# Bio-based polyester fibers – From GWP to a More Comprehensive Environmental Analysis

Tijana Ivanović, Roland Hischier, Claudia Som*

Empa, Swiss Federal Laboratories for Materials Science and Technology,
Lerchenfeldstrasse 5, 9014 St. Gallen, Switzerland
*Address correspondence to claudia.som@empa.ch

## Supporting Information

# Contents

# Production pathways and scenarios

## Fossil-based MEG

Production of fossil-based MEG is a well-established process, which happens worldwide in the existing capacities. It consists of 3 consecutive steps, normally at the same site:

- Ethylene extraction from natural gas
- Conversion of ethylene into ethylene oxide (EO) Conversion of EO into MEG

The underlying chemical reactions that govern the conversion processes are:

$$2\,C_2H_4\,(ethylene)\;+\;O_2\;\rightarrow\;2C_2H_4O\,(ethylene\;oxide)$$ Reaction 1

$$C_2H_4O\;(ethylene\;oxide)\;+\;2H_2O\;\rightarrow\;2C_2H_6O_2\,(MEG)$$ Reaction 2

All three steps combined with global transport of MEG are modeled by applying "*Ethylene glycol {GLO}| market for | Cut-off, U*" dataset.

## Corn-based MEG

MEG is produced from corn grain in USA. The production steps include:

- Cultivation and transport of corn to the ethanol factory
- Consecutive ethanol, bio-ethylene production and bio-ethylene oxide production and bio-MEG at one production site in the US (all intermediary products are considered to be used on site)

The entirety of the cultivation phase which includes planting, growing and harvesting the crop and its transport is captured in the "*Maize grain {RoW}| market for | Cut-off, U*" dataset and is used as a direct input to the next step - ethanol production. Dry milling corn-to-ethanol technology was used as a representative ethanol production process. "*Ethanol, without water, in 95% solution state, from fermentation {US}| ethanol production from maize | Cut-off, U*" was applied which uses 3.2258 kg corn grain/kg ethanol. It includes glucose extraction from corn (via starch hydrolysis), fermentation (with a yeast) and distillation to 95% (solution state) bio-ethanol.

Bio-ethylene is obtained by dewatering ethanol (at 95%) at 481ºC, 11.3bar and in presence of aluminum catalyst. The said industrial process had been modeled based on [1,2]. The simplified chemical transformation in this phase reads:

$$C_2H_5OH\,(bio-ethanol)\;\rightarrow\;C_2H_4(bio-ethylene)\;+\;H_20$$ Reaction 3

An efficiency of 96.6% is assumed as per [2] and the corresponding dataset is available in Table S1. For comparison, US Patent on production of ethylene from ethanol [3] accomplishes a 100% reaction efficiency. The emissions related with from heat production from the original set [2] have not been accounted for here. Water emissions stemming from the reaction 3, have been added to the set, by assuming a 96.6% efficiency.

*Table S1. Inventory data per 1kg of bio-ethylene produced from corn-derived ethanol*

| **Reference product** | **Amount** | **Unit** |
|---|---|---|
| Bio-ethylene | 1 | kg |
| **Input** | | |
| Bio-ethanol from maize production, US | 1.7 | kg |
| Electricity, medium voltage, US | 1.8 | MJ |
| Heat, district or industrial, natural gas at industrial furnace >100kW, RoW | 5.6 | MJ |
| **Output** | | |
| Water, to air | 0.665 | kg |

Thirdly, ethylene oxide is obtained by oxidation of ethylene gas, in the same manner as in the petrochemical chain. This step is modeled using "*Ethylene oxide {RoW}| production | Cut-off, U*". Following changes were introduced:

- All ethylene inputs were modified to bio-ethylene from previous step
- All electricity mix, medium voltage, listings were modified into "Electricity, medium voltage {US}| market group for | Cut-off, U"
- Fossil emissions of carbon dioxide (0.21kg), carbon monoxide (0.00011kg) and methane (7.5e-05 kg) into the air from the set are changed into biogenic carbon dioxide, carbon monoxide and methane respectively.

MEG production was modeled using "*Ethylene glycol {RoW}| production | Cut-off, U*" with following modifications:

- All input ethylene oxide was modified to the previous step
- All electricity mix, medium voltage listings were modified into "Electricity, medium voltage {US}| market group for | Cut-off, U"
- Dataset does not list any fossil inputs, nor emissions of fossil carbon dioxide, carbon monoxide nor methane, thus no emission adaptation are needed.

In the end, transport of MEG was accounted with default scenarios available within "*Ethylene glycol {GLO}| market for | Cut-off*" dataset, where all inputs of ethylene glycol were adapted to the previous step.

## Sugar-MEG, ethanol from direct fermentation

Sugar-based MEG production using a direct fermentation process of sugarcane is similar to that of corn-based MEG. It starts with ethanol production from sugarcane in a direct fermentation process with biomass cogeneration; it follows with ethylene, ethylene oxide and finally MEG. The entire production chain is located at the same site in Brazil, thus no transport is added between steps. Resulting MEG is then transported for polymerization with PTA.

Sugarcane cultivation and ethanol production are addressed jointly. "*Ethanol, without water, in 95% solution state, from fermentation {BR}| sugarcane processing, modern autonomous plant | Cut-off, U*" dataset is applied to this measure and incorporates the direct fermentation of sugarcane and distillation of ethanol to 95%, solution state. The sugarcane, grown in Brazil, represented by "*Sugarcane {BR}| market for | Cut-off,* U" dataset is the principal material input for the fermentation process. The leftover biomass is incinerated for energy needs of the plant.

Ethanol-to-ethylene conversion happens on the same site, immediately after ethanol is produced, thus no transport is included between these two steps. This steps is modeled in the same manner as for the corn-based MEG with an electricity input adapted to Brazil. Ethylene oxide and MEG production as well as MEG transport are produced in the same manner as for corn, except all electricity inputs are changed to Brazil (market group).

## Sugar-MEG, ethanol as by-product

Second version of MEG product from sugarcane involves fermentation of sugar molasses, rather than direct the fermentation of sugarcane. Molasses is obtained as a by-product in the extraction and production of crystal sugar for human consumption in a sugar mill in Brazil. The remained of the setup is the same as for direct fermentation case. After ethanol is obtained, ethylene, ethylene oxide and finally MEG are produced on the same site, hence no transport is accounted for in between these steps. Resulting MEG is again transported for polymerization with PTA. " *Ethanol, without water, in 95% solution state, from fermentation {BR}| sugarcane processing, modern annexed plant | Cut-off, U*" is used to account for ethanol production in this case. The process uses Brazilian sugarcane whose inventory is accounted with "*Sugarcane {BR}| market for | Cut-off,* U". Ethanol-to-ethylene, MEG production and MEG transport are modeled in the same manner as for other sugarcane-based MEG production chain by adapting the corresponding inputs.

## Fossil-PTA

Production of PTA is a well-established process around the globe that has two main phases, happening consecutively at the same production site:

- extraction of para-xylene (PX)
- Amoco process – oxidation of PX and purification to PTA

Para-xylene is produced by catalytic reforming of petroleum. The inventory is modeled with "*Xylene {RER/RoW}| market for xylene | Cut-off, U*" which then acts as the primary input for the PTA production. Crude terephthalic acid is produced by oxidation of para-xylene (reaction 4), which is the purified to obtain purified terephthalic acid (PTA).

$$C_8H_{10}\,(paraxylene) + 3\ O_2 \ \rightarrow\ C_8H_6O_4(\,terephthalic\ acid) \ +\ 2H_2O \qquad \text{Reaction 4}$$

The sum of oxidation and purification process of PTA are modeled with "*Purified terephthalic acid {RER/RoW}| production | Cut-off, U*". All the processes combined with the default scenario for the transportation of PTA are modeled with "*Purified terephthalic acid {GLO}| market for | Cut-off, U*".

## Bio-based PTA

Bio-based PTA production is divided into several major phases, according to which the inventory is assembled as follows:

- Corn cultivation and transport to the entrance of the iso-butanol factory
- Iso-butanol production and Gevo process are performed to obtain paxa-xylene
- PTA is produced from para-xylene using Amocco process

All the production steps after corn cultivation take place on the same production site. The entirety of the cultivation phase which includes planting, growing and harvesting the crop and its transport is captured in the "*Maize grain {RoW}| market for | Cut-off, U*" dataset and is used as a direct input to the next step – iso-butanol production. Fermentation of corn-derived sugar into iso-butanol is approximated with corn sugar-to-ethanol as with [2]. Production of iso-butanol in the natural fermentation can be written as:

$$C_6H_{12}O_6\ \ (sugar\ from\ corn) \ \rightarrow\ \ C_4H_{10}O\ (isobutanol) \ +\ 2CO_2 \ +\ H_2O \qquad \text{Reaction 5}$$

While comparable ethanol production reads:

$$C_6H_{12}O_6\ (sugar\ from\ corn) \ \rightarrow\ 2C_2H_5OH\ (ethanol) \ +\ \ 2CO_2 \qquad \text{Reaction 6}$$

From reaction 5, following stoichiometric relations 1.956kg sugar/1kg ethanol are necessary. The data available from EcoInvent is "*Ethanol, without water, in 95% solution state, from fermentation {US}| ethanol production from maize | Cut-off, U*" state that for corn-based ethanol, 3.2258 kg corn/kg ethanol is needed. Conversion rate of corn to sugar is therefore 1.65. Biogenic (non-fossil) $CO_2$ emitted in the process amounts to 957g $CO_2$/1000g ethanol as per stoichiometric relations. The dataset for ethanol shows an emission of 2.496kg biogenic $CO_2$/kg ethanol, meaning that the difference of 1.539 kg CO2/kg ethanol comes from process itself. From reaction 6, following stoichiometric relations 2432g sugar/1000g iso-butanol is needed. When using the conversion correction factor of 1.65, we conclude that 4.013kg corn/1 kg of iso-butanol is needed. The conversion emits 1.189 kg biogenic CO2/1000 g iso-butanol and adding the process contribution, we obtain a total of 2.758 kg biogenic $CO_2$/kg iso-butanol. We assume the same process between ethanol and iso-butanol production, thus modify no other input/output except corn, biogenic CO2 and water emissions in the dataset "*Ethanol, without water, in 95% solution state, from fermentation {US}| ethanol production from maize | Cut-off*". All the water stemming from the reaction (0.243kg/kg ethanol) is added to the existing water emissions to air and water in the same ratio as for ethanol (51% to air and 49% to water).

Gevo process for the production of para-xylene out of iso-butanol consists of several consecutive steps – i.e. the conversion of iso-butanol into isobutylene, followed by the synthesis of isooctane and its oxidation into para-xylene. Chemical conversion of iso-butanol to iso-butylene is approximated with ethanol-to-ethylene conversion based on [2]. Recalling the reaction 3 for ethanol conversion, the iso-butanol approximation is performed as follows:

$$C_4H_{10}O\ (bio-isobutanol) \ \rightarrow\ C_4H_8(bio-isobutylene) \ +\ H_2O \qquad \text{Reaction 7}$$

From reaction 7, 1 kg of isobutylene needs 1.32 kg of iso-butanol. Additionally, we assume the same process efficiency of 96.6% and same performance for ethylene and iso-butanol as seen in Table S2. Water emissions have been calculated based on reaction 7 with 96.6% efficiency.

*Table S2. Bio-isobutylene production from bio-based iso-butanol*

| **Reference product** | **Amount** | **Unit** |
|---|---|---|
| Bio-isobutylene, US | 1 | kg |
| **Input** | | |
| Bio-based iso-butanol from maize production, US | 1.366 | kg |
| Electricity, medium voltage, US | 1.8 | MJ |
| Heat, district or industrial, natural gas at industrial furnace >100kW, RoW | 5.6 | MJ |
| **Output** | | |
| Water | 0.333 | kg |

Secondly, synthesis of isooctane is done in three sub-steps. The inventory data is obtained and adapted from [2] who had performed an inventory analysis by benchmarking the production sub-steps to the existing data:

- Production of isooctene via dimerization and hydrogenation of C4 components (Table S3)
- Conversion of isooctane into isooctane via hydrogenation of 1-heptene to n-heptane, 100% efficiency (Table S4)
- Oxidation of isooctane into PTA via dehydrocyclization of n-heptane to toluene, 100% efficiency. Note that since products for this reaction include 7.02% hydrogen and 92.98% para-xylene per mass, we chose to assign all the environmental burdens to para-xylene only. (Table S5)

*Table S3. Production of isooctene*[1]

| **Reference product** | **Amount** | **Unit** |
|---|---|---|
| Isooctene | 1 | kg |
| **Input** | | |
| Steam, in chemical industry, market for, GLO | 2 | kg |
| Oxygen, liquid, market for, RoW | 1.32E-03 | kg |
| Bio-isobutylene, US | 1 | kg |
| Water for cooling, unspecified origin, US | 2.40E-03 | kg |
| **Output** | | |
| Water, as average wastewater, RoW | 2.40E-03 | kg |

*Table S4. Production of isooctane from isooctene*

| **Reference product** | **Amount** | **Unit** |
|---|---|---|
| Isooctane | 1 | kg |
| **Input** | | |
| Electricity, medium voltage, US | 0.0483 | kWh |
| Heat, district or industrial, natural gas, at industrial furnace >100kW, RoW | 0.283 | MJ |
| Isooctene, US | 0.982 | kg |
| Hydrogen, liquid, RoW | 0.018 | kg |

*Table S5. Production of para-xylene from isooctane* [2]

[1] Emissions of carbon dioxide, which are part of the original set, are not taken into account to prevent double countring, since stoichiometric relations in Reaction 8 don't have any carbon dioxide emissions.

| **Reference product** | Amount | Unit |
|---|---|---|
| Para-xylene | 1 | kg |
| **Input** | | |
| Electricity, medium voltage, US | 0.0293 | kWh |
| Heat, district or industrial, natural gas at industrial furnace >100kW, RoW | 2.516 | MJ |
| Isooctane, US | 1.0755 | kg |
| **Output** | | |
| Hydrogen, liquid, RoW | 0.0755 | kg |

In the same manner as for the petrochemical, the bio-based crude terephthalic acid is produced using Amocco process by oxidation of para-xylene and the purification step follows to obtain the PTA from its crude form. Hence, "*Purified terephthalic acid {RoW}| production | Cut-off, U*" is adapted to obtain a US-based production of bio-PTA, as follows:

- All electricity, medium voltage inputs have been changes into US inputs
- All natural gas, high pressure inputs were changed to US inputs

Finally, a default scenario for the transportation of PTA was assumed using the existing dataset "*Purified terephthalic acid {GLO}| market for | Cut-off, U*" where input PTA has been changed to the bio-based PTA.

## Polymerization of PET

The last step in polymer production is esterification (polymerization) of the two monomers - PTA and MEG into an amorphous grade PET. To obtain different versions of PET - petrol-based, partially bio-based and fully bio-based different MEG and PTA were combined together as inputs into polymerization process. To model the polymerization process two existing dataset were used:

- "*Polyethylene terephthalate, granulate, amorphous {RER}| production | Cut-off, U*"
- "*Polyethylene terephthalate, granulate, amorphous {RoW}| production | Cut-off, U*"

Because the existing global fossil-based PET production capacities are equally suitable for the production of bio-based PET, the distribution of global production is assumed to remain the same, thus no changes were made to these datasets, except for input MEG and input PTA, according to the matrix in Table S6 below. As $C0_2$, CO and $CH_4$ are not emitted in this unit process, no modification from fossil to bio-based emissions are needed. For all seven scenarios, both datasets (RoW and RER) are produced.

*Table S6. Combination matrix for PET.*

| Combination matrix for PET (Scenarios) | | MEG | | | |
|---|---|---|---|---|---|
| | | Fossil-based | Corn-based | Sugarcane-based (direct fermentation of ethanol) | Sugarcane-based (ethanol as by-product) |
| PTA | Fossil-based | **Scenario 0** Fossil – PET 0% bio-based C | **Scenario 1** Bio (corn/fossil) – PET 20% bio-based C | **Scenario 2A** Bio (sugar/fossil) – PET 20% bio-based C | **Scenario 2B** Bio (sugar/fossil) – PET 20% bio-based C |
| | Corn-based | / | **Scenario 3** Bio (corn/corn) – PET 100% bio-based C | **Scenario 4A** Bio (sugar/corn) – PET 100% bio-based C | **Scenario 4B** Bio (sugar/corn) – PET 100% bio-based C |

Finally, to account for the global transport of PET polymer, defaults market dataset "*Polyethylene terephthalate, granulate, amorphous {GLO}| market for | Cut-off, U*" was applied for all scenarios from Table S6. The following modification were completed beforehand:

- "Polyethylene terephthalate, granulate, amorphous {CA-QC}| production | Cut-off, U" and "Polyethylene terephthalate, granulate, amorphous {US}| polyethylene terephthalate, granulate, amorphous, recycled to generic market for amorphous PET granulate | Cut-off, U", "Polyethylene terephthalate, granulate, amorphous {RoW}| polyethylene terephthalate, granulate, amorphous, recycled to generic market for amorphous PET granulate | Cut-off, U", were approximated with a corresponding RoW dataset
- "Polyethylene terephthalate, granulate, amorphous {Europe without Switzerland}| polyethylene terephthalate, granulate, amorphous, recycled to generic market for amorphous PET granulate | Cut-off, U" and " Polyethylene terephthalate, granulate, amorphous {CH}| polyethylene terephthalate, granulate, amorphous, recycled to generic market for amorphous PET granulate | Cut-off, U", were approximated with corresponding RER dataset

Only then were "*Polyethylene terephthalate, granulate, amorphous {RoW}| production | Cut-off,* U" and "*Polyethylene terephthalate, granulate, amorphous {RER}| production | Cut-off, U*" changed according to the matrix to produce the polymer scenarios from Table S6.

## Bio-based PDO: Production from corn in the USA

Bio-based PDO is using modified bacteria which ferment the corn-derived glucose directly into the bio-PDO after which purification is performed to obtain a higher grade of this monomer [4–6]. The fermentation is preceded by derivation of glucose from corn, meaning that following steps are part of bio-PDO production:

- corn production and transport to the production facility
- corn starch production and its hydrolysis into glucose on one site
- bio-PDO production and purification on the same site

Unlike for ethanol production where integrated datasets are available, e.g. from the crop-to-ethanol, such a set for crop-to-PDO doesn't exist, thus we modeled firstly the steps from corn to glucose, then glucose-to-PDO. The entire chain is presumed to happen on one industrial site in USA, thus transport in between these sub-steps is not accounted for. Transport is included only at the last step, when PDO is shipped to a PTT polymerization facility.

Firstly, just as for MEG, corn cultivation phase includes planting, growing and harvesting of corn which is brought to the PDO factory. For consistency, the inventories for corn cultivation are captured with "*Maize grain {RoW}| market for | Cut-off, U*". Corn grains are subjected to wet milling, that is, soaked with water and acid, the swelled corn is milled and desiccated to extract the starch with is then dried (Urban & Bakshi, 2009). "*Maize starch {DE}| production | Cut-off, U*" was used for this step, where 1.261kg corn grain are used per kg of starch producer. Following modifications are applied to the dataset:

- Electricity, medium voltage into "Electricity, medium voltage {US}| market group, for | Cut-off, U"
- Heat from {Europe without Switzerland} to "Heat, district or industrial, natural gas {RoW}| market for heat, district or industrial, natural gas | Cut-off, U"
- Tap water is adapted to "Tap water {RoW}| market for | Cut-off, U"
- Water emissions from Water, DE to Water, US

Then starch is subjected to an enzymatic process to extract the glucose [5]. The enzymatic reaction takes up to 72h in a heated reactor, for which "*Glucose {RoW}| glucose production | Cut-off, U*" was used. Process uses 0.9 kg starch per 1kg of glucose. Following modification were applied:

- "Electricity, medium voltage {US}| market for | Cut-off, U" was used for all electricity inputs
- Tap water is adapted to "Tap water {RoW}| market for | Cut-off, U"
- "Maize starch {GLO}| market for | Cut-off, U" is changed into the starch from previous step

Bio-based PDO is obtained in the proprietary fermentation process of DuPont Tate & Lyle Bio Products using the genetically modified E.Coli bacteria from the corn-derived glucose [4–6]. Assuming a biomass E.Coli unit of $CH_{1.78}O_{0.6}N_{0.19}$, the underlying chemical reaction can be written as [6]:

$$37C_6H_{12}O_6 + 3NH_3 + 10O_2 \rightarrow 60CO_2 + 16\,H_2O + 50C_3H_8O_2 + 3\,biomass \qquad \text{Reaction 13}$$

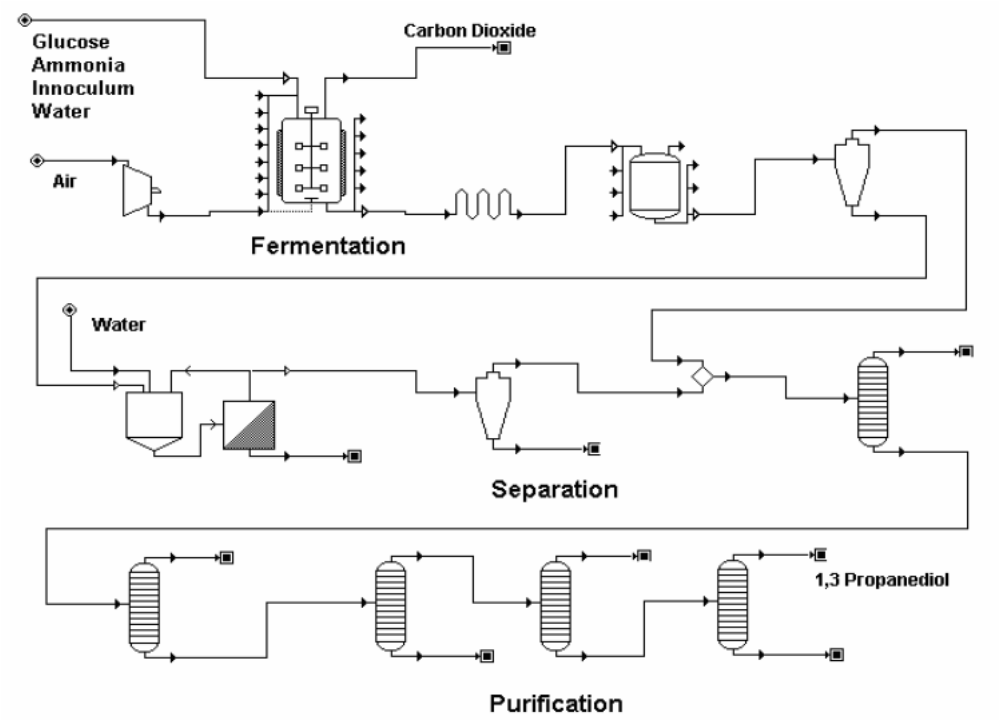


*Figure S1. Process design for bio-based PDO. Source:* [6]

In the absence of the process-level data for bio-PDO production, the process displayed on Figure S1, was simulated in CHEMCAD in the Anex & Ogletree study (2006); assuming the following process variables [6]:

1. Aerobic fermentation at 37ºC and 1 atm for 38h
2. Input concentration of PDO is 135 g/L; rate of production is 3.5 g/L·h;
3. Bio-catalytic growth represented by the standard Monod kinetic model for *E.Coli*: specific growth
   1) rate of 0.50$h^{-1}$, saturation constant at 4.0 mg/l and cell maintenance coefficient of 0.045$h^{-1}$
4. Water requirement are neglected because the starch slurry process [here in step 3] is assumed to provide water
5. Air requirements were neglected as they require little effort and cause negligible impact
6. The inoculum production is neglected since once added, its production is self-sustained
7. The overall efficiency of 89.5% is obtained, that is yield of 0.511 g PDO/g glucose the energy requirement. Under the given efficiency and conditions, the stoichiometric relations in reaction 5 imply that 0.015 kg $NH_3$/kg PDO is necessary ((3x17g)/(50x76gx0.895)). Also, the process emits the biogenic $CO_2$, that is 0.695 kg CO2 /kg PDO ((60x44g)/(50x76gx0.895)).
8. Energy requirements are calculated to total 26 MJ/kg PDO - 90% from the natural gas needed for heating and purification, 10% for electrical energy for the centrifugal separation.

Thus, the resulting list of inputs and outputs for the PDO fermentation process is given in Table S7 [6].

*Table S7. Inventory data per 1kg of bio-PDO produced from glucose.*

| **Reference product** | **Amount** | **Unit** |
|---|---|---|
| Bio-PDO | 1 | kg |
| **Input** | | |
| Ammonium as liquid gas, RoW | 0.015 | kg |
| Glucose, US (from previous step) | 1.96 | kg |
| Electricity, medium voltage, market, US | 2.6 | MJ |
| Heat, district or industrial, natural gas, market, RoW | 23.4 | MJ |
| **Output** | | |
| Carbon dioxide, biogenic | 0.695 | kg |

Transport of PDO to the PTT production site has been modeled using the default market scenarios for the transportation of MEG, in order to adapt the value chain of PET to PTT (seen as that MEG and PDO are comparable monomers, since PTA is shared). "*Ethylene glycol {GLO}| market for | Cut-off, U*" is used to this measure, where the input MEG has been changed with the previously resulting PDO.

## Polymerization of PTT

The last step in producing a polymer suitable for textile industry application is the esterification (polymerization) of the 2 monomers - PTA and PDO into an amorphous-grade PTT. PTT polymerization is approximated with an existing PET polymerization dataset because:

- polymers belong to the same family of chemical compounds – both are polyesters
- both are obtained via esterification in similar environmental conditions
- one monomer (PTA) is shared between the two polymers
- difference in catalyst is overlooked because in theory catalyst is not used up in the reaction (just participates)

Moreover, for the same reasons, it can be expected that PTT is produced in retrofitted PET or new similar facilities around the globe. Default transportation of PET polymer is thus translated to PTT later on.

Same as for PET, two datasets were produced by adapting "*Polyethylene terephthalate, granulate, amorphous {RoW}| production | Cut-off, U*" and "*Polyethylene terephthalate, granulate, amorphous {RER}| production | Cut-off, U*". In each of the two:

- Ethylene glycol input has been changed to PDO according to the matrix in Table S9, with 0.8156kg PDO/ kg of PTT
- PTA input has been changed according to the matrix in Table S9 with 0.3815 kg/kg of PTT

In order to find appropriate quantities of PDO and PTA for PTT polymerization, an approximation was made using the PET reaction stoichiometric as displays in Table S8. Due to the same reaction type, very similar stoichiometric selectivity (84.2% for PET vs 85.1% for PTT), a shared reactant (PTA), same reactant efficiency is assumed for PTA for both reactions; the efficiency of MEG is applied to PDO as calculated in Table S8.

*Table S8. Approximation of PTT Polymerization using PET data*

| **PET Polymerization** | | | | | |
|---|---|---|---|---|---|
| (1) Reactants and products | $C_8H_6O_4$ $(PTA)$ | $+ C_2H_6O_2(MEG)$ | → | $C_{10}H_8O_4$ $(PET)$ | $+ 2\ H_2O$ |
| (2) Stoichiometric relations | 166 g | 62 g | | 192 g **84.2%*** of total products | 36 g 15.8% of products |
| (3) Stoichiometric relations, per kg PET | 0.8646 kg/kg PET | 0.3229 kg/ kg PET | | 1 kg PET | |
| (4) Quantities in EcoInvent from "Polyethylene terephthalate, granulate, amorphous {RoW}| production Cut-off, U" | 0.875 kg/kg PET | 0.334 kg/ kg PET | | 1kg PET | |
| (5) Resulting efficiency per reactant as (3)/(4) | **98,8%** | **96.7%** | | | |
| **PTT Polymerization** | | | | | |
| (6) Reactants and products | $C_8H_6O_4$ $(PTA)$ | $+\ C_3H_8O_2(PDO)$ | → | $C_{10}H_8O_4$ $(PTT)$ | $+ 2\ H_2O$ |
| (7) Stoichiometric relations | 166 g | 76 g | | 206 g **85.1%*** of products | 36g 14.9% of products |
| (8) Stoichiometric relations, per kg PTT | 0.8058 kg/kg PTT | 0.3689 kg/kg PTT | | 1 kg PTT | |
| (9) Resulting quantities to be used in PTT modeling as (8)/(5) (adaptation of "Polyethylene terephthalate, granulate, amorphous {RoW}| production Cut-off, U") | **0.8156 kg/kg PTT** | **0.3815kg/kg PTT** | | **1 kg PTT** | |

Then, the two sets were combined in market data to account for transportation. An approximation was conducted by using PET the dataset "*Polyethylene terephthalate, granulate, amorphous {GLO}| market for | Cut-off, U*" as follows:

- "Polyethylene terephthalate, granulate, amorphous {CA-QC}| production | Cut-off, U" and "Polyethylene terephthalate, granulate, amorphous {US}| polyethylene terephthalate, granulate, amorphous, recycled to generic market for amorphous PET granulate | Cut-off, U", "Polyethylene terephthalate, granulate, amorphous {RoW}| polyethylene terephthalate, granulate, amorphous, recycled to generic market for amorphous PET granulate | Cut-off, U", were approximated with a corresponding RoW dataset
- "Polyethylene terephthalate, granulate, amorphous {Europe without Switzerland}| polyethylene terephthalate, granulate, amorphous, recycled to generic market for amorphous PET granulate | Cut-off, U" and " Polyethylene terephthalate, granulate, amorphous {CH}| polyethylene terephthalate, granulate, amorphous, recycled to generic market for amorphous PET granulate | Cut-off, U", were approximated with corresponding RER dataset

*Table S9. Combination matrix for PTT*

| **Combination matrix for PTT** | | **PDO** | |
|---|---|---|---|
| | | Fossil-based | Corn-based |
| **PTA** | Fossil-based | **Scenario 0**<br>Fossil-based PTT<br>0% bio-based C | **Scenario 1**<br>Partially bio-based PTT<br>27% bio-based C |
| | Corn-based | / | **Scenario 2**<br>Fully bio-based PTT<br>100% bio-based C |

## PLA

PLA is predominantly produced in a ring opening polymerization of lactides. This chemical chain starts of with the corn-derived glucose just like for PDO and corn-MEG (corn cultivation, starch production and glucose extraction preceded the fermentation). The glucose is fermented into crude lactic acid by diverse bacteria which then goes through several continuous extraction and purification steps (acidulation, filtration, evaporation and purification) to obtain an aqueous polymer-grade lactic acid [7]. This intermediary product is transformed into lactides after which an open ring polymerization (at 140-180ºC with a tin-based catalyst) and subsequent pelletization yield the PLA polymer pellets [7,8].

This exact method is used by NatureWorks LLC from Nebraska, USA, the most notable producer of PLA, under its brand name Ingeo [7,9]. The entire cradle-to-gate PLA polymer from corn is well documented in the Ecoinvent dataset "*Polylactide, granulate {GLO}| market for | Cut-off, U*" and is extrapolated from the NatureWorks' plant data. Only one modification was applied – all corn inputs were adapted to "Maize grain {RoW}| market for maize grain | Cut-off, U", for consistency with other corn-based products.

## Melt Spinning

All fibers are produced from homonymous polymers via melt spinning. To model this unit process, the existing set "*Fibre, polyester {RoW}| polyester fibre production, finished | Cut-off, U*" is applied with modifications.

For bio-polyester – only input polymer according is adapted to Table S6 In the case of PTT and PLA fibers, the adaptation of the same set is considered sufficient and appropriate due to proximity of melting temperatures of these polymers to PET. Equally, melt spinning is the single most prominent fiber production method for mass textiles, therefore, no other option is envisaged for bio-based polyester alternatives either. For PLA fiber – input PET is substituted with PLA polymer. For PTT fiber – input PET is substituted with PTT according to table S9. In all cases, $C0_2$, CO and $CH_4$ are not emitted in this unit process, no modification from fossil to bio-based emission is needed.

# Normalization

## Results with default EF

*Table S10. Normalization results with default EF.*

| Impact category | **Scenario 0** | **Scenario 1** | **Scenario 2A** | **Scenario 2B** | **Scenario 3** | **Scenario 4A** | **Scenario 4B** | **Scenario 5** | **Scenario 6** | **Scenario 7** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Climate change** | 0.000503 | 0.000575 | 0.000458 | 0.000457 | 0.000881 | 0.000763 | 0.000762 | 0.000582 | 0.000866 | 0.000465 |
| **Ozone depletion** | 4.04E-06 | 5.64E-06 | 4.33E-06 | 4.29E-06 | 1.15E-05 | 1.02E-05 | 1.02E-05 | 5.98E-06 | 1.15E-05 | 5.83E-06 |
| **Ionising radiation** | 2.76E-05 | 3.68E-05 | 2.68E-05 | 2.67E-05 | 6.35E-05 | 5.35E-05 | 5.33E-05 | 4.04E-05 | 6.53E-05 | 5.29E-05 |
| **Photochemical ozone formation** | 0.000434 | 0.000479 | 0.000454 | 0.000439 | 0.000679 | 0.000654 | 0.000639 | 0.000461 | 0.000647 | 0.000436 |
| **Particulate matter** | 0.000242 | 0.000324 | 0.000297 | 0.000278 | 0.000618 | 0.000591 | 0.000573 | 0.000294 | 0.000568 | 0.000235 |
| **Human toxicity, non-cancer** | 0.000108 | 0.000214 | 0.000168 | 0.00015 | 0.00056 | 0.000514 | 0.000497 | 0.00019 | 0.000514 | 0.000227 |
| **Human toxicity, cancer** | 6.35E-05 | 0.000106 | 6.77E-05 | 6.61E-05 | 0.000222 | 0.000184 | 0.000182 | 9.54E-05 | 0.000203 | 8.8E-05 |
| **Acidification** | 0.000295 | 0.000433 | 0.00038 | 0.00035 | 0.000936 | 0.000882 | 0.000853 | 0.000399 | 0.000867 | 0.00038 |
| **Eutrophication, freshwater** | 0.000109 | 0.0002 | 0.000111 | 0.000108 | 0.000491 | 0.000401 | 0.000399 | 0.000199 | 0.00047 | 0.000325 |
| **Eutrophication, marine** | 0.000177 | 0.000327 | 0.000301 | 0.000265 | 0.000835 | 0.000808 | 0.000772 | 0.000302 | 0.000775 | 0.000391 |
| **Eutrophication, terrestrial** | 0.000184 | 0.000363 | 0.000323 | 0.000282 | 0.000966 | 0.000925 | 0.000884 | 0.000321 | 0.000883 | 0.000364 |
| **Ecotoxicity, freshwater** | 0.001148 | 0.002163 | 0.001326 | 0.001263 | 0.005613 | 0.004777 | 0.004714 | 0.001952 | 0.005169 | 0.002439 |
| **Land use** | 3.69E-06 | 2.7E-05 | 3.14E-05 | 2.4E-05 | 9.96E-05 | 0.000104 | 9.66E-05 | 2.25E-05 | 9.02E-05 | 3.64E-05 |
| **Water use** | 0.000172 | 0.000437 | 0.000158 | 0.000165 | 0.001222 | 0.000944 | 0.00095 | 0.00041 | 0.001142 | 0.000441 |
| **Resource use, fossils** | 0.001278 | 0.001237 | 0.001092 | 0.00109 | 0.001259 | 0.001114 | 0.001112 | 0.001259 | 0.00128 | 0.000759 |
| **Resource use, minerals and metals** | 0.000187 | 0.000432 | 0.000222 | 0.000208 | 0.001107 | 0.000897 | 0.000883 | 0.000235 | 0.000865 | 0.000157 |

# Characterization

## Climate change

*Table S11. Climate change results with default and modified EF*

| | **Default EF, kg CO2 eq.** | **Modified EF, kg CO2 eq.** |
|---|---|---|
| **Scenario 0** | 4.1 | 4.1 |
| **Scenario 1** | 4.7 | 3.5 |
| **Scenario 2A** | 3.7 | 3.1 |
| **Scenario 2B** | 3.7 | 3.3 |
| **Scenario 3** | 7.1 | 2.2 |
| **Scenario 4A** | 6.2 | 1.9 |
| **Scenario 4B** | 6.2 | 2.0 |
| **Scenario 5** | 4.7 | 3.7 |
| **Scenario 6** | 7.0 | 2.5 |
| **Scenario 7** | 3.8 | 1.5 |

## Other midpoint results

*Table S12. Other midpoint results with default EF. Note that modified EF gives the same results for the listed impact categories.*

| | | Sce-nario 0 | Sce-nario 1 | Scenario 2A | Sce-nario 2B | Scenario 3 | Scenario 4A | Scenario 4B | Scenario 5 | Scenario 6 | Scenario 7 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Impact category** | Unit | | | | | | | | | | |
| **Climate change** | kg CO2 eq | 4.074935 | 4.658941 | 3.70747539 | 3.700597 | 7.13066 | 6.179615424 | 6.174038 | 4.710996 | 7.014920889 | 3.762015 |
| **Ozone depletion** | kg CFC11 eq | 2.17E-07 | 3.03E-07 | 2.3232E-07 | 2.3E-07 | 6.18E-07 | 5.47795E-07 | 5.45E-07 | 3.21E-07 | 6.14857E-07 | 3.13E-07 |
| **Ionising radiation** | kBq U-235 eq | 0.116557 | 0.155386 | 0.11313059 | 0.112527 | 0.267857 | 0.225622769 | 0.225001 | 0.170598 | 0.275433533 | 0.223339 |
| **Photochemical ozone formation** | kg NMVOC eq | 0.017626 | 0.019449 | 0.01841784 | 0.017819 | 0.02758 | 0.026549682 | 0.025953 | 0.0187 | 0.026278783 | 0.017707 |
| **Particulate matter** | disease inc. | 1.44E-07 | 1.93E-07 | 1.7651E-07 | 1.66E-07 | 3.68E-07 | 3.51858E-07 | 3.41E-07 | 1.75E-07 | 3.38241E-07 | 1.4E-07 |
| **Human toxicity, non-cancer** | CTUh | 2.48E-08 | 4.91E-08 | 3.8489E-08 | 3.44E-08 | 1.29E-07 | 1.1816E-07 | 1.14E-07 | 4.38E-08 | 1.18013E-07 | 5.22E-08 |
| **Human toxicity, cancer** | CTUh | 1.07E-09 | 1.8E-09 | 1.144E-09 | 1.12E-09 | 3.76E-09 | 3.10194E-09 | 3.07E-09 | 1.61E-09 | 3.43646E-09 | 1.49E-09 |
| **Acidification** | mol H+ eq | 0.016374 | 0.024083 | 0.02108721 | 0.019453 | 0.051988 | 0.048994438 | 0.047365 | 0.022169 | 0.048179208 | 0.02109 |
| **Eutrophication, freshwater** | kg P eq | 0.000175 | 0.000322 | 0.00017788 | 0.000174 | 0.000789 | 0.000645175 | 0.000641 | 0.00032 | 0.000755304 | 0.000522 |
| **Eutrophication, marine** | kg N eq | 0.003468 | 0.006401 | 0.00588465 | 0.005173 | 0.016312 | 0.01579569 | 0.015085 | 0.005911 | 0.015148628 | 0.007644 |
| **Eutrophication, terrestrial** | mol N eq | 0.032595 | 0.064164 | 0.05702636 | 0.049754 | 0.170707 | 0.163573098 | 0.156311 | 0.056778 | 0.156088443 | 0.064406 |
| **Ecotoxicity, freshwater** | CTUe | 49.00052 | 92.30832 | 56.5932255 | 53.89432 | 239.5788 | 203.8672525 | 201.1749 | 83.33144 | 220.604362 | 104.0906 |
| **Land use** | Pt | 3.020747 | 22.10791 | 25.75894 | 19.6947 | 81.61365 | 85.26526273 | 79.20104 | 18.43263 | 73.89878198 | 29.83445 |
| **Water use** | m3 depriv. | 1.972411 | 5.013413 | 1.8174196 | 1.893239 | 14.02034 | 10.82453779 | 10.90028 | 4.700708 | 13.09619554 | 5.06172 |
| **Resource use, fossils** | MJ | 83.08813 | 80.42965 | 71.0312295 | 70.84282 | 81.85001 | 72.45710366 | 72.28067 | 81.88195 | 83.20588832 | 49.32651 |
| **Resource use, minerals and metals** | kg Sb eq | 1.19E-05 | 2.75E-05 | 1.4109E-05 | 1.32E-05 | 7.05E-05 | 5.70797E-05 | 5.62E-05 | 1.5E-05 | 5.50377E-05 | 9.99E-06 |
| **Climate change - Fossil** | kg CO2 eq | 4.064693 | 4.633516 | 3.78359885 | 3.750123 | 7.058541 | 6.2090159 | 6.176869 | 4.689156 | 6.949555927 | 3.731164 |
| **Climate change - Biogenic** | kg CO2 eq | 0.007475 | 0.007739 | 0.03131806 | 0.027441 | 0.007513 | 0.031111308 | 0.027217 | 0.007415 | 0.007205167 | 0.007599 |
| **Climate change - Land use and LU change** | kg CO2 eq | 0.002767 | 0.017686 | -0.1074415 | -0.07697 | 0.064606 | -0.06051178 | -0.03005 | 0.014425 | 0.058159796 | 0.023252 |

*Table S13. Contribution of feedstock to the final impact of fiber. Results of the modified EF are used.*

| | | Scenario 1 | Scenario 2A | Scenario 2B | Scenario 3 | Scenario 4A | Scenario 4B | Scenario 5 | Scenario 6 | Scenario 7 |
|---|---|---|---|---|---|---|---|---|---|---|
| **Impact category** | Unit | | | | | | | | | |
| **Climate change** | kg CO2 eq | -30% | -52% | -37% | -198% | -263% | -226% | -22% | -152% | -95% |
| **Ozone depletion** | kg CFC11 eq | 16% | 4% | 3% | 33% | 30% | 19% | 12% | 30% | 22% |
| **Ionising radiation** | kBq U-235 eq | 8% | 2% | 1% | 20% | 19% | 12% | 6% | 18% | 8% |
| **Photochemical ozone formation** | kg NMVOC eq | 13% | 7% | 5% | 37% | 33% | 19% | 10% | 35% | 20% |
| **Particulate matter** | disease inc. | 30% | 22% | 18% | 64% | 62% | 34% | 26% | 62% | 57% |
| **Human toxicity, non-cancer** | CTUh | 49% | 38% | 31% | 78% | 76% | 44% | 44% | 76% | 65% |
| **Human toxicity, cancer** | CTUh | 40% | 8% | 6% | 78% | 74% | 48% | 35% | 77% | 67% |
| **Acidification** | mol H+ eq | 34% | 27% | 21% | 64% | 63% | 35% | 29% | 62% | 54% |
| **Eutrophication, freshwater** | kg P eq | 42% | 8% | 6% | 70% | 67% | 43% | 33% | 65% | 36% |
| **Eutrophication, marine** | kg N eq | 47% | 42% | 35% | 76% | 75% | 41% | 41% | 74% | 56% |
| **Eutrophication, terrestrial** | mol N eq | 51% | 44% | 37% | 78% | 77% | 43% | 45% | 77% | 71% |
| **Ecotoxicity, freshwater** | CTUe | 45% | 17% | 13% | 72% | 69% | 43% | 40% | 70% | 57% |
| **Land use** | Pt | 85% | 88% | 85% | 94% | 95% | 95% | 80% | 94% | 88% |
| **Water use** | m3 depriv. | 61% | 2% | 1% | 89% | 88% | 57% | 51% | 86% | 85% |
| **Resource use, fossils** | MJ | 5% | 1% | 1% | 20% | 18% | 11% | 4% | 17% | 11% |
| **Resource use, minerals and metals** | kg Sb eq | 17% | 12% | 10% | 27% | 28% | 17% | 25% | 31% | 66% |

## Single score

*Table S14. Single score results with all four impact assessment methods.*

| | Scenario 0 | Scenario 1 | Scenario 2A | Scenario 2B | Scenario 3 | Scenario 4A | Scenario 4B | Scenario 5 | Scenario 6 | Scenario 7 |
|---|---|---|---|---|---|---|---|---|---|---|
| **Default EF** | 344.2 | 453.5 | 347.4 | 337.5 | 832.6 | 726.5 | 716.6 | 426.7 | 780.0 | 368.8 |
| **Default Castellani** | 309.3 | 459.0 | 341.2 | 325.5 | 967.1 | 849.3 | 833.7 | 422.6 | 896.3 | 424.6 |
| **Modified EF** | 344.8 | 422.2 | 332.7 | 325.9 | 703.6 | 614.2 | 607.4 | 401.1 | 663.4 | 311.1 |
| **Modified Castellani** | 309.5 | 449.0 | 336.5 | 321.8 | 925.9 | 813.5 | 798.8 | 414.5 | 859.1 | 406.2 |

## References


1. Liptow, C.; Tillman, A.M. A Comparative Life Cycle Assessment Study of Polyethylene Based on Sugarcane and Crude Oil. *J. Ind. Ecol.* **2012**, *16*, 420–435, doi:10.1111/j.1530-9290.2011.00405.x.
2. Akanuma, Y.; Selke, S.E.M.; Auras, R. A preliminary LCA case study: Comparison of different pathways to produce purified terephthalic acid suitable for synthesis of 100 % bio-based PET. *Int. J. Life Cycle Assess.* **2014**, *19*, 1238–1246, doi:10.1007/s11367-014-0725-2.
3. Jacobs, J.M.; Jacobs, P.A.; Uytterhoeven, J.B. Process for obtaining ethylene from ethanol, United States Patent 4670620,1987.
4. European Commission.*Environmental factsheet: 1,3-propanediol.* 2013. Available online: https://ec.europa.eu/jrc/sites/jrcsh/files/BISO-EnvSust-Bioproducts-13PDO_140930.pdf (last accessed 14 January 2021)
5. Urban, R.A.; Bakshi, B.R. 1,3-Propanediol from fossils versus biomass: A life cycle evaluation of emissions and ecological resources. *Ind. Eng. Chem. Res.* **2009**, *48*, 8068–8082, doi:10.1021/ie801612p.
6. Anex, R.P.; Ogletree, A.L. Life-cycle assessment of energy-based impacts of a biobased process for producing 1,3-propanediol. *ACS Symp. Ser.* **2006**, *921*, 222–238, doi:10.1021/bk-2006-0921.ch017.
7. Vink, E.T.H.; Davies, S. Life Cycle Inventory and Impact Assessment Data for 2014 Ingeo® Polylactide Production. *Ind. Biotechnol.* **2015**, *11*, 167–180, doi:10.1089/ind.2015.0003.
8. Niaounakis, M. *Biopolymers: Processing and Products*; William Andrew Publishing, Amsterdam, The Netherlands, 2015; ISBN 9780323266987.
9. Vink, E.T.H.; Rábago, K.R.; Glassner, D.A.; Gruber, P.R. Applications of life cycle assessment to NatureWorks™ polylactide (PLA) production. *Polym. Degrad. Stab.* **2003**, *80*, 403–419, doi:10.1016/S0141-3910(02)00372-5.