

Life cycle assessment of a biobased process for producing 1, 3 - Propanediol

by

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TABLE OF CONTENTS

TABLE OF FIGURES	v
TABLE OF TABLES	vi
ABSTRACT	vii
CHAPTER 1: INTRODUCTION	1
1.1. Introduction	1
1.2. Sustainability	3
1.3. Life - Cycle Assessment	5
1.4. Objective	6
CHAPTER 2: LITERATURE REVIEW	8
2.1. 1, 3 Propanediol	8
2.2. Literature Review for 1, 3 Propanediol	9
2.3. Review of Literature associated with PTT and Nylon 6.....	12
CHAPTER 3: PROCEDURE	14
3.1 Method of Approach	14
3.2 Fertilizer Production and Transportation.....	15
3.3 Corn Production and Transportation.....	18
3.4. Corn Wet Milling.....	21
3.5. PDO production	27
CHAPTER 4: PDO LIFE CYCLE RESULTS	35
4.1. Discussion of Results.....	35
4.2 Process Improvements	38
CHAPTER 5: PETROCHEMICAL ROUTE TO PDO	40
5.1 Method for Approach for Petrochemical Route	40
CHAPTER 6: LIFE CYCLE COMPARISONS	42
6.1. Comparison Studies	42
CHAPTER 7: SENSITIVITY ANALYSIS	51
7.1 Sensitivity Analysis	51

CHAPTER 8: RESOURCE USE SUMMARY 59

 8.1. Resource Summary 59

CHAPTER 9: CONCLUSIONS AND RECOMMENDATIONS 60

 9.1 Conclusions and Recommendations 60

APPENDIX 63

REFERENCES 69

TABLE OF FIGURES

Figure 1: Life cycle of a biodegradable product made from renewable raw materials	4
Figure 2: LCA framework	6
Figure 3: Molecular structure of 1, 3 Propanediol	8
Figure 4: Metabolic pathway for the production of PDO from glycerol	10
Figure 5: Comparison chart for Sorona, Nylon 6, and PET (Dupont)	13
Figure 6: Systems involved in the biobased production of PDO	14
Figure 7: Schematic diagram of a corn wet mill	22
Figure 8: Corn wet mill energy allocation	26
Figure 9: Metabolic pathway from glucose to PDO showing other by-products	28
Figure 10: Flowsheet for the production of PDO from glucose using the CHEMCAD simulator	32
Figure 11: Life cycle energy for producing biobased PDO	35
Figure 12: Global climate change potential	37
Figure 13: NO _x emissions	38
Figure 14: Petrochemical PDO production	40
Figure 15: Comparison of energy used in biobased process and petrochemical process	43
Figure 16: Climate change potential of the biobased and petrochemical process for PDO ...	43
Figure 17: NO _x emissions of the biobased and petrochemical process for PDO	44
Figure 18: Representation of the entire life cycle from corn to PTT	45
Figure 19: Life cycle energy per one kg of PTT	47
Figure 20: Comparisons of two different petrochemical processes to biobased PTT	48
Figure 21: Global climate change comparison	49
Figure 22: NO _x emissions for biobased PTT, petrochemical based PTT and Nylon 6	50
Figure 23: Climate change potential with coal as the energy source for the corn wet mill ...	53
Figure 24: NO _x emissions with coal as the energy source in the corn wet mill	54

TABLE OF TABLES

Table 1: Properties of 1, 3 Propanediol	8
Table 2: Energy requirements for production of agricultural chemicals and fertilizers	16
Table 3: Emission data for fertilizer and Ag chemical production	17
Table 4: Ag chemical transportation distances	17
Table 5: Energy and emissions for fertilizer and Ag chemical transportation	18
Table 6: Energy and emissions data for corn production and transportation	20
Table 7: Specific allocation factors for the products of the corn wet mill.....	25
Table 8: Reduced allocation factors for the products in the corn wet mill	25
Table 9: Fermentation parameters for the production of PDO from glucose	29
Table 10: Finished product specification	34
Table 11: Sensitivity parameters for the life cycle of PDO	57
Table 12: Sensitivity parameters.....	58
Table 13: Resource use in the production of PDO and PTT.....	59

ABSTRACT

1, 3 Propanediol is a monomer in a range of polycondensation reactions that produce polyesters, polyethers, and polyurethanes. A commercial fermentation route to PDO from corn sugar has been developed by Dupont and Genencor International. This biobased pathway will replace their current petrochemical route from acrolein to PDO. This thesis presents an environmental life cycle comparison of the biobased production of PDO with Nylon 6 and the petrochemical route to PDO. The important key factors evaluated for the biobased process and the petrochemical processes are energy requirements, global climate change, and NO_x emissions. The environmental footprints of the three processes are compared and the sustainability of the biobased process is analyzed. An important result of these comparisons is that the biobased process has the potential of reducing both greenhouse gas emissions and dependence on nonrenewable resources. The life cycle analysis of the biobased production of PDO from corn indicates that the majority of energy used is in the production of PDO from glucose. When comparing the biobased process with the petrochemical process the biobased process requires less energy. The biobased production also has a lesser impact on climate change, while producing approximately the same NO_x emissions as the petrochemical production pathway.

CHAPTER 1

INTRODUCTION

1.1. Introduction

Sustainable development is recognized to be essential for the growth of the economy and industrial productivity (DOE, 2001). Global petroleum reserves are finite, so ultimately there will need to be a new source of carbon-based feedstock for fuels and chemicals. The only known renewable source of carbon is biomass. Renewable materials from crops can provide many of the same chemical building blocks as petrochemical feedstocks (DOE, 2001). Bozell (1993) lists many of the many advantages of integrating renewable feedstocks into the nation's chemical production stream:

- Substituting renewable feedstocks for petroleum based chemical intermediates could potentially lower crude oil demand, thus limiting economic downturns in the chemical industry due to oil price volatility
- Using biomass feedstocks can expand the options of the chemicals industry by increasing feedstock flexibility and by broadening the spectrum of potential chemical products.
- Because imports are reduced as biomass is substituted for fossil resources, the balance of payments deficit can be reduced.
- Producing biobased chemicals may provide an acceptable answer to the current problems that the petroleum-based chemicals industry faces in terms of generating hazardous wastes and responding to public and political pressure to protect the environment.

- Carbon dioxide is recycled when new biomass is grown to replace that harvested for producing chemicals, so there is not a significant contribution to carbon dioxide accumulation in the atmosphere.
- Advances in metabolic engineering, bioprocessing, and separations technologies currently provide an unprecedented opportunity to overcome the key technical and economic hurdles limiting industrial applications.

A new market demand can be created for biobased products based on their life cycle value and ability to satisfy the needs of the consumer. The U.S. Department of Energy says of biobased materials, “The returns to our nation will be great because of the enhanced energy security and environmental quality, stronger economics, and the new employment opportunities that biobased production technologies will offer to the global markets. An effective policy framework will reduce market barriers to biomass and establish science based standards for bioproducts quality, performance and safety” (DOE, 2001).

In contrast to the Department of Energy’s forecast, Gerngross (1999) states, “The benefits of biobased processes have not been critically weighed against an overall inventory of materials and energy required to generate a given product”. In order to identify and maximize the advantages that may exist or result from integrating renewable raw materials into the chemical production stream or replacing conventional plastics with biodegradable polymers, the biobased processes need to be analyzed by process modeling. Currently, one major commercial biobased project of interest is the production PDO from glucose. By performing material and energy balances on this process and using that information to perform life cycle

assessment one can evaluate the environmental impacts associated with the production of this new product.

1.2. Sustainability

Sustained economic growth depends on having a secure and sufficient source of raw materials. Since worldwide materials consumption continues to increase, there is a need to find renewable resources for industrial production and energy needs. The use of crop based resources can possibly provide economical solutions that will meet the needs of the global economy.

The U.S. has a significant number of crop biomass resources such as forestry, rangeland, and the agricultural system (Patel, 2001). Corn is the leading U.S. crop in terms of acreage and production value. In 2000, the total corn production in the U.S. was approximately 215 billion tons. In 2001 and 2002, the total crop production was lower than in 2000. The production totals were roughly 205 billion tons and 194 billion tons respectively (Cook, 2001). As corn yield increases, the specific energy used to produce it generally decreases; therefore, higher yields make corn a more attractive feedstock. Figure 1 shows a typical life cycle of a corn-based product. At the beginning of this life cycle corn is grown and harvested and the corn grain is milled into starch and other useful co-products. The starch is then enzymatically converted to glucose. The glucose is fermented using a biocatalyst to produce a desired chemical. The fermentation product undergoes several separation steps until the required purity is achieved and the product is extracted. In the case of biopolymers the purified fermentation product is generally a monomer that is further processed to modify its properties, for example to increase optical purity. The monomer may

then be polymerized or combined with other chemicals to produce a final product with desired physical properties. The polymer is then molded into the consumer product. After the final product has been used it is either recycled or it is disposed (some products may be dissipated when they are used such as fuels and solvents). Depending on the processing sequence, biobased polymers may or may not be biodegradable. A biodegradable product may be broken down through biological activity and return its components onto the natural cycles, often ultimately resulting in releases of carbon dioxide and water vapor. The released carbon dioxide may be reabsorbed into biomass during subsequent photosynthesis.

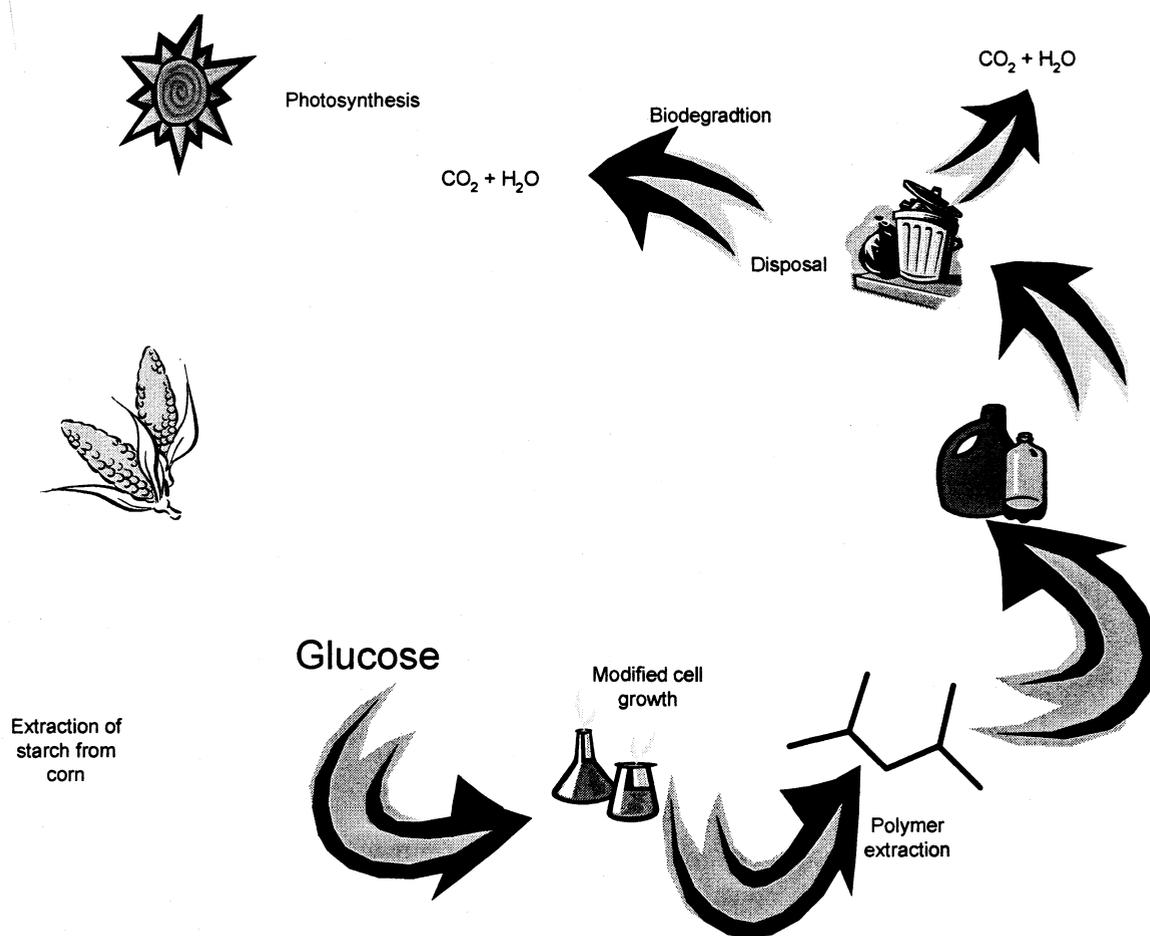


Figure 1: Life cycle of a biodegradable product made from renewable raw materials

1.3. Life - Cycle Assessment

Environmental life-cycle assessment (LCA) analyzes and assesses the environmental impacts of a product or service through out its life cycle – through production, use, and disposal. The four phases of LCA are shown in Figure 2. The first phase depicts defining the Goal and Scope of the assessment. It defines the purpose and extent of the study. An important part of the goal and scope is the functional unit. The functional unit of a product or service delivered serves as the basis for comparison with other systems. The second phase, inventory analysis involves creating an inventory of the emissions and resource used over the life cycle. The data collected are connected to each process as depicted in a process flow diagram. In the third phase, impact assessment, the impacts of the items in the inventory are categorized and compared. The fourth phase, interpretation, uses the results of the life cycle study in making recommendations for the improvements in the system and drawing conclusions regarding the environmental profile of the product or service studied.

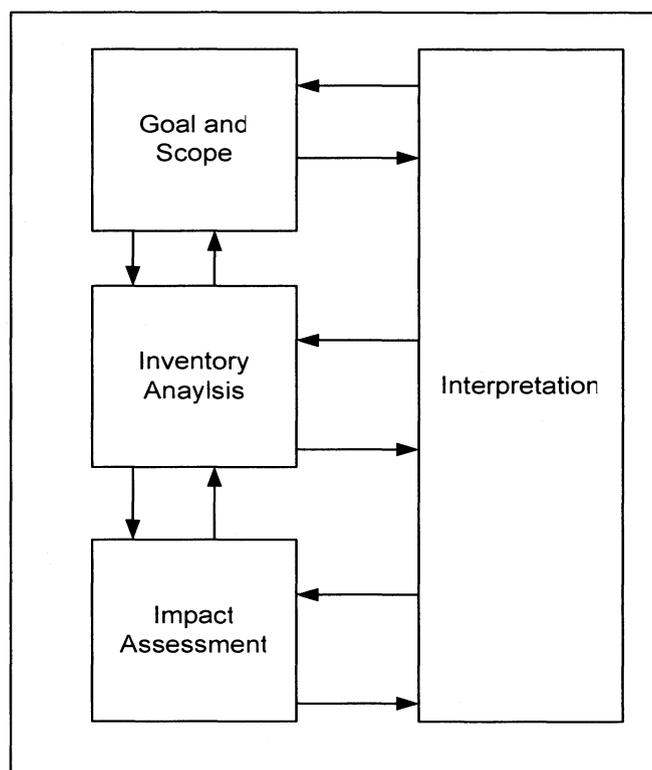


Figure 2: LCA framework

1.4. Objective

In this study, the LCA framework has been applied to the bioproduction of 1, 3 Propanediol (PDO) from corn. For the LCA study of PDO, the following life cycle stages are included: the harvesting of corn, extracting the starch from the corn grain and converting it into glucose, and the fermentation of the glucose into PDO (see Figure 1). The PDO is on the production process including the stages from glucose through polymer extraction is proprietary and thus inventory data were not publicly available at the time of this study. In order to complete an LCA including PDO production, detailed engineering design of the process was required. That section of the life cycle involves fermentation of glucose to the desired intermediate product and its separation and purification. Fermentation processes offer

several advantages over industrial processes for producing polymer intermediates and polymer products. They involve aqueous processing environments, non-toxic waste and the use of renewable, nonfossil feedstocks (Gerngross, 1999). Microbial polymer intermediates derived from glucose through a fermentation process possess favorable material properties and are generally biodegradable. Detailed design and modeling of the bioproduction of PDO from glucose allowed improvement analysis in which performance limiting steps and potential improvements are identified.

The goals of the study are to compare the environmental performance of biobased and petrochemical production of PDO and investigate possible improvements in the process of producing PDO from glucose. Since the boundary conditions are from corn production to the formation of PDO, this is a “cradle-to-factory gate” study and a functional unit of one kg of PDO was chosen. As well as evaluating the energy and environmental impacts of the PDO process, the system can be expanded further and include the production of terephthalic acid process and its combination with PDO to produce polytrimethylene terephthalate (PTT). Dupont markets the PTT polymer under the trade name “Sorona” and also refers to PTT as “3GT”. The biobased PTT life cycle can also be compared to the life cycles of the petrochemical route to PTT and Nylon 6. Through comparison of the life cycle energy and environmental impacts of the PDO biopolymer and its petrochemical equivalent, this study will help inform the on-going debate over the desirability of producing chemicals from biomass feedstock.

CHAPTER 2

LITERATURE REVIEW

2.1. 1, 3 Propanediol

PDO has a number of distinct properties. It is a monomer in a range of polycondensation reactions that produce polyesters, polyethers, and polyurethanes. Figure 3 shows the molecular structure of PDO and Table 1 lists some properties of PDO.

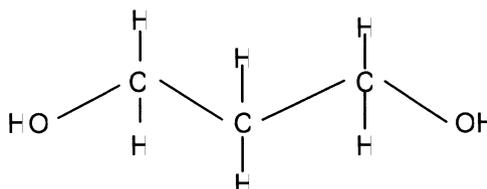


Figure 3: Molecular structure of 1, 3 Propanediol

Table 1: Properties of 1, 3 Propanediol

Property	Value	Units
Molecular Weight	76.09	
Boiling Temperature	214.00	C
Heat of Formation	-480.8	kJ/mol
Free Energy of formation	-304.48	kJ/mol
Heat of vaporization	72.4	kJ/mol
Specific gravity	1.035	

PDO can be used to improve the properties of solvents, adhesives, laminates, resins, detergents, and cosmetics. Until recently, PDO was only used as a solvent because of its high production cost. In 1995, Shell commercialized the 1, 3 Propanediol-based polyester, polytrimethylene terephthalate (PTT). PTT has superior dyeability characteristics that make it attractive in the carpet market. Dyeability plus stretch and rebound properties make it attractive in the apparel market. Shell's route of producing 1, 3 Propanediol from ethylene oxide is a relatively low cost commercialized technology. DuPont and Genencor International have developed a fermentation route to PDO from corn sugar that will replace their current alternate petrochemical production pathway from acrolein to PDO. When DuPont and Genencor commercialize their fermentation route of producing to PDO from glucose it is expected to be lower in cost than Shell's ethylene oxide route. However, whether it will be environmentally superior remains an important question that has not been answered.

2.2. Literature Review for 1, 3 Propanediol

There are a variety of petrochemical and biological pathways to PDO. Naturally occurring yeast can ferment glucose to glycerol and naturally occurring bacteria can convert glycerol to PDO under anaerobic conditions. Experimental studies of the biological production of PDO by fermentation of glycerol utilize the following bacteria: *K. pneumoniae*, *Citrobacter freundii*, and *Clostridium butyricum* (Deckwer, 1995). For the microbial formation of PDO, glycerol is dehydrated to 3-hydroxypropionaldehyde and then reduced to PDO under the consumption of reducing power (NADH₂) (Zeng, 1997). The reducing power generated in the oxidative metabolism of glycerol that makes use of the major glycolysis

reactions and results in the formation of by-products. Figure 4 shows the metabolic pathway for the production of PDO from glycerol. The yield of PDO depends on the combination and stoichiometry of the reductive and oxidative pathways. If a metabolic pathway is chosen so that acetic acid is the sole by-product and the other pathways are used for energy generation then a maximum yield of PDO will be obtained (Zeng, 2000).

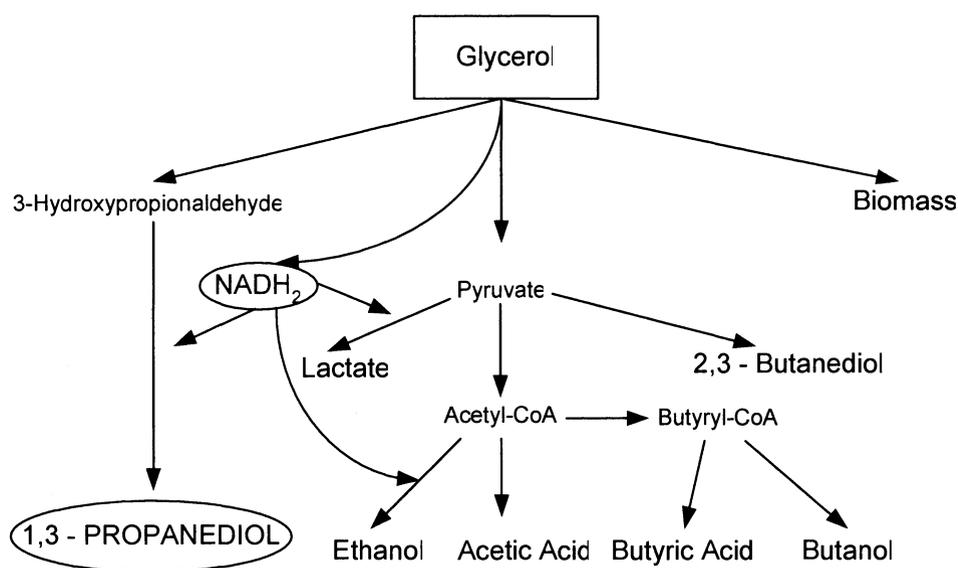


Figure 4: Metabolic pathway for the production of PDO from glycerol

The biological process of converting glycerol to PDO demonstrates that biotechnological production of PDO is promising. For batch processes, the yield of PDO is 67% mol/mol. When cell biomass production is considered in the process, the maximum yield is 64% mol/mol (Zeng, 1997).

There are many factors that affect the production of PDO in the fermentation process: substrate concentration, co-substrates, hydrogen production, and product inhibition (Chotani, 2000). For the glycerol to PDO fermentation process, complete conversion of glycerol is not

possible because of the requirement of an additional reducing equivalent. Adding glucose as a co-substrate allows 100% glycerol conversion to PDO, but glucose inhibition and by-product formation reduce the effectiveness of this strategy (Chotani, 2000). A biological method for producing PDO on an industrial scale requires a low energy input and an inexpensive starting material. A desirable process incorporates a microorganism that has the ability to convert basic carbon sources such as sugars to PDO (Chotani, 2000).

2.2.1. PDO Production Processes from Glucose

Over the past fifteen years, the interests in developing a production process for PDO production from glucose have increased. Dupont completed their first generation biocatalyst for the production of PDO from glucose in the early 1990's and collaborated with Genencor in 1995 to further improve the biocatalyst increasing the yield of PDO from fermentation. By 2000, Dupont was operating a pilot plant producing 90,000 kg/yr of biobased PDO.

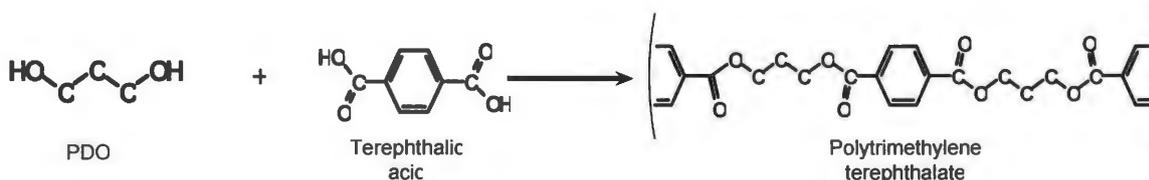
In the meantime, SRI Consulting was developing a process design report on the production of PDO from the many different feedstocks. One of the feedstock selections was an anaerobic fermentation of glucose. In the Process Economics Program (PEP), SRI reported on a process to convert glucose to PDO under anaerobic conditions through a series of continuous fluidized gas-lift fermentors (SRI 1999). Genetically modified *E.-coli* is the single organism used in the fermentation. The fermentation broth from the outlet of the fermentors is filtered to remove the cells. The filtrate is sent to parallel two stage evaporator crystallizers. The overhead vapor from the second stage evaporator containing PDO and water is condensed and fed to a water removal column. The column separates the light ends and the recovered PDO from the bottoms is fed into a purification column and recovered as a

distillate. The PEP design analysis predicted a final PDO yield of 48% in the fermentation (SRI 1999). The process design of the fermentation is a continuous anaerobic fermentation, which is not what is employed by Dupont; therefore the reactants and products of the reaction along with yields are different from what would be expected from the DuPont process. The separation and purification routes designed by SRI are reasonable options for separating PDO from the fermentation broth.

Another source of information regarding the fermentation route to PDO is a design assignment developed at Georgia Tech (Georgia Tech 2004). As a senior design project in the spring of 2004, the students were asked to develop a process that utilizes glucose in fermentation to produce PDO. The student designs relied on different separation and purification routes from those in the SRI report and in this study. In the problem statement used at Georgia Tech, a fermentation system is combined with a spray drying technique to remove the biomass solids (Georgia Tech). The purification route is similar to the one in this study in that there is a distillation train consisting of four distillation columns all operating under a vacuum (Georgia Tech).

2.3. Review of Literature associated with PTT and Nylon 6

Polytrimethylene terephthalate (PTT) is a thermoplastic that is produced by the polycondensation reaction of terephthalic acid and PDO. The overall reaction is shown by Reaction 1. PTT can be spun into both fibers and yarns and has applications in carpeting, textiles and apparel, engineering thermoplastics, non-wovens, films and microfilaments (SRI 1999). PTT has the rigidity, strength, and heat resistance of the polyethylene terephthalate (PET) resins along with the processability of the polybutylene terephthalate (PBT) resins.



Reaction 1: PTT formation from PDO and PTA

Nylon 6 fiber is known for its resiliency, but it does not accept a wide variety of dyes. PET fibers accept a wide range of dyes, but do not have the wearability or the resiliency of Nylon 6 (SRI 1999). PTT fibers have the dyeability of PET and the resiliency and wearability equivalent to that of Nylon 6 (Dupont). Figure 5 shows a comparison chart for each of the different properties for Sorona, Nylon 6 and PET (DuPont).

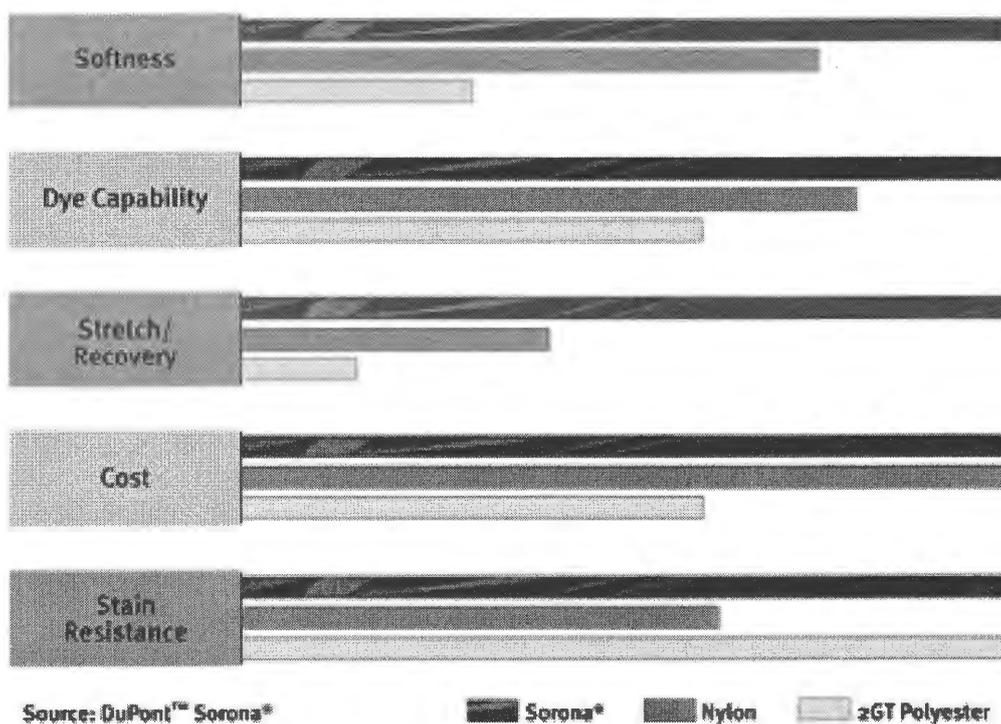


Figure 5: Comparison chart for Sorona, Nylon 6, and PET (Dupont)

CHAPTER 3

PROCEDURE

3.1 Method of Approach

Boundary conditions of cradle-to-factory gate were used in this study of biobased PDO production and are illustrated in Figure 6. The life cycle is divided into six stages. The first stage of the life cycle is the production of fertilizer and agricultural chemicals. The second stage is transport of fertilizer and agricultural chemicals to cornfields. The corn is planted then grown and harvested in the third stage and transported to the corn wet mill in the fourth stage. The corn is converted to glucose and in the final stage, the glucose is fermented to PDO and the final PDO product is separated and purified. The life cycle inventory accounts for raw material and fossil energy inputs and air, water, and solid emissions.

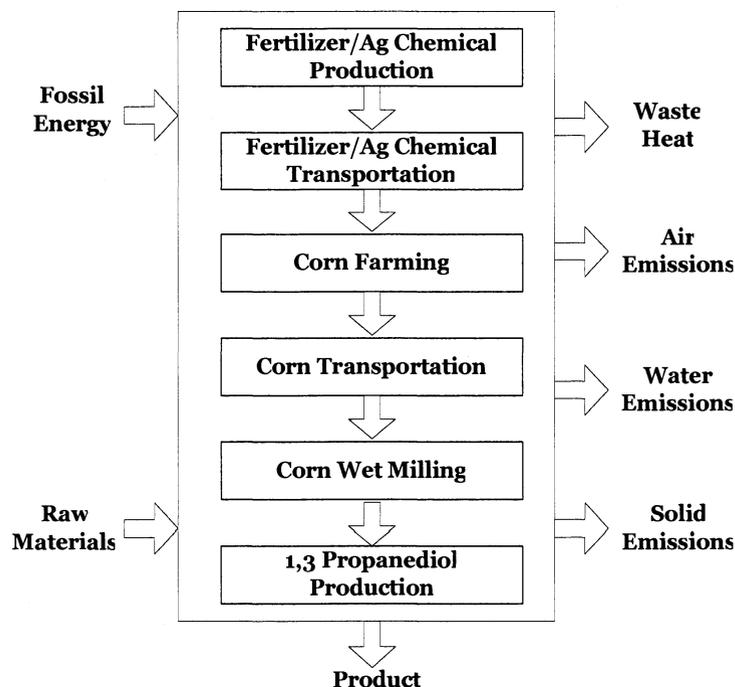


Figure 6: Systems involved in the biobased production of PDO

For the first four stages of the PDO life cycle, the energy and emission data were taken from the Argonne National Laboratory GREET (Greenhouse gas, Regulated Emissions and Energy in Transportation) model (Wang et al 1997). GREET calculates emissions and energy consuming sources and includes various paths including: fertilizer production and transportation and corn production and transportation. It includes emissions of five criteria pollutants: volatile organic compounds (VOC), carbon monoxide (CO), nitrogen oxide (NO_x), particulate matter with size smaller than 10 microns (PM₁₀), and sulfur oxides (SO_x) and three greenhouse gases: methane (CH₄), nitrous oxide (N₂O), and carbon dioxide (CO₂). The corn wet mill energy and emission data were estimated using industry data from Penford Corporation (Quarels) and a report from the Lawrence Berkeley National Laboratory (Galitsy 2003). PDO production was modeled using a chemical engineering simulator (CHEMCAD) and the process energy use and emissions were estimated through simulation. The emissions reported throughout the life cycle are carbon dioxide, methane, nitrous oxide, and nitrogen oxides. Methane and nitrous oxide emission are converted to CO₂ equivalents. The CO₂ mass equivalent conversion for methane and nitrous oxide are 21 and 310 respectively. These conversions are based on a 100 – year time horizon as reported by the Intergovernmental Panel on Climate Change (IPCC).

3.2 Fertilizer Production and Transportation

Field corn cultivation generally requires the application of various agricultural chemicals during the growing season. The production and transportation of fertilizer and agricultural chemicals are therefore included in the life cycle inventory of biobased PDO. Fertilizers include nitrogen, phosphate, potash and lime. Agricultural chemicals include

insecticides and herbicides. There are eight types of N-fertilizer used in significant amounts on U.S. farms, but the three major types are anhydrous ammonia, nitrogen mixtures, and urea. GREET includes three fertilizer mixtures formed from the eight fertilizer components: ammonia, urea, and ammonium nitrate (Wang et al 2003). For GREET simulations, the use of anhydrous ammonia, aqua ammonia, nitrogen solutions are combined together and represented in the model as ammonia (70.7%), the use of ammonium nitrate, ammonium sulfate, and ammonium thiosulfate are combined together and represented by ammonium nitrate (8.3%) and all remaining nitrogen fertilizer use is taken to be in the form of urea (Wang 2003). Table 2 shows the energy requirements for the production of fertilizers and agricultural chemicals used on Iowa farms (Wang, 2003). Table 3 shows all of the emissions associated with the production of those fertilizers and agricultural chemicals.

Table 2: Energy requirements for production of agricultural chemicals and fertilizers

Fertilizer	Energy: MJ/kg PDO
Nitrogen	0.2×10^1
P ₂ O ₅	2.4×10^{-1}
K ₂ O	1.5×10^{-1}
Lime	3.0×10^{-2}
Herbicide	1.6×10^{-1}
Insecticide	2.0×10^{-3}
Total	0.26×10^1

Table 3: Emission data for fertilizer and Ag chemical production

Fertilizer	Emissions: kg/kg PDO			
	CO ₂	NO _x	N ₂ O	CH ₄
Nitrogen	1.2×10^{-1}	1.6×10^{-4}	9.7×10^{-4}	6.4×10^{-3}
P ₂ O ₅	1.6×10^{-2}	3.9×10^{-5}	0	5.4×10^{-4}
K ₂ O	9.4×10^{-3}	2.2×10^{-5}	0	3.2×10^{-4}
Lime	6.1×10^{-3}	3.9×10^{-6}	6.4×10^{-6}	1.0×10^{-4}
Herbicide	8.3×10^{-4}	1.7×10^{-6}	2.9×10^{-6}	3.4×10^{-5}
Insecticide	0	0	0	0

The GREET model estimates energy use and emissions associated with transporting fertilizers and feedstocks based on transportation distance and transportation mode (Wang et al 2003). Transportation of chemicals from manufacturing plants to farms occurs in three steps: from manufacturing plants to bulk distribution centers, from distribution centers to mixers, and from mixers to farms (Wang, et al 1997). Table 4 describes the three transportation steps and associated energy use (Wang, et al 1997).

Table 4: Ag chemical transportation distances

	Step One:	Step Two:	Step Three:
	Plant to Center	Center to Mixer	Mixer to farm
Travel distance (mi)	1060/520	50	30
Transportation mode	Barge/rail	Class 8b truck	Class 6 truck
Energy use (MJ/kg)	0.343	0.122	0.255

In step one, the travel distance is divided into two sections. The transportation by barge is 1060 miles, and the transportation by rail is 520 miles. The energy use listed is in MJ/ kg of nutrient that is being transported. Using the assumptions listed in Table 4, the energy required for transporting the fertilizer and agricultural chemicals were calculated in the GREET model and are listed in Table 5.

Table 5: Energy and emissions for fertilizer and Ag chemical transportation

Description	Value	Units
Energy	4.4×10^{-2}	MJ/kg PDO
Emissions		
CO2	3.9×10^{-3}	kg/kg PDO
NOx	2.0×10^{-5}	kg/kg PDO
N2O	1.9×10^{-5}	kg/kg PDO
CH4	9.3×10^{-5}	kg/kg PDO

3.3 Corn Production and Transportation

U.S. corn yield per acre has increased over the last 30 years by over 50% due to improved corn varieties, better farming practices, and farming conservation measures (Wang, et al 1999). The type of tillage system employed has a significant impact on energy use. Reduced tillage reduces energy use and also decreases runoff of nitrogen that in turn reduces the need for fertilizer application and increases the organic carbon in the soil. While yield has increased, inputs of nitrogen, phosphate and potassium fertilizers have declined per bushel of

corn. The three-year average nitrogen, phosphate and potassium inputs have declined from 1.18, 0.46, and 0.56 pounds per bushel in 1991-93 to 0.94, 0.34, and 0.42 pounds per bushel in 1998-2000 (Graboski 2002). Similarly, total herbicide and insecticide use has declined from 3.22 to 2.48 pounds of active ingredient per acre (Graboski 2002). The fertilizer application, type of tillage, and corn yields significantly impact the overall energy use associated with corn production. In this study the following assumptions were made regarding to corn production:

1. Energy use estimates for corn farming include: land preparation, planting, plowing, weeding, application of chemicals, irrigating, harvesting, and drying
2. The equipment used on the farm is not included in the life cycle
3. The carbon dioxide fixed through photosynthesis is re-emitted so no climate change credit is taken for sequestration of carbon in the soil
4. The location of corn production and conversion to PDO is Iowa

The second assumption reflects that the energy, emissions and materials involved in making a tractor are small compared to the energy and emissions associated with the tractor's use over its lifetime. The third assumption means that there is no carbon sink or source associated with the soils used in growing the corn. Iowa was chosen as the location of the study because there have been several studies of corn production with focus on the state of Iowa. These studies provide useful data on the energy and emissions associated with fertilizer application and corn production. Based on corn production data for the state of Iowa in 2002, estimated yield is 146 bushels/acre (2003 Corn Annual). The energy and emissions associated with corn production and transport are shown in Table 6.

Table 6: Energy and emissions data for corn production and transportation

Description	Corn Production	Corn Transportation	Units
Energy	2.8	4.6×10^{-1}	MJ/kg PDO
Emissions			
CO ₂	1.2×10^{-1}	3.3×10^{-2}	kg/kg PDO
NO _x	9.4×10^{-4}	1.1×10^{-4}	kg/kg PDO
N ₂ O	1.0×10^{-3}	2.4×10^{-4}	kg/kg PDO
CH ₄	4.7×10^{-3}	8.0×10^{-4}	kg/kg PDO

Some of the nitrogen applied to cornfields as nitrogen fertilizer eventually results in N₂O emissions either by direct release from the soil or from runoff water. Both of these types of emissions are caused by nitrification and denitrification processes (Wang, 1997). Adopting the assumption of Wang (1997)), the amount of nitrogen released into the atmosphere as N₂O emissions is taken to be 1.5 % of the nitrogen applied as fertilizer.

Several studies have examined how corn is transported from the farms to the corn wet mill facility. Graboski (2002) reports that of the 1.5 billion bushels of corn hauled off the farm in the state of Iowa, 35.8% was moved in semis, 33.3% in wagons and 30.9% in single and tandem axle trucks. The average hauling distance was 37.2 miles by semi, 4.9 miles by wagon and 9.1 miles by single and tandem axle vehicles. Semi trucks accumulated the majority of the ton-miles required for corn transported to the mill (Graboski 2002). Wang et al. (1997) reports that corn is transported from the farms in a two-step process: first by class

6 trucks (20 miles round trip), then by class 8 trucks (80 miles round trip). The energy required for the transportation according to Graboski is 4600 Btu/ bushel of corn and according to Wang (2002) it is 4100 Btu/bushel of corn. Thus there is a reasonable level of agreement between these two independent estimates of the energy required for corn transportation. The data used in this study shown in Table 6 are from the GREET model (Wang et al, 2002).

3.4. Corn Wet Milling

The purpose of the corn wet mill is to separate corn grain into different marketable products. The five products that are considered in this study are: steep water, germ, gluten feed, gluten meal, and glucose. There are a variety other products that may be associated with corn wet milling, but to reduce the need for life cycle inventory allocation and because of the aggregated form of the industry process data, these five products are taken to be the outputs of the corn wet milling process. A schematic diagram of the corn wet mill is shown by Figure 7 (Galitsky 2003). In addition, it is assumed that the corn wet mill is collocated with the PDO production facility and that all of the starch produced in the corn wet mill is converted to glucose and used in the PDO production facility. This assumption will eliminate from consideration in the LCA any other products that can be formed from starch (e.g., ethanol, high fructose corn syrup) and thus eliminates the need for allocation of the life cycle inventory among these other glucose products.

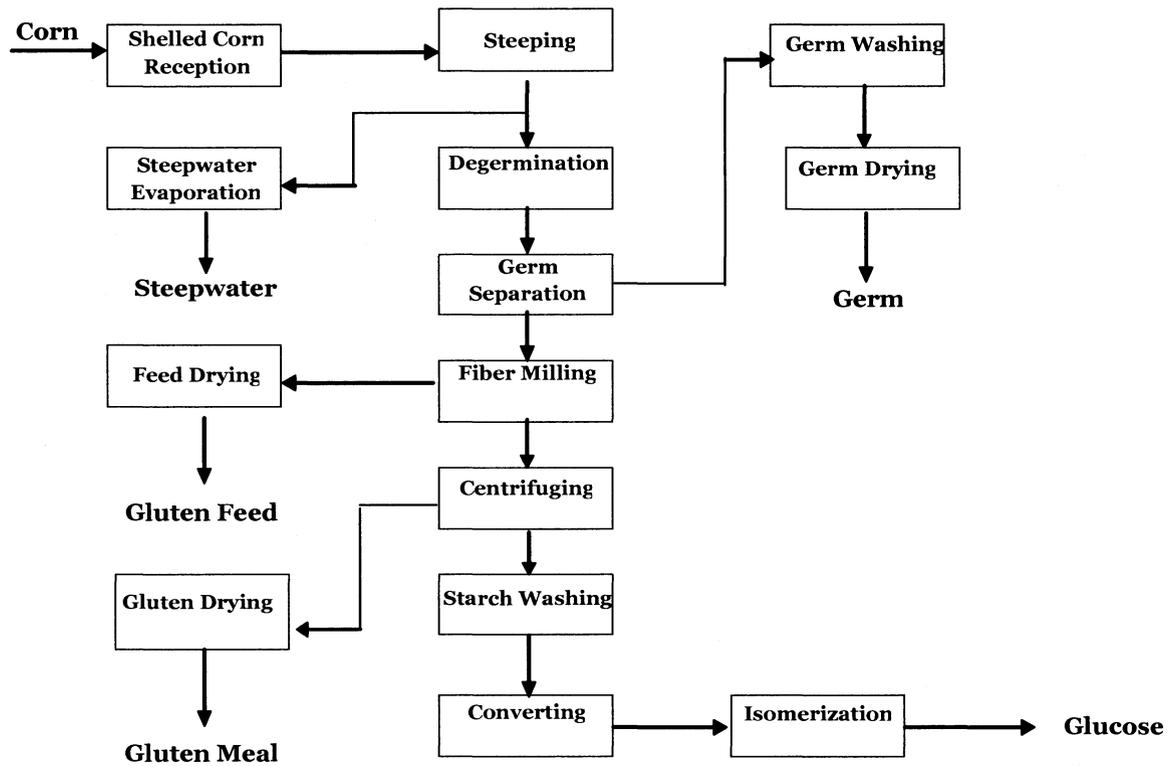


Figure 7: Schematic diagram of a corn wet mill

Allocation is the partitioning and distribution of a life cycle inventory item over several processes and co-product allocation is the partitioning and distribution of the emissions of a multiproduct process over its co-products (Weidema, 2001). The ISO standard 14041 (ISO 1998) recommends the following allocation procedure:

Step 1: Whenever possible, allocation shall be avoided by:

1. Dividing the unit process to be allocated into two or more subprocesses and collecting the input and output data related to these subprocesses;
2. Expanding the product system to include the additional functions related to coproduct.

Step 2: Where allocation cannot be avoided, the inputs and outputs of the system should be partitioned between its products in a way, which reflects the underlying physical relationship between them. These physical relationships can be mass fraction, energy content or volume.

Step 3: Where physical relationship alone cannot be established or used as the basis for allocation, the inputs should be allocated between the products in a way, which reflects other relationships between them.

By eliminating non-PDO uses of glucose from the wet mill obviates the need for some allocation, the procedure cannot be avoided completely. The environmental inventory of the corn wet mill must still be allocated in some way among the five wet mill product streams. Following the recommended ISO allocation procedures, three different methods of allocation were applied to the corn wet milling system. The procedures for allocation were mass allocation, energy content allocation, and market value allocation.

Mass Allocation

For mass allocation, the system was divided according to the mass produced for each product. EQN 1 was used to form the mass allocation factor for each product in the corn wet milling system.

$$AF_A = \frac{M_A}{M_A + M_B + M_C} \quad \text{EQN: 1}$$

The allocation factor for product 'A' is labeled as AF_A . The same labeling scheme would be applied to AF_B and AF_C . In EQN 1, M_A , M_B , and M_C represent the mass for the different products exiting the corn wet mill. Once the mass allocation factor is established, it is applied

to the energy and emissions data to allocate them among to the different products of the system.

Energy Content Allocation

Energy content allocation was associated with the energy content for each product in the corn wet mill. EQN 2 shows the equation used to establish the energy content allocation factor.

$$AF_A = \frac{E_A}{E_A + E_B + E_C} \quad \text{EQN: 2}$$

In EQN 2, E_A , E_B , and E_C represent the energy content for the different products. This factor was then applied to allocate the energy and emissions from the corn wet mill among its five products.

Market Value Allocation

For market value allocation, the market value of each product was used as in EQN 3 to obtain the market value allocation factors for each product.

$$AF_A = \frac{MV_A}{MV_A + MV_B + MV_C} \quad \text{EQN: 3}$$

In EQN 3, MV_A , MV_B , and MV_C represent the market values for the products of the corn wet mill. The market value allocation factor was then applied to the energy and emissions as it was for the other allocation methods. The allocation factors obtained using the different allocation methods are shown in Table 7. Table 8 contains the allocation factors computed if the outputs of the wet mill are aggregated into only two categories: co-products and starch.

Table 7: Specific allocation factors for the products of the corn wet mill

Product	<u>Allocation Factor</u>		
	Output Mass	Energy Content	Market Price
Steep water	5.5 %	0.1 %	0.4 %
Germ	5.2 %	11 %	11 %
Corn Gluten Meal	5.0 %	6.0 %	5.0 %
Corn Gluten Meal	17%	20%	4.0 %
Starch	38 %	63 %	80 %

Table 8: Reduced allocation factors for the products in the corn wet mill

Allocation Method	<u>Allocation Factor</u>	
	Starch	Co-Products
Output Mass	68 %	32 %
Energy Content	63 %	37 %
Market price	80 %	20%

Using those factors listed in Table 8, the energy and emissions required for the corn wet mill were allocated among the different product streams. A comparison of the different allocation methods applied to wet mill energy use is shown in Figure 8.

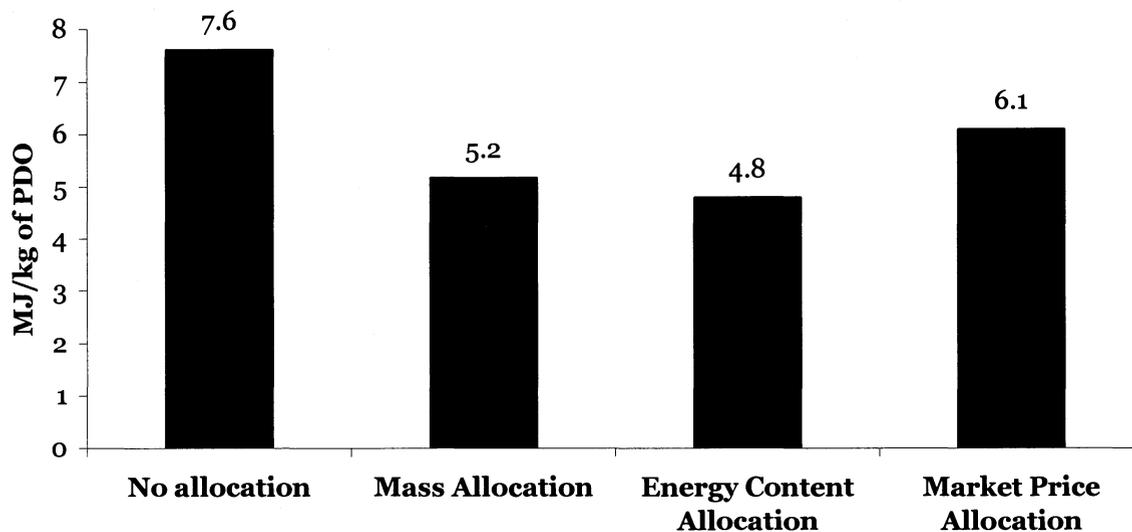


Figure 8: Corn wet mill energy allocation

The first column on the graph represents no allocation for the corn wet mill. “No allocation” reflects the case in which all of the by-products are considered to be waste streams and the only product stream is starch. The results of energy allocation using the other three allocation methods described above are also presented on the graph. The energy units are MJ/kg of PDO since the functional unit is one kg of PDO. There is only a small difference between the results of the allocation methods and after all of the energy from the other stages of the life cycle is added to the energy use in the corn wet mill, then the difference in total energy use between the methods is quite small. It should be noted that there is not a single, correct allocation method. Allocation is a somewhat arbitrary process that is required to make sense of processes with co-products. Because of the small differences observed between the allocation methods evaluated, the mass allocation method was used in this study.

Another allocation method identified in the ISO guidelines and not evaluated here is system expansion. System expansion is performed to maintain comparability of product systems in terms of product outputs by balancing a change in output volume of a co-product that occurs in only one of the product systems by adding an equivalent production in the other systems (Weidema 2001). Unfortunately, a number of drawbacks have been observed in system expansion. For example, the choice of the reference process is not always clear and additional data are required in modeling the expanded system, creating additional data uncertainty (Vink et al. 2004). This method was not applied because of its known weaknesses and because mass allocation is a common and accepted allocation method (Vink et al. 2004).

Another important assumption about the corn wet mill system is the source of energy. About 74% of corn wet mills use coal as their primary fuel and the others use natural gas (Vink et al. 2004). Since natural gas is the cleaner of the two energy sources, the baseline energy source used in the life cycle inventory is natural gas. The impact of this assumption is examined in the sensitivity analysis, where emission data are compared for the coal-fired and the natural gas fueled systems.

3.5. PDO production

Although the biological processes from glucose to glycerol and glycerol to PDO are known, it had never been demonstrated that a single organism could convert glucose to PDO prior to Dupont and Genencor International's organism development in the early 1990's. The organism takes some of the glucose as the starting sugar and allows a portion of it to be completely converted to carbon dioxide that provides more reducing power per glucose

molecule (Chotani, 2000). They have constructed a strain of *E. coli* containing genes from *S. cerevisiae* for glycerol production and the genes from *K. pneumoniae* for PDO production (Chotani, 2000). Figure 9 shows the metabolic pathway of the single organism designed by Genencor International and Dupont for the production of PDO from glucose.

Dupont and Genencor International have publicly released a few of the parameters needed to model the fermentation of glucose to PDO using their engineered organism. The parameters are shown in Table 9.

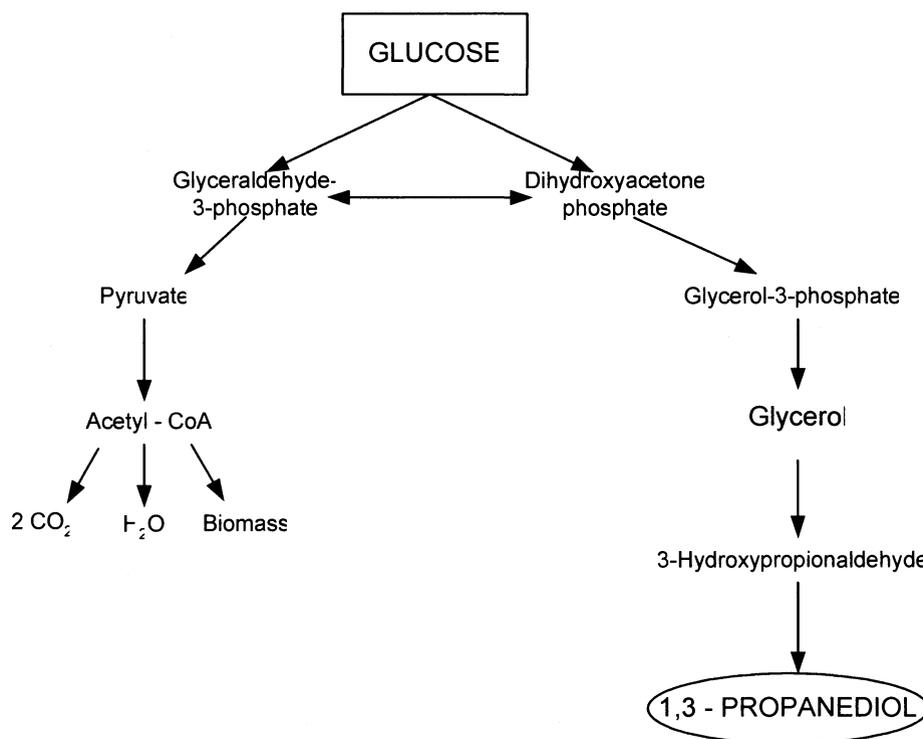


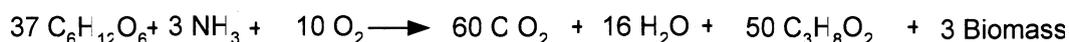
Figure 9: Metabolic pathway from glucose to PDO showing other by-products

DuPont has also supplied some separation and purification choices for the process along with the overall reaction in the fermentor and is shown by Reaction 2. *E. coli* ($\text{CH}_{1.78}\text{O}_{0.6}\text{N}_{0.19}$) is chosen as the representative biomass for the process because it is the

main organism used by Dupont and Genencor International. It provides a rich set of genetic tools: sequenced genome, vectors, and promoters. It is also closely related to the natural PDO producers, *K. pneumoniae* and *C. freundii* (Chotani, 2000). Using values from the literature for *E. coli*, such as growth rate and saturation constants in the Monod model, the reaction given, along with the list of separation and purification choices, the process for the production of PDO from glucose was designed and is shown by Figure 10.

Table 9: Fermentation parameters for the production of PDO from glucose

Description	Value	Units
Concentration of PDO	135	g/L
Rate of Production of PDO	3.5	g/L h
Yield of PDO	0.511	g/g



Reaction 2: Biobased reaction for PDO

As shown in Figure 10, the feed products (S-102), glucose, ammonia, water, inoculum and air (S-133) enter the fermentor. As modeled, the aerobic fermentation proceeds for 38 hours at 37 C, 1 atm with a working volume of 130,000 L. The Monod kinetic model is chosen to describe microbial growth in the aerobic fermentation system. The specific growth rate, saturation constant, and cell maintenance reported in the literature for an aerobic process using *E.coli* are 0.50 h^{-1} , 4.0 mg/L , and 0.045 h^{-1} respectively (Bailey, 1986). For Monod kinetics, the rate of glucose consumption ($-r_s$) is related to the cell growth rate, product generation and cell maintenance as shown in EQN 4.

$$-r_s = Y_{s/c} r_g + Y_{s/p} r_p + m C_c \quad \text{EQN: 4}$$

where,

$Y_{s/c}$: yield of glucose per cells (mol/mol)

$Y_{s/p}$: yield of glucose per PDO (mol/mol)

m : maintenance coefficient (h^{-1})

C_c : cell concentration (mol/l)

r_p : rate of product formation (mol/l h)

r_g : rate of cell growth (mol/l h)

The growth rate of cells is given by EQN 5, where K_s is the saturation constant, C_s is the substrate concentration (mol/l), and μ_{\max} is the maximum specific growth rate (h^{-1}).

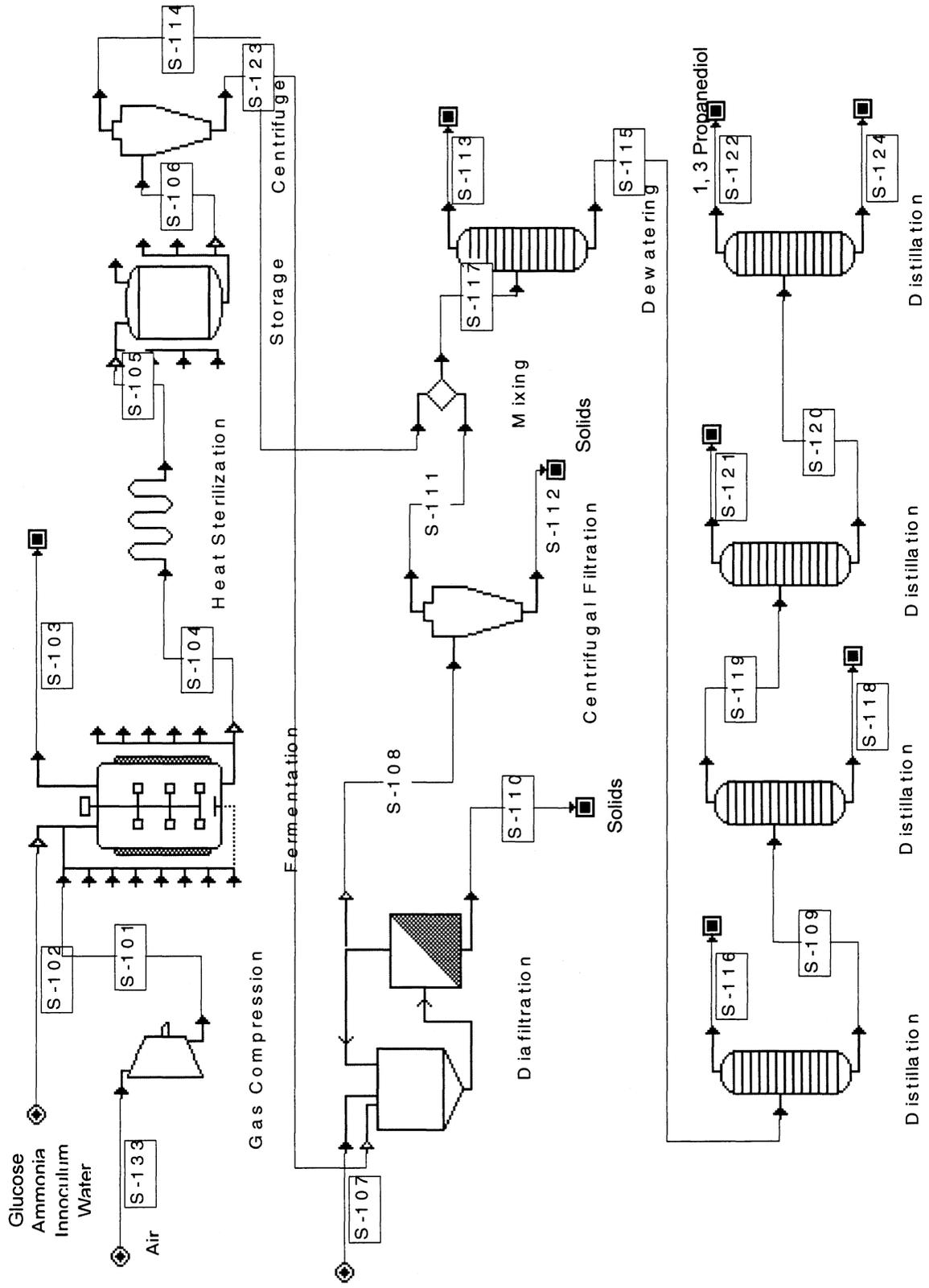
$$r_g = \mu_{\max} \frac{C_s}{K_s + C_s} C_c \quad \text{EQN: 5}$$

The rate of product formation in the growth phase is given by EQN 6, where $Y_{p/c}$ is the yield of PDO per biomass (mol/mol).

$$r_p = r_g Y_{p/c} \quad \text{EQN: 6}$$

After fermentation, the fermentation broth continues to a heat sterilization unit to kill any remaining live organisms (S-104). The heat sterilization unit has a sterilizing temperature of 140 C. Since the fermentation is a batch process, after sterilization the broth is moved to a storage tank (S-105). Leaving the storage tank, the broth (S-106) proceeds to a centrifugal separation system to remove the cell mass from the fermentation liquid to produce a clarified broth containing PDO for further processing. The aqueous product (S-114) continues to a dewatering column while the cell mass (S-123) is further washed to separate out any PDO that remains with the cell mass to improve the overall yield. The washing of the biomass involves a diafiltration system using water as the rinse liquid to extract the residual PDO from the biomass.

Figure 10: Flowsheet for the production of PDO from glucose using the CHEMCAD simulator



The water (S-107) is added to the feed tank at the same rate as the permeate flux, thus keeping the feed volume constant during processing. The aqueous product (S-108) leaving the diafiltration advances to a centrifugal filtration system to remove any biomass that did not exit through the screening process of the diafiltration. The aqueous product from the second centrifugal filtration (S-111) and the first centrifugal system (S-114) are combined and continue on to a dewatering column. The target parameters that need to be met before the aqueous product stream enters the distillation train are:

1. Less than 30% water;
2. No Biomass;
3. Less than 0.1% protein;
4. pH greater than 8.5;
5. Less than 0.1% total dissolved solids; and
6. Less than 0.1% glycerol.

The water is reduced from 90% to 20% in a dewatering column and all of the other design specifications listed above are met either within the dewatering column or upstream before proceeding to the distillation train. All of the columns are operated under a vacuum to reduce operating temperatures and to minimize unwanted reactions and product degradation (SRI 1999). The first column of the distillation train removes water down to less than 3%. The bottom stream (S-109) of the column proceeds to a second distillation column where the heavy impurities, primarily glycerol and residual sugars, are removed (S-118). The third column removes the light components (S-121). The final distillation column purifies the PDO to a dry weight of 99.9% (S-124), along with the other target requirements for the final PDO product. The overall finished product specifications are listed in Table 10. The final

yield of PDO is 3.1 million kg/yr and an overall energy of 26 MJ/kg PDO. The simulator used to model the production of PDO from glucose was CHEMCAD. A stream table for all of the components in kg/yr is provided in the Appendix. Stream names in the Appendix correspond with the stream names shown in Figure 10. The equipment specifications and the energy requirements are also listed in the Appendix with equipment names that correspond to the names of the equipment shown in Figure 10.

Table 10: Finished product specification

Description	Value
Purity on a dry basis wt%	99.98
Glycerol, ppm	50
Water, ppm	500
pH	5.5-7.0

CHAPTER 4

PDO LIFE CYCLE RESULTS

4.1. Discussion of Results

Combining inventory data over all of the life cycle stages and using the functional unit of one kg of PDO, the overall energy use and emissions were obtained for the production of PDO from corn grain. Figure 11 shows the energy required for each stage within the life cycle in units of MJ/kg PDO.

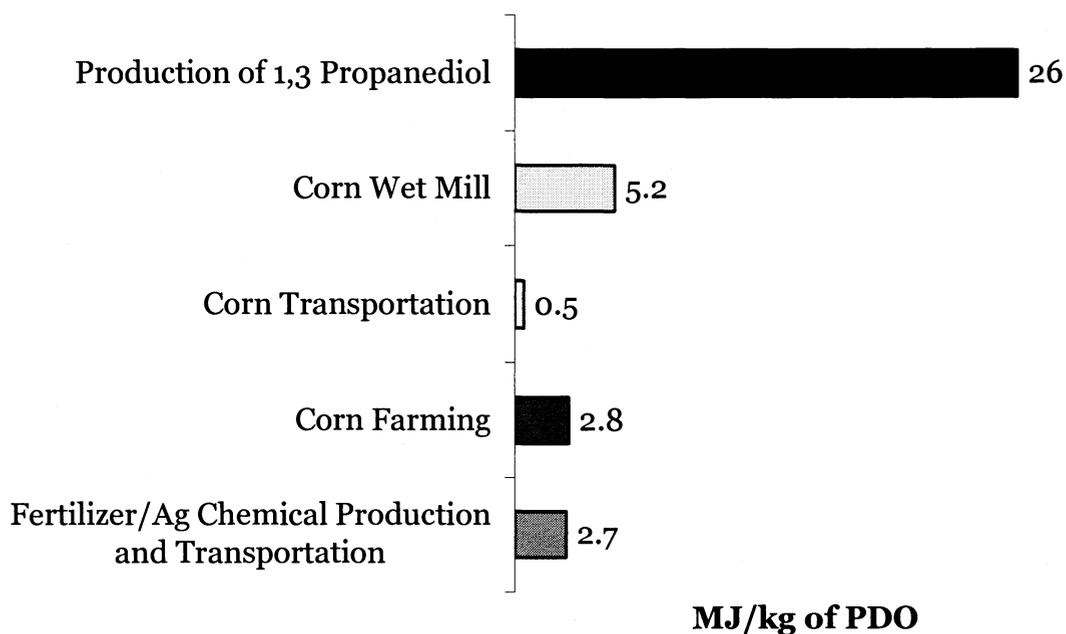


Figure 11: Life cycle energy for producing biobased PDO

The total fossil energy use is 37 MJ/kg of PDO. The total fossil energy use to produce the fertilizer and agricultural chemicals is 2.7 MJ/ kg of PDO. This represents 7% of the total energy requirements for the cradle-to-factory gate life cycle of PDO. Corn farming and

transportation contribute 3 MJ/ kg of PDO to the total fossil energy requirement. This represents only 8% of the total fossil energy used. The energy required to convert the corn into glucose in the corn wet milling system requires 5 MJ/ kg of PDO of fossil energy and accounts for 13 % of overall energy use. The major use of fossil energy in the life cycle is the production of PDO from glucose. The production of PDO requires 26 MJ/kg PDO of energy with around 26% of this energy used in fermentation, 64% in purification and 10% in separation. This process accounts for approximately 70% of the total fossil energy use. In recent studies of other biobased polymer production processes, the life cycle stage requiring the most energy is the production of the polymer intermediate from glucose. In Vink's (2003) study, he finds that lactic acid production from glucose accounts for 49% of the fossil energy used for the production of PLA, while the upstream corn farming and milling processes have energy requirements similar to those found in this study.

In addition to evaluating the energy associated with the production of PDO, the emission of greenhouse gases was analyzed. Figure 12 shows climate change potential for each of the different stages in the life cycle. The units are kg of CO₂ equivalents/kg PDO.

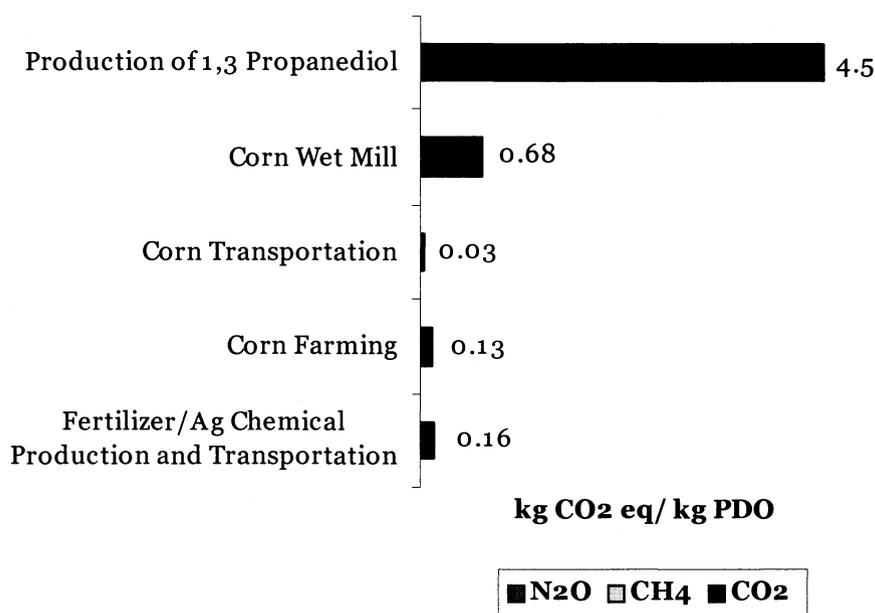


Figure 12: Global climate change potential

Most of the CO₂ emissions are associated with energy use in the production of PDO from glucose, which is naturally related to energy uses shown in Figure 11. The nitrous oxide emissions in corn farming are associated with the fertilizer use in growing corn. As stated earlier, some of the nitrogen in the fertilizer applied to cornfields eventually becomes N₂O emissions either through emissions directly from the soil or from runoff water. Both of these emissions are caused by nitrification and denitrification processes (Wang, 1997).

Other environmental impacts of concern are photochemical smog and acid rain. Nitrogen oxide emissions (NO_x) are one precursor of acid rain. The NO_x emission data are shown in Figure 13 for each stage of the life cycle.

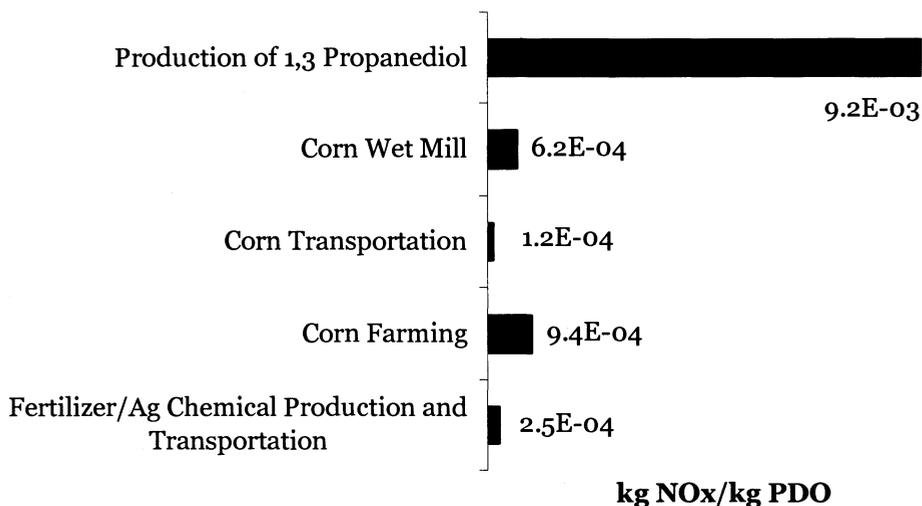


Figure 13: NOx emissions

These results are also correlated with life cycle energy use because one major source of NOx emissions is combustion related to heat and power generation.

4.2 Process Improvements

Since most of the energy in the overall life cycle is in the production of PDO from glucose, an obvious target for improvement of the process is to reduce the amount of energy required. As noted, most of the energy in this process is used in purification and separation of PDO from the fermentation broth. A possibly more efficient purification technique for separating PDO and water is solvent extraction. The preferred solvent would be one that has high selectivity toward PDO and is readily separated from PDO by distillation and has low solubility in water. A likely solvent choice would be an aldehyde because it would have a high selectivity to the PDO because of the complexation between aldehyde and PDO to form acetals (Reaction 3).



Reaction 3: Formation of acetals by PDO and an aldehyde

The PDO could then be back - extracted from the aldehyde. In order to evaluate this alternative method for water removal, data would have to be obtained from Dupont. Candidate techniques for recovering PDO from the biomass more efficiently are spray drying followed by evaporation. This method was proposed by students at Georgia Tech in a design exercise (Georgia Tech). Possible fermentation technique improvements are to minimize the formation of biomass, which would minimize the separation and purification steps in the process. An extraction step after fermentation followed by a recycle loop back into the fermentor could save energy by reducing the amount of biomass in the separation. These alternative designs were not analyzed in detail.

CHAPTER 5

PETROCHEMICAL ROUTE TO PDO

5.1 Method for Approach for Petrochemical Route

In addition to developing a life cycle analysis for the biobased production of PDO, the petrochemical route was evaluated for comparison purposes. Figure 14 shows the abbreviated life cycle stages of the petrochemical route to PDO. Upstream stages not shown in the figure were included in the analysis using data from LCI databases as detailed below.

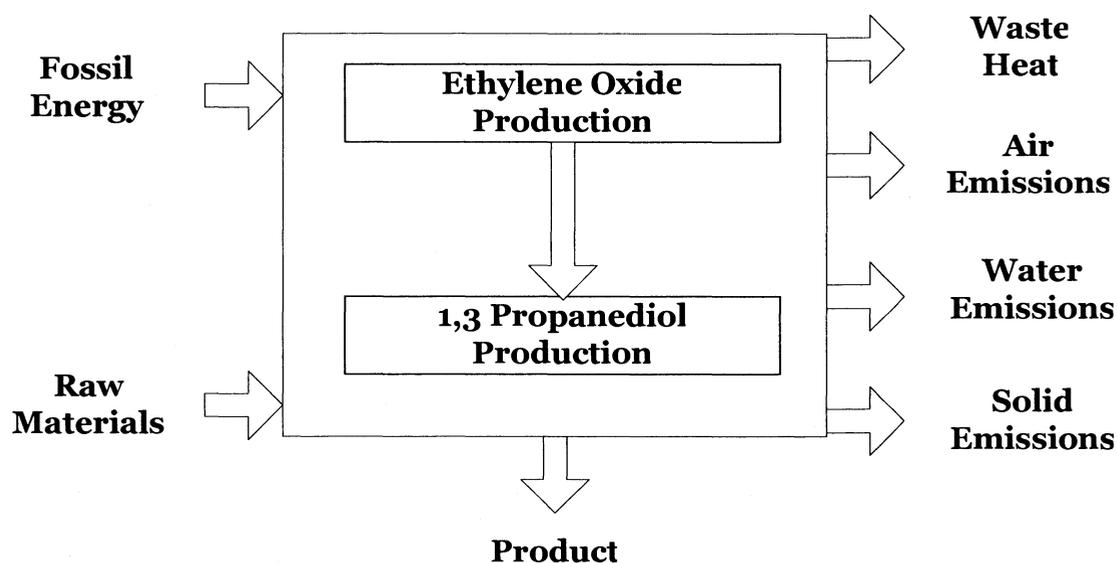
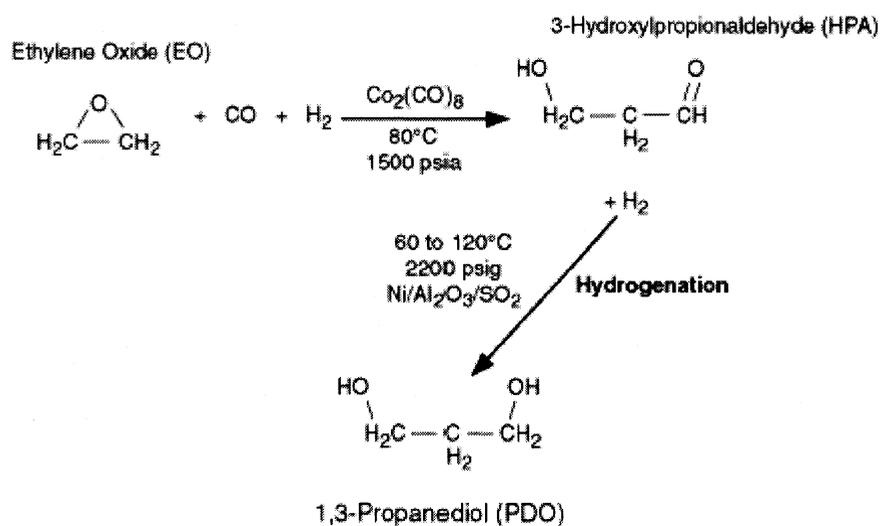


Figure 14: Petrochemical PDO production

The ethylene oxide process data were obtained from SimaPro Life Cycle Assessment software (SimaPro 2002). In this process, ethylene oxide is combined with syngas in a reactor to form Hydroxypropanaldehyde (HPA) (SRI 1999). The HPA is then combined with hydrogen to form PDO. Reaction 4 shows the overall reaction. Using syngas production data (Petrochemical Processes 1989), hydrogen production data (SimaPro 2002), and the energy

and emissions data for the production of PDO from ethylene oxide, the life cycle inventory for the production of PDO from petrochemicals were developed. Using the life cycle inventory data for the petrochemical production of PDO, the process energy, climate change potential, and NO_x emissions were compared to the life cycle inventory of biobased production of PDO.



Reaction 4: Formation of PDO from ethylene oxide and syngas (SRI 1999) SRI report

CHAPTER 6

LIFE CYCLE COMPARISONS

6.1. Comparison Studies

The life cycle inventory data for the biobased and petrochemical processes for production of PDO were compared on the basis of energy, global climate change, and NO_x emissions with the functional unit of one kg of PDO. The energy requirements of the biobased and petrochemical PDO processes are shown in Figure 15. The biobased production pathway requires about 40% less fossil energy than the petroleum-based pathway. Figure 16 shows the climate change potential for both processes (per kg of PDO). The biobased process also appears to have less climate change impact potential than the petrochemical process. There is about a 10%-15% difference in the climate change data for the two production pathways. Even though the biobased process appears not to require as much energy and have less climate change potential, the biobased PDO appears to have marginally more NO_x emissions than the petrochemical process for producing PDO (Figure 17). As shown in Figure 17, there is about a 10% difference in the NO_x emissions with biobased PDO emitting more NO_x. These patterns of NO_x emissions are reasonable since biobased processes require fertilizer to grow the biomass and the fertilizer production and use contributes to N₂O and NO_x emissions as well as CO₂ emissions. Recent LCA studies of biobased processes have shown that they may require less energy and have lower greenhouse gas emissions than petrochemical processes, but these studies have often also shown higher NO_x emissions in biobased systems.

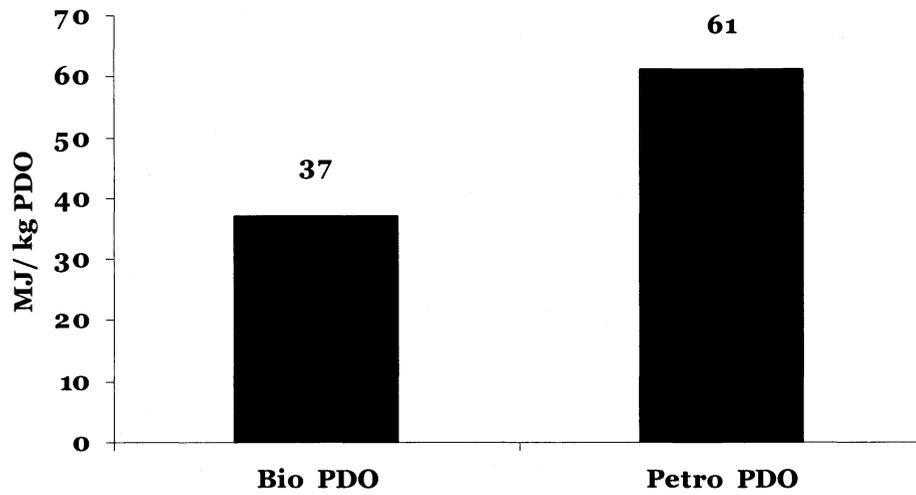


Figure 15: Comparison of energy used in biobased process and petrochemical process

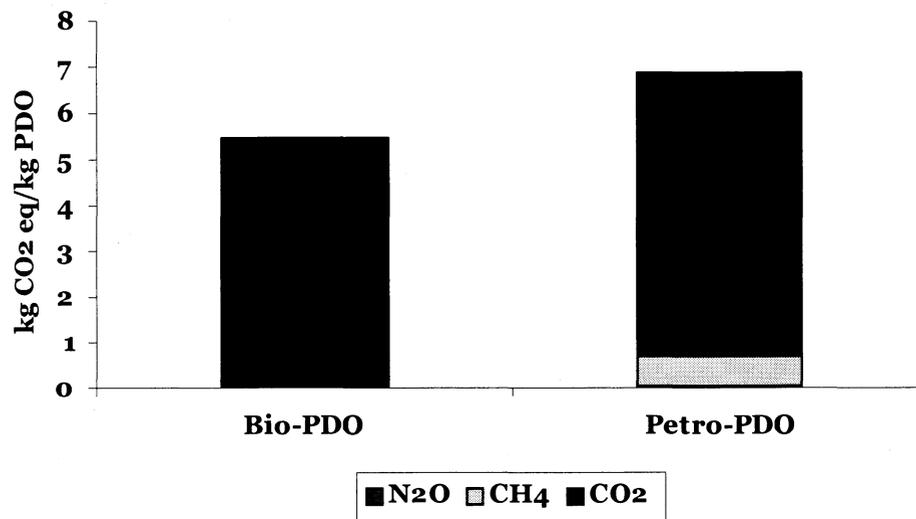


Figure 16: Climate change potential of the biobased and petrochemical process for PDO

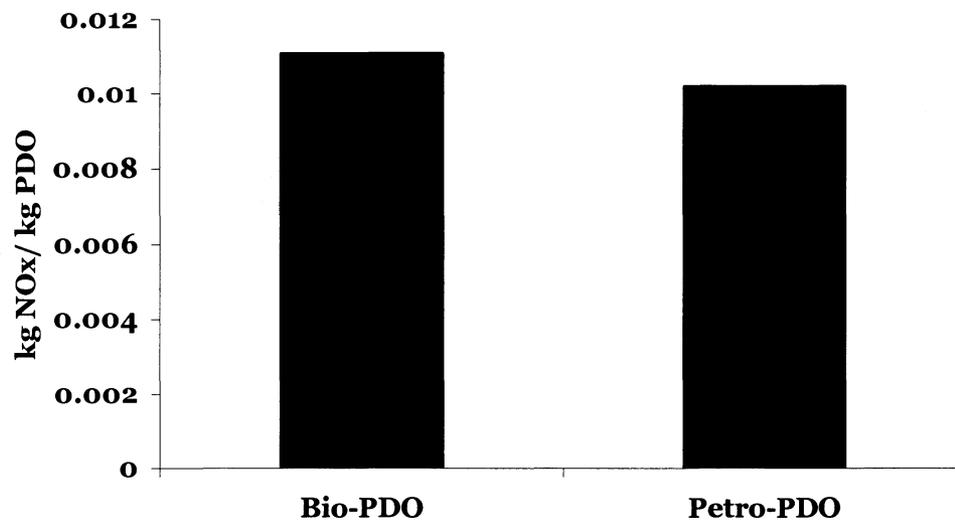


Figure 17: NOx emissions of the biobased and petrochemical process for PDO

Sheehan's report (2002) on the sustainability of ethanol from corn stover found that the ethanol life cycle has NOx emissions that are 13 times that of gasoline per vehicle passenger mile driven. This ethanol life cycle indicated that the additional NOx emissions occur mostly on the farm and particularly through releases from the soil (Sheehan, 2002).

There is a large percentage difference between the two production pathways when comparing the energy requirements. There is of course uncertainty inherent in the life cycle inventory. Quantifying the uncertainty in a life cycle inventory is difficult because many data gathered from databases come with no uncertainty information. Uncertainty in life cycle inventory data is generally taken to be at least 10 – 15%. On this basis, the 45% difference in energy use is probably significant. The climate change potential and NOx emissions comparisons show only a 10-15% difference in the two production pathways, which would fall within the uncertainty of this LCA, and therefore this small difference may not be significant.

In addition to comparing the biobased production of PDO with the petrochemical route to PDO, the system was extended one step further by adding terephthalic acid (PTA) production and the formation of Polytrimethylene terephthalate (PTT) from PDO and PTA (Figure. 18). Figure 18 shows the life cycle up to the production of PTT. The first section (left most box) illustrates the processes of the life cycle inventory data that were obtained from literature for this study.

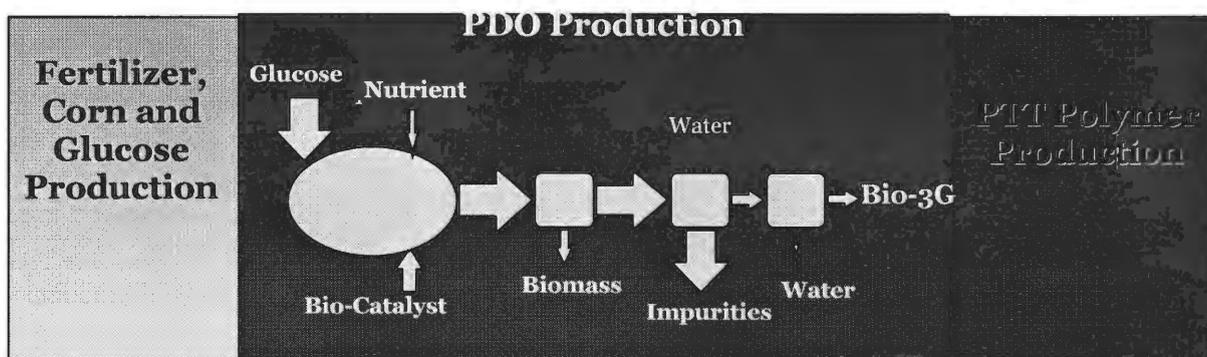


Figure 18: Representation of the entire life cycle from corn to PTT

The middle section represents the PDO production process that was designed and simulated to complete the life cycle of PDO. The last section is the addition of the terephthalic acid process to the life cycle. Terephthalic acid is formed by the oxidation of para -xylene shown by Reaction 5.



Reaction 5: Formation of terephthalic acid from para xylene

Polytrimethylene terephthalate is then formed by the esterification of PDO and terephthalic acid (see Reaction 1).

The data for the petrochemical production of terephthalic acid were obtained from Boustead (2002). The esterification data were estimated using an SRI Process Economics Program Report that modeled this process (SRI 1999). SRI combined PDO with terephthalic acid and a nitrogen purge in a series of two esterification reactors (SRI 1999). After the water removal in the esterification reactors, the ester product then proceeds to a polycondensation reactor train consisting of three columns to achieve the final PTT product (SRI 1999). The PTT life cycle data were then combined with the biobased and petrochemical routes to PDO and the functional unit was changed to one kg of PTT. Figure 19 shows the energy requirements for the production of PTT as well as the full life cycle in terms of the revised functional unit (kg of PTT). When the production of terephthalic acid is included in the life cycle, the energy required in production of PDO is dwarfed by that required for the production of terephthalic acid.

In addition to comparing the biobased production of PTT with the petrochemical route, both processes are compared to Nylon 6 production. As stated earlier, biobased PTT has product performance similar to Nylon 6 for several applications and Dupont's Sorona (3GT) is meant to be a replacement for Nylon 6. Since the biobased production of polytrimethylene terephthalate could be a possible replacement for Nylon 6, it is informative to compare the two life cycles. A complete comparison of PTT and Nylon would consider all life cycle stages, including product use and end-of-life disposition (e.g., disposal or recovery). Consideration of the full life cycle is beyond the scope of this study, so the comparison among the PTT pathways and Nylon is necessarily approximate, considering only the cradle-to-factory gate portion of the life cycle.

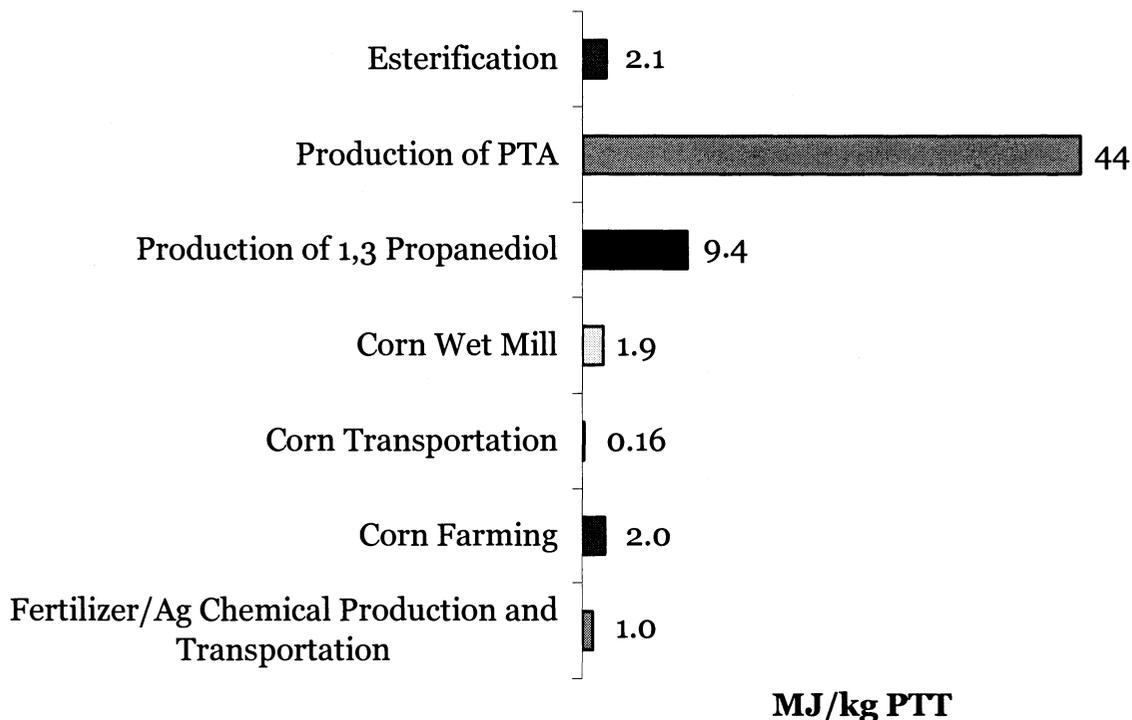


Figure 19: Life cycle energy per one kg of PTT

In order to compare the production of Nylon 6 and the two PTT processes on the same scale, the Nylon 6 process was converted from a functional unit of a kg of Nylon 6 to a functional unit meant to approximate one kg of PTT. This conversion is accomplished by correcting for the density difference of the two compounds. A more correct approach would be to compare environmental emissions per the amount of each material required to provide a similar function in a given application. Because use-specific data are not available for both polymers, life cycle inventory data were normalized based on density as an approximation of the material required for some generic use. The density of Nylon 6 and PDO are 1.14 g/l and 1.35 g/l respectively. The energy requirements for biobased PTT, petrochemical based PTT and Nylon 6 are shown in Figure 20.

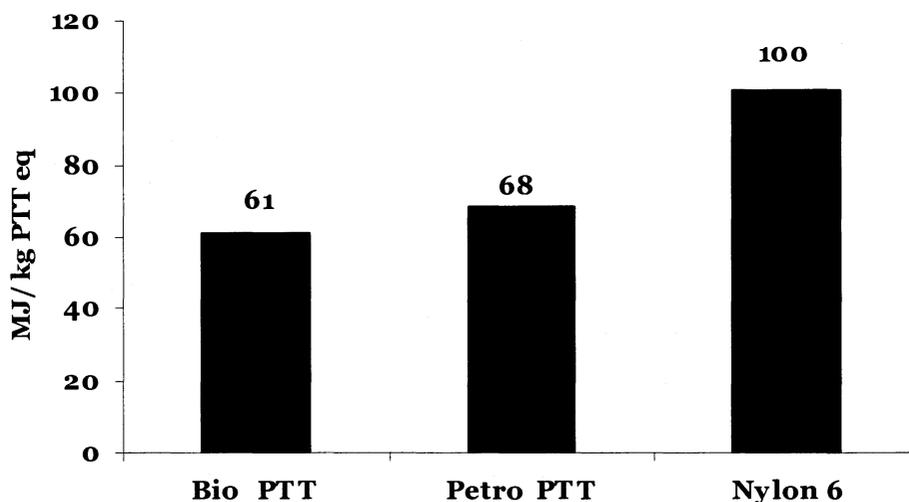


Figure 20: Comparisons of two different petrochemical processes to biobased PTT

Biobased and petrochemical production have the same relative energy requirements as the biobased and petrochemical PDO processes, since the steps from PDO to PTT are identical for both processes. The biobased pathway to PTT also appears to require less energy than Nylon 6 production. There is a larger difference in energy use between the biobased process and Nylon 6 production than between the petrochemical and the biobased routes to PTT. The same comparison applies to greenhouse gas emissions, as shown in Figure 21. There are large N_2O emissions associated with the production of Nylon 6 because Nylon 6 is derived from hexamethylene diamine and adipic acid the manufacture of which results in significant nitrous oxide emissions (Boustead 1995). In comparing NO_x emissions (Figure 22), the biobased and petrochemical processes are similar, and both have considerably lower emissions than the Nylon 6 production process.

These comparisons demonstrate that the biobased production of PTT may require less energy than the petrochemical route to PTT and Nylon 6. Biobased PTT may also emit less

greenhouse gases that Nylon 6 and petrochemical route, but in terms of NO_x emissions, the biobased route to PTT and the petrochemical route to PTT are similar, and both have significantly less emissions than Nylon 6 production. Again, caution must be exercised when drawing conclusions based on these results. There are likely to be significant differences between the use and disposal phases of the PTT and Nylon life cycles that may change their relative environmental attractiveness.

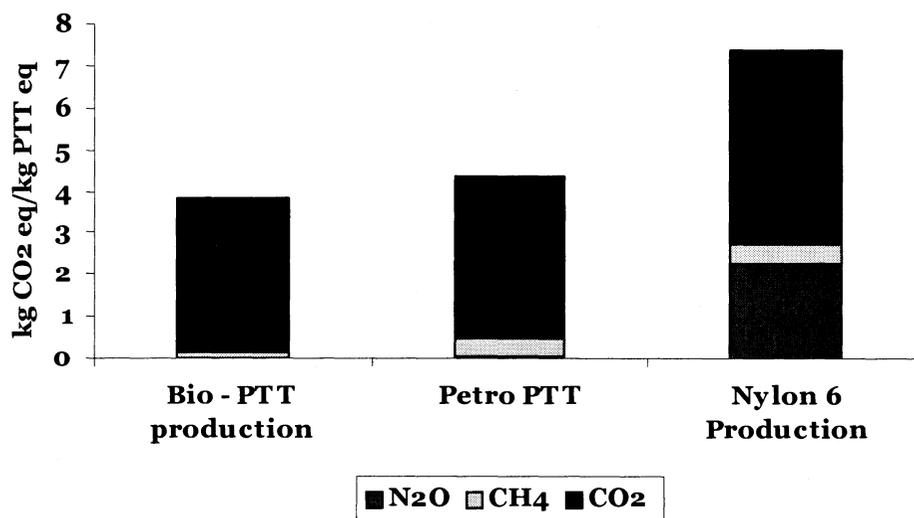


Figure 21: Global climate change comparison

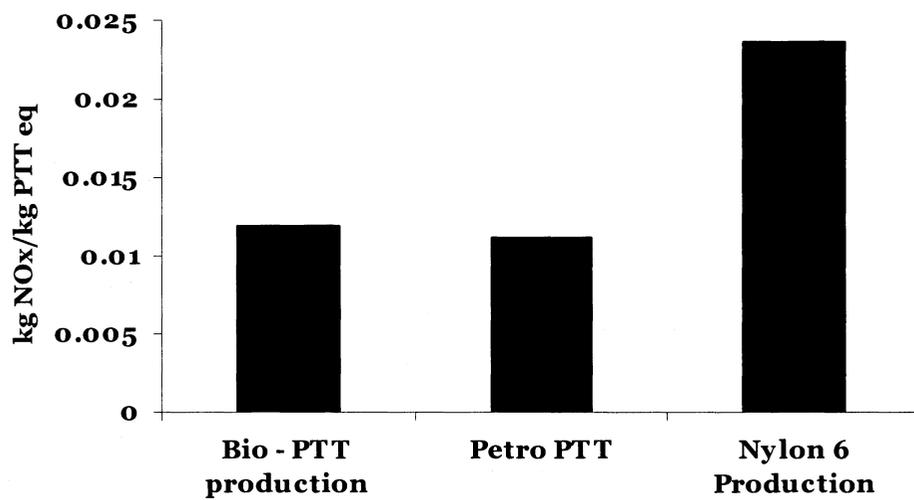


Figure 22: NOx emissions for biobased PTT, petrochemical based PTT and Nylon 6

CHAPTER 7

SENSITIVITY ANALYSIS

7.1 Sensitivity Analysis

In order to begin to understand the uncertainty in the life cycle analysis of the biobased production of PDO, sensitivity studies were performed on the system model. The scenarios examined include:

1. Removal of the diafiltration system
2. Using coal as the fuel in the corn wet mill

In order to be consistent with the previous results for comparison purposes, the mass allocation method is used for all the sensitivity studies.

The first sensitivity study is the use or absence of the diafiltration and centrifugal filtration units that are used to extract the PDO attached to the centrifuged biomass. The original process design is used except that the diafiltration system is removed so that after cycloning, the biomass is discarded and the aqueous liquid proceeds directly to the dewatering column. If a diafiltration system is not used the overall energy use in the production of PDO from glucose is reduced from 26 MJ/kg PDO to 25 MJ/kg PDO. The yield of PDO also decreases slightly from 3.1×10^6 kg/yr to 3.0×10^6 kg/yr. The final purity of the product is also reduced from 99.9 to 99.8 %. According the Shell website, petrochemical PDO can have a minimum purity of 99.7% dry weight (Shell 2004). Dupont has stated that their bioproduction of PDO must produce a PDO product with a dry weight purity of 99.9%.

The level of purity that is required depends, of course, on the intended use of the PDO and the type of impurities present, and may therefore be different for the biobased and petrochemical-based production pathways. There are likely to be trade-offs associated with removing the diafiltration section the evaluation of which requires specific information regarding product use that is not available at this time. For example, it is possible that due to the type of impurities present, the 99.9wt% purity for the bioproduction of PDO would be comparable to the range of purities of 99.9wt% to 99.7wt% for the petrochemical production of PDO. Lacking more detailed information, it is assumed that 99.8 wt% purity is sufficient for all intended applications.

As stated earlier, 74% of corn wet mills use coal as the energy source and others use natural gas. The relative amount of corn processed by these two groups of mills is unknown. In the life cycle assessment results presented thus far, natural gas has been taken as the primary energy source. Since there is a large number of corn wet mills that use coal, the LCI results were also computed using coal as the primary wet mill energy source. Allocation is still done using the mass allocation method. Figure 23 shows that using coal as the primary energy source in the wet mill, the global climate change potential is 4.09 kg CO₂ eq/kg PDO where as using natural gas as the fuel source it was 3.83 kg CO₂ eq/kg PDO (Figure 21).

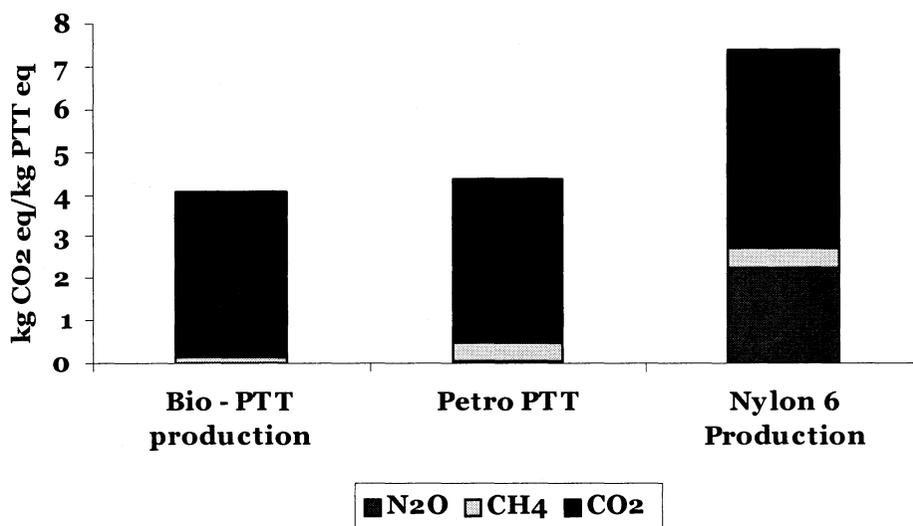


Figure 23: Climate change potential with coal as the energy source for the corn wet mill

Figure 23 shows the climate change potential of the biobased production of PDO (coal), petrochemical production of PDO, and Nylon 6. The petrochemical LCA and Nylon 6 LCA have not changed, but there is a slight increase in the environmental impact of using coal as the fuel source in the corn wet mill for the biobased production of PDO. The same trend is shown in the NO_x emission data (Figure 24). In comparing the NO_x emissions using natural gas (0.012 kg NO_x/kg PDO) and using coal (0.013 kg NO_x/kg PDO), there is also a slight increase in the amount of NO_x emissions for the biobased production of PDO (coal). These results are not surprising since corn wet milling is not the largest use of energy in the biobased PDO life cycle. In summary, the use of coal versus natural gas in the corn wet mill does not have a large impact on the full life cycle inventory results and does not alter conclusions regarding the relative environmental attractiveness of the polymers under consideration.

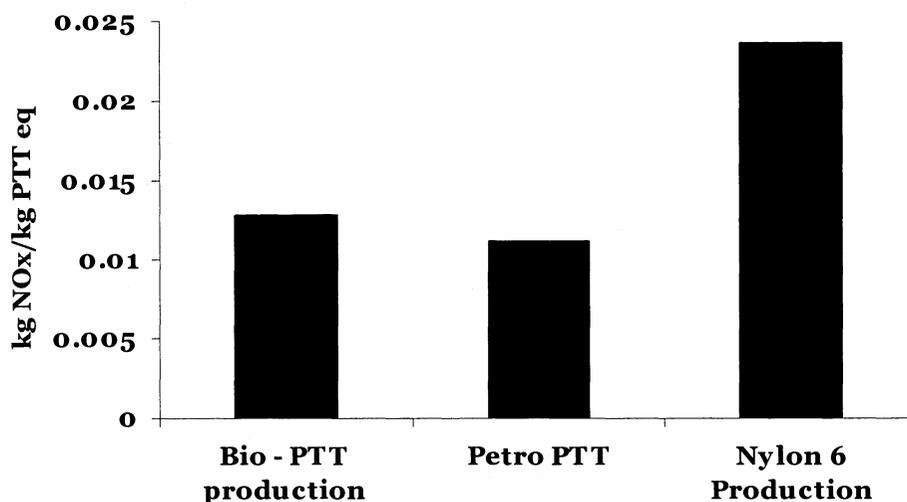


Figure 24: NOx emissions with coal as the energy source in the corn wet mill

The second type of sensitivity analysis performed involved examining the sensitivity of life cycle inventory results to variation in values of various life cycle model parameters. The parameters examined are listed in Table 11. The perturbation chosen to evaluate the change in the system was a 10% difference in the parameter. The new value was incorporated into the LCA and new values for the energy use, greenhouse gas emissions (GHG) and NOx emissions were obtained for the new parameter. The following type of equation (EQN 7), shown here for the change in energy use, was applied to examine the change in greenhouse gas emissions (GHG) and NOx emissions resulting from variation in the selected parameters.

$$\frac{Energy_{New} - Energy_{Base}}{Energy_{New}}$$

EQN: 7

If the terms: $\frac{\Delta Energy}{Energy_{New}}$, $\frac{\Delta NOx}{NOx_{New}}$, and $\frac{\Delta GHG}{GHG_{New}}$, are greater than the 10% perturbation applied to a parameter, then the LCA is deemed sensitive to a change in that parameter. The values of EQN 7 for each parameter are shown in Table 12.

The titer in the fermentation was found to be the most influential model parameter. A 10% change in the titer yields a 35% change in the life cycle energy use, a 44% change in the NOx emissions and a 43% change in the GHG emissions. The changes in energy use, NOx and GHG are greater than 10%, and therefore, the LCA of the production of PDO from corn is sensitive to the concentration of PDO leaving the fermentor. If the titer increases, the energy use, GHG and NOx emissions decrease.

A second influential parameter is the microbial growth constant, K_s . A 10% decrease in the growth constant decreases the yield by 14% and decreases the concentration of PDO leaving the fermentor from 135 g/L to 114 g/L. As shown in Table 12, the 10% change has a greater than 10% effect on the energy use, GHG and NOx emissions.

The amount of inoculum used in the fermentation was also evaluated. As shown in Table 12, the NOx and GHG emissions are the parameters that have a greater than 10% change. Energy use only has an 8.7% change when the perturbation parameter was applied to the amount of inoculum used in fermentation. If the amount of inoculum in the fermentor is reduced by 10%, the titer leaving the fermentation is reduced from 135 g/l to 123 g/l, in turn reducing the overall production capacity to 2.8 million kg PDO/yr.

Another significant parameter is the rejection coefficient in the diafiltration unit. The rejection coefficient is related to how much PDO is separated from the biomass and proceeds to separation and how much proceeds to a wastewater treatment facility. If not as much PDO

is separated from the biomass, then the energy is reduced because there is less power consumed by the diafiltration unit and not as much final product proceeds on the purification. The change in the rejection coefficient did not have as a -great an impact on the LCA as did the previously discussed parameters.

A temperature analysis of each of the distillation columns and dewatering column was also examined. The same type of analysis was performed on the temperatures of each of the columns as shown by Table 12, changing the temperatures by 10% does not have a large impact on life cycle environmental performance relative to the other parameters examined.

Table 11: Sensitivity parameters for the life cycle of PDO

Parameter	Base Value	New Value
Titer	135	148
Growth Constant	0.5	0.45
Innoculum	20800	18720
Rejection Coefficient	0.99	0.89
Corn Wet Mill Energy	75	67.5
Corn Yield	134	120.6
Dewatering Cond. Temp	75	67.5
Dewatering Reb. Temp	90	81
Dist 4 Cond. Temp	178	160.2
Dist 4 Reb. Temp	140	126
Dist 1 Cond. Temp	178	160.2
Dist 1 Reb. Temp	178	160.2
Dist 2 Cond. temp	200	180
Dist 2 Reb. Temp	20800	18720
Dist 3 Cond. Temp	90	81
Dist 3 Reb. Temp	100	90

Table 12: Sensitivity parameters

Parameter	$\frac{\Delta Energy}{Energy_{New}}$	$\frac{\Delta NOx}{NOx_{New}}$	$\frac{\Delta GHG}{GHG_{New}}$
Titer	35%	44%	43%
Growth Constant	11%	13%	12%
Innoculum	8.7%	11%	10%
Rejection Coefficient	6.3%	7.4%	7.3%
Corn Wet Mill Energy	1.4%	0.6%	1.4%
Corn Yield	0.73%	0.24%	0.32%
Dewatering Cond. Temp	0.51%	0.6%	0.6%
Dewatering Reb. Temp	0.51%	0.6%	0.6%
Dist 4 Cond. Temp	0.27%	0.31%	0.31%
Dist 4 Reb. Temp	0.27%	0.31%	0.31%
Dist 1 Cond. Temp	0.27%	0.31%	0.31%
Dist 1 Reb. Temp	0.27%	0.31%	0.31%
Dist 2 Cond. temp	0.27%	0.31%	0.31%
Dist 2 Reb. Temp	0.27%	0.31%	0.31%
Dist 3 Cond. Temp	0%	0%	0%
Dist 3 Reb. Temp	0%	0%	0%

CHAPTER 8

RESOURCE USE SUMMARY

8.1. Resource Summary

The use of agricultural productive land is always a concern in biobased production systems, since this land could alternatively be used to produce food. Since LCI keeps track of all input materials, the amount of corn acres that are required for 1 kg of PDO and PTT can be easily computed. Also, the biobased content of PTT can also be established. Only 36% of PTT is PDO and 64 % is terephthalic acid. The resource use summary is shown in Table 13.

Table 13: Resource use in the production of PDO and PTT

Functional Unit	Amount of Corn	Acre Requirements
1 kg of PDO	1.82 kg	5.5×10^{-4}
1 kg of PTT	0.65 kg	2.0×10^{-4}

There are approximately 70 million acres of corn harvested each year in the U.S. (2003 Corn Annual). If all of the Nylon 6 produced in the U.S. (approximately 907 million kg/yr) were replaced by the biobased production of PTT, only 213,000 acres of corn would be required. This is 0.31% of the total acres of corn harvested in the U.S. during 2002 and a small fraction of the average annual increase in U.S. corn production.

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions and Recommendations

The life cycle analysis of the biobased production of PDO from corn shows that the majority of energy used is in the production of PDO from glucose. When comparing the biobased process with the petrochemical process even with a fair amount of uncertainty, the biobased process seems to require less energy. The biobased production also has a lesser impact on Climate Change, while producing approximately the same NO_x emissions as the petrochemical production pathway. Once the life cycle inventory (LCI) is extended to one kg of PTT and compared to the LCI of Nylon production, the same relative comparisons are made. The biobased production may be environmentally preferable to Nylon and the petrochemical route to PTT, however there is a considerable amount of uncertainty associated with the modeled process for the biobased production of PDO from glucose.

This study examined only a limited number of life cycle inventory categories and there are many other categories that are often included in life cycle assessments. These categories include: human toxicity, eutrophication, ozone depletion, photochemical oxidant creation, acidification, and ecotoxicity. In order to evaluate each of these environmental classifications, each of the systems within the PDO life cycle would require a complete life cycle inventory, including air, water and solid emissions. The data used in this study came from several different sources that only included inventory data on CO₂, CH₄, N₂O and NO_x. Therefore, to remain consistent, only those four emissions were tracked in the LCI of PDO production.

In a recent article by Lynd and Wang (Lynd et al 2003), a framework was developed to estimate fossil fuel displacement of a biological process from biomass in the absence of product specific information. The framework proposed provides a screening process to gain a general insight on a feedstock and process features important in determining the fossil fuel displacement (Lynd et al 2003). Future research could apply the framework developed by Lynd to the bioproduction of PDO and the results compared with other biobased products. The biobased production of PDO would make an interesting test of this framework as it was intentionally designed to use an aerobic process, which is counter intuitive from an energy use perspective.

It seems to be a common perception that if a process is biobased then it must be environmentally superior to a petrochemical process that produces a similar product. It has been shown in this study and many other studies cited here, that biobased does not necessarily mean better. Since biobased processes incorporate an extra element that petrochemical products do not: farming. Farming involves directly in the production process a natural ecological system comprising the soil, water, and biota of the farm environment. Despite many years of study, these systems are not fully understood and impacts are very location specific. This study has not been able to account for many of the impacts of farming such as changes in soil fertility and water quality.

This study has shown that some life cycle characteristics impact the overall system performance more than other parameters and the use of sensitivity analysis allows for the evaluation of these parameters and their importance to the study. In this study, it is shown by the sensitivity analysis that for the limited set of impacts examined, farm practices do not

impact the life cycle inventory as much as the performance of the process of producing PDO from glucose.

These are important benchmarks for biopolymer production and the broader use of renewable feedstock for the production of chemicals. LCA of this biopolymer will inform the on-going debate over the desirability of producing chemicals from biomass feedstock. More importantly, the development of models of the production processes integrated into a life-cycle model will allow for process improvements that may improve the efficiency and reduce the impacts of these production pathways.

APPENDIX

Energy Requirements for the production of PDO from Glucose

Yield (kg PDO/yr)	3E+06	
Process Equipment		MJ/kg PDO
Fermentor		6.271163316
Gas Compression		0.302805364
Heat Sterilization		0.000195047
Storage		0.080309908
Centrifuge		0.082470696
Diafiltration		2.557890009
Centrifuge		0.061853316
Dewatering Column		5.787166375
Distillation 1		2.172430446
Distillation 2		2.151347323
Distillation 3		0.288943858
Distillation 4		2.458307857

Stream table for PDO production

Fermentation Section											
Stream (kg/yr)	S-133	S-101	S-102	S-103	S-104	S-105	S-106				
Glucose			4.9E+06		2.1E+05	2.1E+05	2.1E+05				
Glycerol			8.3E+05		2.9E+05	2.9E+05	2.9E+05				
Ammonia			3.8E+04	1.9E+03	6.0E+02	6.0E+02	6.0E+02				
Oxygen	7.7E+06	7.7E+06		7.5E+06							
Nitrogen	2.9E+07	2.9E+07		2.9E+07							
E-coli			2.1E+04		2.3E+05	2.3E+05	2.3E+05				
Water			1.9E+07		2.0E+07	2.0E+07	2.0E+07				
1,3 Propanediol					1.9E+07	1.9E+07	1.9E+07				
Carbon Dioxide				1.9E+06							
Temperature (C)	25	37.66	25	37	37	35	37				
Pressure (bar)	1.013	1.213	1.013	1.013	1.213	1.213	1.013				

Stream table for PDO production

Purification Section	S-113	S-115	S-116	S-109	S-118	S-119	S-121	S-120	S-124	S-122
Stream (kg/yr)	S-113	S-115	S-116	S-109	S-118	S-119	S-121	S-120	S-124	S-122
Glucose	1.7E+05	4.1E+04	4.2E+03	3.7E+04	3.7E+04	3.7E+00	3.3E+00	3.8E-01	3.7E-01	
Glycerol	2.7E+05	5.6E+03	3.9E+03	1.7E+03	1.6E+03	8.4E+01	4.2E+00	8.0E+01	8.0E+00	7.2E+01
Ammonia	5.9E+02									
Oxygen										
Nitrogen										
E-coli	3.1E+03									
Water	1.8E+07	6.6E+05	5.6E+05	9.9E+04	6.9E+04	3.0E+04	2.1E+04	8.9E+03	8.7E+03	1.8E+02
1,3 Propanediol	3.1E+02	3.1E+06	3.1E+03	3.1E+06	3.1E+04	3.1E+06	3.1E+02	3.1E+06	3.1E+03	3.1E+06
Carbon Dioxide										
Temperature (C)	75	178	90	140	178	75	90	100	200	178
Pressure (bar)	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013

Design Specifications

Air Compressor

Pressure Change 0.2 bar

Power: 275 kW

Overall efficiency is 70%

Fermentation

Volume: 142,000L

Temp: 37 C

Pressure 1.5 bar

Residence time: 38 hr

Height: 11.7 m

Diameter: 3.9 m

Heat sterilization

Sterilization temp: 140 C

Holding tube diameter: 77.6 cm

Holding tube length: 1.3 m

Max throughput: 100 m³/h

Rated throughput: 27.41 m³/h

Centrifuge 1

Velocity of Inlet liquid: 5m/s

Particles in Underflow: 0.2 v/v

Max allowable pressure drop: 3 bar

Body diameter: 0.617 m

Overall length: 3.083 m

Inlet diameter: 0.123m

Underflow diameter: 0.092 m

Diafiltration

Max. Solids Conc. 600 g/l

Denaturation 5%

Filtrate Flux: 20 L/m² h

Membrane Area: 64 m²

Centrifuge 2

Velocity of Inlet liquid: 5m/s

Particles in Underflow: 0.2 v/v

Max allowable pressure drop: 3 bar

Body diameter: 0.617 m

Overall length: 3.083 m

Inlet diameter: 0.123m

Underflow diameter: 0.092 m

Dewatering Column

Pressure: 0.4 bar
Condenser Temp: 75 C
Reboiler temp: 175 C
Max diameter: 2 m
Stage height: 0.4m
Column height: 10 m
Column diameter: 1.851 m

Distillation Column 1

Column Pressure: 0.4 bar
Condenser Temp: 90 C
Reboiler Temp: 140 C
Max diameter: 2 m
Stage height: 0.4m
Column height: 6 m
Column diameter: 0.545 m

Distillation Column 2

Column Pressure: 0.4 bar
Condenser Temp: 75 C
Reboiler Temp: 178 C
Max diameter: 2 m
Stage height: 0.4m
Column height: 11.6 m
Column diameter: 1.064 m

Distillation Column 3

Column Pressure: 0.4 bar
Condenser Temp: 90 C
Reboiler Temp: 100 C
Max diameter: 2 m
Stage height: 0.4m
Column height: 8.4 m
Column diameter: 0.411 m

Distillation Column 4

Column Pressure: 0.4 bar
Condenser Temp: 178 C
Reboiler Temp: 200 C
Max diameter: 2 m
Stage height: 0.4m
Column height: 9.6 m
Column diameter: 0.581 m

REFERENCES

1. Atkinson, B. and Mavituna, F. **Biochemical engineering and biotechnology handbook**. Stockton Press, New York, New York, 1983.
2. Bailey, J. and Ollis, D. **Biochemical engineering fundamentals. 2nd Edition**. McGraw – Hill, New York, New York. 1986.
3. Boswell, Clay. **Bioplastics aren't the stretch they once seemed**. *Chemical Marketing Reporter*. (2001). Vol. 260 (8).
4. Boustead, I. **Eco-profile: Polyethylene Terephthalate**. September 2002. www.apme.org
5. Boustead, I. **Eco-Profile: Nylon 6**. 1995. www.apme.org (retrieved July 2004)
6. Bozell, J.J. and Landucco, R. **Alternative feedstocks program technical and economic assessment**. U.S. Department of Energy.
7. Broek, R. et al. **Green energy or organic food? A life cycle assessment comparing two uses of set – aside land**. *Journal of industrial Ecology*. (2002). Vol. 5 (3), 65 – 87.
8. CHEMCAD Suite Simulator Software 5.4 x. Chemstations (2003). www.chemstations.com
9. Chotani, et al. **The commercial production of chemicals using pathway engineering**. *Biochimica et Biophysica Acta*. (2000). Vol. 1543, 434 – 455.
10. Cook, Jeffrey. **2001 Corn Annual**.
11. Deckwer, Wolf – Dieter. **Microbial conversion of glycerol to 1, 3 Propanediol**. *Microbiology Reviews*. (1995). Vol. 16, 143 – 149.
12. Dove, A. **Experts disagree over color of biomass**. *Nature Technology*. (2000). Vol. 18.
13. Doran, P. **Bioprocess engineering principles**. Academic Press, 1995.
14. Dupont. <http://www.dupont.com/sorona/home3.html>
15. Eissen, M. et al. **Concepts on the contribution of chemistry to a sustainable development**. *Chem. Int. Ed.* (2002). Vol. 41, 414-436.
16. EPA. **Life – cycle assessment: inventory guidelines and principles**. (1993).
17. Fogler, Scott. **Elements of chemical reaction engineering. 3rd Edition**. Prentice Hall, Upper Saddle River, New Jersey, 1999.
18. Freeman, S.L. **Use of stream lined life-cycle assessment for technology R&D investment analysis**. *Air and Waste Management Association*. 1996. 1- 20.
19. Galitsky, Worrell, Ruth. **Energy efficiency improvements and cost saving opportunities for the corn wet milling Industry**. Lawrence Berkley National Laboratory July 2003.
20. Garrett and Grisham. **Biochemistry. 2nd Edition**. Saunders College Publishing, New York, New York 1999.

21. Georgia Tech. <http://swiki.che.gatech.edu/che4505>. (Retrieved July 2004)
22. Gerngross, T. **Can biotechnology move us toward a sustainable society?** *Nature America, Inc.* (1999). Vol. 17, 541-544.
23. Graboski, M. **Fossil energy use in the manufacture of corn ethanol.** August 2002. <http://www.ncga.com/> (Retrieved 2004).
24. Gross, R.A. and Kalra, B. **Biodegradable polymers for the environment.** *Science.* (2002). Vol.297, 803-806.
25. International Organization for Standardization. 1998 <http://www.iso.org/iso/en/ISOOnline.opennerpage> (Retrieved June 2004)
26. Intergovernmental Panel on Climate Change. <http://www.ipcc.ch/>. (Retrieved June 2004).
27. Lynd and Wang. **A Product Non-Specific Framework for Evaluating the Potential of Biomass-Based Products to Displace Fossil Fuels.** *Journal of Industrial Ecology.* (2003). Vol. 7, 17-32
28. McMurry, J. **Organic Chemistry. 4th Edition.** Brooks/Cole, Pacific Grove, California 1996.
29. Patel, M. et al. **Environmental assessment of bio-based polymers and natural fibers.** (2001).
30. Ouarels, Jim. Personal Communication, October 2003. Penford Products
31. Schugerl, K. and Bellgardt, K. **Bioreaction Engineering.** Springer, Frankfurt, Germany, 2000.
32. Shapouri and Duffield. **The energy balance of corn ethanol: An Update.** July 2002. www.usda.gov (Retrieved 2003).
33. Sheehan, et al. **Is ethanol from corn stover sustainable?** National renewable Energy Laboratory. (2002)
34. Shell. http://www.shellchemicals.com/1_3_propanediol/1,1098,301,00.html. (Retrieved April 2003).
35. SimaPro Life Cycle Assessment Software 5.1. (2002) Pre Consultants. www.earthshift.com
36. SRI Consulting. <http://www.sriconsulting.com/>. Process Economics Program. PEP report 227, "1, 3 Propanediol and Polytrimethylene terephthalate" (1999). (Retrieved April 2003)
37. SuperPro Designer Simulator Software v4.7. (1991) Intelligen, Inc. www.intelligen.com
38. U.S. Department of Energy. **Biobased Products and Bioenergy Roadmap 2001.** www.doe.gov. (Retrieved 2003).
39. U.S. Department of Energy. **Biobased Products and Bioenergy Vision 2001.** www.doe.gov. (Retrieved 2003).

40. U.S. Department of Energy. **Plant/Crop – based renewable resources 2020: A vision to enhance U.S. economic security through renewable plant/crop – based resource use. 2001.** www.doe.gov. (Retrieved 2003).
41. Vink et al. “**Applications of life cycle assessment to natureworks polylactide (PLA) production.**” *Polymer Degradation and Stability*. (2003). Vol. 80, 403-419.
42. Wang, Saricks, and Wu. **Effects of fuel ethanol use on fuel-Cycle energy and greenhouse gas emissions.** Center for Transportation Research Argonne National Laboratory. January 1999.
43. Wang, Saricks, and Wu. **Fuel-cycle fossil energy use and greenhouse gas emissions of fuel ethanol produced for U.S. midwest corn.** Center for Transportation Research Argonne National Laboratory. 1997.
44. Weidema, Bo. **Avoiding co-product allocation in life – cycle assessment.** *Journal of Industrial Ecology*. (2001). Vol 4 (3), 11-26.
45. Zeng, A.-P. **Pathway and kinetic analysis of 1, 3 Propanediol production from glycerol fermentation by clostridium butyricum.** *Bioprocess engineering*. (1996). Vol. 14, 169 – 175.
46. Zeng, An – Ping and Biebl, Hanno. **Bulk chemicals from biotechnology: the case of 1, 3 Propanediol production and the new trends.** *Advances in Biochemical Engineering/Biotechnology*. (2000). Vol. 74, 241 – 259.
47. Zeng, A-P., Biebl, H., Deckwer, W. **Microbial conversion of glycerol to 1, 3 Propanediol: recent progress.** *American Chemical Society*. (1997). 265 – 279.
48. Ziney, M.G., et al. **Characterization of growth and metabolite production of Lactobacillus reuteri during glucose/glycerol co-fermentation in batch and continuous cultures.** *Biotechnology Letters*. (1998). Vol.20 (10), 913-916.