LCA COMPARISON OF 100 % BIO-BASED PET
SYNTHESIZED FROM
DIFFERENT PTA PATHWAYS

By

Yasuhiko Akanuma

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

Packaging - Master of Science

2013

ABSTRACT

LCA COMPARISON OF 100 % BIO-BASED PET SYNTHESIZED FROM DIFFERENT PTA PATHWAYS

By

Yasuhiko Akanuma

In this study, environmental impacts of bio-based poly ethylene terephthalate (PET) resin with scenarios of three different purified terephthalic acid (PTA) production methods, which are pathways through muconic acid; isobutanol; and benzene, toluene and xylene (BTX) as intermediates, were compared. In the case of the PTA 1 scenario which goes through muconic acid as intermediate, the unit process of muconic acid production was dominant for all impact categories except for aquatic eutrophication. This unit process was found to be a relatively sensitive process in the pathway to synthesize PTA, according to the sensitivity analysis. This means LCA results from the PTA 1 scenario might contain data limitations to some extent; therefore, further sophisticated LCI data will be useful to provide more accurate comparisons. In the case of the PTA 2 scenario which goes through butanol as intermediate, the unit process of isobutanol production seemed to have large impacts for each environmental index category. In the case of the PTA 3 scenario which goes through BTX as intermediate, even if the data uncertainty (LCIA data output deviation) was considered, this scenario had less impact in the global warming index than that of the other 100 % bio-based PTA scenarios according to a limited Monte Carlo simulation.

ACKNOWLEDGEMENTS

I would like to express my sincerest gratitude to those who, in various ways, have contributed to the work with this thesis. First of all, I am deeply grateful to my family: Mika and Yuta. Without their dedicated support, I wouldn’t have been writing this thesis. Thanks to my company, SUNTORY, for their financial support for my academic life. I hope I can give back to them what I learned in U.S. Thanks to Dr. Selke, my supervisor, for accepting me and giving me all her guidance, support and deep understanding. I could have a lot of useful discussions with her through this study. Thanks to Dr. Auras for all his valuable inputs and guidance. Also, I could learn a lot about sustainability and detail procedure for life cycle assessment through his academic lecture. Thanks to Dr. Joshi for all his valuable inputs and advices, which were really helpful to collect and organize the inventory data. Thanks to all my friends for their support and encouragement, and for all the fun things outside work. I hope we will have a continuing excellent relationship.

TABLE OF CONTENTS

LIST OF TABLES vii

LIST OF FIGURES x

KEY TO ABBREVIATIONS xi

1. INTRODUCTION. 1

2. LITERATURE REVIEW 4
   2.1. BACKGROUND INFORMATION 4
   2.2. LCA STUDY APPLIED TO PLASTIC PACKAGING MATERIALS AND BIOFUELS. 6

3. GOAL AND SCOPE OF THE STUDY. 11
   3.1. GOAL 11
   3.2. SCOPE 11
      3.2.1. PRODUCT SYSTEM BOUNDARIES 12
      3.2.2. DATA COLLECTION, SOFTWARE AND DATABASES 16
      3.2.3. DATA CALCULATION METHOD 18
      3.2.4. FUNCTIONAL UNIT 18
      3.2.5. CUT-OFF CRITERIA 18
      3.2.6. ALLOCATION 18
      3.2.7. LIFE CYCLE IMPACT ASSESSMENT METHODOLOGY, IMPACT CATEGORIES CONSIDERED 19
      3.2.8. DATA QUALITY REQUIREMENTS, AND ASSUMPTIONS 19

4. MUCONIC ACID PATHWAY PRODUCTION 21
   4.1. PROCESS DESCRIPTION AND LCI DATA 21
      4.1.1. BIO-ETHANOL PRODUCTION (MEG SYNTHESIS STEP 1) 21
      4.1.2. ETHYLENE OXIDE PRODUCTION (MEG SYNTHESIS STEP 2) 24
      4.1.3. MONO ETHYLENE GLYCOL PRODUCTION (MEG SYNTHESIS STEP 3) 25
      4.1.4. MUCONIC ACID PRODUCTION (PTA SYNTHESIS STEP 1) 26
      4.1.5. CYCLOHEXA-2,5-DIENE-1,4-DICARBOXYLATE PRODUCTION (PTA SYNTHESIS STEP 2) 28
      4.1.6. PTA PRODUCTION (PTA SYNTHESIS STEP 3) 30
      4.1.7. POLYETHYLENE TEREPHTHALATE RESIN PRODUCTION 33
   4.2. LCI RESULTS 36
      4.2.1. PROCESS ENERGY DEMAND 36
   4.3. LCIA RESULTS (IMPACT 2002+ V2.1) 37

5. ISOBUTANOL PATHWAY PRODUCTION 42
  5.1. PROCESS DESCRIPTION AND LCI DATA 42
    5.1.1. BUTANOL PRODUCTION (PTA 2 SYNTHESIS STEP 1) 42
    5.1.2. ISOBUTYLENE PRODUCTION (PTA 2 SYNTHESIS STEP 2) 44
    5.1.3. ISOOCTENE PRODUCTION (PTA 2 SYNTHESIS STEP 3) 45
    5.1.4. ISOOCTANE PRODUCTION (PTA 2 SYNTHESIS STEP 4) 47
    5.1.5. PARA-XYLENE PRODUCTION (PTA 2 SYNTHESIS STEP 5) 48
    5.1.6. PTA PRODUCTION (PTA 2 SYNTHESIS STEP 6) 49
  5.2. LCI RESULTS 51
    5.2.1. PROCESS ENERGY DEMAND 51
  5.3. LCIA RESULTS (IMPACT 2002+ V2.1) 52

6. BENZENE TOLUENE XYLENE PATHWAY PRODUCTION 58
  6.1. PROCESS DESCRIPTION AND LCI DATA 58
    6.1.1. BTX PRODUCTION (PTA 3 SYNTHESIS STEP 1) 58
    6.1.2. XYLENE PRODUCTION (PTA 3 SYNTHESIS STEP 2) 60
    6.1.3. PTA PRODUCTION (PTA 3 SYNTHESIS STEP 3) 61
  6.2. LCI RESULTS 63
    6.2.1. PROCESS ENERGY DEMAND 63
  6.3. LCIA RESULTS (IMPACT 2002+ V2.1) 63

7. INTERPRETATION 69
  7.1. EVALUATION OF THE RESULTS 69
    7.1.1. COMPLETENESS CHECK 69
    7.1.2. CONSISTENCY CHECK 71
  7.2. ANALYSIS OF THE RESULTS 73
    7.2.1. SENSITIVITY ANALYSIS FOR ENERGY 73
    7.2.2. COMPARISON OF THE SCENARIOS 80
    7.2.3. CONTRIBUTION FROM BIOMASS 84
    7.2.4. UNCERTAINTY ANALYSIS (MONTE CARLO SIMULATION) 86

8. CONCLUSION 87

APPENDICES 91
    Appendix A: Pedigree Matrix
    Appendix B: Classification factors and their environmental mechanism
    Appendix C: LCI Data Calculation Process

REFERENCES 136

LIST OF TABLES

Table 1. The order of priority for selecting the appropriate benchmark processes. 16

Table 2. Input/Output flows for 1 kg of bio-ethanol. 23

Table 3. Input/Output flows for 1 kg of bio-ethylene oxide. 25

Table 4. Input/Output flows for 1 kg of bio-MEG. 26

Table 5. Input/Output flows for 1 kg of muconic acid. 28

Table 6. Input/Output flows for 1 kg of cyclohexa-2,5-diene-1,4-dicarboxylate. 30

Table 7. Input/Output flows for 1 kg of PTA. 32

Table 8. Input/Output flows for 1 kg of PET resin. (step 1: amorphous state) 34

Table 9. Input/Output flows for 1 kg of PET resin (step 2: bottle grade). 35

Table 10. Process energy in the muconic acid pathway, for 1 kg of PET resin. 36

Table 11. Input/Output flows for 1 kg of isobutanol. 43

Table 12. Input/Output flows for 1 kg of n-butanol (GREET). 44

Table 13. Input/Output flows for 1 kg of isobutylene. 45

Table 14. Input/Output flows for 1 kg of isooctene. 46

Table 15. Input flows for 1 kg of isooctane. 47

Table 16. Input/Output flows for 1 kg of para-xylene. 48

Table 17. Input/Output flows for 1 kg of PTA. 50

Table 18. Process energy in the isobutanol pathway, for 1 kg of PET resin. 51

Table 19. Input/Output flows for 1 kg of BTX (from corn). 59

Table 20. Input/Output flows for 1 kg of BTX (through fast pyrolysis). 60

Table 21. Input flows for 1 kg of xylene mixture. 61

Table 22. Input/Output flows for 1 kg of PTA. 62

Table 23. Process energy in the BTX pathway, for 1 kg of PET resin. 63

Table 24. Results of completeness check (self-check). 69

Table 25. Results of consistency check for PTA 1 scenario 1(self-check). 71

Table 26. Results of the sensitivity analysis for uncertainty of PTA scenario 1. 74

Table 27. Results of the sensitivity analysis for uncertainty of PTA scenario 2. 75

Table 28. Results of the sensitivity analysis for uncertainty of PTA scenario 3. 78

Table 29. Biomass amounts for the production of 1kg PET resin (PTA part). 84

Table 30. Pedigree matrix used to assess the quality of data sources. 92

Table 31. Pedigree matrix. 93

Table 32. Bio-ethanol data 109

Table 33. Bio-ethanol data (distillation). 110

Table 34. The demands/emissions for the production of 1000kg adipic acid. 111

Table 35. The demands/emissions for feed material (adipic acid). 112

Table 36. Energy composition for the production of phenol (lignin). 113

Table 37. Feed demands for bacterial growth in bioreactor. 114

Table 38. Cyclehexane production data. 115

Table 39. Para-xylene production data. 117

Table 40. Purified terephthalic acid production data 118

Table 41. PTA production data (from para-xylene) 120

Table 42. Bio-ethanol production data (material mass ratio data) 123

Table 43. N-butanol production data ... 124

Table 44. Bio-ethylene production data. ... 125

Table 45. Isooctene production data (from C_4 component) ... 126

Table 46. N-heptane production energy data. ... 127

Table 47. N-heptane production energy data. (unit change) ... 128

Table 48. Toluene production energy data. ... 129

Table 49. Toluene production energy data (unit change). ... 130

Table 50. BTX production data (from naphtha). ... 131

Table 51. BTX production data (from naphtha, modified) ... 132

Table 52. Bio-oil production data ... 133

Table 53. Poplar production data ... 134

LIST OF FIGURES

Figure 1. Schematic comparison of PET production process. 3

Figure 2. Framework for LCA methodology. 5

Figure 3. PET resin system boundary– inclusions and exclusions. 13

Figure 4. System structure for scenario 1. 38

Figure 5. IMPACT 2002+ v2.1 result of scenario1 39

Figure 6. System Structure for scenario 2. 53

Figure 7. LCIA comparison of production process, for 1 kg of butanol. 54

Figure 8. LCIA results of scenario2 (isobutanol pathway), for 1 kg of PET resin. 56

Figure 9. System structure for scenario 3. 64

Figure 10. LCIA results for the production of 1 kg BTX. 65

Figure 11. LCIA results of scenario 3 (BTX pathway), for 1 kg of PET resin. 67

Figure 12. LCIA results comparison among five scenarios. 82

Figure 13. LCIA results comparison among five scenarios. 83

Figure 14. Comparison of the results with/without biologic related CO_2 credit. 85

Figure 15. Impact result of global warming index, 86

Figure 16. Schematic comparison of PTA production steps. 89

KEY TO ABBREVIATIONS

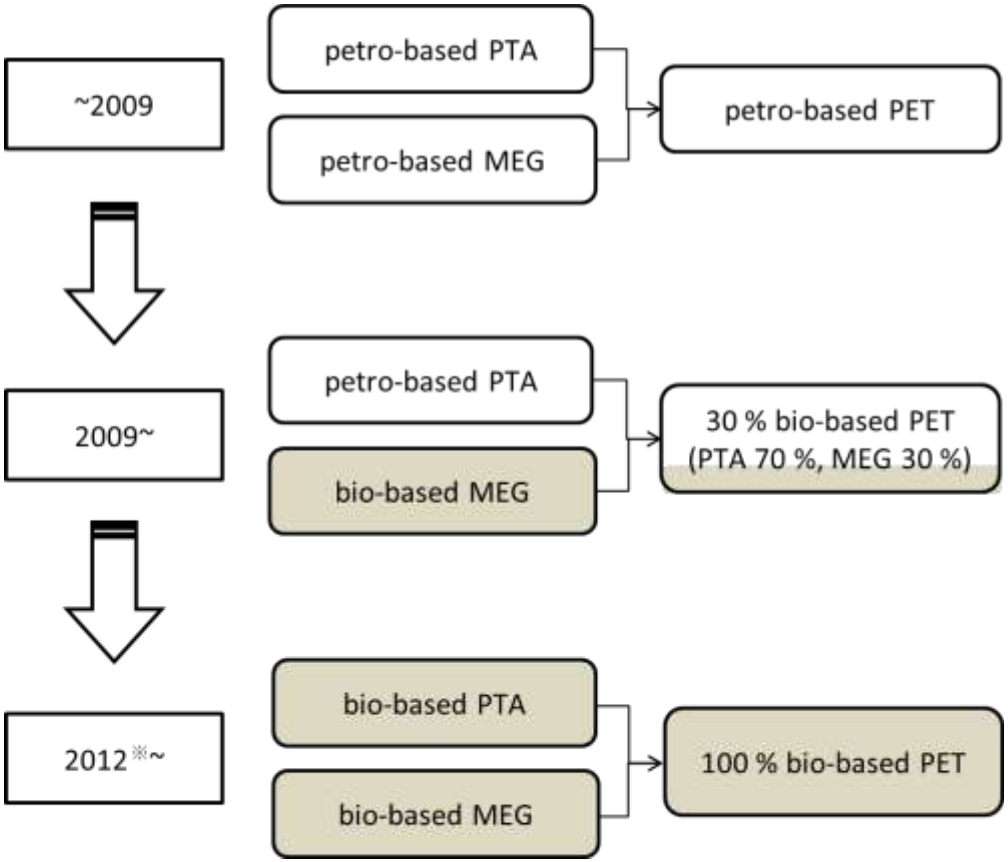
CED	Cumulative Energy Demand
CExD	Cumulative Exergy Demand
GWP	Global Warming Potential
EO	Ethylene Oxide
USEPA	United States Environmental Protection Agency
GHG	Greenhouse Gas
GREET	Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation.
ISO	International Organization for Standardization
IB	Isobutanol
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
MEG	Mono Ethylene Glycol
PET	Polyethylene Terephthalate
PTA	Purified Terephthalic Acid
SPC	Sustainable Packaging Coalition
TPA	Terephthalic Acid
ΔH_f	Heat of Formation

1. INTRODUCTION.

Recently, companies in various industrial categories have tried to move from fossil based resources to more sustainable resources such as biomass or other bio-based material for their products and production processes. This movement is motivated by several factors. The need for development of an environmentally sustainable economy to reduce greenhouse gas (GHG) emissions which are related to the global issue of climate change is one. Besides that, there might be the anticipation that fossil sources would reach peak production in the near future and that prices would climb, as a motivation. This tendency is the same even in the beverage and food category. Market leaders Coca Cola and DANONE started to use “partially” bio-based polyethylene terephthalate (PET) bottles in their bottled water products.[1] Furthermore, some brand owners announced that they would launch a 100 % bio-based PET bottle in the near future. For example, the biggest competitor of Coca Cola, PepsiCo, announced that they would pilot production of the new bottle in 2012. And upon successful completion of the pilot, they intended to move directly to full-scale commercialization.[2]

PET is synthesized by the esterification reaction between about 70 % by mass purified terephthalic acid (PTA) and about 30 % mono ethylene glycol (MEG) with water as a byproduct. Its polymerization process is through a poly-condensation reaction of the monomers. Conventionally, petro based raw materials are used to synthesize this resin. As for MEG, production from renewable resources has been accomplished by several material suppliers already and this enables some brand owners to use bio-based PET. Actually, bottles launched from Coca Cola and DANONE use bio-based MEG resources. Therefore the present bio-based bottle sold in the market can contain only 30 % bio-based material. MEG is produced from ethylene by way of an intermediate substance (ethylene oxide). And, ethylene can be produced through the dehydration of ethanol, or through the thermolysis of naphtha. In the case of bio-based material, these C_2 containing compounds are made from cereal crops, sugar crops or lignocellulosic biomass. On the other hand, PTA has been produced mainly by oxidation of para-xylene, traditionally. Now, several players are developing bio-based para-xylene. Each player is investigating their own production method. It can be said that 100 % bio-based PET bottles could be made after the launch of bio-based para-xylene since they could make use of the existing (petroleum-based) chemical production process line. Figure 1 shows the schematic comparison of PET production processes. The challenging issue is to replace the petroleum-based PTA by a bio-based version to achieve 100 % bio-based PET, and there are several pathways to obtain it.

Since this trend is motivated by environmental consciousness, it is important to know the environmental impact of bio-based PET made by different PTA production methods.



※pilot production

Figure 1. Schematic comparison of PET production process.

Note: For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this thesis.

2. LITERATURE REVIEW

2.1. BACKGROUND INFORMATION

The sustainability movement has spread more broadly in the market. For example, energy conservation is likely to be seen as much more important for companies and consumers than it was before. The United States Environmental Protection Agency (USEPA) considers life cycle assessment (LCA) as one of the markers on the way to sustainability.[3] In this sustainability category, the Sustainable Packaging Coalition (SPC) which is an industry working group dedicated to a more robust environmental vision for packaging , is also trying to promote sustainability as a guiding principle for packaging design.[4] It can be said this movement is closely linked to the concept of producer responsibility. Each producer of a product must be responsible for managing the whole of their production process, which of course includes the products' package.

LCA is one effective tool which can be used to evaluate the tradeoff between natural resources and human activity, with the use of a comparative study. According to USEPA, LCA is a technique to assess the environmental aspects and potential impacts associated with a product or process by compiling an inventory of relevant energy and material inputs and environmental releases, evaluating the potential environmental impacts associated with identified inputs and releases, and by interpreting the results in order to make a more informed decision. LCA can assess environmental impacts, and cover all life cycle stages of the product from the material extraction to the final disposal and recycling.

Since the LCA results are very dependent on, for example, the applied data quality for the systems and other conditions, a procedure was defined by the International Organization for Standardization (ISO) in order to ensure the procedures and the obtained results provided reliable data. As can be seen in Figure 2, LCA methodology consists of the following four steps; goal and scope definition, inventory analysis, impact assessment, and interpretation.

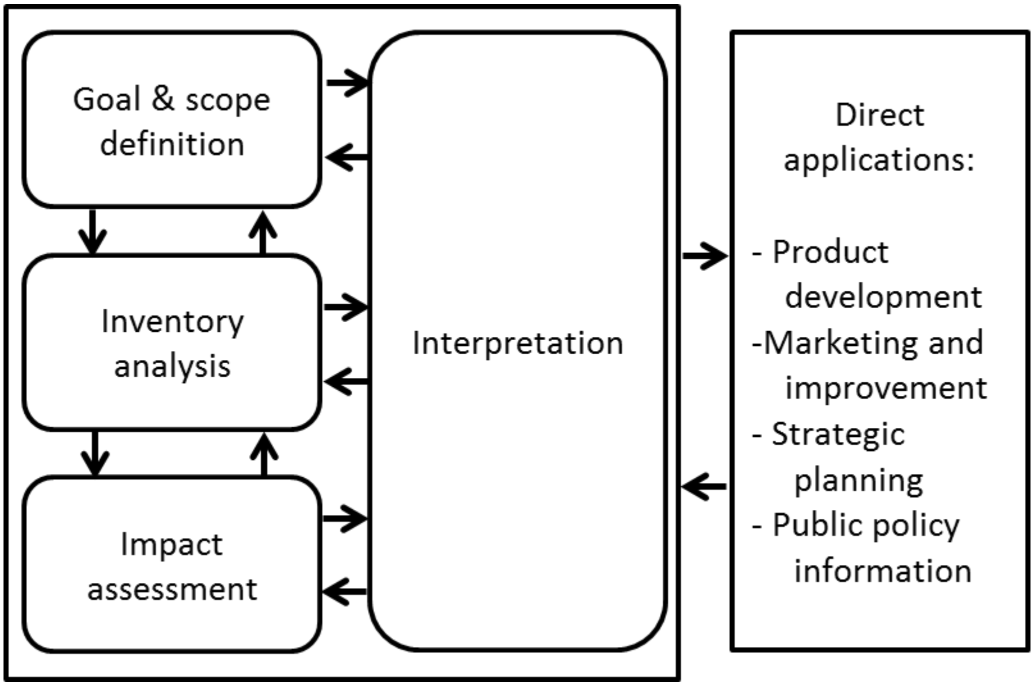


Figure 2. Framework for LCA methodology.

The goal and scope definition is the phase in which the initial choices which determine the working plan of the entire LCA are made.[5] System boundaries must be decided appropriately in this phase. In this study, PET resin production processes from raw materials are the focus; therefore it can be said the type of life cycle boundary is cradle to gate. Inventory analysis is the phase to collect all the data of the unit processes. Since collecting these data is critical to calculate the environmental burdens in the next step, data collecting rules and their quality must be defined strictly. Calculated environmental data are characterized and separated into the appropriate environmental impact categories such as global warming index. These results are evaluated for their consistency and completeness, and then their sensitivity or uncertainty are analyzed in the interpretation phase.

2.2. LCA STUDY APPLIED TO PLASTIC PACKAGING MATERIALS AND BIOFUELS.

LCA is the one of the most powerful methods to estimate such environmental impacts of various products, and of course, of packaging and materials themselves. Various bio-based packaging materials have been investigated and reported. Narayan *et al.* analyzed the LCA of starch based polymers based on the energy usage for production, and compared the results with those of petrochemical based polymers.[6] Also, there is much research about polylactide (PLA). Erwin *et al*. focused on this topic for measuring environmental sustainability and identifying environmental performance-improvement objectives for, in their case, NatureWorks™ PLA.[7] In the same category of biodegradable polymer, polyhydroxybutyrate (PHB) is also drawing international attention. Kim *et al*. estimated the environmental impact of PHB derived from corn grain, and reported that this material could reduce GHG emissions compared to petroleum-derived polymers.[8] In addition, not only base materials used in packaging, but also materials which can add specific functions such as barrier properties are also a focus. For example, there are LCA results about bio-based polyamide resin.[9]

There is also research applied to chemical processes and biofuels. Cherubini *et al*. compared the conventional petro fuel route with several bio-based fuel routes.[10] It was found that GHG emissions can be reduced by use of bioenergy although they concluded that other environmental impacts could be increased. Stichnotte *et al*. estimated and compared two bio-ethanol scenarios derived from household waste.[11] They concluded that GHG emissions could be reduced for a given scenario. Also, considering biomass as a feedstock, there are several LCA studies for the production of bio-ethanol (cellulosic ethanol). Kim *et al*. used corn grain and corn stover as their feedstock.[12] They estimated the U.S. county-level environmental performance for continuous corn cultivation, grown under the current tillage practices for various corn growing locations in the U.S. corn belt. Sauza *et al*. used sugarcane as their feedstock. [13] The objective of their study was to compare a traditional sugarcane ethanol production system with a joint production system, in which ethanol and biodiesel are produced at the same bio-refinery. They also estimated the environmental impact of biodiesel derived from palm oil.

As for the PET category, there is some research about petroleum-derived resin. As described before, PET is synthesized by the esterification reaction between about 70 % by mass purified terephthalic acid (PTA) and about 30 % mono ethylene glycol (MEG) with water as a byproduct. Its polymerization process is through a poly-condensation reaction of the monomers. Following the condensation polymerization, the molecular weight is increased by solid stating in which the dried and crystallized resin chips from the original polymerization are subjected to high temperature and vacuum.[14]

In another environmentally related study, Krugar *et al*. investigated the environmental performance of recycled resin, and compared the results with those of virgin resin. [15] In another study, environmental burdens generated by production of virgin PET resin were compared with the cut-off and open-loop results for recycling the PET resin. [16] Both results showed the use of recycled PET resin could reduce the energy of material resources and also process energy itself, and also GHG emissions could be reduced in proportion to the ratio of recycled parts. In this area, PepsiCo released their actual LCA data which included comparison data for virgin PET and recycled PET resin. They said the use of recycled resin could reduce the environmental burdens compared to virgin PET in eight environmental impact categories.[17] On the other hand, in the category of bio-based PET resin, even though there are already commercially available partly-bio-based PET resins (MEG derived from biomass) and some companies declared they could reduce environmental burdens,[1][2] no published LCA reports are available yet.

To obtain bio-based MEG, producing bio-ethanol is the first step. Sugar crops, cereal crops and lignocellulosic biomass are the main resources for bio-ethanol. For sugar crops, the crops are treated by the process of milling, squeezing the syrup, filtering and pasteurizing through heat along with chemicals. Then, the syrup is fermented before distillation to a higher concentration of alcohol. For cereal (starch) based crops, the process itself is almost the same as that of sugar crops except with the addition of a hydrolysis process. This process is needed to break the long polymers down to monomers so that they can be broken down to the C_6 structure. Starch obtained in the milling process is dissolved into the water, and through acid hydrolysis or enzymes this starch can be converted into sugar. The subsequent processing is the same as with sugar crops.

The difference in process steps between starch and lignocellulosic feedstocks is that lignocellulosic biomass requires a more complicated hydrolysis stage. This is because cellulose in the wood contains carbohydrate polymers. Cellulose is made up of long chains of glucose; therefore more complex (and strong) enzymes are needed to degrade its long chains. That is to say, lignocellulosic bio-ethanol is technically more difficult to produce and currently more expensive compared with bio-ethanol from other sources. But this method is still under development, with the expectation for the future to be able to use forest biomass, cereal, paper, and even municipal solid waste, based on the concept of a bio-refinery. Ethylene can be easily produced through the process of dehydration of bio-ethanol. In the process, 1.7 times the mass of ethanol is required to produce a given mass of ethylene. Then, MEG can be produced from ethylene by way of an intermediate substance (ethylene oxide), which reacts with water to produce ethylene glycol.

On the other hand, PTA is produced mainly by oxidation of p-xylene. Now, several players are developing bio-based PTA by their own methods, which use glucose, sugar, lignocellulose and algae as biomass resources. There are three basic pathways to obtain this bio-based PTA, [18] utilizing muconic acid; isobutanol; and benzene, toluene and xylene (BTX) as the process intermediates.

In this study, LCA of 100 % bio-based PET resin derived from biomass is tackled by using chemically based estimation.

3. GOAL AND SCOPE OF THE STUDY.

3.1. GOAL

The goal of this LCA study is to compare the environmental impact of bio-based PET with three different PTA production method scenarios, which are pathways through muconic acid; isobutanol; and benzene, toluene and xylene (BTX) as intermediates. On the other hand, this is a preliminary study. Therefore, the goal is also to point out which pathway looks most promising from an environmental viewpoint, and what areas of the process are most important to accurately characterize. This goal seems to satisfy current market needs. Interested parties will be mainly the plastic industry, and highly involved consumers such as the consumer beverage industry. On the other hand, this LCA study itself is mainly intended for academic use, not aimed at a public comparative assertion..

3.2. SCOPE

To enable environmental comparisons, a cradle to gate LCA was conducted for the PET polymer synthesis pathway in the United States. This study focuses on the comparison of the production processes. Some process steps needed in real production situations are omitted since they are expected to be very similar for all the cases. These include the transportation phases between processes, utilities and maintenance, labor, and depreciation of the infrastructure.

The time perspectives for the technologies used are during the past 10 years. The study complies with the International Organization for Standardization (ISO) 14040 series of standards governing the use of LCA.[19][20]

3.2.1. PRODUCT SYSTEM BOUNDARIES

Figure 3 shows a summary of what products and processes are considered for the purposes of this LCA study, and the three scenarios that are considered in this study. The boxed arrows on the top indicate the manufacturing input. The arrows on the bottom stand for the outputs (including by-products). All emissions into the environment are included to the extent that data is available. As already mentioned, some processes such as transportation are excluded in order to concentrate on the comparison of the synthesis processes.

Scenario 1 (PTA 1): Muconic acid pathway.

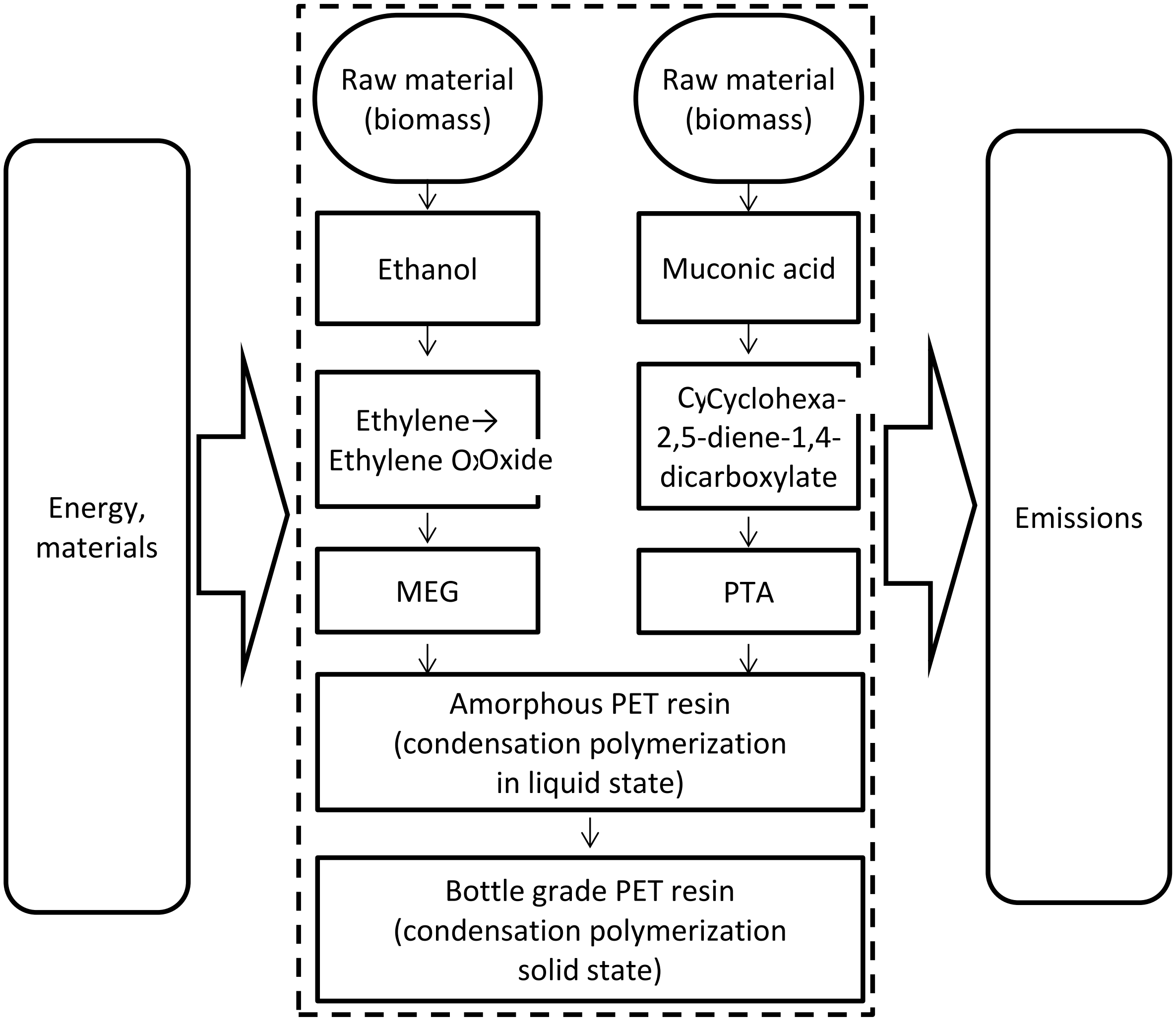


Figure 3. PET resin system boundary– inclusions and exclusions.

Figure 3. (cont'd)

Scenario 2 (PTA 2): Isobutanol pathway.

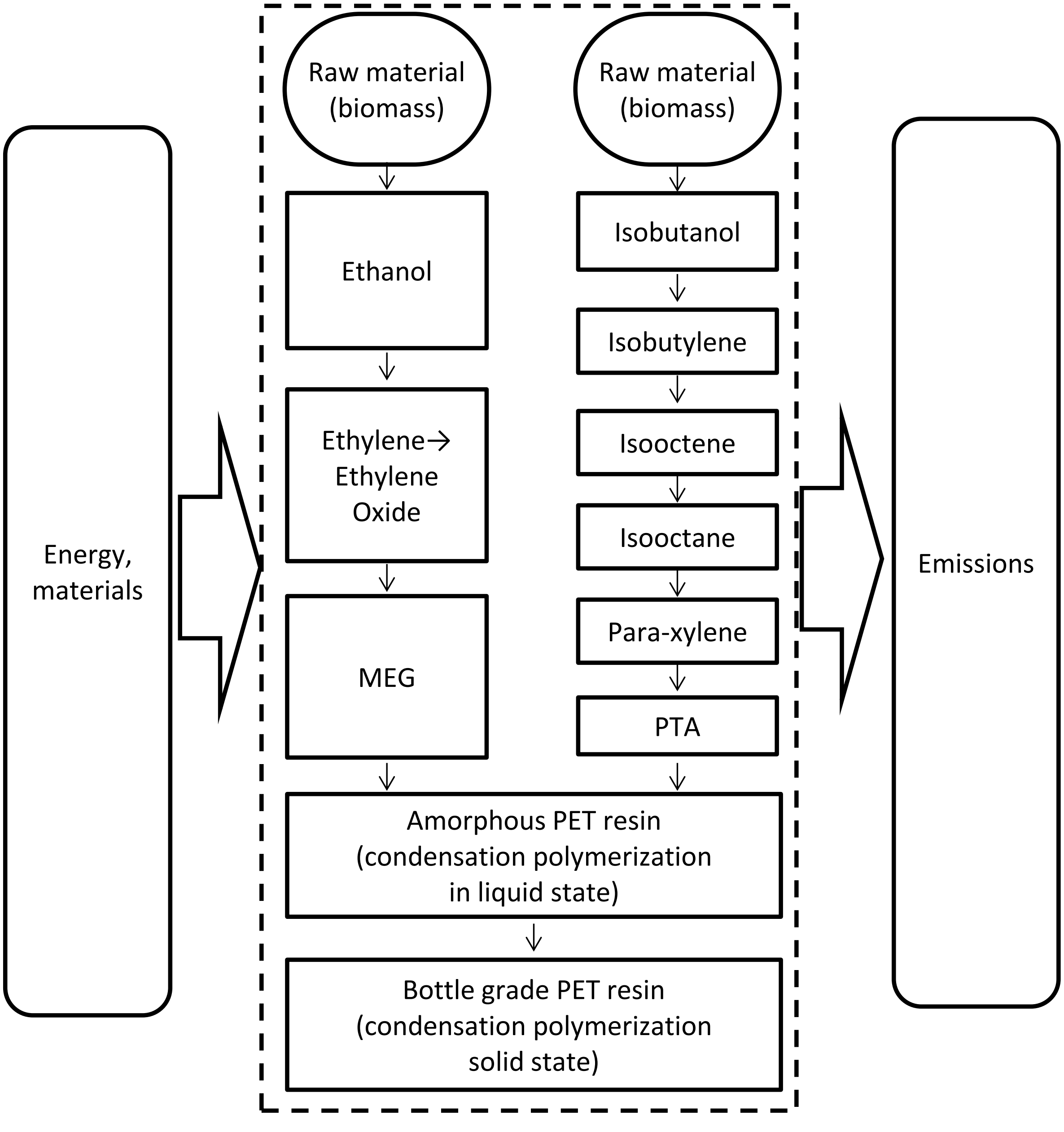
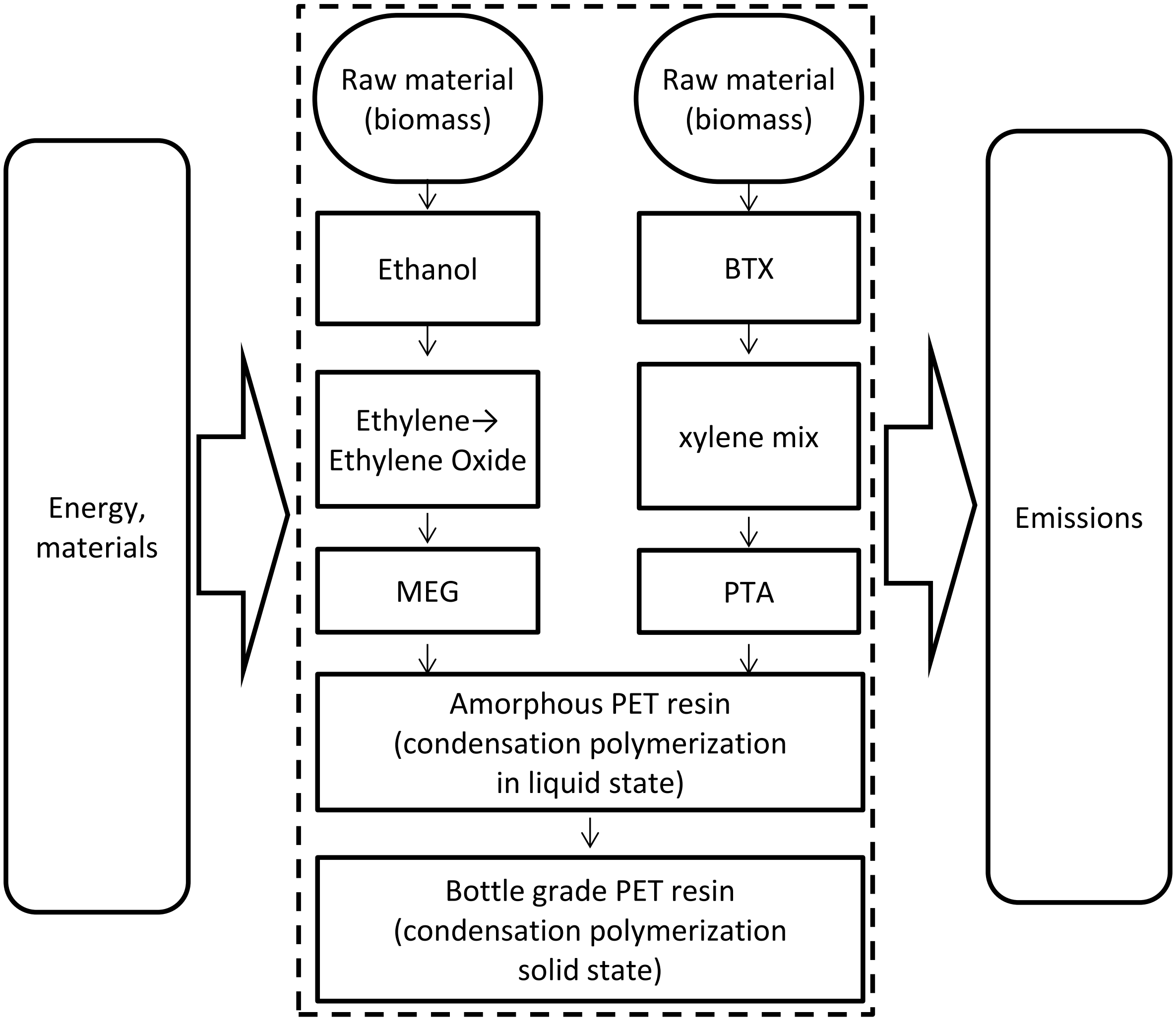


Figure 3. (cont'd)

Scenario 3 (PTA 3): BTX pathway



Included

-Raw material extraction
-Energy and fuel inputs
-Processing of raw materials and intermediate products

Excluded

- Capital equipment and maintenance
- Maintenance and operation of equipment
- Transportation of raw and processed materials
- Human labor

3.2.2. DATA COLLECTION, SOFTWARE AND DATABASES

In accordance with ISO 14040, the following steps were taken in this study. After the definition of system boundaries and objectives, data were collected in the life cycle inventory (LCI) stage. Since enough data from existing public sources could not be obtained, some literature data and patent data were used. In addition, some estimations based on similar chemical reactions and material processes were used. Therefore, the need to select appropriate benchmark processes was inevitable. Table 1 shows the order of priority for selecting the appropriate benchmark processes in this study. Each benchmark process used was selected in accord with these priorities.

Table 1. The order of priority for selecting the appropriate benchmark processes.

↑ priority

1.Chemical reaction type	same	almost same	bit different	different
2. Output material	same	almost same	bit different	different
3. Input material	same	almost same	bit different	different

← priority

The reason that the use of the same chemical reaction process gets the highest priority is that the type of chemical production process is heavily dependent on the type of chemical reaction. These chemical production processes included the machines themselves, their operations and process efficiency, which are important if we try to attach a high value to the process inventory data.

When operational energies were estimated from these benchmark processes, they were estimated as proportional to the output materials' weight. This is because the energy required to operate chemical production processes is typically much larger than the energy involved in the chemical reaction itself. For instance, dehydration of ethanol is an example. This stoichiometry can be written as follows;

$$C_2H_5OH \rightarrow C_2H_4(ethylene) + H_2O, \quad \Delta H_f = 42.91(kJ/mol)$$

Therefore, when1 kg of ethylene was produced, this system requires 1.54MJ of energy (= 1000 g ÷ 28 g/mol × 42.91 kJ/mol × 0.001 MJ/kJ), theoretically. However, it was reported that 7.4 MJ of energy is required to operate this system,[21] which is much higher than that of the theoretically estimated reaction energy demand. This difference seems to come from the operational energy to run the process. Since each target process was assumed to follow the same chemical reaction process as the benchmark, operational energies which were dominant in each production step were estimated as proportional to the output materials' weight. As for material amounts (input and other byproducts in one unit process), the amounts were estimated based on the stoichiometry of those processes.

Obtained data were classified and characterized in the impact analysis stage. In this study, we focused on several environmental midpoint categories and damage categories, which were resource consumption, global warming (climate change), acidification and eutrophication (ecosystem quality). Although this study focused on the U.S. region, the IMPACT 2002+ v2.1 method was selected in order to cover the above described categories. Energy inventory data was replaced with U.S. data.[22]

3.2.3. DATA CALCULATION METHOD

Collected LCI data were calculated using SimaPro 7.3.3.[23]

3.2.4. FUNCTIONAL UNIT

All impacts must be related to the functional unit. In this study, 1 kg of PET resin is the unit. PET resin is chosen because after the resin production, processes such as bottle blowing and assembly are totally the same as with the existing infrastructure, so this study concentrates on the part of the life cycle from raw material extraction to PET resin, where there are differences compared to the existing petroleum based PET synthesis pathway. Reference flows are the several chemical materials which finally can lead to the synthesis of PET resin.

3.2.5. CUT-OFF CRITERIA

In this study, if input and output flows are less than 1 % of the cumulative mass of all the inputs and outputs in each unit process, they are excluded, provided their environmental relevance is not a concern. Therefore, almost all catalysts used in catalytic conversion processes are excluded in this study.

3.2.6. ALLOCATION

Some by-products are generated in some processes. Since these materials are not used in later processes in this study, allocation is applied. Those allocations are applied on the basis of generated mass ratios unless the data sources already applied their own allocation rule. In such cases, we did not modify the allocation rule that had been applied.

For example, the economic allocation had been applied for DDGS (Dried Distillers Grains with Solubles) in the “Ethanol, 95 % in H_2O, from corn, at distillery/US U” data (from Ecoinvent).

3.2.7. LIFE CYCLE IMPACT ASSESSMENT METHODOLOGY, IMPACT CATEGORIES CONSIDERED

As described in section 3.2.2, several environmental impact categories were selected for the investigation in this study. For the purposes of succinct communication of the study results, the following impact categories are investigated:

- Terrestrial acidification/nutrification
- Aquatic acidification
- Aquatic eutrophication
- Global Warming
- Non-renewable energy
- Mineral extraction

3.2.8. DATA QUALITY REQUIREMENTS, AND ASSUMPTIONS

In this study, data quality requirements comply with ISO 14044. Some of the collected data are from the Ecoinvent, US-EI, and U.S. LCI databases. In addition, some literature data and estimated data derived from that literature data are used in this study. All data dates from the past 10 years. As for geographical coverage, all materials and process energy data are based on U.S. data. Since some of the unit processes used in this study are based on data from other countries; the energy sources in these unit processes have been substituted by U.S. energy data. As for technological coverage, data are obtained from databases based on current commercial scale factory operations. On the other hand, some processes are still under investigation or at pilot plant scale. Therefore, these data are estimated based on the assumption that related processes (the same at similar chemical reaction) which are now already at commercial scale or state of the art process operations have a correlation to the relevant processes.

Since this study will contain some limitations of LCI data quality, each production process was assigned a data quality indicator. Although it is difficult to adapt a comprehensive data quality and reliability check on the data reported from several literature sources and databases, consistency and completeness checks for mass and energy balance results were conducted. Also, the quality of each data set was evaluated with the use of a pedigree matrix (Appendix A).

4. MUCONIC ACID PATHWAY PRODUCTION

This study includes the cradle to gate environmental impacts of bio-based PET with the scenario of different PTA production methods. This study concentrates on the steps from raw material extraction to PET resin. This is because only this process range differs from the existing petroleum based PET synthesis pathway. This study has three scenarios, and each scenario has different PTA synthesis processes. In this section, the process of MEG synthesis is described first. Then, the PTA synthesis process through muconic acid is described. Finally, the PET resin synthesis process for bottle grade resin is described.

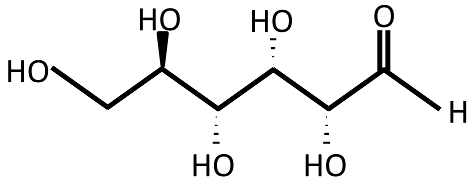
4.1. PROCESS DESCRIPTION AND LCI DATA

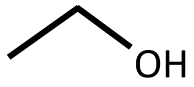
4.1.1. BIO-ETHANOL PRODUCTION (MEG SYNTHESIS STEP 1)

All three scenarios include the same MEG synthesis processes. A raw material which has a C_6 structure such as a starch crop or sugar crop is produced. In the next step, raw materials are converted into C_6 sugar by fractionation and hydrolysis, and then converted to ethanol by fermentation. Obtained ethanol is dehydrated into ethylene, and then oxidized and hydrated into MEG. Synthesized MEG is used in condensation polymerization in order to produce bottle grade PET resin.

In this study, corn (technically the glucose in the corn) harvested in the U.S. is fractionated and goes through hydrolysis and fermentation to be converted into ethanol. The following equation shows the stoichiometry of this process.

$$C_6H_{12}O_6 \quad \rightarrow \quad 2C_2H_5OH\ (ethanol) \quad + \quad 2CO_2$$





Obtained ethanol is then purified to increase its concentration. Table 2 shows the inputs and outputs for this process. Flow values are for 1 kg ethanol production. In this study, all materials' weight and energy balances were checked based on the law of conservation of mass and energy, which is consistent with the stoichiometry. The detailed calculation procedure is described in Appendix C.

Table 2. Input/Output flows for 1 kg of bio-ethanol.

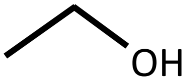
Input		
Water, unspecified natural origin/m^3	1.430E-05	m^3
Water, cooling, unspecified natural origin/m^3	4.840E-03	m^3
Amorphous, polyethylene terephthalate, granulate, at plant/RER with US electricity	7.800E-01	kg
Purified terephthalic acid	1.940E-01	kg
Mono-ethylene glycol, at plant/RER U with US electricity	7.610E-02	kg
Nitrogen, liquid, at plant/RER	3.660E-02	kg
Electricity, medium voltage, production UCTE, at grid/UCTE	1.890E-01	kWh
Heat, heavy fuel oil, at industrial furnace 1MW/RER	2.840E-01	MJ
Heat, light fuel oil, at industrial furnace 1MW/RER	9.460E-02	MJ
Heat, natural gas, at industrial furnace >100kW/RER	3.790E-01	MJ
Heat, at hard coal industrial furnace 1-10MW/RER	1.720E-01	MJ
Steam, for chemical processes, at plant/RER	1.000E-01	kg

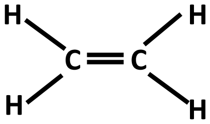
Output		
Heat, waste	6.800E-01	MJ
Particulates, > 10 um	3.200E-07	kg
Particulates, > 2.5 um, and < 10um	4.300E-07	kg
Particulates, < 2.5 um	2.500E-07	kg
NMVOC, non-methane volatile organic compounds, unspecified origin	1.000E-06	kg
BOD5, Biological Oxygen Demand	6.310E-04	kg
COD, Chemical Oxygen Demand	6.310E-04	kg
DOC, Dissolved Organic Carbon	6.410E-07	kg
TOC, Total Organic Carbon	6.410E-07	kg
Suspended solids, unspecified	9.000E-06	kg
Hydrocarbons, unspecified	1.000E-06	kg
Disposal, hazardous waste, 0% water, to underground deposit/DE	4.300E-04	kg
Disposal, average incineration residue, 0% water, to residual material landfill/CH	1.810E-03	kg
Disposal, plastics, mixture, 15.3% water, to municipal incineration/CH	6.300E-04	kg
Disposal, municipal solid waste, 22.9% water, to municipal incineration/CH	4.000E-05	kg

4.1.2. ETHYLENE OXIDE PRODUCTION (MEG SYNTHESIS STEP 2)

Obtained ethanol is then converted into ethylene by a dehydration process. The following equation shows the stoichiometry of this process.

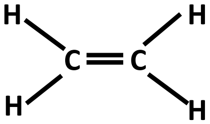
$$C_2H_5OH \quad \rightarrow \quad C_2H_4(ethylene) \quad + \quad H_2O$$





Obtained ethylene is then converted into ethylene oxide by oxidation. The following equation shows the stoichiometry of this process.

$$2\,C_2H_4 \quad + \quad O_2 \quad \rightarrow \quad 2C_2H_4O(ethylene\ oxide)$$



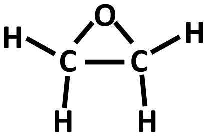


Table 3 shows the inputs and outputs for this process. Flow values are for 1 kg ethylene oxide production. Detailed inventory source data are described in Appendix C.

Table 3. Input/Output flows for 1 kg of bio-ethylene oxide.

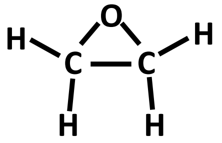
Input		
Oxygen, liquid, at plant/RER with US electricity	4.630E-01	kg
Electricity, medium voltage, production UCTE, at grid/UCTE with US electricity	3.300E-01	kWh
bio Ethanol, 99.7% in H2O, from biomass, at distillation/US	8.250E-01	kg

Output		
Carbon dioxide, fossil	2.100E-01	kg
Carbon monoxide, fossil	1.100E-04	kg
Ethene	2.300E-04	kg
Ethylene oxide	2.000E-05	kg
Heat, waste	1.200E+00	MJ
Methane, fossil	7.500E-05	kg
NMVOC, non-methane volatile organic compounds, unspecified origin	2.400E-04	kg
BOD5, Biological Oxygen Demand	1.900E-04	kg
COD, Chemical Oxygen Demand	1.900E-04	kg
DOC, Dissolved Organic Carbon	2.000E-04	kg
TOC, Total Organic Carbon	2.000E-04	kg
Disposal, catalyst base Eth.oxide prod., 0% water, to residual material landfill/CH with US electricity	5.000E-04	kg

4.1.3. MONO ETHYLENE GLYCOL PRODUCTION (MEG SYNTHESIS STEP 3)

Obtained ethylene oxide is then converted into mono ethylene glycol (MEG) by a hydration process. The following equation shows the main stoichiometry of this process.

$$C_2H_4O \qquad + \qquad 2H_2O \qquad \rightarrow \qquad 2C_2H_6O_2\ (MEG)$$



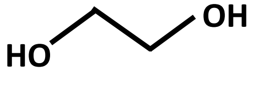


Table 4 shows the inputs and outputs for this process. Flow values are for 1 kg MEG production. As in the previous steps, detailed inventory source data and calculation procedures are described in Appendix C.

Table 4. Input/Output flows for 1 kg of bio-MEG.

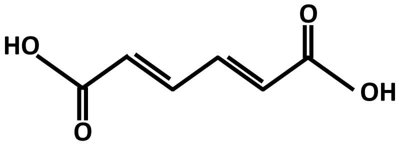
Input		
Water, cooling, unspecified natural origin/m^3	2.400E-02	m^3
Bio Ethylene oxide, at plant/RER with US electricity	5.146E-01	kg
Bio Ethanol, 99.7% in H2O, from biomass, at distillation/US U from no transport corn	5.380E-01	kg
Heat, natural gas, at industrial furnace >100kW/RER	2.000E+00	MJ
Electricity, medium voltage, production UCTE, at grid/UCTE with US electricity	3.330E-01	kWh

Output		
Heat, waste	1.199E+00	MJ
Ethylene oxide	2.619E-03	kg
Ethanol	2.739E-03	kg
Carbon dioxide, fossil	9.245E-02	kg
BOD5, Biological Oxygen Demand	9.160E-03	kg
COD, Chemical Oxygen Demand	9.160E-03	kg
DOC, Dissolved Organic Carbon	2.860E-03	kg
TOC, Total Organic Carbon	2.860E-03	kg

4.1.4. MUCONIC ACID PRODUCTION (PTA SYNTHESIS STEP 1)

In this PTA scenario, raw material which contains lignin is produced. Lignin is the large group of aromatic polymers derived from mainly wood and cell walls of plants.[24] In the next step, lignin is fermented and degraded to muconic acid as shown in the following reaction.

$$lignin \quad \rightarrow (fermentation) \rightarrow \quad C_6H_{12}O_4(mucconic\ acid)\ ,\quad CO_2$$



Since this process is not available in databases, estimation was used to collect LCI data. Duuren *et al*. did an LCA from raw materials to adipic acid in their study.[10] They assumed adipic acid obtained in their process would be produced by hydrogenation of muconic acid under slightly elevated pressure (3.5 bar). Therefore, we assumed that LCI data which excluded this hydrogenation and later processes represents the LCI data between raw material and muconic acid. In this study, since Duuren's study showed their system demands and emissions data with respect to each process (fermentation, hydrogenation, evaporation and crystallization), we used their fermentation process data. Also, the values of feed demands for bacterial growth used in this fermentation process, and feedstock demands for fermentation shown in their study were applied.

In our study, Cumulative Exergy Demand (CExD) which would be useful to estimate the energy efficiency was excluded since we don't need to compare it with the other PTA production scenarios. Also, we replaced the energy source with electricity, gasoline, and diesel data although Duuren used the Cumulative Energy Demand (CED) as input energy. Table 5 is the inputs and outputs for this process. Flow values are for 1 kg muconic acid production. As in the previous steps, detailed inventory source data and the calculation procedures are described in Appendix C.

Table 5. Input/Output flows for 1 kg of muconic acid.

Input		
Electricity, medium voltage, production UCTE, at grid/UCTE with US electricity	5.794	MJ
Gasoline, combusted in industrial equipment/US	0.030	l
Diesel, combusted in equipment/US	0.144	l
Hydrogen	0.028	kg
Ammonium sulphate	0.072	kg
Sodium phosphate	0.051	kg
Sodium hydroxide	0.576	kg
Hydrochloric acid	0.556	kg

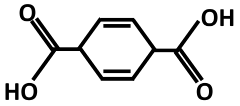
Output		
Carbon dioxide	0.723	kg
Dinitrogen monoxide	0.013	kg

4.1.5. CYCLOHEXA-2,5-DIENE-1,4-DICARBOXYLATE PRODUCTION (PTA SYNTHESIS STEP 2)

Obtained muconic acid is then converted into cyclohexa-2,5-diene-1,4-dicarboxylate using a Diels-Alder process according to the specific patents.[25] In the patent, muconic acid and acetylene are charged in a lab scale Parr reactor, and the reactor is then heated to 200℃ and held at this temperature for 12 hours. An initial pressure of 500 psi is applied. The following equation shows the stoichiometry of this process. The same reaction pathway was assumed in this study.

$$C_6H_6O_4 \quad + \quad C_2H_2$$

$$\rightarrow \quad C_8H_8O_4(\text{Cyclohexa} - 2{,}5 - \text{diene} - 1{,}4 - \text{dicarboxylate})$$



Since this process is not available in databases, estimation was used to calculate LCI data. The benchmarked process was the production of cyclohexane from benzene. As described in section 2.2.2, the same chemical reaction, which is a Diels-Alder reaction in this case, was selected. An LCA study by Zhang[26] compared the inputs and emissions for the production of cyclohexane by solvent-based production and vapor phase industrial production. In this LCA study, LCI data were estimated from Zhang's vapor phase industrial process data. Also, as in section 2.2.2, the energy amount required for this process was estimated as proportional to the output materials' weight ratio. That is to say, in this case, the ratio was based on the relative mass of cyclohexa-2,5-diene-1,4-dicarboxylate and cyclohexane. The material amounts were estimated based on the stoichiometry of this process as described above.

Table 6 shows the inputs and outputs for this process. Flow values are for 1 kg cyclohexa-2,5-diene-1,4-dicarboxylate production. As in the previous steps, detailed inventory source data and calculation procedures are described in Appendix C. Since there is no bio-based LCI data for acetylene, we used the petrochemical based LCI data available in the US-EI database.

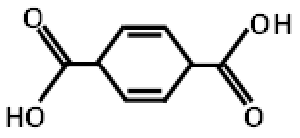
Table 6. Input/Output flows for 1 kg of cyclohexa-2,5-diene-1,4-dicarboxylate.

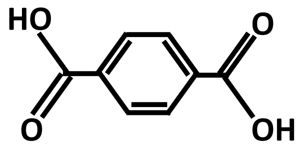
Input		
Electricity, medium voltage, production UCTE, at grid/UCTE with US electricity	4.100E-02	kWh
Steam, for chemical processes, at plant/RER with US electricity	1.000E-01	kg
muconic acid from lignin (wheat stover)	8.450E-01	kg
Acetylene, at regional storehouse/CH with US electricity	1.550E-01	kg
Output		
muconic acid from lignin (wheat stover)	4.270E-04	kg
Acetylene, at regional storehouse/CH with US electricity	2.981E-06	kg

4.1.6. PTA PRODUCTION (PTA SYNTHESIS STEP 3)

Obtained cyclohexa-2,5-diene-1,4-dicarboxylate is then converted into TPA using dehydrogenation processes as described in Burke's patent.[25] According to this patent, subsequent exposure to air or oxygen rapidly converts cyclohexa-2,5-diene-1,4-dicarboxylate to TPA. The following equation shows the stoichiometry of this process.

$$2C_8H_8O_4 \quad + \quad O_2 \quad \rightarrow \quad 2C_8H_6O_4(TPA) \quad + \quad 2H_2O$$





Since this process is not available in databases, estimation was used to calculate LCI data. The benchmarked process is dehydrogenation of xylene to TPA, and its purification to PTA. This benchmark process LCI data was based on the database in the SimaPro software. LCI data were estimated from the benchmark process data. As described in section 2.2.2, the energy amount needed for this process was estimated as proportional to the output materials' weight ratio. The material amounts were estimated based on the stoichiometry of this process as described above. The water mass generated in this chemical reaction was excluded because of its insignificant contribution to environmental impacts. This same approach for water was used in all other steps, even if not explicitly mentioned.

Table 7 shows the inputs and outputs for these processes. Flow values are for 1 kg PTA production. As in the previous steps, detailed inventory source data and calculation procedures are described in Appendix C.

Table 7. Input/Output flows for 1 kg of PTA.

Input		
Water, cooling, unspecified natural origin/m^3	3.420E-04	m^3
cyclohexa-2,5-diene-1,4-dicarboxylate	1.012E+00	kg
Acetic acid, 98% in H2O, at plant/RER with US electricity	5.000E-02	kg
Water, completely softened	4.250E-01	kg
oxygen	9.600E-02	kg
Sodium hydroxide, 50% in H2O, production mix, at plant/RER with US electricity	1.450E-03	kg
Nitrogen, liquid, at plant/RER with US electricity	4.880E-02	kg
Electricity, medium voltage, production UCTE, at grid/UCTE with US electricity	4.690E-01	kWh
Heat, heavy fuel oil, at industrial furnace 1MW/RER with US electricity	6.370E-01	MJ
Heat, light fuel oil, at industrial furnace 1MW/RER with US electricity	2.120E-01	MJ
Heat, natural gas, at industrial furnace >100kW/RER with US electricity	4.580E-01	MJ
Heat, at hard coal industrial furnace 1-10MW/RER with US electricity	3.230E-01	MJ
Steam, for chemical processes, at plant/RER with US electricity	6.400E-01	kg
Electricity, at grid, US	-8.598E-02	kWh
Natural gas, combusted in industrial boiler/US	-1.009E-01	m^3
Liquefied petroleum gas, combusted in industrial boiler/US	-5.020E-03	l
Bituminous coal, combusted in industrial boiler/US	-1.699E-02	kg
Output		
Heat, waste	1.690E+00	MJ
Particulates, > 10 um	2.880E-05	kg
Particulates, > 2.5 um, and < 10um	3.870E-05	kg
Particulates, < 2.5 um	2.250E-05	kg
Hydrocarbons, aromatic	3.780E-04	kg
NMVOC, non-methane volatile organic compounds, unspecified origin	1.100E-04	kg
BOD5, Biological Oxygen Demand	1.300E-03	kg
COD, Chemical Oxygen Demand	1.300E-03	kg
DOC, Dissolved Organic Carbon	1.220E-05	kg
TOC, Total Organic Carbon	1.220E-05	kg
Suspended solids, unspecified	2.560E-04	kg
Hydrocarbons, unspecified	1.400E-05	kg
Disposal, hazardous waste, 0% water, to underground deposit/DE with US electricity U	2.000E-04	kg
Disposal, average incineration residue, 0% water, to residual material landfill/CH with US electricity	6.000E-03	kg

4.1.7. POLYETHYLENE TEREPHTHALATE RESIN PRODUCTION

Polyethylene terephthalate (PET) resin can be obtained through the condensation polymerization process between MEG and PTA. The PET resin is initially in an almost amorphous state, and its viscosity is not appropriate for bottle grade resin. Therefore, the amorphous resin goes through additional polymerization in the solid state in order to increase its viscosity. Tables 8 and 9 show the inputs and outputs for these processes. Flow values are for 1 kg PET resin production. The inventory data sources used are “polyethylene terephthalate, granulate, amorphous, at plant/kg/RER” (from Ecoinvent), which covers condensation polymerization in the liquid state. Then, “ polyethylene terephthalate, granulate, bottle grade, at plant/kg/RER” (from Ecoinvent) is used, by which process amorphous resin goes through the solid state polymerization and bottle grade PET resin can be produced.

Table 8. Input/Output flows for 1 kg of PET resin. (step 1: amorphous state)

Input

Water, unspecified natural origin/m^3	1.630E-04	m^3
Water, cooling, unspecified natural origin/m^3	6.400E-03	m^3
Purified terephthalic acid	8.750E-01	kg
Mono-ethylene glycol, at plant/RER U with US electricuty	3.340E-01	kg
Nitrogen, liquid, at plant/RER with US electricity	2.980E-02	kg
Electricity, medium voltage, production UCTE, at grid/UCTE with US electricity	1.940E-01	kWh
Heat, heavy fuel oil, at industrial furnace 1MW/RER with US electricity	4.940E-01	MJ
Heat, light fuel oil, at industrial furnace 1MW/RER with US electricity	1.650E-01	MJ
Heat, natural gas, at industrial furnace >100kW/RER with US electricity	6.650E-01	MJ
Heat, at hard coal industrial furnace 1-10MW/RER with US electricity	3.060E-01	MJ
Steam, for chemical processes, at plant/RER with US electricity	9.400E-01	kg

Output

Heat, waste	7.000E-01	MJ
Particulates, > 10 um	3.200E-07	kg
Particulates, > 2.5 um, and < 10um	4.300E-07	kg
Particulates, < 2.5 um	2.500E-07	kg
NMVOC, non-methane volatile organic compounds, unspecified origin	9.000E-05	kg
BOD5, Biological Oxygen Demand	1.600E-04	kg
COD, Chemical Oxygen Demand	1.020E-03	kg
DOC, Dissolved Organic Carbon	2.620E-04	kg
TOC, Total Organic Carbon	2.620E-04	kg
Suspended solids, unspecified	1.000E-06	kg
Hydrocarbons, unspecified	4.990E-04	kg
Disposal, hazardous waste, 0% water, to underground deposit/DE with US electricity U	9.000E-05	kg
Disposal, average incineration residue, 0% water, to residual material landfill/CH with US electricity	4.000E-04	kg
Disposal, plastics, mixture, 15.3% water, to municipal incineration/CH with US electricity	2.310E-03	kg
Disposal, municipal solid waste, 22.9% water, to municipal incineration/CH with US electricity	8.800E-04	kg

Table 9. Input/Output flows for 1 kg of PET resin (step 2: bottle grade).

Input		
Water, unspecified natural origin/m^3	1.430E-05	m^3
Water, cooling, unspecified natural origin/m^3	4.840E-03	m^3
Amorphous, polyethylene terephthalate, granulate, at plant/RER with US electricity	7.800E-01	kg
Purified terephthalic acid	1.940E-01	kg
Mono-ethylene glycol, at plant/RER U with US electricity	7.610E-02	kg
Nitrogen, liquid, at plant/RER	3.660E-02	kg
Electricity, medium voltage, production UCTE, at grid/UCTE	1.890E-01	kWh
Heat, heavy fuel oil, at industrial furnace 1MW/RER	2.840E-01	MJ
Heat, light fuel oil, at industrial furnace 1MW/RER	9.460E-02	MJ
Heat, natural gas, at industrial furnace >100kW/RER	3.790E-01	MJ
Heat, at hard coal industrial furnace 1-10MW/RER	1.720E-01	MJ
Steam, for chemical processes, at plant/RER	1.000E-01	kg

Output		
Heat, waste	6.800E-01	MJ
Particulates, > 10 um	3.200E-07	kg
Particulates, > 2.5 um, and < 10um	4.300E-07	kg
Particulates, < 2.5 um	2.500E-07	kg
NMVOC, non-methane volatile organic compounds, unspecified origin	1.000E-06	kg
BOD5, Biological Oxygen Demand	6.310E-04	kg
COD, Chemical Oxygen Demand	6.310E-04	kg
DOC, Dissolved Organic Carbon	6.410E-07	kg
TOC, Total Organic Carbon	6.410E-07	kg
Suspended solids, unspecified	9.000E-06	kg
Hydrocarbons, unspecified	1.000E-06	kg
Disposal, hazardous waste, 0% water, to underground deposit/DE	4.300E-04	kg
Disposal, average incineration residue, 0% water, to residual material landfill/CH	1.810E-03	kg
Disposal, plastics, mixture, 15.3% water, to municipal incineration/CH	6.300E-04	kg
Disposal, municipal solid waste, 22.9% water, to municipal incineration/CH	4.000E-05	kg

4.2. LCI RESULTS

4.2.1. PROCESS ENERGY DEMAND

Table 10 shows the summary of process energy required in this process to produce 1 kg of PET bottle grade resin from raw material extraction. The process energy data can be used to evaluate the sensitivity of each process. The sensitivity check is described in the interpretation section.

Table 10. Process energy in the muconic acid pathway, for 1 kg of PET resin.

		Process energy demand (MJ)
MEG		20.79
PTA 1	step 1	79.07
	step 2	18.82
	step 3	23.94
Amorphous PET resin		13.69
Bottle grade PET resin		9.152
Total		165.5

4.3. LCIA RESULTS (IMPACT 2002+ v2.1)

In this section, the LCIA results of 1 kg of PET resin production through the muconic acid pathway are presented. As described in the previous section, the impact assessment results were calculated using characterization factors published by IMPACT 2002+ v2.1. Figure 4 shows the system structure for the production of 1 kg bottle grade PET resin in this scenario. The indicator used is global warming (kg CO_2 eq). Processes contributing less than 10 % of the total are not shown; therefore not all processes are shown.

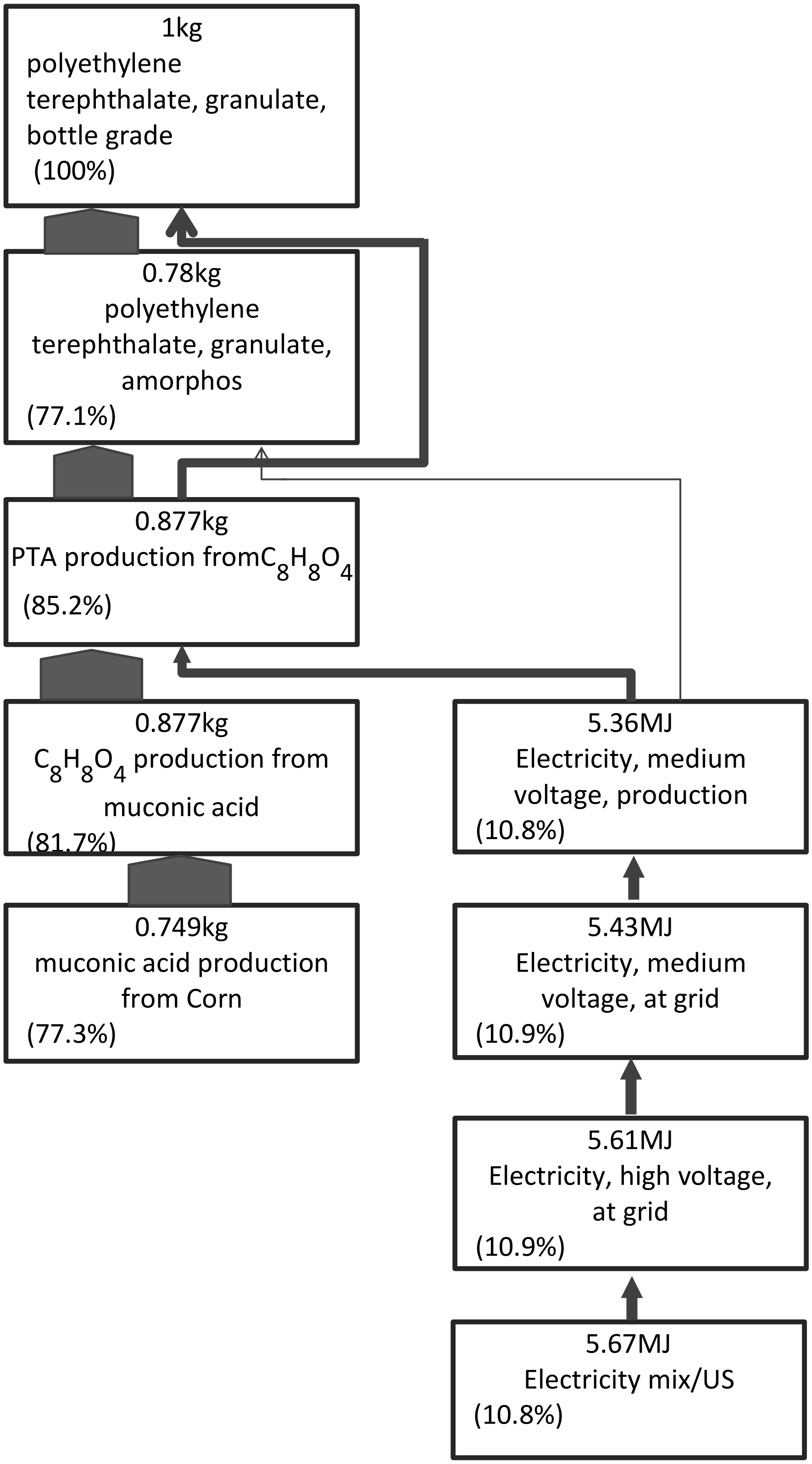


Figure 4. System structure for scenario 1.

Figure 5 shows the results for the terrestrial acidification/nutrification, aquatic acidification, aquatic eutrophication, global warming, non-renewable energy and mineral extraction index for each unit process. The dominant process in all impact categories is PTA 1 (step 1), which is the production process for muconic acid.

The other remarkable feature of these results is that MEG (step 1) , which is the production process of bio-ethanol from corn, has the highest value in the aquatic eutrophication category. This process also has the second highest value in the terrestrial acidification/nitrification category.

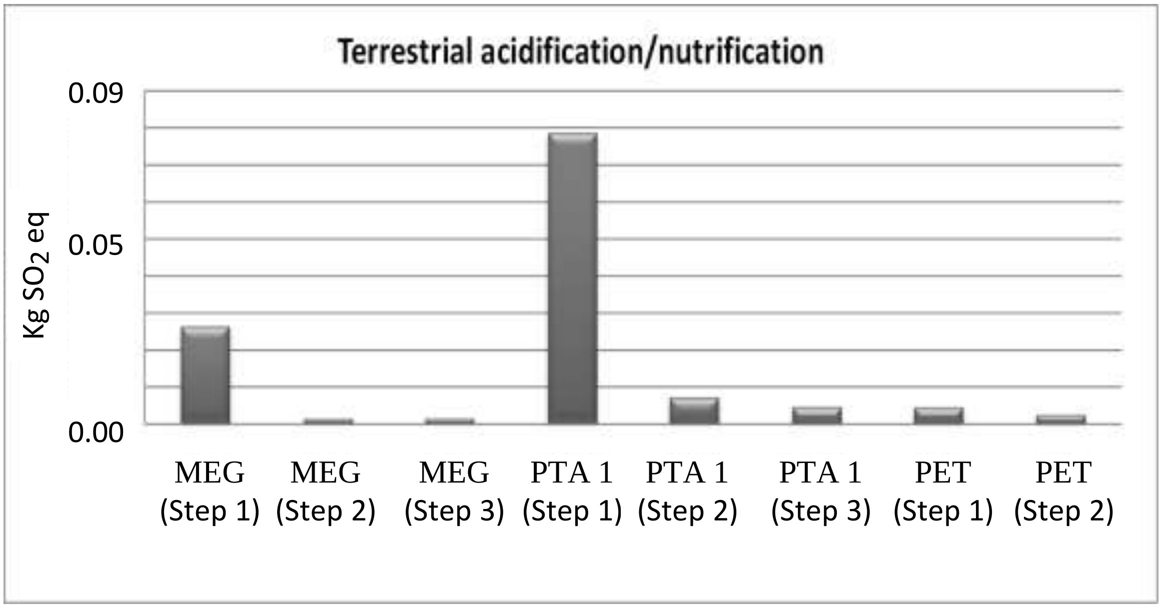
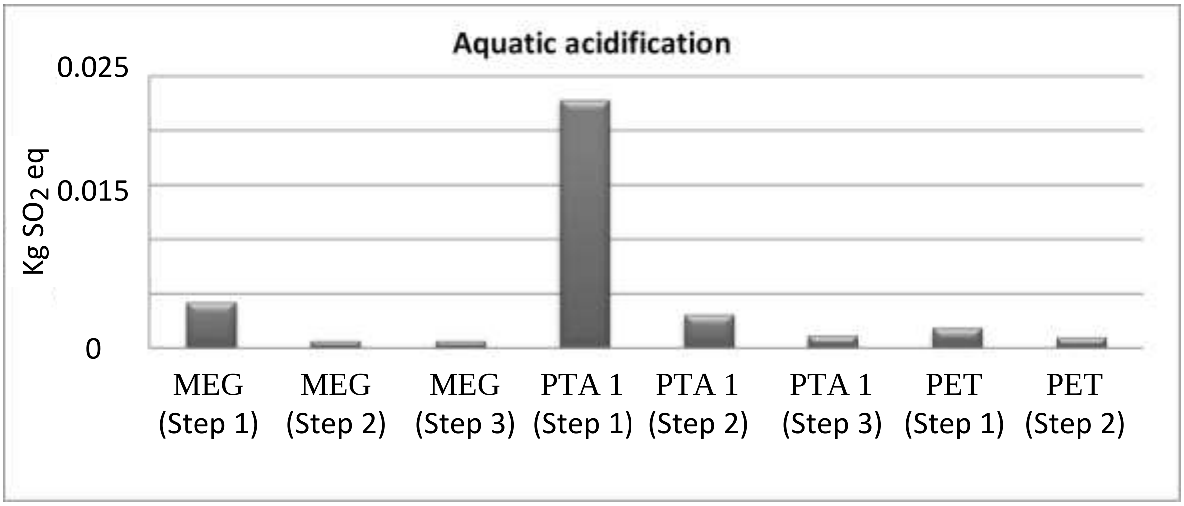
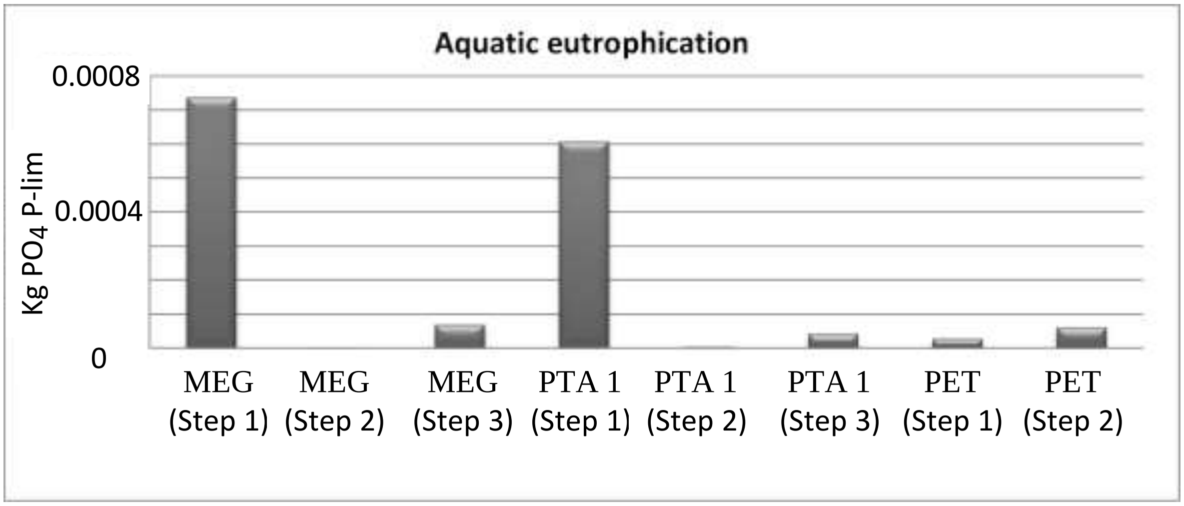


Figure 5. IMPACT 2002+ v2.1 result of scenario1 (muconic acid pathway), for 1 kg of PET resin.

Figure 5. (cont'd)





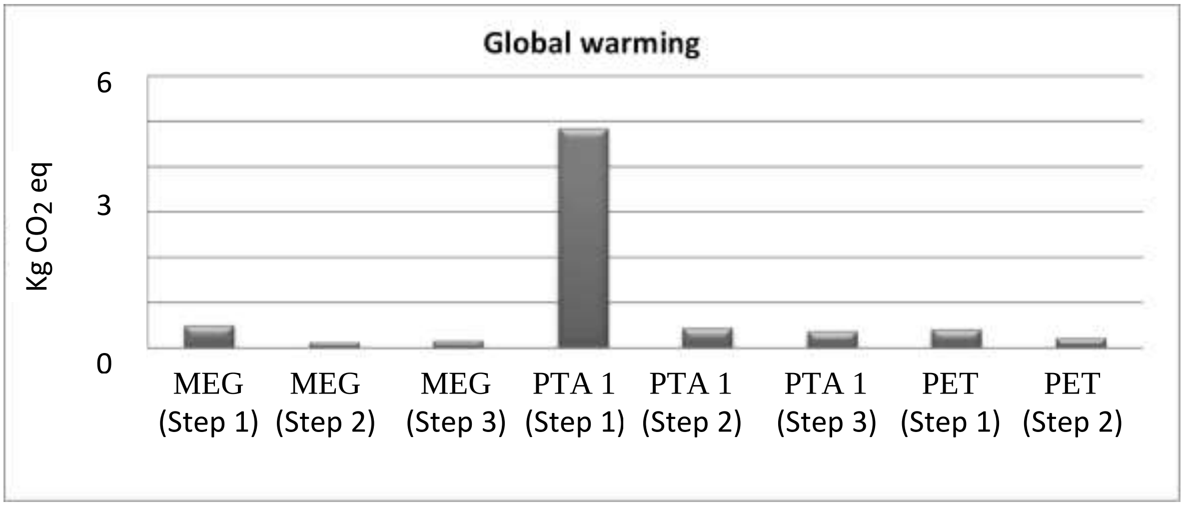
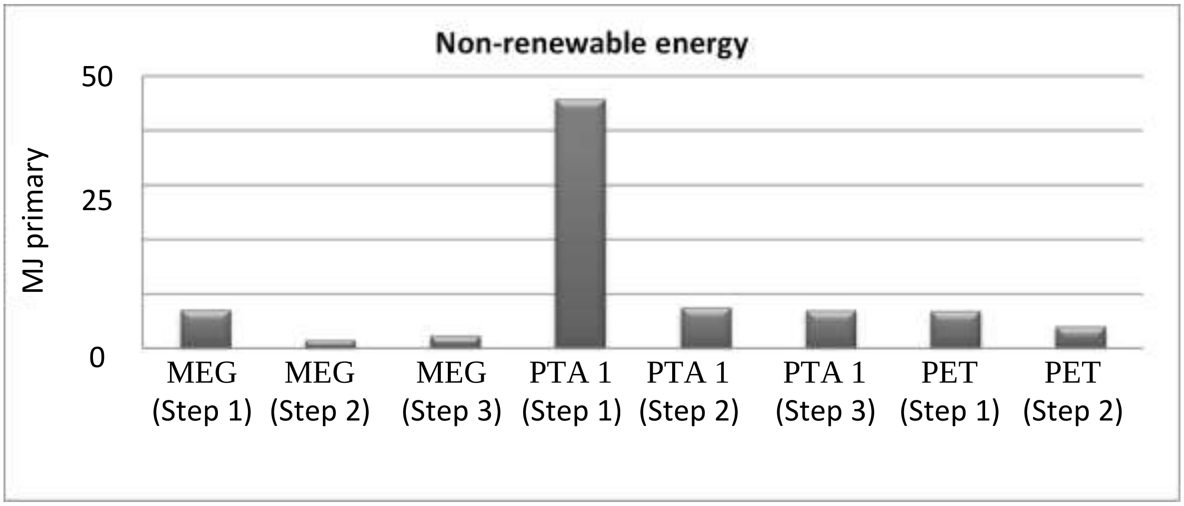
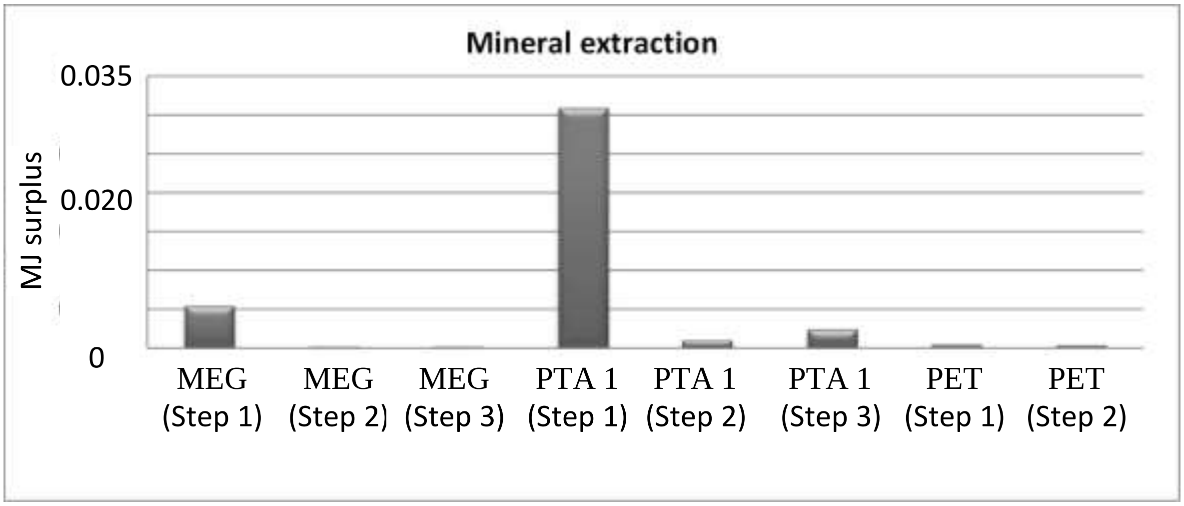


Figure 5. (cont'd)





5. ISOBUTANOL PATHWAY PRODUCTION

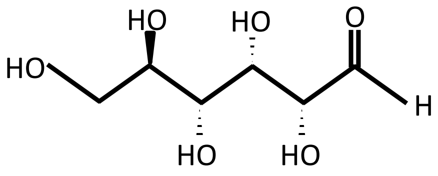
This section describes PTA synthesis through isobutanol as an intermediate.

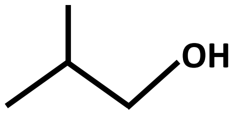
5.1. PROCESS DESCRIPTION AND LCI DATA

5.1.1. BUTANOL PRODUCTION (PTA 2 SYNTHESIS STEP 1)

We considered two pathways to obtain bio-based butanol. In the first pathway, we focused on isobutanol. In this scenario, raw material which contains glucose is produced. Specific yeasts which produce bio-ethanol from a carbon source can be modified to produce isobutanol. [27][28] With the use of such microorganisms, raw materials are fermented and then converted into isobutanol. The following equation shows the stoichiometry of this process.

$$C_6H_{12}O_6 + 7.5H_2O \rightarrow C_4H_{10}O(isobutanol) + 2CO_2 + 8.5H_2O$$





Since this process data is not available in databases, estimation was used to calculate the LCI data. The benchmarked process is fermentation of glucose to ethanol, which is described in the MEG synthesis process. LCI data were estimated from the benchmark process data. As described in section 2.2.2, the energy amount needed for this process was estimated as proportional to the output materials' weight ratio. The material amounts were estimated based on the stoichiometry of this process as described above.

Table 11 shows the inputs and outputs for this process. Flow values are for 1 kg isobutanol production. As in the previous steps, detailed inventory source data and calculation procedures are described in Appendix C.

Table 11. Input/Output flows for 1 kg of isobutanol.

Input		
Corn, at farm/US U	4.013	kg
Tap water, at user/	5.255	kg
Sulphuric acid, liquid, at plant	0.030	kg
Soda, powder, at plant	0.045	kg
Ammonium sulphate, as N, at regional storehouse	0.012	kg
Diammonium phosphate, as N, at regional storehouse	0.012	kg
Heat, natural gas, at industrial furnace >100kW	5.766	MJ
Electricity, medium voltage, at grid/US	0.178	kWh

Output		
Carbon dioxide, biogenic	2.758	kg
Heat, waste	4.211	MJ
Treatment, sewage, from residence, to wastewater treatment, class	0.002	m3

Alternatively, there is inventory data for the production of butanol from corn,[29] using the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model, a full life-cycle model sponsored by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy.[30] However, the butanol type in this process appears to be n-butanol since the production process is the ABE (acetone-butanol-ethanol) fermentation process. This butanol inventory data was considered as a reference process in this study. Table 12 shows the inputs and outputs for this process. Flow values are for 1 kg n-butanol production. As in the previous steps, detailed inventory source data and calculation procedures are described in Appendix C.

Table 12. Input/Output flows for 1 kg of n-butanol (GREET).

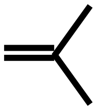
Input		
Corn, at farm/US	5.554	kg
Heat, natural gas, at industrial furnace >100kW/RER	9935	Btu
Electricity	0.152	kWh
Fertiliser (N)	0.036	kg
Fertiliser (P)	0.013	kg
Fertiliser (K_2O)	0.015	kg

Output		
Acetone, liquid, at plant/RER with US electricity	0.149	kg
DDGS, from corn, at distillery/US	0.457	kg

5.1.2. ISOBUTYLENE PRODUCTION (PTA 2 SYNTHESIS STEP 2)

Obtained isobutanol is then converted into isobutylene by dehydration. The following equation shows the stoichiometry of this process.

$$C_4H_{10}O \quad \rightarrow \quad C_4H_8(isobutylene) \quad + \quad H_2O$$



Since this process data is not available in databases, estimation was used to calculate the LCI data. The benchmarked process is dehydration of ethanol to ethylene. Liptow *et al*. did LCA research in this area, and LCI data in this study were estimated from their process data.[21] As described in section 2.2.2, the energy needed for this process was estimated as proportional to the output materials' weight ratio. The material amounts were estimated based on the stoichiometry of this process as described above. Table 13 shows the inputs and outputs for this process. Flow values are for 1 kg isobutylene production. As in the previous steps, detailed inventory source data and calculation procedures are described in Appendix C.

Table 13. Input/Output flows for 1 kg of isobutylene.

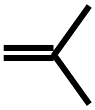
Input		
Heat, natural gas, at industrial furnace >100kW	5.600E+00	MJ
Electricity, medium voltage, at grid/US	1.800E+00	MJ
Bio-isobutanol	1.321E+00	kg

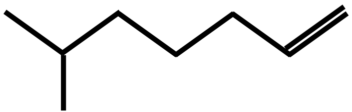
Output		
Methane	1.500E-03	kg
Carbon monoxide	2.000E-04	kg
Carbon dioxide	3.270E-01	kg
Dinitrogen monoxide	1.200E-05	kg
NMVOC	1.100E-05	kg
NOx	1.500E-03	kg
SO_2	1.000E-02	kg

5.1.3. ISOOCTENE PRODUCTION (PTA 2 SYNTHESIS STEP 3)

Obtained isobutylene is then converted into isooctene by a dimerization and hydrogenation process. The following equation shows the stoichiometry of this process.

$$2C_4H_8 \quad + \quad H_2 \quad \rightarrow \quad C_8H_{16}(isooctene)$$





Since this process data is not available in databases, estimation was used to calculate LCI data. The benchmarked process is the production of isooctene from C_4

components. This process is common in the petrochemical industry.[31][32] Such existing process data is for production of isooctene from various components which include 15 % isooctane, and for which it is said that the isobutylene to isooctene reaction is the most dominant.[33] In this study, although we used 100 % isobutylene as the input material, the process efficiency was assumed to be the same as the unpurified input case since there was no basis for any other assumption. Therefore, the energy amount needed for this study's process was assumed to be the same as that of existing process data for isooctene synthesis.

Table 14 shows the inputs and outputs for this process. Flow values are for 1 kg isooctene production. As in the previous steps, detailed inventory source data and calculation procedures are described in Appendix C.

Table 14. Input/Output flows for 1 kg of isooctene.

Input		
Steam, for chemical processes, at plant/RER with US electricity	2.000E+00	kg
Oxygen, liquid, at plant/RER with US electricity	1.319E-03	kg
Isobututylene	1.000E+00	kg
water	2.398E-03	kg

Output		
Carbon dioxide	3.330E-01	kg

5.1.4. ISOOCTANE PRODUCTION (PTA 2 SYNTHESIS STEP 4)

Obtained isooctene is then converted into isooctane by hydrogenation. The following equation shows the stoichiometry of this process.

$$C_8H_{16} \quad + \quad H_2 \quad \rightarrow \quad C_8H_{18}(isooctane)$$

Since this process data is not available in databases, estimation was used to calculate the LCI data. The benchmarked hydrogenation process is the production of n-heptane from 1-heptene.[34] As described in section 2.2.2, the energy needed for this process was estimated as proportional to the output materials' weight ratio. The material amounts were estimated based on the stoichiometry of the process.

Table 15 shows the inputs for this process. Flow values are for 1 kg isooctane production. As in the previous steps, detailed inventory source data and calculation procedures are described in Appendix C.

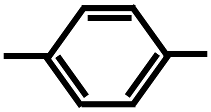
Table 15. Input flows for 1 kg of isooctane.

Input		
Electricity, medium voltage, at grid/US	164.7	Btu
Natural gas, at consumer/RNA with US electricity	267.9	Btu
Isooctene	0.982	kg
Hydrogen, liquid, at plant/RER with US electricity	0.018	kg

5.1.5. PARA-XYLENE PRODUCTION (PTA 2 SYNTHESIS STEP 5)

Obtained isooctane is then converted into para-xylene by dehydrocyclization. The following equation shows the stoichiometry of this process.

$$C_8H_{18} \quad \rightarrow \quad C_8H_{10}(para - xylene) \quad + \quad 4H_2$$



Since this process data is not available in databases, estimation was used to calculate the LCI data. The benchmarked dehydrocyclization process is the production of toluene from n-heptene.[34] As described in section 2.2.2, the energy needed for this process was estimated as proportional to the output materials' weight ratio. The material amounts were estimated based on the stoichiometry of the process.

Table 16 shows the inputs and outputs for this process. Flow values are for 1 kg para-xylene production. As in the previous steps, detailed inventory source data and calculation procedures are described in Appendix C.

Table 16. Input/Output flows for 1 kg of para-xylene.

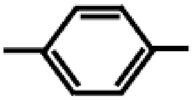
Input		
Electricity, medium voltage, at grid/US	99.95	Btu
Natural gas, at consumer/RNA with US electricity	2385	Btu
Isooctane	1.075	kg

Output		
Hydrogen	0.075	kg

5.1.6. PTA PRODUCTION (PTA 2 SYNTHESIS STEP 6)

Obtained para-xylene is then converted into PTA by oxidation and purification. The following equation shows the stoichiometry of the PTA production process.

$$C_8H_{10} \quad + \quad 3O_2 \quad \rightarrow \quad C_8H_6O_4(TPA) \quad + \quad 2H_2O$$



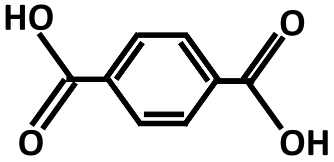


Table 17 shows the inputs and outputs for this process from the SimaPro software. Flow values are for 1 kg PTA production. As in the previous steps, detailed inventory source data and calculation procedures are described in Appendix C.

Table 17. Input/Output flows for 1 kg of PTA.

Input

Water, cooling, unspecified natural origin/m^3	3.420E-04	m^3
Water, completely softened, at plant/RER with US electricity	4.250E-01	kg
para-xylene	6.610E-01	kg
Acetic acid, 98% in H2O, at plant/RER with US electricity	5.000E-02	kg
Sodium hydroxide, 50% in H2O, production mix, at plant/RER with US electricity	1.450E-03	kg
Nitrogen, liquid, at plant/RER with US electricity	4.880E-02	kg
Electricity, medium voltage, production UCTE, at grid/UCTE with US electricity	4.690E-01	kWh
Heat, heavy fuel oil, at industrial furnace 1MW/RER with US electricity	6.370E-01	MJ
Heat, light fuel oil, at industrial furnace 1MW/RER with US electricity	2.120E-01	MJ
Heat, natural gas, at industrial furnace >100kW/RER with US electricity	4.580E-01	MJ
Heat, at hard coal industrial furnace 1-10MW/RER with US electricity	3.230E-01	MJ
Steam, for chemical processes, at plant/RER with US electricity	6.400E-01	kg
Electricity, at grid, US	-8.598E-02	kWh
Natural gas, combusted in industrial boiler/US	-1.009E-01	m^3
Liquefied petroleum gas, combusted in industrial boiler/US	-5.020E-03	l
Bituminous coal, combusted in industrial boiler/US	-1.699E-02	kg

Output

Heat, waste	1.690E+00	MJ
Particulates, > 10 um	2.880E-05	kg
Particulates, > 2.5 um, and < 10um	3.870E-05	kg
Particulates, < 2.5 um	2.250E-05	kg
Hydrocarbons, aromatic	3.780E-04	kg
NMVOC, non-methane volatile organic compounds, unspecified origin	1.100E-04	kg
BOD5, Biological Oxygen Demand	1.300E-03	kg
COD, Chemical Oxygen Demand	1.300E-03	kg
DOC, Dissolved Organic Carbon	1.220E-05	kg
TOC, Total Organic Carbon	1.220E-05	kg
Suspended solids, unspecified	2.560E-04	kg
Hydrocarbons, unspecified	1.400E-05	kg
Disposal, hazardous waste, 0% water, to underground deposit/DE with US electricity	2.000E-04	kg
Disposal, average incineration residue, 0% water, to residual material landfill/CH with US electricity	6.000E-03	kg

5.2. LCI RESULTS

5.2.1. PROCESS ENERGY DEMAND

Table 18 shows the summary of process energy required in this process to produce 1 kg of PET bottle grade resin from raw material extraction. In this table, the isobutanol scenario was selected as step 1. The process energy data can be used to evaluate the sensitivity of each process. The sensitivity check is described in the interpretation section.

Table 18. Process energy in the isobutanol pathway, for 1 kg of PET resin.

		Process energy demand (MJ)
MEG		20.79
PTA 2	step 1	34.83
	step 2	19.85
	step 3	7.943
	step 4	1.066
	step 5	1.994
	step 6	23.94
Amorphous		13.69
Bottle grade		22.84
total		146.9

5.3. LCIA RESULTS (IMPACT 2002+ v2.1)

In this section, the LCIA results of 1 kg of PET resin production through the isobutanol pathway are presented. As described in the previous section, the impact assessment results were calculated using characterization factors published by IMPACT 2002+ v2.1. Figure 6 shows the system structure for the production of 1 kg bottle grade PET resin in this scenario. The indicator used is global warming (kg CO_2 eq), and processes contributing less than 15 % of the total are not shown.

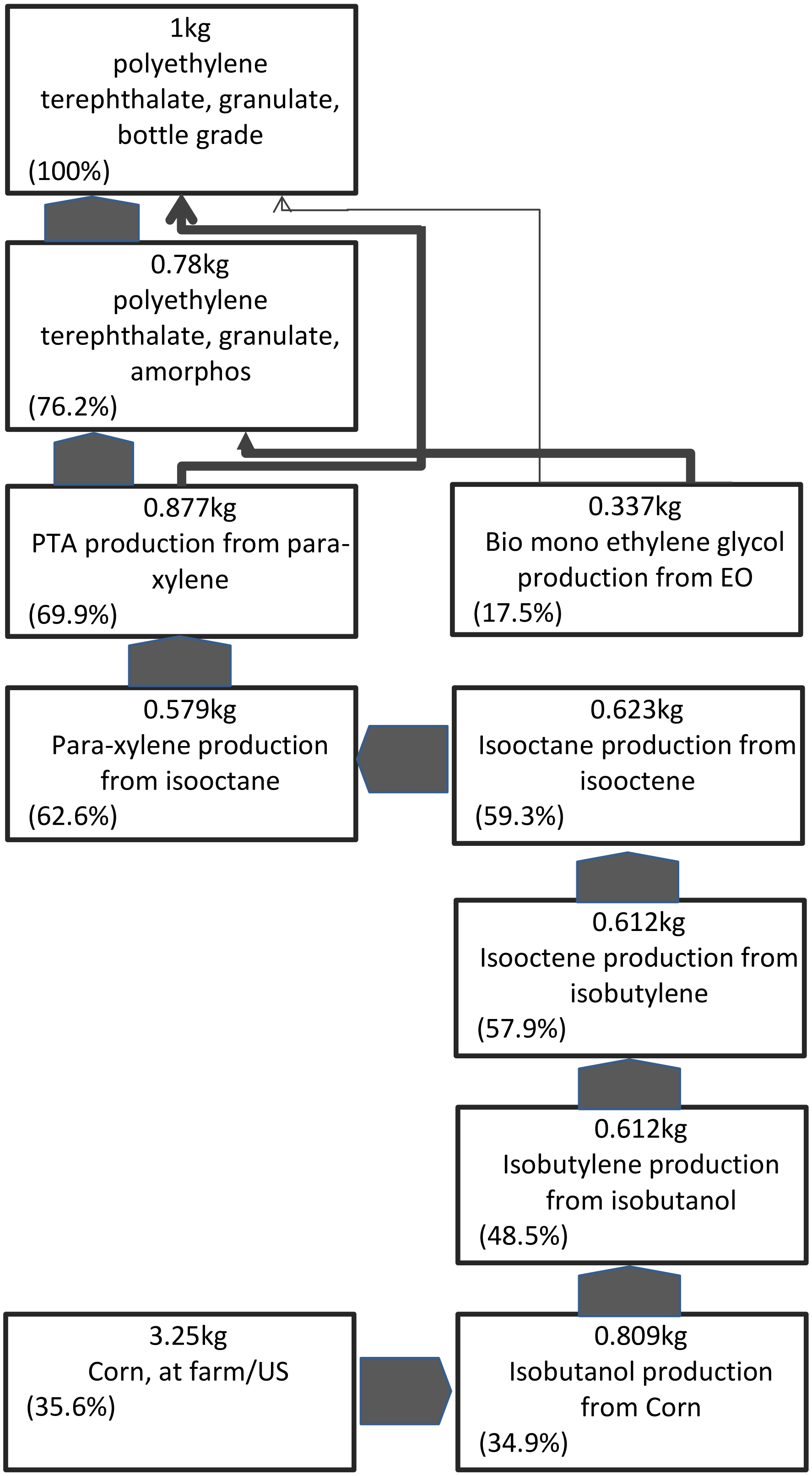


Figure 6. System Structure for Scenario 2.

Figure 7 shows the results for the terrestrial acidification/nutrification, aquatic acidification, aquatic eutrophication, global warming, non-renewable energy and mineral extraction index for the two butanol production processes (PTA 2 step 1). As can be seen, the burdens are similar although the n-butanol process shows higher values in each indicator than those of isobutanol except for global warming and non-renewable energy. Since there was no significant difference between these two butanol processes for global warming, and isobutanol is the pathway used in the market as described in section 2.2, the isobutanol production process was used for PTA 2 step 1 in the remainder of this study even if not explicitly mentioned.

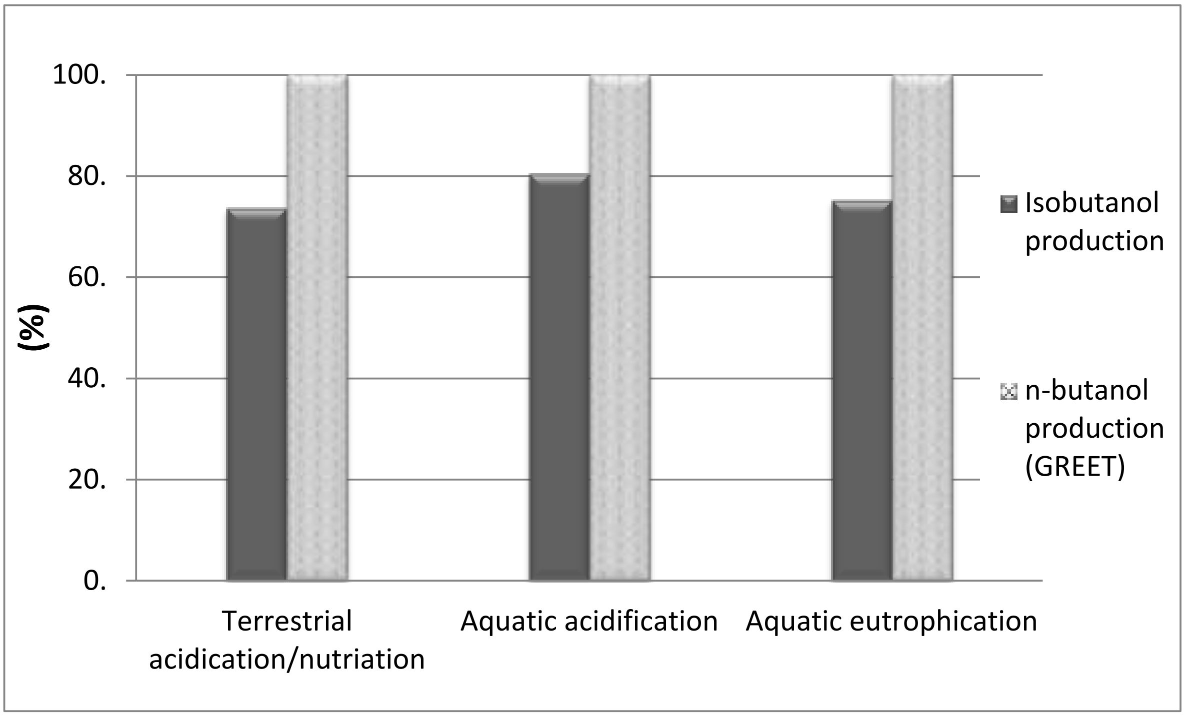


Figure 7. LCIA comparison of production process, for 1 kg of butanol.

Figure 7.(cont'd)

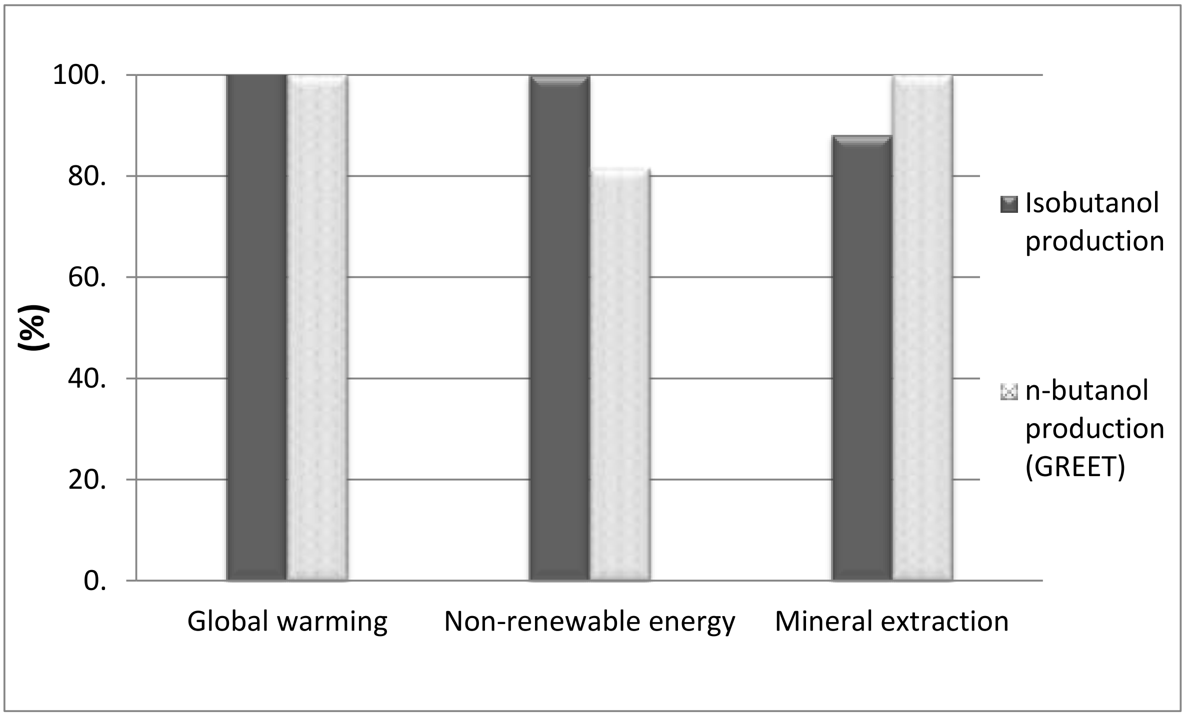


Figure 8 shows the results for terrestrial acidification/nutrification, aquatic acidification, aquatic eutrophication, global warming, non-renewable energy and mineral extraction for each process. The dominant process in all impact categories is PTA 2 (step 1) which is the production of isobutanol. In the global warming and non-renewable energy categories, PTA 2 (step 2), which is the production of isobutylene, has the second highest values.

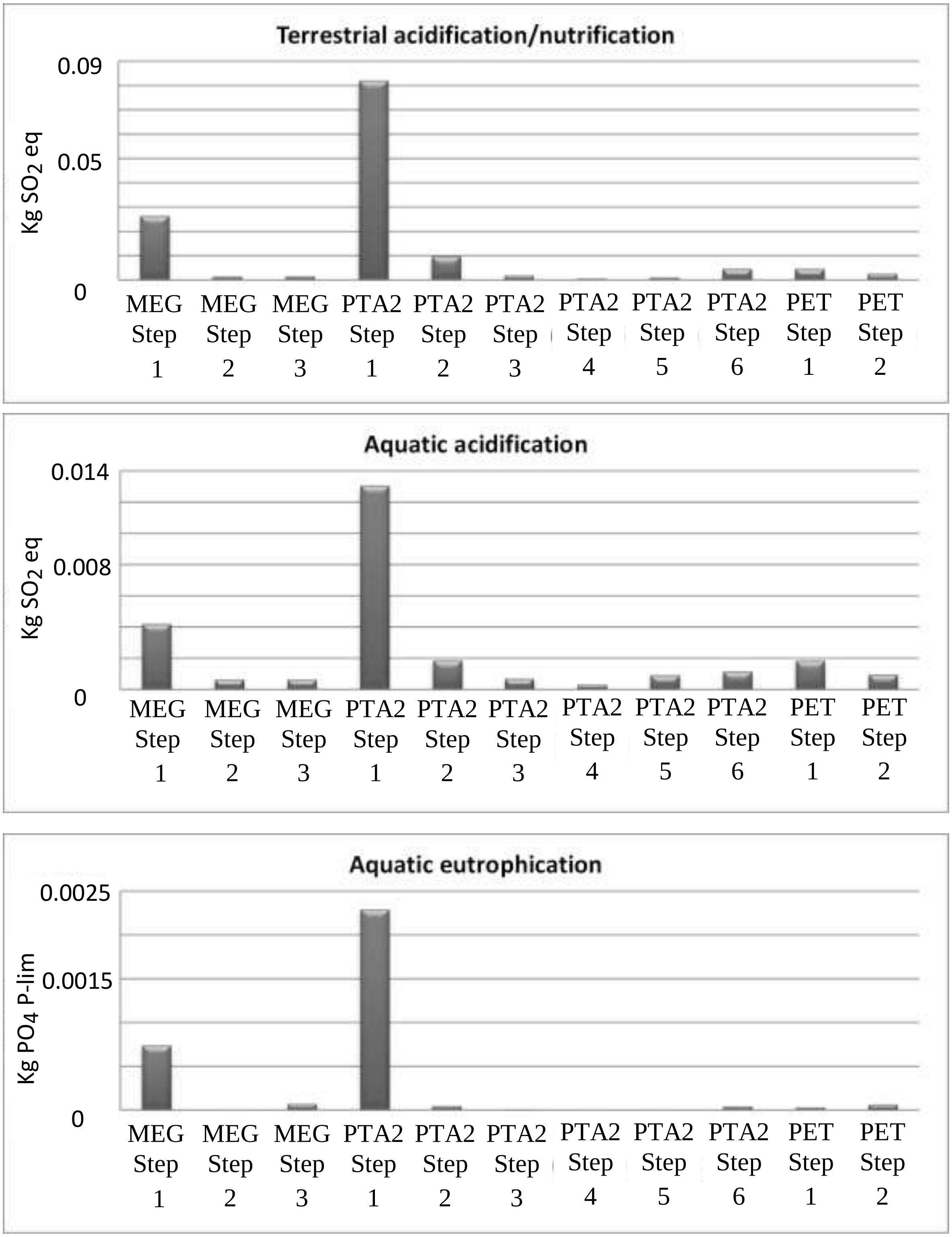
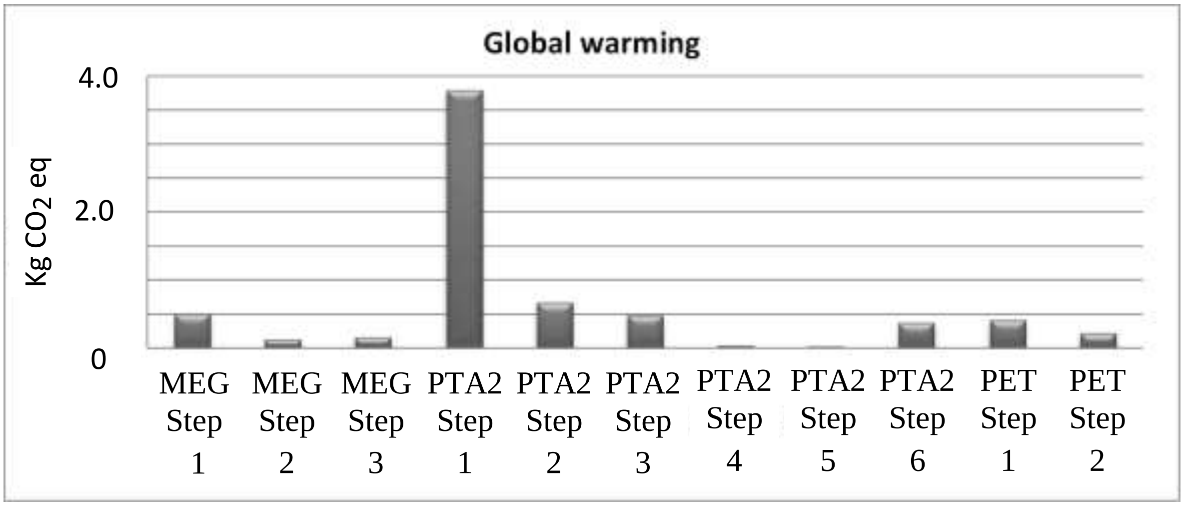
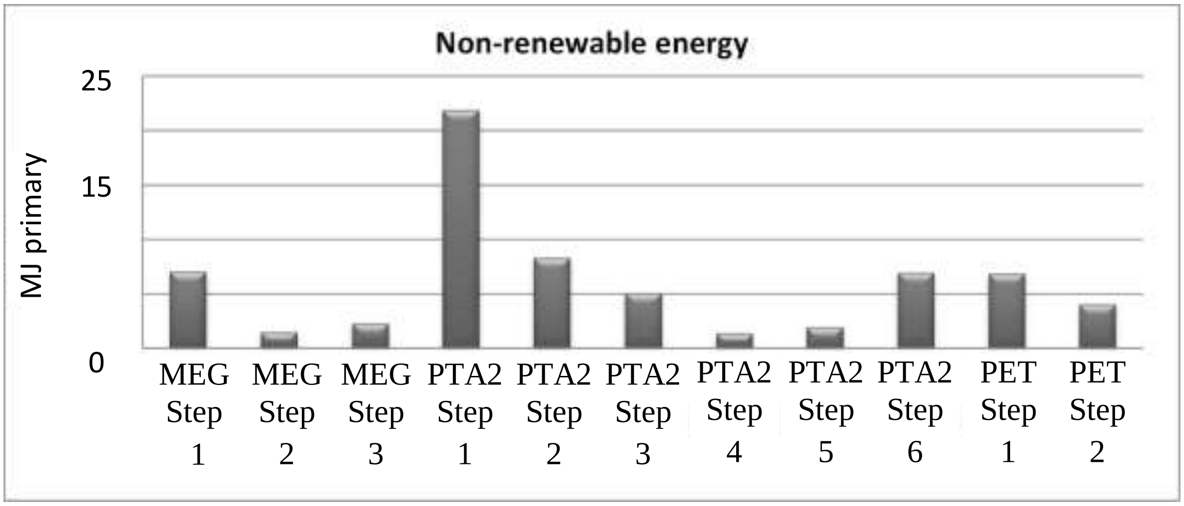
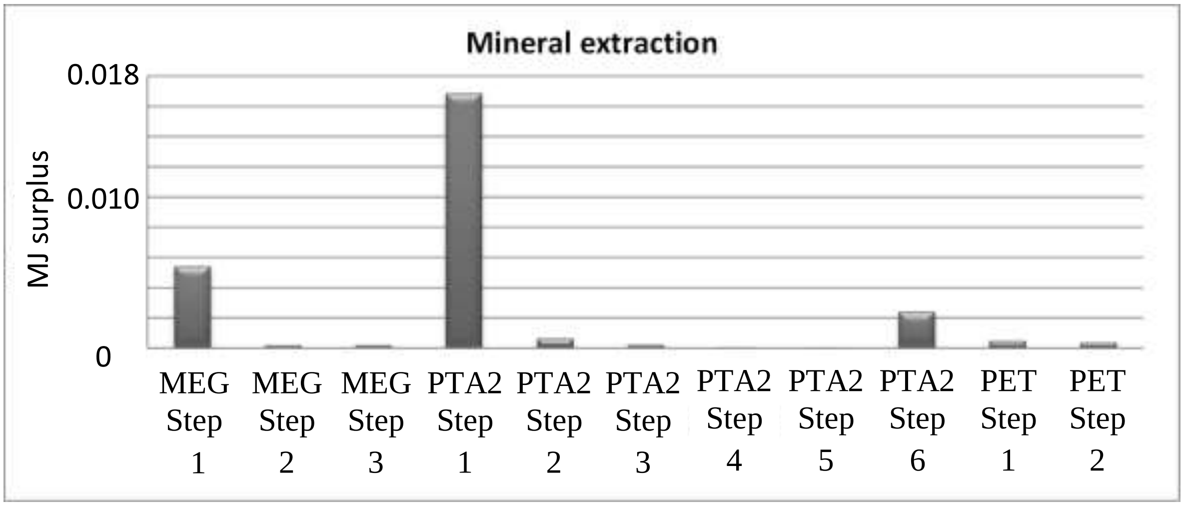


Figure 8. LCIA results of scenario2 (isobutanol pathway), for 1 kg of PET resin.

Figure 8.(cont'd)







6. BENZENE TOLUENE XYLENE PATHWAY PRODUCTION

This section discusses the PTA synthesis process which goes through BTX as the intermediates.

6.1. PROCESS DESCRIPTION AND LCI DATA

6.1.1. BTX PRODUCTION (PTA 3 SYNTHESIS STEP 1)

Two pathways to obtain bio-based BTX were considered. The first pathway was through direct catalytic reformation. In this PTA scenario, biomass which contains glucose and lignin is produced. In the next step, it is catalytically reformed to produce BTX directly. Since this process data is not available in databases, estimation was used to calculate the LCI data. The benchmarked process is the production of BTX from naphtha, which is common in the petrochemical industry.[35] In this study, although we used corn stover as the input material, the process efficiency must be assumed to be the same as the petrochemical input case since we do not have a basis for any other assumption. Therefore, the energy and material amount needed for this process was assumed to be the same as that of existing process data for the naphtha catalytic reforming process.

Table 19 shows the inputs and outputs for this process. Flow values are for 1 kg BTX production. As in the previous steps, detailed inventory source data and calculation procedures are described in Appendix C.

Table 19. Input/Output flows for 1 kg of BTX (from corn).

Input		
Corn stover, at field/kg/US	2.135E+00	kg
Hydrogen, liquid, at plant/RER with US electricity	1.486E-01	kg
Electricity, at grid, US	1.438E-04	MWh
Heat, natural gas, at industrial furnace >100kW/RER with US electricity	8.657E-04	MWh
Output		
LPG FAL	4.461E-02	l
Synthetic gas, production mix, at plant	7.329E-03	l

Alternatively, in the fuel synthesis terrain, there is a pathway to produce bio-oil from biomass and then upgrade the obtained bio-oil to the desired components. This reaction was also benchmarked to estimate the inventory data for the production for BTX.

The benchmarked process uses poplar wood chips as biomass which we also used similarly, to generate bio-oil though fast pyrolysis of a lignocellulosic feedstock in a CFB reactor.[36] Then, the obtained bio-oil was assumed to go through catalytic upgrading with a zeolite catalyst.[37] Table 20 shows the inputs and outputs for this process. Flow values are for 1 kg BTX production. As in the previous steps, detailed inventory source data and calculation procedures are described in Appendix C.

Table 20. Input/Output flows for 1 kg of BTX (through fast pyrolysis).

Input		
poplar (chip)	2.876E+00	kg
Process water, ion exchange, production mix, at plant, from surface water RER	4.767E-02	kg
air	2.734E+00	kg
Electricity, at grid, US	3.735E-01	kWh
Heat, natural gas, at industrial furnace >100kW/RER with US electricity	8.403E-04	MJ

Output		
Charcoal, at plant/GLO with US electricity	4.614E-02	kg
Ash, bagasse, at fermentation plant/BR with US electricity	1.660E-02	kg
O_2	1.941E-01	kg
N_2	2.142E+00	kg
Water	1.431E+00	kg
H_2	1.595E-05	kg
CO	4.084E-03	kg
CO_2	6.840E-01	kg
Methane	1.590E-09	kg
Ethene	3.180E-09	kg
propene	4.765E-09	kg
ammonia	2.383E-09	kg

6.1.2. XYLENE PRODUCTION (PTA 3 SYNTHESIS STEP 2)

Obtained BTX is then distilled into a xylene mixture (ortho-xylene, meta-xylene and para-xylene). We considered extractive distillation process in this step. From the literature,[38] we assumed the use of the sulfolane process which is used to recover high-purity aromatics from hydrocarbon mixtures. Flow values are for 1 kg xylene mix production. As in the previous steps, detailed inventory source data and calculation procedures are described in Appendix C.

Table 21. Input flows for 1 kg of xylene mixture.

Input		
Electricity, medium voltage, at grid/US with US electricity	1.193	MJ
BTX	3.030	kg

6.1.3. PTA PRODUCTION (PTA 3 SYNTHESIS STEP 3)

The obtained xylene mixture is then converted into para-xylene by an adsorption, separation and isomerization process. Then, para-xylene is converted into PTA by oxidation and purification. Table 22 shows the inputs and outputs for this process from the SimaPro software. Flow values are for 1 kg PTA production. As in the previous steps, detailed inventory source data and calculation procedures are described in Appendix C.

Table 22. Input/Output flows for 1 kg of PTA.

Input		
Water, cooling, unspecified natural origin/m^3	3.420E-04	m^3
Water, completely softened, at plant/RER with US electricity	4.250E-01	kg
Xylene mixture	6.610E-01	kg
Acetic acid, 98% in H2O, at plant/RER with US electricity	5.000E-02	kg
Sodium hydroxide, 50% in H2O, production mix, at plant/RER with US electricity	1.450E-03	kg
Nitrogen, liquid, at plant/RER with US electricity	4.880E-02	kg
Electricity, medium voltage, production UCTE, at grid/UCTE with US electricity	4.690E-01	kWh
Heat, heavy fuel oil, at industrial furnace 1MW/RER with US electricity	6.370E-01	MJ
Heat, light fuel oil, at industrial furnace 1MW/RER with US electricity	2.120E-01	MJ
Heat, natural gas, at industrial furnace >100kW/RER with US electricity	4.580E-01	MJ
Heat, at hard coal industrial furnace 1-10MW/RER with US electricity	3.230E-01	MJ
Steam, for chemical processes, at plant/RER with US electricity	6.400E-01	kg
output		
Heat, waste	1.690E+00	MJ
Particulates, > 10 um	2.880E-05	kg
Particulates, > 2.5 um, and < 10um	3.870E-05	kg
Particulates, < 2.5 um	2.250E-05	kg
Hydrocarbons, aromatic	3.780E-04	kg
NMVOC, non-methane volatile organic compounds, unspecified origin	1.100E-04	kg
BOD5, Biological Oxygen Demand	1.300E-03	kg
COD, Chemical Oxygen Demand	1.300E-03	kg
DOC, Dissolved Organic Carbon	1.220E-05	kg
TOC, Total Organic Carbon	1.220E-05	kg
Suspended solids, unspecified	2.560E-04	kg
Hydrocarbons, unspecified	1.400E-05	kg
Disposal, hazardous waste, 0% water, to underground deposit/DE with US electricity	2.000E-04	kg
Disposal, average incineration residue, 0% water, to residual material landfill/CH with US electricity	6.000E-03	kg

6.2. LCI RESULTS

6.2.1. PROCESS ENERGY DEMAND

Table 23 shows the summary of process energy required in this process to produce 1 kg of PET bottle grade resin from raw material extraction. In this table, the fast pyrolysis scenario (poplar as biomass feed) was selected as step 1. The process energy data can be used to evaluate the sensitivity of each process. The sensitivity check is described in the interpretation section.

Table 23. Process energy in the BTX pathway, for 1 kg of PET resin.

		Process energy demand (MJ)
MEG		20.79
PTA 3	step 1	7.109
	step 2	5.430
	step 3	24.56
Amorphous PET resin		13.69
Bottle grade PET resin		9.152
Total		80.73

6.3. LCIA RESULTS (IMPACT 2002+ v2.1)

Figure 9 shows the system structure for the production of 1 kg bottle grade PET resin in this scenario. The indicator used is global warming (kg CO_2 eq), and processes contributing less than 20 % of the total are not shown.

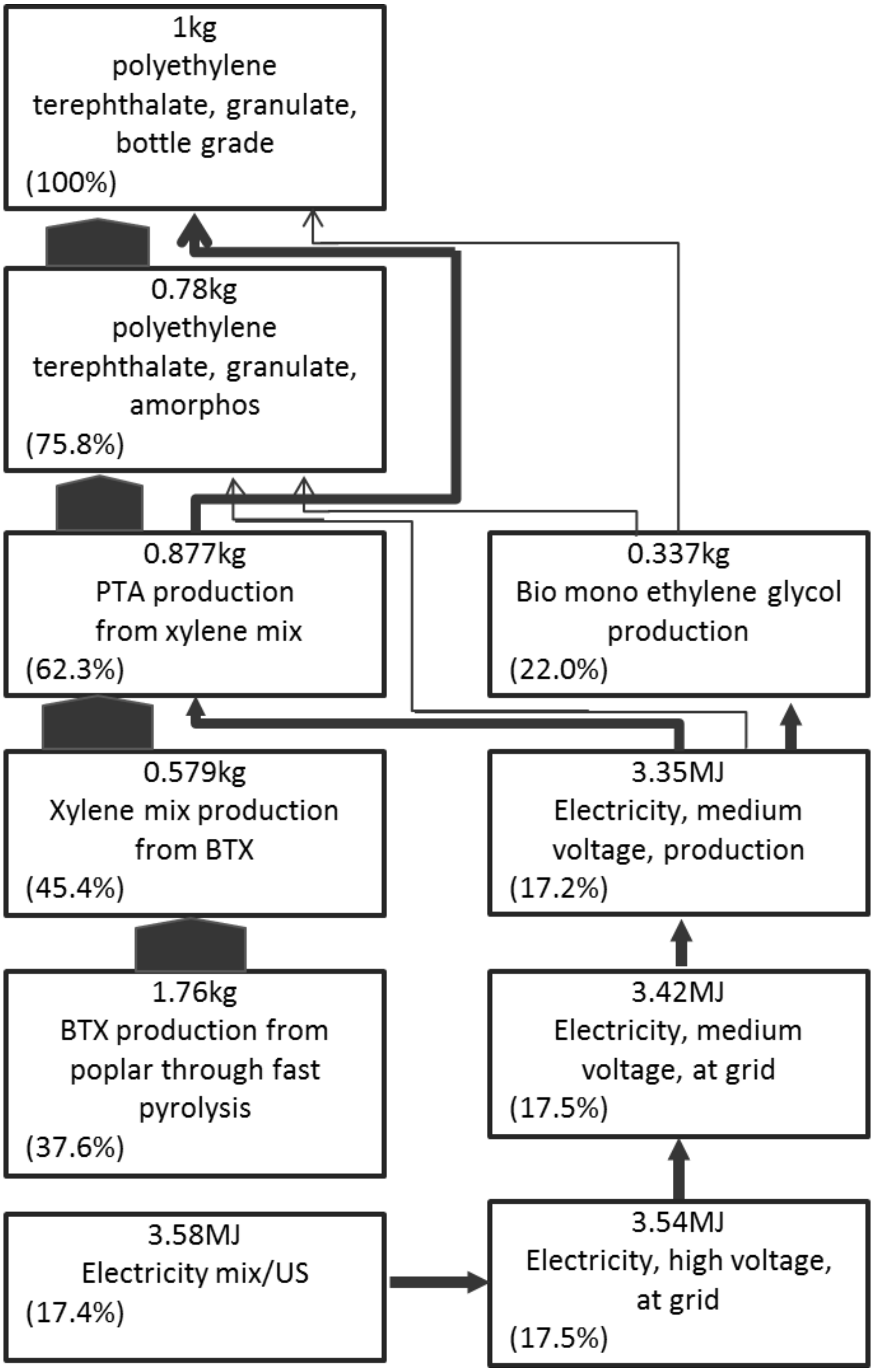


Figure 9. System structure for scenario 3.

Figure 1 shows the results from IMPACT 2002+ v2.1 for BTX production from corn (through direct catalytic reforming) and poplar (through fast pyrolysis). The environmental burdens of the fast pyrolysis model were higher than direct catalytic reforming except for non-renewable energy. Since the direct catalytic reforming scenario does not include any biological treatments such as the pre-processing of biomass, it seems reasonable to use the fast pyrolysis results in this study. Therefore, fast pyrolysis was used for PTA 3 (step 1) in the remainder of this study even if not explicitly mentioned.

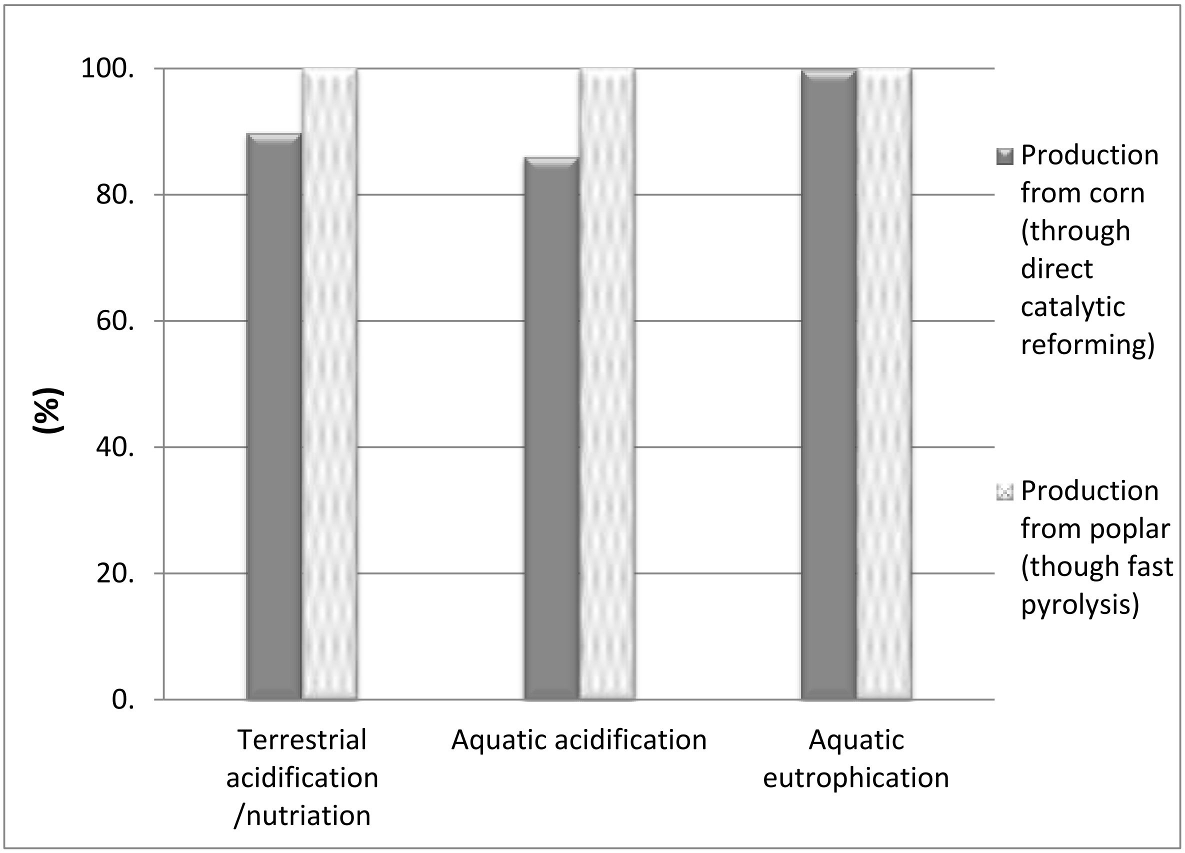


Figure 10. LCIA results for the production of 1 kg BTX.

Figure 10. (cont’d)

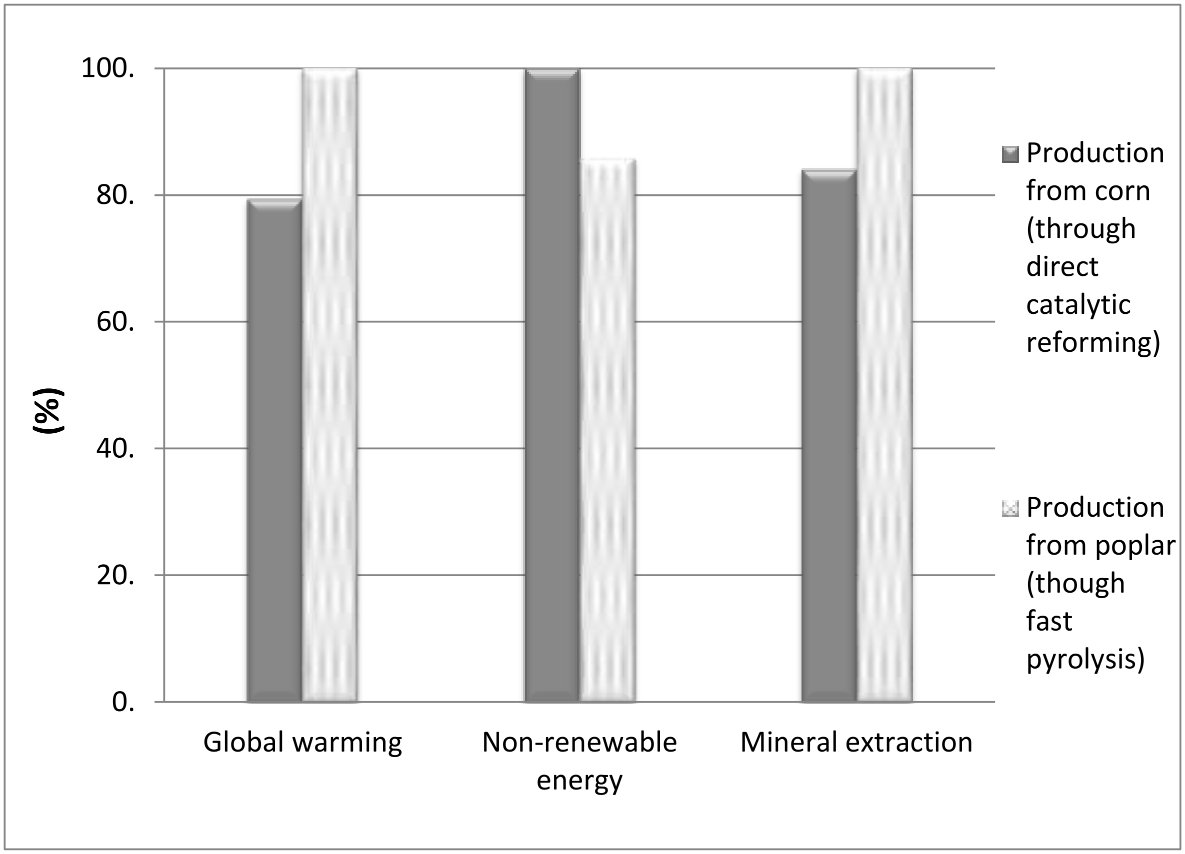


Figure 11 shows the results from IMPACT 2002+ v2.1 for each unit process. As can be seen, PTA 3 process step 1 has the highest values for aquatic acidification and global warming. MEG (step 1) has the highest values for terrestrial acidification /nutrification , aquatic eutrophication and mineral extraction.

Impacts of the PET condensation processes are smaller in every impact category.

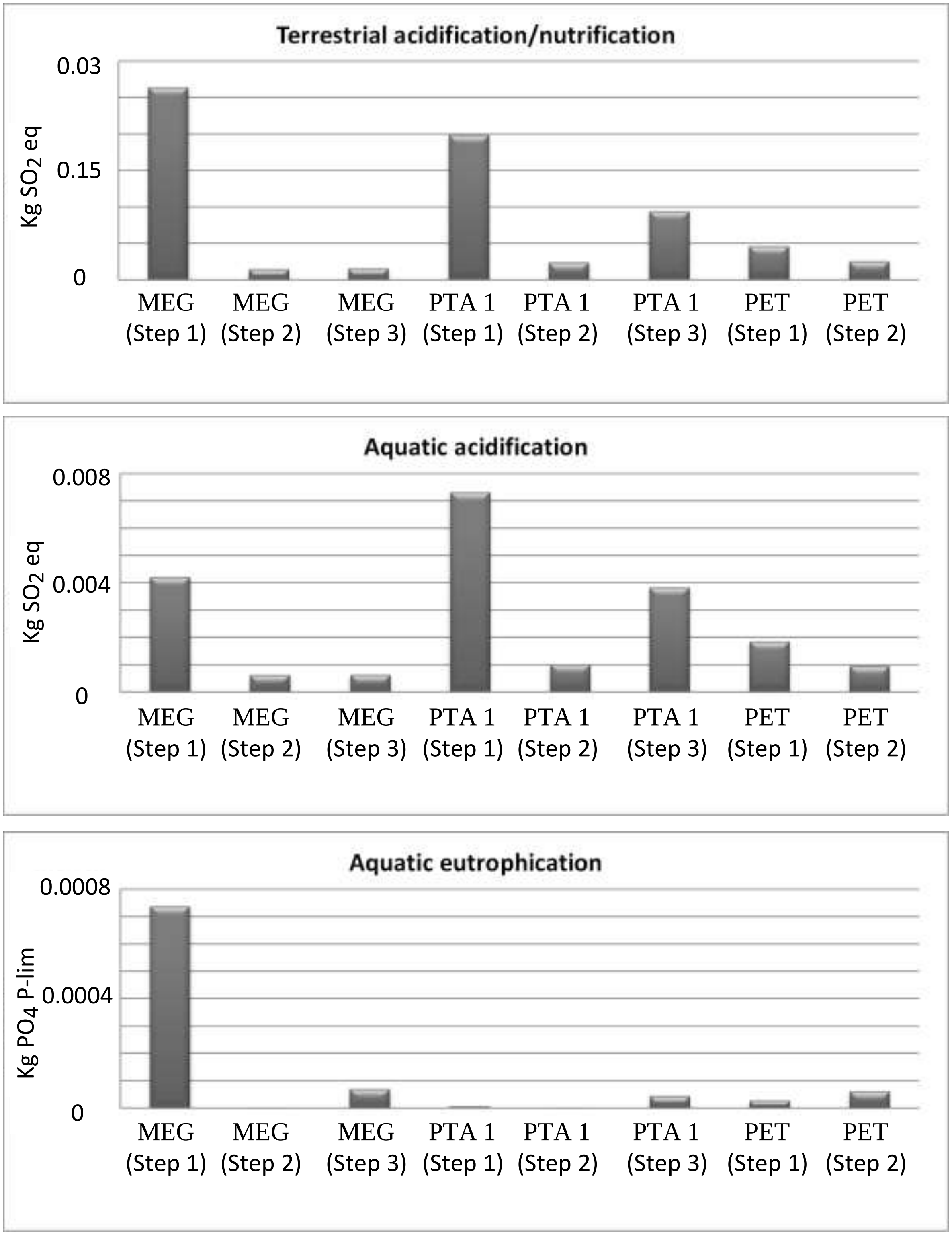


Figure 11. LCIA results of scenario 3 (BTX pathway), for 1 kg of PET resin.

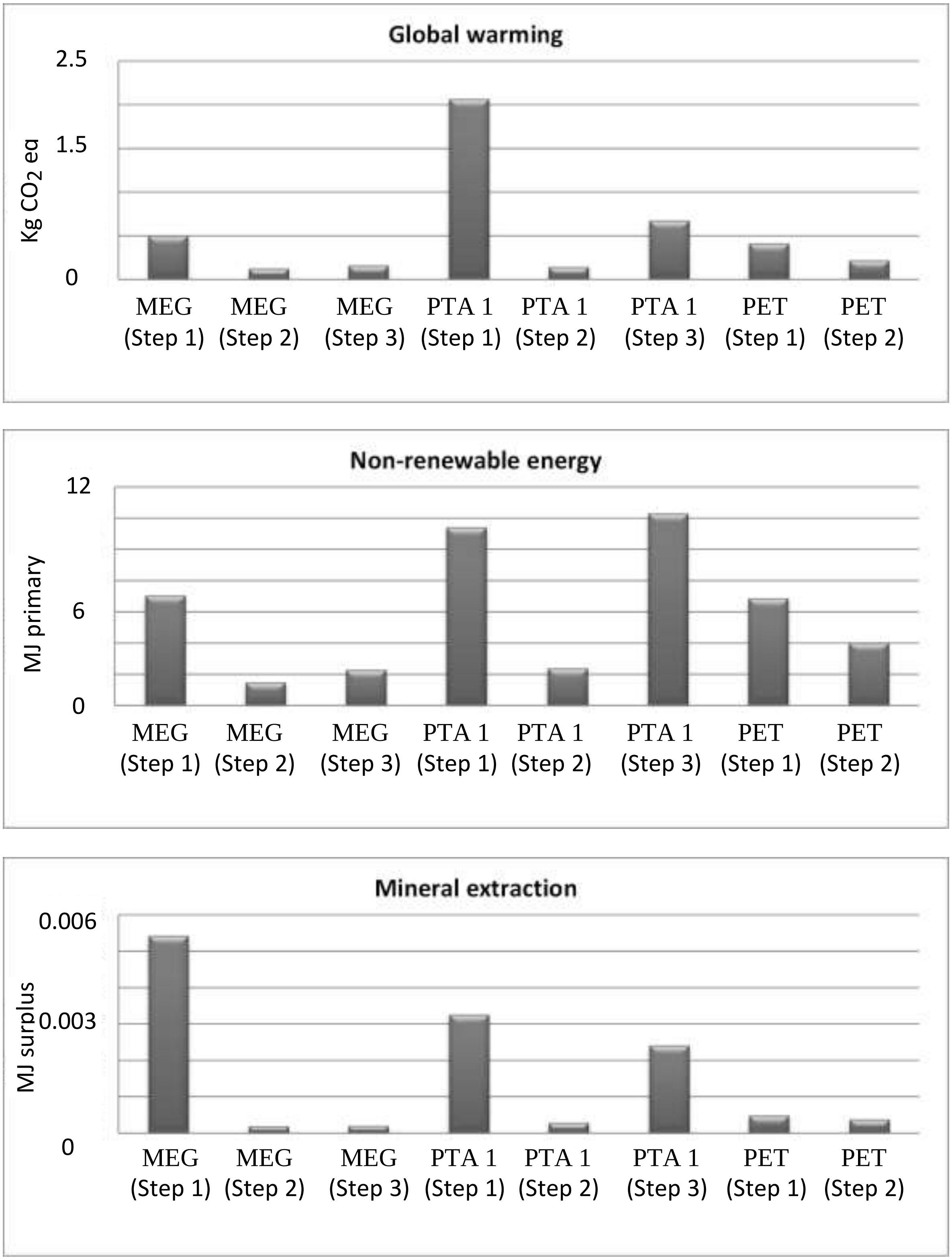


Figure 11. (cont’d)

7. INTERPRETATION

7.1. EVALUATION OF THE RESULTS

7.1.1. COMPLETENESS CHECK

According to ISO14044, obtained LCA results must be checked for completeness first. Completeness check is the process of verifying whether information from the phases of a LCA is sufficient for reaching conclusions in accordance with the goal and scope definition. Table 24 shows the results of the completeness check. In this table, some processes were omitted from this study: transportation, processing, use, and end of life. It can be said that material production and energy supply part have completeness in each production step in each PTA synthesis scenario.

Table 24. Results of completeness check (self-check).

		Material production	Energy supply
PTA 1	step 1	complete	complete
	step 2	complete	complete
	step 3	complete	complete

Table 24. (cont’d).

		Material production	Energy supply
PTA 2	step 1	complete	complete
	step 2	complete	complete
	step 3	complete	※1
	step 4	complete	complete
	step 5	complete	complete
	step 6	complete	complete

		Material production	Energy supply
PTA 3	step 1	※2	complete
	step 2	complete	complete
	step 3	complete	complete

※1: Energy required is assumed to be the same as in the benchmarked process.

※2: Conversion efficiency is assumed to be the same as in the petrochemical case.

7.1.2. CONSISTENCY CHECK

Obtained LCA results must also be checked for consistency. Table 25 shows the result of the consistency check. As can be seen in the tables, some processes are not consistent. But, these inconsistent parts are the targets of this report, so no actions were taken in this case.

In the data accuracy entry, “caution” means some of the LCI data were obtained on the basis of stoichiometric estimation. In the technology coverage entry, “commercial level” means technology used in the specific process is already available at the industrial level. “Pilot” means the technology is not yet available at the mass production level.

Table 25. Results of consistency check for PTA 1 scenario 1(self-check).

		Data source	Data accuracy	Data age	Technology coverage	Geographical coverage
MEG		Database, literature	Good	Within 6 yrs	Commercial level	US
PTA 1	Step 1	Literature	Caution	Within 6 yrs	Pilot (estimation)	US
	Step 2	Database, literature	Caution	Within 6 yrs	Pilot (estimation)	US
	Step 3	Database, literature	good	Within 6 yrs	Pilot (estimation)	US
PET resin		Database	Good	Within 6 yrs	Commercial level	US
Comparison of each process		Consistent	※	Consistent	※	Consistent

Table 25. (cont'd).

		Data source	Data accuracy	Data age	Technology coverage	Geographical coverage
MEG		Database, literature	Good	Within 6 yrs	Commercial level	US
PTA 2	Step 1	Literature	Caution	Within 10 yrs	Pilot (estimation)	US
	Step 2	Literature	Caution	Within 10 yrs	Pilot (estimation)	US
	Step 3	Literature	Caution	Within 10 yrs	Pilot (estimation)	US
	Step 4	Literature	Caution	Within 10 yrs	Pilot (estimation)	US
	Step 5	Literature	Caution	Within 10 yrs	Pilot (estimation)	US
	Step 6	Database, literature	Good	Within 10 yrs	Commercial level	US
PET resin		Database	Good	Within 6 yrs	Commercial level	US
Comparison of each process		Consistent	※	Consistent	※	Consistent

		Data source	Data accuracy	Data age	Technology coverage	Geographical coverage
MEG		Database, literature	Good	Within 6 yrs	Commercial level	US
PTA 3	Step 1	Literature	Caution	Within 6 yrs	Pilot (estimation)	US
	Step 2	Database, literature	Caution	Within 6 yrs	Pilot (estimation)	US
	Step 3	Database	Good	Within 6 yrs	Commercial level	US
PET resin		Database	Good	Within 6 yrs	Commercial level	US
Comparison of each process		Consistent	※	Consistent	※	Consistent

※The differences in data accuracy and technology coverage are the targets of this report.

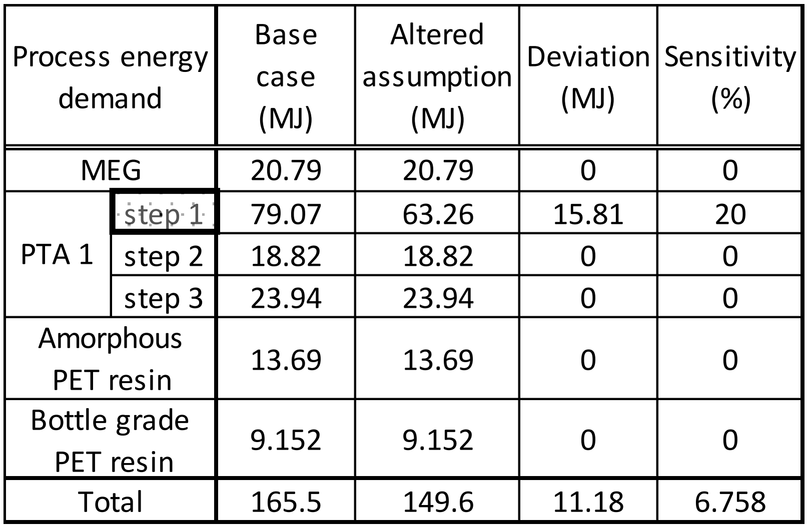
7.2. ANALYSIS OF THE RESULTS

7.2.1. SENSITIVITY ANALYSIS FOR ENERGY

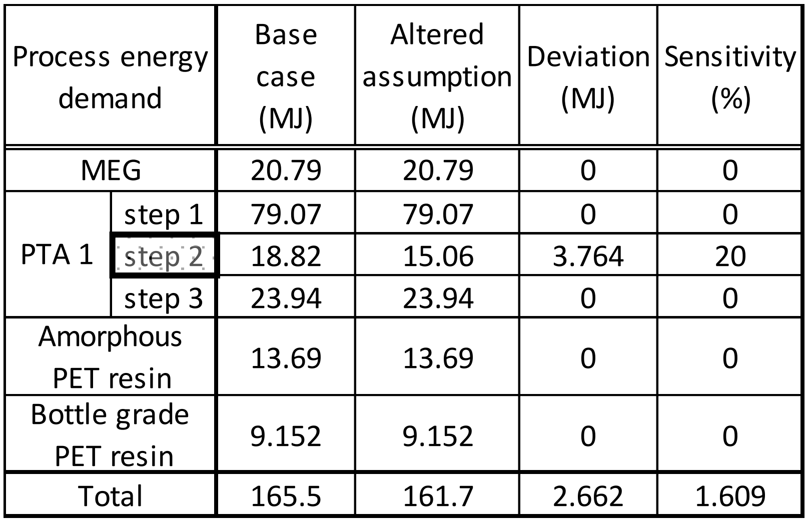
Since this study contains more than two estimations in each scenario's LCI stage, a sensitivity check on energy data uncertainty was performed. We, tentatively, assumed if there was over a 10 % total output change (total sensitivity %) in the case of a 20 % input energy change, it could be concluded the process contained a very sensitive part. Sensitivity (%) was expressed as the absolute deviation (%) of the results.

Table 26 show the results for 1 kg of PET bottle grade resin made with the muconic acid pathway. Input energy amounts were reduced 20 % in each production step. Although significant change (larger than 10 %) was not observed, the PTA 1 step 1 process (muconic acid synthesis) appeared to have the greatest sensitivity in this study since its sensitivity value of 6.758 % was the highest among the three PTA production scenarios. Therefore, if more accurate LCI data were available for this step, a more accurate LCA result would be available.

Table 26. Results of the sensitivity analysis for uncertainty of PTA scenario 1.



Process energy demand		Base case (MJ)	Altered assumption (MJ)	Deviation (MJ)	Sensitivity (%)
MEG		20.79	20.79	0	0
PTA 1	step 1	79.07	63.26	15.81	20
	step 2	18.82	18.82	0	0
	step 3	23.94	23.94	0	0
Amorphous PET resin		13.69	13.69	0	0
Bottle grade PET resin		9.152	9.152	0	0
Total		165.5	149.6	11.18	6.758



Process energy demand		Base case (MJ)	Altered assumption (MJ)	Deviation (MJ)	Sensitivity (%)
MEG		20.79	20.79	0	0
PTA 1	step 1	79.07	79.07	0	0
	step 2	18.82	15.06	3.764	20
	step 3	23.94	23.94	0	0
Amorphous PET resin		13.69	13.69	0	0
Bottle grade PET resin		9.152	9.152	0	0
Total		165.5	161.7	2.662	1.609

Table 26. (cont'd)

Process energy demand		Base case (MJ)	Altered assumption (MJ)	Deviation (MJ)	Sensitivity (%)
MEG		20.79	20.79	0	0
PTA 1	step 1	79.07	79.07	0	0
	step 2	18.82	18.82	0	0
	step 3	23.94	19.15	4.787	20
Amorphous PET resin		13.69	13.69	0	0
Bottle grade PET resin		9.152	9.152	0	0
Total		165.5	160.7	3.385	2.046

Table 27 show the results of 1 kg PET bottle grade resin made with the isobutanol pathway for PTA. The isobutanol process was selected as the PTA step 1 process. Input energy amounts were reduced 20 % in each production step. As can be seen, significant change (over 10 %) was not observed in any step.

Table 27. Results of the sensitivity analysis for uncertainty of PTA scenario 2.

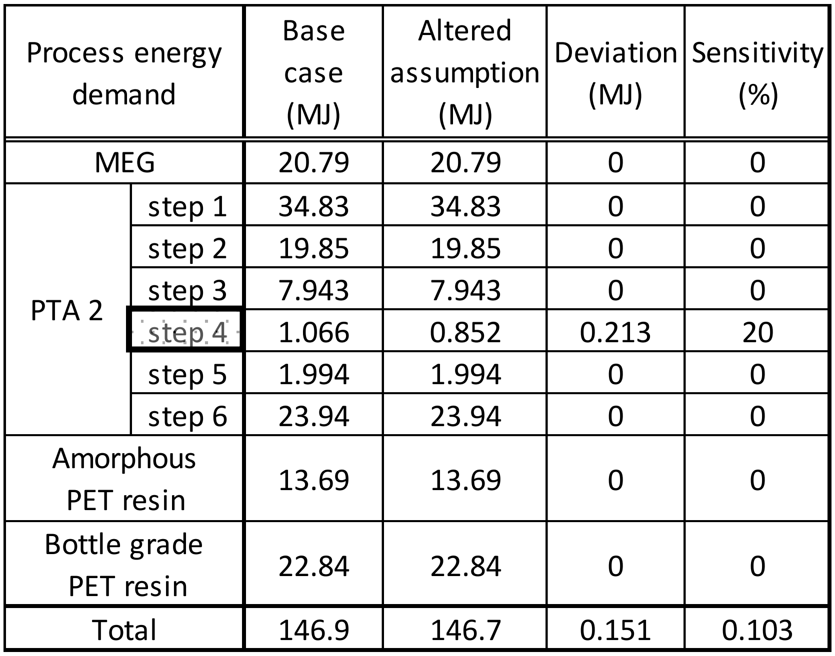
Process energy demand		Base case (MJ)	Altered assumption (MJ)	Deviation (MJ)	Sensitivity (%)
MEG		20.79	20.79	0	0
PTA 2	step 1	34.83	27.87	6.967	20
	step 2	19.85	19.85	0	0
	step 3	7.943	7.943	0	0
	step 4	1.066	1.066	0	0
	step 5	1.994	1.994	0	0
	step 6	23.94	23.94	0	0
Amorphous PET resin		13.69	13.69	0	0
Bottle grade PET resin		22.84	22.84	0	0
Total		146.9	140.0	4.926	3.352

Table 27. (cont’d)

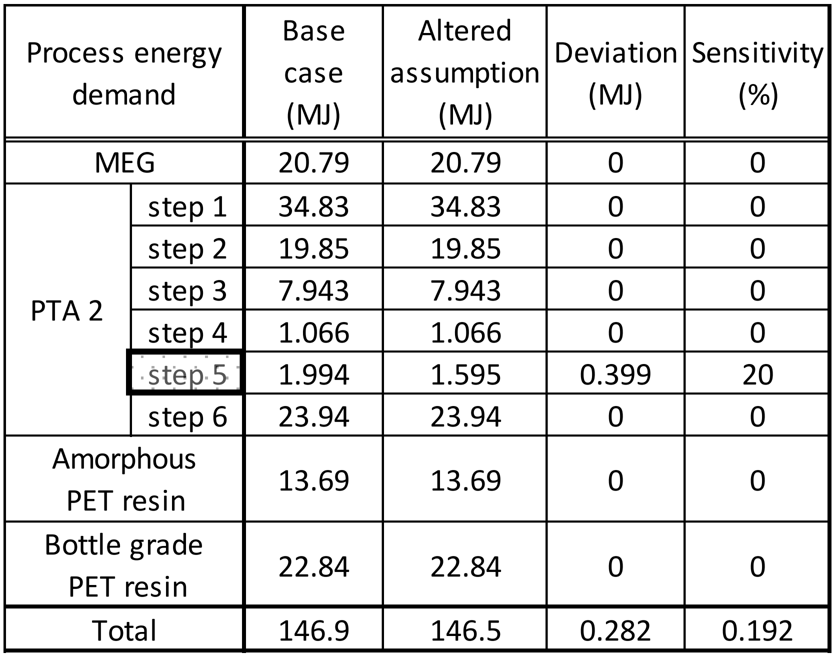
Process energy demand		Base case (MJ)	Altered assumption (MJ)	Deviation (MJ)	Sensitivity (%)
MEG		20.79	20.79	0	0
PTA 2	step 1	34.83	34.83	0	0
	step 2	19.85	15.88	3.970	20
	step 3	7.943	7.943	0	0
	step 4	1.066	1.066	0	0
	step 5	1.994	1.994	0	0
	step 6	23.94	23.94	0	0
Amorphous PET resin		13.69	13.69	0	0
Bottle grade PET resin		22.84	22.84	3.970	20
Total		146.9	143.0	2.807	1.910

Process energy demand		Base case (MJ)	Altered assumption (MJ)	Deviation (MJ)	Sensitivity (%)
MEG		20.79	20.79	0	0
PTA 2	step 1	34.83	34.83	0	0
	step 2	19.85	19.85	0	0
	step 3	7.943	6.355	1.589	20
	step 4	1.066	1.066	0	0
	step 5	1.994	1.994	0	0
	step 6	23.94	23.94	0	0
Amorphous PET resin		13.69	13.69	0	0
Bottle grade PET resin		22.84	22.84	0	0
Total		146.9	145.4	1.123	0.764

Table 27. (cont’d)



Process energy demand		Base case (MJ)	Altered assumption (MJ)	Deviation (MJ)	Sensitivity (%)
MEG		20.79	20.79	0	0
PTA 2	step 1	34.83	34.83	0	0
	step 2	19.85	19.85	0	0
	step 3	7.943	7.943	0	0
	step 4	1.066	0.852	0.213	20
	step 5	1.994	1.994	0	0
	step 6	23.94	23.94	0	0
Amorphous PET resin		13.69	13.69	0	0
Bottle grade PET resin		22.84	22.84	0	0
Total		146.9	146.7	0.151	0.103



Process energy demand		Base case (MJ)	Altered assumption (MJ)	Deviation (MJ)	Sensitivity (%)
MEG		20.79	20.79	0	0
PTA 2	step 1	34.83	34.83	0	0
	step 2	19.85	19.85	0	0
	step 3	7.943	7.943	0	0
	step 4	1.066	1.066	0	0
	step 5	1.994	1.595	0.399	20
	step 6	23.94	23.94	0	0
Amorphous PET resin		13.69	13.69	0	0
Bottle grade PET resin		22.84	22.84	0	0
Total		146.9	146.5	0.282	0.192

Table 27. (cont'd)

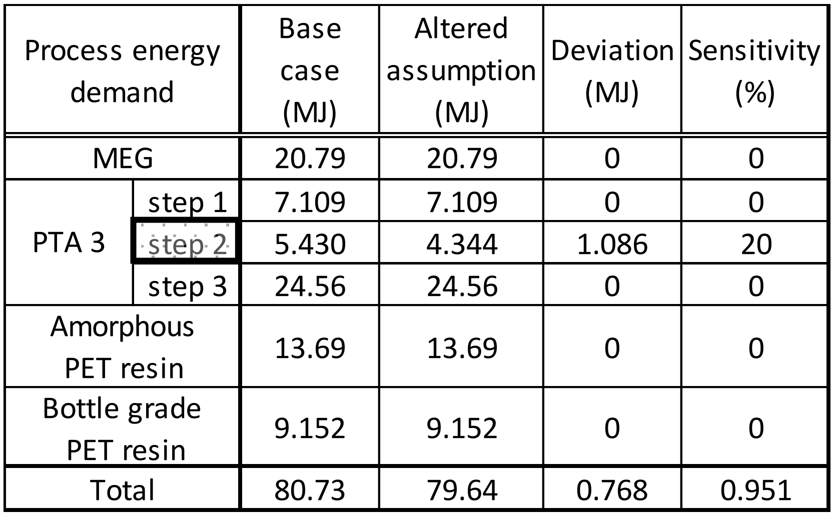
Process energy demand		Base case (MJ)	Altered assumption (MJ)	Deviation (MJ)	Sensitivity (%)
MEG		20.79	20.79	0	0
PTA 2	step 1	34.83	34.83	0	0
	step 2	19.85	19.85	0	0
	step 3	7.943	7.943	0	0
	step 4	1.066	1.066	0	0
	step 5	1.994	1.994	0	0
	step 6	23.94	19.15	4.787	20
Amorphous PET resin		13.69	13.69	0	0
Bottle grade PET resin		22.84	22.84	0	0
Total		146.9	142.2	3.385	2.304

Table 28 show the results for 1 kg PET bottle grade resin made with the BTX pathway to PTA. The fast pyrolysis process which uses poplar was selected as the PTA step 1 process. Input energy amounts were reduced 20 % in each production step. As can be seen, significant change (over 10 %) was not observed in any step.

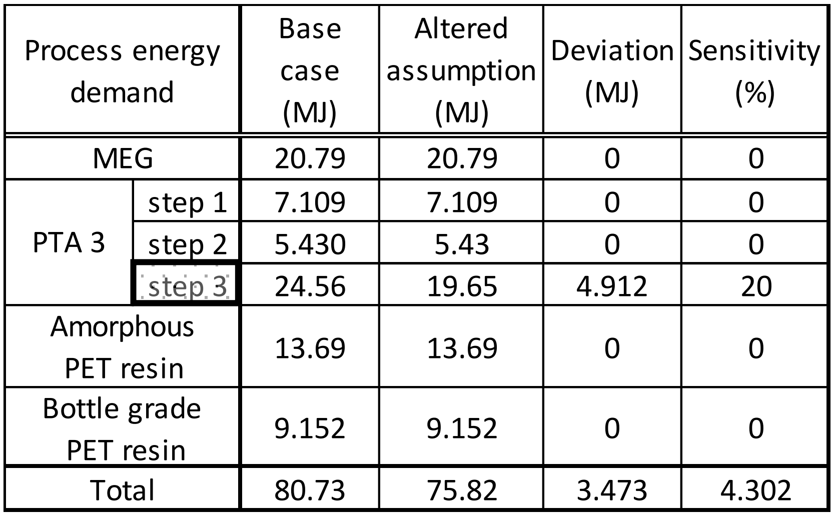
Table 28. Results of the sensitivity analysis for uncertainty of PTA scenario 3.

Process energy demand		Base case (MJ)	Altered assumption (MJ)	Deviation (MJ)	Sensitivity (%)
MEG		20.79	20.79	0	0
PTA 3	step 1	7.109	5.687	1.422	20
	step 2	5.430	5.430	0	0
	step 3	24.56	24.56	0	0
Amorphous PET resin		13.69	13.69	0	0
Bottle grade PET resin		9.152	9.152	0	0
Total		80.73	79.31	1.005	1.245

Table 28. (cont'd)



Process energy demand		Base case (MJ)	Altered assumption (MJ)	Deviation (MJ)	Sensitivity (%)
MEG		20.79	20.79	0	0
PTA 3	step 1	7.109	7.109	0	0
	step 2	5.430	4.344	1.086	20
	step 3	24.56	24.56	0	0
Amorphous PET resin		13.69	13.69	0	0
Bottle grade PET resin		9.152	9.152	0	0
Total		80.73	79.64	0.768	0.951



Process energy demand		Base case (MJ)	Altered assumption (MJ)	Deviation (MJ)	Sensitivity (%)
MEG		20.79	20.79	0	0
PTA 3	step 1	7.109	7.109	0	0
	step 2	5.430	5.43	0	0
	step 3	24.56	19.65	4.912	20
Amorphous PET resin		13.69	13.69	0	0
Bottle grade PET resin		9.152	9.152	0	0
Total		80.73	75.82	3.473	4.302

7.2.2. COMPARISON OF THE SCENARIOS

Figure 12 and Figure 13 present LCIA comparisons for the five scenarios, which include the results of the 100 % petro based PET resin process scenario and the scenario that uses bio-based MEG (PTA is made from a petro base). The results of the 100 % petro based resin scenario were calculated based on SimaPro software, “polyethylene terephthalate, granulate, amorphous, at plant/kg/RER” (from Ecoinvent) and “polyethylene terephthalate, granulate, bottle grade, at plant/kg/RER” (from Ecoinvent). The results of the bio-based MEG resin scenario were calculated using these data sets, with the MEG input parts replaced with the bio-based data described in sections 3.1.1 to 3.1.3.

First, the results from the 100 % petro based PET resin scenario were compared with some existing research results. In this study, the value for aquatic acidification in units of “g eq SO_2” was 12.92. This is very close to the literature value of 11.03,[39] in which the environmental impacts of PET resin production were calculated and compared with other types of resin such as polypropylene, polystyrene and PLA. The value for global warming in “g eq CO_2” was 3028 in this study. This value is also very close to the another literature value of 2798,[40] from a study in which the environmental impacts of nine plastic resins were calculated and compared for the U.S.. Therefore, since the values obtained in this study were similar to results from other research, the processes and production systems considered in this study seem reasonable.

From Figure 12, it is obvious that the values obtained from 100 % bio-based resin scenarios are lower than those of petro based resin for mineral extraction. In addition, it was found that the PTA scenario 2 and PTA scenario 3 had larger reductions in environmental burden for mineral extraction than PTA scenario 1. On the other hand, it seems from Figure 13 that the feedstock transition from petro to bio-base did not reduce the environmental impacts in the other category.

Considering the three 100 % bio-based resin scenarios (PTA scenario 1, PTA scenario 2 and PTA scenario 3), the PTA scenario 2 scenario had the highest value for terrestrial acidification and aquatic eutrophication. As with the global warming index, PTA scenario 1 had the highest and PTA scenario 3 the lowest values.

Here, we must consider that these results are just estimates of output values since each scenario contains unit processes that include a certain amount of uncertainty.

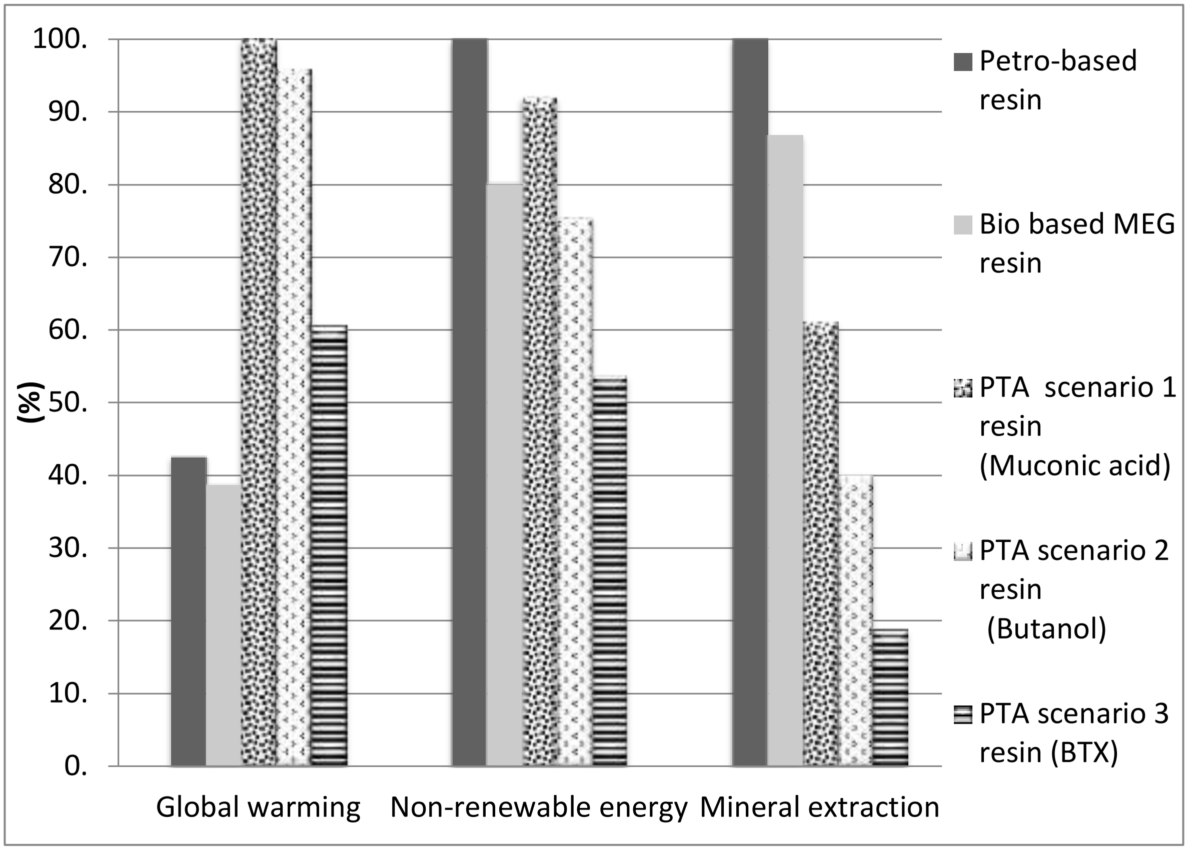


Figure 12. LCIA results comparison among five scenarios.

(Global warming, Non-renewable energy, Mineral extraction)

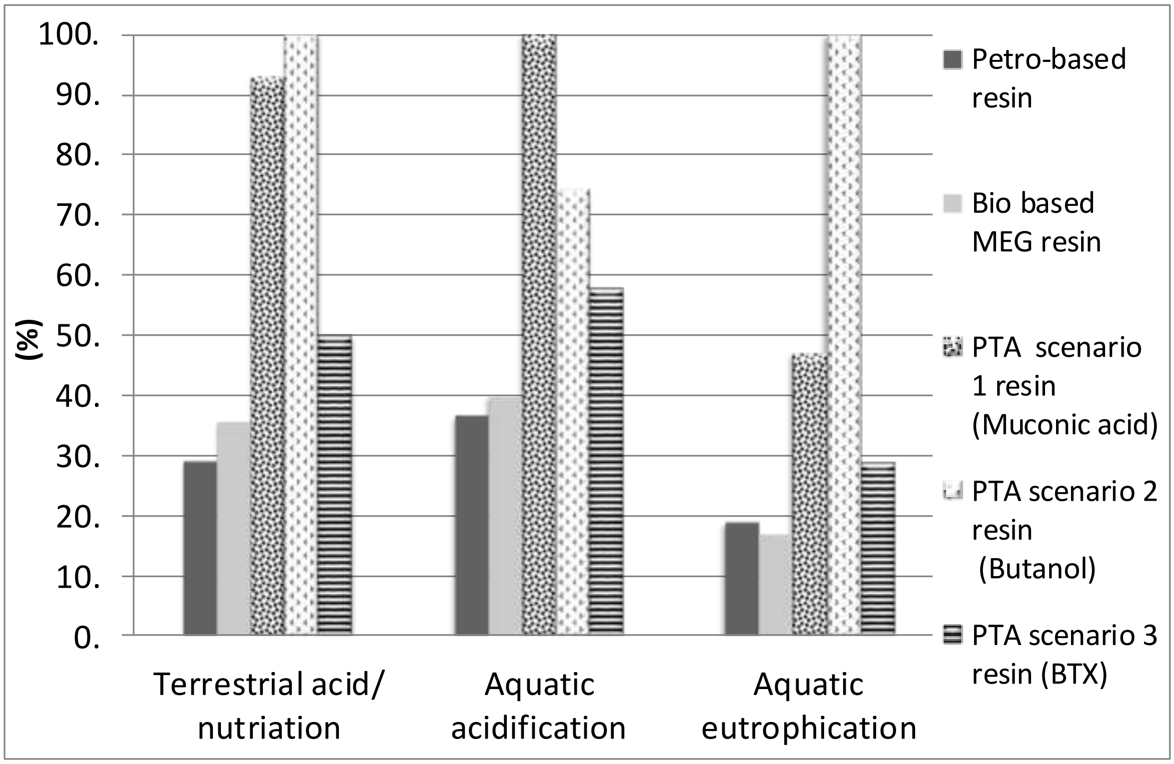


Figure 13. LCIA results comparison among five scenarios.

(Terrestial acid/nutriation, Aquatic acidfication, Aquatic eutrophication)

7.2.3. CONTRIBUTION FROM BIOMASS

In this study, wheat stover, corn, and poplar were considered as biomass sources. Table 29 shows the required biomass amounts for the production of 1 kg PET resin (PTA part). From this table, it is clear that scenario 2 required the smallest amount of biomass. Also, for the MEG part, 1.05 kg of corn was required in this study for the production of 1 kg PET resin.

Table 29. Biomass amounts for the production of 1kg PET resin (PTA part).

	Biomass type	Amount
Scenario 1	Wheat stover	4.412 kg
Scenario 2	Corn	3.250 kg
Scenario 3	Poplar	5.049 kg

Since this study uses IMPACT2002+ v2.1, CO_2 involved in biologic activity, such as the certain amount of CO_2 uptake to the biomass from the atmosphere and biogenic CO_2 emissions, are excluded in this study. In order to consider the situation which takes credit for such CO_2 contribution, we modified the global warming characterization factor in IMPACT2002+ v2.1. The characterization factor for “CO_2, in air” and “CO_2, biogenic” were changed from “0 kg CO_2-eq/kg” to “1 kg CO_2-eq/kg”. We assumed that the carbon in the biomass was completely taken from the air. In scenario 1 (mucconic acid pathway), the amount of CO_2 absorption was estimated by the C-content in the muconic acid, which was 1.859 kg / kg muconic acid. This is because we could not distinguish biotic CO_2 from the other operationally related CO_2. In scenario 2 (butanol pathway), we applied the CO_2 value described in the Ecoinvent corn inventory data, which was 1.347 kg / kg corn. In scenario 3 (BTX pathway), we applied the CO_2 value shown in the literature [41] which we explained in detail in Appendix C. The required CO_2 amount was 1.84 kg / kg poplar. Figure 14 shows the results of the comparison. While with the CO_2 credit, the global warming burden for the 100% bio-based resins are reduced, it still remains higher than the petro-based and partially bio-based PET.

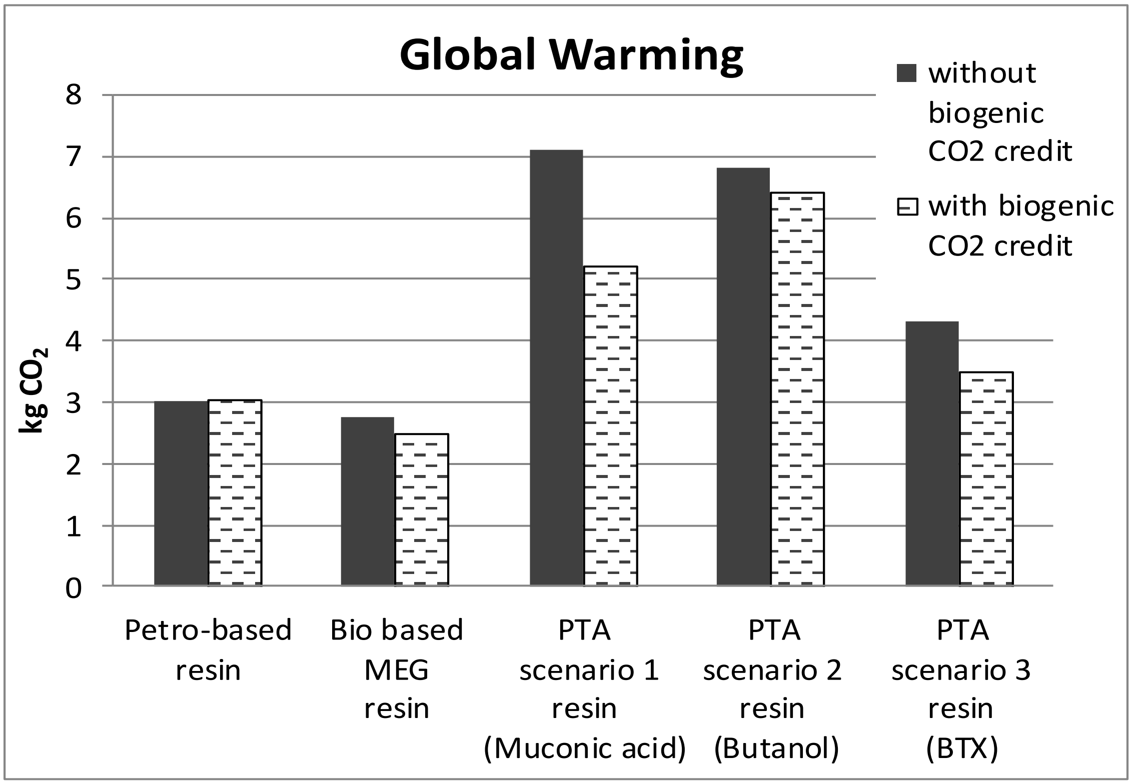


Figure 14. Comparison of the results with/without biologic related CO_2 credit.

7.2.4. UNCERTAINTY ANALYSIS (MONTE CARLO SIMULATION)

Since this study's PTA synthesis scenarios (unit processes) contain several estimations, the obtained LCIA results must be checked with the consideration of data uncertainty. Figure 15 shows the results of Monte Carlo simulations for global warming. The calculation number was 1000 times, and the input values were based on each value's average and standard deviation, which could be calculated from the pedigree matrix in Appendix A. From the figure, it is clear that each scenario's LCIA result has a certain range of output values. Now, when the data of PTA scenario 1 to PTA scenario 3 are compared, it can be concluded that the order (PTA scenario 1 and PTA scenario 2 show a higher value for global warming than PTA scenario 3) will not be changed. This is because, even if there is a certain amount of uncertainty (data deviation) for both scenarios, the difference is large enough to be maintained.

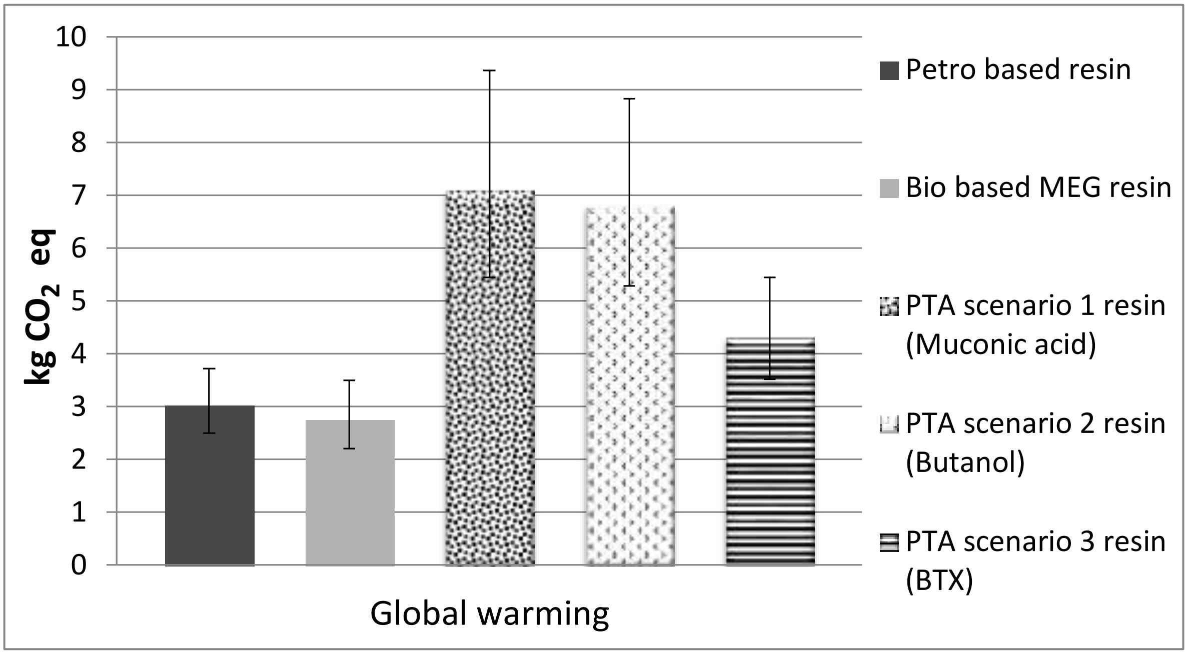


Figure 15. Impact result of global warming index, including data variation among five scenarios.

8. CONCLUSION

In this study, the environmental impacts of bio-based PET resin with scenarios of three different PTA production methods, which are pathways through muconic acid; butanol; and benzene, toluene and xylene (BTX) as intermediates, were compared. Although each scenario contains a certain amount of estimation due to the lack of information in this category, valuable environmental impact data could be obtained.

In the case of the PTA 1 scenario which goes through muconic acid as intermediate, the unit process of muconic acid production was dominant for all impact categories except for aquatic eutrophication. This unit process was found to be a relatively sensitive process in the pathway to synthesize PTA, according to the sensitivity analysis. This means LCA results from the PTA 1 scenario might contain data limitations to some extent; therefore, further sophisticated LCI data will be useful to provide more accurate comparisons.

In the case of the PTA 2 scenario which goes through butanol as intermediate, the unit process of isobutanol production seemed to have large impacts for each environmental index category. This PTA 2 scenario had the largest environmental impacts in the eutrophication categories among the three scenarios.

In the case of the PTA 3 scenario which goes through BTX as intermediate, the unit process of BTX production seemed to have large impacts for aquatic acidification and global warming. As with the global warming index, even if the data uncertainty (LCIA data output deviation) was considered, this scenario had less impact on global warming than that of the other 100 % bio-based PTA scenarios according to a limited Monte Carlo simulation.

Finally, the environmental impacts estimated from the above three 100 % bio-based resin scenarios were compared with those of petro based resin. The values obtained from the 100 % bio-based resin scenarios were found to be lower than those of petro based resin for mineral extraction. On the other hand, it seemed that feedstock transition from petro to bio-base does not appear to significantly reduce the environmental burden for the other impacts evaluated.

On the other hand, this study shows only preliminary results. Figure 16 shows the schematic comparison of PTA production steps, in which gray colored processes required estimation for LCI data. As shown in Figure 16, since some of the LCI data were calculated using chemically based estimations from other data sources in this study, to apply actual industrial process data can provide more accurate comparisons. In future research, the first production steps (PTA 1 step 1, PTA 2 step 2 and PTA 3 step 3) are the most important to accurately characterize the environmental impacts in every scenario since they are the most dominant processes in many impact categories. Also, the biomass feedstocks used in this study for the three scenarios were different from each other, so taking a close look at these differences and their influences will be also valuable.

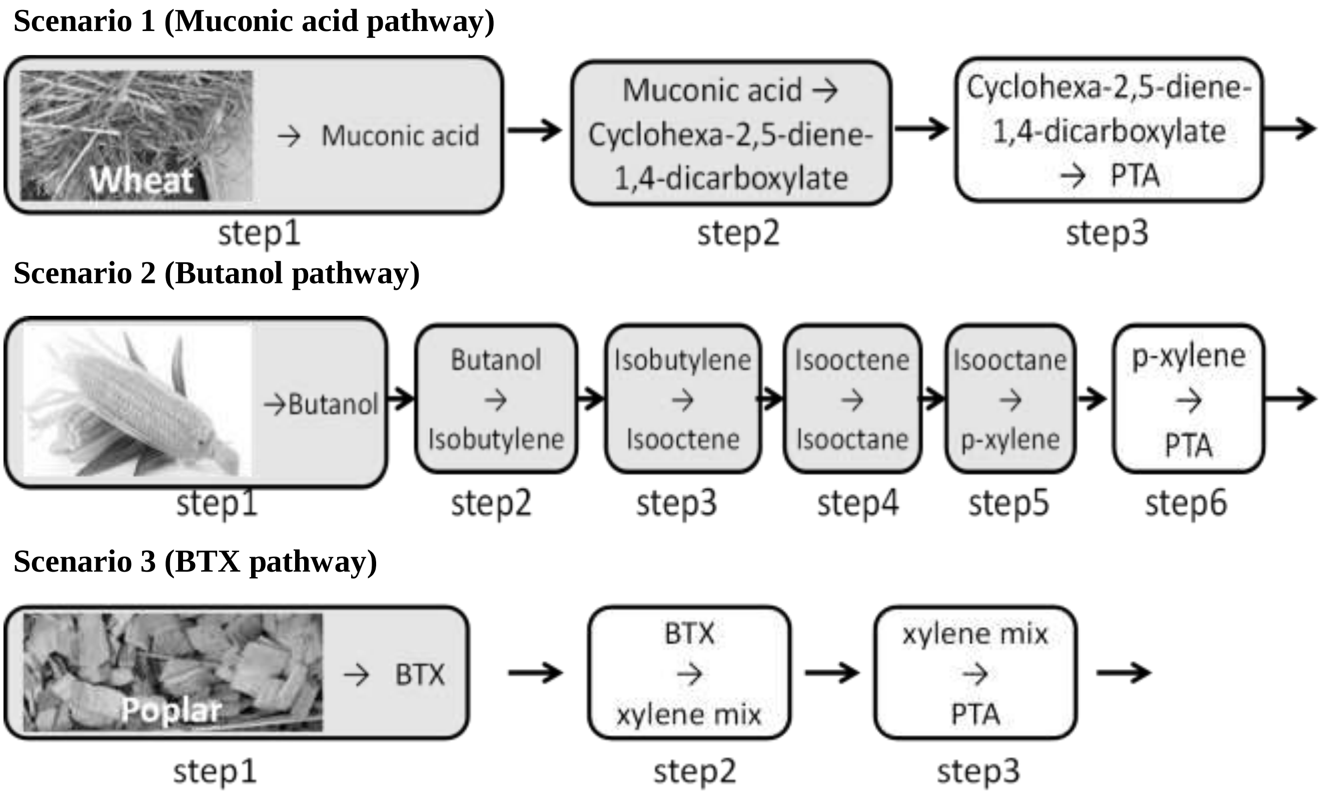


Figure 16. Schematic comparison of PTA production steps.

APPENDICES

Appendix A: Pedigree Matrix

Table 30 shows the pedigree matrix for this study derived from the literature,[42] whose temporal information was modified to our study time. This table indicates each process data quality by the score, and provides an objective analysis of the quality of each production step. Table 31 shows the summarized pedigree matrix, which includes each step's quality value.

The values of standard deviation (SD) in Table 30 were calculated according to the following equation.

$$\mathrm{SD} = \exp\sqrt{\left[\ln(\mathrm{U}_1)^2\right]+\left[\ln(\mathrm{U}_2)^2\right]+\left[\ln(\mathrm{U}_3)^2\right]+\left[\ln(\mathrm{U}_4)^2\right]+\left[\ln(\mathrm{U}_5)^2\right]+\left[\ln(\mathrm{U}_6)^2\right]}$$

U_1 = The corresponding score of reliability.

U_2 = The corresponding score of completeness.

U_3 = The corresponding score of temporal correlation.

U_4 = The corresponding score of geographical correlation.

U_5 = The corresponding score of technological correlation.

U_6 = The corresponding score of sample size.

All corresponding scores are shown in Table 30.

Table 30. Pedigree matrix used to assess the quality of data sources.

score	1	2	3	4	5
U1 (Reliability)	Verified data based on measurements	Verified data partly based on assumptions OR non-verified data based on measurements	Non-verified data partly based on qualified estimates	Qualified estimate; data derived from theoretical information (stoichiometry, enthalpy, etc.)	Non-qualified estimate
	1.00	1.05	1.10	1.20	1.50
U2 (Completeness)	Representative data from all sites relevant for the market considered over an adequate period to even out normal fluctuations	Representative data from >50% of the sites relevant for the market considered over an adequate period to even out normal fluctuations	Representative data from only some sites (<<50%) relevant for the market considered OR >50% of sites but from shorter periods	Representative data from only one site relevant for the market considered OR some sites but from shorter periods	Representativeness unknown or data from a small number of sites AND from shorter periods
	1.00	1.02	1.05	1.10	1.20
U3 (Temporal correlation)	2011 to 2013	2007 to 2010	2003 to 2006	1998 to 2002	before 1997
	1.00	1.03	1.10	1.20	1.50
U4 (Geographical correlation)	Data from area under study	Average data from larger area in which the area under study is	Data from smaller area than area under study, or from similar area	-	Data from unknown OR distinctly different area
	1.00	1.01	1.02		1.10
U5 (Further technological correlation)	Data from enterprises, processes and materials under study (i.e. identical technology)	-	,,or from processes/materials under study but from different technology	,,or on laboratory scale processes and same technology	,,but on laboratory scale of different technology
	1.00		1.2	1.50	2.00
U6 (Sample size)	>100, continous measurement, balance of purchased products	>20	> 10, aggregated figure in env. report	>=3	unknown
	1.00	1.02	1.05	1.10	1.20

Table 31. Pedigree matrix.

			U1	U2	U3	U4	U5	U6	"SD^2" value
PTA 1 (Muconic acid)	step 1	Energies/ Materials	1.1	1.1	1	1.02	1.2	1.1	1.063
	step 2	Energies	1.5	1.1	1.03	1.02	1.2	1.2	1.273
		Materials	1.2	1.1	1.03	1.02	1.2	1.2	1.116
	step 3	Energies/ Materials	-	-	-	-	-	-	-
PTA 2 (Butanol)	step 1	Energies/ Materials	1.2	1.1	1	1.02	1.2	1.05	1.081
	step 2	Energies	1.2	1.1	1.03	1.02	1.2	1.1	1.090
		Materials	1.2	1.1	1.03	1.02	1.2	1.1	1.090
	step 3	Energies	1.1	1.05	1.1	1.02	1.2	1.05	1.058
		Materials	1.2	1.05	1.1	1.02	1.2	1.05	1.084
	step 4	Energies	1.05	1	1.1	1	1.2	1	1.046
		Materials	1.2	1	1.1	1	1.2	1	1.078
	step 5	Energies	1.05	1	1.1	1	1.2	1	1.046
		Materials	1.2	1	1.1	1	1.2	1	1.078
	step 6	Energies/ Materials	-	-	-	-	-	-	-
PTA3 (BTX)	step 1 (from corn)	Energies/ Materials	1.05	1.05	1	1.02	1.5	1.1	1.196
	step 1 (from poplar)	Energies/ Materials	1.05	1.05	1	1.02	1.2	1.1	1.049
	step 2	Energies/ Materials	1.05	1.05	1.1	1.1	1.2	1.05	1.051
	step 3	Energies/ Materials	-	-	-	-	-	-	-

※"-" means, Simapro 7.3.3. database already contains each SD^2 value.

Detailed score reasoning procedures are described below.

PTA 1, Step 1

- Reliability (U1)

The inventory data were not verified, but were estimated on the basis of published research results.[24] The score based on Table 30 was 3.

- Completeness (U2)

The inventory data estimation was based on one data source. The score based on Table 30 was 4.

- Temporal correlation (U3)

The benchmarked process and its results were published in 2011. Therefore, the score based on Table 30 was 1.

- Geographical correlation (U4)

Although the benchmarked literature considered the situation in Europe, the energy related parts were replaced with the energy sources from US infrastructure (power plants). Therefore, the score based on Table 30 was 3.

- Further technological correlation (U5)

The inventory data were based on a related process. So, the score based on Table 30 was 3.

- Sample size (U6)

The sample sizes for the benchmarked process inventory data were unknown. The score on Table 30 was 5.

PTA 1, Step 2

- Reliability (U1)

The energy related amounts, were not verified since it was assumed that the energy related part was proportional to the output materials' weight ratio based on benchmark processes.[26] The score on Table 30 was 5. As for the material related parts, they were estimated on the basis of stoichiometry, so the score was 4.

- Completeness (U2)

The inventory data estimation was based on one data source. The score on Table 30 was 4.

- Temporal correlation (U3)

The benchmarked process and its result were published in 2008. Therefore, the score was 2.

- Geographical correlation (U4)

All inventory data of the benchmarked processes were based on the U.S. The score was 3.

- Further technological correlation (U5)

The inventory data was based on a similar chemical process which was the Diels-Alder reaction. The score was 3.

- Sample size (U6)

The sample size for the benchmarked process inventory data was unknown. The score was 5.

PTA 1, Step 3

All inventory data were calculated by using data in SimaPro software, and they already contained SD values. Those values were applied to this step.

PTA 2, Step 1

- Reliability (U1)

All inventory data were estimated on the basis of a similar chemical process, and derived from stoichiometry. The score was 4.

- Completeness (U2)

The inventory data estimation was based on one data source. The score was 4.

- Temporal correlation (U3)

The benchmarked process was the MEG 1 process which was from SimaPro software. Therefore, the score was 1.

- Geographical correlation (U4)

All inventory data for the benchmarked process were based on the U.S. The score was 3.

- Further technological correlation (U5)

The inventory data was based on a similar chemical reaction. The score was 3.

- Sample size (U6)

The benchmarked process inventory data were reported in SimaPro software. The score was 3.

PTA 2, Step 2

- Reliability (U1)

The inventory data were estimated on the basis of a similar chemical reaction,[21] and those data were a qualified estimation. So, the score was 4.

- Completeness (U2)

The inventory data estimation was based on one data source. The score on Table 30 was 4.

- Temporal correlation (U3)

The benchmarked process and its results were published in 2009. Therefore, the score was 2.

- Geographical correlation (U4)

All inventory data for the benchmarked process were based on the U.S. The score was 3.

- Further technological correlation (U5)

The inventory data was based on a similar chemical process (dehydration). The score was 3.

- Sample size (U6)

The sample size for the benchmarked process inventory data was more than 3. The score was 4.

PTA 2, Step 3

- Reliability (U1)

Inventory data were estimated on the basis of same chemical process (dimerization and hydrogenation).[33] The energy part was not verified but derived from a qualified source, so the score was 3. Material parts were calculated based on stoichiometry. The score was 4.

- Completeness (U2)

The benchmarked data represents the industrial market in this category. The score on Table 30 was 3.

- Temporal correlation (U3)

The benchmarked process and its results were published in 2002. Therefore, the score was 3.

- Geographical correlation (U4)

All inventory data for the benchmarked process were based on the U.S. The score was 3.

- Further technological correlation (U5)

The inventory data was based on a similar chemical reaction (dimerization and hydrogenation). The score was 3.

- Sample size (U6)

The benchmarked process inventory data came from averaged process data. The score was 3.

PTA 2, Step4

- Reliability (U1)

The inventory data were estimated on the basis of the same chemical process (hydrogenation).[34] The energy part was verified and derived from a qualified source, so the score was 2. Material parts were calculated based on stoichiometry. The score was 4.

- Completeness (U2)

The benchmarked data adequately represents the industrial market in this category. The score on Table 30 was 1.

- Temporal correlation (U3)

The benchmarked process and its result were published in 2006. Therefore, the score was 3.

- Geographical correlation (U4)

All inventory data for the benchmarked process were based on the U.S, and their coverage area corresponded to our study area. The score was 1.

- Further technological correlation (U5)

The inventory data was based on a similar chemical reaction (hydrogenation). The score was 3.

- Sample size (U6)

The benchmarked process inventory data came from averaged industrial data. The score was 1.

PTA 2, Step5

- Reliability (U1)

The inventory data were estimated on the basis of the same chemical process (dehydrocyclization).[34] The energy part was verified and derived from a qualified source, so the score was 2. Material parts were calculated based on stoichiometry. The score was 4.

- Completeness (U2)

The benchmarked data adequately represent the industrial market in this category. The score on Table 30 was 1.

- Temporal correlation (U3)

The benchmarked process and its results were published in 2006. Therefore, the score was 3.

- Geographical correlation (U4)

All inventory data for the benchmarked process were based on the U.S, and their coverage area corresponds to our study area. The score was 1.

- Further technological correlation (U5)

The inventory data was based on a similar chemical reaction (dehydrocyclization). The score was 3.

- Sample size (U6)

The benchmarked process inventory data came from averaged industrial data. The score was 1.

PTA 2, Step6

All inventory data were calculated by using data in SimaPro software, and they already contained SD values. Those values can be applied to this step.

PTA 3, Step 1(from corn)

- Reliability (U1)

The inventory data were estimated on the basis of a benchmark process (catalytic reforming),[35] which was verified and derived from a qualified source, so the score was 2.

- Completeness (U2)

The benchmarked data represent the industrial market in this category. The score on Table 30 was 3.

- Temporal correlation (U3)

The benchmarked process and its result were published in 2010. Therefore, the score was 1.

- Geographical correlation (U4)

All inventory data for benchmarked process were based on the U.S. The score was 3.

- Further technological correlation (U5)

The benchmarked processes output material was the same as that of the target process, but the technology itself was not quite the same. Therefore, the score was 5.

- Sample size (U6)

The sample size for the benchmarked process inventory data was based on industrial data (more than 3 sources). The score was 4.

PTA 3, Step 1 (from poplar)

- Reliability (U1)

The inventory data were estimated on the basis of a benchmark process (bio-oil production, catalytic upgrading),[36][37] which was verified and derived from a qualified source, so the score was 2.

- Completeness (U2)

The benchmarked data represent the industrial market in this category. The score on Table 30 was 3.

- Temporal correlation (U3)

The benchmarked process and its results were published in 2012.[36] Therefore, the score was 1.

- Geographical correlation (U4)

Although the benchmarked literature considers the situation of Europe, the energy related parts were replaced with energy sources from US infrastructure (power plant). Therefore, the score on Table 30 was 3.

- Further technological correlation (U5)

The inventory data was based on a related chemical process, and the same technology. So, the score was 3.

- Sample size (U6)

The sample size for the benchmarked process inventory data was based on industrial data (more than 3 sources). The score was 4.

PTA 3, Step 2

- Reliability (U1)

The inventory data were estimated on the basis of a similar chemical reaction,[38] which was verified and derived from a qualified source, so the score was 2.

- Completeness (U2)

The benchmarked data represents the industrial market in this category. The score on Table 30 was 3.

- Temporal correlation (U3)

The benchmarked process and its results were published in 2003. Therefore, the score was 3.

- Geographical correlation (U4)

All inventory data of the benchmarked process were based on the U.S. The score was 3.

- Further technological correlation (U5)

The inventory data were based on a related chemical process, and the same technology. So, the score was 3.

- Sample size (U6)

The benchmarked process inventory data came from averaged process data. The score was 3.

PTA 3, Step 3

All inventory data were calculated by using data in SimaPro software, and they already contained SD values. Those values can be applied to this step.

Appendix B: Classification factors and their environmental mechanism

The following information is cited from literature.[22] In the literature, Jolliet introduced the IMPACT 2002 + methodology which proposed an effective implementation of a combined midpoint/damage approach, with new developments in the comparative assessment of human toxicity and ecotoxicity. This method allows the quantification of stressors that have potential effects on the environment.

- Global warming

Incident shortwave radiation from the sun comes into contact with the earth's surface and is partly absorbed and partly reflected as infrared radiation. The reflected part is absorbed by so-called greenhouse gases in the troposphere and is re-radiated in all directions, including back to earth. This results in a warming effect at the earth's surface.

- Acidification

Acidification is the increasing concentration of hydrogen ion (H) within a local environment. Acidifying pollutants have a wide variety of impacts on soil, groundwater, surface waters, biological organisms, ecosystems and materials.

- Eutrophication/Nutrification

High nutrient concentrations may render surface water unacceptable for drinking water. In aquatic ecosystems increased biomass production may lead to a depressed oxygen levels, because of additional consumption of oxygen in biomass decomposition.

- Resource consumption

Damages due to mineral resource extraction lead to an additional energy requirement for further mining of this resource. Different from mineral extraction, non-renewable energy cannot be potentially accessible for further use, even after waste disposal, dissipated non-renewable energy is not any more available at a functional exergy level.

Appendix C: LCI Data Calculation Process

Bio-Ethanol Production (MEG Synthesis Step 1)

To obtain the ethanol inventory data derived from corn, the existing databases listed below were used. In this data, economical allocation rule was already applied to ethanol.

- Ethanol, 95 % in H_2O, from corn, at distillery/US U (from Ecoinvent)

(For the production of 1 kg of ethanol 95 % in H_2O)

Table 32. Bio-ethanol data.

Input		
Corn, at farm/US U	3.226	kg
Tap water, at user/	4.224	kg
Sulphuric acid, liquid, at plant	0.024	kg
Soda, powder, at plant	0.036	kg
Ammonium sulphate, as N, at regional storehouse	0.010	kg
Diammonium phosphate, as N, at regional storehouse	0.010	kg
Heat, natural gas, at industrial furnace >100kW	3.631	MJ
Electricity, medium voltage, at grid/US	0.134	kWh

Output		
Carbon dioxide, biogenic	2.526	kg
Heat, waste	3.353	MJ
Treatment, sewage, from residence, to wastewater treatment, class	0.001	m^3

- Ethanol, 99.7 % in H_2O, from biomass, at distillation/kg/US (from Ecoinvent)

(For the production of 1 kg of purified ethanol)

Table 33. Bio-ethanol data (distillation).

Input		
ethanol, 95% in H2O, from corn, at distillery/US	1.000E+00	kg
Heat, natural gas, at industrial furnace >100kW	1.005E+00	MJ
Electricity, medium voltage, at grid/US	8.839E-03	kWh

Output		
Heat, waste	3.182E-02	MJ
Treatment, sewage, from residence, to wastewater treatment, class	4.962E-05	m^3

Then, the two tables were combined so that ethanol 95 % could be cancelled and Table 2 could be drawn. This procedure was necessary since the subsequent process (MEG synthesis step 2) required 99.7 % ethanol for its input material.

Note: in this study, all transportation-related and facility-related parts in the input were excluded. This same approach was used in all other steps, even if not explicitly mentioned.).

Bio-Ethylene Oxide Production (MEG Synthesis Step 2)

In this step, an existing database was used.

- Ethylene oxide, at plant/RER with US electricity U (from US-EI)

Here, since this ethylene oxide process has ethanol data as an input stream, we simply replaced that data with the bio-ethanol data obtained from the previous step in order to obtain Table 3.

Bio-Ethylene Glycol Production (MEG Synthesis Step 3)

In this step, an existing database was used.

- Ethylene glycol, at plant/RER with US electricity U (from US-EI)

Here, ethylene oxide data in the input was replaced with bio-ethylene oxide data made in MEG synthesis step 2, in order to obtain Table 4.

Muconic Acid Production (PTA Synthesis Step 1)

In this step, inventory data were estimated based on literature.[24] As described in chapter 3.2, Duuren *et al*. assumed adipic acid obtained in their process would be generated by hydrogenation of muconic acid under slightly elevated pressure. Their study showed the system demands and emissions data with respect to each process (fermentation, hydrogenation, evaporation and crystallization). The following table shows the demands/emissions for the production of 1000kg adipic acid in their study.

Table 34. The demands/emissions for the production of 1000kg adipic acid.

Demands/emissions in each operational stage	CED	CExD	CO_2	N_2O	
	GJ	GJ	kg	kg	
Bioreactor	0.240	0.450	0.010	0	✔
Hydrogenation reactor	15.14	19.47	0.930	0	
Evaporator duty	1.740	3.290	0.110	0	
Crystallizer	0.320	0.710	0.020	0	

In our study, we used their fermentation stage data. Also, as described before, biomass feed for fermentation was required. The following table shows demands/emissions for feed material data to produce 1000 kg adipic acid. In our study, the selected biomass feed was lignin derived from wheat stover.

Table 35. The demands/emissions for feed material (adipic acid).

Demands/emissions for various feed materials	CED	CExD	CO_2	N_2O	
	GJ	GJ	kg	kg	
Benzoic acid	55.86	58.65	3343	0	
Impure aromatics	22.70	24.51	0	0	
Toluene	38.09	40.00	2830	0	
Phenol (lignin)	7.710	9.550	470.6	2.660	✔

In this table, the CED value was replaced with electricity, gasoline, and diesel. This is because energy required for biomass can be divided into two stages, cultivation and factory processing. According to the literature [43] which provided the original data for the above table, 19.6 % of energy was from electricity, and the author stated that the rest of the energy was from thermal energy which consisted of fuel sources. Since the literature itself didn’t describe the fuel composition used in the cultivation stage, we referred to the LCI data for wheat straw from Ecoinvent (“Wheat straw, at field/kg/US”) in order to estimate the used fuel composition. Its composition was gasoline 16.1 % and diesel 83.9 %. We applied the above described energy ratio to the lignin CED value, which means 19.6 % was used for electricity, 12.9 % was for gasoline, and 67.5 % was for diesel, as shown in the following table. For the production of wheat stover, we couldn’t find which allocation rule was applied in their study.

Table 36. Energy composition for the production of phenol (lignin).

Energy composition	Electricity	Gasoline	Diesel	Total
	GJ	GJ	GJ	GJ
Phenol (lignin)	1.512 (19.60 %)	0.995 (12.90 %)	5.203 (67.50 %)	7.710 (100.0 %)

In addition, feed materials for bacterial growth shown in the following table were required. We tried to use existing LCI data for these materials in order to include various emissions which could affect the acidification and the eutrophication index. Duuren used only CED data, which means only energy-related emissions were estimated in their study. Here, since SimaPro software does not have LCI data for potasium phosphate※ and glucose ※ (※ was indicated in the following table), we used their CED demand data and the CO_2/N_2O emission data shown in Duuren's work. (For potassium phosphate, CED: 0.26 GJ and CO_2:10.66 kg were applied. For glucose, CED: 3.62 GJ, CO_2: 221.26 kg and N_2O:10.14 kg were applied.)

Table 37. Feed demands for bacterial growth in bioreactor.

(Option Ⅱ)		
Ammonium sulphate	0.070	ton
Potasium phosphate※1	0.090	ton
Sodium phosphate	0.050	ton
Glucose※2	0.440	ton
Sodium hydroxide	0.560	ton
Hydrochloric acid	0.540	ton

Adipic acid is made from the following stoichiometry.

$$C_6H_6O_4(muconic\ acid) \ + \ 2H_2 \ \rightarrow \ C_6H_{10}O_4(adipic\ acid)$$

The weight of muconic acid could be calculated as 972 kg (= 1000 kg ÷ 146 g/mol × 142 g/mol). In Table 5, values which were the sum of the above data were divided by 972 so that the amount of muconic acid could be set as 1 kg. As described in section 4.1.4, the value of CExD was excluded in our study. Also, CED values (energy input) used in the operation of bio-reactor, and glucose / potassium phosphate used for bacterial growth were replaced with the electricity source.

Cyclohexa-2,5-Diene-1,4-Dicarboxylate Production (PTA 1 Synthesis Step 2)

In this step, a similar chemical process was used to estimate inventory data. The benchmarked process was the Diels-Alder reaction for the production of C_6H_{12}. The following table shows the input and output data for the production of 1 kg of cyclohexane using a vapor phase industrial process, from the literature. [26]

Table 38. Cyclehexane production data.

Input		
C_6H_6	9.300E-01	kg
H_2	7.800E-02	kg
steam	1.000E-01	kg
electricity	4.100E-02	kWh
catalyst	6.200E-05	kg

Output		
C_6H_6	4.700E-04	kg
H_2	1.500E-06	kg
catalyst	6.200E-05	kg

In this process, it seemed a certain amount of C_6H_6 and hydrogen were emitted without reaction. This ratio for hydrogen was calculated as the value of 1.92E-5 (= 1.5E-6/7.8E-2), and 5.1E-4 (= 4.7E-4/9.3E-1) for C_6H_6. Here, as described in chapter 3.5, we assumed the following two conditions to estimate LCI data for the Diels-Alder process for the production of $C_8H_8O_4$. First, the material and energy for the operation were calculated using the proportion of output material weight (in this case, $C_8H_8O_4$). The required material amounts for the chemical reaction were calculated on the basis of stoichiometry. (Note: This same approach was used in all other steps, even if not explicitly mentioned.)

The stoichiometry for this PTA synthesis step 2 is as follows:

$$C_6H_6O_4(muconic\ acid) \ + \ C_2H_2 \\ \rightarrow \ C_8H_8O_4(\mathrm{Cyclohexa-2{,}5-diene-1{,}4-dicarboxylate})$$

Therefore, the weight of $C_6H_6O_4$ was calculated as 845 g (= 1000 g ÷ 168 g/mol × 142 g/mol). Also, the amount of acetylene could be calculated as 155g (= 1000 g ÷ 168 g/mol × 26 g/mol). As with the benchmark process, specific amount of input materials were assumed to be emitted without reaction. For $C_6H_6O_4$, the amount emitted without reaction was calculated as 4.27E-4 g (= 8.45E-1 kg × 5.1E-4). For acetylene, this value was calculated as 2.98E-6 g (= 1.55E-1 kg × 1.92E-5). The catalyst used in the chemical reaction was not included in Table 6, and this exclusion step was also applied to all other steps described later in this appendix.

PTA Production (PTA 1 Synthesis Step 3)

In this step, a similar chemical process was applied to estimate inventory data. The benchmarked process is the dehydrogenation and purification for the production of PTA from para-xylene. Since there was no direct LCI process data from para-xylene to PTA in SimaPro software, it was calculated in an indirect manner with the use of the following two existing databases.

- Para-xylene, at plant/RNA (from U.S. LCI)

(For the production of 1 kg of para-xylene from xylene)

Table 39. Para-xylene production data.

Input		
xylene	1.000E+00	kg
Electricity, at grid, US	1.301E-01	kWh
Natural gas, combusted in industrial boiler/US	1.526E-01	m^3
Liquefied petroleum gas, combusted in industrial boiler/US	7.594E-03	l
Bituminous coal, combusted in industrial boiler/US	2.570E-02	kg

- Purified terephthalic acid, at plant/RER with US electricity U (from Ecoinvent)

(For the production of 1 kg of PTA from xylene)

Table 40. Purified terephthalic acid production data

Input		
Water, cooling, unspecified natural origin/m3	3.420E-04	m3
xylene	6.610E-01	kg
Water, completely softened, at plant/RER with US electricity	4.250E-01	kg
Acetic acid, 98% in H2O, at plant/RER with US electricity	5.000E-02	kg
Sodium hydroxide, 50% in H2O, production mix, at plant/RER with US electricity	1.450E-03	kg
Nitrogen, liquid, at plant/RER with US electricity	4.880E-02	kg
Electricity, medium voltage, production UCTE, at grid/UCTE with US electricity	4.690E-01	kWh
Heat, heavy fuel oil, at industrial furnace 1MW/RER with US electricity	6.370E-01	MJ
Heat, light fuel oil, at industrial furnace 1MW/RER with US electricity	2.120E-01	MJ
Heat, natural gas, at industrial furnace >100kW/RER with US electricity	4.580E-01	MJ
Heat, at hard coal industrial furnace 1-10MW/RER with US electricity	3.230E-01	MJ
Steam, for chemical processes, at plant/RER with US electricity	6.400E-01	kg
Output		
Heat, waste	1.690E+00	MJ
Particulates, > 10 um	2.880E-05	kg
Particulates, > 2.5 um, and < 10um	3.870E-05	kg
Particulates, < 2.5 um	2.250E-05	kg
Hydrocarbons, aromatic	3.780E-04	kg
NMVOC, non-methane volatile organic compounds, unspecified origin	1.100E-04	kg
BOD5, Biological Oxygen Demand	1.300E-03	kg
COD, Chemical Oxygen Demand	1.300E-03	kg
DOC, Dissolved Organic Carbon	1.220E-05	kg
TOC, Total Organic Carbon	1.220E-05	kg
Suspended solids, unspecified	2.560E-04	kg
Hydrocarbons, unspecified	1.400E-05	kg
Disposal, hazardous waste, 0% water, to underground deposit/DE	2.000E-04	kg
Disposal, average incineration residue, 0% water, to residual material landfill/CH with US electricity	6.000E-03	kg

With the use of the above 2 existing processes, the LCI data from para-xylene to PTA was calculated. First, each LCI value in the para-xylene process data was multiplied by 0.661 (Because the input mass of xylene, 0.661 kg, in the PTA production process needs to be cancelled by the mass of xylene in the para-xylene process), and then this value was subtracted from the PTA production process. The following table shows the obtained data for the production of 1 kg PTA from para-xylene.

Table 41. PTA production data (from para-xylene)

Input		
Water, cooling, unspecified natural origin/m^3	3.420E-04	m^3
Water, completely softened, at plant/RER with US electricity	4.250E-01	kg
para-xylene	6.610E-01	kg
Acetic acid, 98% in H2O, at plant/RER with US electricity	5.000E-02	kg
Sodium hydroxide, 50% in H2O, production mix, at plant/RER with US electricity	1.450E-03	kg
Nitrogen, liquid, at plant/RER with US electricity	4.880E-02	kg
Electricity, medium voltage, production UCTE, at grid/UCTE with US electricity	4.690E-01	kWh
Heat, heavy fuel oil, at industrial furnace 1MW/RER with US electricity	6.370E-01	MJ
Heat, light fuel oil, at industrial furnace 1MW/RER with US electricity	2.120E-01	MJ
Heat, natural gas, at industrial furnace >100kW/RER with US electricity	4.580E-01	MJ
Heat, at hard coal industrial furnace 1-10MW/RER with US electricity	3.230E-01	MJ
Steam, for chemical processes, at plant/RER with US electricity	6.400E-01	kg
Electricity, at grid, US	-8.598E-02	kWh
Natural gas, combusted in industrial boiler/US	-1.009E-01	m^3
Liquefied petroleum gas, combusted in industrial boiler/US	-5.020E-03	l
Bituminous coal, combusted in industrial boiler/US	-1.699E-02	kg
Output		
Heat, waste	1.690E+00	MJ
Particulates, > 10 um	2.880E-05	kg
Particulates, > 2.5 um, and < 10um	3.870E-05	kg
Particulates, < 2.5 um	2.250E-05	kg
Hydrocarbons, aromatic	3.780E-04	kg
NMVOC, non-methane volatile organic compounds, unspecified origin	1.100E-04	kg
BOD5, Biological Oxygen Demand	1.300E-03	kg
COD, Chemical Oxygen Demand	1.300E-03	kg
DOC, Dissolved Organic Carbon	1.220E-05	kg
TOC, Total Organic Carbon	1.220E-05	kg
Suspended solids, unspecified	2.560E-04	kg
Hydrocarbons, unspecified	1.400E-05	kg
Disposal, hazardous waste, 0% water, to underground deposit/DE with US electricity	2.000E-04	kg
Disposal, average incineration residue, 0% water, to residual material landfill/CH with US electricity	6.000E-03	kg

The stoichiometry for the production of PTA is

$$C_8H_{10}(para-xylene) \quad + \quad 3O_2 \quad \rightarrow \quad C_8H_6O_4\ (PTA) \quad + \quad 2H_2O$$

Here, as described before, we assumed the following two conditions in this study. The material and energy for the operation were calculated using the proportion of output material weight. The required material amounts for the chemical reaction were calculated on the basis of stoichiometry.

The target process stoichiometry is

$$C_8H_8O_4 \quad + \quad 0.5O_2 \quad \rightarrow \quad C_8H_6O_4\ (PTA) \quad + \quad H_2O$$

Therefore, each material involved in the chemical reaction could be calculated. The weight of $C_8H_8O_4$ consumed was 1012 g (= 1000 g ÷ 166 g/mol × 168 g/mol), that of O_2 was 155 g (= 1000 g ÷ 166 g/mol × 32 g/mol × 0.5. These values were applied to the previous table, and Table 7 was obtained.

Isobutanol Production (PTA 2 Synthesis Step 1)

In this step, a similar chemical process was applied to estimate inventory data. The benchmarked process was the corn to ethanol process as described in MEG step 1, in Table 2. The stoichiometry of this reaction is written as follows.

$$C_6H_{12}O_6 \quad \rightarrow \quad 2C_2H_6O(ethanol) \quad + \quad 2CO_2$$

The weight of CO_2 generated in this reaction was calculated as 957 g (= 1000 g ÷ 46 g/mol × 44 g/mol). Since Table 2 shows the emission of 2526 g biogenic CO_2, it seems 1569 g of CO_2 is the extra contribution from the production system (= 2526 g - 957 g). Also, the weight of glucose consumed in this reaction was calculated as 1957 g (= 1000 g ÷ 46 g/mol × 180 g/mol × 0.5). Therefore, it seems there was a conversion loss from corn to glucose due to the structural composition. We estimated this loss efficiency as 1.65 (= 3226 g ÷ 1957 g).

The target process stoichiometry is

$$C_6H_{12}O_6 \quad \rightarrow \quad C_4H_{10}O(isobutanol) \quad + \quad 2CO_2 \quad + \quad H_2O$$

The weight of CO_2 generated in this reaction was calculated as 1189 g (= 1000 g ÷ 74 g/mol × 44 g/mol × 2). Since the operational contribution of CO_2 must be included, 2758 g CO_2 would be the total amount generated in this case (= 1189 g + 1569 g). The weight of glucose required for this reaction was calculated as 2432 g (= 1000 g ÷ 74 g/mol × 180 g/mol). We must consider the loss efficiency from corn to glucose, resulting in a total amount of corn required of 4013 g (2432 g × 1.65).

As for the other LCI data, since they are generated from the process operation, we assumed each material mass should be increased in proportion to the ratios between the corn mass and the LCI data from the ethanol production model. The following table shows each material's mass ratio.

Table 42. Bio-ethanol production data (material mass ratio data)

Corn to ethanol process			Mass ratio (compared with the corn mass)
Input			
Corn, at farm/US U	3.226	kg	1.000E+00
Tap water, at user	4.224	kg	1.309E+00
Sulphuric acid, liquid, at plant	0.024	kg	7.453E-03
Soda, powder, at plant	0.036	kg	1.118E-02
Ammonium sulphate, as N, at regional storehouse	0.010	kg	2.993E-03
Diammonium phosphate, as N, at regional storehouse	0.010	kg	2.993E-03
Heat, natural gas, at industrial furnace >100kW	4.635	MJ	1.437E+00
Electricity, medium voltage, at grid/US	0.143	kWh	4.439E-02
Output			
Carbon dioxide, biogenic	2.526	kg	
Heat, waste	3.385	MJ	1.049E+00
Treatment, sewage, from residence, to wastewater treatment, class	0.001	m^3	4.004E-04

The obtained mass ratio values, except for the mass of corn and carbon dioxide, were multiplied by the corresponding entries in Table 2, and Table 11 was obtained.

n-Butanol Production (PTA 2 Synthesis Step 1, GREET, for Reference)

Wu *et al*. performed an LCA of corn-based butanol as a bio fuel.[29] In their study, the ABE (acetone-butanol-ethanol) fermentation process was considered as the production process, and the GREET model was used to obtain LCI data. The following table is based on their data. In their study, the amount of corn was calculated using a corn grain feed rate (lb/h) and butanol production rate (lb/h), and the obtained butanol amount was set as 11.587 kg (1 gal of butanol).

Table 43. N-butanol production data

Input		
Corn, at farm/US U	6.435E+01	kg
Heat, natural gas, at industrial furnace >100kW/RER	1.151E+05	Btu
Electricity	1.760E+00	kWh
Fertiliser (N)	4.200E-01	kg
Fertiliser (P)	1.490E-01	kg
Fertiliser (K2O)	1.740E-01	kg

Output		
Acetone, liquid, at plant/RER with US electricity	8.370E+00	kg
DDGS, from corn, at distillery/US	2.568E+01	kg

The data were divided by 11.587 in order to set the output amount as 1 kg, which was shown as Table 12.

Isobutylene Production (PTA 2 Synthesis Step 2)

In this step, a similar chemical process was applied to estimate inventory data.[21] The benchmarked process is the dehydration of bio-ethylene from bio-ethanol. The following table shows the inputs and outputs data for the production of 1 kg of ethylene.

Table 44. Bio-ethylene production data.

Input		
ethanol	1700	g
electricity	1.800	MJ
fuel	5.600	MJ
Output		
CH_4	1.500	g
CO	0.200	g
CO_2	327.0	g
N_2O	0.012	g
NMVOC	0.011	g
NOx	1.500	g
SO_2	0.100	g

The target process stoichiometry is

$$C_4H_{10}O\ (isobutanol) \quad \rightarrow \quad C_4H_8 (isobutylene) \quad + \quad H_2O$$

The weight of C_4H_8 generated in this reaction was calculated as 1321 g (= 1000 g ÷ 56 g/mol × 74 g/mol). This value was applied to modify the above table, and Table 13 was created.

Isooctene Production (PTA 2 Synthesis Step 3)

In this step, a similar chemical process was applied to estimate inventory data. The benchmarked process is the dimerization and hydrogenation for isooctene from C_4 component. The following table shows the input and output data from the literature.[33]

Table 45. Isooctene production data (from C_4 component).

Input		
C_4s (isobutene 15 wt.%)	1.000E+05	lb
Oxygen	2.200E+01	lb
water	4.000E+01	lb
Output		
isooctene	1.668E+04	lb
C_4 Raffinate	8.338E+04	lb

As for operational energy, literature reports that steam consumption of 2 tonnes/tonne isooctene is required based on contractor data, and the process emits 0.3 tonne CO_2-eq/tonne isooctene.[31]

As for the conversion from isobutene to isooctene, it seems almost all isobutene could be converted into isooctene. Although we used 100 % isobutylene as the input material in the target process, the process efficiency was assumed to be the same as with the unpurified input case, that is to say, 10,000 lb isobutylene could be converted into 10,000 lb isooctene in this study.

The isooctene amount was set as 1 kg (every value in the above table were divided by 10,000, and the unit was changed from pound to kg), and steam consumption and CO_2 emissions were added. The obtained LCI data is Table 14.

Isooctane Production (PTA 2 Synthesis Step 4)

In this step, a similar chemical process was applied to estimate inventory data. The benchmarked process is the hydrogenation for n-heptane from 1-heptene. The following table shows the energy data related in this process, described in the literature.[34]

Table 46. N-heptane production energy data.

Energy Source	Specific Energy (10^3 Btu/bbl feed)
Fuel	62.00
Electricity	19.00
Total Energy input	81.00
Hydrogen consumed	30.00
Steam Produced	-31.10

Here, “hydrogen consumed” energy was excluded in our study since this value was used to explain the change of enthalpy for this chemical reaction in the literature.

Since the benchmark process stoichiometry is

$$C_7H_{14}(1-heptene) \quad + \quad H_2 \quad \rightarrow \quad C_7H_{16}(n-heptane)$$

The following table was based on the above table and stoichiometry. (1 bbl = 159 L, density of 1-heptene is 0.697 g/cm^3). Here, we assumed that steam produced energy was recovered and used as an energy source, so that value was subtracted from the fuel energy amount (62000 Btu – 31000 Btu = 30900 Btu).

Table 47. N-heptane production energy data. (unit change)

Input			
Fuel	3.090E+04	Btu	
Electricity	1.900E+04	Btu	
1-heptene	1.108E+02	kg	'＝159 L × 0.697 g/cm3
Hydrogen	2.260E+00	kg	'＝110.823 kg ÷ 98 g/mol × 2 g/mol

Output			
n-heptene	1.153E+02	kg	'＝110.823 kg ÷ 98 g/mol × 102 g/mol

The target process stoichiometry is

$$C_8H_{16}(isooctene) \quad + \quad H_2 \quad \rightarrow \quad C_8H_{18}(isooctane)$$

Therefore, the weight of C_8H_{16} consumed in this reaction was calculated as 113.3 kg (= 115.346 kg ÷ 114 g/mol × 112 g/mol). The weight of hydrogen consumed was calculated as 2.0 kg (= 115.346 kg ÷ 114 g/mol × 2 g/mol). These values were applied to modify the above table, and the isooctane amount was set as 1 kg, yielding the LCI data shown in Table 15.(Data were divided by 115.346.) In Table 15, fuel was replaced with the natural gas.

Para-Xylene Production (PTA 2 Synthesis Step 5)

In this step, estimated data which is based on a similar chemical process was applied. The benchmarked process is dehydrocyclization for the production of toluene from n-heptane. The following table shows the energy data for this process, as described in the literature.[34]

Table 48. Toluene production energy data.

Energy Source	Specific Energy (10^3 Btu/bbl feed)
Fuel	254.0
Electricity	10.00
Total Energy input	264.0
Hydrogen consumed	-479.2
Steam Produced	-15.40

As in the previous step, “hydrogen consumed” energy was excluded in the study since this value was used to explain the change of enthalpy for this chemical reaction in the literature.

The benchmark process stoichiometry is

$$C_7H_{16}(n-heptene) \quad \rightarrow \quad C_7H_8(Toluene) \quad + \quad 4H_2$$

The following table was obtained based on the above table and stoichiometry. (1 bbl = 159L, density of n-heptene is 0.684 g/cm^3). As in step 4, it was assumed that steam produced energy was recovered and used as an energy source, so the value was subtracted from the fuel energy amount (254000 Btu – 15400 Btu = 238600 Btu).

Table 49. Toluene production energy data (unit change).

Input			
Fuel	2.386E+05	Btu	
Electricity	1.000E+04	Btu	
n-heptene	1.088E+02	kg	’＝159 L × 0.684 g/cm^3

Output			
Hydrogen	8.700E+00	kg	’＝(108.756 kg ÷ 100 g/mol ×2 g/mol) ×4
Toluene	1.001E+02	kg	’＝108.756 kg ÷ 100 g/mol × 92 g/mol

The target process stoichiometry is

$$C_8H_{18} \quad \rightarrow \quad C_8H_{10} \quad + \quad 4H_2$$

Therefore, the weight of C_8H_{18} consumed in this reaction was calculated as 107.6 kg (= 100.055 kg ÷ 106 g/mol × 114 g/mol). The weight of hydrogen generated was calculated as 7.55 kg (= 100.055 kg ÷ 106 g/mol × 2 g/mol × 4). These values were applied to modify the above table, with the para-xylene amount set as 1 kg. , The calculated LCI data are shown in Table 16. (All data were divided by 100.055.) In Table 13, fuel was replaced with the natural gas..

PTA Production (PTA 2 Synthesis Step 6)

This process is the same as PTA 1 synthesis step 3, discussed earlier in the appendix.

Benzene Toluene Xylene production (PTA 3 Synthesis Step 1, through Direct Catalytic Reforming)

In this step, estimated data which is based on a similar chemical process was used. The benchmarked process was BTX production from naphtha. The following table shows the mass and energetic rates data in the literature.[35]

Table 50. BTX production data (from naphtha).

Feed	6.061E+04	kg/h
Hydrogen	4.218E+03	kg/h
Fuel Gas	1.040E+02	kg/h
LPG	6.330E+02	kg/h
Reformate	5.565E+04	kg/h
Electricity	4.080E+00	MW
Heat duty	2.457E+01	MW

In this Table, reformate contains C_6 to C_8 aromatics (benzene, toluene, xylenes = BTX), and 51% of reformate is BTX components.[44] Feed means naphtha. Fuel gas, LPG, hydrogen and reformate are the process yields. Therefore, this table can be reformulated as follows.

Table 51. BTX production data (from naphtha, modified).

Input			
Naphtha	6.061E+04	kg	
Hydrogen	4.218E+03	kg	
Electricity	4.080E+00	MWh	
Heat	2.457E+01	MWh	
Output			
LPG	6.330E+02	kg	
BTX	2.838E+04	kg	= 55650*0.51
Fuel Gas	1.040E+02	kg	

In this step, we assumed biomass material could be directly converted into fuel yields so that naphtha was replaced by corn of the same mass. Also, LPG and fuel gas were converted into liters (using a conversion factor of 0.5 kg/l) since SimaPro's data was expressed in liters. These values were applied to modify the above table, and the BTX amount was set as 1 kg. The required LCI data are shown in Table 19.(Inventory data were divided by 28,380 kg.)

Benzene Toluene Xylene production (PTA 3 Synthesis Step 1, through Fast Pyrolysis)

In this step, estimated data based on a similar chemical process was used. The benchmarked process is the production of bio-oil from biomass through the fast pyrolysis of a lignocellulosic feedstock in a CFB reactor.[36] The following table shows the demands and emissions data for the production of bio-oil.

Table 52. Bio-oil production data .

Input		
poplar	5.407E+03	kg
process water	8.964E+01	kg
air	5.141E+03	kg
electricity	7.024E+02	kWh
Natural gas	1.580E+00	MJ

Output		
Bio-oil	2.265E+03	kg
Char	8.675E+01	kg
Ash	3.121E+01	kg
O_2	3.650E+02	kg
N_2	4.028E+03	kg
Water	2.690E+03	kg
H_2	3.000E-02	kg
CO	7.680E+00	kg
CO_2	1.286E+03	kg
Methane	2.990E-06	kg
Ethene	5.980E-06	kg
propene	8.960E-06	kg
ammonia	4.480E-06	kg

For poplar wood's inventory data, literature data [44] was used since there was no existing database in SimaPro software. The table below shows the inventory data for poplar production.

Table 53. Poplar production data .

Input		
Fertilizer(9N/18P/27K)	1.200E+03	kg
Ammonium nitrate	5.000E+02	kg
Glyphosate	4.000E+00	l
Metil pirimifos	1.000E+00	l
Propineb	5.000E-01	l
Diesel	3.464E+02	l

Output		
NH_3	9.950E+00	kg
NOx	3.000E-01	kg
poplar	9.596E+04	kg

In this study, obtained bio-oil was assumed to be directly converted into BTX through the process of catalytic (zeolite) upgrading. The conversion ratio data (0.83) was applied, which was from the related category's literature.[37] In the literature, the overall mass for production of bio-oils from wood by fast pyrolysis followed by conversion into refined liquid fuels by hydrotreating and zeolite upgrading were shown.

Therefore, the bio-oil part in the table was replaced with 1880.3 kg of BTX (= 2265.4 kg × 0.83). This value was applied to modify the above table, and the BTX amount was set as 1 kg, yielding the LCI data shown in Table 20.(Data were divided by 1880.3.)

Xylene Mix Production (PTA 3 Synthesis Step 2)

We considered extractive distillation process in this step. From the literature,[38] we assumed the use of the sulfolane process which is used to recover high-purity aromatics from hydrocarbon mixtures. This process consumes an average 287.5 kcal (1.1932 MJ) of energy per kilogram of the specific aromatics extraction.

Here, since the xylene mix weight % composition is 33.0 in BTX under the highest yield condition,[37] (upgrading temperature is set as 550 ºC), 3.0303 kg BTX is needed to produce 1 kg xylene mix (in this study, 100 % extraction is assumed) In Table 21, the xylene mixes production energy was replaced with electricity.

PTA Production (PTA 3 Synthesis Step 3)

In this step, an existing database was used.

- Purified terephthalic acid, at plant/RER with US electricity U (Ecoinvent)

Here, xylene mixture in the input was replaced with the bio-xylene mix from PTA 3 synthesis step 2, in order to obtain Table 22.

REFERENCES

REFERENCES

[1] Tuck C. O, Pérez E, Horváth I. T, Sheldon R. A, Poliakoff M, "Valorization of Biomass: Deriving More Value from Waste" *Science*. **2012**, 337, 695-699.

[2] Press release, "PepsiCo Develops World's First 100 % Plant-based, Renewably Sourced PET Bottles", **2011**, PepsiCo. Available at:http://www.pepsico.com/PressRelease/PepsiCo-Develops-Worlds-First-100-Percent-Plant-Based-Renewably-Sourced-PET-Bott03152011.html. Access date: 10/13/2012.

[3] USEPA, "Risk Management Sustainable Technology", Available at: http://www.epa.gov/ORD/NRMRL/std/. Access date: 2/25/2013.

[4] SPC, "Essentials of Sustainable Packaging Curriculum", Available at: http://www.sustainablepackaging.org/content/?type=5&id=the-essentials-of-sustainable-packaging-curriculum. Access date: 2/25/2013.

[5] Guinée J. B, "Handbook on Life Cycle Assessment: Operational Guide to the ISO Standards", *Eco-Efficiency in Industry and Science*, **2002**, 7, 708.

[6] Narayan R, Patel M, "Review and Analysis of Bio-based Product LCA's", Available at: http://www3.abe.iastate.edu/biobased/lcareview.pdf. Access date: 1/29/2013.

[7] Vink E. T. H, Glassner D. A, Kolstad J. J, Wooley R. J, O'Connor R. P, "The eco-profiles for current and near-future NatureWorks$^{®}$ polylactide (PLA) production", *INDUSTRIAL BIOTECHNOLOGY*, **2007**, 3-1, 58.

[8] Kim S, Dale B. E, " Energy and Greenhouse Gas Profiles of Polyhydroxybutyrates Derived from Corn Grain: A Life Cycle Perspective", *ENVIRONMENTAL SCIENCE & TECHNOLOGY*, **2008**, 42, 7690.

[9] Company technical report, “Life Cycle Assessment of biobased polyamides VESTAMID® Terra”, **2010**, Evonik Degussa GmbH, Available at: http://www.vestamid.com/sites/dc/Downloadcenter/Evonik/Product/VESTAMID/en/technical-literature/VESTAMID%20Terra%20-%20Life%20Cycle%20Analysis.pdf. Access date: 1/29/2013.

[10] Cherubinia F, Birda N. D, Cowieb A, Jungmeiera G, Schlamadingerc B, Gallasch S. W, “Energy- and greenhouse gas-based LCA of biofuel and bioenergy systems: Key issues, ranges and recommendations”, *Resour. Conserv. Recy.***2009**, 53, 434-447.

[11] Stichnothe H, Azapagic A, “Bioethanol from waste: Life cycle estimation of the greenhouse gas saving potential”, Resour. Conserv. Recy. **2009**,53, 624-630.

[12] Kim S, Dale B. E, Jenkins R, “Life cycle assessment of corn grain and corn stover in the United States”, *Int J Life Cycle Assess*, **2009**, 14, 160-174

[13] Souza S. P, Márcio Turra de Ávila, Pacca S, “Life cycle assessment of sugarcane ethanol and palm oil biodiesel joint production”, *biomass and bioenergy*, **2012,** 44, 70-79

[14] Selke S, Culter J. D, Hernández R. J, “Plastic Packaging-property, processing, application and regulations 2nd edtion,” , *Hanser Publications*, **2004**, 120.

[15] Krüger M, Kauertz B, Detzel A, “Life Cycle Assessment of food packaging made of IngeoTM biopolymer and (r)PET, Final report”, **2009**, IFEU GmbH, Available at: http://www.natureworksllc.com/~/media/The_Ingeo_Journey/Ingeo_vs_rPET/IFEU_LCA__Ingeo_Full_Report_012709_FINAL_pdf.pdf. Access date: 1/29/2013.

[16] Franklin Associates., “FINAL REPORT, LIFE CYCLE INVENTORY OF 100 % POSTCONSUMER HDPE AND PET RECYCLED RESIN FROM POSTCONSUMER CONTAINERS AND PACKAGING”, **2010**, Available at: http://plastics.americanchemistry.com/Education-Resources/Publications/Life-Cycle-Inventory-of-Postconsumer-HDPE-and-PET-Recycled-Resin.pdf. Access date: 1/29/2013.

[17] Ghosh T, Socci E, Cashman S, Sauer B, “Life Cycle Assessment of PepsiCo USA’s Beverage Packaging”, PepsiCo presentation at IAPRI World Packaging Conference, June 17-21, 2012, handout 303-311.

[18] Jong E. D, Higson A, Walsh P, Wellisch M, “Bio-based Chemical - Value Added Products from Biorefineries”, *The IEA Bioenergy Report*, **2012**. Available at: http://www.ieabioenergy.com/DownLoad.aspx?DocId=7312. Access Date: 2/25/2013.

[19] ISO (International Organization for Standardization) , 2006, Environmental Management –Life Cycle Assessment – Principles and Framework, ISO14040

[20] ISO (International Organization for Standardization) , 2006, Environmental Management –Life Cycle Assessment – Requirements and Guidelines, ISO 14044

[21] Christin Liptow, Anne-Marie Tillman, “Comparative life cycle assessment of polyethylene based on sugarcane and crude oil”, **2009**, Chalmers University of Technology. Available at: http://cpmdatabase.cpm.chalmers.se/DataReferences/ESA_2009--14.pdf. Access date: 10/13/2012.

[22] Jolliet O, Margni M, Charles R, Humbert S, Payet J, Rebitzer J, Rosenbaum R, " IMPACT 2002+: A New Life Cycle Impact Assessment Methodology", *Int J. of LCA*, **2003**, 8, 6, 324-330

[23] SimaPro LCA software, “SimaPro 7.3.3”, Released 1/31/12. Available at: http://www.pre-sustainability.com/SimaPro-lca-software. Access date: 2/18/2013.

[24] Van Duuren, J.B.J.H, Brehmer B, Mars A.E, Eggink G, Martins dos Santos V.A.P, Sanders J.P.M, “A Limited LCA of Bio-Adipic Acid: Manufacturing the Nylon-6,6 Precursor Adipic Acid Using the Benzoic Acid Degradation Pathway From Different Feedstocks”. *Biotechnology Bioengineering.* **2011**, 108, 1298–1306.

[25] US. 2011/0124911 A1 (2011), ” Semi-synthetic terephthalic acid via microorganisms that produce muconic acid”, Mark J. Burk, Robin E. Osterhout, Jun Sun.

[26] Zhang Y, “ECOLOGICALLY-BASED LCA AN APPROACH FOR QUANTIFYING THE ROLE OF NATURAL CAPITAL IN PRODUCT LIFE CYCLES”, **2008**, Ph.D. Dissertation, Ohio State University, Chemical Engineering. Available at: http://etd.ohiolink.edu/view.cgi?acc_num=osu1222102539. Access date:1/29/2013.

[27] US. 8,017,375 B2 (2011), “Yeast organism producing isobutanol at a high yield”, Gevo, Inc., Reid M. Renny Feldman, Uvini Gunawardena, Jun Urano, Peter Meinhold, Aristos Aristidou, Catherine Asleson Dundon, Christopher Smith

[28] US. 8,133,715 B2 (2011), “Reduced by-product accumulation for improved production of isobutanol”, Gevo, Inc., Doug Lies, Stephanie Porter-Scheinman, Julie Kelly, Catherine Asleson Dundon, Aristos Aristidou, Andrew Hawkins.

[29] Argonne National Laboratory, “Life-Cycle Assessment of Corn-Based Butanol as a Potential Transportation Fuel”, **2010**, Available at: http://www.transportation.anl.gov/pdfs/AF/448.pdf. Access date:1/29/2013.

[30] GREET model (The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation model), **2012**, Available at: http://greet.es.anl.gov. Access date: 2/18/2013.

[31] Croezen H, Kampman B, ”The impact of ethanol and ETBE blending on refinery operations and GHG-emissions”. *EnergyPolicy*, **2009**, 37, 12; pp. 5226-5238, doi:10.1016/j.enpol.2009.07.072.

[32] Croezen H, Kampman B, Gerdien van de Vreede, Sevenster M,"ETBE and Ethanol: A Comparison of CO_2 Savings”, **2006**, CE Delft. Available at: http://www.ce.nl/publicatie/etbe_and_ethanol%3A_a_comparison_of_co2_savings/715. Access date: 1/29/2013.

[33] Technology profile report, “Conversion of Refinery MTBE Units for Isooctene/Isooctane Production”, CDTECH®, 2004. Available at http://www.cdtech.com/techProfilesPDF/Dimer%208.pdf. Access date: 3/4/2013.

[34] The Industrial Technologies Programs, "Energy Bandwidth for Petroleum Refining Processes", **2006**, Energetics Incorporated for the U.S. Department of Energy Office of Energy Efficiency & Renewable Energy. Available at: http://www1.eere.energy.gov/manufacturing/resources/petroleum_refining/pdfs/bandwidth.pdf. Access date: 1/19/2013.

[35] Portha J. F, Jaubert J. N, Louret S, Pons M. N, "Life Cycle Assessment Applied to Naphtha Catalytic Reforming", *Oil & Gas Science and Technology* , **2010**, 65, 5, pp. 793-805.

[36] Iribarrena D, Petersa J. F, Dufour J, “Life cycle assessment of transportation fuels from biomass pyrolysis”, *Fuel*, **2012**, 97, 812-821.

[37] Huber G.W, Iborra S, Corma A, “Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering”, *Chemical Reviews*, **2006**, 106, 4044-4098

[38] Robert A. M, “Handbook of Petroleum Refining Processes - Third Edition”, *McGraw Hill Professional*, **2003**, chapter 9.

[39] Madivala S, Auras R, Singha S. P, Narayan R, “Assessment of the environmental profile of PLA, PET and PS clamshell containers using LCA methodology”, *Journal of Cleaner Production*, **2009**, 17, 1183-1194.

[40] Franklin Associates., “FINAL REPORT, CRADLE-TO-GATE LIFE CYCLE INVENTORY OF NINE PLASTIC RESINS AND FOUR POLYURETHANE PRECURSORS”, **2010**, Available at: http://www51.honeywell.com/sm/chemicals/enovate/common/documents/FP_Enovate_July_2010_Report_by_the_American_Chemistry_Council_Manual.pdf. Access date: 2/25/2013.

[41] García S. G, Gasolb C. M, Gabarrellb X, Rieradevall J, Moreira M. T, Feijoo G, “Environmental profile of ethanol from poplar biomass as transport fuel in Southern Europe”, *Renewable Energy*, **2010**, 35, 1014-1023.

[42] Weidema B. P, Wesnæs M. S, "Data quality management for life cycle inventories - an example of using data quality indicators", *In: Journal of Cleaner Production*, **1996**, 4(3-4), 167-174.

[43] Brehmer B, “Chemical biorefinery perspectives - the valorisation of functionalised chemicals from biomass resources compared to the conventional fossil fuel production route”, **2008**, , Available at: http://edepot.wur.nl/122048. Access date:3/18/2013.

[44] Technical report, “The BTX Chain: Benzene, Toluene, Xylene”, U.S. Department of Energy Office of Energy Efficiency & Renewable Energy. Available at: http://www1.eere.energy.gov/manufacturing/resources/chemicals/pdfs/profile_chap4.pdf. Access date: 1/31/2013.