conversion process resulted in higher single score impacts for all comparable scenarios than ethanol produced using the thermochemical process, due to the indirect emissions associated with process chemical production (Fig. 6).

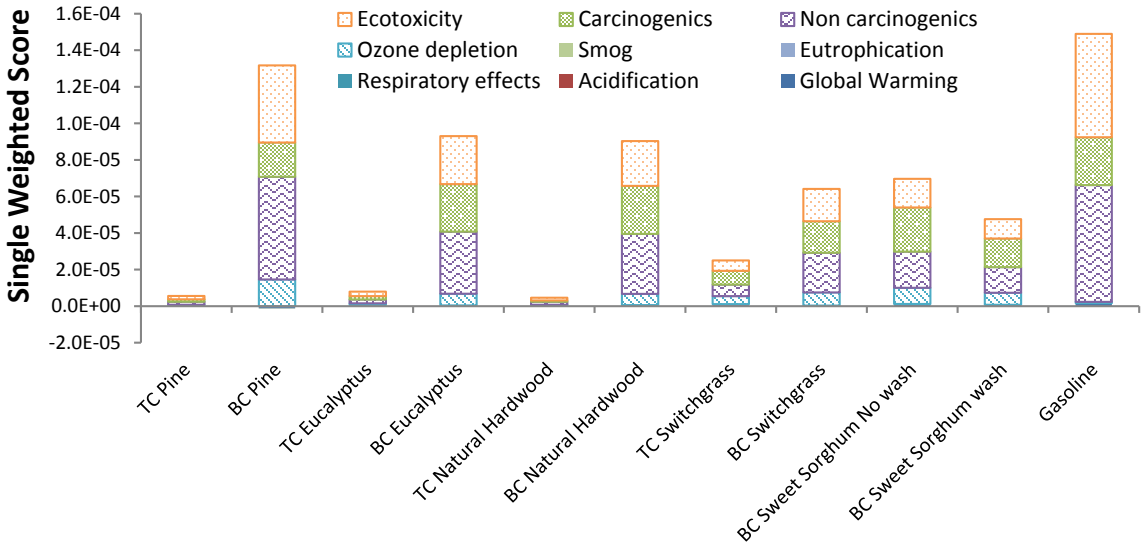

Fig. 6. Single weighted environmental score of 1 MJ of ethanol made from different feedstocks and conversion technologies and gasoline

Mu *et al.* (2010) also found higher indirect environmental impacts for the biochemical process than thermochemical due to higher levels of process chemical consumption. The primary contributors to the single score were eco-toxicity, non-carcinogens, and carcinogens resulting from the production of process chemicals and agricultural chemicals. The thermochemical process requires primarily olivine, a sand-like compound, and a catalyst to operate, while the biochemical conversion process requires a continuous supply of a wider range of chemicals. The ranking of biofuel scenarios from lowest impact to highest is different when comparing the single score result to GHG

emissions. Only considering GHG emissions, as the RFS2 and other policies often do, can have unintended consequence that may lead to reduced GHG emissions at the cost of increased environmental impacts in other categories.

Combined Financial and Environmental Analysis

Greenhouse gas reductions compared to gasoline and fossil fuel energy consumption per MJ of biofuels are other common environmental impact indicators. NPV, internal rate of return (IRR), and MER are common indicators of financial performance of a biofuel production facility. For biofuels producers, both financial outcomes and environmental requirements are integral to being competitive in the long term. For the biochemical and thermochemical conversion pathways, Treasure *et al*. (2014) and Gonzalez *et al.* (2012) examined the financial performance of each biofuel production scenario (Fig. 4) and the environmental performance of each scenario was examined in Daystar *et al.* (2015b) and Daystar *et al.* (2015a), respectively. Since both studies were based on the same process models, yields, and other processing parameters, the environmental performance can be examined in concert with the financial performance.

In all biochemical conversion fuel scenarios other than sweet sorghum with subsequent washing, the MER without subsidies was higher than the ethanol market price, assumed to be $2.42 per gallon (Table 1). MER values for the thermochemical conversion scenarios were all lower than the ethanol market price except in the case of mixed alcohols from switchgrass (Table 2).

For scenarios where the ethanol market price was lower than the MER, the difference represented the subsidy needed per gallon for the facility to be financially competitive at a 12% IRR and in the existing ethanol market. Combining this minimum required ethanol subsidy with GHG reductions resulting from the production and use of bioethanol creates a metric that reflects the cost of CO_2 offsets through biofuel subsidies for each fuel scenario, the minimum carbon price, and MCP (Fig. 7). In the fuel scenarios where the MER was less than the market ethanol price, no additional subsidy was needed for the facility to be profitable. However, more negative MCP values represent scenarios with lower MER and lower GHG emissions. These negative MCP scenarios include all thermochemical conversions except switchgrass and the biochemical conversion with sweet sorghum with washing.

In practice, however, the subsidy given to biofuel producers is not determined by a facility's financial needs with respect to the ethanol market; rather they are determined by policy makers and regulated by the EPA within the Renewable Identification Number (RIN) markets. Recently, the price of a RIN for ethanol has been around $1 per gallon of biofuels but this has fluctuated with changing government policies, availability, and uncertainty due to frequent RIN fraud. For comparison, the $1 per gallon of ethanol RIN value has been used to also calculate the cost of offsetting carbon for each fuel scenario if the facility was to operate at a financial loss (Fig. 7).

The RFS2 carbon price, $1 credit for a gallon of ethanol with 60% greenhouse gas reduction relative to gasoline, and the market price of carbon defined by the Kyoto Protocol are also shown in Fig. 7. The RFS2 carbon price is $135 per ton CO_2. This value is much higher than the market value of carbon offsets, which have for the most part stayed below $20 per ton of carbon offset, as suggested by the Kyoto Protocol. This suggests that without any other considerations, such as national security, the US government is paying more than required to offset CO_2 emissions. The MCP values in Fig. 7 show that, within the current market price of carbon, all thermochemical conversion scenarios and the biochemical

conversion of sweet sorghum with washing are financially feasible based on MCP less than $11/ton.

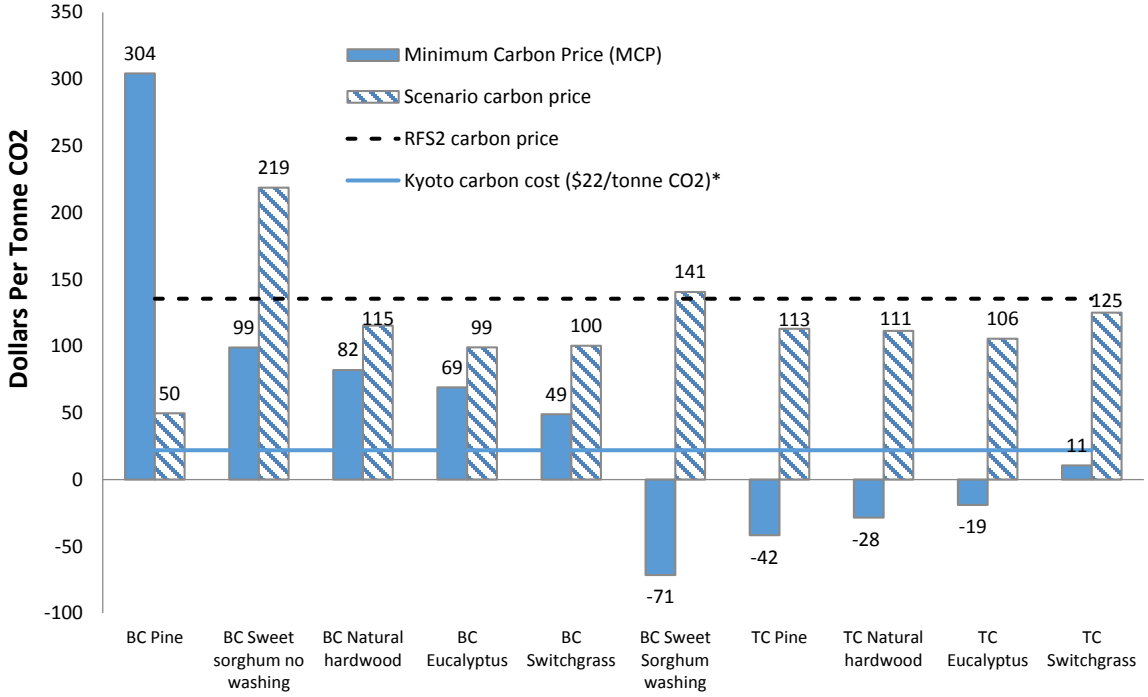

Fig. 7. Cost to avoid CO_2 emissions for different subsidies and fuel scenarios using system expansion co-product treatment method for biochemical conversion process *(Kyoto Protocol 1997)

Table 1. Biochemical Ethanol Conversion Minimum Carbon Price (MCP) Calculation Results (System Expansion)

	Pine	Sweet Sorghum No Washing	Natural Hardwood	Eucalyptus	Switchgrass	Sweet Sorghum Washing
MER ($)	8.53	2.86	3.12	3.11	2.90	1.90
Δ*P* ($) per gallon of ethanol	6.12	0.45	0.71	0.70	0.49	-0.51
% GHG reduction compared to gasoline	163%	37%	70%	82%	81%	58%
GHG avoided emissions (kg) per gallon eth.	20.11	4.57	8.67	10.09	9.98	7.11
Gal ethanol per ton of CO_2 avoided	50	219	115	99	100	141
Dollars per ton carbon avoided (MCP) ($)	**304**	**99**	**82**	**69**	**49**	**-71**

Table 2. Thermochemical Conversion Minimum Carbon Price (MCP) Calculation Results

	Pine	Unmanaged Hardwood	Eucalyptus	Switchgrass
MER ($)	2.04	2.15	2.23	2.49
Δ*P* ($) per gallon of ethanol	-0.37	-0.26	-0.18	0.08
% reduction compared to gasoline	72%	73%	77%	65%
GHG avoided emissions (kg) per gal	8.86	8.98	9.47	8.00
Gal ethanol per ton of CO_2 avoided	113	111	106	125
Dollars per ton carbon avoided (MCP) ($)	**-42**	**-28**	**-19**	**11**

Summary

The profitability of various ethanol conversion technologies and environmental impact reductions compared to gasoline are important to the overall success of the biofuels industry. These two metrics have been compared for both the thermochemical and biochemical ethanol conversion processes. Thermochemical ethanol GHG emissions were lower than biochemical ethanol emissions for the pine, eucalyptus, unmanaged hardwood, and switchgrass scenarios when the energy allocation co-product treatment method was used. The single environmental scores for the thermochemical ethanol fuel scenarios were also lower than the biochemical scenarios due to lower thermochemical conversion process chemical use. Process chemical use was a hot spot resulting in most of the carcinogenic, non-carcinogenic, and ecotoxicity impacts.

The combined financial and GHG metric of MCP was lower for the thermochemical fuel scenarios. The thermochemical MCP values were more negative due to lower MER prices. The biofuels scenarios were ranked within each technology based on MER, GHG emissions, single environmental score, and MCP (Table 3).

Table 3. Biofuel Scenario Ranking Based on Financial and Environmental Performance Metrics

	MER		GHG		Single Score		MCP	
	TC	BC	TC	BC	TC	BC	TC	BC
Pine	1	6	3	1	2	6	1	6
Eucalyptus	3	4	1	2	3	5	3	3
Unmanaged hardwood	2	5	2	4	1	4	2	4
Switchgrass	4	3	4	3	4	3	4	2
Sweet sorghum washing		1		5		2		1
Sweet sorghum no washing		2		6		1		5

CONCLUSIONS

1. Biofuel scenario rankings based on greenhouse gas emissions were different than a single weighted score based on TRACI impacts. This suggests that burden shifting could occur as a result of biofuel production.

2. Ethanol produced *via* the thermochemical conversion pathway required fewer processing chemicals and resulted in lower total environmental impacts based on a single weighted score.
3. Financial and environmental performance was highly dependent on the feedstock composition and conversion pathway scenario.
4. The cost of carbon mitigation through biofuels using a 1 USD RIN value was higher than the market price of carbon defined by the Kyoto Protocol, indicating that the carbon market is not willing to pay as much as the US Government for carbon mitigation through the use of biofuels.
5. All thermochemical conversion scenarios and the biochemical conversion with sweet sorghum with washing were financially feasible with modeled market carbon prices of $22 per ton of CO_2.

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APPENDIX

Table A1. Fossil Fuel Inputs for Ethanol from Cellulosic Materials using the NREL Dilute Acid Pretreatment Biochemical Conversion Route (Daystar *et al.* 2015b)

MJ fossil fuel/MJ ethanol	Loblolly pine	Eucalyptus	Unmanaged hardwood	Switchgrass	Sweet sorghum washing	Sweet sorghum no washing
Feedstock	0.24	0.12	0.14	0.52	0.12	0.17
Process	0.37	0.19	0.18	0.10	0.02	0.04
Purchased Electricity	-0.56	-0.05	-0.04	-0.29	0.09	0.19
Total	**0.05**	**0.26**	**0.28**	**0.33**	**0.23**	**0.39**

Table A2. Dilute Acid Pretreatment Ethanol Conversion Process Simulation Carbon Balance (Daystar *et al.* 2015b)

Tons C/hr	Carbon Content (%)	Pine	Eucalyptus	Natural hardwoods	Switchgrass	Sweet Sorghum Washing	Sweet Sorghum No Washing
Inputs							
Biomass	Varies	43.0	42.5	41.4	39.2	37.4	37.4
Corn steep liquor	8.5	0.2	0.1	0.2	0.1	0.1	0.1
Glucose	40.0	1.4	1.4	1.5	0.8	0.6	0.6
Total in		**44.6**	**44.1**	**43.1**	**40.1**	**38.1**	**38.1**
Outputs							
Enzyme vent	1.7	0.8	0.8	0.8	0.5	0.3	0.3
Aerobic vent	0.6	0.6	1.1	1.3	1.1	0.6	3.3
Brine waste	1.8-12.7	0.6	1.1	0.5	1.8	1.1	1.0
Clean flue gas	12.7	35.6	24.8	22.7	19.9	11.8	17.0
Fermentation vent	27.1	2.3	5.4	5.9	5.6	8.1	5.5
Ethanol	51.8	4.7	10.9	11.8	11.3	16.3	11.0
Total out		**44.6**	**44.1**	**43.1**	**40.1**	**38.1**	**38.1**

Table A3. Process Chemicals Inputs for Ethanol from Cellulosic Materials Using the NREL Dilute Acid Pretreatment Biochemical Conversion Route (Treasure *et al.* 2014)

Process Area	Material	Eucalyptus	Pine	Unmanaged Hardwood	Switchgrass	Sweet Sorghum No Washing	Sweet Sorghum Washing
Feedstock	Biomass	3.15E-01	3.15E-01	3.15E-01	3.15E-01	3.15E-01	3.15E-01
Pretreatment	Sulfuric Acid	2.98E-03	1.18E-08	3.16E-03	2.75E-03	1.41E-03	1.41E-03
	Ammonia	1.99E-03	1.39E-03	2.14E-03	8.86E-04	4.55E-04	4.55E-04
EH + FERM	CSL	2.32E-03	2.69E-03	2.38E-03	1.68E-03	1.58E-03	2.21E-03
	DAP	2.92E-04	3.42E-04	3.01E-04	2.07E-04	1.96E-04	2.79E-04
	Sorbitol	8.75E-05	1.03E-04	8.99E-05	6.15E-05	5.83E-05	8.29E-05
Enzyme Production	Glucose	5.64E-06	5.85E-06	6.00E-06	3.44E-06	2.30E-06	2.30E-06
	CSL	4.73E-04	4.91E-04	5.03E-04	2.88E-04	1.93E-04	1.93E-04
	Ammonia	2.26E-04	2.34E-04	2.40E-04	1.38E-04	9.20E-05	9.20E-05
	Host Nutrient	1.70E-04	1.76E-04	1.81E-04	1.04E-04	6.93E-05	6.93E-05
	Sulfur Dioxide	3.34E-05	3.47E-05	3.55E-05	2.04E-05	1.36E-05	1.36E-05
WWT	Caustic Soda	1.13E-02	6.82E-03	1.21E-02	4.05E-03	2.11E-03	2.07E-03
Other	Lime	1.89E-03	1.80E-03	1.99E-03	1.72E-03	9.00E-04	9.17E-04
	Well Water	2.99E-01	5.25E-01	2.79E-01	3.44E-01	0.00E+00	0.00E+00

Table A4. Cradle to Grave TRACI Impacts of Bioethanol from Cellulosic Feedstocks Made Using the NREL Biochemical Conversion Model and Gasoline per MJ (Daystar *et al.* 2015b)

Impact	Units	Pine	Eucalyptus	Natural Hardwood	Switchgrass	Sweet Sorghum No wash	Sweet Sorghum wash	Gasoline
Global Warming	kg CO2 eq	-5.91E-02	1.67E-02	2.75E-02	1.76E-02	5.86E-02	3.93E-02	9.32E-02
Acidification	H+ moles eq	-3.25E-02	6.52E-03	9.21E-03	3.37E-03	1.36E-02	7.98E-03	9.84E-03
Carcinogenic	kg benzene eq	4.48E-05	6.20E-05	6.25E-05	4.11E-05	5.76E-05	3.75E-05	6.23E-05
Non carcinogenic	kg toluene eq	1.22E+00	7.38E-01	7.15E-01	4.73E-01	4.31E-01	3.04E-01	1.39E+00
Respiratory effects	kg PM2.5 eq	-1.26E-04	2.31E-05	3.28E-05	1.45E-05	4.86E-05	3.02E-05	2.41E-05
Ozone depletion	kg CFC-11 eq	1.68E-04	7.41E-05	7.03E-05	8.20E-05	1.02E-04	7.56E-05	8.54E-06
Eutrophication	kg N eq	1.85E-09	1.02E-09	9.98E-10	5.20E-10	2.96E-10	2.09E-10	3.32E-12
Ecotoxicity	kg 2,4-D eq	2.88E-02	1.79E-02	1.68E-02	1.21E-02	1.07E-02	7.19E-03	3.86E-02
Smog	kg NOx eq	-1.44E-04	1.38E-04	1.57E-04	9.51E-05	1.86E-04	1.29E-04	1.34E-04

Table A5. GHG Emission Factors for Thermochemical Process Chemicals and Non-Wood Inputs (Daystar *et al.* 2015,a)

Material/Process	Units	Emission Factors	Kg CO_2 per MJ Bioethanol (HHV)
Magnesium oxide	kg CO_2/kg	3.77	1.42E-05
Olivine	kg CO_2/kg	3.92E-02	2.34E-05
Molybdenum	kg CO_2/kg	0.108	1.30E-05
Waste treatment	kg CO_2/kg	6.37E-07	8.77E-10
Landfill transportation	kg CO_2/tkm (30km)	0.129	6.93E-06
Landfill	kg CO_2/kg	2.45E-03	2.19E-07
Total chemical and waste GHG emissions			5.78E-05
% of fuel production GHG emissions			0.02%

Table A6. Alcohol Yields for Cellulosic Feedstocks using the NREL Thermochemical Conversion Process (Daystar *et al.* 2015a)

Units (l/OD tonne)	Hybrid Poplar	Loblolly	Eucalyptus	Unmanaged Hard-wood	Switchgrass
Ethanol	349	369	337	356	331
Propanol	62	65	60	63	59
Total Alcohol	441	466	425	449	418

Table A7. Environmental Impacts using TRACI Method for Cellulosic Ethanol Produced Using the NREL Thermochemical Conversion Pathway and Gasoline on a Cradle-to-Grave Basis (Daystar *et al.* 2015a)

	Unit	Pine	Eucalyptus	Unmanaged Hardwood	Switchgrass	Gasoline
Global Warming	kg CO2 eq	2.61E-02	2.17E-02	2.49E-02	3.24E-02	9.32E-02
Acidification	H+ moles eq	2.38E-03	9.44E-03	2.74E-03	2.66E-02	9.84E-03
Carcinogenics	kg benzene eq	3.14E-06	4.40E-06	1.77E-06	1.80E-05	6.23E-05
Non carcinogenics	kg toluene eq	3.52E-02	4.60E-02	3.58E-02	1.36E-01	1.39E00
Respiratory effects	kg PM2.5 eq	8.02E-06	6.59E-05	8.00E-06	1.90E-04	2.41E-05
Eutrophication	kg N eq	2.88E-06	1.09E-05	2.71E-06	5.08E-05	8.54E-06
Ozone depletion	kg CFC-11 eq	9.23E-11	1.49E-10	2.84E-11	9.60E-10	3.32E-12
Ecotoxicity	kg 2,4-D eq	1.23E-03	1.66E-03	9.89E-04	3.89E-03	3.86E-02
Smog	kg NOx eq	2.77E-04	3.06E-04	2.92E-04	3.25E-04	1.34E-04

Table A8. Normalizing Factors (Bare) and Weighting Factors for Different Stakeholder Groups (Modified from Gloria *et al*. 2007) (Daystar *et al.* 2015b)

	Average			
Impact category	All	Producer	User	LCA expert
Global warming potential	39.2	23.2	41.7	61.7
Acidification	4.1	5.8	5.6	1.2
Carcinogens	10.8	11.6	8.3	7.4
Non carcinogens	6.8	15.9	5.6	2.5
Respiratory affects	12.2	10.1	8.3	16.0
Ozone depletion	2.7	4.3	2.8	1.2
Eutrophication	8.1	11.6	8.3	3.7
Ecotoxicity	10.8	11.6	15.3	3.7
Smog	5.4	5.8	4.2	2.5

Note: The weighting factors developed by Gloria *et al*. (2007) were modified for this study removing fossil fuel use as TRACI2 did not track this parameter in SimaPro. The other impact categories were scaled accordingly to reflect this omission. Fossil fuel was tracked separately in the Fossil Fuel Use section.

Table A9. Impacts of a US Citizen Over a Course of a Year Used for Impact Normalization, Bare and Gloria 2006

Impact Category	Per Year per Capita	Total Normalized Value per Capita
Global Warming	kg CO2 eq	2.45E+04
Acidification	H+ moles eq	7.44E+03
Carcinogenics	kg benzene eq	2.58E-01
Non carcinogenics	kg toluene eq	1.47E+03
Respiratory effects	kg PM2.5 eq	7.63E+01
Ozone depletion	kg CFC-11 eq	3.11E-01
Eutrophication	kg N eq	1.80E+01
Ecotoxicity	kg 2,4-D eq	7.38E+01
Smog	kg NOx eq	1.21E+02

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