Changing the Renewable Fuel Standard to a Renewable Material Standard: Bioethylene Case Study

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Supporting Information

ABSTRACT: The narrow scope of the U.S. renewable fuel standard (RFS2) is a missed opportunity to spur a wider range of biomass use. This is especially relevant as RFS2 targets are being missed due to demand-side limitations for ethanol consumption. This paper examines the greenhouse gas (GHG) implications of a more flexible policy based on RFS2, which includes credits for chemical use of bioethanol (to produce bioethylene). A Monte Carlo simulation is employed to estimate the life-cycle GHG emissions of conventional low-density polyethylene (LDPE), made from natural gas derived ethane (mean: 1.8 kg CO₂/kg LDPE). The life-cycle GHG emissions from bioethanol and bio-LDPE are examined for three biomass feedstocks: U.S. corn (mean: 97 g CO₂e/MJ and 2.6 kg CO₂e/kg LDPE), U.S. switchgrass (mean: −18 g CO₂e/MJ and −2.9 kg CO₂e/kg LDPE), and Brazilian sugar cane (mean: 33 g CO₂e/MJ and −1.3 kg CO₂e/kg LDPE). Two new GHG credits for chemical use of bioethanol (to produce bioethylene) and for bio-LDPE are examined for each biomass feedstock. Bio LDPE and bioethanol achieve greater GHG reductions than bio-LDPE. For U.S. production, bioethanol achieves slightly greater GHG reductions than bio-LDPE. For imported Brazilian products, bio-LDPE achieves greater GHG reductions than bioethanol. An expanded policy that includes bio-LDPE provides added flexibility without compromising GHG targets.

INTRODUCTION

In 2007, the United States (U.S.) Energy Independence and Security Act (EISA) expanded the national Renewable Fuel Standard (RFS). 1 The new standard (RFS2), administered by the U.S. Environmental Protection Agency (EPA), requires refiners, blenders, and importers of transportation fuels to meet increased minimum annual biofuel production targets in each of three categories: cellulosic, advanced (anything other than corn ethanol), and renewable (no restrictions). Targets increase annually as shown in the Supporting Information (SI Figure 1). By 2022 RFS2 requires an annual total of 36 billion gallons of renewable fuel, including at least 15 billion gallons of cellulosic, and an additional 5 billion gallons of advanced biofuel. To qualify under RFS2, renewable fuels from facilities constructed after 2007 must achieve at least a 20% reduction in lifecycle greenhouse gas (GHG) emissions relative to baseline (generally gasoline). Steeper reduction targets of 50% and 60% (compared to baseline) are required to qualify as an advanced biofuel or cellulosic biofuel, respectively. Mandated production volumes and GHG reduction targets may be reduced by EPA waiver under certain circumstances. 1

Thus, far, biofuel targets have been met predominantly by blending increasing quantities of bioethanol into conventional gasoline. This practice is approaching its limit at the 10% ethanol (E10) “blend wall”, the upper bound for which the warranty is valid on most cars. 2 Although EPA has issued a partial waiver for use of a 15% ethanol blend (E15) in vehicles from model year 2001 and newer, the Congressional Research Services suggests the “limitation to newer models, coupled with infrastructure issues, are likely to limit rapid expansion of blending rates”. 2 Lack of infrastructure further impedes use of ethanol at higher blends, such as E85, 3 and so the EPA has begun reducing target biofuel production volumes starting in 2014. 4 The difficulties faced by RFS2 can be partially attributed to its limited scope of application (the transportation sector). This simultaneously limits the market for biofuels and places competing uses for bioethanol at a disadvantage in the marketplace. This paper investigates the GHG emissions associated with an alternate use for bioethanol: to produce biobased chemicals. The goal of this analysis is to inform on the potential impact from creating a new, more inclusive federal policy for use of bioethanol, modeled on RFS2. The main question addressed is whether biobased chemicals (specifically bioethylene) from certain feedstocks could achieve similar GHG accounting reductions to the targets laid out in RFS2. Regulatory hurdles and other potential impacts such as those highlighted by the food versus fuel debate (e.g., ref 5) are beyond the scope of this paper but would need to be considered in the future in a broader assessment of the implications of such a policy.

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Bulk chemical production is responsible for about 5–6% of both U.S. GHG emissions and U.S. energy consumption (including feedstock energy). Ethylene is one of the industry’s most important chemicals and can be produced through the dehydration of ethanol. Current U.S. ethylene production is 24 million tons/year. Global production is about 5 times that, making ethylene the world’s largest volume organic chemical. While transportation fuels represent a much larger proportion of U.S. energy use (28%) than bulk chemicals, the latter remains a sizable market. For a point of comparison, the full RFS2 mandate (36 billion gallons of ethanol or ethanol equivalent) represents only about 3% of U.S. energy needs. This paper is focused on bioethylene as a first step toward assessing whether a more comprehensive Renewable Materials Standard (RMS) should be considered as a way to reduce GHG emissions from various sectors. Replacing yearly demand of U.S. fossil ethylene with bioethylene could elevate the demand for bioethanol by roughly the equivalent of current national U.S. ethanol production. In 2014, EPA waiver reduced RFS2 requirements by approximately 3 billion gallons of ethanol; this gap could have been bridged by converting 20% of U.S. ethylene production (5 million tons) to bioethylene.

Bioethylene is chemically and functionally indistinguishable from its conventional fossil-fuel counterpart. This distinguishes it from bioethanol fuel in that bioethylene need only compete on costs, while bioethanol faces a host of other demand-side constraints, such as energy differences per gallon and new infrastructure requirements. Small amounts of bioethylene are already in production, with Brazil having the highest capacity. Nevertheless, bioethylene production remains minimal compared to fossil ethylene (<1% of global ethylene production).

At present, U.S. ethylene production is dominated by steam cracking of light hydrocarbons (65% from ethane and 15 to 20% from propane) derived from natural gas. Cracking of heavy feedstocks (primarily naphtha) accounts for most of the remaining 15 to 20%. Availability of light feedstocks is expected to remain strong for decades, suggesting that ethane cracking will continue to dominate U.S. production for the foreseeable future.

The policy change assessed in this paper would result in a partial shift away from fuel-use of ethanol toward chemical use (for bioethylene). Evaluating the GHG impact of this move requires comparing the difference in GHG emissions between gasoline and bioethanol to the difference in emissions between fossil ethylene and bioethylene. Numerous studies have investigated life-cycle emissions from production of biofuels (reviewed in refs 19–21). Fewer studies investigate the impacts from bioethylene products, and just two of these explicitly considered competition between fuel and chemical use for biomass. Two studies were tailored to a U.S. context, and just one explicitly modeled the emissions from a natural gas derived ethane to ethylene pathway. Only two studies considered emissions from indirect land use change (ILUC). The studies in refs 22–30 generally report that bioethylene based products can achieve reductions in GHG emissions and nonrenewable energy use, though potentially at the expense of other environmental impacts (e.g., acidification and eutrophication).

Figure 1. Pathways considered in the life-cycle assessment. Five unique feedstocks (sugar cane, corn, switchgrass, natural gas, and crude oil) are considered. Target products (energy and LDPE) are indicated at the bottom. The functional unit is 46.9 MJ of energy for fuel or 1 kg of LDPE for chemical use. Key intermediate product flows are shown in black. Coproducts are shown in gray text.
culation). Notable exceptions include one of the scenarios from Liptow and Tillman25 (the “attributional” model with “higher estimate” ILUC shows a 10% increase in GHG emissions from sugar cane polyethylene relative to production from crude oil) and Ghanta et al.30 who find highest GHG emissions for corn ethanol to ethylene (0.67 kg CO₂e/kg ethylene), followed by naphtha (0.50 kg CO₂e/kg ethylene), and finally ethanol (0.42 kg CO₂e/kg ethylene). Alvarenga et al.23 focus exclusively on Brazilian sugar cane and report similar GHG savings for cradle-to-gate GHG emissions for polyethylene production simulation, this paper develops an accounting estimate for the cradle-to-gate GHG emissions for polyethylene production (specifically low-density polyethylene (LDPE)). Although ethylene is used as a raw material for many products, the majority (∼70%) is used to manufacture polyethylene.10 Baseline GHG emissions from fossil-based production (ethane to ethylene) are compared to the expected GHG emissions from biobased ethylene production for three biomass pathways: U.S. switchgrass (a cellulosic feedstock), Brazilian sugar cane (an “advanced” feedstock), and U.S. corn starch. Finally, competing uses for ethanol (as fuel or to produce bioethylene) are examined: the difference in GHG emissions between bioethylene and fossil ethylene is compared to the difference in GHG emissions between ethanol and gasoline. The comparisons drawn in this paper refer to changes in GHG emissions accounting and may not correspond to actual emission changes for several reasons, as elaborated in the Results and Discussion section.

■ METHODS

Pathways Overview. Eight pathways are modeled as shown in Figure 1. Four of these are fuels: gasoline, switchgrass ethanol, corn ethanol, and sugar cane ethanol. The other four are LDPE: natural gas LDPE, switchgrass LDPE, corn LDPE, and sugar cane LDPE. The various pathways produce different products so a consistent functional unit such as kg of product would be misleading. To facilitate comparisons, the functional unit for each pathway is normalized to the same quantity of ethanol (1.74 kg), corresponding to 1 kg of LDPE production or 46.9 MJ energy (lower heating value).

For each biobased pathway, an accounting of the following steps is included: cultivation (including emissions from land-use change), feedstock transportation, and ethanol production via fermentation. The ethanol produced from each pathway is chemically identical and is differentiated only by location (U.S. or Brazil). Corn ethanol is coproduced with dried distiller grains with solubles (DDGS). Switchgrass and sugar cane ethanol are coproduced with unused feedstock components, which may be used to generate electricity. Three additional steps are modeled for fuel-use ethanol: transport to the U.S. (for Brazilian ethanol only), fuel distribution, and combustion. For chemical use (polyethylene production), additional modeled processes include transport of ethanol to the ethylene production facility, dehydration of ethanol to ethylene, polymerization of ethylene to LDPE, and transport to the U.S. (Brazilian LDPE only). These steps are modeled using regionally applicable parameters for Brazilian and U.S. pathways, respectively.

For ethanol fuel, the conventional alternative is gasoline, for which the distribution of GHG emissions are as modeled by Venkatesh et al.31 The conventional pathway for LDPE production in the U.S. is via natural gas derived ethane. The life-cycle analysis includes preproduction, wet natural gas extraction, processing, steam cracking, and polymerization. A number of coproducts are produced throughout the process as shown in Figure 1.

Model Overview and Selection of Distributions and Parameters. The models for switchgrass and corn ethanol production are adapted from Mullins et al.32 The model for sugar cane ethanol is adapted from Liptow and Tillman25 and Seabra et al.33 The former paper was selected as it is among the only papers directly to consider a bio-LDPE pathway for Brazilian sugar cane and is thoroughly documented in an earlier report.34 The study by Seabra et al.33 is among the more recent studies for Brazilian sugar cane ethanol and was based heavily on primary survey data and directly provides parameters for inputs to Monte Carlo simulation. Parameters have been updated where new information is available, as detailed in the text below and in the Supporting Information (SI). Upstream emissions from natural gas associated with the production of ethylene follow the modeling approach from Venkatesh et al.,35 updated with more recent data, the inclusion of preproduction emissions, a more complete allocation of emissions to coproducts, plant-level data for natural gas processing emissions, and the weighting of data prior to fitting each distribution.

When literature sources contain multiple estimates for a single parameter, simple distributions capturing this range are used. Where there is a clear best estimate or a clustering of central estimates, triangular distributions are employed. If only a range is available, then a uniform distribution is used. Where there are a large number of data points, Palisade’s @Risk software is used to fit a continuous distribution.

For the natural gas ethylene pathway, estimates for the emissions from a given process are made separately for each U.S. state (34 in all as the remaining 16 do not produce natural gas), whenever data disaggregated by state are available. In the Monte Carlo analysis, these estimates are the inputs to a discrete distribution with weights being proportional to each state’s share of current national ethane production.

Allocation. Each of the pathways discussed above involves coproducts. Where possible, these are treated by system expansion, as follows. Switchgrass and sugar cane ethanol are credited for surplus electricity production with displaced GHG emissions from U.S. and Brazilian average electricity production emissions factors, respectively. Corn ethanol is credited for DDGS with displaced emissions from other animal feeds as modeled by Argonne National Laboratory’s GREET model.36 Natural gas LDPE is credited for hydrogen production (from ethane steam cracking) with displaced emissions from producing hydrogen via methane steam reforming, the dominant method for hydrogen production in the U.S.37

Emissions from natural gas LDPE production are allocated to remaining products on a mass basis. Though arbitrary, this is a common convention for assigning emissions and allows for a consistent basis of comparison between pathways. Preproduction and extraction emissions are allocated to all products.
produced prior to steam cracking (dry natural gas lease condensate, propane, butane, isobutane, pentanes plus and ethane). Processing emissions and steam cracking emissions were allocated to products at the point of exit from the processing plant (processed dry natural gas, propane, butane, isobutane, pentanes plus and ethane) and cracker (propylene, butadiene, aromatics, and ethylene), respectively. In the estimate for emissions from gasoline, Venkatesh et al. performed allocation of emissions to oil refinery products on a mass basis.

**Global Warming Potential.** Results for this study are reported for the 100-year global warming potential (GWP), using equivalence factors (in kg CO₂e) as reported by the Intergovernmental Panel on Climate Change (IPCC) fifth assessment report (ARS). Equivalence factors are assumed to be normally distributed with uncertainty ranges as presented in the ARS Supplementary Material. Certain sources used as inputs to this paper report only total GWP (not disaggregated by gas) and could not be adjusted to reflect the latest equivalence factors; further details can be found in SI section 1.2.2.

**Fuels and Electricity.** For life-cycle emissions from coal and from petroleum derived fuels (diesel, residual fuel oil, and gasoline), distributions from Venkatesh et al. are used. For emissions from natural gas used as a fuel, an approximate distribution of emissions is fitted to the parameters provided in Venkatesh et al. Emissions from processes taking place in Brazil are modeled using a distribution for average Brazilian grid emissions. Processes taking place in the U.S. employ a distribution for average emissions by North American Electric Reliability Corporation (NERC) region: MRO for corn ethanol production, the combined SPP, TRE, and SERC region for switchgrass ethanol production, and the combined SERC and TRE region for both dehydration of ethanol to ethylene and ethylene polymerization. See SI section 1.2.3 for further explanation.

**Natural Gas Preproduction.** Before a natural gas well becomes operational, various development stages must be concluded, such as the construction of a staging area (the well pad) and well drilling, both of which require energy inputs. In addition, for unconventional wells (e.g., in shale formations), the hydraulic fracturing procedure requires the production of specialty chemicals and the management of large quantities of produced water. These preproduction emissions are modeled using distributions developed in a recent review paper by Weber and Clavin. Emissions from well completions and workovers are described in the SI. See SI section 1.2.4 for more details.

**Natural Gas Extraction (Production).** Emissions from natural gas production arise through the combustion of “lease fuel” used to power the extraction process, through intentional venting and flaring of natural gas, and through unintentional leaks or fugitive emissions. The U.S. Energy Information Administration (EIA) reports total lease fuel consumed (by volume) in each state. Lease fuel is assumed to be composed of CH₄ and CO₂ and to be combusted with 100% efficiency. Emissions are then allocated to the relevant products (and normalized by the total mass of each product) by state. EIA reports natural gas vented and flared in each state. As for lease fuel, vented/flared gas is assumed to be all CH₄ and CO₂, and, following Venkatesh et al., it is assumed that all such gas is flared. Emissions are then allocated and normalized across products by state. Finally, the annual EPA Greenhouse Gas Inventory provides data on other CH₄ emissions from the natural gas production phase by National Energy Modeling System (NEMS) region. The emissions in each NEMS region are fit to a triangular distribution, assuming the relative uncertainty on production emissions within each region is on the same order as for the entire natural gas system (−19% to +30%) as reported by EPA. Emissions from each NEMS region are allocated to each of its constituent U.S. states in proportion to their total natural gas production. See SI section 1.2.5 for details.

**Natural Gas Processing.** Natural gas processing involves the separation of whole gas from the wellhead into different hydrocarbon products including dry natural gas, ethane, propane, n-butane, isobutane, and pentanes plus as well as the removal of nonhydrocarbon gases such as N₂, CO₂, and sulfur containing compounds. Emissions in the stage result from fuel used to power the process, intentional release of scrubbed CO₂, and fugitive emissions of natural gas. Processing emissions were modeled using 2011 data from actual processing facilities as reported to the EPA Greenhouse Gas Reporting Program. To the extent possible, each facility was matched with the corresponding processing plant in the EIA processing capacity database, which gives average daily plant flow from mid-2011 to mid-2012. In all, 222 plants were matched, accounting for 80% of EPA reported daily plant flows. The total GHG emissions from each processing plant (recalculated to reflect the ARS GWP values) are then normalized by its annual plant flow. These emissions are weighted by the plant flow and fit to a continuous distribution. Emissions are then allocated to the relevant products (and normalized by the total mass of each product) on a national basis. See SI section 1.2.6 for more details.

**Steam Cracking.** The conversion of ethane to ethylene is an energy intensive process known as steam cracking. In this process, saturated hydrocarbons like ethane are heated to high temperatures (≥750 °C) in the presence of steam, resulting in a mix of products that is usually optimized for olefins like ethylene. Valuable coproducts result from this process and include ethylene, propylene, butadiene, aromatics (e.g., benzene), and hydrogen. Specific energy requirements for the production of a ton of ethylene via steam cracking of ethane are estimated by a number of sources, as are volumes for coproducts and direct CH₄ emissions. It is assumed that produced methane, C4 components (i.e., butanes), and C5/C6 (i.e., pentanes, hexanes) components are used as fuel to power the steam cracking process and that any residual energy needs are provided by natural gas. Ethylene, propylene, butadiene, and aromatics (treated as benzene) are all treated as products and subject to mass allocation. Hydrogen is treated by system expansion, as discussed above. See SI section 1.2.7 for more details.

**Land Use Change (LUC).** All biobased pathways considered in this study have the potential to cause emissions through the repurposing of land, either directly or as a consequence of indirect market forces. Such emissions may occur over the course of many years, and while there is no agreed methodology to account for their impact, LUC emissions are potentially critical to the GHG impact of biobased products. The U.S. EPA provides estimates for LUC emissions specifically designed to account for the impact of RFS2, these estimates assume a 30-year time horizon and are used for the base-case model in this study. Though arbitrary, a 30-year amortization period is common in the treatment of
LUC emissions. Point estimates for domestic LUC emissions from U.S. corn and switchgrass ethanol production (both are negative, representing carbon sequestration) are combined with triangular distributions fit to EPA’s 95% confidence intervals for international land use change emissions from each feedstock. The confidence intervals provided by EPA ignore uncertainty in their economic model of land-use change. In addition, EPA’s results rely on 2022 as the year of analysis, which creates inconsistencies with other assumptions (based on current technologies) made in this analysis. Furthermore, there is a large range of estimates for LUC emissions in the literature, which is not fully captured by the distribution employed here. Nevertheless, the EPA analysis provides a common set of assumptions for the three feedstocks under study. Sensitivity to LUC emissions is further examined in the SI section 1.4.3

**Cultivation of Biomass Feedstock.** Remaining emissions from agriculture include use of fossil fuels for farming equipment, emissions from agrochemical production, N₂O emissions from volatized nitrogen fertilizer, and CO₂ from calcium carbonate fertilizer. For sugar cane, there are also emissions of CH₄ and N₂O from field burning during harvest. Emissions of CO₂ from field burning are excluded because the carbon source is biogenic, and so the carbon was only recently removed from the atmosphere. For corn and switchgrass pathways, application of synthetic nitrogen fertilizer and crop residue is modeled as in Mullins et al., quantities of other agrochemicals and emissions from fossil fuel use are calculated from the data provided by GREET, using default input parameters. For sugar cane cultivation, distributions for diesel consumption (in L/ha), cane productivity (in t/ha), the quantity of trash burned, and quantities of applied fertilizers and pesticides are taken from Seabara et al., the emissions factor for straw burning is taken from GREET. The emission factor for N₂O from applied fertilizer is modeled stochastically using the uncertainty range provided by the IPCC, although there is some evidence this may underestimate potential N₂O emissions. For all pathways, emissions for the production of agrochemicals are taken from GREET, using separate estimates for U.S. (corn and switchgrass) and Brazilian (sugar cane) production.

**Ethanol Production.** Production of ethanol from sugar cane can be entirely powered by the combustion of bagasse, the dried residue left over after extracting juice from the sugar cane. CO₂ emissions from bagasse burning are annual biogenic emissions and are thus disregarded. Yield of ethanol from sugar cane and quantity of surplus electricity generated by bagasse combustion are modeled as in Seabara et al. See SI section 1.2.8 for more details.

Total heat and electricity required for corn and switchgrass ethanol production, their respective feedstock chemical composition, and yields from the hydrolysis and fermentation processes are as modeled in Mullins et al. In the case of switchgrass, it is assumed that all nonfermentable and unreacted components are combusted in a 68% efficient boiler (higher heating value basis) to produce heat. Any surplus heat is used to drive an 80% efficient turbine, which generates electricity for the process and potentially surplus electricity for sale to the grid. Any heat shortfall in either process is provided by natural gas, while any electricity shortfall is made up by grid electricity.

**Ethanol Dehydration.** For all biobased pathways, ethanol to ethylene conversion follows the fuel and electricity inputs outlined in a 1981 article using the commercial Syndol catalyst, which still represents the dominant technology in use today. Generic uncertainty factors were applied following the method proposed by Geisler et al. Although the data used here is over 30 years old, it is in close agreement with modeling based on a recent patent and results from actual plant data. See SI section 1.2.9 for more details.

**Polymerization.** The last step in the production of LDPE plastic from ethylene is polymerization of individual ethylene molecules to make the final polymer. This process requires both heat (fuel) and electricity. For U.S. pathways, polymerization is modeled using average U.S. industry data. Brazilian polymerization is assumed to follow European parameters, uniformly distributed between the values reported by Liptow and Tillman and PlasticsEurope. Electricity emissions are calculated using Brazil-specific emissions factors. See SI section 1.2.10 for more details.

**Transportation.** At several stages throughout the pathways considered, intermediates must be moved from one location to another. For switchgrass and corn, emissions for feedstock transportation to the ethanol production facility are taken from GREET. For U.S. LDPE production, it is assumed that ethanol is transported by single unit truck using fuel requirements from NREL. For corn ethanol, the transportation distance is assumed to range from 1,000 to 1,800 km, the approximate distance from the U.S. Midwest, where most ethanol biorefineries are located, to the Gulf Coast states, where most ethylene production and infrastructure is located. Switchgrass production is expected to occur primarily in the southeast, resulting in shorter distances (modeled as 0 to 1,500 km with a mode of 1,000 km). For sugar cane, the diesel required for feedstock transportation to the ethanol production facility and subsequent transport of ethanol to the ethylene plant is modeled as in Liptow and Tillman. Transport of the final product (ethanol or LDPE) from Brazil to the U.S. is modeled as a residual fuel oil tanker (fuel requirements from NREL) shipping from Parana, Brazil to Houston, Texas. Fuel distribution for ethanol within the U.S is modeled as in GREET.

**Use Phase and End of Life.** The final stage for both ethanol fuel and gasoline is combustion. For ethanol, all emissions in this phase are biogenic and so are not included in the accounting of GHG emissions. For gasoline, these emissions are already accounted for in the distribution from Venkatesh et al.

For LDPE, use phase and end of life (EOL) are not explicitly modeled as all pathways have converged at the point of production of U.S. LDPE or arrival of Brazilian LDPE to the U.S. While alternative EOL strategies may impact on the life-cycle emissions for LDPE, they will not affect the comparison between fossil-based and biobased production. For the biobased LDPE pathways, carbon taken up during plant growth is now locked away in a nonbiodegradable product. The carbon content of polyethylene accounts for 12/14 of the total mass and is treated as a credit for the amount of CO₂ this carbon would otherwise represent: 3.1 kg CO₂/kg LDPE. More explicit treatment of end of life would not appreciably change the life-cycle emissions for LDPE consumed domestically. In the United States, approximately 85% of plastics are landfilled; the EPA estimates emissions of approximately 0.04 kg CO₂e/kg LDPE landfilled – roughly 2% of fossil LDPE life-cycle GHG emissions. Key parameters for all pathways are given in SI section 1.2.11.
RESULTS AND DISCUSSION

The results presented below must be interpreted with caution. Parameters used in this study are taken as the closest approximation of present operating conditions. However, data is drawn from multiple sources, which could produce inconsistencies. Further, with the exception of land-use change accounting, this study follows an attributional life-cycle assessment (ALCA) approach, which is a form of environmental accounting. It does not predict the actual changes in emissions that would result from increased production of biobased products, for which the use of average electric grid emissions and the implicit assumption of 1:1 displacement of fossil products would be inappropriate. The ALCA approach, however, is indicative of the emissions that may be attributed to each pathway (taken in isolation from market forces) and as such provides a consistent basis to establish how pathways perform relative to EISA targets. To avoid confusion, results are referred to as ‘modeled emissions’ and ‘GHG accounting reductions’.

Simulated life-cycle GHG emissions for each of the 8 pathways considered are shown in Figure 2 (see SI section 1.3.1 for numerical results). To allow comparison between pathways, results are normalized to the amount of ethanol needed to produce 1 kg LDPE, which is 46.9 MJ of ethanol for fuel pathways; fossil-based pathways are likewise scaled to 1 kg LDPE and 46.9 MJ gasoline, respectively. Fuel use of ethanol has higher modeled emissions when compared to LDPE from the same feedstock. This is due primarily to combustion of the produced ethanol as a fuel.

When comparing across biobased pathways, the lowest modeled emissions are for the cellulosic feedstock (switchgrass), followed by the “advanced” feedstock (sugar cane), and finally corn starch. For both sugar cane and switchgrass, nearly all model runs suggest that both LDPE and ethanol fuel will result in decreased modeled emissions relative to their fossil fuel counterparts. On the other hand, corn products result in higher modeled emissions with a high degree of confidence (~90% of model runs for LDPE and ~70% of model runs for ethanol). A substantial number of model runs predict negative emissions (net carbon sequestration) for the switchgrass and sugar cane LDPE pathways. This suggests that no amount of improvement to the fossil LDPE pathway (e.g., via recycling) would lead to the fossil route being preferred. Switchgrass ethanol for fuel may also result in negative modeled emissions if displacement of grid emissions by surplus electricity generation occurs. This is not the case for sugar cane ethanol, as less surplus electricity is produced, plus displaced Brazilian electricity has a relatively low carbon intensity.

Following the “risk of policy failure” framework developed by Mullins et al., Figure 3 shows the modeled probability

Figure 2. Modeled life-cycle GHG emissions from all pathways. a) Simulated GHG emissions from production of LDPE from corn, natural gas (NG), sugar cane (SC), or switchgrass (SW). b) Simulated GHG emissions for the production and combustion of 46.9 MJ of fuel, using corn ethanol, gasoline, sugar cane (SC) ethanol, or switchgrass (SW) ethanol. The functional units (1 kg LDPE or 46.9 MJ) represent equivalent quantities of ethanol. For clarity, the y-axis refers to “probability density” but should only be interpreted as a relative proportion of model runs.

Figure 3. Proportion of model runs in which modeled GHG emissions from each biobased pathway are below those of the fossil fuel counterpart (at 0%) or below some policy target. 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, y-axis refers to “probability” but should only be interpreted as a proportion of model runs.
values on the y-axis represent higher confidence (i.e., measured in percentage of model runs) that a given GHG reduction target can be achieved. A more conventional cumulative distribution function is presented in SI section 1.3.2, with numerical results presented in SI Table 15.

Corn pathways achieve the “renewable biofuel” 20% reduction target in very few model runs, which is in agreement with results previously presented by Mullins et al.\textsuperscript{(32)} Both sugar cane pathways can meet the “advanced biofuel” 50% reduction target. Both switchgrass pathways achieve the “cellulosic biofuel” 60% reduction target in nearly all model runs—a slightly more optimistic result than presented by Mullins et al.,\textsuperscript{(32)} due to higher estimates of feedstock energy and GHG intensity of displaced electricity employed here.

Feedstock choice (corn, sugar cane, or switchgrass) has a larger impact on modeled GHG accounting savings than how the ethanol is used (for fuel or LDPE). For U.S. production (corn and switchgrass), fuel use of the ethanol stochastically dominates (greater GHG accounting savings) chemical use, while the reverse is true for Brazilian production (sugar cane). The difference stems first from the lower emissions of Brazilian electricity used in ethanol dehydration and ethylene polymerization and second from the reduced weight of shipping LDPE relative to ethanol when transporting the end-products to the U.S.

Finally, Figure 4 presents the GHG accounting savings (if any) that bio-LDPE can achieve above and beyond the modeled GHG accounting savings from bioethanol fuel. Results are expressed as a percent of gasoline life-cycle emissions. U.S. production of bio-LDPE would require a relaxation of expected emission reductions compared with bioethanol fuel (e.g., by 17% of gasoline emissions for 80% of model runs confidence level). Brazilian production would allow for additional GHG accounting savings (e.g., by 5% of gasoline emissions for 80% of model runs confidence level). Numerical results (in kg CO$_2$e/fuel) are available in SI Table 16. A major advantage of this presentation is that it is independent of the emissions from ethanol production (ethanol emissions are subtracted out when taking the difference between net emissions from bioethanol and bio-LDPE) and can be readily applied to new feedstocks or other studies on cradle-to-gate ethanol emissions.

An alternative way to frame this discussion would be to establish a GHG equivalence factor between bio-LDPE and bioethanol fuel for policy achievement purposes—that is, for every unit of ethanol diverted from fuel use, how much ethanol must go toward bio-LDPE to achieve the same GHG accounting reductions. More details are available in SI section 1.3.3. Figures 3 and 4 implicitly assume that biobased products replace their conventional fossil counterparts on a 1:1 basis. Though 1:1 replacement is accurate in physical terms, the resulting changes in market prices make 1:1 replacement unlikely across the entire market. This is discussed further in the sensitivity analysis. Alternate versions of Figures 3 and 4, which also incorporate indirect market effects, are available in SI section 1.4.4.

Sensitivity Analysis. For each biobased pathway, inputs were ranked by their impact on mean net emissions (see SI section 1.4.1). For corn and switchgrass pathways, modeled uncertainty in emissions from the biobased pathways is larger than modeled uncertainty in emissions from the displaced fossil fuel counterparts. The reverse is true for sugar cane pathways. Top uncertainties in corn and sugar cane pathways are related to fertilizer N$_2$O emissions and emissions from land-use change. For switchgrass, key uncertainties are all related to emissions reductions from displaced electricity. In several pathways, important contributors to uncertainty are the global warming potentials for CH$_4$ and N$_2$O — parameters whose uncertainty is often overlooked.

Sensitivity to emissions from land-use change (LUC), to the treatment of displaced electricity, to the use of marginal electricity, to the choice of feedstock for displaced fossil LDPE, and to the assumption of 1:1 displacement of fossil products are also presented in SI sections 1.4.2 to 1.4.5. Noteworthy findings are described here. Removal of land-use change (LUC) emissions allows corn pathways to achieve net GHG accounting savings but provides only limited ability to achieve EISA targets (60% of model runs for ethanol and 30% for LDPE); for switchgrass and sugar cane, high values of LUC may prevent those pathways from achieving EISA targets but are unlikely to result in a net increase in emissions relative to fossil products. Without credit for displaced electricity, switchgrass LDPE is less likely to meet EISA’s cellulosic biofuel targets (50% of model runs), although substantial GHG accounting savings are still achieved. The choice of feedstock for displaced fossil LDPE, credit for displaced electricity for switchgrass ethanol or for sugar cane pathways, and the use of average rather than marginal electricity emissions factors affect net emissions for each pathway but without overturning conclusions regarding the ability to meet EISA GHG targets. Finally, while market effects, such as the indirect fuel use effect,\textsuperscript{(74)} may significantly affect the GHG accounting savings from biofuel pathways, bio-LDPE pathways are far less vulnerable to similar market-induced indirect demand increases for fossil LDPE (due to the relatively low emissions from fossil LDPE). Alternate end of life scenarios (e.g., incineration) for LDPE could overturn this result. Further discussion of this effect, which we term indirect demand change (IDC), is available in SI section 1.4.4.

Cost Considerations. Production costs for bioethanol and bioethylene have been estimated by the International Renewable Energy Agency.\textsuperscript{(14)} Ranges for the cost of production of fossil ethylene and gasoline were estimated from recent historical data and official sources.\textsuperscript{(75–79)} Details are available in SI section 1.3.4. Bioethylene (from any source) is

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\textbf{Figure 4.} Proportion of model runs in which modeled GHG accounting reductions from fossil LDPE replacement are superior to those from gasoline replacement (at 0% on the x-axis) or in excess of some policy target. Positive values indicate that more stringent accounting reductions can be met through LDPE replacement. Negative values represent needed relaxation in the target emissions reductions (as a % of gasoline emissions). For clarity, the y-axis refers to "probability" but should only be interpreted as a proportion of modeled runs.
substantially more expensive to produce than ethane-derived ethylene. In contrast, ethanol, particularly from sugar cane, may already be competitive with gasoline. Implicit carbon prices were calculated by simulating cost data along with GHG emissions.

While bioethanol appears to be a reasonable GHG mitigation strategy (leading to implicit carbon prices of $200 to $300/ton CO₂e for sugar cane and $0 to $100/ton CO₂e for switchgrass), bioethanol can only be justified at current production costs (corresponding to implicit carbon prices of 150 to 350 $/ton CO₂e for sugar cane and 200 to 500 $/ton CO₂e for switchgrass) if substantial cobenefits are expected. Nevertheless, private investment into bioethanol is already taking place.80,81 Adopting a more flexible standard in place of RFS2 will likely decrease the overall cost of compliance, particularly as market prices change and new production technologies evolve. Further details and results are available in SI section 1.3.4.

The Way Forward. The relative desirability of the pathways studied here depends on both market conditions and the goals of the policy effort. The preamble to EISA makes clear that its goals include both energy security and independence as well as the promotion of “clean” renewable fuels.1 Currently, U.S. ethane production is almost entirely used for the production of ethylene. Ethane displaced from ethylene production may be included (to a limited extent) in existing natural gas streams or used as fuel for upstream fossil fuel production, displacing methane and thereby increasing the availability of natural gas. It should be noted, however, that the U.S. is already expected to become a net exporter of natural gas by 2020.18 In contrast, the EIA reference scenario assumes continued reliance on imports for liquid fossil fuels through 2040.18 Thus, from the standpoint of energy independence, there is less to be gained by incentivizing bioethanol production and focus should remain on fuel use of ethanol with an emphasis on domestic production.

If the policy goal is simply to encourage production of biofuels (e.g., for rural development, to achieve learning by doing cost savings, etc.), then any expansion of biobased production should be viewed favorably, and so incentives for bioethanol production would be beneficial. In light of existing constraints on biofuel consumption discussed at the outset of this paper, continued expansion of bioethanol production may need to rely on new pathways like bioethylene.

The focus of this analysis, however, is the impact of strategies for biomass use on GHG emissions. From a global warming perspective, the choice of feedstock is significantly more important than whether it is used for fuel or ethylene production. This suggests that in an environment of constrained demand for ethanol fuel, promoting bioethylene would be a promising alternative. Indeed, between the imported Brazilian products, biobased LDPE is actually the preferred route (as modeled) for GHG mitigation. Under the specific scenario of U.S. production with supply side constraints (as is currently the case for cellulosic biofuel), and no demand-side limitations, then fuel-use for ethanol should be given priority. If GHG equivalence factors are employed as discussed above, then there is no need for policy makers to choose between bio-LDPE and bioethanol fuel.

The expanded policy analyzed in this paper constitutes a partial departure from the energy security emphasis of EISA and the transportation fuels focus of RFS2. Nevertheless, increasing incentives for biobased chemicals would open new opportunities to conserve fossil fuels, to reduce GHG emissions, and to bolster the ethanol industry by shifting toward higher value products. Further work is needed to establish the details of a new standard and its economic, social, and sustainability implication. One possibility would be to allow manufacturers of bioethylene to sell credits into the existing renewable identification number market for biofuels. A carefully revised policy has the potential to provide added flexibility to obligated parties while having no adverse impact on GHG emission accounting targets.

ASSOCIATED CONTENT

Supporting Information
Detailed explanation of methods and modeling parameters employed, additional results, and references. This material is available free of charge via the Internet at http://pubs.acs.org.

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