

Life cycle assessment of the manufacture of lactide and PLA biopolymers from sugarcane in Thailand

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Abstract

Background L-lactide is the monomer for the polymer poly-L-lactic acid (PLLA). PLLA can be made from renewable resources, and is used in an increasing amount of applications. The biopolymer PLLA is one type of polymer of the family of polylactic acids (PLAs). Purac produces L-lactide and D-lactide, and supports partners with know-how to produce their own PLA from lactide. This life cycle assessment (LCA) study supporting market development presents the eco-profile of lactides and PLA biopolymers. **Method** An LCA was carried out for L-lactide, D-lactide, PLLA, and two PLLA/PDLA blends made from cane sugar in Thailand, and were compared with that of fossil-based polymers. The LCA complies with ISO standards, and is a cradle-to-gate analysis including sugarcane cultivation, sugarcane milling, auxiliary chemicals production, transport, and production of lactide and PLAs. In the analysis, process data were taken from the designs of full-scale plants for the production of lactic acid, lactides, and PLA. The data were combined with ecoprofiles of chemicals and utilities and recalculated to the following environmental impacts: primary renewable and non-renewable energy, non-renewable abiotic resource usage, farm land use, global

warming, acidification, photochemical ozone creation, human toxicity, and eutrophication.

Results and discussion On a weight-by-weight basis, PLLA results in significantly lower emissions of greenhouse gasses, and less use of material resources and non-renewable energy, compared to fossil-based polymers. With the present calculations, the Global Warming Potential (GWP) in L-lactide production is 300–600 kg CO₂ eq./tonne and for PLLA 500–800 kg CO₂ eq./tonne. The range indicates the sensitivity of the GWP to the energy credit for electricity production from bagasse in the sugar mill. The GWP of PLLA/PDLA blends with increased heat resistance is also lower compared to fossil based polymers with similar durable character. Being based on an agricultural system the biobased PLA gives rise to higher contributions to acidification, photochemical ozone creation, eutrophication, and farm land use compared to the fossil polymers.

Conclusions The application spectrum of PLAs is expanding, and there are opportunities to replace various fossil-based polymers. This facilitates climate change mitigation and reduces dependence on fossil and scarce resources while promoting the use of local and renewable resources. It is evident that in emerging green economies agricultural technology will form an integral part in the changeover towards a more sustainable industry and society.

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1 Introduction

Bioplastics are receiving much attention in the emerging topic of green chemistry since they can be made from

renewable resources or will degrade easily later in nature or under industrial conditions (Narayan 2004). The use and application of the biopolymer poly lactic acid (PLA) has seen a tremendous growth in the last years since the PLA plant of NatureWorks in Blair, Nebraska, came on stream in 2001 (Vink et al. 2003).

The biopolymer PLA is made from lactic acid that can be produced from sugars by fermentation. Lactic acid has a carboxylic and hydroxyl group and through esterification PLA, chains of lactic acid moieties, may be formed. In practice, PLA is normally made through ring opening polymerisation of lactide, a ring structure formed by self-esterification of two lactic acid molecules (Fig. 1).

Lactic acid has two stereo-isomers: L(+) lactic acid and D(-) lactic acid, the first being most common in nature. Lactide can be made from lactic acid and exists in three forms: L-lactide, D-lactide, and meso-lactide composed of L(+) and D(-)-lactic acid. The production of L(+) lactic acid and further to L-lactide is more mature than the D-lactide route. Consequently, the production of poly L-lactic acid (PLLA) has the greater commercial relevance. Since the presence of D(-) lactic acid moieties in PLLA has a large influence on the properties of polymer, the origin and fate of meso-lactide is important in an overall production process. Meso-lactide arises from the formation of the D(-) form in a L(+)-lactic acid fermentation and from racemisation of the L(+) form to the D(-) form mainly in the high temperature process steps. From a techno-economic point of view, the desired lactide purity and the

yield of lactide on lactic acid is intricately linked to the production process of choice. Although the D-lactide process is less mature costwise, the purities and process yields are similar to that of L-lactide.

Purac has over 70 years of experience in L(+)-lactic acid production, and has started up a modern low-cost lactic acid plant near Rayong in Thailand in 2007, using sugar from sugarcane as the raw material. Since the early 1990s, Purac manufactures high quality L-lactide and D-lactide monomers and copolymers for medical applications at the production site in Gorinchem, The Netherlands. In 2008, Purac started up a new facility in Spain for production of larger volumes of L-lactide or D-lactide, and a new large-scale lactide plant will become onstream at Purac's site in Thailand in 2011. As a lactide supplier, Purac is teaming up with Sulzer Chemtech for PLA production technology, and with customers for PLA production and application development, e.g., with Synbra in the Netherlands for expanded PLA foam (Biofoam®).

Purac produces for its PLA production partners L-lactide and D-lactide with high purity. With these pure monomers the biopolymers PLLA and PDLA and a variety of (block-) co-polymers can be produced. A special class of PLAs consists of blends of PLLA and PDLA: nucleated PLA (nPLA) may contain up to 5% PDLA next to PLLA, and stereocomplex PLA (scPLA) up to 40% PDLA. nPLA and scPLA have new properties, notably through various degrees of crystallinity of the polymer blend. For example, the increased heat resistance of PLLA/PDLA blends allow for application in drinking cups for hot drinks, or in technical applications such as films for solar cells, automotive fibers or plastics (Garlotta 2002). In contrast PLA resin containing a certain amount of meso-lactide has a limited heat resistance, and applications may be restricted to, e.g., packaging material.

A well-documented recent overview of the PLA business is given by Shen et al. (2009). NatureWorks is the main PLA producer at this moment with a plant on the Cargill site in Blair, Nebraska, with a name plate capacity of 150 kt. It is forecasted that the biopolymer market in general will grow fast; and for PLA, the company announcements indicate a growth to 800 kt in 2020. For Western Europe, it has been estimated that 82% of the polymer market, including fibers, may be substituted by biopolymers, given the current and expected future technical performance.

Figure 2 visualizes the types of PLA, current applications of PLA and lists well-known fossil-based polymers that are used presently in similar fields of applications. The figure indicates with arrows the increased demand for performance polymers, and the continued search for new applications of biobased polymers. In Section 3 in a comparable fashion, the global warming potential (GWP)

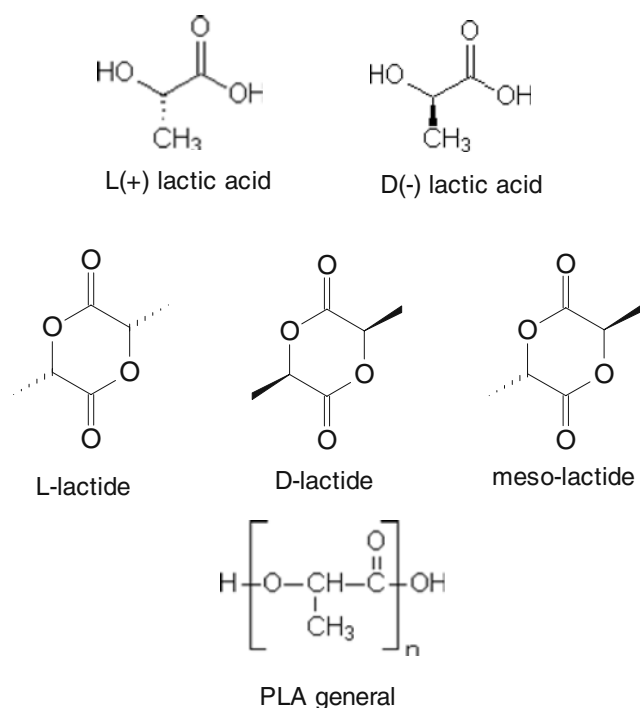
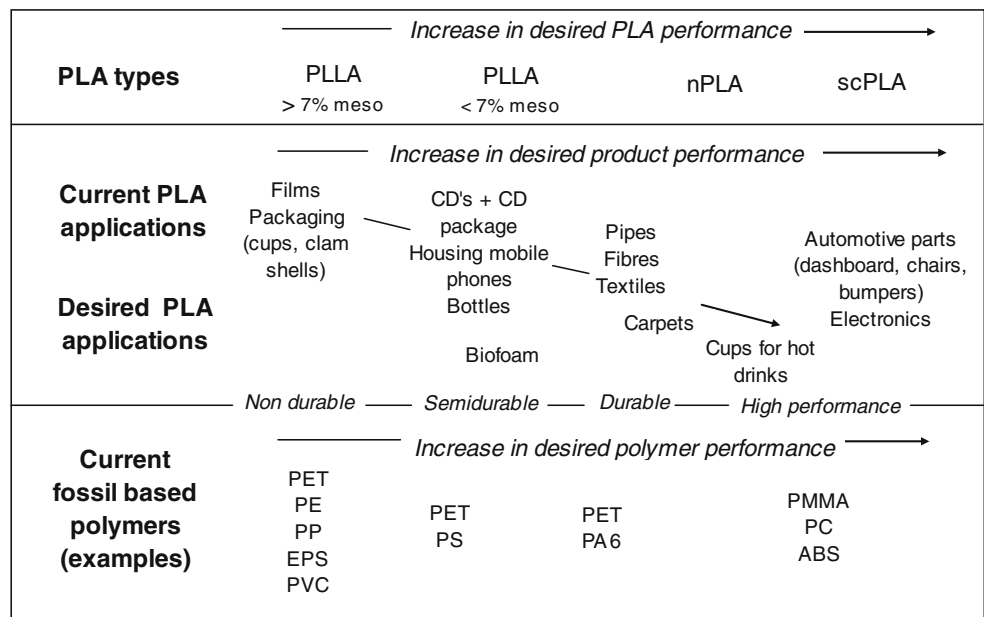


Fig. 1 Structures of lactic acid, lactide, and PLA

Fig. 2 Applications of PLAs. *PVC* polyvinylchloride, *PMMA* polymethylmetacrylate, *PET* polyethylenetereftalate, *PA6* polyamide 6, *PC* polycarbonate, *PP* polypropylene, *PE* polyethylene, *PS* polystyrene, *EPS* expanded polystyrene, *ABS* acrylonitrile butadiene styrene



of PLA biopolymers and fossil-based polymers will be presented. Figure 2 may suggest that polymers are used in a pure form; however, in plastics applications, the polymers are used normally as a mix with other polymers, plasticisers, fillers, etc. Consequently in PLA applications, the PLA content may be well over 90%, but in other applications, it may be below 50%, and the ecoprofile of the plastic obviously will be influenced by that.

At present, PLA is already used in a great number of consumer products (Shen et al. 2009). The applications are in the form of a biobased plastic alone, or in blends with other polymers, or reinforced with e.g., cellulose fibers. The largest application field of PLA is in packaging of a host of products (IFEU et al. 2006). Another emerging application for PLA is in fibers being used in textiles.

In the global trend towards an increased use of annually renewable feedstocks, sugarcane as a crop will become more important. Cane sugar, sucrose, is considered a versatile raw material for the fermentation industry to yield green chemicals. An important aspect of sugar production is that normally the bagasse, the cellulosic plant leftover from sugarcane extraction, is burnt to yield steam to run the sugar mill, while the surplus steam is converted to electricity supplied to the grid. In Thailand, there are rights and regulations for industry to buy renewable energy, comparable to the Renewable Energy Certificates system in the USA. Thus, the production of biobased polymers from sugarcane promotes the use of green energy.

Life cycle assessment (LCA) is a commonly used tool to assess the environmental performance of products and is currently recognized as best practice to holistically identify the ecological burden and impact of a production system and the ecological consequences of changes in the

economic system/exchange of products. Thus, LCA was chosen as the instrument for investigating the environmental profiles of Purac's products, and how these compare with the environmental profiles of traditional and fossil-based alternative polymers. The aims of the LCA are to:

- Quantify the potential environmental impacts associated with the forthcoming production of lactide from sugarcane in Thailand, and the production of PLLA, PDLA, nPLA, and scPLA.
- Compare the potential environmental impacts of Purac's biopolymers with that of fossil based polymers on a weight by weight basis
- Identify the critical environmental aspects in Purac's lactic acid, lactide and PLA production chain in order to facilitate systems optimization and development of more sustainable products.

Similar studies have been carried out by NatureWorks for PLLA derived from corn starch (Vink et al. 2003; Vink et al. 2007, press releases on Internet), and indicate the beneficial GWP profile for PLLA compared to fossil-based plastics. These studies also reflect the continuous process improvements in present-day industry to arrive at attractive bioplastics made from renewable resources, and the role of an LCA as a guideline.

2 Methodology, data, and system description

This LCA models the production systems associated with the manufacture of lactide and PLA biopolymers from cane sugar in Thailand and was carried out to comply with the International Standardization Organization's (ISO) ISO

14040 (ISO 2006a) and ISO 14044 (ISO 2006b) standards on LCA.

The LCA is a cradle-to-gate analysis, with the functional unit of 1 tonne of material at the factory gate in Thailand. The materials that are assessed are L-lactide, D-lactide, PLLA, nPLA (PLLA with low levels of PDLA), and scPLA (PLLA with increased levels of PDLA). The study includes the sugarcane agricultural system, industrial activities related to auxiliary chemicals, distribution of raw materials, processing of sugarcane into sugar and final production of lactic acid, lactides, and PLA biopolymers.

In Section 3, the biobased polymers are compared on an equal weight basis with fossil-based polymers, such as mentioned in the applications graph of Fig. 2. The environmental profiles of the fossil-based polymers were retrieved from the European Plastics Association's database and represent the average of several production sites in Europe (plasticseurope.org 2009). These fossil-based polymers have different technical and physical properties, and they are used, like PLAs, in different amounts in the final application. In case of polyethyleneterephthalate (PET), a polymer that may be replaced by PLA to a large extent, the substitutability of PET by PLA on a weight basis in practical applications is close to 1:1.

The inventory phase of this LCA study comprised of the following steps:

- Inventory analysis of sugarcane growing and sugar milling. Use of publicly available databases for agrochemicals, other chemicals, fuels, electricity, transportation and waste treatment, and adapted to conditions in

Thailand when deemed relevant. Building and demolition of industrial plants and machines have been included as well.

- Inventory analysis for the lactic acid, lactide, and PLA plant.
- The application of a cut off criteria for some material inputs constituting in total less than 1 wt.% of the total material input to the overall production system.
- Allocation: system expansion has been used to avoid allocation for the electricity co-product in the sugar mill process. For all other valuable by-products, economic allocation based on selling prices has been used.

Average data have been applied for all production activities. A schematic of the production chain from agriculture to lactide and PLA is given in Fig. 3. Relevant info on the different phases of the life cycle assessment will now be described in more detail.

2.1 Sugarcane agriculture

The agriculture of sugarcane growing is firmly established in countries such as Brazil, South Africa, Australia, Thailand, and India. Numerous textbooks exist with detailed knowledge on the growing of crops, and the milling of sugarcane to produce crystal sugar (Van der Poel et al. 1998; Chen and Chou 1993). Recently also, a number of LCA studies on sugar production from cane have appeared, notably the extensive PhD report of Nguyen on the LCA for the Thailand case of sugarcane farming and milling (Nguyen 2007). Some relevant data on the inventory

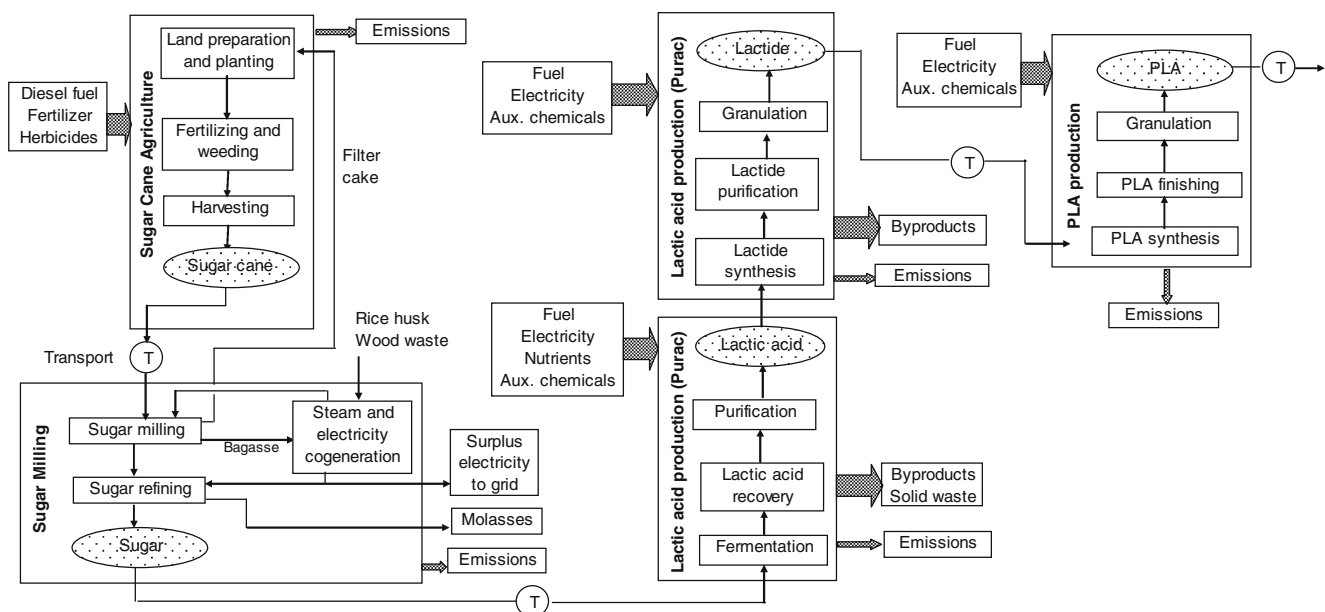


Fig. 3 Schematic of the production chain from agriculture to PLA

analysis of sugarcane agriculture from this PhD study, and references on inventories of products and activities used in this LCA, are:

- Sugarcane yield: 57 tonne/ha year (Nguyen 2007)
- Cane trash: 11 tonne/ha year (Nguyen 2007). This cane trash is burned on the field.
- Fertilizer (Davis and Haglund 1999; Nemecek and Kägi 2007): use of agrochemicals (code names) in kg/ha year: 15-15-15:140; 16-8-8:27; 46-0-0:99; 21-0-0:180; 16-2-0:28; 16-16-8:45; 16-20-0:7.7; 20-20-0:12; 25-7-7:11
- Pesticides and herbicides (Davis and Haglund 1999; Nemecek and Kägi 2007): use in kg/ha year: Paraquat: 1.1, Glyphosate: 0.16, Ametryn: 3, Atrazine: 3.9; 2,4D: 2.5
- Emissions during cane growing: for nitrogen it was assumed that of the total N applied 10% will be volatilized as NH₃ and 20% will be lost to water via surface runoff and percolation. 1% and 1.5% of the N that is not volatilized as NH₃ is assumed to be volatilized as NO_x and N₂O respectively (for NH₃ and NO_x emission, see also Wang et al. (1997); IPCC (2000); Hall et al. (1996)). For phosphorous, it was assumed that there is a surface runoff of 10% (see also Ometto et al. 2009).
- Use of diesel in harvesting, soil preparation, etc. (Börjesson and Berglund 2003): 63 l/ha year
- Use of diesel for transport of cane, agrochemicals, etc. (GaBi 2006): 110 l/ha year

The soil was considered to be part of the technosphere and only air and water emissions are accounted for. The soil is not considered to function as a carbon sequestration and storage.

2.2 Sugarcane milling

The case of a typical sugar mill in Thailand is taken into account with the intake of cane and the production of crystal sugar, molasses, and electricity. Relevant data were taken from the Nguyen study, and are summarized in Table 1 (this table gives total flows and does not address the water balance of the mill). Economic allocation for the environmental burden in sugarcane milling was based on 2006 prices of sugar and molasses. It is practice in Thailand to burn rice husk and wood waste along with bagasse to generate steam and electricity. The magnitude of the electricity credit will be discussed further in the Section 3.

2.3 Lactic acid, lactide, and PLA plant

In the inventory analysis, the mass and energy balances of Purac's existing 100 kt lactic acid in Thailand, and the forthcoming 75 kt lactide plant was used. For the PLA, plant data from the Sulzer Chemtech design for Synbra was used. In the overall mass balance, sugar, hydrated lime, and sulfuric acid constitute approximately 96 wt.% of the inputs of chemicals. The environmental profile for sugar has been treated above. For the environmental profile of all other chemicals, utilities, byproducts, and waste water treatment AkzoNobel's databanks and publicly available databases were used. In Section 3, the sensitivity of the LCA outcome to different numbers in databanks will briefly be addressed. In the present calculations, the following main assumptions were made:

- The steam is produced from natural gas (Dones et al. 2007). Data on green house gasses (GHG) emission from steam production from various energy sources

Table 1 Data on the sugar mill

Flow	Unit	Amount	Type	Related activity	Eco-profile for activity
Inputs					
Sugarcane	kg/ton sugar	9,653	Product input	Farming	Nguyen 2007
Bagasse	kg/ton sugar	2,722	Internal flow	Burning for steam and electricity	Dones et al. 2007
Rice husk	kg/ton sugar	68	Waste input—no env. load	Burning for steam and electricity	Dones et al. 2007
Wood waste	kg/ton sugar	42	Waste input—no env. load	Burning for steam and electricity	Dones et al. 2007
Diesel	L/ton sugar	1	Product input	Production and combustion of diesel for transport process fuels	GaBi 2006
Outputs					
Sugar	kg/ton sugar	1,000	Product output, ref flow		
Molasses	kg/ton sugar	436	By-product	Replacing soybeans as animal feed in Europe	
Bagasse	kg/ton sugar	2,722	Internal flow	Burning for steam and electricity	Dones et al. 2007
Electricity sold to the grid	kWh/ton sugar	164	By-product	Generation of average Thai electricity, including fuel production	Dones et al. 2007; IEA 2009; Vattenfall 2009; Brännström-Norberg et al. 1996

- vary; but for natural gas, the data are relatively consistent.
- The average Thai electricity mix is based on data presented for the year 2006 (IEA 2009). Inventories for the generation of electricity from different fuels were taken from public databases (Dones et al. 2007; Vattenfall 2009; Brännström et al. 2009).
 - Lime production in a modern kiln and with burning of heavy fuel oil and average Thai electricity as energy sources (Kellenberger et al. 2007)
 - The inventory for the production of sulfuric acid represents 50% elemental sulfur burning and 50% smelter gas burning (Althaus et al. 2007). The smelter gas is considered to be a waste product and hence no environmental load is assigned to this sulfuric acid. Electricity input is considered to be average Thai electricity. Normally, sulfur burning leads to the cogeneration of steam (average ~3.5 MJ/kg 100% H₂SO₄; Althaus et al. 2007); but in this study, no steam credit was taken into account.
 - In Purac's lactic acid business, food grade lactic acid and lactates, and lactide are the main products; but in the production processes, also byproducts are generated: gypsum, biomass, and feed grade and technical grade lactic acid. In Thailand, the gypsum is being used in a cement plant, thereby replacing the mining of gypsum and having no environmental burden. In other lactic acid plants, the gypsum may be used for other purposes, or is landfilled, and the LCA analysis will be more complex. The biomass is applied in agriculture, with a main application of alleviating problems with acidification of soil. From a practical point of view, both gypsum and biomass are cost neutral, and do not affect the GHG outcome through economic allocation. The feed grade lactic acid contains mainly the residual components from the fermentation, and can be used for animal feed. The technical grade lactic acid can be used in applications such as leather tanneries. Both feed grade and technical grade lactic acid have net positive selling prices and have an effect on the GHG outcome through economic allocation.
 - Design data on extruders were used to estimate the energy costs of compounding PLLA and PDLA resin to nPLA and scPLA resin.
 - Data on D(-)-lactic acid production were taken from campaigns in Purac Spain in 2008. The D(-)-mass balance was then combined with the large scale design of the Thai plant, and the environmental loads were calculated in the same way as for L(+) lactic acid.

The next phase in the LCA concerns the life cycle impact assessment (LCIA) which is the stepwise aggregation and

translation of inventory data into potential chemical and physical environmental impacts. The potential environmental impacts covered in this LCA are: primary renewable and non-renewable energy demand (PED-ren and PED-non ren, GWP = carbon footprint), acidification potential (AP), eutrophication potential (EP), photochemical ozone creation potential (POCP), non-renewable abiotic resource depletion potential (ADP), farm land use, and human toxicity potential (HTP). The characterization factors for each environmental impact category and intervention are presented in Table 2.

3 Results and discussion

3.1 Global warming potential of L-lactide and PLLA

In this section, first, the GWP profile of Purac's L-lactide, and PLLA made from this lactide will be addressed. Figure 4 shows the additive parts in GHG emissions in making PLLA. The starting point, by convention, is the amount of renewable CO₂ fixated in the PLLA itself, – 1833 kg CO₂/tonne PLLA. This starting point needs further clarification:

- In the sugarcane plant CO₂ is sequestered in the sugar and the plant itself. In the sugar mill, the sugar is recovered and the plant becomes available as bagasse. This bagasse is burnt to yield energy. In terms of CO₂ fixation, in this cradle-to-gate calculation, the CO₂ sequestered is found back only in the sugar.
- The sugar recovered is in the form of crystal sugar and molasses. The CO₂ uptake related to molasses is allocated to the molasses, and the CO₂ balance is zero for the sugar.
- In a cradle-to-grave analysis, the end-of-life option of incineration of the polymer would release again 1,833 kg CO₂/tonne polymer again, so that the CO₂ balance is zero for the carbon feedstock (see Section 3.5).
- The methodologies to quantify CO₂ sequestration for carbon footprinting receive considerable attention in the LCA community, and at this point also reference is made to the PAS 2050 standard (PAS 2050).

With the starting point of –1,833 kg CO₂/tonne PLLA, the CO₂ emissions in all steps to manufacture PLLA from sugar will now start adding up. In these sequential additions, the yield of these process steps are taken into account, the higher yield of PLLA on sugar giving rise to a low addition. In Fig. 4, the additive parts in the build of the GHG emission represent the following distinctive groups of processing activities:

- Sugar production: cultivation of sugarcane and the processing of sugarcane into sugar at the sugar mill, including operation of machines and production and

Table 2 The environmental impact categories and characterization factors applied in the LCIA

Category Flow	GWP100 CO2 eq	AP SO2 eq.	EP generic air/water/soil PO4-3 eq.	POCP C2H4 eq.	ADP Crude oil eq./kg	HTP kg DCB eq.
Emissions to air						
CO2	1					
SOx		1		0.048		0.096
NOx		0.7	0.13	0.028		1.2
CH4	25			0.006		
NM-VOC				0.416		0.058
CFC's						
NH3		1.88	0.35			0.1
N2O	298					
HCl		0.88				0.5
CO						
Particles				0.027		0.246
H2S		1.88				0.22
Emissions to water						
COD			0.022			
BOD						
N-tot			0.42			
NH4-N			0.424			
P-tot			3.06			
AOX						
HC						
SO4-2						
Cl-						
Abiotic depletion data						
Natural gas					1.153	
Crude oil					1	
Hard coal					0.6667	
Brown coal					0.2393	
Biomass					0	
Uranium in ore					0.1428	
Iron in ore					4.194E-06	
Copper in ore					0.09652	
Bauxite					1.045E-07	
Sulfur in ore					0.01781	
Limestone					2.090E-07	

GWP values: IPCC 2007. Other values: Guinée et al. 2002

AP acidification potential, EP eutrophication potential, POCP photochemical ozone creation potential, ADP abiotic resource depletion potential, HTP human toxicity potential

- distribution of agrochemicals. Figure 4 includes a zoom-in on the electricity credit generated in the sugar mill that has been taken into account (see later in this section).
- Production of other chemicals: auxiliary chemicals needed in the lactic acid production: lime, sulfuric acid, fermentation nutrients, etc.
- Purac inbound transportation: transportation of sugar and auxiliary chemicals to Purac's production site in Thailand
- Electricity needed in the lactic acid, lactide, and PLA process.
- Steam needed in the lactic acid, lactide, and PLA process

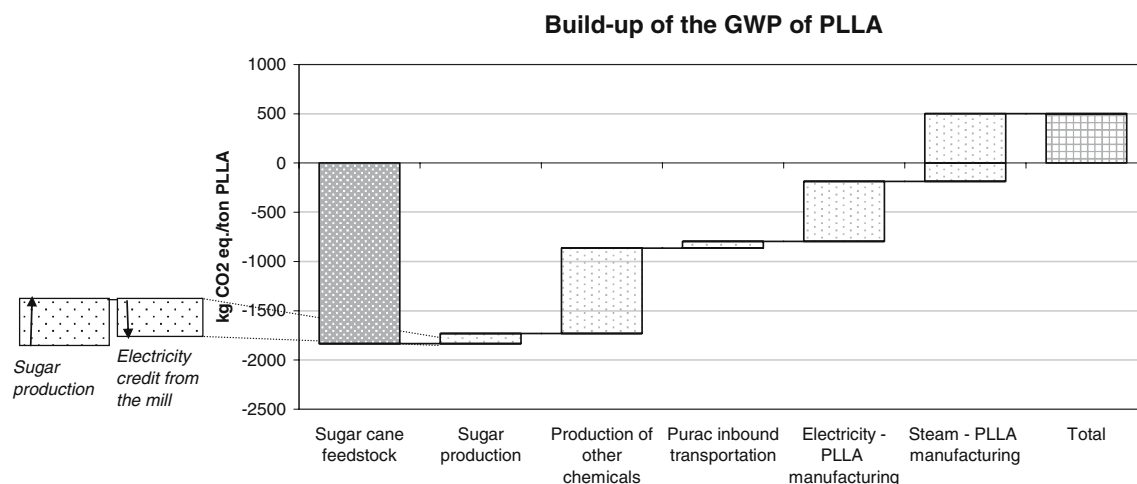


Fig. 4 GWP build-up in the PLLA production chain

For the correct view on Fig. 4, a number of important assumptions will be repeated:

- The data are based on the designs of the plants to produce lactic acid, lactide, and PLLA.
- System expansion was used to account for the electricity credit from the sugar mill. Economic allocation was used to account for the valuable byproducts, so that the total GWP of the plant is actually higher, but a small part of that is attributed to byproducts
- It is assumed that PLLA is made from L-lactide on the same site.

Figure 4 then shows that the GHG emission of PLLA production is a net positive number. Purac strives to lower this number through process improvements in the lactic acid and lactide plant and through fine-tuning with the sugarcane industry (Section 3.6).

The waterfall plot in Fig. 4 is for PLLA, but the build-up of this plot is almost identical for L-lactide because the production of PLLA from L-lactide involves a small addition of emissions through steam and electricity use, and a yield close to 100%. Hence, Purac uses the following ranges of GHG emission of L-lactide and PLLA.

GHG emission of PLLA: 500–800 kg CO₂ eq./tonne PLLA

GHG emission of L-lactide: 300–600 kg CO₂ eq./tonne L-lactide

It is chosen at this point to present a range because of the variability of the electricity credit from a sugar mill and the effect of that number on the LCA. The high GHG emission numbers are derived with an electricity credit from the mill of 17 kWh/tonne cane according to the Nguyen study. From an LCA perspective, this number is very well documented as it also addresses the practice of burning rice husk and

wood waste in the furnace of the mill. Public reports on cogeneration of electricity from bagasse in all sugar mills in Thailand are also available (EPPO 2009). Numbers on the electricity credit as high as 95 kWh/tonne cane are cited; however, since documentation on the cofiring of the furnace with rice husk and wood waste is missing, caution must be taken with the interpretation. In this study, calculations were also done with 55 kWh/tonne cane, the weighted average of the public numbers: this leads to the lower GHG emissions given above. In practice, Purac considers the GHG emission of L-lactide to be 500 kg CO₂ eq./tonne PLLA and 300 kg CO₂ eq./tonne L-lactide as it is assumed that the weighted average electricity credit of 55 kWh/tonne cane resembles the current reality.

Figure 5 further shows the dependence of the GHG emission on the electricity production at the mill. It is clear then that there is great potential through using optimal technology in the sugar mill to decrease the GHG emission of biopolymer production and increase sustainability (see also Section 3.6).

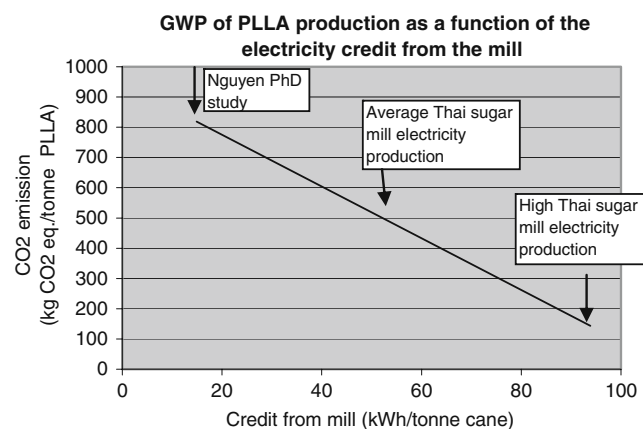


Fig. 5 GHG emission of PLLA as a function of the electricity production from the mill

It is acknowledged that in the calculation of the GHG emission of PLLA, many parameters have an influence on the outcome. It is beyond the scope of this study to do a full sensitivity analysis, but for the electricity credit from the mill this sensitivity is shown as is intricately linked to the issue of energy from renewable resources. Other parameters that will be relevant to a sensitivity analysis are: facts and data on sulfuric acid production, pricing of molasses and sugar in the allocation of molasses, pricing of byproducts in the allocation of CO₂ to PLLA and byproducts, and data in databanks on the electricity mix. From a development point of view, these sensitivities are less important than process parameters. The main determining factors in the CO₂ emission are: the steam and electricity use in the production process and the yield of PLLA on sugar.

3.2 Comparison of the global warming potential and energy demand of biobased PLLA and fossil-based polymers

In this section, the incentive to shift in society from fossil-based polymers to biobased polymers will be quantified. Numbers on the GWP of several common fossil based polymers are well documented and can be found on the Internet site of the European Plastics Association (EPA 2009). For example, for polyethylene, polypropylene, and other polymers, a vast list of emissions is given, including emissions of GHG. In Fig. 6, the GWP for PLLA and these polymers is shown.

Figure 6 shows that the global warming potential of PLLA is much lower than for fossil based polymers, and this is one of the main drivers today for producing biopolymers. Though this comparison is clear, a number of remarks are relevant as background information. The GWP of PLLA is lower because CO₂ is sequestered from

the atmosphere and fixated in the polymer (see Fig. 4) and this is accounted for in this cradle-to-gate study. The GWPs of the fossil polymers refer only to the energy related and process-related emissions of GHG which have not recently been sequestered from the atmosphere, e.g., emissions related to recovering crude oil, transportation, refining, and production of the polymer resin. Considerations on the origin of carbon content of these polymers only become visible in a cradle-to-grave analysis for incineration as the end-of-life option of the polymer (see Section 3.5).

A second way of comparing the ecoprofile of biopolymers and fossil-based polymers is to address the gross energy demands. This energy demand is the combination of the energy used in the process and the feedstock related energy; for PLA the feedstock is the sugar plant, and for fossil-based polymers it is oil. The feedstock-related energy represents the energy of fuel-type materials that are fed in the system, but used as carbon based building blocks rather than fuels (see also EPA internet site). Figure 6 shows the comparison on the gross energy demand for PLLA and fossil-based polymers. A further division into renewable and non-renewable energy now splits the total into four parts.

- The feedstock related renewable energy. This number reflects the average energy content of the sugar substrate.
- The process-related renewable energy. This number is high for PLLA as it represents the energy in the bagasse (excludes energy equivalents for coproduced power fed to the grid). For fossil-based polymers, this number is very small and represents, e.g., the use of wood in addition to natural gas or oil in national energy based economy

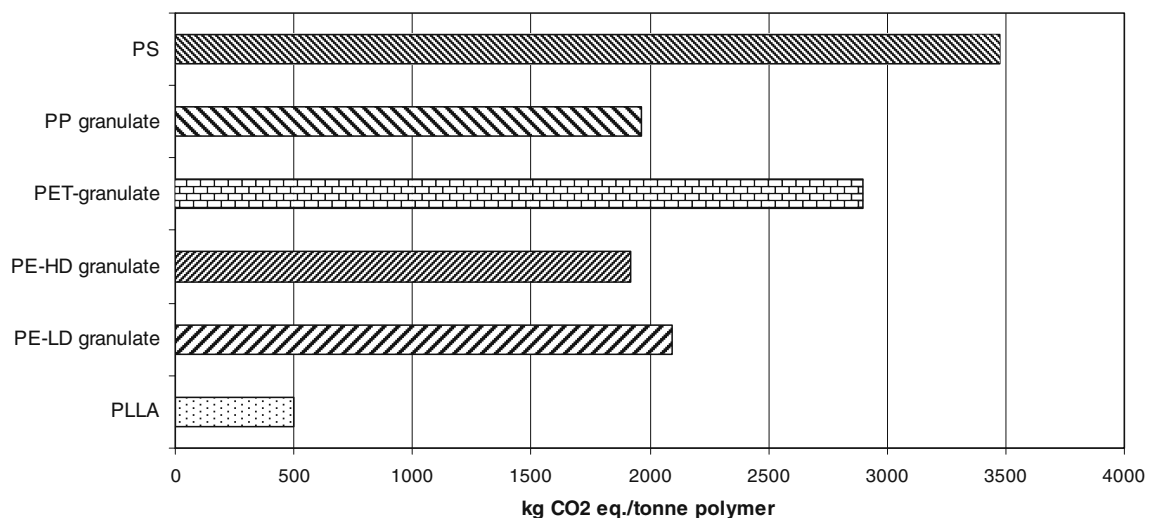


Fig. 6 GWP involved with the production of PLLA and other polymers

- The process related non-renewable energy used to make the polymer (recovery of crude oil, transportation, refining for steam, and electricity production to make the polymer)
- The feedstock related non-renewable energy. This number is zero for biopolymers. In case of fossil-based polymers, this number reflects the average energy content of the feedstock.
- NO_x , SO_x and CO from cane trash burning in the field
- Uncontrolled NO_x and SO_x emissions in cane cultivation

Thus, Fig. 7 show that the sum of renewable and non-renewable energy may be in the same order of magnitude for biobased and fossil-based polymers. This, however, does not suggest that, energy-wise, making a biopolymer does not present an advantage compared to fossil-based polymers. With biopolymers, a large part of the total energy was supplied for free by the sun, and was used to fixate CO_2 in the sugarcane plant.

3.3 Other ecological factors

In this LCA study, data also were generated on the abiotic depletion potential, acidification potential, eutrophication potential, photochemical ozone depletion potential, human toxicity potential, and farm land use. Table 3 gives the results for these impact categories for the production of PLLA in absolute numbers, and Fig. 8 gives all environmental impact data for PLLA and a number of fossil-based polymers, normalized for the highest data points. SO_x emissions are partly related to sulfuric acid production. Furthermore, it is found then that PLLA has a disadvantageous score in the impact categories that are related to sugarcane cultivation and processing. The most important impacts that contribute to eutrophication, acidification, and photochemical ozone creation are:

- N-leakage and NH_3 volatilization from an ammonia-based fertilizer in the soil

Agriculture is also starting now to categorize and quantify these factors and relating them to detailed know-how on agricultural practices. It is evident that in emerging green economies, agricultural technology will form an integral part in the strive for sustainability.

3.4 Ecoprofile of PLLA and PLLA/PDLA blends

Polymers are characterized by a variety of properties and the heat of distortion temperature (HDT) is an important factor in the use of the polymer in applications at different temperatures. Therefore, the ecoprofiles of both PLLA and PLLA/PDLA blends are presented in relation to the HDT. PLLA has a rather low HDT (45°C), and can be regarded to belong to a class which also encompass polyethylenes and polypropylenes, versatile but less durable polymers used in various low temperature applications such as packaging material (see Fig. 2). In so called nPLA, a blend containing 95% PLLA and 5% crystalline PDLA the HDT increases to $90\text{--}100^\circ\text{C}$, a range also encompassing polystyrene, polyethylene terephthalate and the nylon PA6. With scPLA, stereocomplex PLA at a ratio 40/60 PLLA/PDLA, the heat of distortion temperature will further increase to $150\text{--}170^\circ\text{C}$, e.g., for high-performance applications in cars or electronics. In this range, the counterpart fossil-based polymers are often compounded plastics, rather than neat polymers. The compounding materials can be various, and, e.g., glass filled nylons can be considered, and the determination of the ecoprofile will be more complicated.

The GWP of nPLA and scPLA were based on the GHG emissions of PLLA and PDLA production, and assumptions on the energy use for compounding.

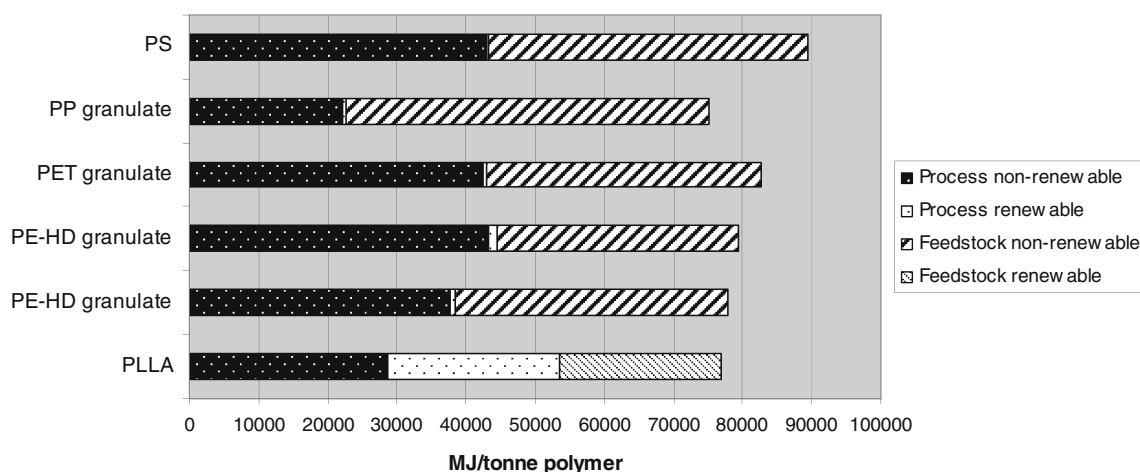


Fig. 7 Primary energy demand involved with the production of PLLA and other polymers

Table 3 The environmental impact potentials for the production of PLLA divided on different stages of the production system

	PED non-ren MJ	PED ren. MJ	ADP kg oil eq.	GWP 100 kg CO2 eq.	AP kg SO2 eq.	EP kg PO43-eq.	POCP kg C2H4 eq.	HTP kg DCB eq.	Farm land m2. year
Sugarcane feedstock	N.A.	23,233	N.A.	-1,833	N.A.	N.A.	N.A.	N.A.	N.A.
Sugar production	-3,392	31,699	-79	103	8.8	4.3	2.6	4.1	2,081
Lime production	3,594	42	75	553	0.7	0.1	0.1	0.5	0
Sulfuric acid production	1,575	34	31	89	8.6	0.1	0.4	1.4	0
Production other auxiliary chemicals— PLLA manufacturing	4,167	95	74	222	1.0	0.1	0.1	0.6	0
Purac inbound transportation	1,014	1	22	67	0.4	0.1	0.0	0.6	0
Electricity—PLLA manufacturing	10,814	403	243	610	0.7	0.1	0.1	0.8	0
Steam—PLLA manufacturing	12,737	25	299	689	0.5	0.0	0.1	0.4	0
WWT—PLLA manufacturing	35	4	0	2	0.0	0.2	0.0	0.0	0
Total	30,545	55,536	665	502	21	5.0	3.4	8.5	20

Industrial processes to make D(-) lactic acid, the ingredient for PDLA, can be considered to be less mature than that for L(+) lactic acid, and consequently the GWP will be higher.

Figure 9 shows the GWP of various polymers and is now plotted versus the heat of distortion temperature for the sake of visualization. The data for non-PLA polymers are all from the EPA, and refer to neat resins, i.e., virgin noncompounded materials. The data for PLA is for virgin resin, and for nPLA and scPLA for a resin blend.

It is thus shown that the GWPs of nPLA and scPLA are somewhat higher than for PLLA, but still much more favorable than for fossil based polymers on a weight by weight basis.

3.5 End-of-life options of PLA

In this study, the cradle-to-gate approach for PLA was used, but after the application of a bioplastic in society, it will, e.g., degrade and will release CO₂ again. Thus, the end-of-life options of the polymer and cradle-to-grave thinking should form an integral part of an LCA study.

The end-of-life options of PLAs are summarized in Table 4. This table lists the options as well as the implications of these options in terms of ecological impact. In this study, only the impacts with respect to GWP are considered; but in practice, also other impacts must be considered, e.g., when the polymer in the form of the actual plastic in the end-of-life option also leads to the emissions of other compounds, such as fillers, plasticizer, etc. The

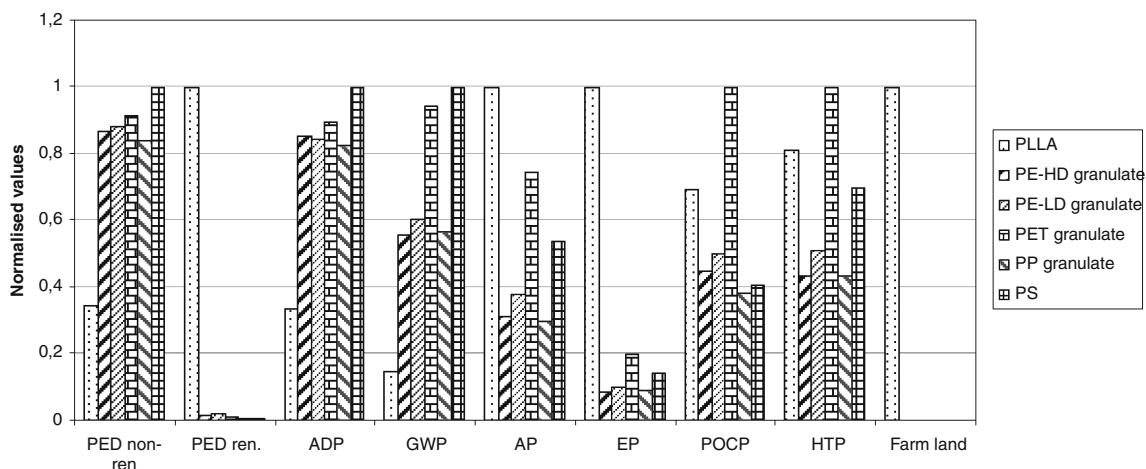
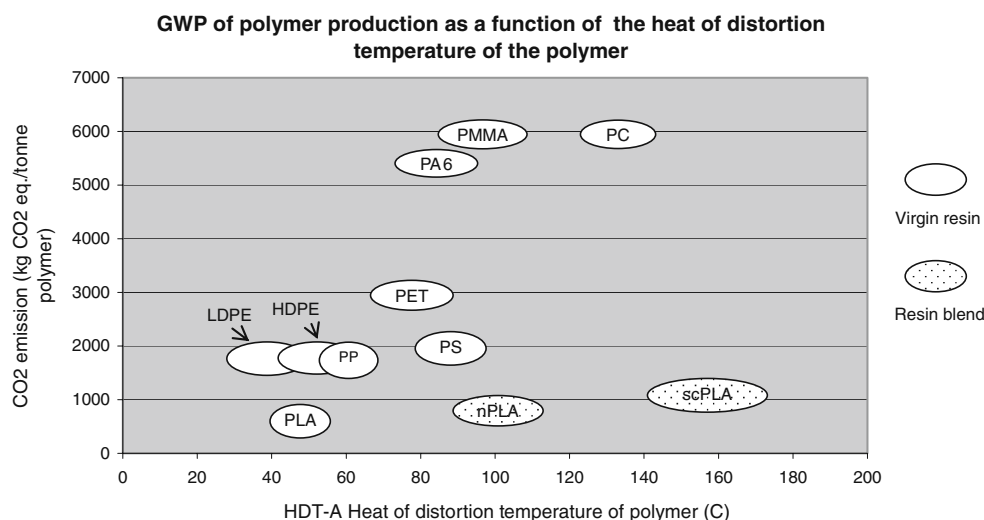


Fig. 8 Comparison of the most relevant ecological factors involved in the production of PLLA and fossil-based derived polymers

Fig. 9 GWP of various PLLA, nPLA and scPLA and fossil-based polymers. Abbreviations see Fig. 3; HDT-A heat distortion temperature at 0.45 MPa



GWP now also depends on whether the polymer is actually recycled and processed further to again polymer or another chemical, and the end-of-life of this new compound. In all cases, assuming that there will be shift to a low carbon society over the next decades, the time frame in which a compound is ultimately converted to CO₂ in the atmosphere is important.

It can be seen from Table 4 that the analysis of the end-of-life options of PLA is a multifaceted task and that satisfactory solutions will evolve in time through technological and organizational developments.

Some remarks to Table 4 are:

– Recycle of PLA

Recycle of PLA via lactic acid will lead to the advantage of a prolonged life-time before final breakdown to CO₂. For a detailed study on the recycling of PLA packaging material, see the IFEU study (IFEU et al. 2006). Methods have been described to convert PLA to lactic acid, but it must be mentioned that continued processing will lead to

further racemization, and thereby will effect yields, or lead to PLA with higher meso content and applications limited to, e.g., packaging material. New recycle methods go hand-in-hand with innovative technologies to sort plastics based on chemical composition.

– PLA recycling to lactic acid derivatives

Useful compounds that can be made out of PLA are, e.g., the lactate esters, e.g., ethyllactate through esterification with (bio)ethanol. Any effect of racemization in PLA recycling does not play a role, since the presence of L- or D-lactic acid in the ester is not relevant for the majority of ester uses. Ethyllactate or other esters can have a prolonged lifetime e.g., as degreasing agent in the electronics industry with recovery through distillation. Ethyllactate can also be used as biodiesel.

– Composting

In composting, part of the compound will be released as CO₂ relatively quick, and part is fixated in compost and

Table 4 End of life options of PLAs

PLA destination	CO ₂ emission based on sorting, cleaning, collection, transport	Process related CO ₂ emission	Carbon retention	Timeframe of CO ₂ emission to atmosphere
PLA recycling to PLA via lactic acid	High	High	High	10 years
PLA recycling to lactic acid derivatives	High	Moderate	High	2 years
Mechanical recycling	Moderate	Low	High	5 years
Composting	Low	Low	Moderate	>6 months up to years
Anaerobic digestion	Low	Low	Low (energy value)	<1 month
Incineration	Low	Low	Low (energy value)	<1 month
Landfill	Low	High, in case of CH ₄ emission	Low	>10 years

liberated later. While in central composting, conditions can be controlled well, improvements are needed in home composting of PLAs to avoid uncontrollable unwanted emissions.

– Landfill

In the US and Europe, there is legislation that waste must be pretreated and diverted from landfill. Landfill of biopolymers is not considered sustainable, as well as that littering of biopolymers is considered non-sustainable, even though they may be biodegradable. In landfill also, anaerobic processes can give rise to production of methane, a pronounced greenhouse gas.

– Incineration

This section is ended with Fig. 10 on the total GWP related to the production and incineration as the end-of-life option of PLLA and fossil-based polymers (no credit for possible heat recovery has yet been considered).

It is again evident that the GWP involved with polymer production clearly favors the low number for PLLA compared to other polymers. Note that the GWP of PLA in Fig. 10 now has been built up from the 1,833+500 kg/tonne from Fig. 4. At this point also, the CO₂ fixated in the polymer has been liberated again, and the feedstock-related CO₂ emission at the end-of-life from fossil carbon with PLLA is zero. The feedstock related CO₂ emission at the end-of-life however is substantial of course for the fossil based polymers. Only polyvinylchloride (PVC) appears similar, however, it has been recognized that due to the presence of chlor atoms in the PVC, the PVC may create ecological issues of its own in the end-of-life. The feedstock-related CO₂ emission of other fossil-based polymers containing more oxygen such as PMMA may be relatively low, but the GWP related to the production of these polymers offsets the benefits of this.

Fig. 10 CO₂ emission of polymers in a cradle-to-gate + incineration analysis. Abbreviations, see Fig. 2

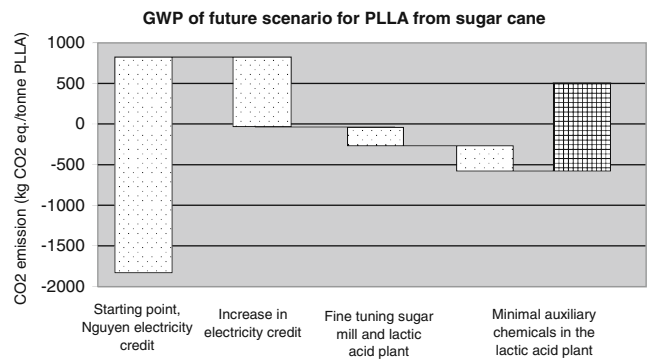
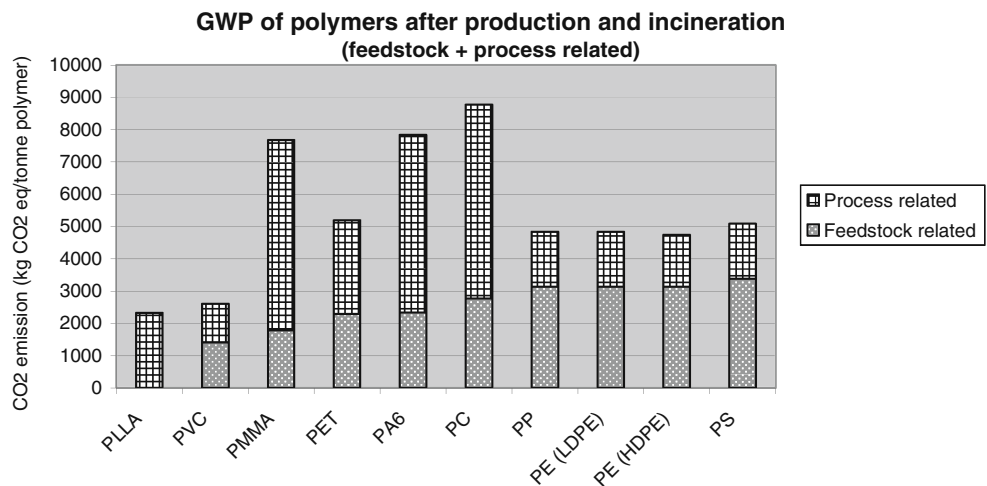


Fig. 11 CO₂ emission profile of PLLA in future process scenario

The approach reflected in Fig. 10 is also advocated by Narayan (2009) for business-to-business communication of the carbon footprint of polymers. The approach in general has its advantages when blends of biobased and fossil-based compounds are considered, e.g., blends of PLA and other polyesters. In that case, the origin of feedstock-related carbon content in the incineration scenario is distinctly visible. Also, while the emission profile of a recycled fossil-based polymer-like PET might significantly be improved, graphs like in Fig. 10 will indicate that a significant amount of the final CO₂ emitted is originally fossil based.

As a final remark, it is evident that in the direction towards more green economies, the options on the end-of-life of a polymer need considerable attention. Improvements should include technological maturation of biopolymers, recycling of polymers, plastic take back schemes, biodegradability, etc.

3.6 Future developments

Developments in the emerging world of biopolymers will continue to be evaluated against the trend of sustainable

technology for chemical production, energy production, and emission control. In this multidisciplinary field, various technologies alone or in combination will improve the LCA of PLA further. Figure 11 shows a future scenario of PLLA made from sugarcane, and indicates that it is economically viable to produce PLA with a net negative GWP at the factory gate.

A further explanation to this graph is:

- Step 1 Starting point with a well documented electricity of 17 kWh produced electricity/tonne sugarcane as presented in this article.
- Step 2 Improvements in sugarcane agriculture and sugar milling.

In sugarcane agriculture, various developments take place, such as the use of crops with high sugar yield, decreased fertilizer use, and emission control. In the sugar milling process, evaporation and crystallization steps may be optimized in energy use to yield grades of sugar sources that can be fine tuned with the fermentation and downstream processing in a lactic acid plant. The production of energy from bagasse, at least in Thailand, is considered integral part of the energy requirements of the society. Thailand aims at having electricity from renewable resources to be 20% of the national total by the year 2022, and energy from bagasse forms an important share of this renewable energy.

- Step 3 Improvements in the lactic acid, lactide and PLA industry.

Detailed know-how on fermentation, chemical, and separation technology will allow industry to optimize and integrate processes further and improve the ecoprofile. Gypsum-free processes will be developed that will substantially lower the GWP involved with auxiliary chemicals.

Finally, the farm land use aspect will be addressed. In a future green economy, next generation processes will be developed to produce fuels and products from cellulose containing wastes, like bagasse in sugarcane production. PLLA from bagasse as the feedstock will avoid competition for land for growing of crops for food applications in regions where farm land is scarce. This is best illustrated with a change-oriented LCA also considering that bagasse has an environmental value as a fuel for electricity generation.

4 Conclusions

The production technology of L-lactide and PLLA at Purac and partners has a GHG emission level and use of non-renewable energy and material resources lower than that of fossil-based polymers. This finding confirms the increasing relevance of bioplastics to offset environmental issues

strongly related to the use of fossil resources. The opportunities for PLLA/PDLA blends in bioplastic applications with improved durability are also confirmed by a GHG emission level more favorable compared to that of fossil-based polymers with similar durability.

The emission profile for PLA production is less favorable for environmental impacts linked to agriculture, e.g., emissions of nutrients to water. In the future, the production of biobased polymers will become intricately linked to producing renewable resources with agriculture, and the cogeneration of bioenergy, such as steam and electricity production from bagasse will continue to have an important role. Also, emissions in agriculture itself will need to be reduced.

The end-of-life options for PLA need to be developed further, but the ecoprofiles are generally positive. The options include mechanical or chemical reuse, energy production through incineration or biogas production, composting, etc.

The current calculations in the LCA are based on plant designs, and for the future, certification of Purac's plants is foreseen. For technology development, the LCA has indicated opportunities in lactic acid production and sugarcane milling to further minimize environmental impacts.

For LCA methodology development, more attention is needed for the sensitivity to data from databanks and to manufacturing technologies such as for sulfuric acid. In the expected competition of agricultural feed stocks for food, chemical products, and energy, more sophisticated allocation and system expansion methods are needed to identify the structure of the emission profiles.

LCA is an indispensable tool to quantify the impacts of industrial production on the environment, and guide industry towards the development of green chemicals.

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