LIFE CYCLE ASSESSMENT AND GREEN DESIGN: AN ASSESSMENT OF GREEN DESIGN IN A CASE STUDY OF PLASTICS

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In this thesis, a cradle-to-gate life cycle assessment (LCA) for the production of bio-based polyethylene terephthalate (B-PET) is completed and then used along with LCAs of 11 other packaging plastics to evaluate the efficacy of green design principles such as the "12 Principles of Green Chemistry," the "12 Additional Principles of Green Chemistry," and the "12 Principles of Green Engineering."

The chemical composition of B-PET is identical to traditional polyethylene terephthalate (PET) and the production methods for both polymers are similar. B-PET production differs from traditional PET production by using (in part) sugarcane molasses as a material source in place of natural gas and petroleum. Results from this study show that B-PET production, compared to PET, represents a 28% reduction in global warming potential and a 12% reduction in non-renewable energy (NREU) use. However, a normalization of impacts in all categories using estimates of total U.S. emissions in 1999 shows that the magnitudes of both reductions are small when compared to increases in human health and exotoxicity impacts.

Adhering to green design principles was shown to decrease life cycle environmental impacts for petroleum based polymers and bio-polymers separately. Biopolymers rank highly in terms of green design, however cause increases in life cycle environmental impacts from production in almost every measureable category. This thesis recommends qualifying the "use renewable sources" principle to exclude agriculture products shown to have large, deleterious environmental impacts durign farming. Both the use of renewable sources and the design

products that biodegrade should be qualified to avoid increasing the number of chemical processing steps to achieve each goal.

This thesis does not criticize the inclusion of green chemistry and other green design principles into national research policies or marketing initiatives. It instead uses a case study to evaluate the effectiveness of previously used design principles, outlines possible issues, and makes recommendations for improvements.

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NOMENCLATURE

AC	acidification potential
B-PET	bio-polyethylene terephthalate (plastic material made from both petroleum and agriculture sources)
CAR	carcinogenic human health hazard potential
CED	cumulative energy demand impact assessment method, created by ecoivnent.
ETX	ecotxicity
GHG	greenhouse gas
GPPS	general purpose polystyrene (plastic material)
GWP	global warming potential
HDPE	high density polyethylene (plastic material)
LDPE	low density polyethylene (plastic material)
NCA	non-carcinogenic human health hazard potential
NREU	non-renewable energy use (includes all depleting energy sources, e.g., fossil fuels and nuclear)
OZ	ozone depletion potential
PC	polycarbonate (plastic material)
PET	polyethylene terephthalate (plastic material)
PHA	polyhydroxyalkanoate- biodegradable plastic material made from either corn grain or corn stover
PHA-G	polyhydroxyalkanoate produced from corn grain (plastic material)
PHA-S	polyhydroxyalkanoate produced from corn stover (plastic material)

PLA	polylactic acid biodegradable plastic material made from corn grain (plastic material)
PLA-G	polylactic acid produced under a general scenario (plastic material)
PLA-NW	polylactic acid produced by NatureWorks™ LLC (plastic material)
PP	polypropylene (plastic material)
PVC	polyvinyl chloride (plastic material)
RE	respiratory effects
SMOG	photochemical smog potential
TRACI	Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts

1.0 INTRODUCTION

Sustainable, or 'Green,' products increased in prevalence over the past 10-20 years, as evidenced by growth in bio-based materials, green labeling initiatives, etc. This growth represents an increase in consumer concern for the environment, and an increase in corporate concern for pre-adopting sustainable practices which will soon be necessary. Unfortunately there is no universally recognized standard system for evaluating the sustainability of a product. Instead, organizations generating sustainable products are guided by principles, such as the "12 Principles of Green Chemistry," the "12 Additional Principles of Green Chemistry," and the "12 Principles of Green Engineering" (Anastas and Warner 2000; Anastas and Zimmerman 2003; Gonzalez and Smith 2003) as well as other conceptions of green design such as "Cradle to Cradle," "Design for the Environment," "Industrial Ecology," and "Pollution Prevention" (Graedel and Allenby 1970; Graedel and Allenby 1996; McDonough and Braungart 2002). While these principles intend to reduce the negative impacts of production/manufacturing on the environment, the impacts of technology and industry are broad in scope and difficult to identify. Thus implementing one or more of these principles as a change to current product may cause intended environmental benefit as well as unintended environmental detriment. For example, the

manufacture of plastics from biological materials may reduce the amount of petroleum needed for production, however the fertilizer and pesticide used to grow crops for biomass may cause significant detriment to the ecosystem quality in nearby bodies of water (Landis and Theis 2006). In order to evaluate various intended and unintended environmental impacts, Life Cycle Assessment (LCA) methods are used to quantify environmental impacts caused by the production, use, and disposal of a product. In this thesis, a cradle-to-gate life cycle assessment (LCA) for the production of bio-based polyethylene terephthalate (B-PET) is completed and then used along with LCAs of 11 other packaging plastics to evaluate the efficacy of green design principles.

1.1 GREEN DESIGN PRINCIPLES

Sustainable design is guided by principles such as the "12 Principles of Green Chemistry," the "12 Additional Principles of Green Chemistry," and the "12 Principles of Green Engineering" (Anastas and Warner 2000; Anastas and Zimmerman 2003; Gonzalez and Smith 2003), as well as by similar conceptions sustainable design, such as "Cradle to Cradle," "Design for the Environment," "Industrial Ecology," and "Pollution Prevention" (Graedel and Allenby 1970; Graedel and Allenby 1996; McDonough and Braungart 2002). A list of green design principles used in this thesis are displayed in Figure 3.1 in Chapter 3 of this thesis.

Green principles increased in status over the past two decades with the creation of the United States Environmental Protection Agency (EPA) “Green Chemistry Program” in 1993, the adoption of similar government programs in Italy and the United Kingdom, and the inaugural publication of the journal *Green Chemistry* by the Royal Society of Chemistry in 1999 (Anastas and Kirchhoff 2002). At a recent international conference on Sustainability Science and Engineering, organized by both the American Institute for Chemical Engineers and the EPA, one chemical company even presented a metric system in order to quantitatively measure its products’ adherence to the 12 principles of green chemistry (Cohen 2009). The application and efficacy of green chemistry and other green design principles are documented for many case studies, including biodegradable polymers, and the production of polymers from biomass (Anastas and Lankey 2000; Anastas and Warner 2000; Anastas and Lankey 2002; Anastas and Kirchhoff 2002; Lankey and Anastas 2002).

The institutions upholding green chemistry and the resulting enthusiasm for achieving environmental goals through chemical technology are admirable. However, the principles now guiding environmental technology were never set in stone, and the constant addition of more principles and more green design conceptions reflect a necessity for constant evaluation and improvement.

1.2 LIFE CYCLE ASSESSMENT

Life cycle assessment is an evaluative tool which measures the environmental impacts resulting from the production, use, and disposal of a product or process. LCA has many benefits for making well informed environmental decisions: (1) products are compared in well defined environmental impact categories, which can be conceptualized by real environmental detriment, (2) unintended environmental trade-offs can be identified between these impact categories or different stages of the life cycle and (3) a standardized methodology allows life cycle assessments from separate studies to be used to compare product choices (Guinée 2002).

LCA methodology, standardized by the International Organization for Standards (ISO 14040-14043), contains four stages. The first stage is the goal and scope definition which articulates the product(s) to be studied, the purpose of the LCA, and the final metrics to be assessed. The second stage is the life cycle inventory (LCI) which calculates the amount of pollutant emissions produced and the resources used during the production, use, and disposal of the product. The third stage is the life cycle impact assessment (LCIA) which characterizes emissions from the inventory to quantify the resulting impacts in various ecosystem impact categories such as global warming potential or photochemical smog formation. The final stage of an LCA is an improvement analysis, where the results are assessed and recommendations are made.

Two major decisions are made during the goal and scope definition of an LCA, the boundaries of the assessment and the functional unit of comparison. Examples of assessment boundaries are "cradle-to-gate" which include only the environmental impacts from the extraction of raw materials and the production of a product, and "cradle-to-grave" which include all emissions during the production, use, and disposal of a product. A functional unit of comparison is the metric by which products in a life cycle assessment are compared. For example, the environmental impacts of producing one kilogram of a plastic versus one liter of a plastic are different. If a study (such as this one) is comparing plastics of varying density, this decision of functional until will affect the relative emissions in the life cycle assessment. Decisions of boundaries and functional units are made to meet the goals of the LCA within data constraints.

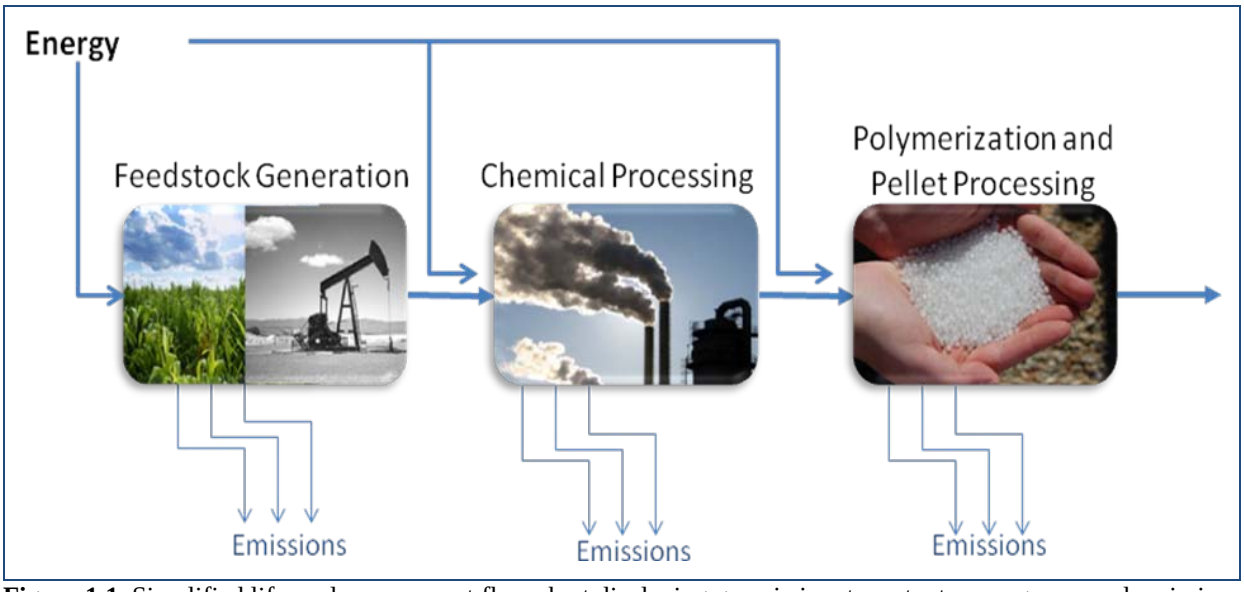

Figure 1.1. Simplified life cycle assessment flow chart displaying generic inputs, outputs, energy use and emissions for plastic production.

As shown in Figure 1.1, the life cycle of a product is made up of multiple processes, each requires energy and material inputs, and each produces pollutant emissions and a product output. The life cycle inventory stage uses information for each process in a product's life cycle and quantifies the total emissions and energy use required to produce one functional unit of product. The results of a life cycle inventory include hundreds to thousands of pollutant emissions to the ground, water and air as well as the total energy use classified by type of energy (e.g, electricity from coal, natural gas for heating, renewable biomass burning, etc.). Data for each process in the life cycle are collected via voluntary surveys/studies, government reports, or pre-published databases. Further explanation of the ecoinvent database, which is used in this thesis, can be found in Section 2.1.1.

Detail and allocation are the two most important characteristics of life cycle inventories. The emissions/energy from production processes with multiple outputs must be allocated to each output, often this allocation is proportional to the relative mass, stored energy, carbon content, or market price of each output. Decisions on allocation can be avoided by increasing the detail of inventory data and breaking up large production steps into smaller ones, however achieving this high level of detail is limited by the type of process and the transparency offered by the manufacturer.

Life cycle impact assessment (LCIA) characterizes the emissions and energy use from the inventory into measurable environmental impacts. For example, the global warming potentials for all greenhouse gasses are well documented by the Intergovernmental Panel on Climate

Change. During the LCIA, greenhouse gas emissions are adjusted to reflect their global warming potential relative to carbon dioxide (CO_2) and measured in equivalent emissions of CO_2 ($kgCO_2e$). Given a common unit of measurement, all greenhouse gas emissions can be added together to reflect overall global warming potential measured in $kgCO_2e$. LCIA methods vary greatly, some attempt to create a single measure of ecosystem detriment while others strive to measure multiple impacts in different areas of environmental damage. The effect of LCIA method choice can be significant due to the varying level of academic consensus concerning methods for measuring the impact of emissions in specific ecosystems categories (Landis 2008). This thesis uses the Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI) for impact assessments, as described in Section 2.2.4.

1.3 PLASTICS STUDIED

In this thesis, plastics are used both as examples of applied green chemistry and as commonly studied products in life cycle assessments. Plastic design, synthesis and production have provided excellent examples of applied green chemistry principles, most visibly the use of renewable sources and the design for degradability. Seven petroleum derived plastics (polymers) are assessed in this thesis: high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polycarbonate (PC),

and polyvinyl chloride (PVC). These 7 plastics are widely used in everyday products, over 20 million tons are produced in the U.S. each year (2008). Four polymers assessed in this study are both biodegradable and generated from renewable sources. All four are classified as either polylactic acid (PLA) or polyhydroxyalkanoate (PHA). One polymer studied is generated in part from renewable sources and is not biodegradable, bio-polyethylene terephthalate (B-PET).

1.4 THESIS OUTLINE

This thesis uses life cycle assessment to evaluate the effectiveness of current green design principles in a case study of packaging plastics. Chapter 1 includes background on green design, life cycle assessment, and polymers included in the case study. Chapter 2 presents a life cycle assessment of a new polymer, bio-based polyethylene terephthalate (B-PET). Chapter 3, which will be submitted as a research article to the journal *Environmental Science & Technology,* assesses the benefits and limitations of current green design principles with respect to life cycle environmental impacts using a case study of 12 packaging plastics, including B-PET. Chapter 4 offers overall conclusions.

2.0 LIFE CYCLE ASSESSMENT OF BIO-BASED POLYETHYLENE TEREPHTHALATE (B-PET)

Polyethylene terephthalate (PET) is best known for its use in soda bottles and textiles. 3.7 million tons of PET were produced in 2007, accounting for 12.5% of all plastic production and 1.5% of total U.S. municipal waste (2008). Currently, 18.1% of all PET produced is recycled; the recycling rate is substantially higher for PET soft drink bottles at 36.6%. Most recycled PET is mechanically ground into RPET where it can be used to produce textiles, non-food containers, carpets, or (in part) new plastic bottles (Brooks, Giles et al. 2002).

PET is most commonly produced from petroleum feedstocks (chemicals refined from oil and/or natural gas). A process schematic of PET production from both petroleum and renewable sources is shown in Figure 2.1. PET is polymerized from two monomers, terephthalic acid, and ethylene glycol. Terephthalic acid is a di-carboxylic acid generated from the oxidation of xylene over a bromine or magnesium catalyst bed; xylene is refined from oil. Ethylene glycol results from the repeated oxidation of ethylene into ethylene oxide then into ethylene glycol, where ethylene generated from natural gas (Brooks, Giles et al. 2002; Kumar and Gupta 2003; Scheirs and Long 2003).

In order to use renewable biomass, ethylene can alternately be generated from the dehydration of ethanol which is fermented from sugarcane molasses, also shown in Figure 2.1. By using biomass, this production route avoids the use of non-renewable sources, sequesters the greenhouse gas CO_2 during plant growth, and follows the principle of green chemistry to use renewable feedstocks (Anastas and Warner 2000).

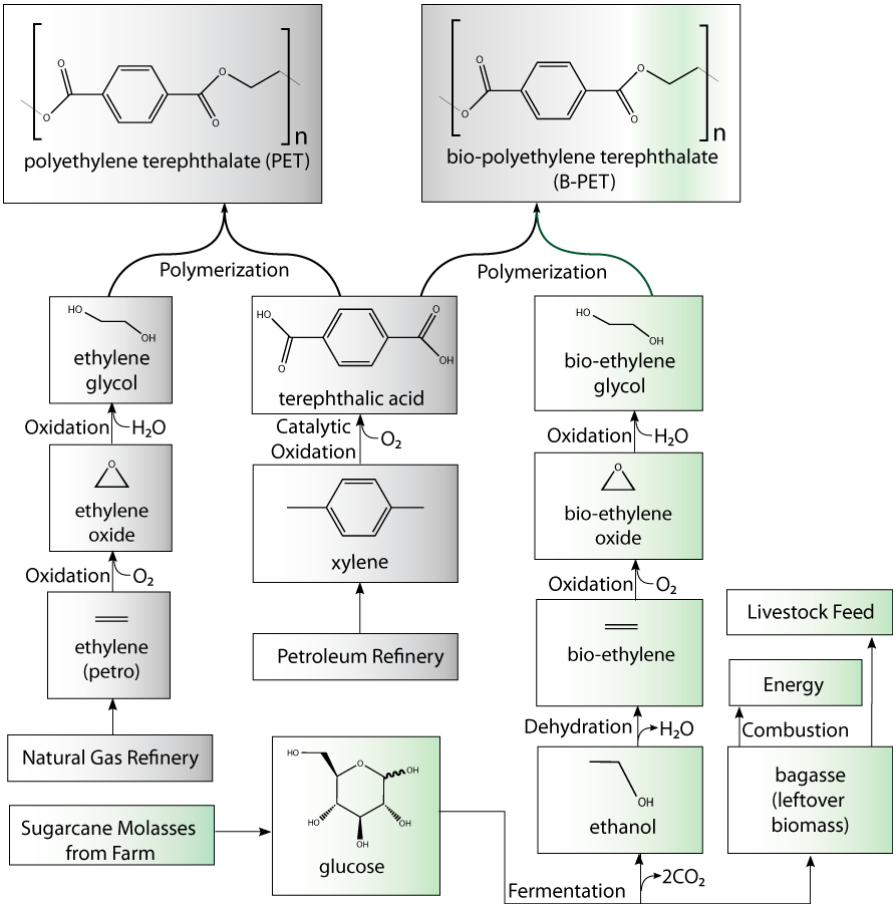

Figure 2.1. Synthesis of polyethylene terephthalate from either biological sources (B-PET) or petroleum sources (PET). A green background represents biomass products and a grey bachground represents petroleum products.

2.1 LITERATURE REVIEW

As shown in Figure 2.1, B-PET differs from PET by deriving ethylene glycol from biomass, namely sugarcane molasses. The traditional feed chemical for ethylene glycol formation is ethylene which is refined from natural gas. In the biomass scenario, this ethylene is instead produced by the dehydration of ethanol, where ethanol is produced from the fermentation of biomass. A literature review of commodity chemicals produced from biomass, specifically bio-ethylene, is presented below.

Academic reviews for the synthesis of commodity chemicals from biomass (bio-commodities) focus on metabolic pathways (Catia Bastioli 2001; Bruce E Dale 2003; Carole, Pellegrino et al. 2004; Basil J. Nikolau 2008; Jacco van Haveren 2008), the economic feasibility of current and past bio-based chemical technology (Hermann and Patel 2007; Dornburg, Hermann et al. 2008; Morschbacker 2009), and the environmental impacts of such technologies (Hermann, Blok et al. 2007; Dornburg, Hermann et al. 2008; Ben Brehmer 2009). The process of dehydrating ethanol to bio-ethylene has been used in industry since the late 1970's however lost popularity as oil and natural gas prices decreased in the 1980's and 90's (Morschbacker 2009). Patents for processes dehydrating ethanol were all filed before 1990 and are now expired (Tsao and Zasloff 1979; Pearson 1983; Jacobs, Jacobs et al. 1987). Many chemical companies (Halcyon, ICI, Petrobras, and Union Carbide) used the process in the past, taking advantage of areas with large sugarcane ethanol production such as Brazil, Peru, India, and Pakistan. Most

plants were shut down in the 1990's, only one company, India Glycols Limited, continues to use the process (Morschbacker 2009). Both Dow Chemicals and Braskem plan new ethylene from ethanol production in Brazil by 2010 (Ben Brehmer 2009).

The environmental impacts of bio-ethylene production were studied in (Patel, Crank et al. 2006; Hermann, Blok et al. 2007; Dornburg, Hermann et al. 2008; Ben Brehmer 2009). All of these studies use data from *The BREW Project* (Patel, Crank et al. 2006), a collaborative research project funded by the European Commission, performed by academic institutions in the Netherlands, Spain, and Germany and contributed to by nine different chemical manufacture companies. *The BREW Project* assesses the economic viability and environmental effects bio-commodities under current and proposed policy scenarios. *The BREW Project* reports only one environmental impact category, life-cycle Non-Renewable Energy Use (NREU). Effects of bio-commodity production on greenhouse gas emissions and land use are later reported by authors of *the BREW project* (Hermann, Blok et al. 2007). Dornburg 2007 is a continuation of the Hermann study where market projections are used to predict the use of bio-commodities with or without policy incentives and the subsequent effect on greenhouse gas emissions, energy use, and land use (Dornburg, Hermann et al. 2008). Brehmer 2009 specifically assesses production of biobased ethylene from sugarcane ethanol in Brazil and uses a Net Energy Value impact assessment method and an impact assessment methods created by the chemical company, BASF. Relevant results from these studies are shown in Table 2.1. Values reported in Table 2.1 are in

terms of "savings," which represent the impact reduction caused by using the "chemical product," in place of the "reference product" defined in columns one and two.

Table 2.1. Relevant results from life cycle impact assessments in *The BREW Project* and Brehmer 2009.

Chemical Product	**Reference Product**	**Study**	**Non-renewable Energy Savings MJ/kg Chemical**	**Global Warming Potential Savings kg CO_2/kg**
Ethanol	LHVof Gasoline	Brehmer	25-50	N/A
Ethanol	Petro Ethanol Production	BREW	65-85	N/A
Ethanol	Nothing	BREW	13.7, 18.7	N/A
Bio-Ethylene	Ethylene, Petroleum	Brehmer	90	N/A
Bio-Ethylene	Ethylene, Petroleum	BREW	95	1.9
Bio-Ethylene	Nothing	BREW	29.9	N/A

Neither *the BREW Project* nor the Brehmer study report environmental impacts other than global warming potential and non-renewable energy use. While the BASF impact assessment method requires "all pollutants" to be quantified, the emissions are then aggregated along with human safety, energy use, and raw material consumption into one "ecological impact" value (Saling, Kicherer et al. 2002). Thus, from the BASF Impact assessment results, it is impossible to assess individual environmental impact categories.

2.1.1 The ecoinvent database

The eco-invent database is a product of the Swiss Centre for Life Cycle Inventories and contains inventories for many production processes. Ecoinvent inventories contain pollutant emissions, energy requirements, input materials/services and output materials/services.

Ecoinvent's methods are documented both in its user's manual as well as in peer reviewed journals (Frischknecht, Jungbluth et al. 2003; Frischknecht, Jungbluth et al. 2005; Hischier, Hellweg et al. 2005). The ecoinvent methodology for inventorying emissions for chemical processes was published by Hischier in 2005 (Hischier, Hellweg et al. 2005).

Hischier outlines a method for estimating emissions from a chemical process where no industry data can be found. In Hischier's method, the reaction equation is used to assess inputs, and conversion of 95% of reactants is assumed. Of the 5% of unconverted inputs, 96% are assumed to be emissions to water and the remaining 4% are assumed to be emissions to air. Hirschier notes that this method results in highly speculative data and should only be used when no other data is available (Hischier, Hellweg et al. 2005).

2.1.2 The dehydration of ethanol to ethylene

No emissions inventory could be found for the dehydration of ethanol process, however product stream compositions were found in academic studies (Takahara, Saito et al. 2005; Inaba, Murata et al. 2006) and patent applications (Tsao and Zasloff 1979; Jacobs, Jacobs et al. 1987). Both academic publications report conversions of over 90% with byproducts including acetaldehyde, diethyl ether, olefins of 3 carbons and greater, and aromatics (Takahara, Saito et al. 2005; Inaba, Murata et al. 2006). A recent review of industrial production reports average ethanol conversions of over 99% with an ethylene selectivity of 97-99% (Morschbacker 2009).

One patent, awarded to Jacobs et al. in 1987 reports product compositions from over 120 ethanol dehydration experiments using various catalysts at varying temperatures. Of these dehydration experiments, 37 reported conversion and ethylene selectivity over 95%. A summary of the data from these 37 experimental results is shown in Table 2.2. The byproducts from experiments reported in the patent are consistent with those found in academic sources. Data reported in the patent does not specify the sterochemical structure for large alkanes and alkenes nor does it report specific aromatic compounds.

Table 2.2. Summary of data from experimental results reported in patent awarded to Jacobs et al. in 1987 (Jacobs, Jacobs et al. 1987). All percentages are by mass.

	Unit	Average	Standard Deviation
Temperature	K	607	66
ethanol Conversion	%	99.2	1.74
ethylene Selectivity	%	98.8	1.8
Product Stream Composition			
acetaldehyde	%	0.29	0.88
diethyl ether	%	0.09	0.43
water	%	38.75	1.13
methane	%	0.01	0.05
ethylene	%	60.15	1.10
ethane	%	0.00	0.01
propylene	%	0.21	0.26
butanes	%	0.03	0.10
butenes	%	0.13	0.28
pentanes	%	0.01	0.05
pentenes	%	0.01	0.08
C5+ (non aromatic)	%	0.32	1.33
aromatics	%	0.07	0.28

2.1.3 Allocation between ethanol and bagasse

The process of fermenting sugars from molasses to ethanol also biomass product called bagasse (leftover biomass), shown in Figure 2.1. At this juncture all cumulative emissions and energy use must be allocated either to bagasse or to ethanol. The ecoinvent database allocates all greenhouse gas emissions based on the carbon content of either product, and all other emissions based on mass. Both *the BREW project* and Brehmer 2007 allocate based on the energy content of either product.

One use of bagasse is combustion for energy. Both the ecoinvent database and the previous studies assume that the fermentation facility uses bagasse as a renewable energy source. However, the sugarcane molasses fermentation process produces more bagasse than needed to provide energy for the facility. The ecoinvent database allocates all unused renewable energy as embedded in the leftover bagasse, which can then be sold for energy use in another facility or as livestock feed. Both the Brehmer study and *the BREW project* allocate the renewable energy in the unused bagasse to the ethanol product, regardless of its final use.

2.2 LIFE CYCLE ASSESSMENT

Life cycle assessments were completed using the methodology defined in ISO standards 14040-14043 (Guinée 2002). Four stages are defined for ISO standardized life cycle

assessments, (1) goal and scope definition, (2) life cycle inventory (LCI), (3) life cycle impact assessment (LCIA), (4) improvement analysis. The fourth stage is eliminated for the purpose of this study. For more information on each stage see Chapter 1 of this thesis.

SimaPro life cycle assessment software was used to complete all life cycle assessments. SimaPro software contains multiple life cycle inventory databases including ecoinvernt and allows users to define new processes by inputting the inputs, outputs, energy use, and pollutant emissions. Processes in SimaPro are placed in life cycle networks by referencing all material inputs to outputs of other processes. Using these networks, emissions inventories are computed quickly. SimaPro also contains life cycle impact assessment methods and can characterize an inventory into an impact assessment using previously published methods such as TRACI.

2.2.1 Goal and scope definition

The goal of this LCA is twofold, to compare the environmental impacts of PET and B-PET, and two, to include the LCIA of B-PET in a later study assessing the efficacy of green design principles in packaging plastics. The LCA in this chapter is presented both as a comparative assessment, to show the benefits and tradeoffs of using B-PET in place of PET, and as a national assessment, to show the impacts in each category relative to annual U.S. emissions. The functional unit of comparison between PET and B-PET is mass, this functional unit is appropriate given the equivalent physical properties of both polymers. The boundaries of this

LCA are cradle-to-gate, this scope is appropriate given the equivalent use and disposal scenarios for both polymers.

2.2.2 Life cycle inventory

Data for the life-cycle inventory of B-PET was generated from the ecoinvent database and from the literature review. Explicit processes used for each stage of the B-PET life cycle inventory are shown in Table 2.3. Emissions and energy use for one process, the dehydration of ethanol to ethylene, were entered manually as described in Section 2.1.2. Material inputs/outputs for all processes were edited in order to include the appropriate bio-based chemicals. For example, the ethylene input for the ethylene glycol production process was removed and replaced with the bio-ethylene process created for this study; the output of the production process was then changed to "bio-ethylene glycol." It is assumed that the ethylene glycol used in the PET polymerization process is transported to the U.S. from India and travels and estimated 15,000 km by a barge tanker.

Table 2.3. Processes in SimaPro used for the production of B-PET, edits to processes are included in the description

Process	Database	Process Name and Edits
B-PET polymerization	ecoinvent	Polyethylene terephthalate, granulate, bottle grade, at plant/RER U **Edit:** 15,000 miles of transport added; ethylene glycol input replaced with bio-ethylene glycol
Transport of ethylene glycol to US	ecoinvent	Transport, barge tanker/RER U
bio-ethylene glycol production	ecoinvent	ethylene glycol, at plant/RER U **Edit**: ethylene oxide input replaced with bio-ethylene oxide
bio-ethylene oxide production	ecoinvent	ethylene oxide, at plant/kg/RER **Edit**: ethylene input replaced with bio-ethylene
bio-ethylene production (two emissions scenario)	literature	ethylene, at plant, kg. from molasses ethanol; two emissions scenarios are entered as described in Section 2.2.2.1
ethanol production (High and Low emissions scenario)	ecoinvent	Ethanol, 95% in H2O, from sugarcane molasses, at sugar refinery/BR U **Edit**: high and low emissions estimates described in Section 2.2.2.2

The life cycle inventory of traditional petroleum based PET is completed, in full, in the ecoinvent database. The process used is named Polyethylene terephthalate, granulate, bottle grade, at plant/RER U, no edits were made. The process was created by the Swiss Center for Life Cycle Inventories for the Association of Plastics Manufactures in Europe as requested by the European Commission.

2.2.3 Creation of the ethylene production process

The eco-invent methodology for chemical processes lacking data (Hischier, Hellweg et al. 2005), and the average emissions data from patent documents (shown in Table 2.2) were used

to create two separate processes for the dehydration of ethylene. Both methods have drawbacks. The Hirsher method is speculative and assumes selectivity and yield below that published by industry. The patent data does not specify many types of emissions. For the patent data inventory, all butanes and pentanes are assumed to be in the "n" form and all aromatics are assumed to be benzene. For both scenarios, energy requirements reported in Brehmer 2009 were used. All energy is assumed to be high voltage Brazilian mix electricity.

2.2.4 Farming data correction

The ecoinvent inventory for sugarcane farming in Brazil reports several emissions which are significantly higher than those of any other farming product in the database. Emissions from the sugarcane farming process were compared to the emissions resulting from 12 other farm product inventories in the ecoinvent database listed in Table 2.4.

Table 2.4. ecoinvent farm product inventories used to compare to the sugarcane farming in Brazil

Farming Inventories Compared
Rye straw extensive, at farm/CH U
Rye straw IP, at farm/CH U
Rye straw organic, at farm/CH U
Silage maize IP, at farm/CH U
Silage maize organic, at farm/CH U
Soy beans IP, at farm/CH U
Soy beans organic, at farm/CH U
Soybeans, at farm/BR U
Soybeans, at farm/US U
Straw IP, at farm/CH U
Straw organic, at farm/CH U
Straw, from straw areas, at field/CH U
Sugar beets IP, at farm/CH U

6 of the 700 emissions resulting from sugarcane farming were more than 10 standard deviations above the mean emissions resulting from the 12 other agriculture products, displayed in the "t" column of Table 2.5. A high estimate was created using emissions values of 2 standard deviations above the mean of the other 12 farm products. A low emissions estimate was created by completely removing all six outlying emissions. Table 2.5 displays the outlier emissions, the initial and high estimate values for sugarcane farming, and statistical information from the 12 compared farm products.

Table 2.5. Corrected emissions for ecoinvent sugarcane farming in Brazil using statistics from 12 other farming product's emission inventories

Emission	Media	unit	Average Emissions	Standard deviation	Sugarcane Value	t	High-Estimate	Low-Estimate
aldrin	soil	mg	$3.83x10^{-07}$	$5.16x10^{-07}$	35.65	$6.91x10^{+07}$	$1.42x10^{-06}$	0
arsenic	soil	mg	$1.68x10^{-04}$	$2.07x10^{-04}$	2.54	$1.23x10^{+04}$	$5.82x10^{-04}$	0
carbon monoxide	air	g	$8.03x10^{-03}$	$8.64x10^{-03}$	30.00	$3.47x10^{+03}$	$2.53x10^{-02}$	0
methane	air	mg	.427	.419	286.09	682	1.27	0
particulates	air	g	$3.72x10^{-02}$	$3.96x10^{-02}$	3.01	75	$1.16x10^{-01}$	0
tin	soil	µg	$7.56x10^{-04}$	$8.82x10^{-04}$	-64.14	$-7.28x10^{+04}$	$2.52x10^{-03}$	0

2.2.5 Life cycle impact assessment

The Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI), was developed by the U.S. Environmental Protection Agency and was used to generate environmental impact assessments from the life cycle inventories (Bare, Norris et al. 2002). In SimaPro this impact assessment method is abbreviated TRACI 2 V3.01. TRACI characterizes emissions of over 700 different pollutants into environmental burdens in ten

different impact categories: acidification, carcinogenic human health hazards, ecotoxicity, eutrophication, global warming potential, non-carcinogenic human health hazards, ozone depletion, respiratory effects, smog, and non-renewable energy use. Though TRACI includes NREU as an impact category, SimaPro does not calculate NREU in its TRACI impact assessment method. Thus the impact assessment method "Cumulative Energy Demand V1.05" was used in order to quantify NREU.

The impact assessment results were also adjusted to reflect total U.S. production of PET in 2005, (2008) and normalized using national environmental impacts for the year 1999 as published by Bare et al. in (Bare, Gloria et al. 2006) and national fossil fuel consumption as published in the National Institute of Standards and Technology (NIST) manual for Building for Environmental and Economic Sustainability (Lippiatt). From this additional assessment, the impact of switching total U.S. PET production to B-PET is measured in reference to total U.S. environmental impact.

2.3 RESULTS

Results for the comparative assessment of B-PET and PET are shown in Figure 2.2. High and low emissions estimates for sugarcane farming and the dehydration of ethanol contributed to less than 5% of overall impact in any category. The Hirsher method along with

high estimate for farming emissions are used in the following assessments. B-PET is the most significant contributor in all impact categories except for global warming potential (GWP) and non-renewable energy use (NREU). The NREU benefit awarded to bio-based PET is largely due to the renewable energy use resulting from the burning of bagasse, a byproduct of ethanol production from molasses. The GWP benefit of B-PET is due to the CO_2 sequestration achieved during the growth of sugarcane during farming, represented by an extension of the GWP bar below the 0% line. The generation of bio-based PET represents 5% to 40% increases in all other environmental impact categories, namely a 40% increase in photochemical smog formation (SMOG). As shown in Figure 2.2, the generation of ethanol and sugarcane farming account for 21% of SMOG, 19% of the acidification impact (AC), ecotoxicity impact (ETX) and respiratory effects impact (RE), 17% of the non-cancer health impact (NCA), and 14% of the cancer health impact (CAR). Due to the similarity of B-PET production to PET, the generation of feedstock also accounts for most of the disparity between the two LCAs. Other acronyms presented in the results are eutrophication (EU), non-carcinogenic health hazards (NCA), and ozone depletion (OZ).

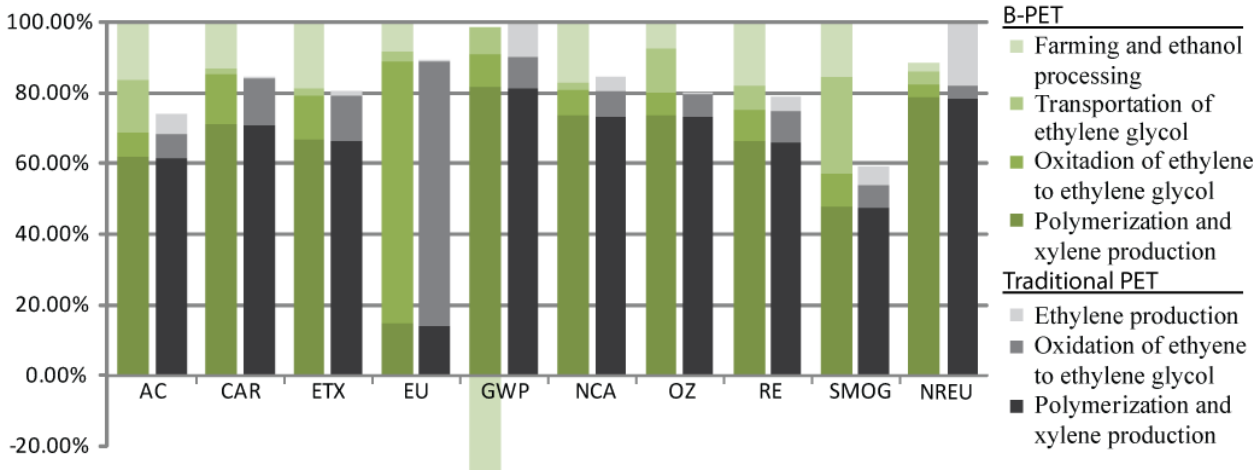

Figure 2.2. Comparative results for lifecycle environmental impacts of PET manufacture using either petroleum based ethylene (PET) or ethanol based ethylene (B-PET). Results normalized by largest impact in each category. Carbon sequestration resulting from sugarcane faming is represented as a bar extended below the x axis.

Following the impact assessment, the results for both products were adjusted to reflect annual production of PET for soda bottles in 2005, 1.01 million short tons (2008). The emissions for the annual production of all soft drinks bottles in the U.S. were then normalized to 1999 annual emissions as reported by Bare et al. (Bare, Gloria et al. 2006). Results for the normalization are shown in Figure 2.3. By completely switching PET production to use bio-based ethylene, increases of 3%, 7%, and 4% in national environmental impacts of CAR, ETX, and NCA respectively. The same switch only decreases the GWP of national greenhouse gas emissions by 0.01% and national NREU by 0.11%. While these results are striking, it should be noted that U.S. normalization factors are a nascent tools and not yet completely applicable. It is unlikely that PET bottle production alone accounts for over 15% of national ecotoxicity impact.

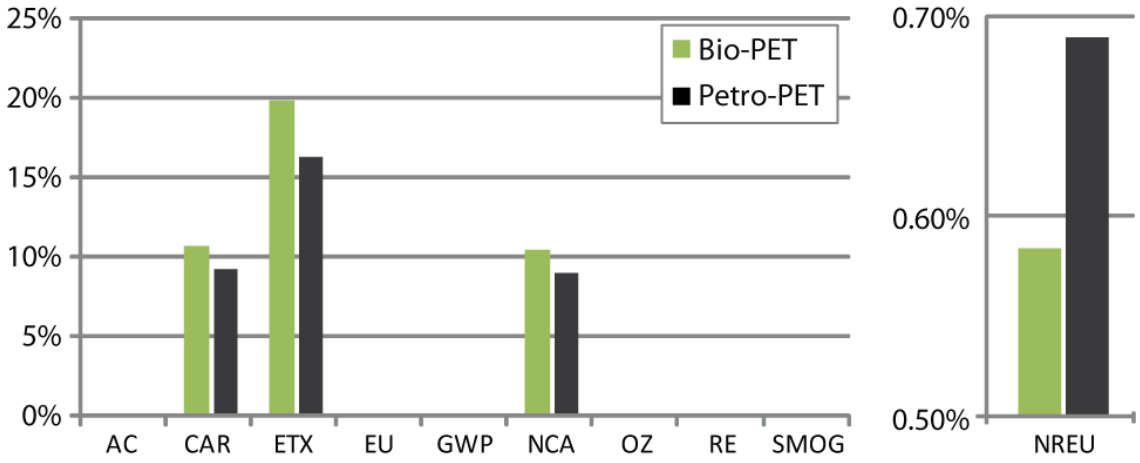

Figure 2.3. LCIA results for both B-PET and PET normalized to 1999 US emissions (Bare, Gloria et al. 2006).

2.3.1 Comparison to Previous NREU Studies,

Both *the BREW project* and the Brehmer 2009 paper consistent findings of NREU savings which differ from the findings from this study, shown in Table 2.6. This disparity results from the accounting for renewable energy produced by the combustion of bagasse. By allocating the renewable energy embedded in unused bagasse as non-renewable energy savings in the fermentation plant, the two previous studies find significantly higher energy savings than this study. The ecoinvent database allocates all renewable energy embedded in the byproduct bagasse to the bagasse. Thus any unused bagasse will count as renewable energy for a future process that uses the by-product as an energy source, not for the fermentation process. Using data from Brehmer 2009, a reallocation of was performed where renewable energy from the unused bagasse was not allocated to the ethylene product, shown in the last two rows of **Table 2.6**.

Following the reallocation, the current study's assessment is within 15MJ of *the Brew project*'s assessment.

Table 2.6. Comparison of results to previous studies

	BREW (MJ/kg ethylene)	**Brehmer (MJ/kg ethylene)**	**Current Study (MJ/kg ethylene)**
Bio-ethylene Production	-29.9	Not Reported (-28)	8.41
Petro-ethylene Production	65.6	67.03	65.208
Savings	95.5	95	56.79
Energy produced from excess bagasse	27.1	27.1	N/A
Recalculation of savings (allocating renewable energy to both excess bagasse and ethylene).	68.4	67.9	56.79

2.4 CONCLUSIONS

The use of B-PET in place of traditional PET contributes to both climate and energy goals, however it also represents increased detriment in every other environmental impact evaluated. The detriments of B-PET production are attributable to primarily to the generation of ethanol, which accounts for 21% of the photochemical smog impact, 19% of the acidification, ecotoxicity and respiratory effects impact, 17% of the non-cancer health impact, and 14% of the cancer health impact. Due to the similarity of B-PET production to PET, the generation of feedstock also accounts for most of the disparity between the two LCAs.

3.0 SUSTAINABILITY METRICS: LIFE CYCLE ASSESSMENT AND GREEN DESIGN IN PACKAGING PLASTICS

The following chapter is written for submission to the journal *Environmental Science & Technology*. If accepted and printed in *Environmental Science & Technology*, copyrights for all material will be owned by the journal publisher, the American Chemical Society (ACS). References to supporting information are adjusted, where appropriate, to reference Chapter 2 of this Thesis. In-text citations are reformatted to reference the existing bibliography.

Sustainability metrics: Life cycle assessment and "green design" in polymers

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3.1 ABSTRACT

This study evaluates the efficacy of green design principles such as the "12 Principles of Green Chemistry," the "12 Principles of Green Engineering" with respect to environmental impacts as found using Life Cycle Assessment (LCA). A case study of twelve polymers are used for comparison, seven derived from petroleum, four derived from biological sources, and one derived from both. Each polymer is assessed using LCA methodology standardized by the International Organization for Standards (ISO) and assessed for its adherence to green design principles using metrics generated specifically for this paper. Metrics include atom economy, mass of product from renewable sources, biodegradability, percent of product recycled, distance of furthest feedstock, price, and life cycle health hazards and energy use. A decision matrix is used to generate single value metrics for each polymer evaluating either adherence to green design principles or life cycle environmental impacts. Results from this study show a qualified positive correlation between adherence to green design principles and a reduction of the environmental impacts of production. The qualification results from a disparity between biopolymers and petroleum polymers. While biopolymers rank highly in terms of green design, they exhibit larger than expected environmental impacts from production.

KEYWORDS: Green Chemistry, environmental design, green design principles, biopolymer, renewable feedstocks, life cycle assessment.

3.2 INTRODUCTION

Sustainable, or green, products are increasing in popularity, as evidenced by the growth in green labeling initiatives, eco-marketing, and bio-based materials. Unfortunately there is no universally recognized standard system for evaluating the sustainability of a product or process. Instead, sustainable design is guided by principles such as the "12 Principles of Green Chemistry," the "12 Additional Principles of Green Chemistry," and the "12 Principles of Green Engineering" (Anastas and Warner 2000; Anastas and Zimmerman 2003; Gonzalez and Smith 2003), as well as by similar conceptions sustainable design, such as "Cradle to Cradle," "Design for the Environment," "Industrial Ecology," and "Pollution Prevention" (Graedel and Allenby 1970; Graedel and Allenby 1996; McDonough and Braungart 2002). These principles increased in status over the past two decades with the creation of the United States Environmental Protection Agency (EPA) "Green Chemistry Program" in 1993, the adoption of similar government programs in Italy and the United Kingdom, and the inaugural publication of the journal *Green Chemistry* by the Royal Society of Chemistry in 1999 (Anastas and Kirchhoff 2002). The application and efficacy of green chemistry and other green design principles are documented for many case studies, including biodegradable polymers, and the production of polymers from bio-materials (Anastas and Lankey 2000; Anastas and Warner 2000; Anastas and Lankey 2002; Anastas and Kirchhoff 2002; Lankey and Anastas 2002).

Life Cycle Assessment (LCA) is an evaluative tool which measures the environmental impacts resulting from the production, use, and disposal of a product or process. LCA has many benefits for making well informed environmental decisions: (1) products are compared in well defined environmental impact categories, which can be conceptualized by real environmental detriment, (2) unintended environmental trade-offs can be identified between impact categories and (3), a standardized methodology allows life cycle assessments from separate studies to be used to compare product choices (Guinée 2002). Previous publications have outlined the effect of green chemistry on various aspects of a product's life-cycle (Anastas and Lankey 2000). Lankey et al. points out the benefit of using LCA within green chemistry to assess the tradeoffs in switching between supply chemicals or processes (Lankey and Anastas 2002). However, no published study quantitatively assesses the effect of green design principles on the life cycle environmental impacts of similar products.

This study empirically identifies the benefits and limitations of current green design principles with respect to life cycle environmental impacts using a case study of packaging plastics. Twelve polymers are assessed in this study. Seven polymers from petroleum or other fossil fuel feedstocks: polyethylene terephthalate (PET), high and low density polyethylene (HDPE, LDPE), polypropylene (PP), polycarbonate (PC), polyvinyl chloride (PVC), and general purpose polystyrene (GPPS). Two biopolymers are assessed via different production scenarios: polylactic acid made via a general scenario (PLA-G) and a scenario produced by NatureWorks© LLC (PLA-NW) as defined in the ecoinvent database, and polyhydroxyalkanoate was assessed

separately as derived from corn grain (PHA-G) and from corn stover (PHA-S). Lastly, one hybrid bio/petroleum polymer is assessed, bio-polyethylene terephthalate (B-PET) which is made from one fossil fuel feedstock and one biological feedstock.

3.3 METHODS

Life cycle assessments were completed for each polymer using the ecoinvent *v1.2* database, the EPA Tool for the Reduction and Assessment of Chemical and other environmental Impacts (TRACI 2 v.3.01) (Bare, Norris et al. 2002), literature reviews, and SimaPro life cycle assessment software. Green Design Principles found in the literature were reduced into quantifiable green design metrics, shown in Figure 3.1. Each polymer's adherence to green design principles was assessed via these metrics. A decision matrix was used to normalize the results of both assessments and rank each polymer for preference in either assessment. Single-value metrics generated by the decision matrix were also used to compare the adherence to green design principles and the life cycle environmental impacts in a two dimensional chart.

3.3.1 Life Cycle Assessment

Life cycle assessments were completed using the methodology proposed in ISO standards 14040-14043 (Guinée 2002). The functional unit of comparison is defined as one liter of

polymer pellets. Previous material assessments compared impacts based on mass; however volume is used in this study to reflect the material requirements of common plastic products (Vink, Rabago et al. 2003; Erwin T. H. Vink 2004; Shen and Patel 2008). The scope of each life cycle assessment is "cradle-to-gate," including only the impacts resulting from the production of each plastic and not the use or disposal. This limitation is reasonable because each material has varied applications and the environmental impacts of biopolymer disposal have yet to be studied.

Life cycle inventories in the ecoinvent *v1.2* database in SimaPro were used for all petroleum based polymers (PET, HDPE, LDPE, PP, PC, PVC, GPPS) and both polylactic acid scenarios (PLA-G and PLA-NW). The B-PET life-cycle inventory was completed specifically for this study, and is discussed in further detail in the following paragraph. No inventory was available for PHA; instead data from the impact assessment stage was obtained using a literature review of published life cycle assessments (Heyde 1998; Kurdikar, Fournet et al. 2000; Akiyama, Tsuge et al. 2003; Kim and Dale 2005; Pietrini, Roes et al. 2007; Kim and Dale 2008; Yu and Chen 2008).

A life cycle inventory for B-PET was created for this study. The chemical composition of B-PET is identical to traditional PET and the production methods for both polymers are similar. In the B-PET production method, one monomer, ethylene glycol, is generated from sugarcane ethanol instead of natural gas. Eco-invent inventory data on ethanol fuel and PET as well as literature sources were used to complete this inventory. See the Chapter 2 of this thesis for a full process outline including data sources and preliminary results.

In the B-PET method, the xylene feed remains refined from petroleum; however the ethylene feed is manufactured in India and is produced from sugarcane derived ethanol (2003). The chemical manufacturing of ethylene from sugarcane includes bio-ethanol, a commonly used transportation fuel included in the ecoinvent v1.2 database (see Figure 2.1 in Chapter 2). The dehydration of ethanol to ethylene was not available in SimaPro databases, thus emissions and energy use were approximated using previously published energy assessments and process patents (see Section 0). Additional ethylene glycol transportation of 15,000 miles by a tanker barge was included for the transportation of bio-ethylene glycol from India to the United States. Full data and process outlines for this life cycle assessment are included in Chapter 2 of this thesis.

The Tool for the Reduction and Assessment of Chemical and environmental Impacts (TRACI), was used to generate environmental impact assessments from the life cycle inventories (Bare, Norris et al. 2002). TRACI, developed by the U.S. Environmental Protection Agency, uses a mid-point assessment in order to aggregate the emissions of over 700 different pollutants into environmental burdens on ten different impact categories: acidification, carcinogenic human health hazards, ecotoxicity, eutrophication, global warming potential, non-carcinogenic human health hazards, ozone depletion, respiratory effects, smog, and Non-Renewable Energy Use (NREU).

No life cycle inventory data was available for PHA within the SimaPro databases. Impact assessment data was obtained from previously published life cycle assessments, shown in Table

S.1 of the supporting information (Heyde 1998; Kurdikar, Fournet et al. 2000; Akiyama, Tsuge et al. 2003; Kim and Dale 2005; Pietrini, Roes et al. 2007; Kim and Dale 2008; Yu and Chen 2008). All studies used contained assessments of NREU and greenhouse gas emissions. Only one study also included eutrophication potential, smog formation, and acidification potential, shown in Table S.2 of the supporting information (Kim and Dale 2005). To maintain complete assessments for use in the decision matrix, the average impact from the PLA scenarios is used to as substitutes for PHA's impacts on human health, respiratory effects, ozone depletion, and ecotoxicity.

3.3.2 Green Design Metrics

Figure 1 displays previously published green design principles used in this study. Principles were reduced into "themes" which are quantitatively or qualitatively evaluated by metrics. Table 3.1 lists each theme, each associated metric, and specific principles each theme/metric references. The metrics from Table 3.1 were evaluated for each polymer in order to measure adherence to each design principles. Metrics are explained in detail below.

Waste Prevention

Waste reduction is measured through atom economy, defined in Equation 1 where M_{input} is the mass of chemical product input to all reactions and $M_{product}$ is the mass of the chemical product. Atom economy, originally defined for single reactions, is evaluated for the entire

synthesis of each polymer using the method defined within Blowers et al. (Blowers, Zhao et al.). The scope of each atom economy calculation begins with chemicals refined from petroleum (or fructose in the case of plant sugars) and ends with the final chemical structure of the polymer.

Equation 1 $$Atom\ Economy = \frac{M_{product}}{M_{input}}$$

Material Efficiency

The ability of a material to promote efficient use is measured through its density, which is reflected in the volumetric as a functional unit for all assessments. Less dense materials are able to serve the same purpose with less mass, thus a lower density is more preferable.

Avoid Hazardous Materials and Pollution

The avoidance of hazardous materials and pollution is measured via an average of the normalized life-cycle impacts in TRACI categories of respiratory effects, human health cancer, human health non-cancer, and ecotoxicity (Bare, Norris et al. 2002). For categories where PHA does not contain data, averages of the PLA scenarios are used.

Maximize Energy Efficiency

Overall energy efficiency was measured by the cumulative life cycle energy-use found by the Cumulative Energy Demand LCIA method. This energy demand includes all energy use in the production of the product, as well as any embedded energy in input materials such as oil, natural gas, or biomass. Embedded energy is calculated using the higher heating value (HHV) as explained Huijbregts et al. (Huijbregts, Rombouts et al. 2005).

Use of Renewable Sources

The use of renewable sources is measured by the percent of material from biological sources in the final product, by mass.

Design products for recycle

Adherence to these principles is measured through the percent recovery of a material in the U.S. municipal recycle stream (2008).

Design Biodegradable Products

The biodegradability of a product is measured categorically. Materials are classified as either non-biodegradable, biodegradable in an industrial facility, or biodegradable in typical backyard conditions. For quantitative purposes, these categories are assigned values of 1, 2, and 3, respectively.

Use Local Sources

The categorical distance of the furthest feedstock location is assessed as a metric. Petroleum sources are categorized as international, often traveling to the U.S. through Canada or from the Middle East. Renewable sources may be local or not, bio-ethylene for use in B-PET is only produced in India, where PLA and PHA are often produced from national or regional corn crops. For quantitative purposes, categorical distances of international, national, and regional are assigned values of 1, 2, and 3, respectively.

Cost Efficiency

Sustainable products need to be competitively priced to effectively integrate into markets. The cost effectiveness of these polymers was measured via a median price per liter of the polymer, as reported by ICIS (2010).

3.3.3 Decision Matrix

A decision matrix was used to create two single-value-metrics for each polymer, one evaluating each polymer for life cycle environmental impacts and the other evaluating each polymer for adherence to green design principles. Results from both assessments are normalized to the average across all polymers, shown in Equation 2, where N_{ij} is the normalized value for polymer *i* in metric/impact *j*, V_{ij} is the value of polymer *i* in metric/impact *j*, *n* in the total number of polymers studied, and Ψ_j is a multiplication factor which is 1 for metrics/impacts in which higher values are more preferable and -1 for metrics/impacts in which lower values are more preferable. The resulting normalized values in each category all average to either 1 or -1 depending on the value of Ψ_j.

Equation 2 $N_{ij} = \frac{V_{ij} * n}{\sum_i (V_{ij})} * \Psi_j$

To create single-value metrics that enable ranking of the polymers with respect to adherence to green design principles or LCA, the normalized impacts of each polymer's life cycle environmental impact and the normalized metrics for each polymer's green design metrics were summed separately. Each impact category or green design metric is equally weighted in

the single value metric system. While equal weighting is arguably non-ideal, it reduces bias toward specific metrics or impacts and maintains clear transparency. An alternate normalization method employing the maximum value in place of the average value was also completed for comparison.

3.4 RESULTS

3.4.1 Life Cycle Assessment Results

The cradle-to-gate environmental impacts resulting from the production of each packaging polymer are shown in Figure 3.2. The resulting life cycle impacts are normalized to the largest impact in each category. Figure 3.2 shows biopolymer production resulting in the highest impact in five of the ten categories: ozone depletion, acidification, eutrophication, carcinogens, and ecotoxicity. PLA-G results in the greatest eutrophication potential, most likely as a result of fertilizer use (Landis, Miller et al. 2007). B-PET results in the greatest impact in ecotoxicity and human health cancer categories, this impact is largely attributed to sugarcane farming and ethanol production which account for anywhere from 13 to 21% of impacts in each category (See Chapter 2 for a more detailed assessment). It should be noted that high impacts of B-PET are not solely due to agriculture/ethanol; PET is the second highest in each of these categories. PHA-G results in the greatest acidification impact.

The polyolefin polymers, (HDPE, LDPE, and PP) do not result in the maximum impact in any impact category. This result is due to the limited chemical processing required for polyolefin polymers. Monomers for polyolefin polymers are the direct products of oil refining. The more complex petro-polymers (PET, PC, and PS) require additional synthetic steps between the oil refinery and polymerization. Additional processing requires additional transportation and chemical process emissions, thus increasing the likelihood of emissions and environmental impact.

3.4.2 Green Principles Assessment Results

Table 3.2 shows the results of the green principles assessment for each of the 12 polymers studied. The biopolymers adhere well to several green design principles: the use of renewable and regional resources, low emissions of carcinogens and particulates. Polyolefin polymers exhibit the highest atom economy, the lowest price, and low pollutant emissions.

3.4.3 Comparison

Rankings generated by the decision matricies are shown in Table 3.3. The two ranking systems represent design choices based on either the green design principles or the life cycle assessment results. Biodegradable polymers sit on top of the green design rankings, owing mostly to their low energy demand, use of renewable materials, and biodegradability.

Comparing the green design rankings to the life cycle assessment rankings, the bio-polymers, which ranked, 1, 2, 3 and 4, in the green design system, are 6, 4, 8, and 9 respectively in the LCA rankings (as shown in Table 3.3). Polyolefins, PP, LDPE, HDPE, rank 1,2, and 3 in the LCA rankings. As mentioned earlier, polyolefins benefit from limited production steps, thus producing fewer byproducts and requiring less energy use during production. Complex polymers, such as PET, PVC, and PC placed at the bottom of both ranking systems. Specifically, B-PET ranked 8th in the green design ranking and last in the LCA ranking. The production of B-PET requires agriculture, fermentation, and multiple chemical processing steps, resulting in a low atom economy and a large potential for emissions and environmental impact.

To further study the relationship between green design metrics and environmental impacts, the single-value metrics used to rank each polymer are presented in Figure 3.3, where the x-axis represents adherence to green design principles and the y-axis represents life cycle environmental impacts. The close relationship between many of the polymers in the green design principles dimension shows the relatively small differentiation between rankings 1-5, as well as rankings 6-8. In contrast, single-values in the life cycle environmental impacts dimension are relatively continuous, exhibiting tight differentiation only between the polyolefin polymers, ranking 1-3.

The relationship between green design principles and life cycle environmental impacts shows a distinct difference between biopolymers and petroleum polymers. With the exception of PET, petroleum polymers exhibit lower life cycle environmental impacts as they adhere more strictly

to green design principles. While biopolymers exhibit a range of life cycle environmental impacts, their rank based on green design principles does not vary widely, with the exception of B-PET. While adhering to green design principles reduces environmental impact in either the petroleum or biological polymer categories, switching from petroleum feedstocks to a bio-feedstocks does not necessarily reduce environmental impacts.

Normalization in the decision matrix using maximum values instead of average values does not change the LCA ranking however does change the green design rankings. Regardless of normalization, the overall disparity between biological and petroleum polymers remains. Results for the maximum normalization method can be found in Figure S.3.4 of the supporting information.

3.5 DISCUSSION

Results from this study show a qualified positive correlation between adherence to green design principles and a reduction of the environmental impacts of production. The qualification results from the difference between biopolymers and petroleum polymers. While biopolymers uniformly rank highly in terms of green design, they exhibit larger than expected environmental impacts from production. As shown through the LCA results, a decrease in fossil fuel use from switching to renewable resources results in large increases in other impact categories such as

eutrophication, human health impacts, and eco-toxicity. These impacts result both from fertilizer use, pesticide use, and land use change required for agriculture production as well as from the fermentation and other chemical processing required to turn the biomaterial into useful plastic (Landis, Miller et al. 2007).

Principles regarding the use of renewable resources should be redefined to prevent trade-offs related to the use of harmful chemicals on crops and the energy/emissions in the production and use of fertilizers and pesticides. For example the use of renewable sources could be limited to those which require below average pesticide and fertilizer use. Principles should be further qualified to address the trade-offs involved in chemical processing from bio feedstock or chemicals. This study's example, B-PET, first required the conversion of sugar starch into ethanol, a process already under scrutiny for its environmental benefit (Searchinger, Heimlich et al. 2008). Following this conversion, B-PET must go through the same production process as traditional PET, thus resulting in greater environmental impacts in all impact categories with the exception of fossil fuel depletion and greenhouse gas emissions, shown in Figure S-2 of the Supporting Information.

The number of production steps may be a simple approximation for environmental impact and can be added to the "use renewable resources" principle to prevent trade-offs. As mentioned earlier, polyolefin polymers require only one synthetic step after oil or natural gas refining and exhibit, by far, the lowest environmental impacts. In stark contrast, PC, PET, and B-PET require multiple synthetic steps between feedstock and final polymer and exhibit the greatest

environmental impact. However, the impacts of different synthetic stages in chemical plants vary widely; for example the production of ethylene glycol from ethylene oxide result in an unusually high eutrophication impact, and the production of chlorine gas from salt requires significantly high energy use.

The LCAs in this study have a limited scope and the exclusion of disposal scenarios may affect conclusions for biodegradable polymers or commonly recycled plastics. However, given biodegradation process for many bio-polymers, disposal scenarios are unlikely to reduce life cycle environmental impacts. In 2007, recycling facilities in the U.S. processed 18% of total PET production, 10% of all HDPE production, and 5% of all LDPE production (2008). Had the effect of recycled plastics on the reduction of virgin plastic production been included in the life cycle assessment, impacts resulting from each of these plastics would be reduced. However, the environmental impacts of the recycling process would also have to be included, most likely resulting additional impacts depending on the specific recycling process. Also, the environmental impacts of other waste scenarios such as incineration, land filling, and the composting of biodegradable polymers would have to be included. The obvious benefits of biodegradable products are a reduction in landfill waste as well as avoided transportation to industrial waste facilities. However biodegradation will inherently produce greenhouse gasses which can exceed the negative impact of carbon sequestration during plant growth. Also, given the proliferation of waste incinerators with energy recovery, other disposal options may continue to reduce the landfill waste while also providing an energy benefit to the life cycle. Finally, the

environmental and human health impact of chemical byproducts PLA or PHA biodegradation have yet to be studied.

Acknowledgment

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Supporting Information Available

A process outline and inventory information for the life cycle assessment of bio-polyethylene terephthalate, results for the B-PET LCA arranged by life cycle stage, data used from the literature review on PHA production, and tabular results from all life cycle assessments. This material is available free of charge at http://pubs.acs.org.

3.6 FIGURES

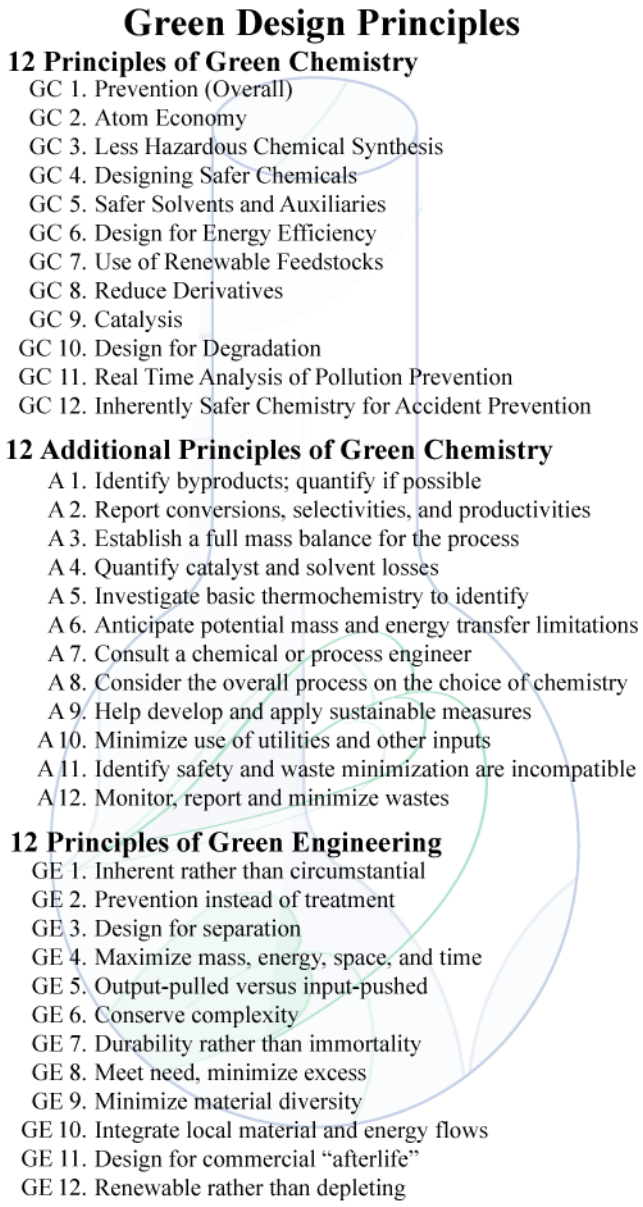

Figure 3.1. Previously published green design principles.

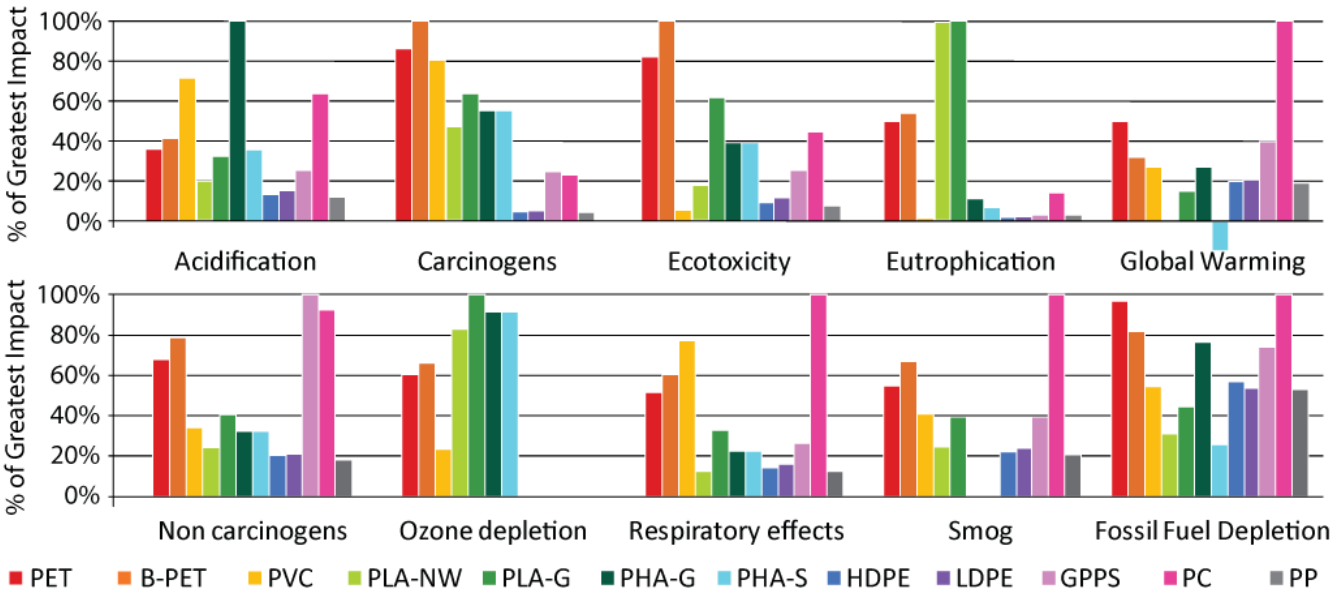

Figure 3.2. Life cycle assessment results for each of the polymers in TRACI impact categories, normalized by the greatest impact each category.

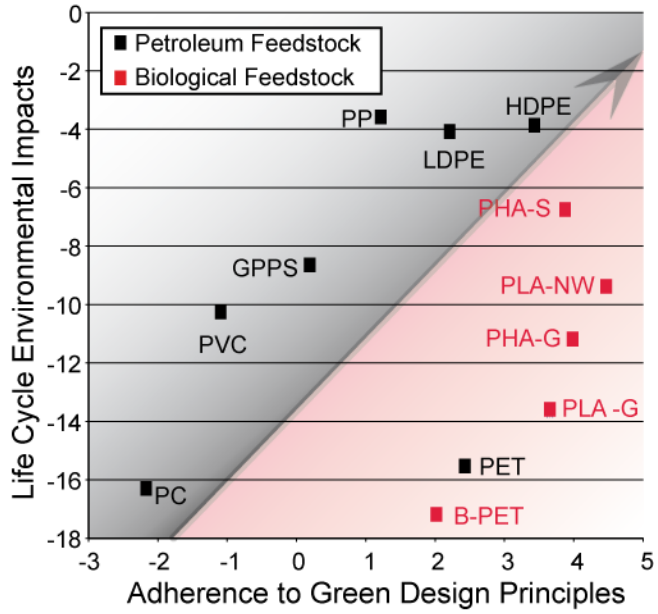

Figure 3.3. Polymer assessments displayed in two dimensions, “adherence to green design principles” and “life cycle environmental impacts” in the y-axis.

3.7 TABLES

Table 3.1. Reduction of green design principles to metrics.

Theme	Metric	Principles Referenced
Avoid Waste	Atom Economy	GC 2, A1, A3
Material Efficiency	Density	GE 8, GE4
Avoid Hazardous Materials/Pollution	TRACI Health and Ecotoxicity Impacts	GC 3-5, 11; GE 2
Maximize Energy Efficiency	Total Energy Demand	GC 6, A 10, GE 3,4, 10
Use of Renewable Sources	Percent from Renewable Soruces	GC 7, GE 12
Use Local Sources	Feedstock Distance	GE 10
Design products for recycle	Percent Recycled	GE 3,6, 9, and 11
Design to Degrade	Biodegradability	GC 10
Cost Efficiency	Price	GE 9

Table 3.2. Evaluation of polymers using green design metrics.

Material	Overall Atom Economy (%)	Carcinogens (kg benz. eq /L)	Non-Carcinogens (kg tolu. eq/ L)	Respiratory Effects (kg PM2.5 eq/ L)	Ecotoxicity (kg benz. eq/ L)	Cumulative Energy Demand (MJ eq/ L)	%Renewable Material	Distance of Feedstocks	% Recovery	Biodegradeable	Price (USD/ L)
PET	80%	$1.1x10^{-2}$	62.9	$4.9x10^{-3}$	5.72	123.8	0%	Intern.	18%	N/A	4.13
B-PET	62%	$1.3x10^{-2}$	72.7	$5.7x10^{-3}$	6.98	146.2	15%	Intern.	18%	N/A	4.13
PVC	55%	$1.1x10^{-2}$	31.7	$7.3x10^{-3}$	0.40	82.9	0%	Intern.	0%	N/A	4.02
PLA-NW	80%	$6.1x10^{-2}$	22.5	$1.2x10^{-3}$	1.21	79.4	100%	Region.	0%	Indus.	4.66
PLA-G	80%	$8.4x10^{-3}$	37.5	$3.1x10^{-3}$	4.31	98.3	100%	Region.	0%	Indus.	4.66
PHA-G	48%	$7.2x10^{-3}$	30.0	$3.1x10^{-3}$	2.76	91.5	100%	Region.	0%	Backyard	6.20
PHA-S	48%	$1.1x10^{-2}$	30.0	$2.1x10^{-3}$	2.76	91.5	100%	Region.	0%	Backyard	6.20
HDPE	100%	$6.5x10^{-4}$	18.7	$1.3x10^{-3}$	0.65	73.4	0%	Intern.	10%	N/A	1.52
LDPE	100%	$6.9x10^{-4}$	19.6	$1.5x10^{-3}$	0.82	72.3	0%	Intern.	5%	N/A	1.58
GPPS	98%	$3.2x10^{-3}$	92.7	$2.5x10^{-3}$	1.79	92.2	0%	Intern.	1%	N/A	2.35
PC	59%	$3.0x10^{-3}$	85.6	$9.5x10^{-3}$	3.13	128.9	0%	Intern.	0%	N/A	5.25
PP	100%	$5.8x10^{-4}$	16.8	$1.2x10^{-3}$	0.54	67.6	0%	Intern.	0%	N/A	1.78

Table 3.3. Rankings for each of the polymers based the normalized green design assessment results and the normalized life cycle assessment results.

Material	Green Design Rank	LCA Rank
PLA (NatureWorks)	1	6
PHA (Utilizing Stover)	2	4
PHA (General)	2	8
PLA (General)	4	9
High Density Polyethylene	5	2
Polyethylene Terephthalate	6	10
Low Density Polyethylene	7	3
Bio-polyethylene Terephthalate	8	12
Polypropylene	9	1
General Purpose Polystyrene	10	5
Polyvinyl chloride	11	7
Polycarbonate	12	11

3.8 SUPPORTING INFORMATION

Table S.1 Literature review of life cycle impact results of global warming potential and non-renewable energy use of PHA production.

Study	Feed Source	Non renewable energy (MJ/kg)	Global Warming (kg CO2/kg PHA)
Current technology (Kim and Dale 2005)	Corn Grain	88.00	2.85
Gerngoss (Gerngross 1999)	Corn Grain	80.42	4.40
Lynd (Lynd and Wang 2003)	Corn Grain	76.73	X
Near Future technology (Kim and Dale 2005)	Corn Grain	68.60	1.72
Heyde (Heyde 1998)	Corn Grain	66.10	X
Akiyma (Akiyama, Tsuge et al. 2003)	Corn Grain	59.17	0.48
Yu (Yu and Chen 2008)	Corn Stover	44.00	0.49
Pietrini (Pietrini, Roes et al. 2007)	Corn Stover	38.60	0.00
IS Grengross (Gerngross 1999; Kim and Dale 2005)	Corn Stover	31.50	-0.28
IS current technology (Kim and Dale 2005)	Corn Stover	24.90	-0.70
IS near future (Kim and Dale 2005)	Corn Stover	17.80	-1.20
IS akiyma (Akiyama, Tsuge et al. 2003; Kim and Dale 2005)	Corn Stover	12.30	-1.90
Kim integrated system (Kim and Dale 2008)	Corn Stover	2.50	-2.30

Table S.2 Literature review of life cycle impact results in other impact categories as reported by Kim and Dale et al. in (Kim and Dale 2005).

Study	Photochemical smog [mg–NOx eq. m–1 kg–1]	Acidification [moles H+ eq. kg–1]	Eutrophication [g–N eq. kg–1]
IS Grengross (Gerngross 1999; Kim and Dale 2005)	30.7	2.41	2.02
IS current technology (Kim and Dale 2005)	27.7	2.14	1.90
IS near future (Kim and Dale 2005)	22.5	1.62	1.68
IS akiyma (Akiyama, Tsuge et al. 2003; Kim and Dale 2005)	20.6	1.56	1.43

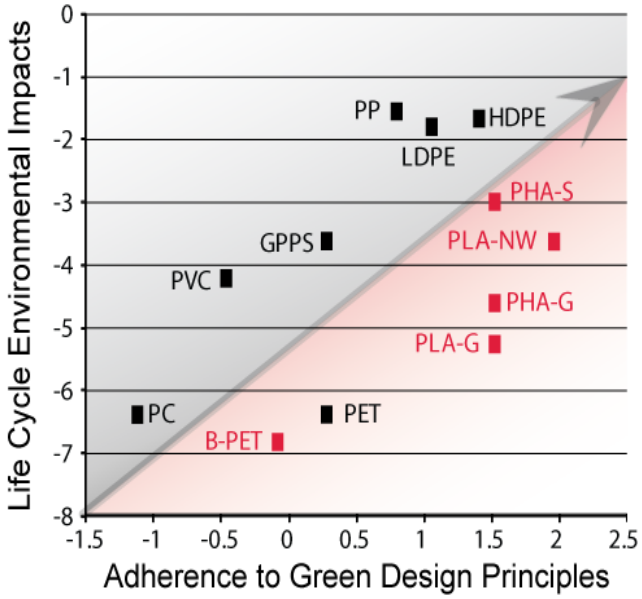

Figure S.3.4. Polymer assessments displayed in two dimensions, with results normalized to the maximum value among all polymers studied.

4.0 CONCLUSION

In this thesis, a life cycle assessment for the production of polyethylene terephthalate made from bio-based ethylene glycol (B-PET) is completed and then used along with those of 11 other packaging plastics to evaluate the effectiveness of green design principles.

B-PET production compared to its petroleum derived equivalent, PET, represents a 28% reduction in global warming potential and a 12% reduction in non-renewable energy (NREU) use. However the magnitudes of these reductions are small when compared to 1999 U.S. greenhouse gas emissions and NREU (<0.2%).

Green design principles, on the whole, were evaluated favorably. Increasing atom economy (which encompasses a vast amount of Green Chemistry) correlates well with reduced life cycle environmental impacts. However principles associated with using renewable resources and/or designing materials that biodegrade were found to increase environmental impacts of production, even when accounting for the benefits of using non-depleting sources and greenhouse gas sequestration. The principle for using renewable sources should be qualified to exclude agriculture products shown to have large, deleterious environmental impacts. Both the

use of renewable sources and the design for products that biodegrade should be qualified to avoid increasing the number of chemical processing steps needed to achieve each goal.

Principles are both necessary and dangerous aspects of environmental design and environmental research. By defining achievable outcomes, they offer needed guidance to new technology and turn environmental protection into a goal industry and society can share. However, as the results of this study show, following principles can lead to unintended side-effects which should to be taken into account sometime between the research/design process and widespread production and acceptance. As opposed to principles, evaluative metrics like life cycle assessments take time and a large amount of data to complete. It is categorically impossible to predict the effects of a chemical technology while it is still being developed on the lab bench and it remains hard to understand the effects new industrial technologies even after they have begun large scale production. As environmental principles continue to be applied, they must also be evaluated in light of changing technology and new environmental concerns.

Future work for the evaluation of green design principles includes studying their affect on the life cycle of existing products. By including more examples of "green production," more tradeoffs can be identified. Following the completion of environmental assessments of biopolymer disposal scenarios and polymer recycling, complete cradle-to-grave life cycle assessments can be created for each polymer. Such an assessment will be better able to evaluate green principles which apply to disposal, such as "design for products that biodegrade." Finally,

in place of creating additional green principles, current principles should be periodically restated to promote avoidance of likely environmental tradeoffs.

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