

Changing the Renewable Fuel Standard to a Renewable Material Standard: Bio-ethylene Case Study

SUPPORTING INFORMATION

I. Daniel Posen^{†‡}, W. Michael Griffin[†], H. Scott Matthews^{†‡} Inês L. Azevedo[†]*

Department of Engineering & Public Policy and Department of Civil & Environmental Engineering, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, Pennsylvania 15213.

*Corresponding author phone: (412) 268-2670; fax:(412) 268-3757; e-mail: daniel.posen@gmail.com

[†] Department of Engineering & Public Policy.

[‡] Department of Civil & Environmental Engineering

Number of pages: 55

Number of figures: 20

Number of tables: 19

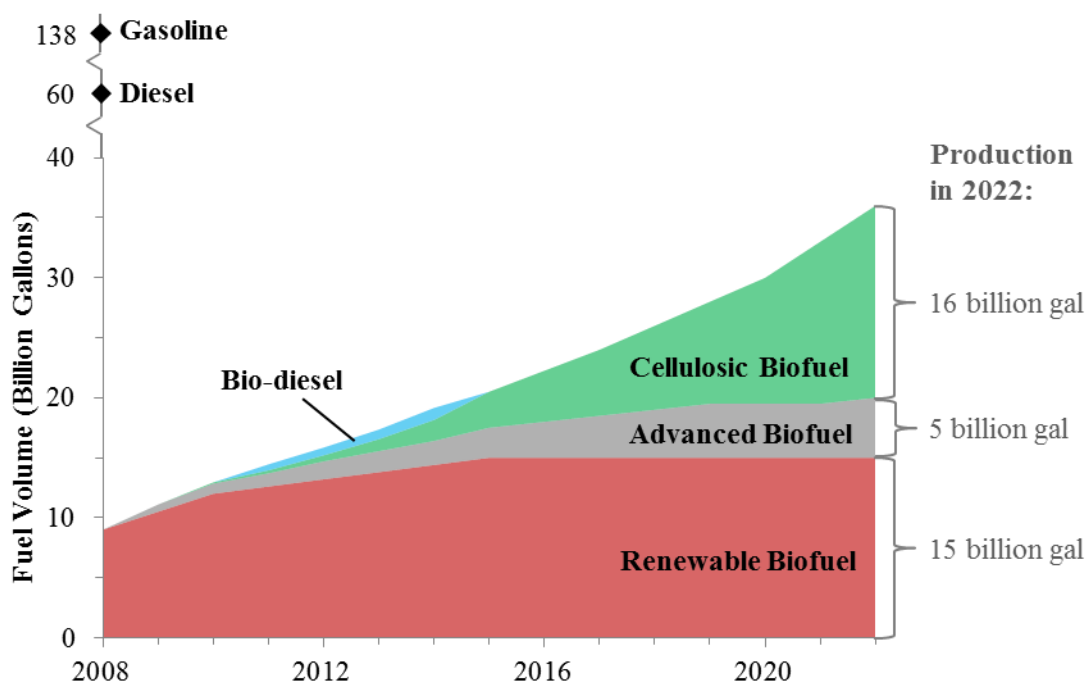
1. Supporting Information

Contents

1. Supporting Information	2
1.1 Additional Details Regarding RFS2	3
1.2 Model and Data	3
1.2.1 Allocation	3
1.2.2 Global Warming Potential	4
1.2.3 Fuels and Electricity	4
1.2.4 Natural Gas Pre-Production	5
1.2.5 Natural Gas Production	7
1.2.6 Natural gas processing	8
1.2.7 Steam Cracking	10
1.2.8 Ethanol Production	11
1.2.9 Ethanol Dehydration	12
1.2.10 Polymerization	12
1.2.11 Model Parameters	12
1.3 Results and Discussion	27
1.3.1 Summary Statistics	27
1.3.2 CDF of Net GHG Emissions	30
1.3.3 Bio-LDPE GHG Equivalence Factor	31
1.3.4 Cost Analysis	32
1.4 Importance analysis and sensitivity	35
1.4.1 Importance Analysis	35
1.4.2 Sensitivity to treatment of electricity:	39
1.4.3 Sensitivity to land use change	42
1.4.4 Sensitivity treatment of displaced fossil products	44
1.4.5 Sensitivity to other select assumptions	51
1.5 References	54

1.1 Additional Details Regarding RFS2

As explained in the main text, RFS2 targets increase annually until 2022 (see SI Figure 1). For years beyond 2022, targets are at the discretion of the Environmental Protection Agency in consultation with other government departments.



SI Figure 1. Renewable biofuel targets established under the Energy Independence and Security Act of 2007. ‘Renewable biofuel’ refers to any renewable source, ‘advanced biofuel’ refers to any renewable source other than corn starch and ‘cellulosic biofuel’ refers to fuel derived from cellulose, hemicelluloses or lignin. Reference gasoline and diesel production volumes are shown for 2008. Figure is adapted from (1).

1.2 Model and Data

1.2.1 Allocation

Production volumes for each natural gas co-product are established as follows. EIA reports annual production by state for dry natural gas (2), lease condensate (3), and combined natural gas plant liquids¹ (NGPLs) (4) as well as annual production of disaggregated NGPLs² by refining

¹ Data is by state of origin of the gas (as opposed to state of processing).

² Categories reported are: ethane, propane, isobutane, normal butane and pentanes plus.

district.³ The combined NGPLs from each state are assumed to be distributed among individual products in the same (volumetric) proportion as the refining district(s) to which that state belong(s). Unless otherwise specified, all data used in this paper pertains to reporting year 2011 (the most recent available data). Allocation is performed on a state by state basis and integrated into a discrete distribution for each process modeled, as discussed in the main text. Mass and energy densities of relevant substances can be found in SI Table 7.

1.2.2 Global Warming Potential

Whenever possible, GHG emissions were modeled explicitly by gas before conversion to CO₂ equivalent. For natural gas pre-production emissions (well pad construction, well drilling, hydraulic fracturing chemicals and water management) (5), and life-cycle emissions for fuels (6-8), only the total GWP was available. Emissions from natural gas used as fuel, fugitive CH₄ from production, liquids unloading, processing, transmission, distribution and combustion were modeled explicitly as per Venkatesh *et al.* (6) and used to update the life-cycle GHG estimate accordingly. No adjustment was made to the other inputs listed above.

1.2.3 Fuels and Electricity

As indicated in the main text, emissions from U.S. electricity production are modeled by North American Electric Reliability Corporation (NERC) region (9). For corn ethanol, the majority of existing ethanol biorefineries are located in the region spanned by the Midwest Reliability Organization (MRO) (10). For switchgrass, the EPA predicts production primarily in the regions spanned by the Southwest Power (SPP), the Texas Regional Entity (TRE) and the Southeast Electric Reliability Council (SERC) (11), and so it is assumed these are the regions where most switchgrass biorefineries will be located. Finally, the majority of existing ethylene production capacity is located in the region spanned by TRE and SERC (12). Due to difficulties in transporting ethylene gas and the large scale of existing chemical manufacturing complexes, it is assumed that bio-ethylene production and ethylene polymerization will take place near existing ethylene infrastructure (i.e. in TRE and SERC). For each region, multiple sources were consulted

³ Refining districts are subdivisions of petroleum administration for defense districts (PADDs).

and a uniform distribution was employed that spans the ranges of the different estimates. For aggregated regions, distribution bounds represent the extreme estimates for any of the constituent regions. For electricity consumption, emissions factors account for transmission line-losses; when grid electricity is displaced, it is assumed that line-losses still occur, resulting in lower emissions savings. Line losses are taken to be 5.8% for U.S activities (representative of the Eastern Interconnect) (13) and 16% for Brazil (14).

Electricity emissions factors employed in this paper are nominally for average electricity generation (15-19). Nevertheless, the range employed for each U.S. region encompasses the marginal electricity emissions factor for that region as reported by Siler-Evans *et al.*, after adjusting for line-losses and upstream emissions from coal and natural gas (6, 8, 13, 14). Following Liptow and Tillman (20), natural gas is assumed to be the marginal electricity source in Brazil; this is examined further in the sensitivity analysis below.

1.2.4 Natural Gas Pre-Production

Emissions (in CO₂e/unit gas produced) from well pad construction, well drilling, production of chemicals for hydraulic fracturing, and water management from fracturing employ the same inputs as Weber and Clavin (5) and are modeled as triangular distributions. The two distributions pertaining to hydraulic fracturing are multiplied (on a state by state basis) by the percentage of gross gas withdrawals that are from unconventional wells (2).

Weber and Clavin report their distributions as g CO₂e/MJ, which results from allocating all emissions to dry natural gas. These figures are converted to CO₂ emissions per unit volume assuming the same energy density as Weber and Clavin (35.95 MJ/m³) and then allocated across products (and normalized per unit mass of each product).

Further, for both conventional and unconventional wells, there is the potential for a release of fugitive natural gas emissions during the final pre-production phase (well completions) or from remedial operations to increase production (workovers). Well completions and workovers are

divided into 3 categories according to EPA nomenclature: conventional wells, unconventional⁴ wells (uncontrolled emissions) and unconventional wells (controlled emissions⁵) as outlined below.

Fugitive emissions from conventional completions and workovers are taken from 2010 revised estimates by EPA (21). These are coupled with conservative (low) estimates for well lifetime and an estimate of daily production from Venkatesh *et al.* (6) to obtain emissions per MMscf of gross withdrawals. Further, a conservative (high) number of workovers (1 per year) is assumed. Even with conservative assumptions in place, conventional well workovers and emissions amount to less than 1% of the total emissions from ethylene production and so the uncertainty was not characterized further.

For unconventional wells, potential emissions from uncontrolled completions or workovers are much higher and could have a large effect on the final results. Following a 2012 EPA background technical support document, an uncontrolled completion or workover is assumed to release a normally distributed volume of methane (22). This is converted to release of whole gas using the EPA assumed methane content of 83.24%. The result is coupled with a distribution for estimated ultimate recovery from Weber and Clavin (5) to normalize the emissions of whole gas per volume of gas produced. Finally, whole gas released is converted to emissions of methane and carbon dioxide per MMscf of production, assuming respective methane and carbon dioxide contents in each state equal to that of the hydraulically fractured wells in the National Energy Modeling System (NEMS) region (23) to which that state belongs⁶ (tables A-130 and A-139 of (24)). For reduced emission completions (RECs), it is assumed that 90% of flowback is captured (25); all other calculations are the same as for uncontrolled emissions. Finally, following Jiang *et al.* (26), a uniform distribution is assumed for the percent of released gas which is flared; flare efficiency is taken to be 98%. For the base case, EPA projects that, in the absence of regulations,

⁴ Following the U.S. EPA, unconventional wells are assumed to involve hydraulic fracturing, and include tight sand, shale, and coal bed methane formations. (21 p.84)

⁵ Controlled completions are also known as ‘green completions’ and ‘reduced emission completions’ (RECs)

⁶ For states that belong to multiple NEMS regions (Texas and New Mexico), CO₂ and CH₄ contents are modeled as uniform distributions across the values for the relevant regions.

51% of completions would be performed with reduced emissions in 2015 (22). However, current regulation requires flaring for all new completions, and green completions with flaring for all completions subsequent to January 2015. Simulating a ‘regulated scenario’ assuming 100% RECs, and 100% flaring had no noticeable effect on the final results.

For unconventional workovers, the well pad will already be fitted with appropriate gathering equipment, and so we assume that any refractures will be performed with reduced emissions as described above. Using various data sources, the U.S. EPA finds that the annual refracture rate among unconventional wells is approximately 1% (22). Although the number of workovers is likely positively correlated with the estimated ultimate recovery, employing a correlation parameter had little effect on the final results.

Workover and completion emissions are multiplied by the corresponding (conventional or unconventional) percent of gross withdrawals on a state by state basis for 2011 (2). Completion emissions from oil well completions are much smaller overall (25) and it is assumed that the portion allocated to the associated gas will be negligible.

1.2.5 Natural Gas Production

The annual EPA GHG Inventory provides data on CH₄ emissions from the natural gas production phase (24). From the 2013 EPA GHG Inventory, table A-124 is used to determine potential production emissions by NEMS region. Workovers and completions are removed, as these have been accounted for in the above pre-production analysis. Reductions by the Natural Gas STAR program (table A-132) and from other regulations (table 1-133) are allocated to each NEMS region in proportion to that region’s share of total emissions from the relevant category.⁷ Because production volumes are only known by state and some states (New Mexico and Texas) are covered by more than one region, it was necessary (for normalization by production volumes) to merge certain NEMS regions, leaving 3 regions in all: West Coast, North East and

⁷ For example, the North East region accounts for 33.5% of all potential emissions from Kimray pumps (table A-124), and so 33.5% of CH₄ reductions for Kimray pumps (Table A-132) are likewise attributed to the North East.

the combined Midcontinent, Rocky Mountains, Gulf Coast and South West region. EPA further reports uncertainty from -19% to +30% for CH₄ emissions from the entire natural gas system (27), for which field production is the single largest category (accounting for just over a third of system wide emissions). It is assumed that the relative uncertainty on production emissions within each region is on the same order as for system wide emissions, and so a triangular distribution is used for the emissions within each region. Production CH₄ emissions from each region are then normalized by gross withdrawals for all states within that region (2); These emissions are then allocated across products (and normalized per unit mass of each product) on a state by state basis.⁸ The overwhelming majority of CO₂ emissions from the natural gas production phase reported in the EPA GHG Inventory are from gas flaring, which has already been taken into account above using direct EIA data.

1.2.6 Natural gas processing

The following is an account of statistical methods that were used in analyzing the data from the EPA GHG inventory after matching with EIA processing flows.

Using ordinary least squares (OLS) regression of normalized emissions on plantflow confirms there is no overall trend for normalized emissions in function of plantflow ($p=0.12$) – suggesting that the data may be drawn from a static distribution. Visual inspection of the data (in tons CO₂e/MMcf processed) suggested a small number of outliers with abnormally high emissions. This is confirmed with a number of statistical tests, as described below.

In the end, the five points with the highest normalized emissions were removed from the dataset as they are believed to represent data errors rather than true heterogeneity in emissions. All such points were more than 3 times the interquartile range above the 75th percentile of the distribution. One of the outliers was driven by exceedingly high normalized CH₄ emissions – 4 times higher than the next highest entry and nearly 14 standard deviations above the mean.

⁸ Each state is assumed to have the same emission intensity as the region to which it belongs. Alaska, which is not part of any region, is assumed to have the same emission intensity as all regions combined (i.e. national emission intensity).

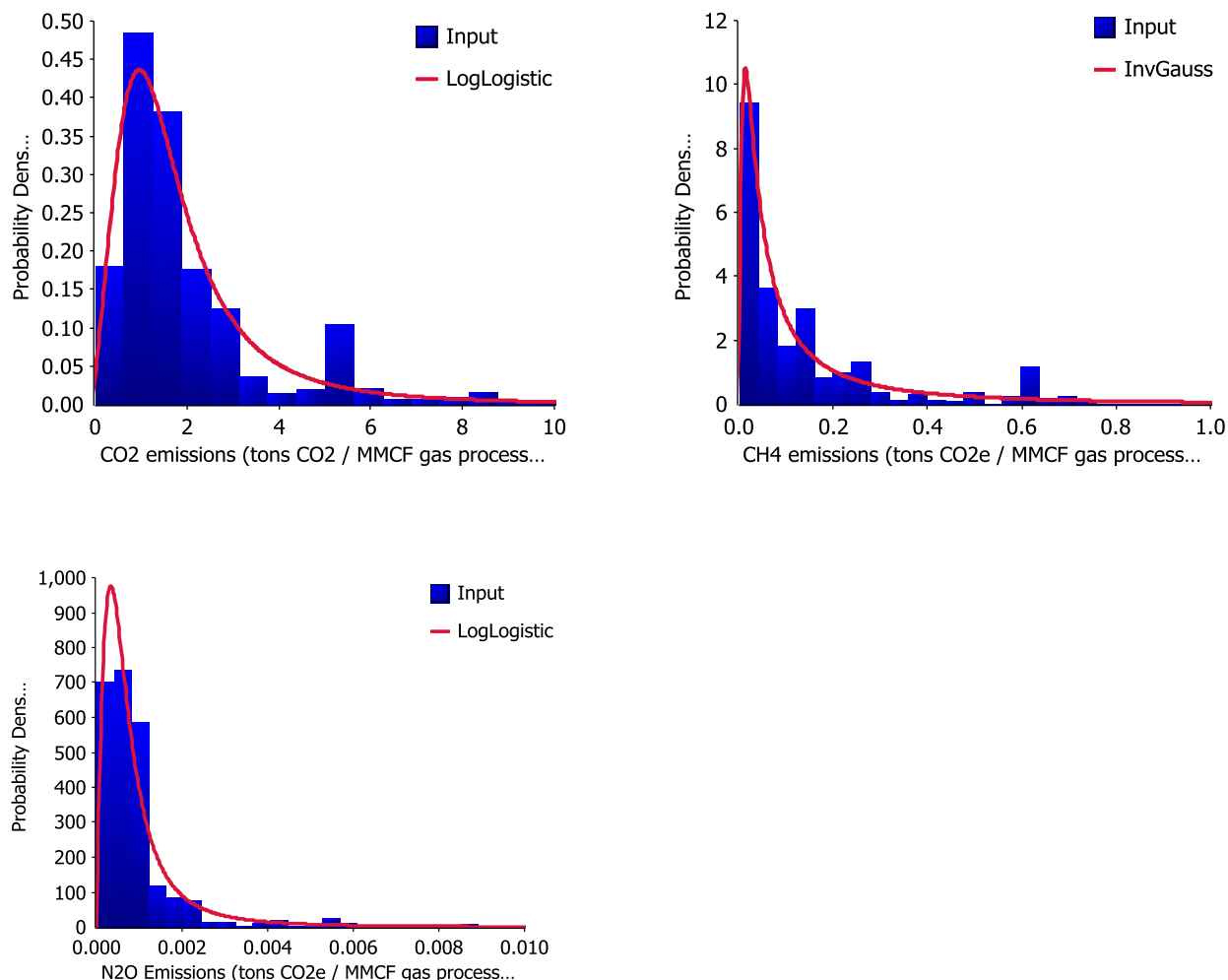
Initial attempts to fit the data suggested that a lognormal distribution would be appropriate, and indeed a Shapiro-Wilk test on the log-data (post-removal of outliers) does not reject the null hypothesis of normality at the 5% level. Thus, further tests were run on the natural logarithm of the normalized emissions. The remaining four suspected outliers are all greater than 1.5 times the interquartile range above the 75th percentile in the log data. Further all were beyond 3 standard deviations away from the mean, giving less than 0.3% chance they belong to the (assumed normal) distribution.

Of five eliminated outliers, three were for the lowest plantflows in the dataset (1.22, 1.7 and 2 MMcf/day), and the 4th was among the 11 smallest (9 MMcf/day). While it is possible that these results suggest a steep upward trend in normalized emissions for small plants, plants below the size of 9 MMcf/day account for less than 1% of all natural gas processing (according to the complete EIA dataset). A more likely explanation is that the facilities with low plant flow have processing as a secondary operation in a larger facility, thereby falsely inflating emission estimates for natural gas processing. The 5th outlier was close to average plant flow (145 MMcf/day), but had well below average utilization (21%), suggesting that the EIA reported plantflow may not be representative of the true processing flows for the (slightly mismatched) time period of the EPA reported emissions. Inclusion of all outliers would increase mean processing emissions by approximately 20%, which represents only a small (<2%) increase in life-cycle GHG emissions for LDPE.

Upon removal of the outliers OLS regression of normalized emissions on plantflow now predicts a significant downward trend in normalized emissions in function of plantflow, but with an absolute coefficient so small as to be irrelevant.

Through a series of OLS regressions and Goldfeld-Quandt tests for heteroskedasticity, it is determined that the variance of total emissions increases approximately linearly with plant flow; this result is as expected if one imagines total emissions in each plant to be the result of a sum of emissions from multiple discrete unit plant flows for that plant.

Normalized emissions of greenhouse gases for each plant are then used to fit continuous distributions (weighted by the plant flow for each facility) as shown in SI Figure 2. This has the advantage of accounting for the fact that larger plants yield more efficient estimates for normalized emissions. To the extent that normalized emissions may not actually be constant with increasing plant size, this method will also weight each observation in proportion to the likelihood that gas was processed at the corresponding plant.



SI Figure 2. Input data (histogram) and fitted distributions for emissions from natural gas processing

1.2.7 Steam Cracking

Specific energy requirements (lower heating value) for the production of a ton of ethylene via steam cracking of ethane are estimated by a number of sources (28-30). The ranges given are

very similar, and are used as the parameters of a uniform distribution. The resulting distribution is renormalized per ton of ethane input using the stochastic output of ethylene determined below.

Volumes for each product resulting from steam cracking ethane are also given by a variety of sources (28-32). Production volumes from each source are normalized to 1 ton of ethane input (using the stochastic distribution for product losses across sources if the original value is given only as a ratio of products). From these estimates are formed distributions for each product (triangular if there is a modal clustering across sources, or uniform otherwise). Since product/loss draws are performed independently, there is no guarantee of mass balance; all products (and losses) are scaled equivalently to restore mass balance for each Monte Carlo draw.

It is assumed that methane, C4 components (i.e., butanes) and C5/C6 (i.e., pentanes, hexanes) components are all used to power the steam cracking process. Combustion is assumed to be complete, and so CO₂ emissions are determined stoichiometrically for each product. Lower heating values for each component (SI Table 7) are used to determine the quantity of energy provided. Any residual energy needs are assumed to be provided by natural gas, with a stochastic life-cycle emission factor set to approximate the results reported by Venkatesh et al. (6). Finally, direct CH₄ emissions are modeled as reported by the IPCC GHG guidelines (33).

1.2.8 Ethanol Production

Sugarcane ethanol is co-produced with electricity from the combustion of bagasse. Seabra *et al.* (34) report both co-production of electricity and an additional quantity of bagasse which they assume displaces fuel oil. This paper takes a more conservative approach assuming that this additional bagasse is instead used for electricity generation, which is in line with existing trends toward greater electricity export from ethanol mills (34). This produced bagasse is assumed to have a moisture content of 50% (19); electricity generation is assumed to take place with a LHV efficiency of 30% (35) and to displace Brazilian grid electricity.

1.2.9 Ethanol Dehydration

Following Liptow and Tillman (36), modeled emissions from ethanol dehydration to ethylene are limited to fuel and electricity use reported by Kochar *et al.*(37) for polymer grade bio-ethylene. As no other published estimates are readily available, generic uncertainty factors were applied. Following Geisler *et al.* (38), both fuel and electricity requirements were assumed to follow a lognormal distribution with dispersion factor (ratio of 97.5th percentile to the median) of 2, which is typical of the uncertainty in energy requirements for chemical production.

1.2.10 Polymerization

For U.S. pathways, polymerization is modeled using average U.S. industry data as reported by Franklin Associates (39). Grid electricity, natural gas, LPG and residual oil are treated on a life-cycle basis. Following the recommendation of Franklin Associates, recovered energy from waste gas is treated as LPG (excluding upstream emissions) with combustion emissions as in Venkatesh *et al.* (7); for bio-based pathways, waste gases are assumed to be biogenic (no net emissions). Primary energy for electricity cogeneration is divided between natural gas (59%), coal (28%) and waste gases (13%) as reported by Franklin Associates; these percentages were used in a probability mixture model as the probabilities for each fuel type (drawn from a discrete distribution).

Following Liptow and Tillman, polymerization in Brazil is assumed to follow European parameters (20, 36), involving higher electricity use and lower on-site fuel use than in the United States (36, 40). Due to the low emissions factor for Brazilian electricity, this results in relatively low emissions for Brazilian polymerization, consistent with the values reported by Kikuchi *et al.*(41).

1.2.11 Model Parameters

The following tables present a list of the key parameters for each of the models developed in this paper. SI Table 1 shows parameters specific to the production of ethylene from natural gas derived ethane. SI Table 2 shows parameters specific to the production of ethanol from U.S. corn

starch. SI Table 3 shows parameters specific to the production of ethanol from U.S. switchgrass. SI Table 4 shows parameters specific to the production of ethanol from Brazilian sugarcane. SI Table 5 shows parameters for life-cycle stages that are common across models. SI Table 6 shows employed global warming potentials along with emission factors for fuels, electricity and agrochemicals. SI Table 7 shows the energy and mass densities used throughout this paper.

SI Table 1. Summary of key parameters for ethylene production pathway via natural gas derived ethane

Parameter	Value or distribution	Units	Source
<i>Pre-Production</i>			
Well pad construction	Triangular (0.05, 0.13, 0.3)	g CO ₂ e/MJ	(5)
Well Drilling	Triangular (0.1, 0.2, 0.4)	g CO ₂ e/MJ	(5)
Hydraulic Fracturing Chemicals	Triangular (0.04, 0.23, 0.5)	g CO ₂ e/MJ	(5)
Hydraulic Fracturing Water Management	Triangular (0.04, 0.07, 0.1)	g CO ₂ e/MJ	(5)
Gas venting for conventional well completions	0.71	tons CH ₄ /completion	(21)
Gas venting for conventional well annual workovers	0.05	tons CH ₄ /workover	(21)
Conventional well workovers	1	workover/year	(6)
Operating Lifetime of Conventional well	5	Years	(6)
Daily production for conventional well	0.15	MMscf/day	(6)
Uncontrolled gasvented/flared for unconventional completions and workovers	Normal (8900,2006067)	Mcf “CH ₄ ”/completion	(22)
Unconventional Well Estimated Ultimate Recovery	Triangular (0.5, 2, 5.3)	Bcf	(5)
Flowback Captured in Reduced Emission Completions	90%	%	(25)
Percent of released gas which is flared	Uniform (51,100) (100% for regulated scenario)	%	(26) (42)
Flare Efficiency	98%	%	(26)
Number of refractures per unconventional well	Bionomial (p = 0.01, n= 30)	#	(22) for p (43) for n
Green Completion Percentage	51% 100% (for regulated scenario)	%	(22) (42)
Conventional and unconventional percent of growth withdrawals	State by state	%	(2)
2011 CO ₂ and CH ₄ content in raw natural gas	By NEMS region for each state	%	(24) (data from 2011 reporting year)

<i>Production</i>																			
Lease Fuel Consumed	State by state (discrete distribution)	MMcf/year	(44) (data from 2011 reporting year)																
Gas Vented and Flared	State by state (discrete distribution)	MMcf/year	(2) (data from 2011 reporting year)																
Production CH ₄ Emissions	Triangular (.81*best, best, 1.30*best) by (aggregated) NEMS region(s)	Mg CH ₄ /year	(24) (data from 2011 reporting year)																
<i>Processing</i>																			
CO ₂ Emissions	Log-logistic(-0.089,1.59,2.28) (truncated at 0)	tons CO ₂ /MMcf processed	Own Analysis of (45, 46)																
CH ₄ Emissions	Inverse Gaussian (0.00880,0.00284,-0.000287) (truncated at 0)	tons CH ₄ /MMcf processed	Own Analysis of (45, 46)																
N ₂ O Emissions	Log-logistic (9.08*10 ⁻¹⁰ , 2.12*10 ⁻⁶ , 1.66) (truncated at 0)	tons N ₂ O/MMcf processed	Own Analysis of (45, 46)																
Correlation Matrix for processing emissions	<table border="1"> <tr> <td></td><td>CO₂</td><td>CH₄</td><td>N₂O</td></tr> <tr> <td>CO₂</td><td>1</td><td></td><td></td></tr> <tr> <td>CH₄</td><td>0.36</td><td>1</td><td></td></tr> <tr> <td>N₂O</td><td>-0.03</td><td>-0.05</td><td>1</td></tr> </table>		CO ₂	CH ₄	N ₂ O	CO ₂	1			CH ₄	0.36	1		N ₂ O	-0.03	-0.05	1	N/A	Own Analysis of (45, 46)
	CO ₂	CH ₄	N ₂ O																
CO ₂	1																		
CH ₄	0.36	1																	
N ₂ O	-0.03	-0.05	1																
<i>Steam Cracking</i>																			
Specific Energy Required	Uniform (15,25)	GJ/t ethylene	(28-30)																
Ethylene Produced	Triangular (764, 803, 840)	kg/ton ethane	(28-32)																
Propylene Produced	Triangular (14.1, 16, 29.9)	kg/ton ethane																	

Butadiene Produced	Triangular (17.4, 19.9, 23)	kg/ton ethane	
Aromatics Produced	Uniform (0, 19.9)	kg/ton ethane	
Hydrogen Produced	Triangular (57.9, 60, 89.7)	kg/ton ethane	
Methane Produced	Triangular (58.8, 61, 70.1)	kg/ton ethane	
C4 Components Produced	Triangular (0, 6, 8.1)	kg/ton ethane	
C5 and C6 Components Produced	Uniform (0, 26)	kg/ton ethane	
Product Losses	Uniform (5, 20)	kg/ton ethane	
Emissions from Hydrogen Production via steam reforming (for system expansion)	Uniform (9.3, 14.2) ^a	kg CO ₂ e/kg H ₂	Multiple sources consulted. Lower bound from (47) as cited in SimaPro software. Upper bound from (19)
Direct CH ₄ emissions from ethane cracker	Triangular (5.45, 6, 6.6)	kg CH ₄ /t ethylene	(33)

Distributions are written as: Triangular (lower, mode, upper), Normal (mean, standard deviation), Uniform (lower, upper), Binomial (p = probability of event, n = number of draws), Log-Logistic (location, scale, shape), Inverse Gaussian (mean, shape, shift)

(a) Mean bounds are shown. Actual bounds are stochastic due to uncertainty in GWP.

SI Table 2. Summary of key parameters for ethanol/ethylene production pathway via U.S. Corn Starch

Parameter	Value or Distribution	Units	Source
<i>Land-use Change</i>			
Domestic Land Use Change	-4	kg CO ₂ e/mmBtu	(11)
International Land Use Change	Triangular (20.9, 31.8, 44.7)	kg CO ₂ e/mmBtu	Fit to confidence interval given by (11)
<i>Agricultural Operations</i>			
Corn Yield	Beta ($\alpha=21.62$, $\beta=5.86$, [0,14.3])	Mg dm/ha	(48)
Nitrogen Application	Triangular (141, 150, 160)	kg N / ha	(49) as cited in (48)
Crop residue applied	Triangular (73, 80, 86)	kg N / ha	From (50) as modeled by (48)
CaCO ₃ applied	1150	g / bushel	(19)
K ₂ O applied	172	g / bushel	(19)
P ₂ O ₅ applied	148	g / bushel	(19)
Herbicides applied	4.75	g / bushel	(19)
Insecticides applied	0.4	g / bushel	(19)
Fossil Fuel Use	894 1.97 0.023	g CO ₂ / bushel g CH ₄ / bushel g N ₂ O / bushel	(19)
Dry matter fraction of bushel	87%	%	(50)
<i>Ethanol Production</i>			
Corn starch content	Triangular(62.6, 67.3 ,72)	%w of dry matter	(51) and (52) as used in (48)
Heat input	Triangular (0.32, 0.42, 0.51)	MJ heat / MJ EtOH	(51, 53, 54) as cited in (48)
Electricity input	Triangular (0.023,0.038,0.049)	MJ elec/MJ EtOH	
Co-product credit	7.4	g CO ₂ /MJ EtOH	(19)

	0.017 0.018	g CH ₄ /MJ EtOH g N ₂ O / MJ EtOH	
Transportation			
Feedstock transportation	434 0.549 0.007	g CO ₂ / bushel g CH ₄ / bushel g N ₂ O / bushel	(19)
Trucking distance for ethanol to ethylene plant	Uniform(1000,1800)	km	Approximate distance from existing corn ethanol refineries (10) to gulf states ethylene infrastructure (12).
Truck fuel consumption	0.0203	L diesel / t-km	(55)

Distributions are written as: Triangular (lower, mode, upper), Normal (mean, standard deviation), Uniform (lower, upper), Beta (α , β , [lower bound, upper bound]).

SI Table 3. Summary of key parameters for ethanol/ethylene production pathway via U.S. Switchgrass

Parameter	Value or Distribution	Units	Source
<i>Land-use Change</i>			
Domestic Land Use Change	-2.5	kg CO ₂ e/mmBtu	(11)
International Land Use Change	Triangular (7.9, 15.1, 23.7)	kg CO ₂ e/mmBtu	Fit to confidence interval given by (11)
<i>Agricultural Operations</i>			
Switchgrass Yield	Beta ($\alpha=21.62$, $\beta=5.86$, [0,21.6])	Mg dm / ha	(48)
Nitrogen Application	Triangular (55, 74, 100)	kg N/ ha	(56, 57) as cited in (48)
Crop Residue Applied	Triangular (133.5, 171.7, 210)	kg N / ha	From (50) as modeled by (48)
K ₂ O Applied	227	g / ton dm	(19)
P ₂ O ₅ Applied	114	g / ton dm	(19)
Herbicide	31.8	g / ton dm	(19)
Fossil Fuel Use	20.7 0.314 26.7	g CO ₂ / kg SW g N ₂ O / kg SW g CH ₄ / kg SW	(19)
<i>Ethanol Production</i>			
Glucan Content	Triangular (31, 34.4, 37.2)	% w	(58) as cited in (48)
Xylan Content	Triangular (20.6, 23.0, 26.0)	% w	
Mannan Content	Triangular (0.29, 0.32, 0.36)	% w	
Galactan Content	Triangular (0.67, 1.0, 1.2)	% w	
Arabinan Content	Uniform (2.6, 3.4)	% w	
Lignin Content	Triangular (17.3, 19.2, 21.1)	% w	
Energy Input	Uniform (0.44, 0.72)	MJ / MJ EtOH (treated as HHV)	(59, 60) as cited in (48)
Percent of energy to electricity, heat	10% / 90%		
Boiler efficiency	68%		
Turbine Efficiency	85%		

<i>Transportation</i>			
Feedstock Transportation	15	g CO ₂ e/ kg SW	Calculated from (19)
Trucking distance for ethanol to ethylene plant	Triangular (0,1000,1500)	km	Approximate distance from projected switchgrass ethanol facilities (11) to gulf states ethylene infrastructure (12)
Truck fuel consumption	0.0203	L diesel / t-km	(55)

Distributions are written as: Triangular (lower, mode, upper), Normal (mean, standard deviation), Uniform (lower, upper), Beta (α , β , [lower bound, upper bound]).

SI Table 4. Summary of key parameters for ethanol/ethylene production pathway via Brazilian Sugarcane

Parameter	Value or Distribution	Units	Source
<i>Land-use Change</i>			
Land-use change (total)	Triangular (-5.8, 4.3,13)	g CO ₂ e/MJ EtOH	Fit to confidence interval given by (11)
<i>Agricultural Operations</i>			
Harvest Yield	Normal(86.7,13.4)	t cane / ha	(34)
Diesel Consumption	Normal (274,75)	L diesel /ha	(34)
Nitrogen Application	Triangular (39, 777, 1515)	g N/t cane	(34)
CaCO ₃ applied	Triangular (162,5183,13755)	g / t cane	(34)
K ₂ O applied	980	g / t cane	(19)
P ₂ O ₅ applied	249	g / t cane	(19)
Herbicides applied	44	g / t cane	(19)
Insecticides applied	3	g / t cane	(19)
Trash burning	Triangular (3,82,126)	kg CO ₂ e/t cane	(34)
Emissions from Trash Burning	113	g CO ₂ e / kg straw	(19)
<i>Ethanol Production</i>			
Ethanol yield	Normal (81.1, 4.3)	L EtOH/ t cane	(34)
Surplus Electricity	Exponential (10.7)	kWh/t cane	(34)
Surplus Bagasse	Exponential (8.7)	kg/t cane	(34)
Bagasse moisture content	50%	%	(19)
Bagasse boiler LHV Efficiency	30%	%	(35)
<i>Transportation</i>			
Field to ethanol mill, fuel use	10300	kcal diesel/t cane	(61) as cited in (36)
Ethanol to ethylene plant, fuel use	0.217	MJ diesel / kg ethanol	(36)
Shipping distance, Brazil (Parangua) to U.S. (Houston)	10700	Km	(62)
Ship fuel consumption (Ocean Freighter)	4.93 *10 ⁻³	L residual fuel oil/t-km	(63)

Distributions are written as: Triangular (lower, mode, upper), Normal (mean, standard deviation), Uniform (lower, upper), Exponential (mean).

SI Table 5. Summary of key parameters for processes which are common across models

Parameter	Value	Units	Source
Ethanol Production (used for switchgrass and corn)			
Hydrolysis yield	Uniform (0.85, 0.95)	%	(64) as cited in (48)
Fermentation yield from glucose	Uniform (0.85, 1)	%	
Fermentation yield from other sugars	Uniform (0.75, 0.9)	%	
Ethanol Fuel Distribution			
Emissions from fuel distribution	1.2	g CO ₂ e/MJ	Calculated from (19)
Ethanol dehydration to ethylene			
Ethylene yield	0.58	kg ethylene / kg ethanol	Calculated from (37)
Fuel used	Lognormal (1.67, 0.611)	MJ /kg ethylene (Assumed to be LHV)	Mean from (37); standard deviation calculated based on (38)
Electricity Used	Lognormal (1.12, 0.41)	MJ electricity/ kg ethylene	Mean from (37); standard deviation calculated based on (38)
U.S. Polymerization (used for switchgrass and corn)			
Fuel for electricity cogeneration	5.66	MJ HHV / kg LDPE	(39)
Natural gas (additional)	2.02	MJ HHV / kg LDPE	(39)
LPG	9.64*10 ⁻⁴	MJ HHV/ kg LDPE	(39)
Residual oil	0.064	MJ HHV / kg LDPE	(39)
Recovered energy	0.4	MJ HHV / kg LDPE	(39)
Brazilian Polymerization (used for sugarcane only)			
Electricity required	Uniform (3.4,4.0)	MJ electricity / kg LDPE	Lower bound calculated based on (65) as per (36). Upper bound from

			(40).
Emissions from fuel use: <i>estimate 1</i>	57 1.9 6.5×10^{-4}	g CO ₂ / kg LDPE g CH ₄ / kg LDPE g N ₂ O / kg LDPE	Calculated from (65) as per (36).
Emissions from fuel use: <i>estimate 2</i> (net heat required; treated as natural gas)	-0.25	MJ HHV / kg LDPE	(40) for energy required; emissions calculated as per SI Table 6
Emissions from fuel use: total	Uniform (<i>estimate 2, estimate 1</i>)	g CO ₂ e/kg LDPE	Calculated from (65) as cited in (36)

Distributions are written as: Uniform (lower, upper), lognormal (mean, standard deviation)

SI Table 6. Global warming potentials and emission factors for fuels, electricity and agrochemicals

Parameter	Value	Units	Source
<i>Global warming potentials</i>			
CH ₄ GWP	Normal (36, 8.5)	g CO ₂ e / g CH ₄	(66, 67)
N ₂ O GWP	Normal (298, 52.5)	g CO ₂ e / g N ₂ O	
<i>Fuel Emissions</i>			
Gasoline life-cycle emissions	Log-logistic (2.2, 0.2, 80)	g CO ₂ e/MJ (LHV)	(7)
Diesel life-cycle emissions	Log-logistic (2.3, 0.2, 82)	g CO ₂ e/ MJ (LHV)	
Residual fuel life-cycle emissions	Log-logistic (2.3, 0.3, 83)	g CO ₂ e/ MJ (LHV)	
LPG life-cycle emissions	Log-logistic (2.1, 0.2, 77)	g CO ₂ e/ MJ (LHV)	
LPG combustion emissions	Triangular (66.7, 68.4, 71.2)	g CO ₂ e/ MJ (LHV)	
Natural gas life-cycle emissions (prior to updating GWP)	Normal (66, 3.5)	g CO ₂ e/MJ (HHV)	Approximate fit to parameters from (6);
Natural gas CH ₄ and N ₂ O emissions (for updated GWP)	Various	Various	See (6)
Natural gas life-cycle emissions (after updating GWP)	Normal (70, 5.0) Normal (78, 5.5)	g CO ₂ e/MJ (HHV) g CO ₂ e/MJ (LHV)	Fit to modeled distribution based on (6)
Coal life-cycle emissions	Log-logistic (3.05, 0.14, 74)	g CO ₂ e/ MJ (HHV)	(8)
<i>Electricity Emissions</i>			
Brazilian electricity (average)	Uniform (20, 81) ^a	g CO ₂ e/MJ	Lower bound from (19). Upper bound from (18)
Brazilian electricity (marginal): Natural gas turbine	Uniform (179, 207) ^a	g CO ₂ e/MJ	Lower bound from (19). Upper bound from (68) and (69) as cited in (20) SI.
MRO electricity	Uniform (200, 313) ^a	g CO ₂ e/MJ	Lower bound from (19). Upper bound from (16)
TRE and SERC electricity	Uniform (164, 220) ^a	g CO ₂ e/MJ	Lower bound from (19) for TRE. Upper bound from (15).

TRE, SERC and SPP electricity	Uniform (164, 308) ^a	g CO ₂ e/MJ	Lower bound from (19) for TRE. Upper bound from (17)
Agrochemicals			
U.S. production of CaCO ₃	0.0137 ^a	kg CO ₂ e / kg CaCO ₃	Calculated from (19)
U.S. production of K ₂ O	0.688 ^a	kg CO ₂ e / kg K ₂ O	
U.S. production of P ₂ O ₅	1.83 ^a	kg CO ₂ e / kg P ₂ O ₅	
Brazilian production of CaCO ₃	0.0205 ^a	kg CO ₂ e / kg CaCO ₃	
Brazilian production of K ₂ O	0.371 ^a	kg CO ₂ e / kg K ₂ O	
Brazilian production of P ₂ O ₅	0.630 ^a	kg CO ₂ e / kg P ₂ O ₅	
Corn Herbicides	21.4	kg CO ₂ e / kg herbicide	
Corn Insecticides	25.0	kg CO ₂ e / kg insecticide	
Switchgrass Herbicides	21.3	kg CO ₂ e / kg herbicide	
Switchgrass Insecticides	25.0	kg CO ₂ e / kg insecticide	
Sugarcane Herbicides	15.6	kg CO ₂ e / kg herbicide	
Sugarcane Insecticides	18.0	kg CO ₂ e / kg insecticide	
Direct CO ₂ emissions from CaCO ₃	0.44	kg CO ₂ / kg CaCO ₃	Calculated
Direct N ₂ O from synthetic fertilizer and crop residue	Triangular (0.003, 0.01, 0.03)	kg N ₂ O-N/kg N applied	(50)
Volatilization from synthetic fertilizer	Triangular (0.03, 0.1, 0.3)	(kg NH ₃ -N + kg NO _x -N) / kg N	
Indirect N ₂ O from volatilized N	Triangular (0.002, 0.01, 0.05)	kg N ₂ O-N / (kg NH ₃ -N + kg NO _x -N)	
Runoff/Leaching of N from synthetic fertilizer and crop residue	Triangular (0.1, 0.3, 0.8)	kg N runoff / kg N applied	
Indirect N ₂ O from runoff	Triangular (0.0005, 0.0075, 0.025)	kg N ₂ O-N/kg N runoff	

Distributions are written as: Triangular (lower, mode, upper), Normal (mean, standard deviation), log-logistic (location of the underlying logistic, scale of the underlying logistic, shift)

(a) Mean values (point estimate or distribution bounds) are shown. Actual values are stochastic due to uncertainty in GWP.

SI Table 7. Energy and mass densities used throughout this paper.

<u>Liquids</u>			
Item	LHV Energy Density (btu/gal)	HHV Energy Density (btu/gal)	Mass Density
Gasoline	112,194 ^a	120,439 ^a	2,836 ^a g/gal
Diesel/distillate, etc.	128,450 ^a	137,380 ^a	3,167 ^a g/gal
Residual Fuel Oil	140,353 ^a	150,110 ^a	3,752 ^a g/gal
Ethanol	76,330 ^a	84,530 ^a	2,988 ^a g/gal
Ethane (liquefied)	-	-	546.5 ^d kg/m ³
Propane (liquefied)	84,250 ^a	91,330 ^b	582 ^d kg/m ³
<i>n</i> -Butane (liquefied)	94,970 ^a	103,000 ^b	601.4 ^d kg/m ³
Isobutane (liquefied)	90,060 ^a	94,620 ^b	593.4 ^d kg/m ³
Pentanes plus	-	110,000 ^b	651 ^c kg/m ³
<i>n</i> -Hexane	105,125 ^a	-	655 ^a kg/m ³
<u>Gasses</u>			
Item	LHV Energy Density (btu/ft ³)	HHV Energy Density (btu/ft ³)	Mass Density
Natural gas	983 ^a	1,089 ^a	22 ^a g/ft ³
Methane	962 ^a	1,068 ^a	20.3 ^a g/ft ³
Hydrogen	290 ^a	343 ^a	2.55 ^a g/ft ³
<u>Solids</u>		<u>Solids</u>	
Item	HHV Energy Density (MJ/kg)	Item	HHV Energy Density (MJ/kg)
Glucan/Cellulose	16.9 ^e	Glucose	15.6 ^f
Xylan	17.4 ^e	Xylose	15.6 ^f
Mannan	16.6 ^e	Mannose	15.6 ^f
Galactan	17.2 ^e	Galactose	15.5 ^f
Arabinan	16.9 ^e	Arabinose	15.6 ^f
Lignin	25.1 ^e	Non-sugar, non- lignin switchgrass components	11.8 ^e
Sugarcane Bagasse	14.4 ^e (LHV)		

(a) Data from Wang 2013 (19)

(b) Calculated from (70)

(c) Calculated using composition data from (71) and standard density information

(d) Liquid density at boiling point (kg/m³) from (72)

(e) Calculated from (59)

(f) (73)

1.3 Results and Discussion

1.3.1 Summary Statistics

The following tables present summary statistics for 10,000 simulations of each of the pathways modeled in this paper. For the tables in this section, “lower 90% CI” and “upper 90% CI” is constructed as a percent of model runs, and should not be interpreted as a traditional statistically based confidence interval.

SI Table 8. Summary Statistics for the GHG emissions from the life cycle stages for production of LDPE from natural gas derived ethane in the U.S.

Life-cycle Stage	Mean (kg CO ₂ e/kg LDPE)	Standard Deviation	Coefficient of Variation	Lower 90% CI	Upper 90% CI
Pre-Production	0.04	0.01	0.26	0.03	0.06
Production	0.27	0.09	0.34	0.17	0.37
Processing	0.13	0.16	1.26	0.02	0.33
Steam Cracking	0.65	0.27	0.42	0.20	1.10
Polymerization	0.74	0.08	0.11	0.64	0.87
Ethylene Subtotal	1.1	0.34	0.31	0.58	1.6
LDPE Total	1.8	0.35	0.20	1.3	2.4
Fitted Distribution	Log-logistic (location = 1.04, scale = 2.84, shape = 14.8)				

SI Table 9. Summary Statistics for the GHG emissions from the life cycle stages for production of U.S. corn ethanol fuel

Life-cycle Stage	Mean (g CO ₂ e/MJ)	Standard Deviation	Coefficient of Variation	Lower 90% CI	Upper 90% CI
LUC	27	4.6	0.17	19	35
Corn Farming	43	9.8	0.23	30	61
Co-Product Credits	-13	0.9	-0.07	-14	-12
Ethanol Production	35	4.7	0.13	27.7	43
Transportation	4.0	0.2	0.05	3.7	4.3
Ethanol Fuel Total	97	12	0.12	79	120
Fitted Distribution	Gamma (shape = 17.3, scale = 2.77, shift = 48.8)				

SI Table 10. Summary Statistics for GHG emissions from the life cycle stages for production of U.S. corn LDPE

Life-cycle Stage	Mean (kg CO ₂ e/kg LDPE)	Standard Deviation	Coefficient of Variation	Lower 90% CI	Upper 90% CI
LUC	1.3	0.22	0.17	0.91	1.6
Corn Farming	2.0	0.46	0.23	1.40	2.9
Co-Product Credits	-0.61	0.04	-0.07	-0.68	-0.54
Ethanol Production	1.7	0.22	0.13	1.3	2.0
Ethanol Dehydration	0.34	0.09	0.28	0.21	0.51
Polymerization	0.71	0.08	0.11	0.62	0.85
Transportation	0.31	0.03	0.10	0.26	0.36
EOL (growth credit)	-3.1	-	-	-	-
LDPE Total	2.6	0.57	0.22	1.7	3.6
Fitted Distribution	Gamma (shape = 21.0, scale = 0.123, shift = -0.0209)				

SI Table 11. Summary Statistics for the GHG emissions from the life cycle stages for production of U.S. switchgrass ethanol fuel

Life-cycle Stage	Mean (g CO ₂ e/MJ)	Standard Deviation	Coefficient of Variation	Lower 90% CI	Upper 90% CI
LUC	12	3.1	0.25	7.4	18
Switchgrass farming	12	2.8	0.24	8.2	17
Ethanol production & electricity credit	-45	24	-0.52	-87	-9.4
Transportation	3.2	0.1	0.04	3.1	3.4
Ethanol fuel Total	-18	23	-1	-59	18
Fitted Distribution	Weibull (shape = 6.18, scale = 135, shift = -143)				

SI Table 12. Summary Statistics for the GHG emissions from the life cycle stages for production of U.S. switchgrass LDPE

Life-cycle Stage	Mean (kg CO ₂ e/kg LDPE)	Standard Deviation	Coefficient of Variation	Lower 90% CI	Upper 90% CI
LUC	0.58	0.14	0.25	0.35	0.83
Switchgrass Farming	0.57	0.13	0.24	0.38	0.81
Ethanol Production & electricity credit	-2.1	1.1	-0.52	-4.1	-0.44
Ethanol Dehydration	0.34	0.09	0.28	0.21	0.51
Polymerization	0.71	0.08	0.11	0.62	0.85
Transportation	0.20	0.04	0.20	0.13	0.26
EOL (growth credit)	-3.1	-	-	-	-
LDPE Total	-2.9	1.1	-0.39	-4.9	-1.2
Fitted Distribution	Weibull (shape = 5.64, scale = 5.90, shift = -8.34)				

SI Table 13. Summary Statistics for the GHG emissions from the life cycle stages for production of Brazilian sugarcane ethanol fuel

Life-cycle Stage	Mean (g CO ₂ e/MJ)	Standard Deviation	Coefficient of Variation	Lower 90% CI	Upper 90% CI
LUC	4	3.7	1.0	-2.6	10
Sugarcane farming	20	4.5	0.23	13	28
Ethanol production & electricity credit	-1.4	1.3	-0.9	-3.8	-0.20
Transportation	11	0.65	0.06	11	12
Ethanol fuel Total	33	6.0	0.18	24	43
Fitted Distribution	Normal (mean = 33.3, standard deviation = 5.95)				

SI Table 14. Summary Statistics for the GHG emissions from the life cycle stages for production of Brazilian sugarcane LDPE

Life-cycle Stage	Mean (kg CO ₂ e/kg LDPE)	Standard Deviation	Coefficient of Variation	Lower 90% CI	Upper 90% CI
LUC	0.2	0.17	1.0	-0.1	0.5
Sugarcane Farming	0.93	0.21	0.23	0.62	1.3
Ethanol production & electricity credit	-0.067	0.059	-0.9	-0.18	-0.01
Ethanol Dehydration	0.2	0.05	0.31	0.1	0.3
Polymerization	0.2	0.08	0.33	0.1	0.4
Transportation	0.5	0.03	0.06	0.4	0.5
EOL (growth credit)	-3.1	-	-	-	-
LDPE Total	-1.3	0.30	-0.22	-1.8	-0.8
Fitted Distribution	Normal (mean = 1.34, standard deviation = 0.299)				

SI Table 15. Summary Statistics for the net GHG emissions from each bio-based pathway. Reported emissions include 1:1 displacement of the relevant fossil fuel product (gasoline or fossil LDPE). The functional unit is scaled so that equivalent volumes of ethanol are considered, resulting in 1kg LDPE or 46.9 MJ energy.

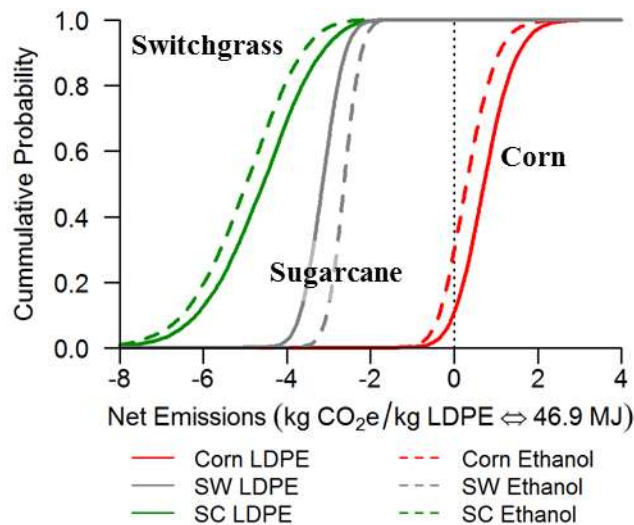
Pathway	Mean net emissions (kg CO ₂ e/functional unit)	Standard Deviation	Coefficient of Variation	Lower 90% CI	Upper 90% CI
Corn ethanol	0.33	0.57	1.73	-0.54	1.3
Corn LDPE	0.74	0.63	0.85	-0.22	1.8
Switchgrass ethanol	-5.0	1.13	-0.22	-7.0	-3.3
Switchgrass LDPE	-4.7	1.16	-0.25	-6.7	-2.9
Sugarcane ethanol	-2.6	0.33	-0.12	-3.2	-2.1
Sugarcane LDPE	-3.2	0.45	-0.14	-3.9	-2.5

SI Table 16. Summary Statistics for comparing GHG accounting reductions achieved by bio-LDPE to those achieved by bio-ethanol (as per figure 4 of the main text). Positive values imply that bio-LDPE achieves greater GHG accounting reductions than bio-ethanol. Negative values imply that bio-ethanol achieves greater GHG accounting reductions than bio-LDPE. Results assume bio-products achieve 1:1 displacement of the relevant fossil fuel product (gasoline or fossil LDPE). The functional unit is scaled so that equivalent volumes of ethanol are considered, resulting in 1kg LDPE or 46.9 MJ energy.

Pathway	Mean difference in net emissions (kg CO ₂ e/functional unit)	Standard Deviation	Coefficient of Variation	Lower 90% CI	Upper 90% CI
U.S. Production	-0.41	0.39	-0.96	-1.0	0.2
Brazilian Production	0.51	0.41	0.79	-0.13	1.1

1.3.2 CDF of Net GHG Emissions

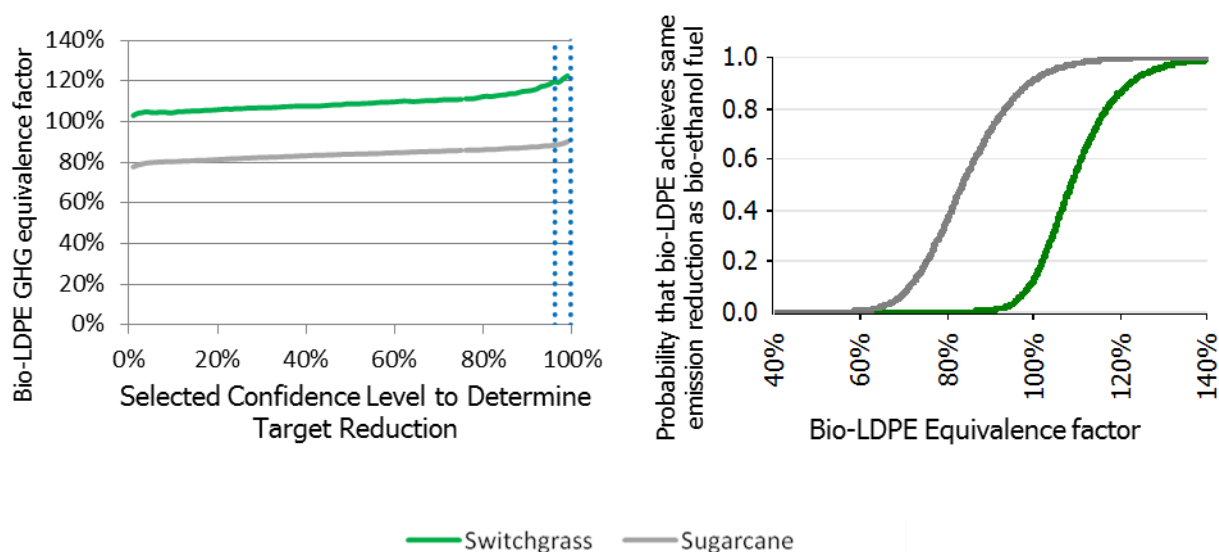
SI Figure 3 presents, the cumulative probability distribution functions for net GHG emissions from each bio-based pathway. Net GHG emissions are calculated by subtracting the emissions of the relevant fossil counterpart from the emissions for each bio-based product. Each curve thus represents the net increase (positive values) or decrease (negative values) in GHG emissions from replacing a fossil product with its bio-based counterpart. Key conclusions from this figure are already discussed in the main text.



SI Figure 3. Net emissions from examined bio-based pathways. The figure shows the cumulative distribution function for net emissions from both chemical (LDPE) and fuel use of bio-based ethanol, including any savings from 1:1 displacement of the relevant fossil fuel product (gasoline or fossil LDPE). The functional unit is scaled so that equivalent volumes of ethanol are considered. For clarity, the y-axis refers to ‘probability’, but should only be interpreted as a proportion of modeled runs.

1.3.3 Bio-LDPE GHG Equivalence Factor

The main text introduces the possibility of establishing a bio-LDPE to bio-ethanol GHG equivalence factor. To do so, policy makers could first choose an acceptable level of confidence (y-axis in main text Figure 3) as suggested by Mullins *et al.* (48), legislate the corresponding percentage target for ethanol fuel (x-axis in main text Figure 3), then scale bio-ethylene requirements to achieve the same GHG accounting reduction and confidence (% of model runs). The required scaling for switchgrass and sugarcane is shown on the left in SI Figure 4 for different confidence thresholds. Alternatively, results may be reported as the result of a direct simulation on the ratio of GHG emissions accounting savings from bio-LDPE to bio-ethanol fuel, as shown on the right of SI Figure 4.



SI Figure 4. Bio-LDPE ethanol use equivalence factor for achieving the same emission reduction targets as bio-ethanol fuel. LEFT: relative quantity of ethanol used in bio-LDPE (y-axis) to achieve the same reduction target as bio-ethanol fuel for a reduction target set by fixed level of confidence (x-axis) as applied to main text Figure 3. The vertical dotted lines at 99% and 96% show respectively the degree of confidence with which sugarcane ethanol and switchgrass ethanol can achieve EISA targets (50% reduction for sugarcane and 60% reduction for switchgrass). **RIGHT:** probability that bio-LDPE will achieve the same reduction in emissions as bio-ethanol fuel (y-axis) in function of the quantity of ethanol used for bio-LDPE (x-axis) relative to a unit amount of ethanol used for fuel. References to “probability” and “confidence levels” should only be interpreted as a proportion of modeled runs.

SI Figure 4 (left) shows that bio-LDPE and bio-ethanol fuel could achieve the EISA reduction targets with the same level of confidence if ~1.2 units of ethanol used toward switchgrass bio-LDPE or ~0.9 units of ethanol used toward Brazilian bio-LDPE were given the same credit as 1 unit of ethanol fuel. These values correspond to confidence levels (proportion of model runs) of approximately 90% and 75% respectively that emission reductions from bio-LDPE will be at least as good as from bio-ethanol fuel (SI Figure 4 right).

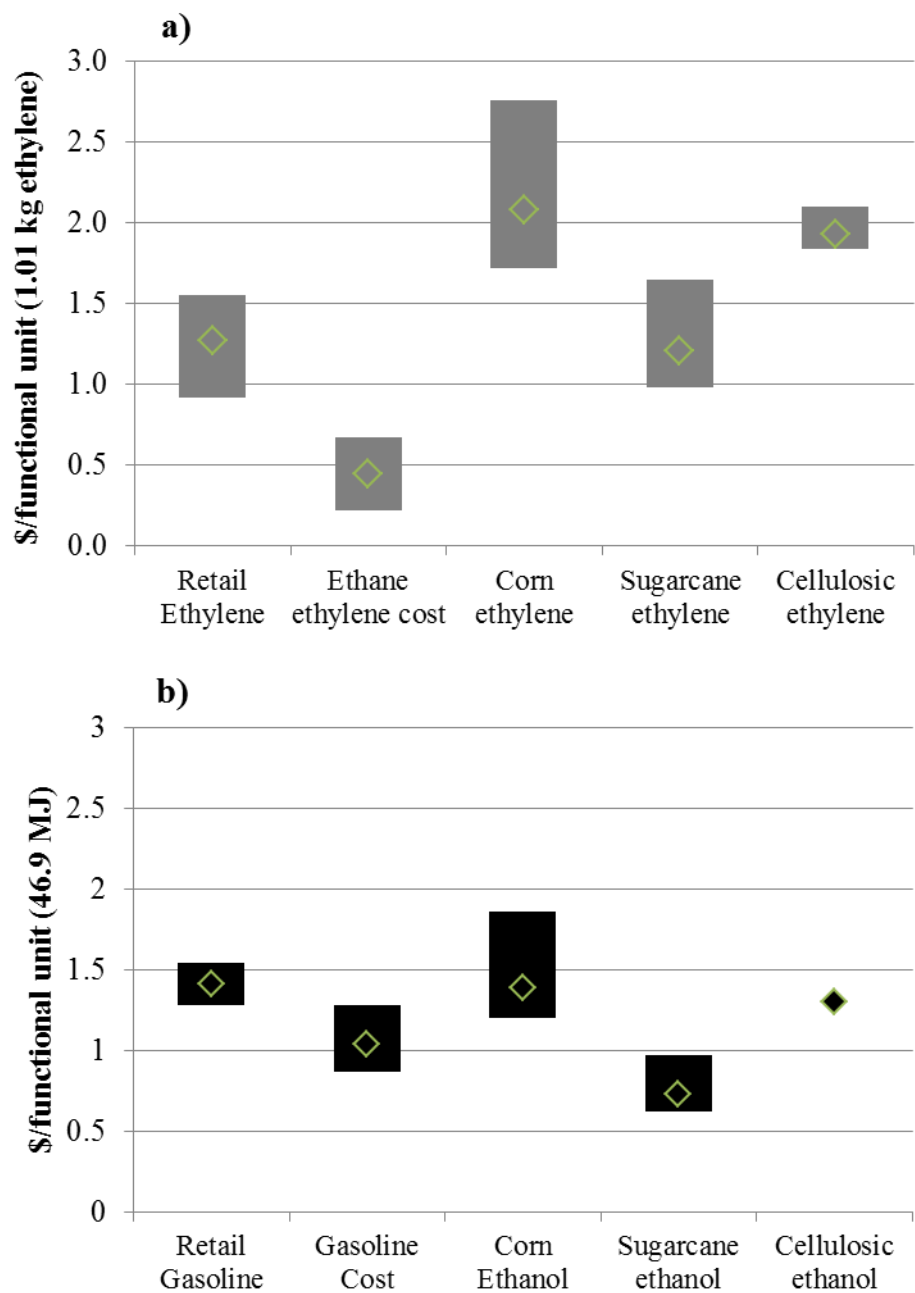
1.3.4 Cost Analysis

Production costs for bio-ethanol and bio-ethylene have been estimated by the International Renewable Energy Agency (74); where mean and confidence interval were provided, these data were used as the parameters (min, mode and max) for triangular distributions. The cost for fossil

ethylene was estimated from historical data by subtracting ethane cracker margins from the retail price of ethylene as reported by multiple sources (75-77). The minimum and maximum values obtained from these sources for the period from January 2012 to July 2013 (the latest data available) were used to parameterize a uniform distribution.

Gasoline production costs are estimated as the sum of crude oil and refining costs. EIA provides monthly data on the components of the average U.S. gasoline price over time (78). The data does not separate refining costs from refiner margins. Instead, refiner margins were estimated using data from the International Energy Agency (IEA) (79). IEA data is available annually from 2004 to 2010 and quarterly for 2011. For each U.S. refinery type, the refiner margin is calculated as a percent of net product worth (also provided by IEA). For each available time period, the refinery margin percentage is simulated as a uniform distribution ranging over all U.S. refinery types. This percent markup is then converted back into a dollar value (restricted to positive values) using net product worth calculated from the EIA data (averaged across the IEA time periods) (78). For each IEA time period, refiner costs are calculated by subtracting these refiner margins from the average gross refining contribution to retail gasoline prices reported by EIA for that period (78). Total refining cost is then simulated as a uniform distribution across the available time periods and fitted to a single continuous distribution to reduce computational intensity. Crude oil costs are simulated as a uniform distribution spanning the minimum and maximum monthly crude oil costs reported by EIA from January 2012 to January 2014 (78). Finally crude oil and refining costs are assigned a correlation of 0.5 based on historical data.

Results of the cost analysis are presented in SI Figure 5. Bio-ethylene (from any source) is substantially more expensive to produce than ethane-derived ethylene. In contrast, ethanol, particularly from sugarcane, may already be competitive with gasoline.



SI Figure 5. Simulated costs per functional unit. Rectangles show the range of simulated costs and diamonds show the mean or best estimate for each feedstock. a) Retail price and feedstock specific cost of production for 1.01 kg ethylene. b) Retail price and feedstock specific cost per 46.9 MJ of fuel.

For each bio-based pathway net GHG accounting savings are combined with cost estimates to simulate an implicit carbon price. Results are presented in SI Table 17. No value is shown for corn pathways as no net GHG accounting savings are achieved. While bio-ethanol appears to be a

reasonable GHG mitigation strategy, bio-ethylene can only be justified (at current production costs) if substantial co-benefits are expected. Nevertheless, *private* investment into bio-ethylene is already taking place (80, 81). Adopting a more flexible standard in place of RFS2 can only decrease the overall cost of compliance, particularly as market prices change and new production technologies evolve.

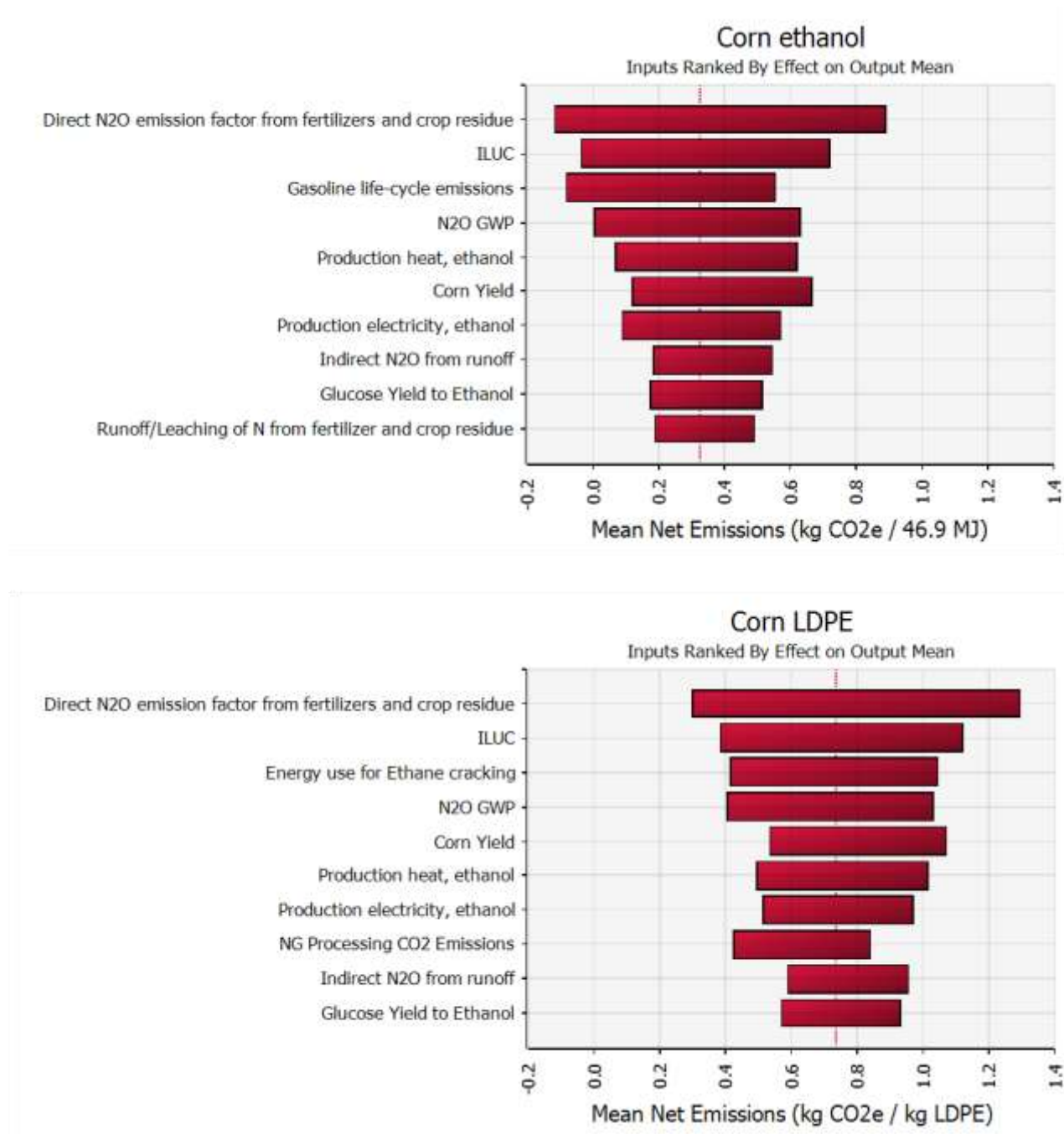
SI Table 17. Implicit Carbon Price for bio-ethanol and bio-ethylene (90% confidence interval, \$/ton CO₂e). Confidence interval is formed as a percent of model runs, and may not represent true probability.

	Corn	Sugarcane (\$/tonCO ₂ e)	Switchgrass (\$/tonCO ₂ e)
Bio-ethanol	N/A	-200 to 0	0 to 100
Bio-ethylene	N/A	150 to 400	200 to 550

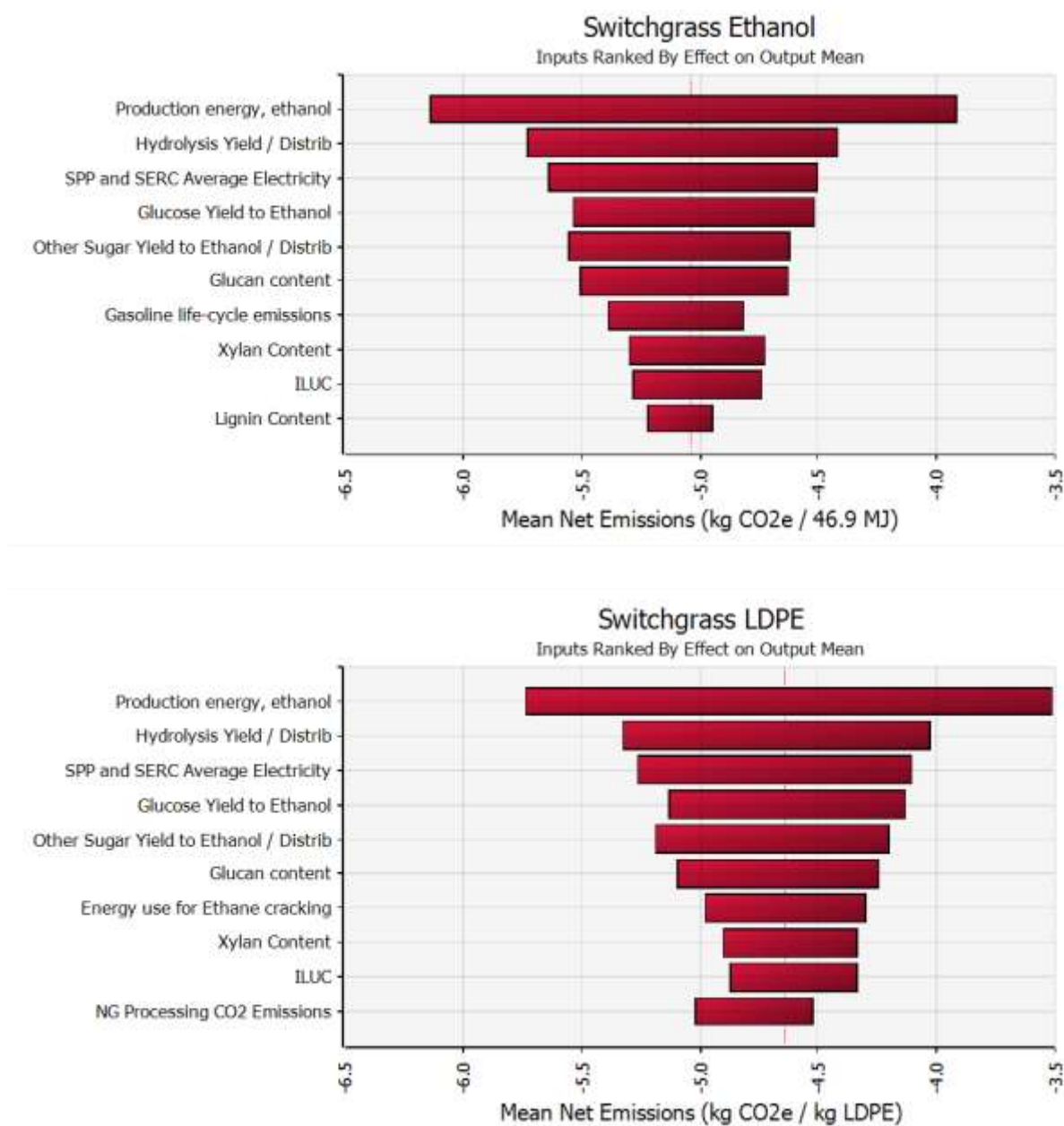
1.4 Importance analysis and sensitivity

1.4.1 Importance Analysis

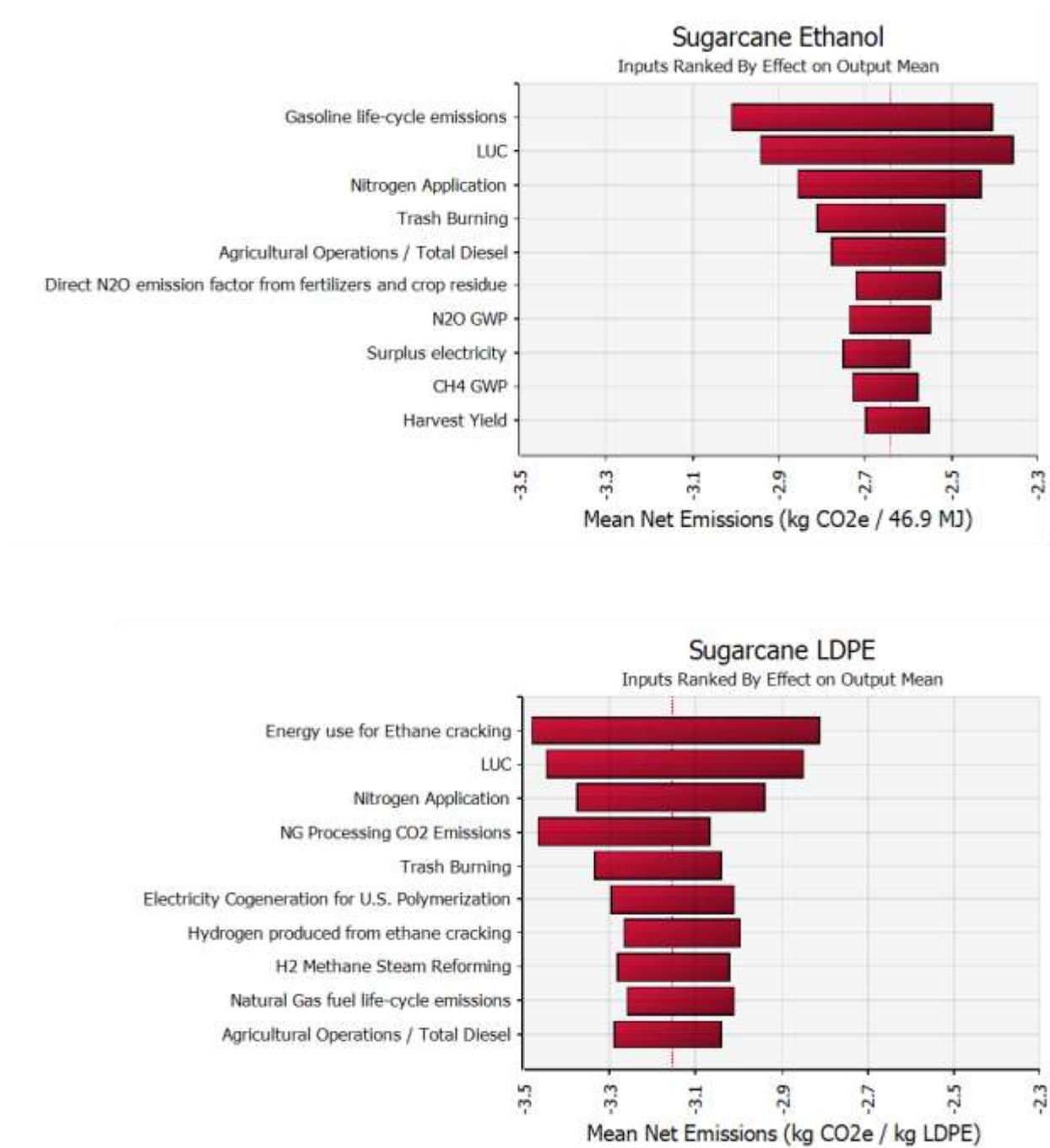
The following figures show sensitivity to mean *net* GHG emissions to model inputs for each of the 6 biomass pathways modeled in this paper. The results include 1:1 displacement of the relevant fossil fuel product (gasoline or fossil LDPE). The tornado plots are generated using Palisade's @RiskTM software. The edges of the tornado bars show the output mean for the simulations representing lowest (respectively highest) 10% of values for the selected input. The model is first run for 10,000 iterations. Each input is then divided into deciles (10 ascending bins). The output mean is calculated for each of these bins. The lowest of the 10 output means becomes the left edge of the tornado plot for that input; the highest of the 10 output means becomes the right edge of the tornado plot for that input. This method implicitly accounts for correlations and non-linearities in the output response.



SI Figure 6. Sensitivity of mean net GHG emissions of corn pathways to model inputs. The results include 1:1 displacement of the relevant fossil fuel product (gasoline or fossil LDPE). The edges of the tornado bars show the output mean for the simulations representing lowest (respectively highest) 10% of values for the selected input.



SI Figure 7. Sensitivity of mean net GHG emissions of switchgrass pathways to model inputs. The results include 1:1 displacement of the relevant fossil fuel product (gasoline or fossil LDPE). The edges of the tornado bars show the output mean for the simulations representing lowest (respectively highest) 10% of values for the selected input.



SI Figure 8. Sensitivity of mean net GHG emissions of sugarcane pathways to model inputs. The results include 1:1 displacement of the relevant fossil fuel product (gasoline or fossil LDPE). The edges of the tornado bars show the output mean for the simulations representing lowest (respectively highest) 10% of values for the selected input.

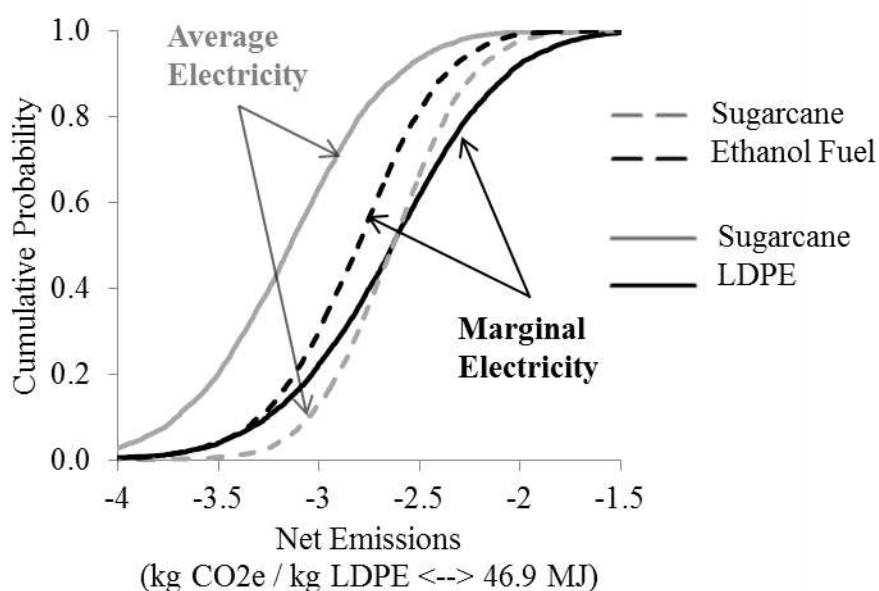
Within the fossil LDPE pathway (disaggregated results not shown), uncertainty/variability on natural gas processing emissions, primary energy source for U.S. polymerization electricity cogeneration, the global warming potential of CH₄ and inputs for the steam cracking phase (total energy requirements, H₂ produced, and offset emissions from H₂ production) are all prominent contributors to overall uncertainty.

For corn and switchgrass pathways, modeled uncertainty in emissions from the bio-based pathways is larger than uncertainty in emissions from the displaced fossil fuel counterparts. For sugarcane, modeled uncertainty from ethanol production is lower, allowing uncertainty from the fossil fuel pathways to play a more prominent role. For all biomass pathways (especially corn and sugarcane), land-use change (LUC) emissions play a prominent role; this is in spite of employing a relatively narrow distribution that does not fully capture the range of literature estimates for LUC emissions. For corn pathways, most of the other important contributors to uncertainty relate to N₂O from fertilizer use (e.g. direct and indirect N₂O emission factors, N₂O GWP, nitrogen runoff and corn yield per hectare) and energy used for ethanol production. For switchgrass pathways, the most important inputs are those affecting the availability of surplus electricity: energy required for ethanol production, hydrolysis yield, ethanol yield, composition of switchgrass. Carbon intensity of displaced electricity is also an important contributor to uncertainty.

1.4.2 Sensitivity to treatment of electricity:

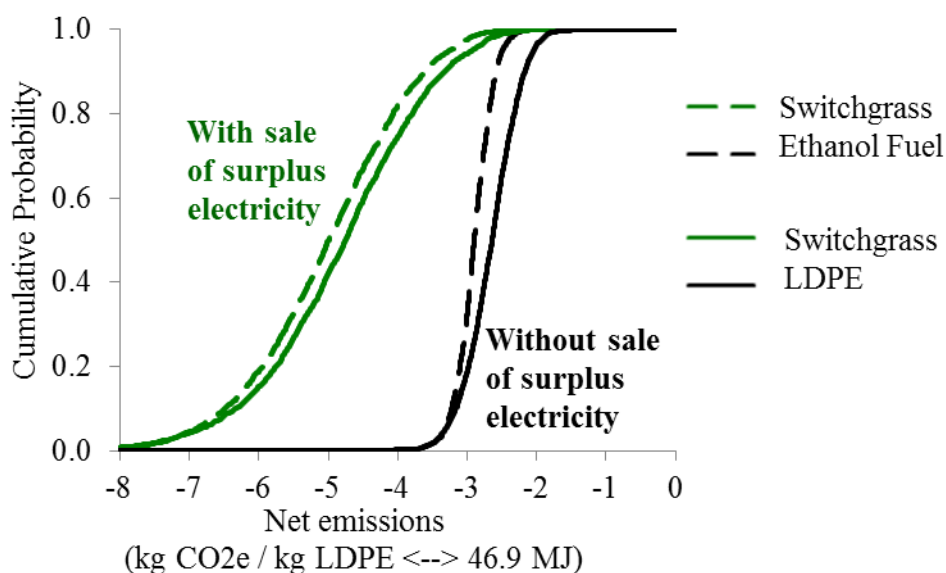
The treatment of electric grid emissions is an important parameter subject to a large degree of spatial and temporal variability. The large ranges employed capture much of this uncertainty, notably encompassing both estimates of ‘average’ and ‘marginal’ carbon intensity for the U.S. NERC regions as discussed above. For Brazilian electricity, however, there is a significant difference between average electricity (dominated by hydro power) and marginal generation, which is generally attributed to natural gas (82, 83). Thus, for the sugarcane route only, an additional model run was performed using marginal (Brazilian) electricity emissions factors. Results are presented in SI Figure 9

As is evident from the figure, switching to marginal electricity reduces the net emissions from the fuel pathway while increasing the emissions from the LDPE pathway; this is because the ethanol pathway is a net producer of electricity (due to surplus bagasse), while the LDPE pathway is a net consumer of electricity due to large electricity requirements further downstream (ethylene production and polymerization). Sugarcane ethanol fuel now achieves slightly greater GHG accounting savings. Both pathways continue to meet EISA targets (50% GHG accounting reduction relative to gasoline) with confidence levels in excess of 85% of model runs.



SI Figure 9. Net emissions from sugarcane pathways using either average or marginal Brazilian electricity emissions factors. The figure show the cumulative distribution function for net emissions from both chemical (LDPE) and fuel pathways, including savings from 1:1 displacement of the relevant fossil fuel product (gasoline or fossil LDPE). The functional unit is scaled so that equivalent volumes of ethanol are considered. For clarity, the y-axis refers to ‘probability’, but should only be interpreted as a proportion of model runs.

As discussed above, emission credits from the sale of surplus electricity are critical to both switchgrass pathways. An additional case is modeled with no credits for surplus electricity for the event that ethanol production facilities are unable to sell this product to the grid. Results for switchgrass pathways are shown in SI Figure 10. Removing credits for surplus electricity makes little difference to the baseline model for sugarcane pathways.



SI Figure 10. Net emissions from switchgrass pathways both with and without credits for the sale of surplus electricity. The figure show the cumulative distribution function for net emissions from both chemical (LDPE) and fuel pathways, including savings from 1:1 displacement of the relevant fossil fuel product (gasoline or fossil LDPE). The functional unit is scaled so that equivalent volumes of ethanol are considered. For clarity, the y-axis refers to ‘probability’, but should only be interpreted as a proportion of model runs.

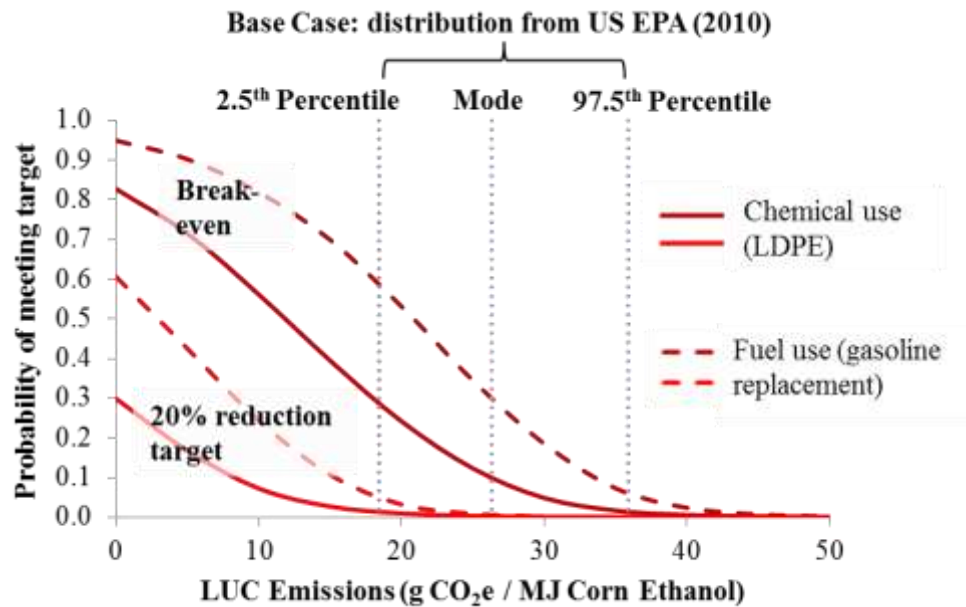
Inability to sell surplus electricity considerably increases the net emissions from switchgrass pathways while decreasing the modeled uncertainty. Although switchgrass ethanol fuel retains a high likelihood (>95% of model runs) of meeting the EISA target for cellulosic ethanol (60% accounting reduction relative to gasoline), the LDPE pathway can only meet the same EISA target in 50% of model runs, a substantial drop from the base case. Without credits for surplus electricity, there is now substantial overlap in emissions between switchgrass and sugarcane pathways. Summary results for this section are presented in SI Table 18.

SI Table 18. Summary of net emissions (including 1:1 displacement of the baseline fossil fuel product) for alternate assumptions regarding emissions from electricity.

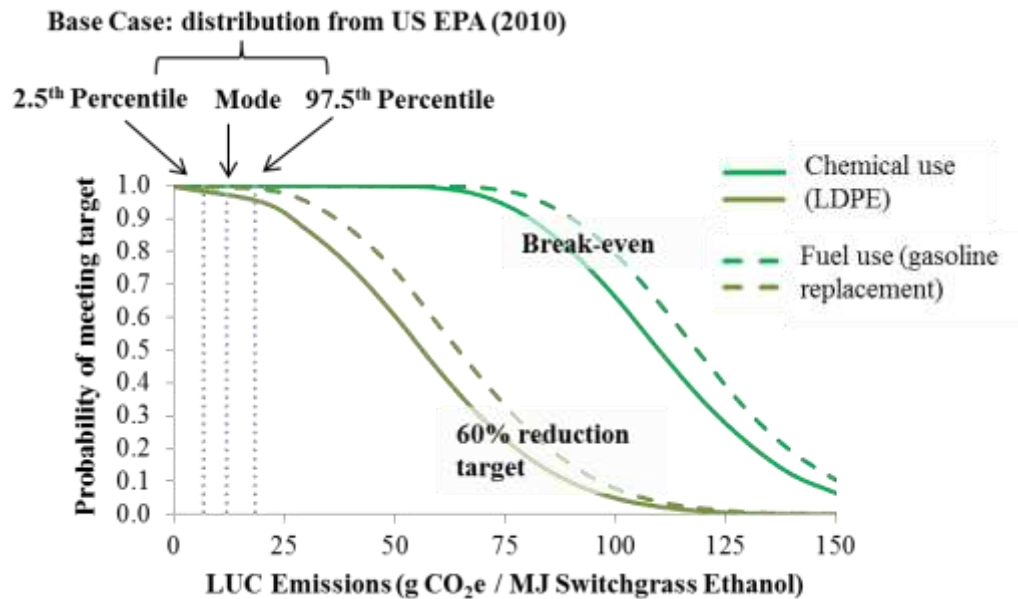
	Mean simulated net emissions (kg CO ₂ e/functional unit)		
	Base Case	Marginal Electricity	No sale of surplus electricity
Corn Ethanol	+0.33	–	–
Corn LDPE	+0.74	–	–
Sugarcane Ethanol	-2.6	-2.8	-2.6
Sugarcane LDPE	-3.2	-2.7	-3.1
Switchgrass Ethanol	-5.0	–	-2.9
Switchgrass LDPE	-4.7	–	-2.5

1.4.3 Sensitivity to land use change

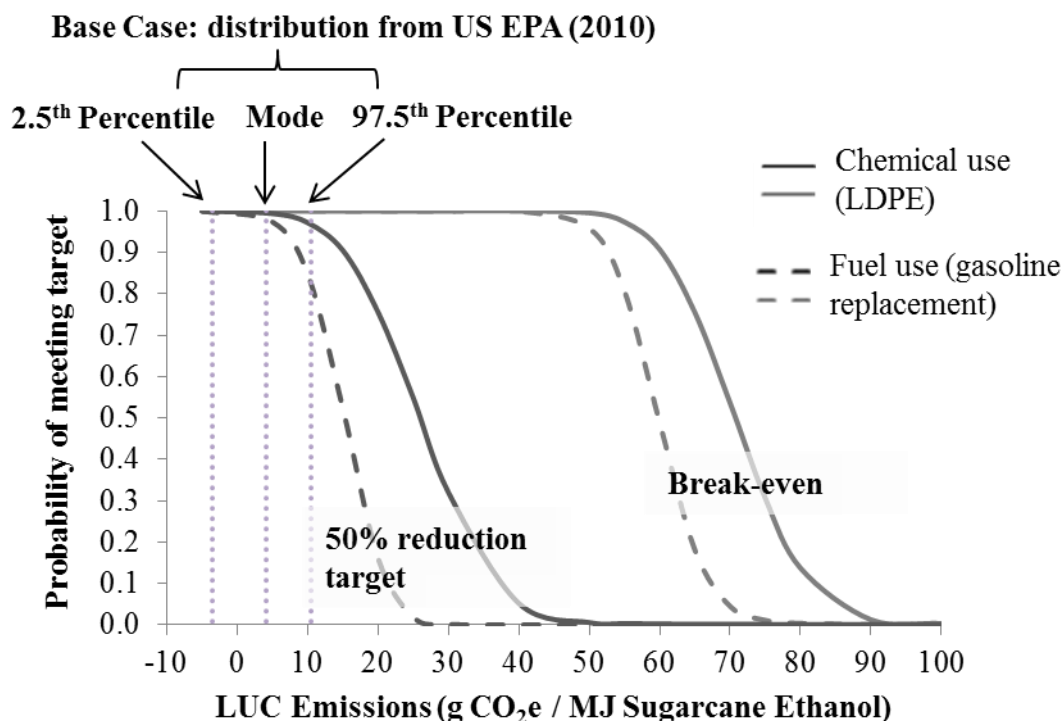
Emissions from land use change are highly uncertain and subject to much controversy. In SI Figure 11 to SI Figure 13, land use change is treated parametrically for each of the biobased pathways considered. Excluding land use change (i.e. 0 g CO₂e / MJ) leads to a high proportion of model runs in which corn ethanol and LDPE achieve some emission accounting reduction (i.e. “break-even”) relative to gasoline and fossil LDPE, respectively. It is still only in a limited proportion of model runs that either bio-product achieves the 20% emission accounting reduction required by EISA. For switchgrass and sugarcane, a modest increase in LUC emissions could threaten the ability to meet EISA reduction targets. Only the most extreme estimates for LUC are likely to lead to a net increase in emissions relative to gasoline or fossil LDPE.



SI Figure 11. “Probability” that GHG emissions from corn ethanol and corn LDPE are below gasoline and fossil LDPE respectively (“break-even”), or below the RFS2 renewable biofuel reduction target (20% reduction compared to gasoline) as a function of LUC emissions. For clarity, the y-axis refers to ‘probability’, but should only be interpreted as a proportion of model runs.



SI Figure 12. “Probability” that GHG emissions from switchgrass ethanol and switchgrass LDPE are below gasoline and fossil LDPE respectively (“break-even”), or below the RFS2 cellulosic biofuel reduction target (60% reduction compared to gasoline) as a function of LUC emissions. For clarity, the y-axis refers to ‘probability’, but should only be interpreted as a proportion of model runs.

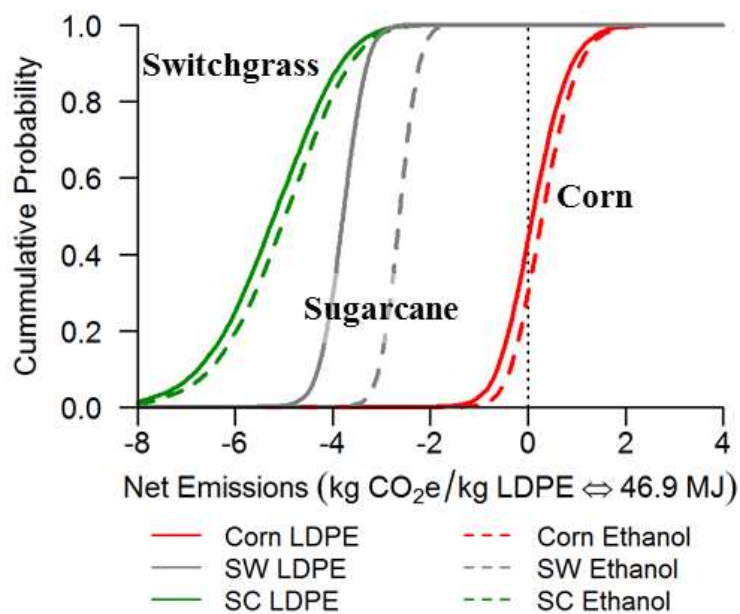


SI Figure 13. “Probability” that GHG emissions from switchgrass ethanol and sugarcane LDPE are below gasoline and fossil LDPE respectively (“break-even”), or below the RFS2 advanced biofuel reduction target (50% reduction compared to gasoline) as a function of LUC emissions. For clarity, the y-axis refers to ‘probability’, but should only be interpreted as a proportion of modeled runs.

1.4.4 Sensitivity treatment of displaced fossil products

This analysis makes several important assumptions regarding displaced fossil products. First, fossil ethylene is assumed to be derived from natural gas ethane. Although ethane is the dominant feedstock in the U.S., heavier feedstocks like naphtha still account for close to 15 to 20% of domestic ethylene production (84-86). As naphtha crackers tend to display lower profit margins (75, 87), heavier feedstocks would likely be displaced first by an increase in bio-ethylene production. To investigate this possibility, a model was developed to account for the emissions from naphtha-derived ethylene. Life-cycle emissions from naphtha production are assumed to be equivalent to the reported emissions for gasoline production reported by Venkatesh *et al.* (7). Emissions from naphtha cracking were modeled in the same way as emissions from ethane cracking, using naphtha-specific estimates for energy requirements (28) and co-product volumes (32).

Naphtha-derived LDPE is found to be approximately 25% more GHG intensive than ethane-derived LDPE. Mean modeled emissions for Naphtha LDPE are 2.4 kg CO₂e / kg LDPE with 90% of model runs from 2.0-2.9 kg CO₂e / kg LDPE. Net emissions for each bio-based pathway assuming displacement for naphtha-derived LDPE for bio-LDPE pathways are presented in SI Figure 14 (compare with SI Figure 3). Under the assumption that naphtha-derived LDPE is displaced (rather than ethane-derived LDPE), bio-LDPE is marginally preferred over bio-ethanol fuel even for U.S. pathways. The ability for each pathway to meet the relevant EISA GHG reduction target is not significantly affected.

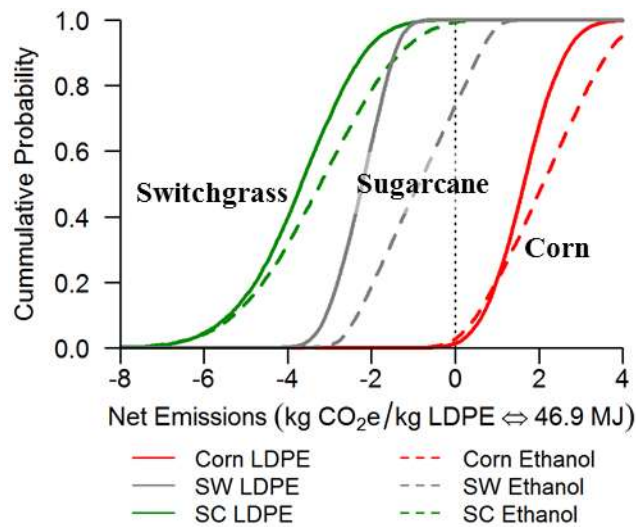


SI Figure 14. Net emissions from examined bio-based pathways treating naphtha as the feedstock for fossil ethylene. The figure shows the cumulative distribution function for net emissions from both chemical (LDPE) and fuel use of bio-based ethanol, including any savings from 1:1 displacement of the relevant fossil fuel product (gasoline of naphtha-derived LDPE). For clarity, the y-axis refers to ‘probability’, but should only be interpreted as a proportion of model runs.

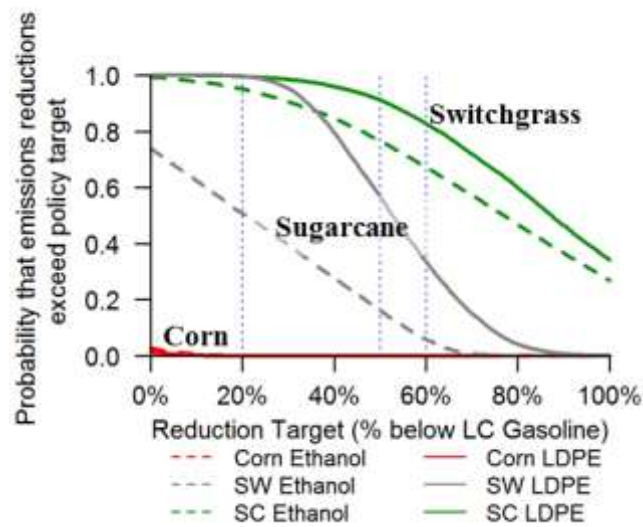
Another important assumption in this paper is that GHG accounting savings for bio-based pathways are calculated assuming 1:1 displacement of the corresponding fossil fuel product (gasoline or fossil LDPE). While 1:1 replacement is accurate on a physical basis, the resulting changes in market prices make 1:1 replacement unlikely across the entire market. Policies which encourage the use of biofuel or bio-based chemicals may cause a variety of market-mediated effects, some of which have already been accounted for by including emissions from indirect land-use change. Another important market-mediated effect involves the global market for fossil fuel products and has been termed the

indirect fuel use effect (IFUE), see for example ref. (88). Mandates like RFS2 decrease demand for fossil products and may result in a global change in demand as fossil prices drop, resulting in replacement of fossil products that is less than 1:1. On the other hand mandates like RFS2 increase the price of the final product mix in regulated sectors which could also result in a negative IFUE (for example, if people drive less in response to higher fuel prices). The increase in global demand for fossil products relative to the counterfactual of 1:1 replacement with bio-products is sometimes called “rebound,” however to avoid confusion with the energy efficiency literature we prefer the terms “IFUE” (for fuel markets) or more generally “indirect demand change” (IDC) for fossil products. As an example, a +20% “indirect demand change” for LDPE indicates that introducing 1 unit of bio-LDPE into the market will lead to a net decrease of 0.8 units of fossil LDPE.

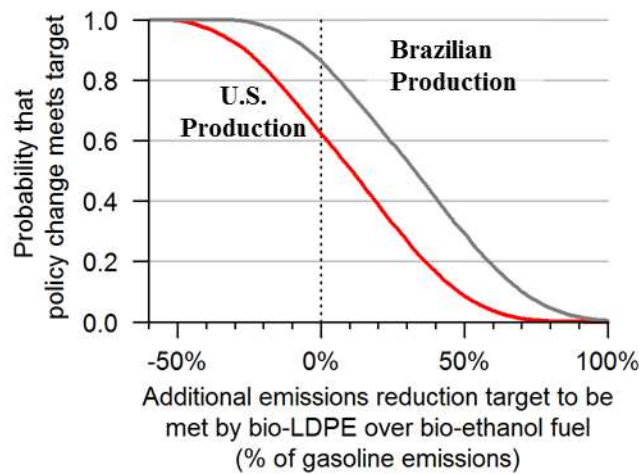
A limited number of studies have investigated the magnitude of IFUE, and were the subject of a recent critical review by Smeets *et al.* (89). To capture the range presented, indirect demand change for gasoline (due to the introduction of bio-ethanol) is simulated with a uniform distribution ranging from -1% to 85% (i.e. introduction of 1 MJ of ethanol results in a market wide decrease in gasoline use ranging from 1.01 MJ to 0.25 MJ). The upper bound (85%) deliberately excludes cases presented in (89), which relate to tax credits rather than an RFS2-style mandate. No studies were available to estimate indirect demand change in the fossil ethylene market, and so a fossil LDPE indirect demand change is simulated with a uniform distribution from 0% to 100%. Results are presented in SI Figure 15 to SI Figure 17. Inclusion of indirect demand change effects increases the modeled net emissions in all pathways. Nevertheless, sugarcane LDPE and both switchgrass pathways continue to meet EISA targets in a large proportion of model runs. For reasons discussed below, indirect demand change has a larger effect in the fuels market (despite lower modeled indirect demand change percentages). As a result, bio-LDPE is now the preferred pathway for both U.S. and Brazilian pathways (SI Figure 17).



SI Figure 15. Net emissions from examined bio-based pathways. The figure shows the cumulative distribution function for net emissions from both chemical (LDPE) and fuel use of bio-based ethanol, including savings displacement of the relevant fossil fuel product (gasoline or fossil LDPE), with market induced indirect demand change. The functional unit is scaled so that equivalent volumes of ethanol are considered. For clarity, the y-axis refers to ‘probability’, but should only be interpreted as a proportion of model runs.



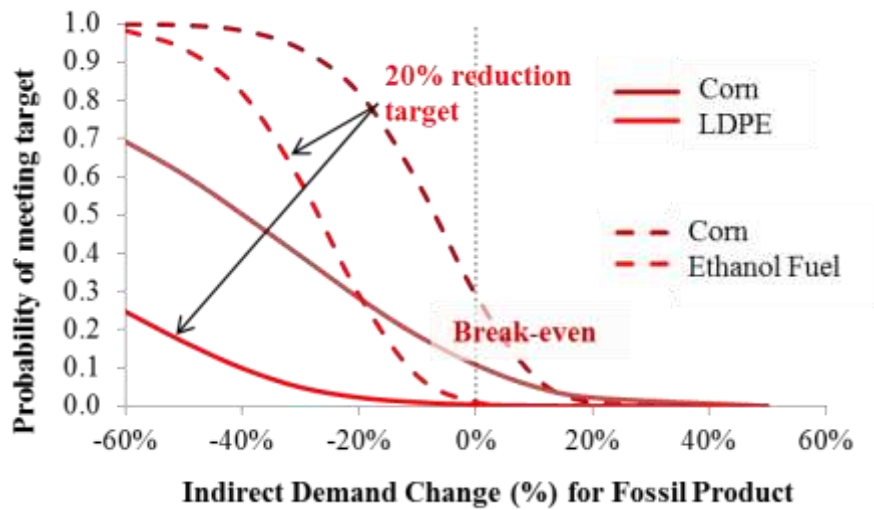
SI Figure 16. Proportion of model runs in which modeled GHG emission from each bio-based pathway are below those of the fossil fuel counterpart (at 0%) or below some policy target. Fossil product displacement is modeled with uncertain market-induced indirect demand change. Policy targets are given as a percent reduction relative to simulated gasoline life-cycle (LC) emissions. EISA targets (20% for corn biofuel, 50% for advanced biofuels and 60% for cellulosic biofuels) are shown with vertical blue lines. For clarity, the y-axis refers to ‘probability’, but should only be interpreted as a proportion of model runs.



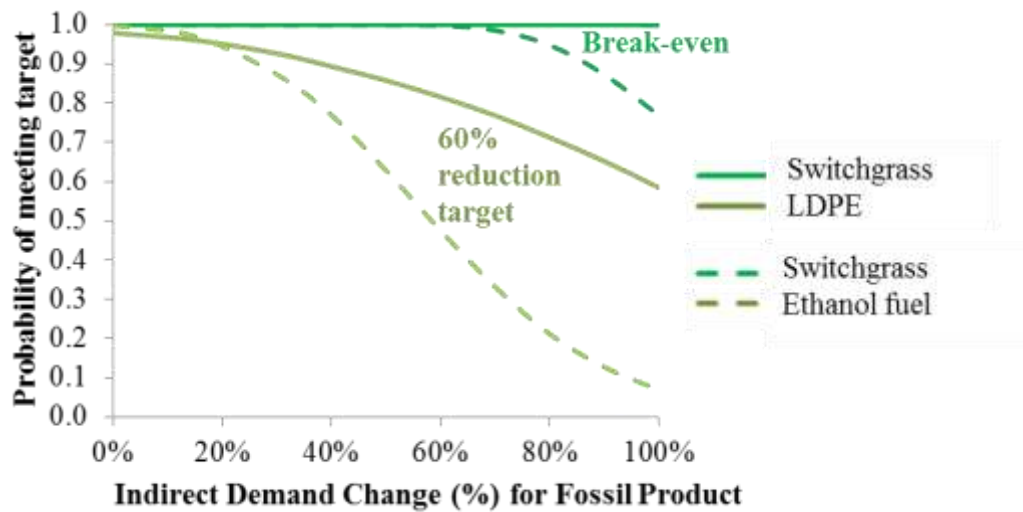
SI Figure 17. Proportion of model runs in which modeled GHG savings from bio-LDPE are superior to those from bio-ethanol (at 0% on the x-axis) or in excess of some policy target. Positive values indicate that more stringent reductions can be met with bio-LDPE. Negative values represent needed relaxation in the target emissions reductions (as a % of gasoline emissions). Figure includes market-induced indirect demand change effects. For clarity, the y-axis refers to ‘probability’, but should only be interpreted as a proportion of model runs.

In SI Figure 18 to SI Figure 20, indirect demand change in the fossil product market (gasoline or fossil LDPE) is treated parametrically for each of the biobased pathways considered.

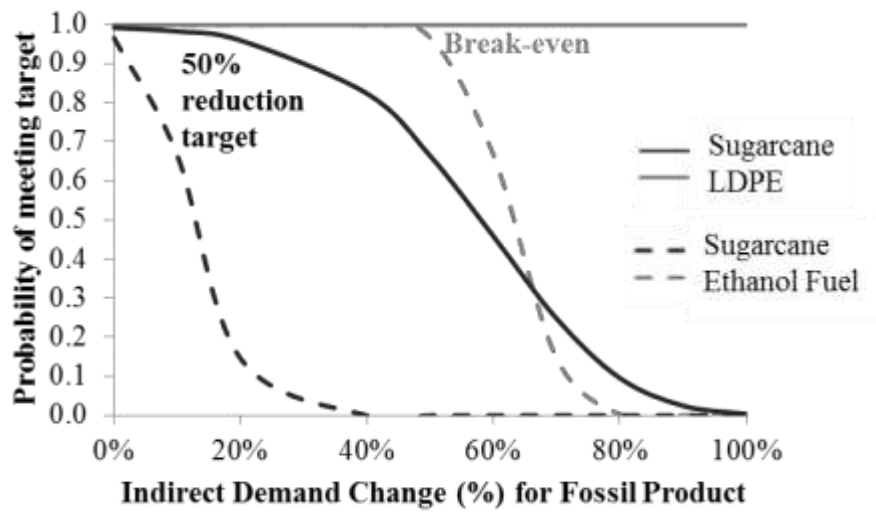
Indirect demand change in the gasoline market has a higher impact than indirect demand change in the LDPE market; this is because gasoline has higher emissions per functional unit than fossil LDPE. For corn ethanol, substantial *negative* indirect demand change is required before RFS2 targets can be met; even with such indirect demand decreases, corn LDPE remains unable to meet the RFS2 20% accounting reduction target, as modeled. For sugarcane ethanol pathways, modest gasoline indirect demand increases threaten RFS2 targets, while only relatively large indirect demand increases would cause net increase in emissions. For sugarcane LDPE and both switchgrass pathways, high levels of indirect demand change could interfere with RFS2 targets but a net increase in emissions is almost never observed in the model (reflecting the high proportion of model runs resulting in negative emissions for these pathways even excluding fossil product displacement).



SI Figure 18. Probability that corn ethanol and corn LDPE achieve net GHG emission reductions (“break-even”), or the RFS2 renewable biofuel reduction target (20% reduction compared to gasoline) as a function of market-induced indirect demand change in the fossil product market. For clarity, the y-axis refers to ‘probability’, but should only be interpreted as a proportion of model runs.



SI Figure 19. Probability that switchgrass ethanol and switchgrass LDPE achieve net GHG emission reductions (“break-even”), or the RFS2 cellulosic biofuel reduction target (60% reduction compared to gasoline) as a function of market-induced indirect demand change in the fossil product market. For clarity, the y-axis refers to ‘probability’, but should only be interpreted as a proportion of model runs.



SI Figure 20. Probability that sugarcane ethanol and sugarcane LDPE achieve net GHG emission reductions (“break-even”), or the RFS2 advanced biofuel reduction target (50% reduction compared to gasoline) as a function of market-induced indirect demand change in the fossil product market. For clarity, the y-axis refers to ‘probability’, but should only be interpreted as a proportion of model runs.

1.4.5 Sensitivity to other select assumptions

SI Table 19. Selected assumptions and their impact on main conclusions of the study:

Category	Assumption	Impact on Study Conclusions
General Assumptions		
Choice of product	LDPE chosen as the reference ethylene-based product	Low impact: stages taking place after the production of ethylene are only important for Brazilian production. Products with higher electricity requirements would reinforce the conclusion that Brazilian bio-ethylene is preferred to bio-ethanol. Products with lower electricity requirements would result in GHG accounting savings for bio-ethylene that are similar to the accounting savings from bio-ethanol fuel.
Point estimates	All pathways contain a small number parameters for which uncertainty is not modeled	Underestimation of uncertainty. No model will ever capture all uncertainty. Nevertheless, calculated ranges presented here are likely to be representative of the modeled pathways.
Gasoline		
Baseline life-cycle emissions	Life-cycle emissions modeled as in Venkatesh <i>et al.</i> (7); mean not scaled to match EPA reported value	Low Impact: the mean value employed here is 89 g CO ₂ e/MJ, compared to 93 g CO ₂ e/MJ reported by EPA. Calibrating gasoline emissions so that the mean matches the EPA reported value favors bio-ethanol fuel routes but does not overturn any qualitative conclusions.
Natural Gas LDPE		
Allocation	Production and processing products treated by mass allocation	Low impact: allocation by energy content would slightly decrease the emissions from fossil LDPE (increasing the net emissions from bio-LDPE)
Allocation	Hydrogen from steam cracking treated by system expansion.	Moderate impact: treating H ₂ as fuel slightly increases the emissions from fossil LDPE (decreasing net emissions from bio-LDPE). Treating H ₂ by mass allocation (the least favorable possible assumption) substantially increases the emissions from fossil LDPE such that bio-LDPE is preferred over fuel ethanol even for U.S (corn and switchgrass) routes.

Allocation	Non-Hydrogen products from steam cracking treated by mass allocation	Low impact: non-hydrogen co-products are very minor compared to ethylene. Treatment by (HHV) energy allocation would slightly increase the emissions from fossil LDPE (decreasing net emissions from bio-LDPE).
Correlation between well workovers and estimated ultimate recovery	No correlation	Low impact: correlation would reduce variance, but contribution from workovers to final results is minimal
Lease fuel and plant fuel composition	Composed entirely of CO ₂ and CH ₄	Low Impact: In 2011, CO ₂ and CH ₄ together accounted for 87.6% of national natural gas content (24). The remaining composition will be a mixture of inert gasses (like nitrogen, argon and helium) and higher hydrocarbons (like ethane, propane, butane and pentane). The latter will increase the (per unit volume) CO ₂ emissions while the former will reduce them.
Production site vented and flared gas	All flared	Under estimation of fossil LDPE emissions. Even if all gas were vented (an extreme scenario), emissions for fossil LDPE would rise only by about 10% and net emissions for bio-LDPE would fall by 5 percentage points (expressed as a percent of gasoline emissions).
Displacement of fossil LDPE	Bio-LDPE replaces ethane-based LDPE	Under estimation of fossil LDPE emissions: although ethane is the dominant feedstock for U.S. ethylene production, there is no guarantee that it will be on the margin (i.e., that this is the feedstock bio-LDPE will replace). Heavier feedstocks are generally reported to have higher emissions for ethylene production, which would therefore decrease net emissions from bio-LDPE products. This was discussed in section 1.4.4.
Displacement of fossil LDPE	Bio-LDPE replaces fossil LDPE on a 1:1 ratio	High impact: market forces make it unlikely that bio-LDPE would actually replace fossil LDPE on a 1:1 basis. The sign and magnitude of emission changes due to secondary market interactions is unclear. This was discussed in section 1.4.4.

<i>Switchgrass Pathways</i>		
Allocation	Surplus electricity treated by system expansion	Moderate impact: system expansion represents the most optimistic possible assumption for surplus electricity. The most pessimistic assumption (no credit for surplus electricity has already been discussed). Treating surplus electricity by energy content allocation lies in between these extremes.
<i>Sugarcane Pathways</i>		
Allocation	Surplus electricity treated by system expansion	Low impact: surplus electricity production is small

1.5 References

1. Mullins, K. Evaluating Biomass Energy Policy in the Face of Emissions Reductions Uncertainty and Feedstock Supply Risk. Ph.D. Thesis, Carnegie Mellon University, Pittsburgh, PA, 2012.
2. U.S. Energy Information Association (U.S. EIA). Natural Gas Gross Withdrawals and Production. 2013. http://www.eia.gov/dnav/ng/ng_prod_sum_a_EPG0_FGW_mmcf_a.htm (Accessed August 14, 2013).
3. U.S. Energy Information Association (U.S. EIA). Lease Condensate Production. 2013. http://www.eia.gov/dnav/ng/ng_prod_lc_sl_a.htm (Accessed September 2, 2013).
4. U.S. Energy Information Association (U.S. EIA). Natural Gas Plant Liquids Production. 2013. http://www.eia.gov/dnav/ng/ng_prod_ngpl_sl_a.htm (Accessed September 2, 2013).
5. Weber, C. L.; Clavin, C., Life Cycle Carbon Footprint of Shale Gas: Review of Evidence and Implications. *Environ Sci Technol* **2012**, *46*, (11), 5688-5695.
6. Venkatesh, A.; Jaramillo, P.; Griffin, W. M.; Matthews, H. S., Uncertainty in Life Cycle Greenhouse Gas Emissions from United States Natural Gas End-Uses and its Effects on Policy. *Environ Sci Technol* **2011**, *45*, (19), 8182-8189.
7. Venkatesh, A.; Jaramillo, P.; Griffin, W. M.; Matthews, H. S., Uncertainty Analysis of Life Cycle Greenhouse Gas Emissions from Petroleum-Based Fuels and Impacts on Low Carbon Fuel Policies. *Environ Sci Technol* **2011**, *45*, (1), 125-131.
8. Venkatesh, A.; Jaramillo, P.; Griffin, W. M.; Matthews, H. S., Uncertainty in Life Cycle Greenhouse Gas Emissions from United States Coal. *Energ Fuel* **2012**, *26*, (8), 4917-4923.
9. North American Electric Reliability Corporation (NERC). Regional Entities. 2013. <http://www.nerc.com/AboutNERC/keyplayers/Pages/Regional-Entities.aspx> (Accessed December 10, 2013).
10. Renewable Fuels Association (RFA). Biorefinery Locations. 2013. <http://www.ethanolrfa.org/bio-refinery-locations/> (Accessed December 10, 2013).
11. United States Environmental Protection Agency (U.S. EPA), *Renewable Fuel Standard Program (RFS2) Regulatory Impact Analysis*; EPA-420-R-10-006; Office of Transportation and Air Quality: Washington, DC, 2010.
12. Koottungal, L., *International Survey of Ethylene from Steam Crackers - 2013*; Oil & Gas Journal: 2013.
13. United States Environmental Protection Agency (U.S. EPA), *The Emissions & Generation Resource Integrated Database (eGRID): Ninth Edition with Year 2010 Data (Version 1.0)*; 2014.
14. The World Bank Group. Electric Power Transmission and Distribution Losses (% of output). 2014. <http://data.worldbank.org/indicator/EG.ELC.LOSS.ZS> (Accessed April 15, 2014).
15. *Ecoinvent 3 - Allocation: Market for Electricity, Medium Voltage TRE, US only*; Swiss Center for Life Cycle Inventories: 2012.
16. *Ecoinvent 3 - Allocation: Market for Electricity, Medium Voltage MRO, US only*; Swiss Center for Life Cycle Inventories: 2012.
17. *Ecoinvent 3 - Allocation: Market for Electricity, Medium Voltage SPP, US only*; Swiss Center for Life Cycle Inventories: 2012.
18. *Ecoinvent 3 - Allocation: Market for Electricity, Medium Voltage BR*; Swiss Center for Life Cycle Inventories: 2012.
19. Wang, M., *The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model, Version GREET1 2013*; Argonne National Laboratory: 2013.
20. Liptow, C.; Tillman, A. M., A Comparative Life Cycle Assessment Study of Polyethylene Based on Sugarcane and Crude Oil. *J Ind Ecol* **2012**, *16*, (3), 420-435.

21. United States Environmental Protection Agency (U.S. EPA), *Greenhouse Gas Emissions Reporting from the Petroleum and Natural Gas Industry: Background Technical Support Document*; Washington DC, 2010; pp 1-144.
22. United States Environmental Protection Agency (U.S. EPA), *Oil and Natural Gas Sector: Standards of Performance for Crude Oil and Natural Gas Production, Transmission, and Distribution: Background Supplemental Technical Support Document for the Final New Source Performance Standards*; Washington DC, 2012; pp i-C14.
23. U.S. Energy Information Association (U.S. EIA). The National Energy Modeling System: An Overview. 2009. <http://www.eia.gov/oiaf/aeo/overview/> (Accessed 28 November, 2013).
24. United States Environmental Protection Agency (U.S. EPA), *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2011 (Annexes)*; Washington DC, 2013; pp A1-A429.
25. United States Environmental Protection Agency (U.S. EPA), *Oil and Natural Gas Sector: Standards of Performance for Crude Oil and Natural Gas Production, Transmission, and Distribution: Background Supplemental Technical Support Document for Proposed Standards*; Washington DC, 2011; pp i to 8-42.
26. Jiang, M.; Griffin, W. M.; Hendrickson, C.; Jaramillo, P.; VanBriesen, J.; Venkatesh, A., Life cycle greenhouse gas emissions of Marcellus shale gas. *Environ Res Lett* **2011**, 6, (3).
27. United States Environmental Protection Agency (U.S. EPA), *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2011*; Washington DC, 2013; pp 3-60 to 3-72.
28. European Commission (EC), *Integrated Pollution Prevention and Control (IPPC): Reference Document on Best Available Techniques in the Large Volume Organic Chemical Industry (February 2003)*; European Commission: Brussels, Belgium, 2003.
29. Ren, T.; Patel, M.; Blok, K., Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes. *Energy* **2006**, 31, (4), 425-451.
30. Worrell, E.; Phylipsen, D.; Einstein, D.; Martin, N., *Energy Use and Energy Intensity of the U.S. Chemical Industry*; LBNL-44314; Energy Analysis Department, Environmental Energy Technologies Division, Ernest Orlando Lawrence Berkeley National Laboratory: Berkeley, 2000.
31. Neelis, M. L.; Patel, M.; Gielen, D. J.; Blok, K., Modelling CO₂ emissions from non-energy use with the non-energy use emission accounting tables (NEAT) model. *Resour Conserv Recy* **2005**, 45, (3), 226-250.
32. American Chemistry Council (ACC), *Ethylene Product Stewardship Guidance Manual (December 2004)*; 2004.
33. Harnisch, J.; Jubb, C.; Nakhtin, A.; Cianci, V. C. S.; Lanza, R.; Martinsen, T.; Mohammad, A. K. W.; Santos, M. M. O.; McCulloch, A.; Mader, B. T., *2006 IPCC Guidelines for National Greenhouse Gas Inventories, Volume 3 Chapter 3: Chemical Industry Emissions*; Intergovernmental Panel on Climate Change (IPCC): 2006.
34. Seabra, J. E. A.; Macedo, I. C.; Chum, H. L.; Faroni, C. E.; Sarto, C. A., Life cycle assessment of Brazilian sugarcane products: GHG emissions and energy use. *Biofuel Bioprod Bior* **2011**, 5, (5), 519-532.
35. *Biomass for Power Generation and CHP*; International Energy Agency (IEA): 2007.
36. Liptow, C.; Tillman, A.-M., *Comparative Life Cycle Assessment of Polyethylene Based on Sugarcane and Crude Oil*; 2009:14; Department of Energy and Environment, Chalmers University of Technology: Göteborg, Sweden, 2009; pp 1-147.
37. Kochar, N. K.; Merims, R.; Padia, A. S., Ethylene from Ethanol. *Chem Eng Prog* **1981**, 77, (6), 66-70.
38. Geisler, G.; Hellweg, S.; Hungerbühler, K., Uncertainty analysis in life cycle assessment (LCA): Case study on plant-protection products and implications for decision making. *Int J Life Cycle Ass* **2005**, 10, (3), 184-192.

39. *Cradle-to-Gate Life Cycle Inventory of Nine Plastic Resins and Four Polyurethane Precursors*; Franklin Associates: Prairie Village, Kansas, 2011.
40. *Eco-Profiles and Environmental Product Declarations of the European Plastics Manufacturers: HDPE, LDPE, LLDPE*; PlasticsEurope: 2014.
41. Kikuchi, Y.; Hirao, M.; Narita, K.; Sugiyama, E.; Oliveira, S.; Chapman, S.; Arakaki, M. M.; Cappa, C. M., Environmental Performance of Biomass-Derived Chemical Production: A Case Study on Sugarcane-Derived Polyethylene. *J Chem Eng Jpn* **2013**, 46, (4), 319-325.
42. [Federal Register], Environmental Protection Agency. 40 CFR Parts 60 and 63. Oil and Natural Gas Sector: New Source Performance Standards and National Emission Standards for Hazardous Air Pollutants Reviews. *Federal Register* **2012**, 77, (159), 49490-49600.
43. U.S. Energy Information Association (U.S. EIA). Technically Recoverable Shale Oil and Shale Gas Resources. 2013. <http://www.eia.gov/analysis/studies/worldshalegas/> (Accessed September 14, 2013).
44. U.S. Energy Information Association (U.S. EIA). Natural Gas Consumption by End Use. 2013. http://www.eia.gov/dnav/ng/ng_cons_sum_a_epg0_vcl_mmcfa.htm (Accessed August 14, 2013).
45. United States Environmental Protection Agency (U.S. EPA). Greenhouse Gas Reporting Program: 2011 Data Sets. 2013. <http://www.epa.gov/ghgreporting/ghgdata/2011data.html> (Accessed July 9, 2013).
46. U.S. Energy Information Association (U.S. EIA). Natural Gas Annual Respondent Query System (EIA-757 Data through 2012). 2013. http://www.eia.gov/cfapps/ngqs/ngqs.cfm?f_report=RP9&f_sortby=&f_items=&f_year_start=&f_year_end=&f_show_compids=&f_fullscreen (Accessed August 14, 2013).
47. Boustead, I., *Eco-Profiles of the European Plastics Industry: Reformer Hydrogen*; Plastics Europe: 2005.
48. Mullins, K. A.; Griffin, W. M.; Matthews, H. S., Policy Implications of Uncertainty in Modeled Life-Cycle Greenhouse Gas Emissions of Biofuels. *Environ Sci Technol* **2011**, 45, (1), 132-138.
49. Paz, J. O.; Batchelor, W. D.; Babcock, B. A.; Colvin, T. S.; Logsdon, S. D.; Kaspar, T. C.; Karlen, D. L., Model-based technique to determine variable rate nitrogen for corn. *Agr Syst* **1999**, 61, (1), 69-75.
50. Klein, C. D.; Novoa, R. S. A.; Ogle, S.; Smith, K. A.; Rochette, P.; Wirth, T. C.; McConkey, B. G.; Mosier, A.; Rypdal, K., *2006 IPCC Guidelines for National Greenhouse Gas Inventories, Volume 4 Chapter 11: N₂O Emissions from Managed Soils, and CO₂ Emissions from Lime and Urea Application*; Intergovernmental Panel on Climate Change (IPCC): 2006.
51. Kwiatkowski, J. R.; McAloon, A. J.; Taylor, F.; Johnston, D. B., Modeling the process and cost of fuel ethanol production by the corn dry-grind process. *Industrial Journal of Crop Production* **2006**, 23, 288-296.
52. Boyer, C. D.; Shannon, J. C., Carbohydrates of the Kernel. In *Corn: Chemistry and Technology*, 2 ed.; White, P. J.; Johnson, L. A., Eds. American Association of Cereal Chemists: St. Paul, MN, 2003; pp 289-311.
53. Perrin, R. K.; Fretes, N. F.; Sesmero, J. P., Efficiency in Midwest US corn ethanol plants: A plant survey. *Energ Policy* **2009**, 37, (4), 1309-1316.
54. McAloon, A. J.; Taylor, F.; Yee, W.; Ibsen, K.; Wooley, R., *Determining the Cost of Producing Ethanol from Corn Starch and Lignocellulosic Feedstocks*. 2000.
55. National Renewable Energy Laboratory (NREL). U.S. Life-Cycle Inventory Database: Transport, Single Unit Truck, Long-Haul, Diesel Powered. 2013. <https://www.lcacommons.gov/nrel/process/show/b06e2d43-7ecc-4a2f-ac4e-fac9bee76fc6> (Accessed September 20, 2013).
56. McLaughlin, S. B.; Walsh, M. E., Evaluating environmental consequences of producing herbaceous crops for bioenergy. *Biomass Bioenerg* **1998**, 14, (4), 317-324.

57. Schmer, M. R.; Vogel, K. P.; Mitchell, R. B.; Perrin, R. K., Net energy of cellulosic ethanol from switchgrass. *P Natl Acad Sci USA* **2008**, *105*, (2), 464-469.
58. U.S. Department of Energy (U.S. DOE). Biomass Program: Biomass Feedstock Composition and Property Database. 2009. http://www1.eere.energy.gov/biomass/feedstock_databases.html (Accessed March 18, 2009).
59. Aden, A.; Ruth, M.; Ibsen, K.; Jechura, J.; Neeves, K.; Sheehan, J.; Wallace, B.; Montague, L.; Slayton, A.; Lukas, J., *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover*; National Renewable Energy Laboratory (NREL): Golden, Colorado, 2002.
60. Luo, L.; van der Voet, E.; Huppes, G., Life cycle assessment and life cycle costing of bioethanol from sugarcane in Brazil. *Renew Sust Energy Rev* **2009**, *13*, (6-7), 1613-1619.
61. Macedo, I. d. C.; Leal, M. R. L. V.; Silva, J. E. A. R. d., *Assessment of greenhouse gas emissions in the production and use of fuel ethanol in Brazil*; Government of Sao Paulo, 2004.
62. Sea-Rates. Transit Time, Distance Calculator & Port to Port Distances. 2013. <http://www.searates.com/reference/portdistance/> (Accessed September 10, 2013).
63. National Renewable Energy Laboratory (NREL). U.S. Life-Cycle Inventory Database: Transport, Ocean Freighter, Residual Fuel Oil Powered. 2013. <https://www.lcacommons.gov/nrel/process/show/b06e2d43-7ecc-4a2f-ac4e-fac9bee76fc6> (Accessed September 20, 2013).
64. 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* **2003**, *7*, (3-4), 117-146.
65. Borealis, A. B., *Miljörapport 2008 [Environmental report 2008]*; Borealis AB: Stengunsund, Sweden, 2008.
66. IPCC, *Climate Change 2013: The Physical Science Basis. Working Group I Contribution to the IPCC Fifth Assessment Report, Chapter 8*; Intergovernmental Panel on Climate Change (IPCC): 2013; p '8.58'.
67. IPCC, *Climate Change 2013: The Physical Science Basis. Working Group I Contribution to the IPCC Fifth Assessment Report, Chapter 8 Supplementary Material*; Intergovernmental Panel on Climate Change (IPCC): 2013; pp "8SM-19".
68. Pilavachi, P. A.; Stephanidis, S. D.; Pappas, V. A.; Afgan, N. H., Multi-criteria evaluation of hydrogen and natural gas fuelled power plant technologies. *Appl Therm Eng* **2009**, *29*, (11-12), 2228-2234.
69. Bargigli, S.; Raugei, M.; Ulgiati, S., Comparison of thermodynamic and environmental indexes of natural gas, syngas and hydrogen production processes. *Energy* **2004**, *29*, (12-15), 2145-2159.
70. U.S. Energy Information Administration (U.S. EIA), *Annual Energy Review 2011*; 2012.
71. Gage, B. D.; Driskill, D. L., *Analyses of Natural Gases 1917-2007*; Bureau of Land Management 2008.
72. Air Liquide. Gas Encyclopedia. 2013. <http://encyclopedia.airliquide.com/Encyclopedia.asp?GasID=41> (Accessed August 14, 2013).
73. Haynes, W. M., *CRC Handbook of Chemistry and Physics*. 94th ed.; Boca Raton, FL, Internet Version 2014.
74. International Renewable Energy Agency (IRENA), *Production of Bio-Ethylene: Technology Brief*; 2013.
75. Lippe, D., US Olefins First-Half 2013: Ethylene Production Prospects Clouded by First Half Turnarounds. *Oil & Gas Journal* **2013**, *111*, (9).
76. Platts McGraw Hill Financial. US Natural Gas and Ethane Spot Prices. 2014. http://www.platts.com/news-feature/2013/petrochemicals/global-margins/us_natgas (Accessed February 20, 2014).

77. Dewitt & Company Incorporated. Petrochemical Portal: Ethylene Vs. Ethylene Cash Cost from Ethane. 2014.
<http://www.dewittworld.com/portal/GraphAnalysis/ShowLogiXML.aspx?ModuleID=3&GraphID=260&ProductID=101&MainActiveTab=Americas&SubActiveTab=Prices&PageIndex=0> (Accessed February 25, 2014).
78. U.S. Energy Information Association (U.S. EIA). Gasoline and Diesel Fuel Update. 2014.
http://www.eia.gov/petroleum/gasdiesel/gaspump_hist.cfm (Accessed 28 March, 2014).
79. *Oil Market Report: Annual Statistical Supplement*; International Energy Agency (IEA): 2012; p 30.
80. Procter & Gamble. P&G Announces Plan to Use Innovative Sustainable Packaging. 2014.
<http://news.pg.com/press-release/pg-corporate-announcements/pg-announces-plan-use-innovative-sustainable-packaging> (Accessed May 25, 2014).
81. The Coca-Cola Company. PlantBottle: Frequently Asked Questions. 2012. <http://www.coca-colacompany.com/stories/plantbottle-frequently-asked-questions> (Accessed May 25, 2014).
82. Campbell, J. E.; Block, E., Land-Use and Alternative Bioenergy Pathways for Waste Biomass. *Environ Sci Technol* **2010**, 44, (22), 8665-8669.
83. *Detailed California-Modified GREET Pathway for Brazilian Sugar Cane Ethanol*; California Environmental Protection Agency, Air Resources Board: 2009.
84. Nexant, *North American Shale Gas: Opportunity or Threat for Global Ethylene Producers (Prospectus)*; Nexant: New York, 2012; p 7.
85. Rappaport, H., *Ethylene and Polyethylene Global Overview (presentation)*; CMAI: 2011.
86. Lippe, D., 2012 ethylene production bounces back; turnarounds in early 2013 to curb output. *Oil&Gas Journal* **2013**, 111, (3).
87. Platts McGraw Hill Financial. US Ethane and Lt. Naphtha Cracker Margins. 2014.
http://www.platts.com/news-feature/2013/petrochemicals/global-margins/us_ethane (Accessed February 20, 2014).
88. Rajagopal, D., The fuel market effects of biofuel policies and implications for regulations based on lifecycle emissions. *Environ Res Lett* **2013**, 8, (2).
89. Smeets, E.; Tabeau, A.; van Berkum, S.; Moorad, J.; van Meijl, H.; Woltjer, G., The impact of the rebound effect of the use of first generation biofuels in the EU on greenhouse gas emissions: A critical review. *Renew Sust Energ Rev* **2014**, 38, 393-403.