Comparative Life Cycle Assessment of Fossil and Bio-based Polyethylene Terephthalate (PET) Bottles

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Abstract

Both biofuels and bioplastics are often regarded as sustainable solutions to current environmental problems such as climate change, fossil depletion and acidification. However, both have been criticized for being economically costly, competing with other societally beneficial goods such as food, and offering limited environmental benefits compared to their fossil counterparts. This study provides a comparative environmental Life Cycle Analysis (LCA) for 100% bio-based polyethylene terephthalate (PET) bottles, versus fully fossil-based and partially bio-based PET bottles. An attributional life cycle assessment (aLCA) and sensitivity analysis of key assumptions is carried out to compare cradle-to-factory-gate impacts (i.e. feedstock extraction, component production and product manufacturing) of twelve PET bottle production scenarios. Results indicate that woody-biomass based PET bottles have 21% less global warming potential and require 22% less fossil fuel than their fossil based counterparts, but perform worse in other categories

such as ecotoxicity and ozone depletion impacts. Results are sensitive to impact allocation assumptions as well as parameter input assumptions related to isobutanol production. In most categories, with avoided impact credits considered, forest residue feedstocks result in overall better environmental performance than corn stover feedstocks for bio-PET bottle production. The variability in avoided burdens could alter the relative environmental rankings for fossil and bio-PET bottles. Depending on the biomass feedstock, extraction and pre-processing are likely more emission-intensive than the corresponding fossil refinery processes due to the significant upstream emissions embodied in the application of fertilizers, and the significant chemical and energy inputs required to break recalcitrant lignocellulosic bonds.

Keywords Comparative Life Cycle Assessment (LCA); Polyethylene Terephthalate (PET); Paraxylene (PX); Bioplastics; Bio-Polyethylene Terephthalate (Bio-PET) Bottle.

1 Introduction

In response to growing concerns about climate change, many countries have enacted stringent carbon policies to limit greenhouse gas emissions of domestic industries. As a result, growth of traditional fossil refineries and fossil power facilities, which together generate the leading share of total carbon emissions, has slowed. However, global demand of energy supplies will continue to grow, with a 37% increase by 2040 (USEIA, 2013). Consequently, there is an urgent need to identify and utilize renewable resources to meet this increasing demand. Biomass is recognized as a sustainable alternative due to its abundant availability, carbon-neutrality and low sulfur content. Countries like the United States, India, China, South Africa, and those in the European Union have all set ambitious goals to achieve a higher share of biofuels in their overall fuel mix (Vivekanandhan et al., 2013). Nonetheless, the commercialized first generation biofuels have been criticized for competing with food crops (Pimentel et al., 2008; Sims et al., 2010), causing considerable environmental impacts during biomass farming (Valipour, 2015a; Valipour, 2015b) and having limited greenhouse gas emission reductions (De Fraiture et al., 2008; Fargione et al., 2008;

Melillo et al., 2009; Zaines et al., 2013). To address those issues, second generation biofuels have been developed primarily from non-food crops, agricultural wastes, and forest residues (Hsu et al., 2010), although the high cost of processing enzymes and building new facilities currently hinders their commercialization (Stephen et al., 2012). So far, government subsidies are the primary force propelling biomass resource utilization (Vivekanandhan et al., 2013), but these are temporary and can be decreased or even suspended if no further economic benefits are generated with biofuels (USEIA, 2013).

A promising solution to the problem is establishing integrated biorefineries, where biochemicals and biomaterials are coproduced with biofuels. This is inspired by fossil fuel refineries, where less than 10% of fossil oil is used to produce non-energy products, but it accounts for nearly half of the total economic value of the whole petroleum refinery system (Hatti-Kaul, 2010; Nelson and Powell, 2010). Biochemicals and biomaterials have similar potential to reduce the per unit operation costs of biofuel production and to better utilize biomass feedstocks (Bergeron et al., 2012; Cherubini, 2010; Fernando et al., 2006; Kamm et al., 2008; Kelloway and Daoutidis, 2013). Unfortunately, biomaterials receive much less attention than their biofuel counterparts. Challenges arise from a scarcity of data on the not-yet-industrialized biomass conversion process, as well as issues related to the allocation of environmental impacts or costs between different co-products. Such uncertainty might lead to diverse or even completely reverse results (Shen et al., 2012; Spatari et al., 2005; Tabone et al., 2010; Williams et al., 2009). Furthermore, the pool of potential biochemicals and biomaterials is vast, making it difficult to identify the best candidate to maximize profits and minimize emissions.

As public awareness of sustainable packaging has grown, the possibilities of bioplastics has emerged as a potential alternative to petro-based plastics. Though currently occupying a trivial share of the plastics market (less than 1%), worldwide bioplastics production has been forecast to spike starting in 2018 (Scharathow, 2012). The term “bioplastics” implies either that the polymer is generated from renewable resources, or that the plastic is biodegradable or compostable at the end-of-life (Gironi and Piemonte, 2011). At first, scholars targeted biodegradable bio-based polymers such as Polylactic Acid (PLA),

claiming that they were more environmentally friendly than petro-plastics (Shen et al., 2012; Vink et al., 2003). However, market expansion of those materials is limited by their low-barrier properties (Harada et al., 2007; Jamshidian et al., 2010), and has therefore triggered an interest in strong, non-biodegradable bioplastics such as bio-PET. PET is widely used in construction, transportation, packaging and engineering. In 2007, global PET production reached 46 million metric tons, taking 15% of the worldwide synthetic polymer production capacity (Shen et al., 2012). The United States consumes the largest portion of the PET market, with 9.5 kg PET per capita use in 2011 (Koncept Analytics, 2013).

Despite its popularity, only a few efforts have been made to analyze the life cycle impacts of producing bio-based PET materials, and they mostly focus on partially bio-based PET, where only one of the two precursors, ethylene glycol (EG), is produced from biomass; the other precursor, purified terephthalic acid (PTA), due to technical constraints, remains fossil based (Shen et al., 2012; Tabone et al., 2010). To remedy this exclusion, our study presents a novel manufacturing process to produce both partially and fully bio-PET bottles using lignocellulosic biomass from forest residues. The abundance of available forest residues allows us to extract energy from biomass without competing with food farming (Gan and Smith, 2007; Repo et al., 2012). After using an integrated method to convert forest residues to isobutanol (IBA) (Feldman et al., 2011), the IBA can be processed into paraxylene (PX) (Peters et al., 2010), a key prerequisite for PTA production, or processed into biofuels, although the current study will focus on the former pathway. The Coca-Cola Company plans to use woody biomass-based PTA to produce 100% bio-based PET beverage bottles (citation), suggesting the timely nature of this study. The aim of this study is to conduct a comparative Life Cycle Assessment (LCA) for the traditional petroleum-based PET bottles and bio-based PET bottles. Results of the study will provide an important reference to policy makers, bioplastic researchers, industry partners and purchasers, and will contribute to the optimization of integrated biorefinery system design.

2 Methods and Materials

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105 2.1 Attributional Life Cycle Assessment (aLCA) Model

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107 This study applied the Life Cycle Assessment (LCA) methodology, which is used for the estimation and
108 evaluation of environmental impacts attributable to the life cycle of a product (Rebitzer et al., 2004). It
109 encompasses the material and energy flows within the system boundary and calculates relevant impacts
110 generated by each unit process, such as greenhouse gas emissions, toxic impacts to an ecosystem, water
111 contamination, and so forth (Bare et al., 2012). The LCA model was established through the thinkstep GaBi
112 software (GaBi, 2014), complying with ISO 14040 and 14044 standards (ISO, 2006). Considering the data
113 availability of pilot and demonstration biorefinery facilities, a traditional attributional life cycle assessment
114 (aLCA) model was applied with sensitivity analysis of key assumptions in the system. Based on this initial
115 report, future research could focus on developing consequential LCA models.

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117 2.2 Goal, Scope, System Boundary and Functional Unit (FU) of the Study

118

119 The goal of this study is to quantify and compare environmental impacts of PET bottles produced through
120 traditional petroleum refineries and through biorefineries in the context of the United States. The aim of
121 including various feedstock options is also to explore the system-wide advantages or limitations of fully
122 bio-based PET bottle production scenarios over partially bio-based and fossil-derived PET bottles.

123

124 A cradle-to-factory-gate approach was applied in this paper, given that the upstream processes (feedstock
125 extraction, component production and product manufacturing) of PET bottle life cycles are what primarily
126 differentiates bio-based PET from fossil PET. The consumer use phase and the end-of-life phase (disposal
127 or recycling) are excluded from the analysis, given the complexity of possible options available to
128 adequately handle bioplastics in the current waste streams and that consumer use impacts will be identical

between scenarios (Komly et al., 2012; Shen et al., 2011; Zhang and Wen, 2013); however, end-of-life impacts are worth further exploration in future work.

Regarding the production of PET bottles, the two chemical precursors, PTA and EG, are synthesized separately. In the traditional production of PET, both PTA and EG were fossil refinery products. Petroleum refiners first separate out PX from a xylene mixture and then oxidize it to PTA. Similarly, ethylene produced from the alkene co-products of natural gas production are processed through hydration and oxidation to produce EG. These two precursors are then polymerized to amorphous-grade PET granulate, which is then turned into bottle grade granulate through solid-state polycondensation processes. Finally, PET bottles are shaped through injection blow molding. For partially bio-based PET bottles (30% or 70%), one of the two fossil precursors is substituted with a bio-based material; for fully bio-based PET bottles, both are produced from biomass. The processing of bio-PTA and bio-EG into PET bottles is identical to the processes described for petro-PET. Bio-based versions of PTA and EG can be produced from a variety of biomass materials, the environmental impacts of which are explored in different scenarios (see ‘Scenario Description’). Fig. 1 illustrates the process flow diagrams for producing fully bio-based PET bottles, which represents the system boundary of the study.

For the functional unit (FU), the environmental impact per 1 kg of PET bottles was investigated. This equals the weight of approximately 100 bottles with 0.5-liter capacity, and is kept consistent for all compared scenarios in order to yield meaningful comparative results (Curran, 1996; NAPCOR, 2016).

published literatures. Detailed assumptions and dataset descriptions are documented in the Supporting Information (SI) of this study.

2.4 Scenario Description

PTA accounts for approximately 70% of the weight of PET resin, while EG contributes to the rest (PE INTERNATIONAL AG., 2014). PET bottles with bio-based EG and fossil-based PTA are therefore referred to as 30% bio-based bottles; these are already available on the market, as in the Dasani water bottles from the Coca-Cola Company. Currently the bio-EG used for Dasani bottles is manufactured in Indonesia, and the company seeks to begin producing bio-PTA in order to be a leader in producing 100% bio-based PET bottles (Schut, 2012). Although no real ‘bio-PTA + fossil EG’ scenarios have been proposed for commercialization, these scenarios were nonetheless included in this study (Scenario 5 and Scenario 9) for comparison purposes. Bio-based EG is processed from biomass-derived ethanol, which has life cycle inventory data available from a variety of feedstocks. In this study, corn, switchgrass and wheat straw were considered as raw materials of bio-EG, while corn stover and forest residues were selected as feedstock for bio-PTA. Together with fossil- based PTA and EG, 12 PET bottle production scenarios were established, as shown in Table 1.

Table 1

Scenarios of Fossil-based and Bio-based PET Bottles

Scenario	Feedstock of PTA	Feedstock of EG	% of Biomass	Scenario	Feedstock of PTA	Feedstock of EG	% of Biomass
1 ^a	Fossil	Fossil	0	7	Wood	Switchgrass	100
2	Fossil	Corn	30	8	Wood	Wheat Straw	100
3	Fossil	Switchgrass	30	9	Corn Stover	Fossil	70
4	Fossil	Wheat Straw	30	10	Corn Stover	Corn	100

5	Wood	Fossil	70	11	Corn Stover	Switchgrass	100
6	Wood	Corn	100	12	Corn Stover	Wheat Straw	100

^a Baseline scenario.

2.4.1 Forest Residues

Every year, the amount of solar energy stored by plants is about 10 times greater than the total amount of worldwide energy used by humans. About 13 billion metric tons (dry weight) of wood are produced annually, providing an abundant material resource for renewable energy (Kumar et al., 2008). Much of this material is harvested for wood-based products production. However, harvesting operations currently collect only 60% of above-ground forest biomass, leaving the remainder as residues. Typically, harvest residues are either collected and burned, or left to decompose on the forest floor (Ganguly et al., 2014). Replacing fossil fuels with biofuels derived from forest residues could help to mitigate climate change (Gan and Smith, 2007; Repo et al., 2012). Removal of extra forest residues also helps reduce fire hazards and improve forest health (Perlack et al., 2011) without threatening industrial wood supplies or contributing to deforestation (Smeets and Faaij, 2007). Douglas fir softwood forest residues from the Pacific Northwest region of the United States were chosen as the source of the raw material for the bio-refinery. Fuel demand for forest regeneration, thinning and harvesting operations were summarized by Puettmann et al. (2012). We used forest inputs representing the weighted average management intensity, which is characterized by three forest management scenarios (high, medium and low intensity). Upon harvesting, the woody biomass transportation scenario for equipment and distances, as described by Ganguly et al. (2014), were accounted for and documented in the SI.

2.4.2 Avoided Burdens and Allocation

For a multi-output system, the main problem of LCA lies in how to allocate material and energy flows between primary products and co-products, as well as how to attribute environmental debits or credits among them. According to ISO 14040 and 14044 standards, allocation should be avoided either by dividing the multifunction process into separate subsystems and collecting data for these sub-processes individually, or by expanding the investigated system boundary to include an alternative production system of exported functions (ISO, 2006). The displacement/substitution method was developed based on the concept of system expansion, where the impacts associated with the alternative production of exported functions were subtracted from the investigated system to determine the potential avoided burdens (Guinée, 2002; Tillman, 1994; Wang et al., 2011). In the biomass processing scenarios considered in this study, four kinds of avoided impacts were accounted for, with further details recorded in the SI.

- a. Avoided impacts from slash pile burning (for forest residues). Note that in the Pacific Northwest, to reduce the risk of wildfire, non-merchantable harvesting residues are collected and burned to ashes, thereby increasing emissions due to incomplete combustion (Ganguly et al., 2014; Stevens and Verhé, 2004). When bioenergy was harvested from residues, the avoided impacts from slash pile burning were credited to the biofuel production system (Ganguly et al., 2014) and thus subtracted from the emissions of the investigated bio-PET bottle system.
- b. Avoided impacts from fossil-based steam and electricity production. In the bio-PET bottle production system scenarios, energy supplies were assumed to be internally fulfilled by co-producing energy from a combined heat and power biomass boiler/generator utilizing fermented lignin residues. It was also assumed that any excess electricity produced would be sold back to the grid to displace an equivalent amount of U.S. average electricity supply. Impacts generated by fossil-derived energy production were thereby avoided and subtracted from bio-PET bottle systems.
- c. Avoided impacts from non-energy co-products (for corn feedstocks). Corn grain, soybean meal and urea are the products considered in this study that are displaced with co-products produced from the advanced dry mill corn ethanol production system (Hsu et al., 2010).
- d. Carbon storage credits for biomass derived bottles. As bio-PET bottles are chemically equivalent to their fossil counterparts, they will be used and recycled in the same way, and hence the emissions

associated with these downstream processes will be the same. The carbon in the bio-PET bottles used to be a part of the natural carbon cycle. Now, they are sequestered from the atmosphere in a recyclable plastic product. Therefore, although the end-of-life stage is not included in the scope of this analysis, we find it reasonable to include sequestered biogenic carbon as a credit to bio-PET bottle scenarios (Narayan, 2011; Roberts et al., 2010).

When it is not possible to avoid allocation, impacts need to be assigned to different product flows based on physical relationships and corresponding functions (ISO, 2006). Usually, impacts will be allocated based on mass, energy content or economic values. In this study, mass allocation was applied on the forest resource extraction phase, as is recommended in Jungmeier et al 2002 for increased consistency in results. as the primary product of the system was used as a chemical material, not an energy product, and no market value was assigned to the 100% bio-PET bottles yet. Approximately 39% of impacts generated during timber production were allocated to residues (Ganguly et al., 2014). Impacts from the woody biomass boiler were allocated to the IBA and PX processes based on the amount of steam and electricity required for each process. Economic allocation could be evaluated in future studies.

2.4.3 Transport Adjustment

Transport associated with the various inputs for industrial processes was included in life cycle inventory databases. For some inputs, however, modifications were made to reflect particular assumptions. For example, to lower costs and emissions caused by bulky wood delivery, a woody biomass-based IBA processing facility was assumed to be located near softwood harvesting sites in Oregon (Leu et al., 2013). Pilot plants for PX manufacturing are located in the southern U.S., from where they would transport crystallized PX products to Coca-Cola's largest bottling facility, Coca-Cola Bottling Co. Consolidated (CCBCC), in Charlotte, North Carolina (CCBCC, 2016). CCBCC is responsible for manufacturing PTA from PX and producing PET bottles from PTA and EG. With regard to EG, Iowa was selected as the

location that corn, switchgrass, and wheat are planted, harvested and processed into EG. Detailed documentation for transport assumptions is provided in the SI.

3 Results and Discussion

3.1 Life Cycle Impact Assessment (LCIA)

Impacts are evaluated at the midpoint instead of at endpoint categories in order to reduce uncertainties, since endpoint impacts are subjected to overall much larger uncertainties (Finnveden et al., 2009; Pawelzik et al., 2013). Eight impact categories were analyzed in this study. Most were calculated based on The Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI v2.1), which is designed by the U.S. Environmental Protection Agency and normalized to reflect the context of the U.S. industries (Bare et al., 2012). However, exceptions were made on eutrophication and ozone depletion. Life cycle impact characterization models usually take different approaches with eutrophying impacts for land and water systems. Aquatic eutrophication suffers from weak modeling, whereas terrestrial eutrophication is better characterized using the Accumulate Exceedance model (Hauschild et al., 2011) and was thereby adopted in this study. For ozone depletion, results generated from TRACI v2.1 are significantly different from the ReCiPe v1.08 Hierarchy model, despite both being based on the ozone depletion model from the World Meteorological Organization (WMO). Ultimately, the impact indicator from ReCiPe v1.08 was chosen instead of TRACI v2.1 because ReCiPe offers a more detailed method documentation and addresses uncertainties in the model, whereas TRACI v2.1 only briefly explains how those results are generated (Bare et al., 2012; Zelm, 2009).

The comparative LCIA results are illustrated in Fig. 2. Solid color bars refer to impacts without including displacement credits, indicating that in almost all categories, bio-PET bottles (both partial and fully bio-

based ones) have worse performance than their 100% fossil-based counterparts. However, if avoided impacts are counted (depicted as impact offsets by the hashed sections on bars), bottles made from woody biomass PTA show significant advantage over fossil PTA and corn stover PTA bottles. Fig. 3 gives a more detailed profile of impacts from each unit process along the 12-scenario life cycles, with no avoided impacts included. Each bar refers to the impacts generated from producing PTA and EG for each scenario, and does not include PET bottle manufacturing processes because these processes are identical throughout all scenarios (esterification/polymerization, solid state poly-condensation, and injection stretch blow molding). Each color block indicates the impacts derived from a specific unit process; for example, block 'PX' shows emissions from upgrading IBA to PX.

Fig. 2. Life Cycle Impact Analysis results for 12 PET bottle production scenarios (per kg PET bottles).

*The blue gradient is for PTA production whereas the red is for EG manufacturing.

** For fossil-based PTA, no IBA was produced. PX is directly processed from a series of petroleum refinery co-products. Therefore, the IBA blocks for fossil PTA actually refers to impacts from petroleum refinery co-products.

Fig. 3. Unit process impacts for 12 different PET bottle production scenarios.

Climate change impacts (Global Warming Potentials, GWPs) of forest residue-derived bottles is about 4.14 to 4.92 kg CO₂-equivalent per kg PET bottles. This results in 27% lower CO₂-eq than those produced from corn stover PTA bottles (~5.49 to 6.48 kg CO₂-eq/kg PET bottles) and 21% lower than those from fossil PTA bottles (~4.74 to 6.36 kg CO₂-eq/kg PET bottles) on average. If no credits were taken into account, however, forest residue PTA bottles would have higher GWPs than fossil PTA bottles. The processes that contribute greatest to each of the scenario impacts are presented in Fig. 3a. Extraction of crop residues was found to be a particularly impactful phase; specifically, the establishment of cornfields, together with the harvesting and handling of corn stover, made raw material extraction a big emitter of greenhouse gases. Another primary contributor of impact is the IBA production process in wood PTA scenarios. The process involves several steps including pretreatment, enzymatic hydrolysis, and fermentation - where polysaccharides are turned into fermentable sugars and then processed to IBA. Woody-biomass has a higher lignin content than non-woody biomass. Lignin binds cellulose and hemicellulose together and forms lignocellulose, which is highly recalcitrant to microbial and enzymatic digestion (Zhu and Pan, 2010). Hence, compared to other kinds of biomass (such as sugar, molasses and starch), a considerable amount of extra energy is required to destruct lignocellulose in woody biomass (Hendriks and Zeeman, 2009; Mosier et al., 2005), leading to an overall higher environmental impact than petroleum-based PX extraction processes. It is notable that switchgrass production yielded high impacts compared to that of wheat straw and corn grain. However, since switchgrass has not yet been produced as a commercial crop, the data uncertainty is relatively higher, which may potentially lead to its worse environmental profile (Hsu et al., 2010; Spatari et al., 2005). Uncertainty about the estimated IBA process inputs is discussed in the sensitivity analysis section.

Compared to GWP impacts, the results of the fossil fuel consumption category are more intuitive, confirming that bio-PET bottles generally consume less fossil energy than fossil PET bottles (Fig. 2b). Producing wood PTA bottles with displacement credits (~8.10 to 10.41 MJ surplus energy/kg PET bottles) required even fewer fossil fuels (22% and 9% lower than the fossil PTA and corn stover PTA groups, respectively). It is obvious that extracting petroleum-derived resources consumes a large amount of fossil

energy. However, it is worth mentioning that the production of IBA is the leading consumer of fossil energy in the production of woody biomass PTA, whereas feedstock extraction generated the largest share for corn stover PTA. As mentioned previously, significant amounts of energy are required to destruct lignocellulose to fermentable sugars and convert them to IBA. Also, compared to forest residues extraction, the corn stover production stage is energy intensive (including corn farming and corn stover collection), driven by fertilizer production, tillage and harvesting processes (e.g. grinding and drying) (Valipour, 2014; Valipour, 2012; Valipour et al., 2015; Hsu et al., 2010; Luo et al., 2009).

The corn stover PTA group has the greatest acidification impact, followed by wood and fossil PTA groups (Fig. 2c). Avoiding slash pile burning results in approximately 0.014 kg SO₂ equivalent/kg bottles of impact offsets for forest residue PTA bottles, but still results in 27% higher acidification impact than their fossil-based counterpart. Further, it's clear that bio-based EGs on average release more acidifying emissions than fossil-based EGs (Fig. 3c). Bio-chemical processing of IBA once again represented a large portion of the acidification impacts for wood-PTA scenarios (~30%), primarily due to use of processing chemicals and combustion of fuels. Fig. 3c reveals that in the fossil-PTA + bio-EG scenarios the agricultural stages of corn, switchgrass and wheat straw all released considerable amounts of acidifying compounds, resulting in feedstock extraction being the decisive stage responsible for overall higher acidification impacts. Specifically, switchgrass extraction took up more than half (~53%) of the total acidification impacts from fossil-switchgrass bottles, primarily due to fertilizer production (Monte et al. 2009) and application (Fu et al., 2003). For corn stover-PTA scenarios, corn stover production stage took the largest share with roughly 63% of overall impacts from PTA and EG. Other than fertilizing and harvesting operations, this could also be explained by the impact allocation choices made between corn grains and corn stover (Williams et al., 2009). Similarly, retrieving forest residues generated additional acidification impacts compared to fossil feedstock (~0.0096 kg SO₂-eq/kg bottles), due primarily to the fossil fuel combustion required by forestry management, as forests need very limited fertilization (Spellman, 2011).

For eutrophication impacts on terrestrial ecosystems, wood PTA bottles have a similar performance to fossil PTA bottles. The corn stover PTA group, however, generated significantly higher eutrophying emissions, equaling approximately 5 times the eutrophying impacts of those driven by fossil and wood PTA groups on average. It was evident in Fig. 3d that retrieving crop biomass in general released more N-nutrients to the soil ecosystem than fossil and forest residue extraction. For corn stover acquisition, emissions come from two dominant impact drivers, namely fertilizer and hay production, with each contributing to approximately 50% of the unit process impacts. Note that low-quality hay was used to substitute corn stover as over-winter feed, and therefore the environmental burden brought by hay processing needs is included. The only emissions documented for processing fertilizer and hay were NH_3 and NO_x , which were driven by N-related physical input conversions, such as ammonia, urea, and ammonium nitrate (Hsu et al., 2010). The eutrophication indicator chosen here, accumulated exceedance, takes exactly NH_3 and NO_x to calculate overloaded N nutrients deposition (Seppälä et al., 2006). Hence, it was expected that those two processes were eutrophication intensive. Fertilization may also explain the large share of eutrophication impacts from producing corn grain, switchgrass and wheat straw in fossil PTA + bio-EG bottle scenarios (~46%, 70% and 44%, respectively). In addition, switchgrass required more bailing inputs, leading to extra emissions (Hsu et al., 2010). Producing IBA from wood residues was the decisive factor for eutrophication impacts for forest residue bottles, mostly due to the N-based materials applied in the bio-chemical conversion process. However, since forestry requires very limited fertilization (Puettmann et al., 2012), the eutrophication impacts are trivial compared to corn stover PTA scenarios.

Human Health Particulate emissions are interpreted in kg PM_{2.5} equivalent per kg PET bottles, shown in Fig. 2e. On average, forest residue PTA bottles with displacement credits have the lowest impacts (~ -0.043 to -0.041 kg PM_{2.5}-eq/kg PET bottles), but were comparable to other scenarios without avoided impacts incorporated (~ 0.0037 to 0.0059 kg PM_{2.5}-eq/kg PET bottles). While avoided particulate emissions from slash pile burning accounts for most of the credits (Ganguly et al., 2014), this assumption could vary due to differences on geographical areas, types of woody biomass, and forestry logistics scenarios. For this reason, we address this potential variability in a sensitivity analysis. It was clear in Fig. 3e that if no avoided

impacts are applied, particulate emissions become significant in the forest residue extraction phase as well as the wood-IBA processing stage. Corn stover and wheat straw extraction impacts, on the other hand, are primarily attributed to the grinding process and electricity usage. For switchgrass production, bailing during the harvest operation is the primary contributor to impact, whereas for corn grains, fertilizer production, tillage and irrigation processes are responsible for the majority of particulate emissions.

To evaluate the eco-toxicity potential, TRACI v2.1 uses the USEtox model which is based on the metric ‘comparative toxic units’ (CTUe) (Rosenbaum et al., 2008). Note that the USEtox model includes both recommended and interim characterization factors, where the latter ones need to be used with caution (Bare, 2011; Hauschild et al., 2011). To reduce uncertainty, GaBi only considers recommended factors (GaBi, 2014). The majority of eco-toxicity potential impacts are due to bio-EGs and bio-PTAs. Electricity consumption and grinding processes are the most impact-intensive factors for corn stover PTA and wheat straw EG, whereas the bailing process is responsible for most of the eco-toxicity impacts from switchgrass EG. Corn grain EG bottles, on the other hand, gain their eco-toxicity mainly from pesticide and fertilizer production. Finally, bio-PTAs production in 70% bio-based bottles (i.e. wood PTA and corn stover PTA paired with fossil EG) have extremely high eco-toxicity impacts due to wood IBA processing and corn stover extraction, respectively.

With regard to smog effects, compared to corn stover and fossil counterparts, bio-PTA bottles have higher emissions than fossil PTA bottles. Primary offsets come from the avoidance of slash pile burning, but Fig. 3g shows that forest logistics remain the primary cause of smog generation, as the handling of bulky wood logs and branches is energy intensive. Similarly, just as with eco-toxicity and human health particulates, smog impacts increased greatly with the extraction of agricultural feedstocks due to the fuel combustion from operating agricultural machinery (for tillage, grinding, drying and bailing). Energy consumption in supplementary material production (fertilizer, pesticide and hay) contribute as well. These are also decisive factors behind the high ozone depletions with the production of bio-based PTA bottles, whereas bio-EG generated close to 100% ozone depletion impacts when paired with a fossil PTA.

3.2 Sensitivity Analysis and Limitations

LCIA results for woody biomass-derived PET bottles (Scenario 5 – 8) were found sensitive to several factors. Sensitivity analysis results are presented as percentage changes of the initial credited Scenario 5 (Wood PTA + Fossil EG) impacts. Complete results can be found in SI.

Currently the U.S. national PET container recycling rate is about 30% (NAPCOR, 2015). Therefore, figure 4 explores the possibility of PET bottles being landfilled or burned for energy use by illustrating GWP results for the 12 scenarios with and without carbon sequestration credits. It is obvious that if those credits are excluded, partially/fully bio-based PET bottles (Scenario 2-12) would lose their advantage over fossil PET bottles (Scenario 1).

Fig. 4. Comparison of scenario GWP results (per kg PET bottles) with/without carbon sequestration credits.

Table 2 addresses the uncertainty in paraxylene and IBA processing inputs, and assumptions of avoided impacts from slash pile burning by altering the quantities of input values and assessing the change in impacts. Apparently, variability in both slash pile burning and IBA impact estimates considerably influence final results, but changes in PX processing impacts have relatively minimal influence on final results. Climate change, acidification and smog were all vulnerable to modified assumptions of IBA production inputs, with a 55% reduction in IBA inputs (leaving only 45% of baseline IBA input values in the system) leading to 16%, 12% and 6% decreases in the corresponding impacts of credited Scenario 5. Acidifying emissions also decrease by 32% if 55% of the slash pile burning credits were removed. Particulate emissions are also largely dependent on the avoided slash burn assumption, with a 55% credit reduction resulting in a 60% increase in fine particulate impacts. Smog would also have a dramatic increase of 73%. Collectively, such uncertainty could largely alter the conclusion of environmental rankings for fossil and bio-PET bottles. Future studies should address data refinement issues in order to increase confidence in relative results.

Table 2

Percentage changes of selected impacts of credited scenario 5 results introduced by changing input quantities in different unit processes.

	Upgrading IBA to PX (%)			Isobutanol Process (%)			Slash Pile Burning (%)		
% of Baseline Input Values	45% *	70%	135%	45% *	70%	135%	45% *	70%	135%
Climate Change	-2.3	-1.3	+1.4	-16.1	-8.8	+10.2	+3.3	+1.8	-2.1
Acidification	-0.3	-0.2	+0.2	-11.8	-6.4	+2.1	+32.3	+17.6	-20.6
Particulates	-0.0	-0.0	+0.0	-0.4	-0.2	+0.1	+59.7	+32.6	-38.0
Smog	-0.6	-0.3	+0.4	-6.3	-3.5	+1.2	+73.3	+40.0	-46.6

*Discussion provided in text.

We compared our results with relevant LCIs for validation. Adom et al. (Adom et al. 2014) studied the life cycle greenhouse gas emissions of IBA produced from corn stover, and revealed a 2.7 kg CO₂e/kg IBA impact, which is very close to the number in our study using wood residues (2.70 kg CO₂e/kg IBA impact).

Akanuma et al. 2014 documented life cycle impacts from different 100% bio-based PET production scenarios and they found a GHG emission of 6.81 kg CO₂e/kg PET for their butanol pathway, which is comparable to this study's forest residue PTA + corn EG PET bottle emissions (6.23 kg CO₂e/kg PET bottles, without carbon sequestration credits), but lower than those from the corn-stover PTA + corn EG scenario (7.79 kg CO₂e/kg PET bottles without carbon sequestration credits).

A limitation of the study lies in the data availability of the fossil fuel scenarios. LCI information about fossil PTA and EG production specific to U.S. conditions are available in GaBi, but only in aggregated format. Therefore, unit process data was estimated based on the percentage share each unit stage takes, which was calculated based on corresponding data from Ecoinvent (Weidema et al., 2013). In such a case, the comparative results of biomass unit processes and fossil unit processes must be considered with caution.

4 Conclusions and Recommendations

According to the aforementioned outcomes, mixed results were found across impact categories when comparing the environmental performances of partially and fully bio-based PET bottles versus fossil-based ones. In most categories, with avoided impact credits considered, forest residues had a better or comparable environmental profile to corn stover when used as feedstock for bio-PET bottles. The conclusion is subject to uncertainty, where variability in avoided burdens could alter the conclusion of environmental rankings for fossil and bio-PET bottles. Moreover, a summary of unit process impacts implies that biomass feedstock extraction and pre-processing are likely more emission-intensive than corresponding fossil refinery processes, either due to the extra energy required for agricultural operations, or because of the production and application of required chemicals. As a result, future research should focus on: 1) improving the availability and reliability of LCI data; 2) developing more detailed avoided impact scenarios; 3) optimizing biorefinery processes; 4) determining a sustainable residue collection rate (Andrew,

2006); 5) incorporating economic analyses to deliver a more robust and comprehensive sustainable portfolio of PET bottle bio-refineries.

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672 **Figure and Table Captions with Size Suggestions**

673 **Fig. 1.** Cradle-to-Gate system boundary for 100% bio-based PET bottles

674 Preferred magnification factor: 1.5 column

675 **Fig. 2.** Life Cycle Impact Analysis results for 12 PET bottle production scenarios (per kg PET bottles).

676 Preferred magnification factor: Double column (full width)

677 **Fig. 3.** Unit process impacts for 12 different PET bottle production scenarios.

678 Preferred magnification factor: Double column (full width)

679 **Fig. 4.** Comparison of scenario GWP results (per kg PET bottles) with/without carbon sequestration credits.

680 Preferred magnification factor: 1.5 column

681 **Table 1** Scenarios of Fossil-based and Bio-based PET Bottles.

682 **Table 2** Percentage changes of selected impacts of credited scenario 5 results introduced by changing input
683 quantities in different unit processes.

Figure

*The blue gradient is for PTA production whereas the red is for EG manufacturing.

**For fossil-based PTA, no IBA was produced. PX is directly processed from a series of petroleum refinery co-products. Therefore, the IBA blocks for fossil PTA actually refers to impacts from petroleum refinery co-products.

Figure

Table 1

Scenarios of Fossil-based and Bio-based PET Bottles.

Scenario	Feedstock of PTA	Feedstock of EG	% of Biomass	Scenario	Feedstock of PTA	Feedstock of EG	% of Biomass
1 ^a	Fossil	Fossil	0	7	Wood	Switchgrass	100
2	Fossil	Corn	30	8	Wood	Wheat Straw	100
3	Fossil	Switchgrass	30	9	Corn Stover	Fossil	70
4	Fossil	Wheat Straw	30	10	Corn Stover	Corn	100
5	Wood	Fossil	70	11	Corn Stover	Switchgrass	100
6	Wood	Corn	100	12	Corn Stover	Wheat Straw	100

^a Baseline scenario.

Table 2

Percentage changes of selected impacts of credited scenario 5 results introduced by changing input quantities in different unit processes.

% of Baseline Input Values	Upgrading IBA to PX (%)			Isobutanol Process (%)			Slash Pile Burning (%)		
	45%	70%	135%	45%	70%	135%	45%	70%	135%
Climate Change	-2.3	-1.3	+1.4	-16.1	-8.8	+10.2	+3.3	+1.8	-2.1
Acidification	-0.3	-0.2	+0.2	-11.8	-6.4	+2.1	+32.3	+17.6	-20.6
Particulates	-0.0	-0.0	+0.0	-0.4	-0.2	+0.1	+59.7	+32.6	-38.0
Smog	-0.6	-0.3	+0.4	-6.3	-3.5	+1.2	+73.3	+40.0	-46.6