

LIFE CYCLE INVENTORY FOR POLYLACTIC ACID PRODUCTION in GREET® 2019

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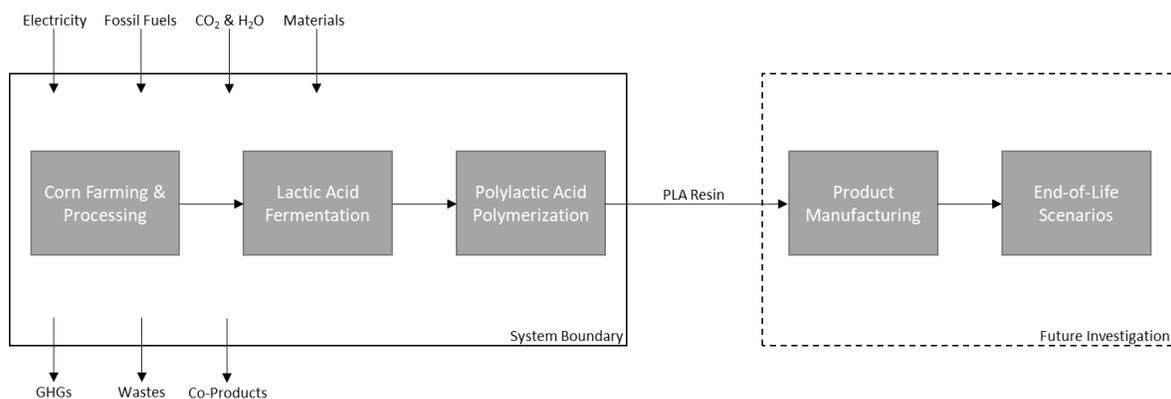
Introduction

Poly(lactic acid) (PLA) is a linear aliphatic thermoplastic polyester with three stereochemical forms: poly-L-lactide, poly-D-lactide, and poly-D,L-lactide [Nampoothiri et al. 2010]. In 2017, PLA production accounted for around 10% of global bioplastic production (232,749 tons) and is expected to have a significant increase in production capability to 50% percent by 2022 compared [European Bioplastics 2017; Detzel et al. 2013]. It is estimated that bioplastics can replace as much as 90% of the application used by conventional plastics, which show the great potential of bio-based plastics [Shen et al. 2010]. PLA has a proven track record as a substitute for more commonly used plastics such as polypropylene (PP), high density polyethylene, acrylonitrile butadiene styrene, and more [Guo and Crittenden 2011; Groot and Boren 2010]. PLA is a potential replacement for conventional plastics applications such as cups, bottles, to-go containers, packaging, films, and textiles [Henton et al. 2005; Binder and Woods 2009; Vaes et al. 2006; Gironi and Piemonte 2011; Vink et al. 2003].

In this document, we present a life-cycle inventory (LCI) for PLA production that can be used to evaluate the energy and material inputs with the greatest effect on the life-cycle energy use and greenhouse gas (GHG) emissions of PLA production. For this purpose, we used the Greenhouse gases, Regulated Emissions, and Energy use in Transportation (GREET) model, which Argonne National Laboratory developed [GREET 2018]. GREET was used to collect data for the upstream processes of PLA production including energy use and emission factors.

Poly(lactic acid) Production

The flow diagram in Figure 1 illustrates the system boundaries used in the assessment. The diagram includes major material and energy flows and describes the general process. The system boundary starts with the feedstock production, in this case corn, which includes production of corn seed, addition of fertilizers and pesticides, fuels and water used during the agricultural activities, and processing the feedstock. The boundary is followed by conversion of the feedstock, which includes dextrose production, lactic acid fermentation, and resin production (including lactide production and PLA polymerization) [Vink et al. 2007; Nampoothiri et al. 2010; Groot and Boren 2010].



Once the corn is harvested, it is transported to a corn wet mill (CWM) for processing. At the CWM, the corn is cleaned to remove foreign matter and particulates and analyzed to determine its composition (i.e. percent moisture, protein, starch, etc.). The corn is steeped in a water/sulfur dioxide solution at ~51°C for 36 hours [Ramirez et al. 2008]. The germ, fiber, and gluten content of the corn are recovered individually, and a high purity starch solution is produced. The liquefied starch is transferred to a reactor vessel where enzymes (e.g. glucoamylase) are added. As a result, dextrose is produced and then filtered out. The unreacted starch solution is recycled back into the reactor vessel. Fermentation of dextrose into lactic acid occurs under anaerobic conditions using nitrogen gas. Chirality and purity of the product is controlled by the selection of lactic acid bacteria used in the fermentation process. *Lactobacillus lactis* is the fermenting microorganism most commonly used in the production of L-lactic acid from dextrose [Dunn et al. 2015]. L-lactic acid is used almost exclusively in the industrial production of PLA [Groot and Boren 2010]. Fermentation by lactic acid bacteria only occurs near neutral pH levels, but production of L-lactic acid lowers the pH of the fermentation broth. To counter-act the lowered pH in the fermentation broth, calcium carbonate (CaCO₃) is added to the broth, converting L-lactic acid to calcium lactate. During purification, sulfuric acid (H₂SO₄) is added to the calcium lactate solution. The freed L-lactic acid is recovered, and gypsum (CaSO₄) precipitates out the solution. The CaSO₄ is filtered out, and the lactic acid solution is concentrated by evaporation.

PLA production occurs in a two-step process: the formation of lactide dimers through a condensation reaction, and polymerization of those dimers into high molecular weight PLA. In the first stage, water is removed from the purified L-lactic acid solution by evaporation, and the solution is deposited into the prepolymer reactor. As the solution condenses, L-lactic acid undergoes direct condensation plasticization producing low molecular-weight PLA (prepolymer). The prepolymer is transferred to the lactide reactor where it is de-plasticized in a “back-biting” reaction catalyzed by tin(II) 2-ethylhexanoate [Castro-Aguirre et al. 2016; Auras et al. 2004]. This results in the formation of L-lactide, a dimer of L-lactic acid. The molten L-lactide solution is purified by distillation, and any unreacted L-lactic acid or prepolymer is recycled back into the system. The purified L-lactide molecules undergo a ring-opening plasticization reaction catalyzed by tin(II) 2-ethylhexanoate. The result is high molecular-weight PLA. The PLA is then devolatilized, crystallized, and pelletized [Vink et al. 2010]. The production processes described here are mainly from NatureWorks, the biggest producer of PLA in the world, which manufactures more than 150,000 metric tons of PLA annually [Castro-Aguirre 2016].

This report presents the production of PLA resin (i.e., the system boundary specified in Figure 1), but it does not include the information on consumer product manufacturing inputs and end-of-life of the product. Thus, the results represent a cradle-to-gate that focuses on the GHG emissions, fossil fuel consumption associated with upstream, and PLA production stages.

Input Data and Parametric Assumptions

NatureWorks is the only large-scale manufacturer of PLA resin in the world. This means the production methods used by NatureWorks are the primary methods used in PLA production worldwide [Detzel and Kruger 2006; Detzel et al. 2013]. The data collected for this inventory was gathered from an eco-profile published by Vink et al. 2007, for NatureWorks, LLC in 2007. The eco-profile describes the material and energy inputs required for the production of PLA, from corn production to resin pelletization based on the system boundary presented in Figure 1. The material inputs required for the production of one ton of PLA resin are presented in Table 1. Material inputs from the literature were matched to existing entries in the GREET 2018 model. In case a matching entry did not exist, a material with similar characteristic was selected. The material substitutions include common clay and bentonite as kaolin (a highly refined type

of clay), sulfur (bonded) as sulfuric acid, and steel scrap as recycled steel. The limestone entry covers both limestone and chalk (CaCO₃). The only material input excluded from the inventory was gravel, which is only used in extremely small quantities (0.9 grams per ton of PLA) and has an insignificant effect on total GHG emissions. Air was another excluded input. For more detail regarding the PLA inventor, see Appendix A.

Table 1 Material and Energy Input to Produce One Ton of PLA Resin (Cradle-to-Gate)

Material Input	kg material/ton PLA
Barite ¹	0.51
Bauxites	0.01
Sodium Chloride	103.81
Kaolin	19.33
Iron	0.30
Lead	1.81e-3
Limestone	715.67
Sand	9.11
Phosphate	5.90
Sulfur (elemental)	12.64
Dolomite	3.63e-3
Oxygen	0.16
Nitrogen	8.35
Olivine	2.72e-3
Potassium Chloride	13.21
Sulfuric Acid	230.66
Recycled Steel	0.06
Feedstock (corn, dry)	1161.87
Energy Input	mm Btu/ton PLA
Electricity	5.74
Coal	0.21
Oil	2.92
Natural gas	16.94
Hydrogen	0.08
Total Energy	25.88

¹ Barite information was calculated from Pettersen (2007).
See Appendix B for material and energy input of Barite production.

Table 1 also presents the energy inputs required to produce one ton of PLA. The quantity of electricity consumed in the production of one ton of PLA resin was determined from the renewable energy credits (RECs) reported in the eco-profile [Vink et al. 2007]. According to Vink et al., “The environmental burden of electricity used in the PLA production system is offset 1:1,” by the purchase of RECs. This information was not available in more recent eco-profiles.

Cradle-to-Gate PLA GHG Emissions and Fossil Fuel Consumption

Figure 2 illustrates the GHG emissions associated with PLA production. The graph shows GHG emissions divided between feedstock production and the conversion of feedstock into PLA. Biogenic carbon is carbon taken from the atmosphere (in the form of CO₂) by growing corn that is converted into PLA. Corn production accounts for 10.1% of the GHGs emitted by the system, so the remaining 89.9% is a result of the conversion process. The net GHG emission on a cradle-to-gate bases are 1.22 tCO₂e per one t of PLA produced. Biogenic carbon (carbon uptake from the atmosphere during feedstock production that is present in PLA resin) is taken into account.

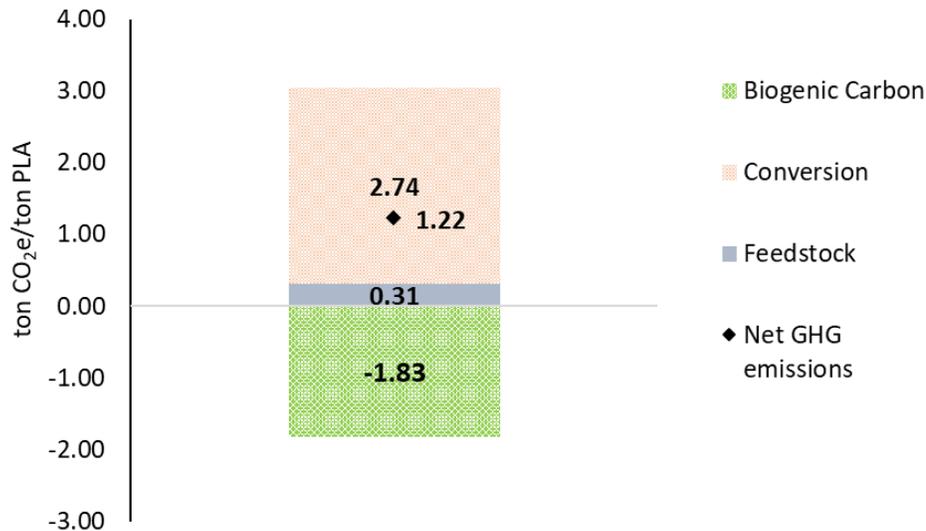


Figure 2. Cradle-to-gate GHG Emissions from PLA Production (in CO₂ equivalents/ton PLA produced).

The share of GHG emissions by input can be found in Table 2. The inputs (excluding feedstock) represent the conversion process as seen in Figure 2. Natural gas (NG) and electricity account for the majority of GHG emissions, even when production and transportation of the material inputs are considered. The quantity of energy consumed from natural gas (16.9 million [mm] Btu/ton PLA) is nearly three times the amount of electrical energy consumed (5.7 mm Btu/ton PLA), but the share of GHG emissions associated with NG is only one-and-a-half times the share of GHG emissions associated with electricity.

Table 2 Cradle-to-Gate GHG Emissions

Input	tons CO₂e/ton PLA	% Contribution
Feedstock	0.31	10.1
Materials	0.09	2.9
Natural Gas	1.36	44.6
Electricity	0.94	30.8
Residual Oil	0.32	10.5
Coal	0.02	0.8
Hydrogen	0.01	0.3

Table 3 describes the amount of energy from fossil fuel sources that is required to produce one ton of PLA, 33.8 mm Btu. In GREET, fossil fuel consumption is divided into three categories, coal (6 mm Btu/ton PLA), NG (23.9 mm Btu/ton PLA), and petroleum (3.9 mm Btu/ton PLA). These values include fossil fuels consumed directly, in the production of electricity, and upstream during the production of material inputs. Fossil fuels consumed during feedstock production (1.09 mm Btu/ton PLA) made up 3.2% of the total quantity of fossil fuels consumed by the system, while conversion corresponds to 97.1% of the total fossil fuels.

Table 3. Fossil Fuel Consumption during PLA Production Broken Down by Fuel Type

Feedstock	mm Btu/ton PLA	% total energy
Coal	0.02	0.0
Natural Gas	0.72	2.1
Petroleum	0.35	1.0
Subtotal	1.09	3.2
Conversion	mm Btu/ton PLA	% total energy
Coal	6.02	17.7
Natural Gas	23.24	68.8
Petroleum	3.64	10.5
Subtotal	32.91	97.1
Total Feedstock + Conversion	33.88	100

Note: Fossil fuels consumed during feedstock production have been differentiated from those consumed during the conversion process (mm Btu/ton PLA).

Conclusions

This work presents the life-cycle GHG emissions and fossil fuel consumption of producing PLA bioplastic. Production of PLA (cradle-to-gate) is responsible for the net release of 1.22 tons CO₂e (3.04 tons CO₂e gross emissions — 1.83 tons CO₂e biogenic carbon credit) and consumes 33.8 mm Btu of fossil fuel energy per ton of PLA. Conversion was the major contributor of GHG emissions in the supply chain. Conversion of feedstock into PLA resin consumes 32.91 mm Btu of fossil fuel energy (~97% total fossil fuel consumption) and produces 2.74 tons of CO₂e per ton of PLA produced.

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Appendix A: Assumptions

Data collection was limited to the eco-profile published by Vink et al. 2007. This is because it was the only published eco-profile, which provided a value for the total electricity used in the PLA production process. In addition, the information in more recently published eco-profiles represented the energy and material inputs for a different (potentially more refined) process than the one described in the 2007 publication. The 2007 eco-profile treats PLA production as a single process, obscuring the distribution of material and energy inputs throughout the system. As a result, identification of an individual process or processes with the greatest impact and changes to those processes cannot be simulated. Here are the major assumptions:

- The LCI of Vink 2007 was used because it provided the necessary information for the analysis presented here. Although newer LCI exists [Vink et al. 2010, 2015], it lacked information on the distribution of energy use (electricity, diesel, fuel oil, etc.).
- Data on bentonite and common clay production do not currently exist in GREET and could not be located during the data collection phase of the assessment. Kaolin is a clay that requires the same or more energy to be mined and processed. Data for kaolin clay was used to represent the bentonite and common clay used in the PLA production process. Kaolin is a clay used as a catalyst. This catalyst requires extensive processing during production, and it is held to a higher standard than common clay or bentonite. This could result in an overestimation of the energy requirements due to clay use; however, the discrepancy in energy from bentonite is insignificant as only 39g of bentonite is required to produce one ton of PLA.
- One gram of gravel is used in the production of one ton of PLA. Information for gravel production is not currently available in GREET. The energy costs of gravel production were assumed to be most similar to the energy costs of sand production because sand and gravel (aggregate) are frequently mined simultaneously [Drew et al. 2002]. The quantity of gravel used in each ton of PLA production is inconsequential (grams per ton of PLA), thus gravel was excluded from the analysis.
- According to Vink 2007, CaSO_4 is co-produced along with PLA. One part of gypsum can be sold for land application and the other part can be landfilled. However, Vink 2007 does not provide details for the quantity of CaSO_4 used for land use, so estimating the credits of avoided emissions due to raw CaSO_4 production is difficult. Therefore, the impact of this co-product was ignored for the purpose of this assessment.
- Iron was assumed to be cast iron and to not require further processing.
- Sulfur (bonded) was assumed to represent sulfuric acid, while sulfur (elemental) was assumed to represent elemental sulfur. Sulfur energy input was converted to mass (heating value = 9.2 MJ/kg) and accounted for with the material inputs (no sulfur category exists in GREET for energy inputs) [Muller 2003].
- Air was assumed to represent compressed air used in the one or more of the production processes. Atmospheric air is not “produced,” so no upstream GHG emissions or fossil fuel consumptions were needed to consider. Any electricity (energy) used to compress the air would be included in the energy inputs provided by Vink 2007.
- Limestone and chalk values were combined in GREET as CaCO_3

- “Recovered Energy” was given as an entry in the energy inputs data from Vink 2007. We assumed the inputs as “recovered” from natural gas (natural gas energy input was reduced by 1.49 MJ/kg PLA).
- Water use provided by Vink 2007 was calculated without considering irrigation water because the crop production in the GREET model already takes irrigation water into account.
- Corn data were provided for corn at 15% moisture [Vink et al. 2007], this was recalculated to the dry mass of the corn
- GREET data for corn wet milling were used for the feedstock production.
- It was not reported if the nuclear energy in the eco-profile was used in the production of electricity or for other uses, such as the production of steam. Nuclear energy only comprised 0.5% of the total energy inputs into the system, so it was decided that nuclear energy would not significantly impact the results of this inventory, so it was excluded.
- The results presented in Vink 2007 used a different electricity grid than the one use in GREET 2018. This grid was recreated to compare the results. Data published by the Mid-Continental Area Power Pool (MAPP) and US EPA eGRID 2005 data from the U.S. Environmental Protection Agency (EPA) were used for the Table A comparison. The results obtained with the GREET 2018 model agree well with the results presented by Vink 2007 results, with a difference of around 4%.

Table A. MAPP 2005 Grid Mix (Recreated with Data from US EPA 2005) [Mid-Continent Area Power Pool 2007; US EPA 2005]

Energy Source	% Grid Mix
Residual Oil	19.30
Natural Gas	9.70
Coal	58.30
Nuclear Power	2.10
Biomass	0.10
Other	10.50

Appendix B: Life-Cycle Inventory for the Production of Barite

For Barite production, energy inputs were obtained from Pettersen 2007 based on mining operations by Norbar minerals. Barite production is divided into two process extraction (mining) and refining. Table B presents the energy used during mining and refining of Barite, including energy due to the used of diesel trucks, generators, and compressors.

Table B. Energy Input Used during Barite Extraction and Refining [Pettersen 2007]

	Extraction (mm btu/ton)	Refining (mm btu/ton)
Natural Gas		0.057
Residual Oil	0.034	0.051
Diesel fuel	0.055	