Electronic Supplementary Material (ESI) for Green Chemistry.

Hybridised sustainability metrics for use in Life Cycle Assessment of bio-based products: Resource efficiency and circularity

Supplementary Annex

1. Description of case studies: Details of the production processes, assumptions, allocations and cut-off criteria

1.1. Comparison of bio-based versus fossil-derived packaging films

BoPLA packaging films: The BoPLA-based packaging film is sourced from 100% bio-based PLA resin. The lactic acid used for the sybthesis of this resin has been produced via bacterial fermentation using glucose as the carbon source. The glucose was derived from three different renewable feedstocks (i.e. corn, lignocellulosic corn-stover and sugar-beet pulp). Corn is converted to the fermentable carbon source, via wet milling process, while cornstover and sugar-beet pulp required pre-treatment and chemical hydrolysis to improve the treatment's access to the biomass's cellulosic content. The environmental burden of these processes has been taken into consideration to quantify the impacts of sourcing glucose from the different feedstocks. However, their cultivation processes and subsequent pre-treatment and pre-processing approaches have not been reported in this study.

The PLA production process can be divided into three stages:

- Pre-treatment of lignocellulosic and starch-rich feedstock for the production of fermentable sugars (for the *cornstover-to-glucose* and *corn-to-glucose* routes respectively),
- Lactic acid production via fermentation including downstream separation and purification, and
- Polymerization stage for the production of PLA.

The production process for the PLA packaging film and its baseline candidate (BoPP packaging films production) has been graphically presented in Figure A. 1, with the processes captured within this study highlighted with a red dashed border. Detailed quantifications have already been reported in the paper. The energy/ mass balances and the sequence of unit operations (i.e. chemical pre-treatment and enzymatic hydrolysis) used for corn stover hydrolysate production was based on the report published by the National Renewable Energy Laboratory (Humbird et al. 2011)[1]. The fermentation medium is prepared by mixing the carbon source with nutrients and water in a mixing tank. The fermentation

medium is subsequently sterilized and then added into the bioreactor. The material and energy balances for fermentation media, continuous sterilisation, bioreactor operation and inoculum preparation were based on the work undertaken by Dheskali et al (2017)[2]. Fermentation efficiency data for lactic acid production (i.e. productivity, final lactic acid concentration and yield) using the bacterial strain *Bacillus* sp. 2-6 was based on the work by Qin et al. (2009)[3]. The pH is controlled during fermentation using calcium carbonate ($CaCO_3$) as neutralizing agent resulting in the formation of calcium lactate. At the end of fermentation, the broth is fractionated and purified for the production of polymer-grade lactic acid for which the process reported by Bapat et al. (2014) [4] was adopted. This process can be divided into three stages:

- The first stage begins after the separation of spent cells from the fermentation broth via centrifugation, followed by the treatment of calcium lactate with sulfuric acid. This reaction yields water soluble lactic acid and solid calcium sulfate, which is separated via centrifugation. The lactic acid concentration in the effluent from centrifugation is increased via water evaporation to about 50 % (w/w).
- In the second stage, the lactic acid-rich stream from the evaporator is sent to a bioreactor, where it is esterified with methanol to produce methyl lactate and water. The reactor outlet stream is heated and sent to a reactive distillation column.
- The third stage involves the hydrolysis of methyl lactate to polymer grade L-lactic acid in a reactive distillation column. Lactic acid stream flows at the bottom of the column, while the produced methanol and excess water outflows as a distillate. Most of the initial amount of methanol is recovered and recycled back to the second step via distillation.

The material and energy data and the sequence of unit operations for the polymerization stage were calculated based on the process reported by Gruber et al, 1992 [5]. The purified polymer grade L-lactic acid is then condensed leading to the formation of pre-polymers (low-molecular weight polylactic acid) which are further separated from water using appropriate columns. The pre-polymer is then mixed with the catalyst in the lactide reactor where the oligomers depolymerize and form lactide rings. The liquid outflow of the lactide reactor contains unreacted oligomers, which are recycled back into the reactor. Besides lactide, the vapour stream contains unreacted lactic acid, lactic acid oligomers and water, which are also recirculated. The purification of lactide takes place in a series of two distillation columns operated under vacuum, where water and the residual lactic acid is separated. The overhead product of all three distillation columns contains a significant amount of lactic acid, which is collected and recycled back to the lactic acid recovery stage. The purified lactide stream is mixed with catalyst (stannous octoate) and fed into the polymerization reactor,

where high molecular weight PLA is produced via ring-opening polymerization of lactide. The resulting product stream contains a substantial amount of unreacted lactide. The residual lactide is removed under vacuum in a devolitilizer and recycled back into the polymerization reactor. The refined PLA stream undergoes pelletization.

The pelletized PLA resin is melted with co-polymers and polymer additives and finally subjected to oriented-film extrusion to produce biaxially-oriented packaging films. Oriented extrusion is an essential step which renders moisture resistance, optical clarity and high tensile strength to the packaging films, ideal for their application to packaging fresh produce and food. These wastes have been assumed to be disposed onto landfill. The lactic acid monomers resulting from the “polymerisation” step are assumed to be recovered and recirculated back into the process to achieve optimal conversion yield. The cooling water used throughout this process has been recovered and reused. Based on the industrial data provided on the chemical composition of the resin used to prepare packaging films of the proposed specifications, the biogenic carbon content per functional unit of analysis was determined to be 5.58 g[6].

BoPP packaging films: Biaxially oriented polypropylene (BoPP) has been chosen as the baseline candidate against whom the environmental performance of BoPLA will be compared. The inventory associated with polypropylene, which is available in the Ecoinvent 3.5 database, was adopted and modified to suit the assumptions, processes and sub-processes for BoPP film production that was adopted for the comparative study. For disaggregated information required for the quantification of the hybridised indicators, published literature by Plastics Europe was consulted[7]. The processes and sub-processes that were captured within the scope of this report are as follows. BoPP, sourced from petroleum derived Naphtha, is subjected to cracking resulting in the formation of polypropylene monomers. These monomers are then polymerised to produce polypropylene resin which is then oriented- film extruded into BoPP. For finer details associated to the production of polypropylene, please refer to the suggested reference. Assumptions related to transportation, distribution of intermediates and finished products and formulation (extrusion), BoPLA-based assumptions were employed. Please refer to Figure A.1 for a visualisation of the various life cycle processes involved in the production of bio-based and fossil-derived packaging films. However, A red demarcation identifies those specific processes that have been subjected to the environmental impact assessment (system boundary for this study). The sources of data for the inventory prepared for each of the case studies are provided in Table A. 1.

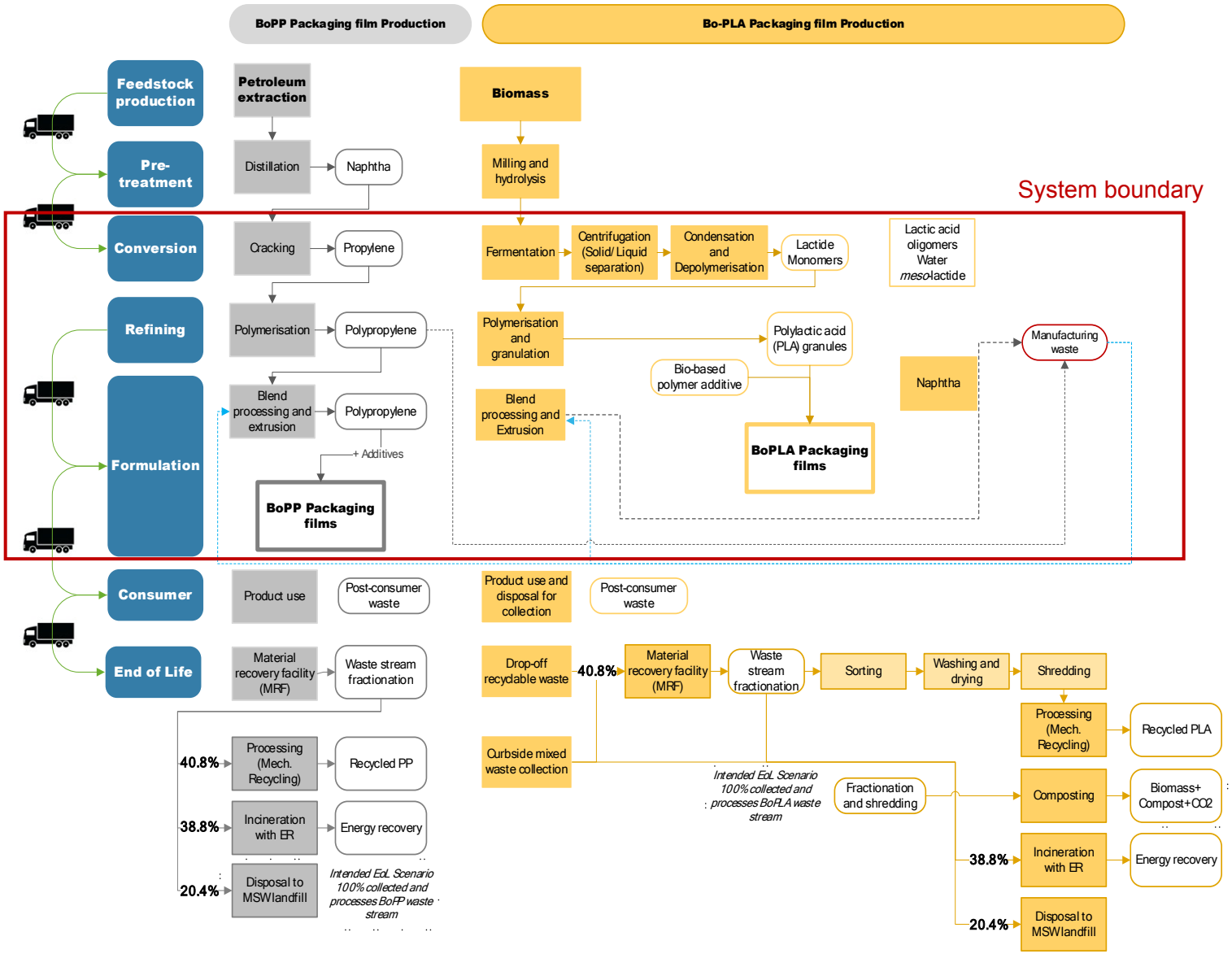

Figure A. 1: Assumed life cycle processes and the system boundary for the exemplary environmental evaluation of the 100% bio-derived BoPLA and fossil-derived BoPP based packaging films *(Note: end-of-life scenario for the bio-based case study- hypothetical and out of the scope of this paper)*

1.2 Comparison of bio-based Vs fossil-derived mulch films

PLA-based Mulch films: The soil-biodegradable mulch film, adopted for this study, has a more complex composition than the packaging films and is only partially bio-based. The mulch film is a bio-based co-polyester synthesised from PLA and a semi-crystalline, translucent co-polymer, containing additives that provide thermal stability, and puncture resistance. The co-polymer is synthesised from bio-derived 1,4-butanediol and petro-derived adipic acid and terephthalic acid. The finer details of composition of the bio-based mulch film have not been provided to their confidential nature. A inventory and the production method, similar to the one described in section 1.1, has been adopted for PLA that is incorporated into the PLA based mulch films.

The inventory for the co-polymer blend was adopted from the published industrial reports and patents [8–10] where further details of their composition may be found. This section, will however, give an account of the synthesis of the 100% bio-based 1,4-Butanediol (bio 1,4-BDO) that forms a part of the co-polymer blend. The bio 1,4-BDO was produced from an industrial side stream, sugar beet pulp. This pectin-rich feedstock has been converted into fermentable sugars that are required to produce bio 1,4-BDO via chemical pre-treatment and enzymatic hydrolysis. The fermentable sugars which are mixed with other nutrients and subsequently sterilized in a continuous sterilisation system. The material and energy balances in the fermentation stage were estimated using the data published by Burgard et al [11] using a genetically engineered *Escherichia coli* strain. Fermentation is carried out at pH 7 under microaerobic conditions (0.02 vvm) for 36 h. The final 1,4 -BDO concentration is 125 $g \cdot L^{-1}$ with a yield of 0.4 g of $BDO \cdot g^{-1}_{sugars}$. After fermentation, the broth is centrifuged to remove bacterial cells and then processed with a series of cationic and anionic resin columns to remove the organic acids. The resins are regenerated with HCl and NaOH, while the outlet stream is treated via reverse osmosis. The resin-treated stream is concentrated using a mechanical vapour recompression forced circulation evaporation system. 1,4-BDO is finally purified via distillation where the remaining by-products are separated. The fermentation and organic waste streams were assumed to be disposed onto a landfill.

During the formulation phase of the agricultural mulch, a mixture of PLA and the co-polymer blend is melted and co-blended with REACH-permissible polymer additives (UV stabilisers and carbon black). The mixture is then assumed to be blow-film extruded to the desired thickness, aired and packaged for distribution to retailers, and ultimately, to the consumers. Please note that the exact composition of the mulch film has not been disclosed, in the interest of the industrial partners and data confidentiality. Based on information from a previous study, the biogenic carbon content of the product of analysis was determined to be 59.8 kg per functional unit of analysis (152 kg of mulch film needed to cover a hectare of

agricultural land) [12]. This may be confirmed by a ^{14}C experimental analysis, as suggested within the CEN/TC/411 standard for bio-based carbon content estimation (EN 16785-2015).

LLDPE mulch films: In the case of the baseline candidate, LLDPE mulch films are assumed to be synthesised from 100% virgin petro-derived polymers. The data inventory for the production of LLDPE resin was adopted from that available in the Ecoinvent 3.5 database. The material and energy input for the production of mulch films were adopted from published literature [13] and modified to the technical specifications of our chosen functional unit. In this study, the starting material was ethylene, derived from cracking Naphtha, which is then polymerised to produce LLDPE resin. Similar to the bio-based case study, the LLDPE granulates were assumed to be melted and co-blended with appropriate additives (UV stabilisers and carbon black), then blow-film extruded to produce mulch films of the desired thickness. The blown films are then aired and packaged for distribution to retailers and ultimately, consumers. For further details on the production of LLDPE, please refer to the literature suggested above [13].

The process involved in the production of PLA based mulch film and its conventional baseline candidate LLDPE mulch films has been graphically presented in Figure A. 2.

Inventory	Source	Packaging films	Mulch films
Polylactic acid	6,14,15	x	x
1,4- Butanediol	11,16,17		x
Adipic acid	Ecoinvent 3.5 database		x
Terephthalic acid	Ecoinvent 3.5 database		x
Extrusion	6,18–20	x	x
Linear Low-density Polyethylene	13,18		x
Polypropylene	6,7,21,22	x	

Table A. 1: Sources of data for process inventory development and environmental impact assessment

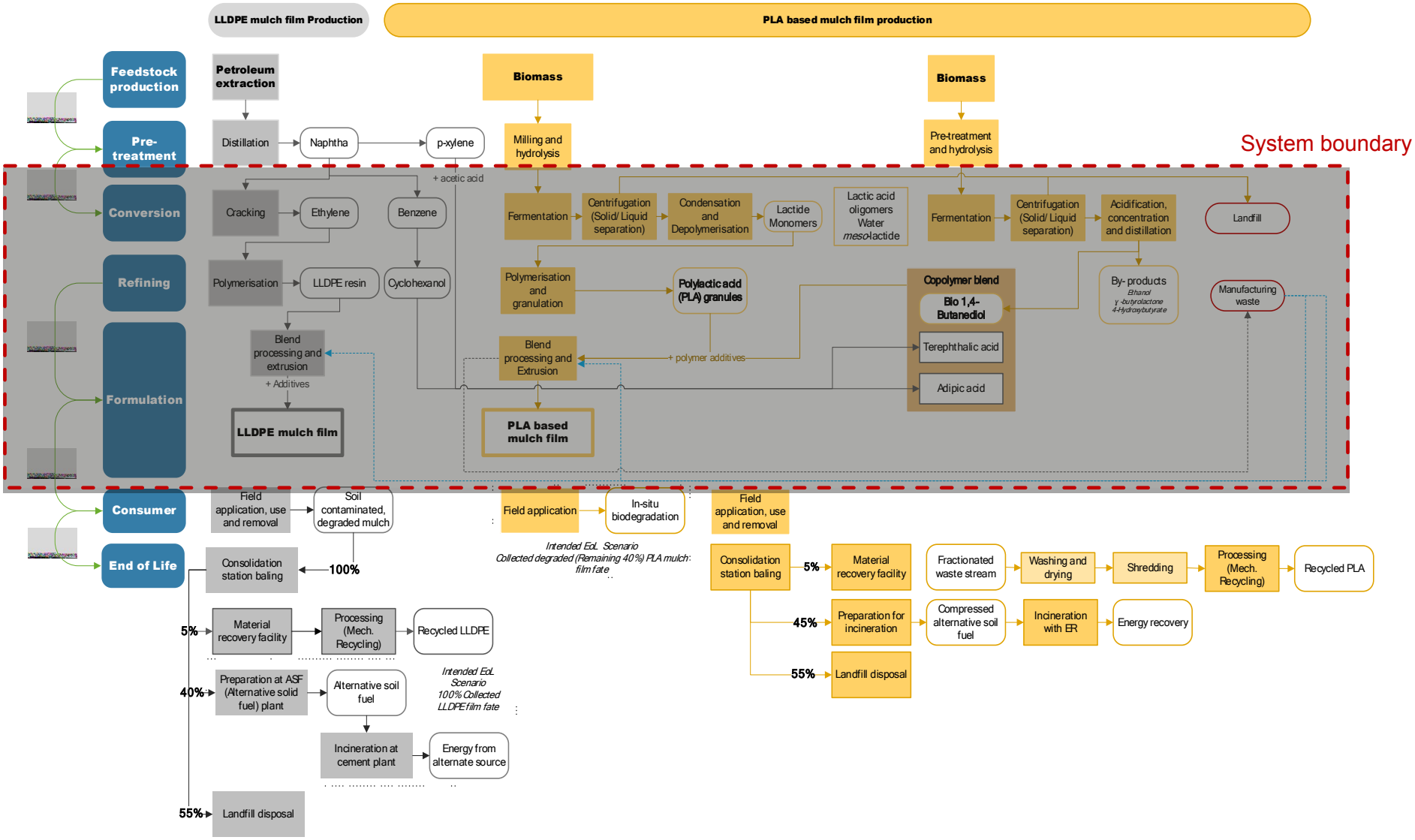

Figure A. 2: Life Cycle processes and the system boundary for the exemplary environmental evaluation of the partially bio-derived PLA and fossil-derived LLDPE based mulch films *(Note: end-of-life scenario for the bio-based case study- hypothetical and out of the scope of this paper)*

1.4 Assumptions and other considerations

- **Allocation methods**: This study does not adopt any form of impact allocation methods between the different feedstocks since the starting materials considered, within the scope of this assessment, is glucose (sourced from different biomass). Avoidance of any form of allocation was undertaken to ensure that the impacts associated to the choice of biomass is not double-counted between the upstream (cradle-factory gate) and downstream (manufacturing to distribution to consumer) stages.
- **Transportation:** In terms of the transportation processes, the pelletized intermediates from the refinery were assumed to be freighted to the end-producer located at a distance of 250 km using 7.5 tonne low-sulphur diesel truck. From the end-product producers, the packaging films (unit of 500,000 pieces were assumed to be distributed to the regional warehouse located at a distance of 150 km, before finally the product reaches the retailer located at a distance of 10 km. A single item of film-wrapped fresh produce is assumed to be bought and transported by a consumer in a small petrol vehicle over a distance of 5 km.
- **Fate of waste from processes**: The waste from the fermentation stage comprising the spent cells and fermentation broth is assumed to be disposed of to a landfill.
- **Recovered and reused material within the process:** Process water and some inorganic acids that are employed in the downstream processes (isolation, purification, evaporation and reactivation of acid columns) of bio-based L-lactic acid and are assumed to be recovered and reused at an efficiency of 98%. Unreacted components, including the lactic acid monomers in the polymerization step to PLA are assumed to be recovered and recycled. For further details on which specific process auxiliaries are recovered and reused, please refer to the suggested literature[23].
- **Transformation efficiencies**: The efficiency of extracting L-lactic acid from the fermentation broth was assumed to be at an industrial average of 95%. The polymerisation and transformation of L-lactic acid to PLA resin is assumed to occur at an efficiency of 80%. Unreacted monomers are extracted and subjected to another round of polymerisation. Undesirable meso-lactide formed in the process is assumed to be removed and disposed onto a landfill. Wastage of PLA resin from loss on the factory floor was assumed to be 0.5%. The reprocessable nature of the PLA resin allows any waste resulting from the refining and formulation phase to be recirculated into the process at an assumed efficiency of 90%. Similar assumptions have been

adopted for the synthesis of PLA and co-polyester blend involved in the mulch film production.

- **Process Uniformity**: For the non-LCA indicators, the processes, sub-processes, materials and energy inputs associated to the production of BoPLA and PLA based mulch film sourced from the different feedstock (corn-derived glucose, corn stover and sugar beet pulp) have been assumed to be the same. The rationale for this assumption is that in the manufacturing phase (starting point within the scope of this assessment), the primary feedstock is assumed to be sugars (glucose or dextrose).
- **Out of scope:** Temperatures, pressures, pH and other technical details have not been captured within this study as they fall outside the scope. Water scarcity has been reported only for freshwater that was directly integrated into the process. Product use and disposal have been excluded from this study.

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