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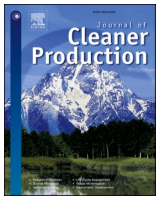

Towards the production of net-negative greenhouse gas emission bio-based plastics from 2nd and 3rd generation feedstocks

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ABSTRACT

Here, we show production pathways for greenhouse gas (GHG)-negative bio-based plastics from 2nd and 3rd generation feedstocks. We focus on bio-based plastics that are technically capable of replacing 80% of the global plastic market. By presenting life cycle inventories and discussing GHG-emissions hotspots, this work will inform stakeholders along the plastic supply chain of the necessary steps to achieving net-zero emissions by 2050, and potentially, how to drive net-uptake. This work is of critical importance given the overwhelming mass of plastic produced annually and the resulting CO_2 emissions. To conduct this assessment, we derive life cycle inventories for nine different bio-based plastics and address the impact of methodological choices, such as allocation method, on the resulting 100a global warming potential (GWP). Our findings show that resources used and processing methods implemented have significant effects on the potential for us to derive carbon-negative plastics. Furthermore, we find that environmental impact quantification methods greatly influence the perceived GWP of such processes. For example, economic and mass allocation methods resulted in an apparent increase in GWP of up to 39% and 166%, respectively, compared to no allocation for bio-based plastics made from 2nd generation crops, whereas mass allocation resulted in the lowest GWP for bio-based plastics made from 1st generation crops. In considering environmental impact hotspots, our findings show that decarbonization of thermal energy and electricity, reduced use of ammonia-based fertilizer, renewable hydrogen production, use of bio-based alternatives for petrochemicals and plasticizers, enzyme production pathways from 2nd generation crops, and more efficient biomass conversion processes to reduce feedstock inputs may be critical steps in creating GHG-negative bio-based plastics in the future.

1. Introduction

The mass of plastics in use today amounts to twice the mass of all animals on earth - 99% of which is made from petroleum-based feedstocks (Elhacham et al., 2020; European Bioplastics, 2022). The petrochemical industry as a whole is responsible for 18% of global industrial greenhouse gas (GHG) emissions, making it the third largest CO_2-emitting industry (International Energy Agency, 2018). While many efforts have been taken to decarbonize common materials such as concrete (Monteiro et al., 2017; Miller et al., 2016a, 2018, 2021) and steel (Yu et al., 2021; Fan and Friedmann, 2021; Bataille, 2020; Rissman et al., 2020), the methods for plastic production and disposal have remained largely the same. Minimizing the demand for plastics would help alleviate some of these issues, but consumption trends indicate plastics will continue to play a vital role in our economy in the coming years. In fact, plastics may contribute a significant role in the global transition to net-zero emissions by 2050 through their use in renewable energy, electric vehicles, medical devices, food packaging, and many other applications. Therefore, there is a need to identify strategies that allows for the continued growth of plastics while simultaneously mitigating GHG emissions from their production, and ideally converting this growing class of materials to becoming a pathway to uptake GHGs (herein referred to as "GHG-negative plastics").

Various studies have examined the potential for plastics to act as a carbon sink and although the methodologies and scopes differ, the same general conclusion is reached: there is no single solution to achieve GHG-negative plastics. Initial exploration of decarbonization of petroleum-based plastics have indicated that achieving net-zero emissions, let alone net-negative, will be a challenge. Even with the use of renewable energy and recycling, there are several "carbon lock-ins" associated with petroleum-based plastic production, such as emissions from steam cracking, that require carbon capture technology to achieve

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net zero emissions (Bauer et al., 2022). Frequently, bio-based plastics, which use biomass as the carbon feedstock instead of petroleum resources, have been examined as a way to reduce GHG emissions (Walker and Rothman, 2020; Hottle et al., 2013; Yates and Barlow, 2013). Authors who have explored these pathways still note potentially high emissions from energy-intensive production processes (Schulze et al., 2017) and land-use change (Piemonte and Gironi; Brizga et al., 2020), changes in material performance that can alter use-phase impacts (Tamburini et al., 2021; Molina-Besch, 2022), and end-of-life pathways that could lead to GHG emissions, such as incineration or biodegradation (Van Roijen and Miller, 2022). As such, findings indicate that the transition to GHG-negative plastics will require a combination of process electrification, improved waste management, as well as the use of non-edible biomass feedstocks (Suh and Bardow, 2021).

Recent studies have indicated pathways worthy of deeper exploration when deriving carbon-negative plastics. Sun et al. (2022) examined pathways to reach carbon-neural plastics and found that the use of biomass contributed the most to GHG reductions, with remaining strategies such as recycling only contributing 5–7%. Zibunas et al. (2022) found that combining renewable energy with increased recycling rates of plastics could drive down emissions, but it would result in the highest cost compared to strategies that utilize biomass. Stegmann et al. (2022), incorporated socio-economic factors to determine future CO_2 emissions from plastics and found that a combination of increased CO_2 prices, plastic recycling, and biomass use, could lead to carbon-negative approaches for plastic manufacturing. Similarly, Meys et al. (2021) found that combining recycling, biomass utilization, and carbon capture and utilization (CCU) could lead to net-carbon-negative plastics that have lower cost and energy demands than petroleum-based plastics with CCU. While findings have been promising, many of these studies have only considered CO_2 emissions. However, to reach the Intergovernmental Panel on Climate Change (IPCC) targets of 1.5 °C by 2050, a 50% and 22% reduction in CH_4 and N_2O must simultaneously be achieved alongside decarbonization strategies (Rogelj and Lamboll, 2024). Considering the role of chemicals in biomass cultivation and plastic production, it is critical to understand the impact of other GHGs (e.g., N_2O from fertilizers (Goglio et al., 2018)) on creating net-negative emissions pathways. In addition, most existing studies utilize models that rely on large data sets with life cycle assessment (LCA) data coming from various sources, thereby limiting the ability to (1) utilize a consistent approach among all materials, (2) determine what is contributing most to the environmental impacts of each material, and (3) determine how biomass feedstock type or LCA methodology can impact the results.

Carbon feedstock sources and modeling assumptions have been proven to play a large role in uptake potential for bio-based plastics in the literature (Miller et al., 2016b). De Oliveira et al. (2021) performed bottom-up LCAs of bio-based plastics and found that carbon-negative bio-based plastics could be achieved when considering long-term applications (e.g., the use Bio-HDPE or Bio-PVC in construction). However, this study only examined 1st generation feedstocks which compete with food production. Deriving all plastics from such a resource would require roughly 5% of global arable land (Bishop et al., 2022). Alternatively, 2nd generation feedstocks, or inedible plant-based materials, and 3rd generation feedstocks, or feedstocks that have negligible land footprints (i.e. food waste, algae, or biogas), are being investigated in the literature as potential resources for bio-based plastic production. Given the extra processing steps required for utilizing these materials (e.g., pretreatment and enzymatic hydrolysis), it remains unclear if they could offer substantial GHG emission reductions compared to 1st generation bio-based plastics or petroleum-based plastics made from renewable energy. Studies have investigated the environmental impacts of bio-based plastics from 2nd and 3rd generation biomass such as corn stover (Zhong et al., 2009; Muñoz et al., 2014; Adom and Dunn, 2017), wheat straw (Parajuli et al., 2017), sugarcane bagasse (Daful et al., 2016), switchgrass (Chen et al., 2016), vetiver leaves (Raman and Gnansounou, 2015), cheese whey (Koller et al., 2013; Asunis et al., 2021), wastewater (Andreasi Bassi et al., 2021; Vogli et al., 2020), landfill gas (Rostkowski et al., 2012), and used cooking oil (Moretti et al., 2020). However, given the variability in methodologies, literature reviews of LCAs of bio-based plastics from 2nd and 3rd generation feedstocks report inconclusive results, with analyses considering the same 2nd generation feedstock leading to both higher and lower GHG emissions than their 1st generation counterpart (Wellenreuther and Wolf, 2020). Furthermore, transparent life cycle inventory (LCI) data are not consistently provided, limiting the ability to reproduce results (Bishop et al., 2021). To determine the large-scale impacts of a bio-based plastic economy, harmonization of data is necessary to support reproducible LCAs and to inform quantitative, systematic assessment of mechanisms to drive carbon-uptake.

In this work, we derive LCIs for nine major bio-based plastics: (1) polylactic acid (PLA); (2) polyhydroxyalkanoate (PHA); (3) thermoplastic starch (TPS); (4) high-density polyethene (Bio-HDPE); (5) polyethylene terephthalate (Bio-PET); (6) polyvinylchloride (Bio-PVC); (7) polypropylene (Bio-PP); (8) polyurethane (Bio-PUR); (9) polytrimethyl terephthalate (Bio-PTT). All of these plastics at least partially utilize 2nd and 3rd generation feedstocks. We use these inventories to perform cradle-to-gate environmental impact assessments for each material. The influence of methodological decisions, namely the allocation method, and hotspots in production that could be targeted to create carbon-negative plastics are analyzed. The term “GHG-negative” refers to a below-zero value for the combined emissions of CO_2, CH_4 and N_2O with 100a global warming potentials (GWP) (other GHGs, such as water vapor and hydrofluorocarbons, are outside the scope of this analysis due to their minimal impact on resulting GWP for the production processes examined herein (Environmental Protection Agency, 2023; Sherwood et al., 2018)). Pathways to achieve GHG-negative cradle-to-gate bio-based plastics and the remaining sources of GHG emissions are discussed to identify areas for further improvement.

2. Methods

2.1. Scope and goals

The goal of this work is to derive LCIs of plastics that can lead to GHG-negative pathways during their production, assess methodological assumptions that could alter outcomes, and identify processes that should be targeted to drive emissions reductions. The declared unit for all inventories formulated in this work is 1 kg of bio-based plastic. The system boundary includes biomass cultivation, refinement, conversion, processing, and bio-based plastic production. The manufacturing of specific products (bottles, containers, etc.), the use phase, and end-of-life stage of bio-based plastics is not considered in this study. However, we note that the literature indicates these stages, specifically end-of-life, can contribute greatly to overall life cycle GHG emissions (Van Roijen and Miller, 2022) and should be addressed in future work.

To create a systematic basis for inventory development, additional assumptions are made. Where possible, consistent LCI data sources are used for similar production processes, and when multiple LCI data sources exist, average values of the literature are used. We harmonize LCI flows and modeling assumptions to create a unified method for assessment and comparison of environmental impacts from bio-based plastics. Direct land use change associated with feedstock cultivation is included in these inventories. However, the inventories are based on an attributional approach, and therefore do not include indirect impacts from land-use change. In the derivation of inventories, for non-biodegradable bio-based plastics, some downstream processes are identical to petroleum-based plastics, and therefore are assumed to have the same process-based emissions, such as particulate matter emissions. To determine the feasibility of GHG-negative bio-based plastics, all electricity and energy demands of the main processes are assumed to be satisfied by wind electricity and biogas. In addition, a biogenic carbon

credit is applied based on the carbon content of the plastic. For example, if a plastic has a carbon content of 0.6 kg C/kg plastic, then a CO_2 credit of −2.2 kg CO_2/kg plastic is applied (determined by multiplying the carbon content by the molar mass ratio of CO_2 to carbon, or 3.67 kg CO_2/kg C).

Three allocation methods were considered to determine the cradle-to-gate GHG emissions for each material: (1) mass, (2) economic, and (3) no allocation. With no allocation, main crops (such as corn) are assigned 100% of the impact, while any by-products (such as corn stover) are attributed 0%. While the International Organization for Standardization (ISO) recommends system expansion whenever possible (International Organization for Standardization, 2006), this method is outside the scope of this work. The life cycle CO_2-equivalents (CO_2e) for each material is determined based on CO_2, CH_4 and N_2O emissions. Global warming potentials of 28 and 273 are used for CH_4 and N_2O, respectively, based on the IPCC sixth assessment report (IPCC, 2021).

2.2. Life cycle inventories of feedstocks

The following feedstocks are considered for bio-based plastic production: corn, corn stover, wheat straw, sugarcane sugar, sugarcane molasses, sugarcane bagasse, rapeseed oil, used cooking oil, reclaimed potato starch, and biogas. Sugarcane, corn, and wheat were considered in this analysis given their abundant production volumes. Together, along with rice, these crops accounted for half of all primary crops produced globally in 2020 (Food and Agriculture Organization of the United Nations, 2000), with sugarcane and corn being the two most produced crops globally (Food and Agriculture Organization of the United Nations, 2000). While palm oil and soybean oil are the largest produced vegetables oils (Food and Agriculture Organization of the United Nations, 2000), here we model rapeseed oil, making up 12% of global vegetable oil production in 2019. The selection of rapeseed oil for our inventories was due to the availability of detailed LCI data (Fridrihsone et al., 2020a, 2020b). Data availability for soy (Helling and Russell, 2009) and palm-based polyol (Zolkarnain et al., 2015) LCIs have not been as robustly reported in the literature. We also consider 3rd generation feedstocks, such as landfill biogas, reclaimed potato starch, and used cooking oil. While many 3rd generation feedstocks have potential applications in bio-based plastics production, we again made the selection of these resources based on data availability.

We model biomass inventories based on large global producers of these crops. Land use requirements for every crop are determined by calculating the global weighted average crop yield from 2017 to 2020 using data from the Food and Agricultural Organization of the United Nations (FAO) (Food and Agriculture Organization of the United Nations). The mass and economic allocation factors for each feedstock are determined from the literature (Table 1).

For corn and corn stover production, we base our feedstock models on corn cultivation in the United States (US), the largest global producer of corn (Food and Agriculture Organization of the United Nations), with inventory values based on data from the ecoinvent 2.2 database (Frischknecht et al., 2005). To quantify production of stover, we assume 1 kg of corn stover is produced per kg of corn, as presented in the ecoinvent database. Although this value is representative of the US, it is close to the global average harvest index for corn, 0.45 kg corn/total biomass (Ludemann et al., 2022). Some studies have found that 30–70% of the corn stover can be left on the field as a soil amendment to prevent erosion and maintain appropriate soil organic carbon levels (Wilhelm et al., 2010; Ruis et al., 2017; Johnson et al., 2013); therefore, we assume only 70% of corn stover is available for bio-based plastic production.

For sugarcane sugar, bagasse, and molasses, we base our feedstock models on Brazil, the world's largest producer of sugarcane (United States Department of Agriculture). This ecoinvent inventory is supplemented with agricultural inputs such as fertilizer and pesticide use extracted from Seabra et al. (2011) (representative of the 2008/2009 growing season in Brazil). Data for sugarcane processing are from literature, using average values reported for Brazil (Seabra et al., 2011; Tsiropoulos et al., 2014), India (Tsiropoulos et al., 2014), and Thailand (Groot and Borén, 2010), which are the three largest sugarcane-producing countries (United States Department of Agriculture). The yield of sugar from sugarcane is determined by taking the average values from studies by Groot and Borén (2010) (Thailand) and Tsiropoulos et al. (2014) (India). We note that sugarcane mills commonly utilize the lignocellulosic by-product, bagasse, as an internal energy source. However, bagasse can be extracted for use in other applications (such as bioethanol or polylactic acid production), and here we aim to address potential benefits of use in bio-based plastics, where the carbon can be stored for a longer period of time.

For wheat straw, LCI data for wheat cultivation, including yield

Table 1
Mass and economic allocation factors for the feedstocks considered in this study.

Feedstock type	Feedstock	Mass allocation factor	Economic allocation factor	Reference
1st generation	Corn	0.50	0.86	Mass: (Frischknecht et al., 2005) Economic: (Patel et al., 2017)
	Corn starch (from corn wet milling)	0.67	0.79	Mass: (Ramirez et al., 2007) Economic: (Ramirez et al., 2007; United States Department of Agriculture, 2012)
	Rapeseed	0.23	0.5	Mass: (Gupta et al., 2022) Economic: (Stelzer et al., 2021)
	Rapeseed oil	0.40	0.62	Mass: (Gupta et al., 2022) Economic: (Fridrihsone et al., 2020a; Malça et al., 2014)
	Sugar, from sugarcane	0.10	0.88	Mass: (Groot and Borén, 2010) Economic: (Changwichan and Gheewala, 2018; Silalertruksa and Gheewala, 2020; Tsiropoulos et al., 2015)
2nd generation	Molasses, from sugarcane	0.05	0.09	Mass: (Groot and Borén, 2010) Economic: (Changwichan and Gheewala, 2018; Silalertruksa and Gheewala, 2020; Tsiropoulos et al., 2015)
	Bagasse, from sugarcane	0.31	0.03	Mass: (Groot and Borén, 2010) Economic: (Changwichan and Gheewala, 2018; Silalertruksa and Gheewala, 2020; Tsiropoulos et al., 2015)
	Wheat straw	0.57	0.13	Mass: (Frischknecht et al., 2005) Economic: (Patel et al., 2017; Forte et al., 2016)
	Corn stover	0.55	0.14	Mass: (Ludemann et al., 2022) Economic: (Patel et al., 2017)
3rd generation	Used cooking oil	0	0	n/a
	Landfill biogas	0	0	n/a
	Reclaimed potato starch	0	0	n/a

ratios for wheat straw relative to grain, are taken from ecoinvent 2.2 (Frischknecht et al., 2005). This inventory is based on average values for wheat production in the US, the largest producer out of the countries available in the ecoinvent database for wheat production, and the fourth largest wheat producer globally (Food and Agriculture Organization of the United Nations, 2000). The harvest index reported in this inventory, 0.45 kg wheat/total biomass, agrees with recent reported average values for wheat across the US (Dai et al., 2016). Similar to corn stover, studies have shown that roughly 2/3 of wheat straw can remain on the field as a soil amendment (Borrion et al., 2012). Therefore, we assume only 1/3 of wheat straw is available for bio-based plastic production.

LCI data for rapeseed production is taken from Gupta et al. (2022), which is representative of rapeseed production in Europe, the world's largest rapeseed oil producer (United States Department of Agriculture). The LCI data for agricultural processes, such as fertilizer and pesticide application rates, are based on rapeseed production guidelines provided by New Holland Agriculture. Large-scale rapeseed oil production data, reported in Gupta et al. (2022), is based on industry data.

Potato starch can be retrieved as a residue from manufacturing sliced potato products, where starchy wastewater is generated, and starch can be extracted via centrifugation. For this carbon feedstock, we use LCI data for reclaimed potato starch from Broeren et al. (2017). Due to limited availability of data, the centrifugation process used to isolate the starch components is left out of the analysis. Broeren et al. found that this is a fair omission given that the energy requirements for this step are much lower than the subsequent evaporation steps that are captured in the inventory, and that it is part of the wastewater treatment process and, therefore, should be at least partly allocated to the primary product.

For landfill biogas as a feedstock for bio-based plastic production, we model the composition of landfill biogas based on a study by Rasi et al. (2007). It is assumed that if the biogas were not used as a feedstock for bio-based plastic production, then it would otherwise be burned. Therefore, the avoided CO_2 emissions from burning methane are applied as a credit (or negative emissions) to the system.

2.3. Life cycle inventories of bio-based plastic production processes

The various bio-based-plastic production pathways analyzed herein are outlined in Fig. 1. Together, these bio-based plastics can substitute roughly 80% of today's petroleum-based plastic market. To determine the substitution potential of each bio-based plastic within the current plastic market, we use the technical replacement potential of bio-based plastics reported by Shen et al. (2009), which is based on mechanical performance characteristics, coupled with the current global market of petroleum-based plastics (Plastics Europe, 2022). Sugarcane molasses is investigated as a feedstock for bioethanol production given that roughly 95% of molasses is currently used for ethanol production (Tsiropoulos et al., 2014). Both corn stover and wheat straw are modeled as feedstocks for bio-based ethanol, a key intermediate for Bio-HDPE, Bio-PET, and Bio-PVC production. Using a mass-based allocation approach with the life cycle inventories outlined herein, corn stover-based ethanol was found to have lower GHG emissions (3.7 kg CO_2e/kg ethanol, not including biogenic carbon) than wheat straw-based ethanol (5.97 kg CO_2e/kg not including biogenic carbon). Therefore, only corn stover-based ethanol is used for Bio-PET and Bio-PVC production. Corn is modeled as a feedstock for ethanol and lactic acid to allow for comparisons of environmental impacts between 1st, 2nd, and 3rd generation feedstocks. All electricity and heat requirements were assumed to be satisfied by wind and biogas (modeled using ecoinvent datasets outlined in supplemental materials data sheet "Ecoinvent datasets"). See supplemental materials for a full list of the resources (including ecoinvent datasets) used to generate the LCIs.

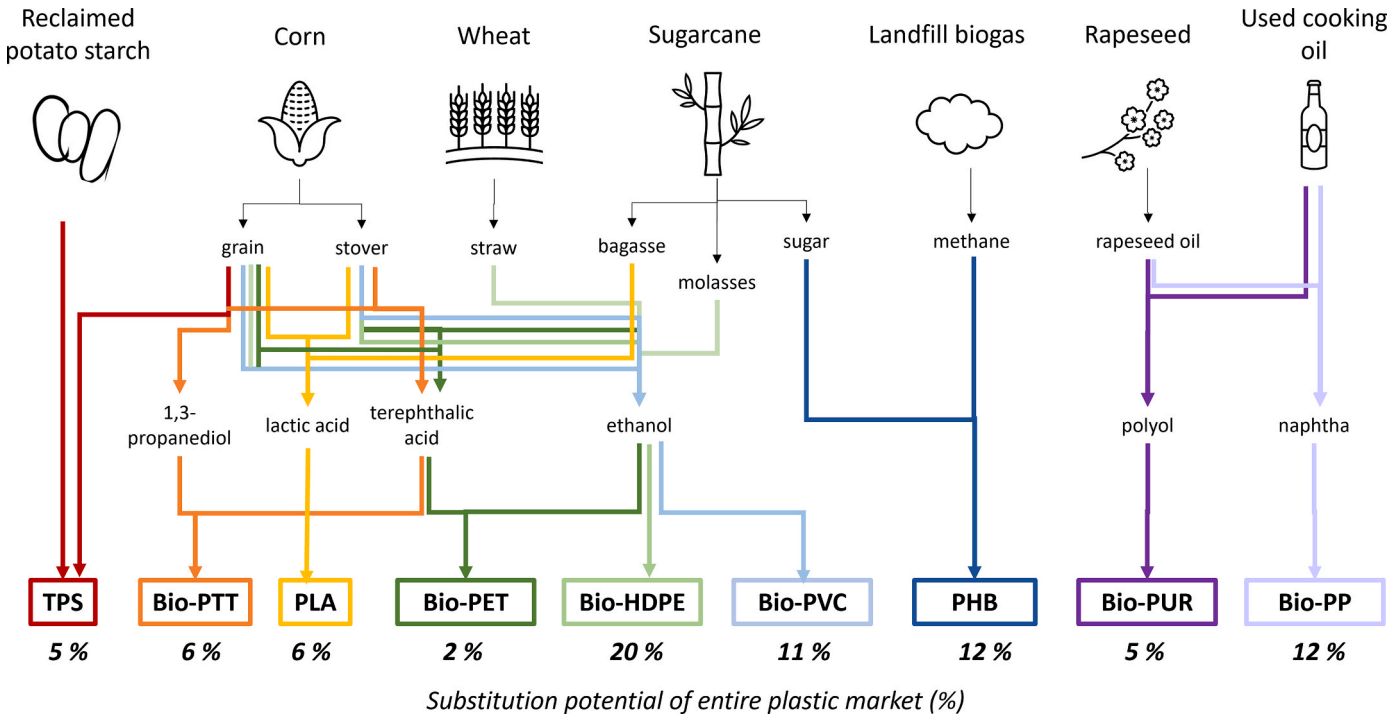

Fig. 1. Overview of bio-based plastic production pathways examined in this study. This figure does not include all the process steps required for the conversion of feedstock to bio-based plastic, but rather highlights the general production routes with key intermediates. The theoretical substitution potential of each bio-based plastic within the current petroleum-based plastic market is presented underneath in italics. These values were obtained by combining the technical substitution potential of each bioplastic (based on material performance), with the current plastic market. Note that these substitution potentials are not reflective of the resource availability of the feedstocks used. Note the following acronyms: thermoplastic starch (TPS), polytrimethyl terephthalate (Bio-PTT), polylactic acid (PLA), polyethylene terephthalate (Bio-PET), high-density polyethene (Bio-HDPE), polyvinylchloride (Bio-PVC), poly(3-hydroxybuturate) (PHB), polypropylene (Bio-PP), polyurethane (Bio-PUR).

2.3.1. LCIs for biodegradable bio-based plastics

PLA is a biodegradable, thermoplastic polyester that has been proposed as a substitute for traditional plastics such as polypropylene (PP), acrylonitrile butadiene styrene (ABS), polystyrene (PS), polyethylene (PE) and polyethylene terephthalate (PET), in food packaging and biomedical applications (Narancic et al., 2020; Hamad et al., 2018). The LCI for PLA from corn is derived from NatureWorks, the largest global producer of PLA (Vink et al., 2003). However, their published LCI data is highly aggregated and therefore difficult to modify. Therefore, we model the LCI for PLA from corn stover and sugarcane bagasse based on work by Ioannidou et al. (2022) and Daful et al. (2016), respectively. Producing lactic acid from lignocellulosic feedstocks involves four main steps. First, the feedstocks must be pre-treated, breaking down the biomass prior to enzymatic hydrolysis. LCI data for the pretreatment process of corn stover is based on a report from the National Renewable Energy Laboratory (NREL) on bioethanol production which includes two steps: (1) deacetylation and (2) dilute acid pretreatment. In this study, the LCI for this pretreatment process is slightly modified based on improvements to the design reported in a more recent report from NREL (Davis et al., 2015) (namely, reducing the loading of sulfuric acid from 22 mg/g dry solid to 9 mg/g dry solid). LCI data for the pretreatment of sugarcane bagasse is based on a steam explosion process. After pretreatment, the slurry is sent to a reactor for enzymatic hydrolysis using cellulase to convert cellulose into glucose. Glucose is then fermented to produce lactate. Traditionally, calcium carbonate is used as a neutralizing agent to reduce the negative effects of low pH on metabolic activities. However, in the LCI of bagasse-PLA, magnesium-hydroxide and triethylamine are used for the neutralization process to reduce the generation of gypsum waste products (Daful et al., 2016). To recover pure L-lactic acid, bacterial biomass is first separated from the fermentation broth via centrifugation, then the lactate is treated with 50% sulfuric acid to produce dilute lactic acid. Lactic acid is concentrated via evaporation and then reacted with methanol to produce methyl lactate. Finally, a distillation column is used for the hydrolysis of methyl lactate to produce polymer grade L-lactic acid. The LCI data for PLA production from lactic-acid via ring-opening polymerization reported in Ioannidou et al. (2022) is based on a study by Gruber et al. (1993). Due to the lack of necessary data around reaction rates and the thermodynamics of intermediate products, the authors conducted a simulation of the components to calculate mass and energy balances of the process.

PHAs are microbially produced, readily biodegradable polyesters. They are suitable to replace traditional plastics in medical and food packaging applications, but scaling has been limited to date due to high costs of production (Khatami et al., 2021). One of the most common types of PHA, poly(3-hydroxybuturate) (PHB), can be produced from either 1st or 3rd generation feedstocks using a similar process involving: (1) the accumulation of microbes in a reactor, (2) nutrient limitation (such as nitrogen or phosphorous) to form intracellular PHB, and (3) extraction of PHB from cells and purification. The LCI data for PHB production from sugar is based on Harding et al. (2007), and the LCI data for PHB production from biogas is based on Rostkowski et al. (2012). We note that Rostkowski et al. (2012) examined various extraction methods including solvent extraction, selective dissolution, and surfactant digestion. Solvent extraction was found to be the least favorable method in terms of GHG emissions, but is used in the LCI for this study to remain consistent with the LCI for biogas-PHB and because it is the most commonly used PHB extraction method (Jacquel et al., 2008).

Starch is a widely abundant and cheap bio-based plastic, making up roughly 20% of global bioplastic production capacity (European Bioplastics, 2022), but to achieve desired properties it is typically blended at high temperatures with plasticizers to form TPS, making it only partially bio-based (Khan et al., 2017). The LCI for TPS is based on the ecoinvent inventory for modified starch (Frischknecht et al., 2005), which uses aggregated data from Novamont, the producer of a common TPS bioplastic called Mater-Bi (Storz and Vorlop, 2013). This inventory is representative of TPS made from only 34% bio-based content. Here, starch is derived from corn wherein a milling process breaks down the corn into its components (corn starch, meal, germ, and feed). Mass allocation values reported in Ramirez et al. (2007), are utilized in combination with market values reported by the United States Department of Agriculture (United States Department of Agriculture, 2012) to determine economic allocation factors for this multi-output process. To model TPS production from reclaimed potato starch, the same inventory is used with reclaimed potato starch replacing corn starch.

2.3.2. LCIs of non-biodegradable bio-based plastics

Bioethanol is a common precursor in the production of bio-based, non-biodegradable plastics. We consider bioethanol production from two 2nd generation crops, corn stover and wheat straw, based on LCI data from Byun and Han (2021) and Borrion et al. (2012), respectively. The production of ethanol from lignocellulosic crops involves the following steps: (1) the hemicellulose fraction of the biomass is converted to xylose using sulfuric acid catalyst pretreatment; (2) the remaining fraction (cellulose) is converted into glucose using the cellulase enzyme; and then (3) the biomass derived glucose is fermented with a yeast catalyst, corn steep liquor, and diammonium phosphate to produce an ethanol-rich stream. We also consider bioethanol production from corn and sugarcane molasses. The corn to ethanol conversion process is taken from Akanuma et al. (2014). The LCI data for molasses to ethanol conversion is adapted from Tsiropoulos et al. (2014) and is a simple process, which only requires fermentation and distillation steps to produce ethanol.

Here we model a fully bio-based PET LCI using data for the production of bio-based ethylene glycol and bio-based terephthalic acid (TPA) from corn stover using models from Chen et al. (2016) and Benavides et al. (2018). We model TPA production from isobutanol intermediate - an established, high-volume commercial process. This process includes: (1) pre-treatment of corn stover to destruct lignocellulose into cellulose/hemicellulose; (2) enzymatic hydrolysis to convert polysaccharides into monosaccharides, which can be fermented into isobutanol; (3) conversion of isobutanol to paraxylene through dehydration, oligomerization, and dehydro-cyclination; and (4) oxidation of paraxylene into TPA. This final step results in the production of electricity and diesel blendstock, but these byproducts are considered outside of the scope of this work and all environmental impacts of these processing stages are attributed to the main product, TPA. The production of TPA from corn (based on Akanuma et al. (2014)) is similar to corn stover derived TPA but without the pretreatment step. The LCI for bio-based ethanol from corn stover and corn are the same as discussed above, and the conversion process of ethanol to ethylene is based on Chen et al. (2016). The remaining processing steps (conversion to ethylene oxide, ethylene glycol and polymerization to PET) are identical to petroleum-based plastic production processes, which we base on ecoinvent 2.2 (Frischknecht et al., 2005).

Bio-PVC is produced from the reaction between bio-based ethylene and chlorine. LCI data for PVC production is therefore the same as petroleum-based PVC production, reported in ecoinvent, with the exception that ethanol is derived from biomass using the methods described above, and again, the conversion process of ethanol to ethylene is based on Chen et al. (2016).

We model Bio-PP production from a 3rd generation feedstock, used cooking oil, and 1st generation feedstock, rapeseed oil. The only difference between the two production routes is the upstream production of both used cooking oil and rapeseed oil. From there, the process starts with the pretreatment and de-oxygenation of oil, producing bio-based naphtha, a by-product of hydrotreated vegetable oil (HVO). The LCI data for this multi-output process is from Neste, a biorefinery located in the Netherlands (Johnson, 2017). Mass allocation is applied where HVO is the main product (91 wt%), followed by bio-propane (6 wt%), bio-naphtha (2 wt%), and water (1 wt%). Bio-based naphtha is then converted to smaller hydrocarbons (including propylene) via steam

cracking. Given that steam cracking produces multiple products, mass allocation is applied. Ethylene is the major product when naphtha feedstock is used (35 wt%), followed by pyrolysis gas (20 wt%), methane (16 wt%), bio-propylene (14%), C4 (8%), pyrolysis fuel oil (5%) and hydrogen (2%). This process is assumed to be the same for both rapeseed oil and used cooking oil, given that both feedstocks result in HVOs with similar properties and yield similar products upon steam cracking (Karaba et al., 2021). Mass allocation factors for this steam cracking process are based on current US average industry data (Young et al., 2022). The final step of polymerization is identical to the petroleum-based polymerization process, and we model this process based ecoinvent data (Frischknecht et al., 2005).

Bio-PUR is modeled based on the conversion of rapeseed oil or used cooking oil to bio-based polyol via amidization with diethanolamine (DEA). The LCI data for the conversion process comes from a cradle-to-gate LCA study on rapeseed oil-based polyol production (Fridrihsone et al., 2020b) and is assumed to be the same for used cooking oil. While it is possible to have transesterification of rapeseed oil/used cooking oil with triethanolamine, we model the DEA route due to its known lower GHG emissions. The LCI for the final step (the generation of polyurethane foam) is obtained from ecoinvent as it is assumed to be identical to petroleum-based PUR foam production (Frischknecht et al., 2005). Given that the bio-based polyol content varies depending on the type of foam, both rigid and flexible PUR foam are modeled herein.

We model Bio-PTT production based on the two main ingredients, 1,3-propanediol (PDO) and TPA. The LCI for PDO production from corn glucose was obtained from Urban and Bakshi (2009), which involves a commercialized fermentation process using genetically engineered E. coli. The impacts from inoculum production are assumed to be negligible because once they are produced, they are self-sufficient, and the CO_2 emissions from glucose fermentation are determined stoichiometrically. The LCI for TPA production from corn stover is the same one that is used for Bio-PET. Given the similarities in chemical structure between PET and PTT, the electricity and heat requirements for the polymerization of PTT from PDO and TPA are assumed to be the same as PET.

3. Results

3.1. Greenhouse gas emissions and identifying environmental impact hotspots

Our findings show that it is possible to synthesize GHG-negative cradle-to-gate emissions for all bio-based plastics assessed with appropriate selection of feedstock (Fig. 2). These net-negative fluxes are achieved primarily by satisfying all energy demands with renewable electricity and heat, coupled with the biogenic carbon storage in bio-based plastic. These pathways were selected as the means to reduce GHG emissions due to known energy contributions to plastics production (Daehn et al., 2022) and the role of renewable carbon feedstocks on net-GHG emissions (Rosenboom et al., 2022). When utilizing the 2018 global average electricity mix (see supplemental data sheet 1), along with traditional fossil-fuel heat sources such as coal and natural gas, energy-derived emissions are responsible for up to 96% of production emissions for these bio-based plastics (see supplemental data sheet 19

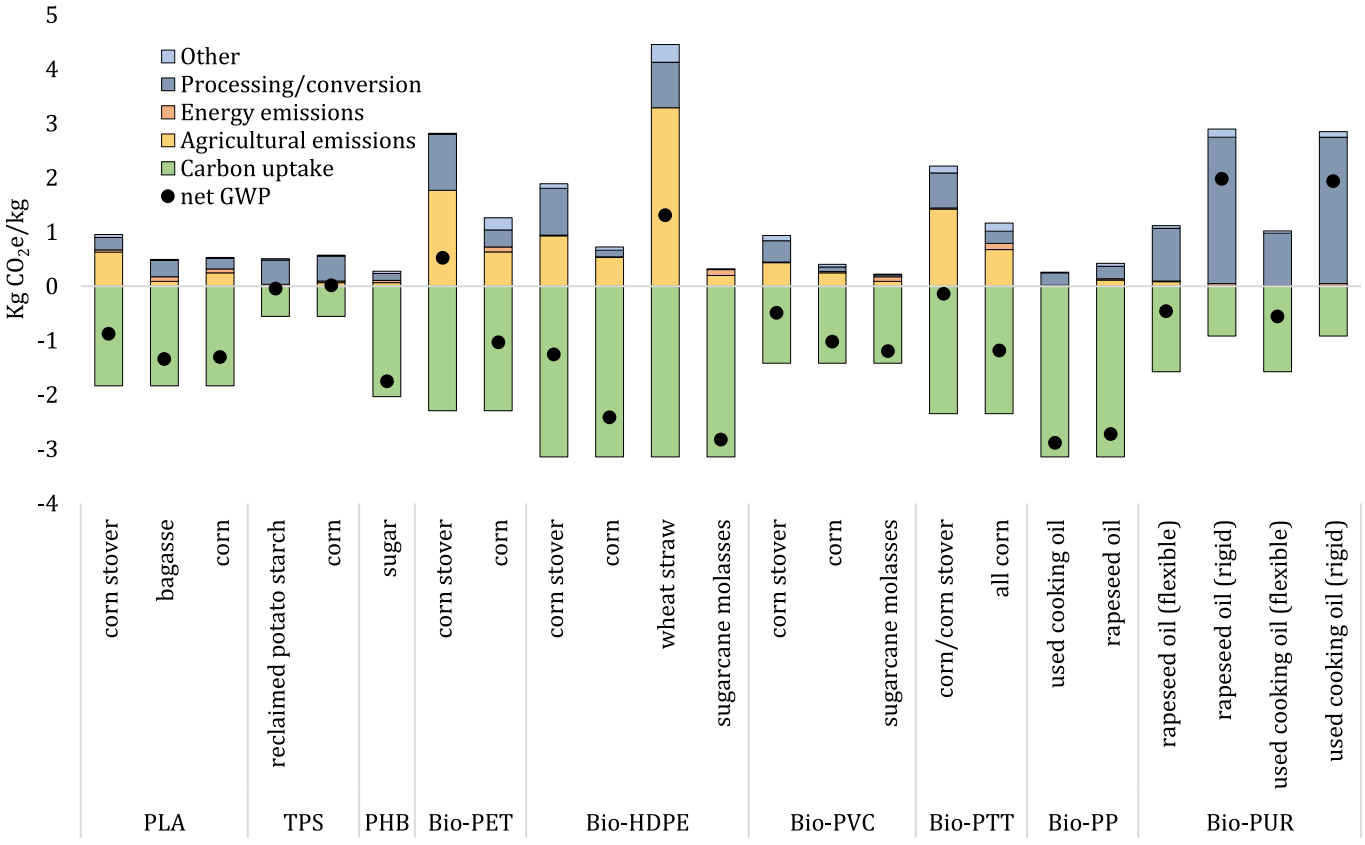

Fig. 2. Process contributions for cradle-to-gate GHG emissions of bio-based plastics using a mass-allocation approach. Process contributions are broken down by carbon uptake (green), agricultural processes (yellow), energy emissions (orange) from renewable energy, processing and conversion (blue/gray), and "other" processes contributing to less than 5% of overall emissions (light blue). Net GWP is shown by the black dots. GWP (or CO_2e) is calculated using GWP factors for CO_2, CH_4 (28) and N_2O (273) emissions. Note the following acronyms: polylactic acid (PLA), thermoplastic starch (TPS), polyethylene terephthalate (Bio-PET), high-density polyethylene (Bio-HDPE), polyvinylchloride (Bio-PVC), polytrimethyl terephthalate (Bio-PTT), polypropylene (Bio-PP), and polyurethane (Bio-PUR). See supplemental data sheet 17 for full figure data and PHB from biogas data. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

for a detailed breakdown of process contributions without renewable energy). By nearly eliminating energy-related emissions through the use of renewables, life cycle GHG emissions can be up to 30 times lower for some bio-based plastics (as is the case for PLA from sugarcane bagasse). Similarly, the cradle-to-gate impacts for PHB from landfill biogas amounted to −0.53 and 11 kg CO_2e/kg with and without the use of renewable energy, respectively. Despite the potential for GHG-negative bio-based plastics, agricultural and chemical processes for bio-based plastics are still emissions intensive. Therefore, the following section provides a breakdown of the environmental impact hotspots that exist when energy-related impacts are nearly eliminated. Noting that process modifications can help reduce these emissions (Miller et al., 2013), here we utilize a mass-based allocation approach to examine sources of these emissions, broadly categorized as: (1) "Agricultural emissions" for emissions related to the cultivation of agricultural feedstocks (agricultural machinery, fertilizer inputs, irrigation, etc.); (2) "Energy emissions" for emissions associated with renewable energy use; (3) "Processing/conversion emissions" for emissions related to conversion of feedstocks to bio-based plastics (such as industrial chemical production); or (4) "Other emissions" for sources of emissions that contribute to less than 5% of the overall GHG emissions and therefore are not examined on an individual basis.

In general, we find that a primary driver in environmental impacts of these materials is the type of feedstock used. For example, Bio-PET, Bio-HDPE, Bio-PVC and Bio-PTT have lower GWP when they are produced from 1st generation feedstocks, such as sugarcane sugar or corn, rather than 2nd generation feedstocks, such as corn stover or wheat straw, due to the removal of pretreatment steps and lower enzyme loading, thereby reducing impacts associated with enzyme and chemical production. In addition, even though some of the bio-based plastics are partially petroleum-based such as PUR and TPS, they are still able to reach GHG-negative emissions when renewable energy is used. Therefore, future increases in biomass content in bio-based plastics could offer the ability to uptake even more CO_2 during production and potentially drive greater GHG-negative fluxes.

3.1.1. Agricultural

Fertilizer production and use is one of the largest contributors to emissions of 2nd generation feedstocks, such as corn stover and wheat straw. For example, 17% of CO_2 emissions associated with PLA production from corn stover came from the production of ammonia for corn cultivation. Industrial ammonia production emits more CO_2 than any other chemical-producing process (Boerner, 2019) resulting from extremely high energy demand and the use of hydrogen via the Haber-Bosch process. Even when high-temperature and high-pressure process requirements are met with renewable energy (as it is modeled here), the production of hydrogen required for the reaction is currently made from natural gas, coal, or oil, via a process that accounts for more than half of the CO_2 emissions from ammonia production. To minimize these emissions, hydrogen could be produced from renewable resources via electrolysis (Smith et al., 2020) and alternatives to the Haber-Bosch process that may improve efficiency could be investigated (Humphreys et al., 2021).

In addition to the production of ammonia, its application contributes significantly to N_2O emissions due to biological processes, such as nitrification and denitrification. In 2005, only 17% of nitrogen produced for agriculture remained in the final product (Mathivanan et al., 2021; Jan Willem Erisman et al., 2008). As a result, for bio-based plastics with high agricultural feedstock inputs, such as Bio-PET and Bio-HDPE (7.5 and 4.04 kg corn stover, respectively), N_2O emissions from corn stover cultivation led to substantial GHG emissions - roughly 34 and 29% of the total mass-allocated GWP for these plastics, respectively. The same relative contributions hold true for Bio-PVC from corn stover and Bio-PTT from corn/corn stover, with roughly 27% and 35% of GWP coming from N_2O field emissions, respectively. To reduce the magnitude of nitrogen emissions from fertilizers, various agricultural process improvements could be implemented such as: (1) drainage systems to help maintain optimal moisture content and reduce denitrification of ammonia; (2) inserting ammonia-based fertilizer deeper into the soil to reduce ammonia volatilization; and (3) utilizing a need-based approach for fertilizer application to reduce excess nitrogen runoff (Wang et al., 2021).

3.1.2. Processing/conversion

Enzyme production is a significant source of processing and conversion emissions for bio-based plastics made from lignocellulosic materials. Enzymes are required for the enzymatic hydrolysis of lignocellulosic feedstocks, which is an energy and emissions intensive process. Here we modeled this enzyme production based on the ecoinvent LCI for potato starch-derived enzymes. A notable fraction of the emissions from this enzyme production process, once energy-emissions are eliminated, are attributable to the agricultural processing of potatoes. In addition to reducing fertilizer use, another potential process improvement would be to investigate the use of 2nd and 3rd generation feedstocks for enzyme production (Mihajlovski et al., 2021). Furthermore, reducing enzyme loading while maintaining high yields could lower energy requirements, as well as make the process more economically desirable (Wiloso et al., 2012). It has been suggested that such loading could be lowered by 50% (Humbird et al., 2011). Studies have also investigated an alternative to enzymatic hydrolysis – a one-step chemical hydrolysis process – that can help reduce GHG emissions by 54% compared to enzymatic hydrolysis (Byun and Han, 2021).

Beyond enzymes, chemicals required to convert biomass feedstocks to bio-based plastics can contribute to cradle-to-gate GHG emissions. For example, triethylamine and magnesium hydroxide ($Mg(OH)_2$), both required for the neutralization of lactic acid in the production of PLA from sugarcane bagasse, contribute 22% to cradle-to-gate mass-allocated GWP. Similarly, the extraction of PHB from microbial cells, regardless of the initial feedstock, is an energy and chemical-intensive process; we note again, different methods (Rostkowski et al., 2012) could be used for extraction and we model a solvent-based method here due to wide use. It is likely that the process efficiency for PHB extraction will improve once production reaches commercial scale (Valappil et al., 2007). Moving forward, utilizing less carbon-intensive chemicals, such as NaOH instead of chloroform, could also reduce emissions (López-Abelairas et al., 2015).

For bio-based plastics that are partially petroleum-based such as Bio-PUR or TPS, petrochemical production processes can amount to 84–97% of the production-related emissions. This factor is well exemplified by flexible and rigid Bio-PUR foam, whose LCIs differ in the ratio of biomass to petroleum feedstocks and the type of petroleum feedstock used (toluene diisocyanate (TDI) vs. methylene diphenyl diisocyanate (MDI)). Driven by its higher biomass to petroleum feedstock ratio, the cradle-to-gate mass-allocated GWP for the flexible Bio-PUR are over 100% lower than rigid foam. However, even with increased biomass content, the majority (55%) of GWP for flexible PUR foam comes from the production of diethanolamine, a chemical required to produce polyol from vegetable oil, whereas for rigid PUR foam, the majority (78%) of the GWP comes from the production of MDI. Despite the use of renewable energy, both plastics result in significant emissions due to the petroleum feedstocks required for production. While this work focuses on GHG fluxes, there are also human health concerns that should be addressed, with MDI and TDI resulting in increased asthma risk for occupational workers in foam manufacturing (Muñoz, 2016). Therefore, deriving less harmful, bio-based alternatives to TDI, MDI, and DEA is a necessary area for study. Bio-based non-isocyanate urethanes derived from plant oil have been produced on a lab-scale, but they still require an in-depth analysis of their potential environmental impacts (Mahendran et al., 2012).

Given that there are no upstream environmental impacts attributed to the feedstock, used cooking oil, for Bio-PP production, the majority (93%) of mass-allocated GWP comes from the hydrotreatment process of

oil. This process requires hydrogen which is produced via natural gas reformation. To reduce production related emissions, the production of hydrogen via electrolysis using renewable energy could be explored. In addition to using waste oil as a feedstock, GHG-negative Bio-PP could be made by synthesizing methanol from atmospheric CO_2 and H_2, again, assuming all energy demands and hydrogen production are satisfied by renewables (Kuusela et al., 2021).

In addition to the environmental impacts of agricultural and chemical production processing, a significant source of emissions come from inefficiencies in the bio-based plastic production processes. For example, due to inefficiencies in the extraction process of PHB from microbial cells, 5.26 kg of CH_4 from landfill biogas are required to produce 1 kg of PHB, resulting in significant CO_2 emissions. If the CO_2 from biogas were to be captured and utilized as a feedstock for plastic production, the cradle-to-gate emissions for PHB and associated production costs could be reduced. Similarly, the production of Bio-PET and Bio-HDPE requires 7.5 and 4.04 kg corn stover, corresponding to 3.3 and 1.8 kg of carbon, but only 20 and 48% of the carbon ends up in the final product, respectively. Therefore, process improvements for these materials include increasing the efficiency of TPA and ethanol production pathways to reduce losses and minimize primary feedstock inputs. A more efficient production route for TPA via direct fermentation of sugars could reduce the loss of carbon as well as minimize capital and operating costs (Benavides et al., 2018). Engineering bio-based plastics can capitalize on such methods.

3.2. Role of methodological assumptions

When determining the environmental impact of an agricultural by-product, such as corn stover or wheat straw, the upstream impacts (such as emissions associated with land-use, fertilizer production and application, and fuel consumed by agricultural machinery) need to be applied to both the main crop and the by-product. ISO 14040 recommends applying system expansion to avoid allocation, thereby encompassing the impacts associated with all of the products and byproducts within a system (International Organization for Standardization, 2006). However, applying system expansion is data intensive and requires making assumptions on the behavior of the system, which can lead to high uncertainty. Alternatively, the impacts of these upstream processes can be divided up (or allocated) based on economic or physical relationships or can be entirely attributed to one "main" product. Three common allocation methods are examined herein: (1) mass allocation, utilizing physical relationships to allocate impacts; (2) economic allocation, addressing economic value of products, which can drive production rates and market behavior; and (3) no allocation, which attributes all impacts to one product and is commonly used in LCAs examining 2nd and 3rd generation feedstocks (Moretti et al., 2020; Cherubini and Ulgiati, 2020; Angili et al., 2021). Economic allocation provides the benefit of potentially reflecting real-world resource consumption patterns based on market values of materials. However, economic values vary greatly over time and across different regions, leading to high variability among results. Mass allocation provides the benefit of remaining consistent by utilizing a physical relationship to allocate impacts. However, applying mass-allocation may result in attributing a large amount of environmental impacts to inevitable waste streams and simultaneously undervaluing the impacts of the main product.

Our findings show that GWP-negative production pathways are possible depending on the allocation method used. Fig. 3 shows the impact of varying allocation methods on the cradle-to-gate GWP of the bio-based plastics considered in this work. Our findings show that mass allocation results in the highest apparent GWP for all materials made from 2nd generation feedstocks (e.g., from corn stover or wheat straw),

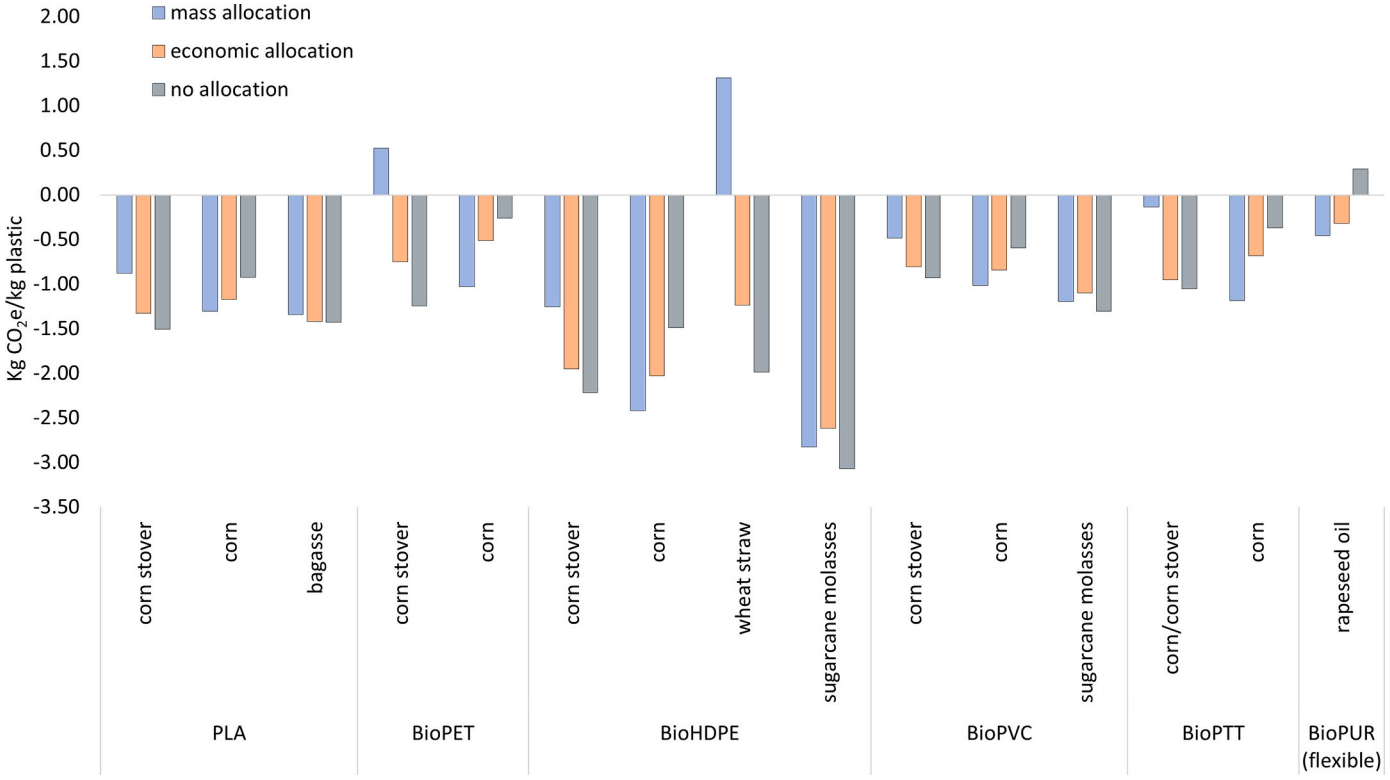

Fig. 3. Cradle-to-gate GWP of bio-based plastics from various feedstocks, using 100% renewable energy, and allocating impacts based on a mass (blue), economic (orange), and no allocation approach (gray). CO_2e was calculated using GWP factors for CO_2, CH_4 (28) and N_2O (273) emissions. Note the following acronyms: polylactic acid (PLA), polyethylene terephthalate (Bio-PET), high-density polyethylene (Bio-HDPE), polyvinylchloride (Bio-PVC), polytrimethyl terephthalate (Bio-PTT), and polyurethane (Bio-PUR). See supplemental data sheet 18 for full figure data. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

with economic allocation and no allocation resulting in 137% and 170% lower GWP on average. These findings are expected given that the mass allocation factor for 2nd generation crops is typically higher than the economic allocation factor (Luo et al., 2009). No allocation results in the highest impact for bio-based plastics from 1st generation feedstocks (e.g., from corn or rapeseed oil). On average, no allocation and economic allocation resulted in 69% and 28% higher GWP compared to mass allocation for 1st generation bio-based plastics. These findings are expected given that under no allocation, all upstream impacts from crop cultivation are attributed to the 1st generation feedstock. The key exceptions to these trends are for the bio-based plastics made from sugarcane molasses. Sugarcane molasses, a second generation feedstock, has a higher factor for economic allocation than for mass allocation (see Table 1) because it is typically sent to distilleries for ethanol production (Chauhan et al., 2011). However, it is not considered the main product of sugarcane, which is sugar, therefore no allocation results in the lowest GWP.

How biogenic carbon is addressed in the GHG fluxes for plastics production affects not only the GHG emissions profile for the plastic, but also the extent to which selecting a different allocation method alters the net impact. Biogenic carbon accounting is a common source of variability among bio-based plastic LCA studies (Wiloso et al., 2012; Luo et al., 2009). In this study, biogenic carbon credit is applied based on the carbon content of the bio-based plastic, meaning that the benefits of removal of atmospheric CO_2 is the same regardless of the allocation method. We selected this method of accounting as it reflects the bound carbon in the material. However, other authors have used other methods. For example, Luo et al. (2009) allocated biogenic carbon the same way that other emissions, such as N_2O, are allocated. For an assumption like Luo et al.'s, mass allocation correlates to a higher biogenic carbon credit than economic allocation for 2nd generation feedstocks. This difference in methodology results in the opposite trend than what is observed herein, with mass allocation resulting in lower GHG emissions compared to economic allocation for bio-based plastics from 2nd generation crops. This notable difference in results highlights the need for standardization among allocation methods in LCAs, specifically for 2nd and 3rd generation bio-based materials.

The sensitivity of GHG emissions (or magnitude of net-uptake) to the allocation methodology used depends on the type of bio-based plastic. For plastics where the biomass resource used contributes low amounts to GHG emissions, there is lower variation resulting from selecting a different allocation method. For plastics where a substantial amount of the GHG emissions profile is driven by the biomass resource, greater fluctuation in findings can occur by applying a different allocation method. For example, given that the feedstock inputs are much higher for Bio-PET than they are for PLA, the impact of allocation methods are much more significant.

4. Discussion

The goal of this study is to present LCI data for GHG-negative bio-based plastic production pathways from 2nd and 3rd generation feedstocks. While GHG-negative production pathways were identified, it is important to address some of the barriers and limitations of such methods. For example, although the electricity and energy requirements are modeled as using renewable resources, there are some scenarios where transitioning to renewable energy could be challenging given the high-temperature or high-pressure requirements of a given process. The Haber-Bosch process for ammonia production requires temperature and pressures above 700 °C and 200 bar (Daehn et al., 2022). Although some renewable energy technologies (such as solar thermal energy), are technically capable of satisfying high temperature requirements, the capacity of such technologies are not yet sufficient to meet the energy demands of the plastic industry. The petrochemical industry consumes 30% of total final industrial energy use globally (Bauer et al., 2022), whereas wind and solar energy currently only make up 2.7% of total global energy demand (International Energy Agency). Similarly, despite the growth in installed bioenergy capacity over recent years, biomass energy only contributes ~9% to total global energy demand (International Energy Agency). Therefore, while the environmental hotspots discussed herein are still relevant, it is important to note that decarbonizing the plastic industry remains a challenge. Proposed solutions to the environmental hotspots addressed herein, outside of energy demand, include the use of renewable hydrogen, decreased fertilizer demand, isocyanate-free PUR production, and alternative methods for enzymatic hydrolysis. It is crucial to acknowledge that implementing these solutions in the near future may face challenges such as high cost, insufficient infrastructure for scaling, and absence of established value chains. For example, despite the technological maturity of green hydrogen production, 99% of hydrogen is still produced from fossil fuels largely due to cost barriers (Eni and Mattei, 2020).

Another potential limitation to the solutions proposed herein is the availability of 2nd and 3rd generation feedstocks. While these biomass residues provide a source for plastic production without limiting food availability, the total quantity produced may not be sufficient to meet global plastic demand. In this work, we present LCIs for bio-based plastics capable of replacing 80% of current petroleum-based plastic. This assumption is based on their technical performance, rather than on resource availability. To reach the 80% substitution rate referenced herein, alternative production routes such as CO_2-based plastics, may need to be developed. However, if closed-loop end-of-life strategies are implemented for bio-based plastics (such as chemical recycling), annual biomass demand for bio-based plastic production would only amount to 23% of the projected untapped biomass resources (such as lignocellulose and food waste) estimated to become available due to improved farming (Meys et al., 2021).

While this study focused on cradle-to-gate impacts of bio-based plastic production, end-of-life impacts remain significant. These end-of-life impacts may be notable for biodegradable bio-based plastics (PLA, PHA, TPS), since anaerobic biodegradation of these materials at end-of-life can release methane (Van Roijen and Miller, 2022). Therefore, it is important to note that achieving cradle-to-grave net-negative emissions for bio-based plastics may only be feasible under certain end-of-life conditions, such as recycling, anaerobic digestion or composting. Another potential limitation to this study is that some of the LCI data that is used is region-specific (for example, corn and corn stover production are based on US average values). Grabowski et al. (2015) reviewed currently available datasets for bio-based plastic feedstocks, and found that 60% of the available datasets were based on two regions: North America and Europe. They also found that the data for most crops were out-of-date. In this study, this temporal data gap is partially addressed by using updated crop yield statistics, but it remains a concern for other inputs such as fertilizer and harvesting methods, which can vary greatly by region as well as over time. Furthermore, given the attributional approach of this study, the impacts of alternative scenarios and/or interconnected processes are not captured. For example, we model sugarcane bagasse as a feedstock for bio-based plastic production, when it is typically used as an energy-source. Future work could apply system expansion in such cases to capture the impacts of such alternative scenarios.

Countless studies have discussed the necessity to decarbonize the petrochemical industry, and the global theoretical potential to make the petrochemical industry net-zero has been explored. However, pathways to create net-zero or net-uptake systems need to be systematically quantified and assessed. By creating a harmonized method for systematically quantifying GHG fluxes for bio-based plastics, this work shows the necessary technological advancements to eliminate GHG emissions from the production process of plastics. As noted, the plastics examined in this work have the technical potential to substitute roughly 80% of the current petroleum-plastic market. Given that depending on the allocation method considered, GHG-negative plastic production methods were identified, findings can be used to inform stakeholders along the plastic

supply chain of mechanisms to drive GHG-negative plastics. However, this shift towards bio-based plastics would not be an economically viable emissions mitigation strategy if only 1st generation crops are used due to land-use change impacts and competition with food (Brizga et al., 2020). By presenting production pathways for bio-based plastics from non-edible feedstocks, new markets for agricultural byproducts can be driven (Ni et al., 2021). Such alteration would not only mitigate reliance on petroleum resources for consumer products, but also potentially mitigate inefficient utilization of, and create new markets for, the roughly 1 billion tonnes of agricultural and food waste generated globally each year (Rosenboom et al., 2022). Such a shift in resource use could contribute to the reduction of resource transportation, the mitigation of harmful emissions from petroleum refinement (Ragothaman and Anderson, 2017), and the limitation of insecurities associated with supply chain dynamics if implemented properly.

5. Conclusion

In this study, GHG-negative production pathways were identified for nine bio-based plastics. Harmonized LCIs were derived for these plastics to facilitate comparison, analysis, and improved production. This level of transparency will not only support scientific advancements, but also help eliminate the black box that exists in many petrochemical production methods. Together, the plastics explored are technically capable of substituting roughly 80% of current petroleum-based plastic demand, suggesting a potential for the plastic market to become a carbon sink rather than a significant carbon source. Furthermore, all of the bio-based plastic production pathways examined herein at least partially utilize 2nd or 3rd generation feedstocks, which reduce competition with food and land-use change impacts - two major problems typically associated with bio-based plastic production.

Applying the LCIs synthesized in this work, our analysis of GHG emissions hotspots highlighted the need for various process improvements outside of decarbonizing energy and electricity demands, including:

- reducing ammonia-based fertilizer use
- engineering greener methods for H_2 production, such as electrolysis via renewable energy
- using bio-based, isocyanate-free PUR production pathways
- using 2nd-generation feedstocks for enzyme production
- determining alternatives to enzymatic hydrolysis, such as one-step chemical-hydrolysis
- engineering bio-based alternatives to typical petroleum-based TPS blends
- improving process efficiencies in TPA and ethanol production pathways to reduce CO_2 emissions from biomass loss

Our work also considers the sensitivity of modeling outcomes to allocation methods. Generally, mass allocation of 2nd generation feedstocks resulted in the highest GWP, while economic or no allocation resulted in the highest GWP for 1st generation feedstocks. However, these results can shift due to changes in methodology such as biogenic carbon accounting (e.g., either applying biogenic carbon credits based on the carbon content of the final product or based on an allocation factor). Therefore, there is a need for standardization and clear guidelines regarding biogenic carbon accounting and allocation methods as they apply to bio-based materials.

When considering drastic changes in production processes, such as shifting from petroleum-based to bio-based plastics, it is important to reduce burden shifting or reducing one environmental impact category at the expense of another. Therefore, future work should aim to understand the environmental and human health impacts outside of GHG emissions of the bio-based plastic production pathways presented herein, such as particulate matter emissions and eutrophication impacts from fertilizer use (Wyer et al., 2022), human health burdens from the combustion and conversion of fuels for energy generation (Macor, 2020; Shindell and Smith, 2019), and increased water demand associated with bio-based feedstocks (Brizga et al., 2020). In addition, investigating the consequential impacts of large-scale bio-based plastic production, such as indirect land-use change and shifts in biomass markets, should be further analyzed. Data gaps that exist in plastic production inventories, such as the use of additives, should be investigated to better understand the impact of these materials on the environment, and continued integration of updated life cycle inventory data, particularly when geographically and temporally relevant, should be studied. Finally, to achieve net-zero plastics, the end-of-life impacts must also be considered. Therefore, determining the impact of waste management strategies on the GHG-negative potential of bio-based plastics is critical.

CRediT authorship contribution statement

Elisabeth Van Roijen: Data curation, Formal analysis, Methodology, Validation, Visualization, Writing – original draft. **Sabbie A. Miller:** Supervision, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All relevant data is attached in the supplemental materials

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2024.141203.

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