ABSTRACT

A COMPARISON OF ANHYDROUS ETHANOL PRODUCTION FROM ETHYLENE AND FROM CORN UTILIZING LIFE CYCLE ANALYSIS METHODOLOGY

by
Gregory Morse

There is currently much concern with the impact on the environment due to industrial processes. One method to assess this impact is to perform a Life Cycle Analysis (LCA) on the process. Life Cycle Analysis is made up of three stages; Life Cycle Inventory Analysis, Life Cycle Impact Assessment, and Life Cycle Improvement Assessment. In this study, Life Cycle Inventory Analysis methodology was applied to two industrial processes for producing anhydrous ethanol. The first process is the fermentation of corn, and the second is the hydration of ethylene using water and a catalyst. Each process was first modeled using the BioPro Designer, a process simulator, to generate the material and energy balances associated with each process. The result of the Life Cycle Inventory Analysis on each process was an eco-vector which contained all material inputs, energy inputs, and emissions associated with each step of each of the processes.

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by
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CHAPTER 1

INTRODUCTION

Concern about energy usage and natural resource depletion has led to efforts to develop methods to evaluate a product's impact on the environment. As a result, Resource Environmental Profile Analysis (REPA) was developed in the 1970's by the Midwest Research Institute (Hunt et. al., 1992). This methodology evolved to become what is known today as Life Cycle Analysis (LCA). This methodology attempts to quantify natural resource consumption, energy usage, and emissions at every stage of a product's life from raw materials acquisition to eventual disposal. The result is a product's environmental "charge" indicating its impact on the environment. This information is useful for companies trying to reduce the impact on the environment from manufacturing processes as well as for consumers who would like to buy environmentally friendly, or "green", products. Although there is no universal agreement at this time on how to rate a product based upon its resource consumption and generation of emissions, the methodology to calculate the quantity of resource consumption and emissions is well established and widely accepted. This virtual universal acceptance is due primarily to the work performed by the various International Organisation for Standardisation (ISO) LCA subcommittees (Marsmann, 1994).

The objective of this study is to use this established life cycle inventory analysis methodology to compare two ethanol production processes. One process uses ethylene as a feedstock, whereas the second one uses corn as a feedstock. These processes will be modeled using BioPro Designer, a computer simulation program developed by Dr. Demetri Petrides of the New Jersey Institute of Technology. The results of the simulation will then be analyzed using the life cycle analysis methodology to generate a Life Cycle Inventory Report. These data will provide the information required to compare the natural resource and energy consumption of the two processes, as well as emissions generation. This information can then be used in future studies to determine the relative environmental impact of each process on a per kilogram of anhydrous ethanol basis.

CHAPTER 2

BACKGROUND INFORMATION

As mentioned in the previous chapter, there has been an increasing interest in resource and energy consumption, as well as emissions, from manufacturing activities. Recently, methodologies have been developed to calculate these quantities and assign relative environmental impacts to these quantities. The following two sections describe the historical development of Life Cycle Analysis (LCA), or Resource Environmental Profile Analysis (REPA) as it was formerly known, and the development of the methodology to perform the necessary calculations The third section describes BioPro Designer, a process simulation program. The fourth and fifth section of this chapter will describe the fundamentals of ethanol production from ethylene and from corn, respectively.

2.1 Historical Development of LCA

Life cycle analyses strive to quantify the degradation of human, plant, and animal health as well as the depletion of finite natural resources (Hunt et. al., 1992). These effects are often difficult to quantify because many of them are indirectly related to the manufacturing, use, and ultimate disposal of a product.

The first attempt to perform a Life Cycle Analysis was by Harry Teasley of The Coca-Cola Company in 1969 (Hunt et. al., 1992). A study was conducted by Midwest Research Institute (MRI) to analyze different beverage containers to determine which type consumed the fewest natural resources and generated the least amount of emissions. At that time, such a study was known as a Resource and Environmental Profile Analysis (REPA). This type of study focused on cataloging the consumption of resources, such as materials and energy, and emissions of a product throughout its life. The study did not attempt to assess the impact on the environment as a result of these quantities.

As interest grew in this area because of concerns about energy usage and generation of solid waste, the Life Cycle Analysis method became more refined and complete. The process became divided into three distinct stages: Life Cycle Inventory, Life Cycle Impact Analysis, and Life Cycle Improvement Analysis. The definitions of these terms as they appear in Kolluru (1994) are the following:

> 1. **Life cycle inventory:** "A data based process of quantifying energy and raw material requirements, air emissions, waterborne effluents, solid waste, and other environmental releases incurred throughout the life cycle of a product, process, or activity."
>
> 2. **Life cycle impact analysis:** "A technical, quantitative and/or qualitative process to characterize and assess the effects of the environmental loadings identified in the inventory component. The assessment should address both ecological and human health considerations, as well as other effects such as habitat modification and noise pollution."
>
> 3. **Life cycle improvement analysis:** "A systematic evaluation of the needs and opportunities to reduce the environmental burden associated with energy and raw materials use and waste emissions throughout the whole life cycle of a product process or activity. This analysis may include both qualitative and quantitative measures of improvements, such as changes in product design, raw materials use, industrial processing, consumer use, and waste management."

Each of these three distinct stages builds upon the information generated by the previous stage. Currently, the methodology of the first stage is well developed and is widely accepted. The second and third stages are not as well developed and there is much debate concerning the quantification of the effect a particular pollutant has on the environment. The International Standardisation Organisation (ISO) currently has Life Cycle Analysis (LCA) subcommittees developing a standard method for these types of assessments. The charge of the subcommittees has been defined in Marsmann (1993) as the following:

> "[The purpose of the subcommittee is to create] standardisation in the field of life cycle assessment as a tool for environmental management of product and service systems. It encompasses the assessment of impacts on the environment from the extraction of raw materials to the final disposal of waste."

This subcommittee is made up of five working groups, each focused on a particular segment of the process. An excellent description of these activities can be found in Marsmann (1993).

The scope of this study is limited, and therefore the focus will be on the life cycle inventory stage of the process. The life cycle inventory stage itself is made up of six different stages. These stages are defined in Kolluru (1994) as the following:

> 1. **Raw materials acquisition:** "The boundary for the raw material stage of the inventory begins with all the activities needed for the acquisition of raw materials and energy and ends at the first manufacturing or processing stage that refines the raw material."
>
> 2. **Manufacturing, processing, and formulation:** "The processing step for the inventory component analyzes the conversion of feed stocks or raw materials to final products."
>
> 3. **Distribution and transportation:** "Transportation is the movement of materials or energy between operations at different locations and can occur at any stage in the life cycle. Distribution is the transfer of the manufactured product from its final manufacturer to its end user. A common attribute of both distribution and transportation is that, although they involve a change in the location or physical configuration of a product, they do not involve a transformation of materials."
>
> 4. **Use, reuse, and maintenance:** "The boundary for this stage of the life cycle inventory begins after the distribution of products or materials and ends at the point at which those products or materials are discarded and enter a waste management system."
>
> 5. **Recycle:** "The recycling stage encompasses all activities necessary to take material out of the waste management system and deliver it back to the manufacturing/processing stage."
>
> 6. **Waste Management:** "Waste streams are generated at each phase of the life cycle. Waste is any material released to any environmental medium-air, water, or land. Waste management systems include any mechanisms for treating or handling waste prior to its release to the environment."

Using these definitions, it is possible to characterize each stage of a product's life. The most convenient method of analysis is to utilize a flow chart, where each stage is represented by a "black box." The actual mechanics of the process are important only in that it is necessary to catalog all inputs and outputs leading to and from this "black box." Because of the scope of this project, only the manufacturing, processing, and formulation stages will be considered in detail. For a complete description of the entire analytical process, see Kolluru (1994).

Once the product's life is mapped out in a flow chart, it is necessary to quantify the inputs and outputs at each stage. The inputs include natural resources, energy, and water. Outputs include product(s) and emissions such as air pollution, water pollution, and solid waste. Energy is generally expressed in units of MegaJoules (MJ). Water input only includes water that is permanently removed from its source; cooling water that is returned to the source is not considered to be an input to the process. However, if the water quality is changed in any way, for example, by an increase in temperature, the water output will be considered water pollution.

Environmental emissions, or outputs from the process stage, are generally reported in units of mass of pollutant per unit mass of product. Different types of emissions are defined in specific ways. Air emissions are those emissions that are released to the air despite any pollution control devices. Examples of air emissions are particulates, nitrogen oxides (NO_X), sulfur oxides (SO_X) , carbon monoxide (CO), carbon dioxide (CO_2), and volatile organic compounds (VOCs). Similarly, water pollution is defined as any materials that are discharged into a receiving body of water. These materials can include, but are not limited to, any of the following: suspended solids, dissolved solids, metals, oils and grease, sulfides, phosphates, chemical oxygen demand (COD), and/or biological oxygen demand (BOD). The definition of solid waste is not as clear as the definitions of air emissions and water pollution. Solid waste is only considered to be material that is landfilled or otherwise disposed of, but not recycled. Usable scrap or other materials recovered for reuse or recycling are also not considered solid waste. Solid waste, although most commonly measured in mass, may be measured in volume in order to estimate the landfill space it will occupy. Examples of solid waste include waste water treatment sludges, solids from air pollution control devices, and post consumer solid waste.

Once all the inputs and outputs are known for each process in each stage of a product's life, one can then begin to allocate natural resource depletion and environmental emissions to the product. This allocation will be described in the next section.

2.2 Methodology of Environmental Impact Allocation

The allocation procedure for simple processes is very straightforward. However, if there are multiple products generated during one process, or if there are recycle streams or streams between processes, calculations can become difficult and cumbersome. In some cases, the resulting calculations involve many equations that must be solved simultaneously. Because many industrial processes generate more than one product and may involve recycle streams, a methodology using "eco-vectors" has been documented (Castells, 1994). Use of these eco-vectors makes the allotment of natural resource depletion and environmental emissions much easier. These eco-vectors also simplify the solution of the simultaneous equations when they arise.

An eco-vector is defined as "a multidimensional vector in which every dimension corresponds to a particular pollutant or [environmental] burden" (Castells, 1994). Each mass flow associated with a process, whether it be an input, emission, or product, has an associated eco-vector. The elements within each eco-vector are in units of mass of pollutant or burden per unit mass of material in the flow. In the case of eco-vectors associated with energy flows into a process, the units of the elements in the eco-vector are mass of pollutant or environmental impact per MegaJoule (MJ) of energy. Many times, however, the environmental impact associated with an input or output is not known. If this is the case, then the eco-vector components are made up of the mass of material per kilogram of product or energy input per kilogram of product. An example of this type of eco-vector can be found in Figure 1. The subscript "w" indicates that the material is a waste product, or emission. Also, the subscript "S-104" indicates that this is the eco-vector associated with material stream S-104 in the process flow diagram.

$$\begin{bmatrix} Ethylene \\ Water \\ Heating \\ Power \\ Cooling \\ (Ethylene)w \end{bmatrix}_{S-104} = \begin{bmatrix} .55 \\ .41 \\ 41 \\ .70 \\ 9.0 \\ 0 \end{bmatrix}_{S-104}$$

Figure 1: Example of an Eco-vector

Thus, when the mass flow of the material is multiplied by the eco-vector, the result is the total amount of each pollutant or environmental burden associated with that stream. If the environmental burden associated with each input and output is not know, as in the example above, the result is the total amount of inputs and outputs associated with that stream. Examples of elements contained in the eco-vector include solid wastes, water pollution, and air emissions. In some cases, environmental impacts that cannot be measured by mass are included, such as radiation and noise.

Once these eco-vectors are defined for process inputs and outputs other than products, it is possible to perform an environmental impact balance on the process in order to allocate the environmental impact to the product or products. In order to perform the balance, however, it is necessary to define the elements of the eco-vector associated with emissions to be negative quantities. This will allow all environmental impacts associated with a process to be allocated to the product or products. The environmental impact balance is performed in the same manner in which one would perform a material balance on a system or process. The following example was adapted from Castells, 1994.

Consider a process with two raw material inputs, one waste stream, and one product stream (Figure 2). The mass flow rates of the streams, in units of kg/s, are R1, R2, W, and P respectively. Assume that the two raw material streams and the waste stream each have nitrogen oxides as an element in their respective eco-vectors. These quantities are indicated by $[NO_x]_{R1}$, $[NO_x]_{R2}$, and $[NO_x]_W$. An environmental impact balance can be performed for the nitrogen oxide as follows:

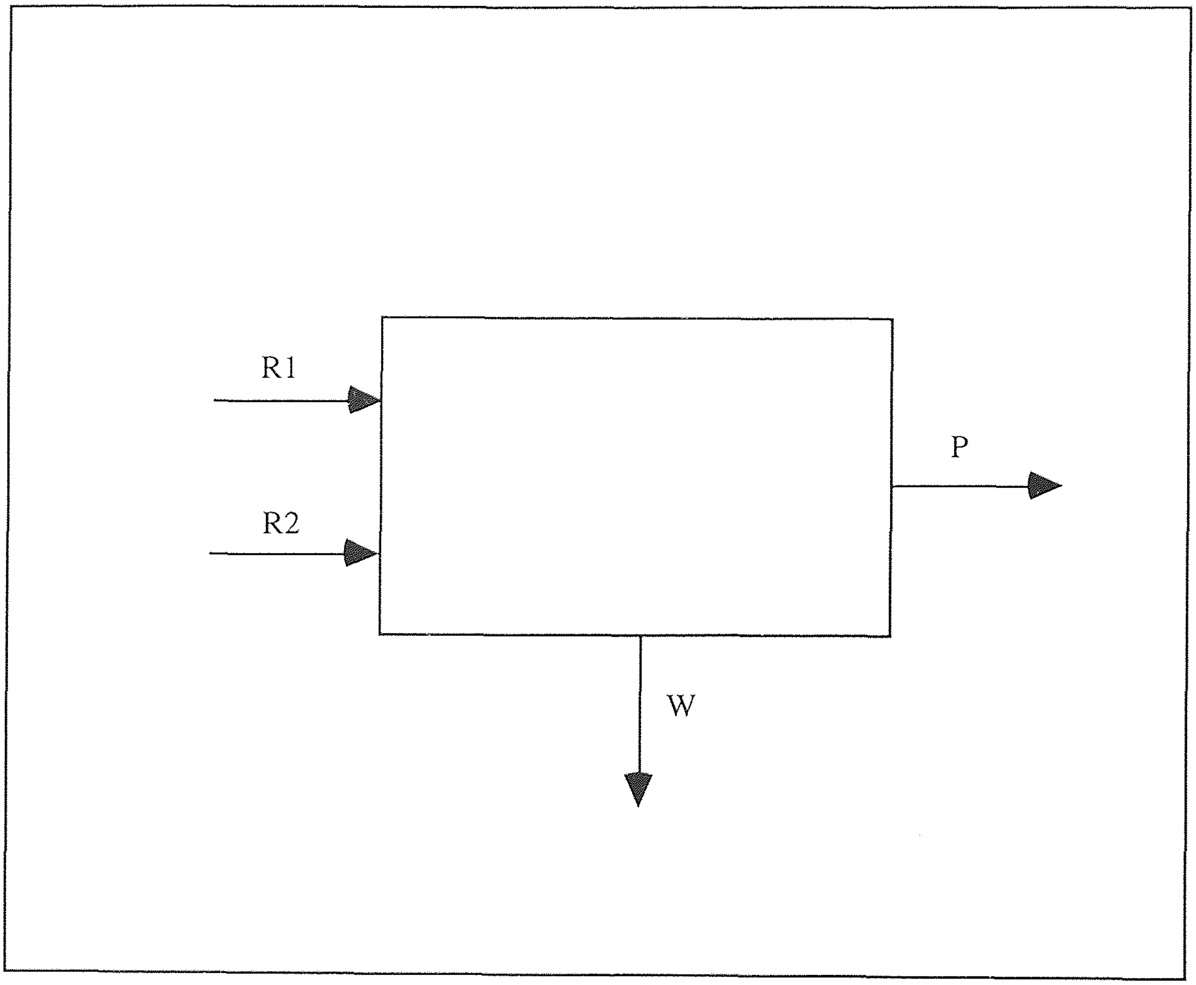

Figure 2 Sample Flow Diagram for Process 1

Inputs:

$$(R1) \bullet \begin{bmatrix} 0 \\ [NOx]_{R1} \\ 0 \end{bmatrix} + (R2) \bullet \begin{bmatrix} 0 \\ [NOx]_{R2} \\ 0 \end{bmatrix} \qquad (1)$$

Outputs:

$$(W) \bullet \begin{bmatrix} 0 \\ -[NOx]_{W} \\ 0 \end{bmatrix} + (P) \bullet \begin{bmatrix} 0 \\ [NOx]_{P} \\ 0 \end{bmatrix} \qquad (2)$$

In this specific case, only the non-zero components of the eco-vector are of interest. Therefore the environmental impact balance will be performed on NO_X. Because there is no accumulation of environmental impact within any of the streams, it can be assumed that the following statement is true:

$$\text{(environmental impact input) - (environmental impact output)} = 0 \qquad (3)$$

Substituting equations (1) and (2) into equation (3) and disregarding the zero components of the eco-vectors, yields the following equation:

$$(R1) \bullet \left[[NOx]_{R1}\right] + (R2) \bullet \left[[NOx]_{R2}\right] - (W) \bullet \left[-[NOx]_{W}\right]$$

$$- (P) \bullet \left[[NOx]_{P}\right] = 0 \qquad (4)$$

Because the flow rates R1, R2, W, and P, and the environmental impact components of the eco-vectors associated with R1, R2, and W are known, it is possible to solve for the environmental impact associated with P. The result is the following:

$$[[NOx]_P] = \left[\frac{(R1) \bullet [NOx]_{R1} + (R2) \bullet [NOx]_{R2} - (W) \bullet [-NOx]_W}{P} \right] \quad (5)$$

Equation (5) states that the environmental impact associated with NO_X in product stream P will be the sum of the NO_X components in the eco-vectors of the two input streams plus the amount generated by the process itself (found in waste stream W). This same procedure could have been performed for each non-zero component of the eco-vectors. This product stream and its associated eco-vector will then be one of the inputs into the next process in the product's life cycle.

The former example is highly simplified for the purpose of illustration. The next example, also adapted from Castells (1994), is the situation where two products are generated during a single process. The use of eco-vectors will allow the environmental impact to be fairly distributed between the products.

Consider a process with one raw material input, one energy input, one waste stream, and two product streams (Figure 3). The flow rates of the streams, in units of kg/s for the mass streams or kJ/s for the energy input, are R1, E, W, P1, and P2 respectively. Assume that the raw material stream, energy stream, and the waste stream each have nitrogen oxides as an element in their respective eco-vectors. These quantities are indicated by $[NO_X]_{R1}$, $[NO_X]_E$, and $[-NO_X]_W$, respectively. An environmental impact balance can be performed for the nitrogen oxides as follows:

Inputs:

$$(R1) \bullet \begin{bmatrix} 0 \\ [NOx]_{R1} \\ 0 \end{bmatrix} + (E) \bullet \begin{bmatrix} 0 \\ [NOx]_E \\ 0 \end{bmatrix} \quad (6)$$

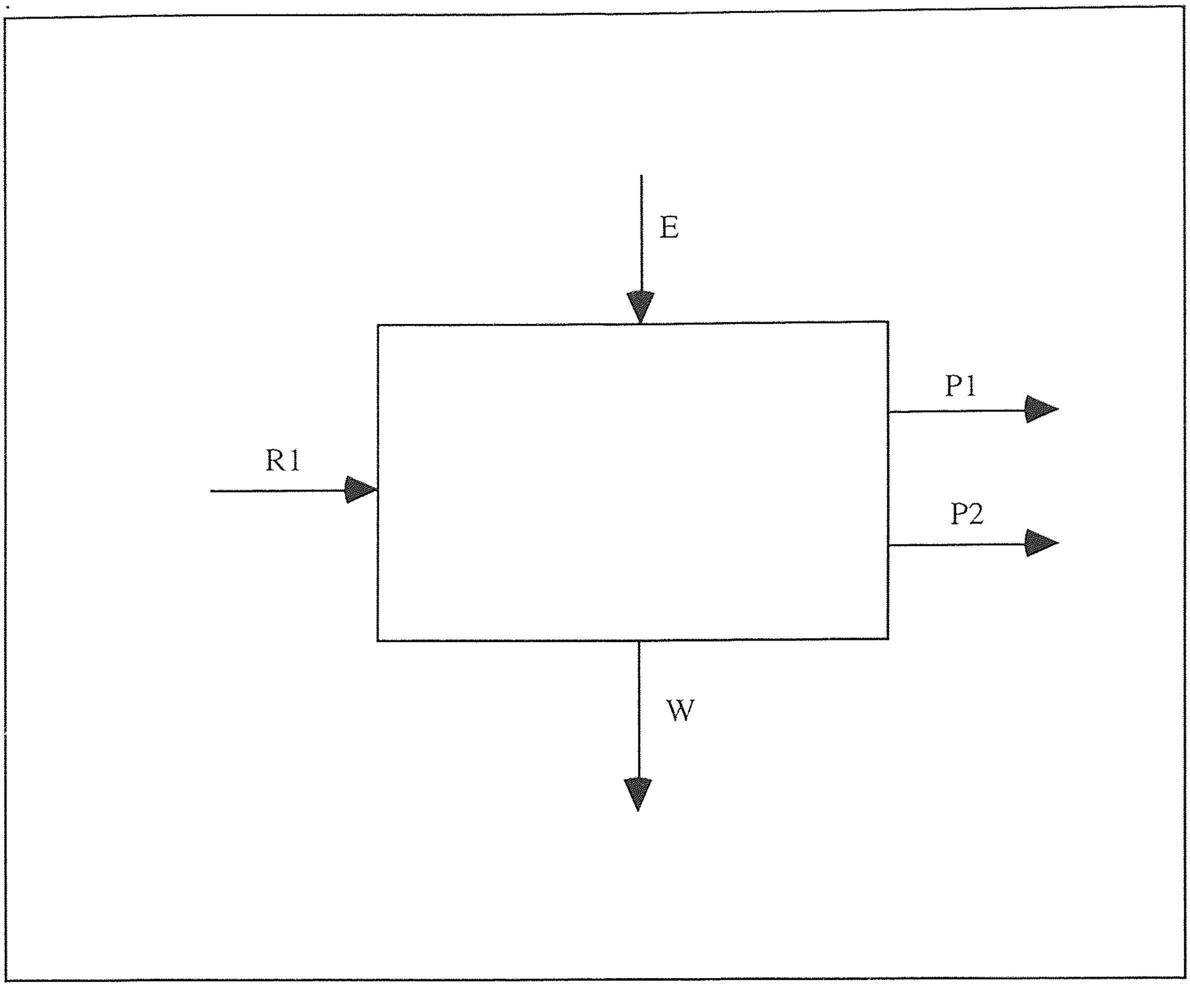

Figure 3 Sample Flow Diagram for Process 2

Outputs:

$$(W) \bullet \begin{bmatrix} 0 \\ -[NOx]_W \\ 0 \end{bmatrix} + (P1) \bullet \begin{bmatrix} 0 \\ [NOx]_{P1} \\ 0 \end{bmatrix} + (P2) \bullet \begin{bmatrix} 0 \\ [NOx]_{P2} \\ 0 \end{bmatrix} \qquad (7)$$

In this specific case, only the non-zero components of the eco-vectors are of interest. Therefore the environmental impact balance will be performed on NO_X. As in the previous example, there is no accumulation of environmental impact within any of the streams, and it can be assumed that the following statement is true:

$$\text{(environmental impact input)} - \text{(environmental impact output)} = 0 \tag{8}$$

Substituting equations (6) and (7) into equation (8) and disregarding the zero components of the eco-vector yields the following equation:

$$(\mathrm{R1}) \bullet \left[[NOx]_{R1}\right] + (\mathrm{E}) \bullet \left[[NOx]_{E}\right] - (\mathrm{W}) \bullet \left[-[NOx]_{W}\right] - (\mathrm{P1}) \bullet \left[[NOx]_{P1}\right]$$

$$- (\mathrm{P2}) \bullet \left[[NOx]_{P2}\right] = 0 \tag{9}$$

Because the flow rates R1, E, W, P1, and P2, and the environmental impact components of the eco-vectors associated with R1, E, and W are known, it is possible to solve for the environmental impact associated with P1 and P2. However, before that can be done it is necessary to calculate the distribution of the environmental impacts between streams P1 and P2. These distribution factors, defined as f1 for stream P1 and f2 for stream P2, can be calculated as follows (Castells, 1994) when based upon mass flow rates:

$$\mathrm{f1} = \frac{P1}{(P1 + P2)} \tag{10}$$

and

$$\mathrm{f2} = \frac{P2}{(P1 + P2)} \tag{11}$$

These distribution factors can also be based upon the relative market value of the product streams instead of mass flow. This would be desirable when one or more of the streams contains a product of high value, such as a pharmaceutical drug, and the other contains a low value solvent. In this example, however, the distribution factors will be based upon mass flow. Therefore, the environmental impact balance for stream P1 can now be written as follows:

$$(\mathrm{R1}) \bullet (\mathrm{f1}) \bullet [[NOx]_{R1}] + (\mathrm{E}) \bullet (\mathrm{f1}) \bullet [[NOx]_{E}] - (\mathrm{W}) \bullet (\mathrm{f1}) \bullet [-[NOx]_{W}]$$

$$- (\mathrm{P1}) \bullet (\mathrm{f1}) \bullet [[NOx]_{P1}] = 0 \tag{12}$$

Equation (12) can be solved for the environmental impact associated with stream P1:

$$[[NOx]_{P1}] = \left[\frac{(R1)\bullet(f1)\bullet[NOx]_{R1} + (E)\bullet(f1)\bullet[NOx]_{E} + (W)\bullet(f1)\bullet[-NOx]_{W}}{P1}\right] \tag{13}$$

A similar expression can be obtained for the environmental impact associated with stream P2:

$$[[NOx]_{P2}] = \left[\frac{(R1)\bullet(f2)\bullet[NOx]_{R1} + (E)\bullet(f2)\bullet[NOx]_{E} + (W)\bullet(f2)\bullet[-NOx]_{W}}{P2}\right] \tag{14}$$

Using this methodology allows the environmental impact of a process to be allocated to one or more products. The result is that it is possible to identify process steps in a product's life cycle that have a substantial impact on the environment. This information can then be used in pollution prevention and waste minimization efforts.

As is evident from the previous example, the calculations for environmental impact allotment rapidly become cumbersome as the process increases in complexity. The use of computer simulation programs to model complex processes has become increasingly popular in recent years. These programs can perform material and energy balances on a variety of different unit operations that are found in all types of industries. By using these types of programs, it is possible to easily allocate environmental impacts to a great number of products generated in a complex process. BioPro Designer is an example of such a program. This program was used in this project to model the ethanol production from both corn and ethylene

2.3 BioPro Designer

BioPro Designer is a computer simulation program developed by Dr. Demetri Petrides of the New Jersey Institute of Technology, Department of Chemical Engineering, Chemistry, and Environmental Science. Industrial processes can be modeled by constructing a flow sheet consisting of a series of unit operations. BioPro Designer performs material and energy balances, estimates the size of the specific pieces of equipment, and provides detailed economic evaluation information. Information such as cooling water requirements, steam requirements, electrical usage, and waste generation is readily available through reports generated by the program. This information is very important for performing life cycle inventories. This program will be utilized to model the ethanol production processes using corn and ethylene as feed stocks. Once the process is modeled and the reports are generated, a life cycle inventory will be performed on both processes.

2.4 Anhydrous Ethanol Production from Corn

The process of ethanol production from corn utilizes fermentation by microbes to convert sugars to alcohol and carbon dioxide. There are four basic steps to this process; preparation of a sugar solution from the feed stock, fermentation, distillation, and removal of water to produce anhydrous ethanol. These four steps, as well as any associated reactions, are outlined below. This material is based upon guidelines provided by the

Office of Alcohol Fuels, Department of Energy report "Preliminary Design Report for a Small-Scale Fuel Alcohol Plant," 1980.

The first step in the process is the preparation of the sugar solution from the feed stock. This feed stock commonly is made up of materials such as corn, wheat, sugar beets, or potatoes. For purposes of this study, only corn will be considered. This material must be properly processed prior to preparation of the sugar solution. This processing includes cleaning to remove dirt, screening to remove foreign objects, and milling to obtain a 20 mesh final product size (.040 inch). Once the feed material has been purified and milled to the correct size, it is then cooked to prepare it for the saccharification process. The feed material is made into a slurry and is cooked at 200°F. This slurry becomes rich with dextrins as the starches are hydrolyzed. This slurry now is put through the process of saccharification. The slurry is cooled to 140°F and is treated with alpha-amylase (α-amylase) and glucoamylase enzymes to convert the dextrins to sugars. The end result is a slurry that is rich in sugar and ready to be fermented.

The process of fermentation utilizes yeast to convert the sugars to ethanol, yeast biomass, and carbon dioxide by anaerobic respiration. This is carried out at a temperature of 85°F and a pH of 4.9. After a batch is fermented to the desired alcohol content, it is necessary to purify the alcohol from the rest of the broth. This is done by removing the solids and distilling the ethanol.

Once the solids have been removed from the alcohol mixture, the process of distillation can begin. A series of columns is used to produce commercial grade alcohol (95% alcohol). The residue that is removed before and during the distillation process can be used as feed for livestock. Once the desired alcohol purity is obtained, it can be further purified by the process of dehydration.

Dehydration is the process of removing the water from the alcohol solution to obtain anhydrous alcohol. This product is desirable because many industrial applications require the use of anhydrous alcohol. Techniques for dehydrating alcohol include membrane separations, adsorption techniques, distillation using a third component, and vacuum distillation processes. In this paper, distillation using benzene will be considered.

2.5 Anhydrous Ethanol Production from Ethylene

Ethanol production from ethylene accounted for more than 95% of all ethanol generated in the Unites States in the 1970's (Shreve and Brink, 1977). In the 1930's, however, ethanol production from corn via fermentation processes dominated the market. The increased popularity of ethanol production from ethylene is due primarily to the development of large scale hydrolysis and hydration plants. Hydrolysis, the older of the two methods, is gradually being replaced by the process of hydration due to its superior yield and avoidance of problems associated with sulfuric acid. Both of these processes are described in greater detail below.

The first step of hydrolysis is the absorption of ethylene into 90%-98% sulfuric acid. This step is carried out at a temperature of 50°C-85°C and a pressure of 1.0 MPa-1.4 MPa. The following are the reactions associated with this step (Kniel, 1980):

$$CH_2{=}CH_2 + H_2SO_4 \rightarrow CH_3CH_2OSO_3 \qquad (15)$$

$$2CH_2{=}CH_2 + H_2SO_4 \rightarrow (CH_3CH_2)_2SO_4 \qquad (16)$$

After this is completed, the absorbate containing mixed sulfates is hydrolyzed with water at 70°C to ethanol, dilute sulfuric acid, and small amounts of diethyl ether. The diluted sulfuric acid is separated and concentrated for reuse in the process. The yield is approximately 88% ethanol by weight. These processes have the following associated reactions (Kniel, 1980):

$$CH_3CH_2OSO_3 + H_20 \rightarrow CH_3CH_2OH + H_2SO_4 \qquad (17)$$

$$(CH_3CH_2)_2SO_4 + 2H_2O \rightarrow 2CH_3CH_2OH + H_2SO_4 \qquad (18)$$

$$(CH_3CH_2)SO_4 + CH_3CH_2OH \rightarrow CH_3CH_2OSO_3H + CH_3CH_2OCH_2CH_3 \qquad (19)$$

$$2CH_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_20 \qquad (20)$$

Reactions (17) and (18) generate dilute sulfuric acid as a byproduct, and equations (19) and (20) generate diethyl ether as byproducts.

The next process, called hydration, utilizes a phosphoric acid catalyst supported on diatomaceous earth. The support is impregnated with an aqueous acid solution to a concentration of 75-85%. A concentrated ethylene stream is compressed to 7 MPa, mixed with water, vaporized, and further heated to a reaction temperature of 300°C. This mixture is then passed multiple times over the catalyst and is directly hydrated to ethanol by the following reaction (Kniel, 1980):

$$CH_2{=}CH_2 + H_20 \rightarrow CH_3CH_2OH \qquad (21)$$

The overall yield is approximately 95%, with traces of acetaldehyde and ethyl ether as byproducts. This method is now the one most widely used in industry for reasons previously stated.

CHAPTER 3

ANHYDROUS ETHANOL PRODUCTION FROM CORN CASE STUDY

The following chapter describes the use of BioPro Designer to model the production of ethanol from corn. The first section documents the modeling process and presents the data generated by the simulation program. The second section discusses this data and presents a life cycle inventory on the process. The result will be a cataloging of all inputs and outputs of the process, both energy and material, on a per kilogram of anhydrous ethanol basis.

3.1 Process Simulation

The entire flow diagram associated with this simulation can be found in Figure 4. The first step in the simulation is the processing of corn to cornmeal. Because there no milling unit operation available in the current version of BioPro Designer, this first step is simulated by a generic box and consists of grinding, screening, and separation. This generic box is represented by the box labeled "Milling" on the process flow diagram. The material and energy inputs and outputs can be found in Table A-1 in Appendix A. The energy requirements for the milling operation were adapted from the Office of Alcohol Fuels, United States Department of Energy, report titled "Preliminary Design Report: Small-Scale Fuel Alcohol Plant," published in June, 1980.

The next step in the simulation is the conversion of the cornmeal to dextrin (starch) by the process of hydrolysis. For this Step, a well mixed reactor was used. For simplicity, only one reactor is shown on the process flow diagram; the actual process will consist of nine reactors each with a volume of 90.7 m^3. This reaction requires the addition of water. The reaction takes place at a temperature of approximately 93 °C and a pressure of 1.7 bar, with a conversion of approximately 70% by mass. The remaining 30% of the mass cannot be converted to dextrins and will remain in the process as corn

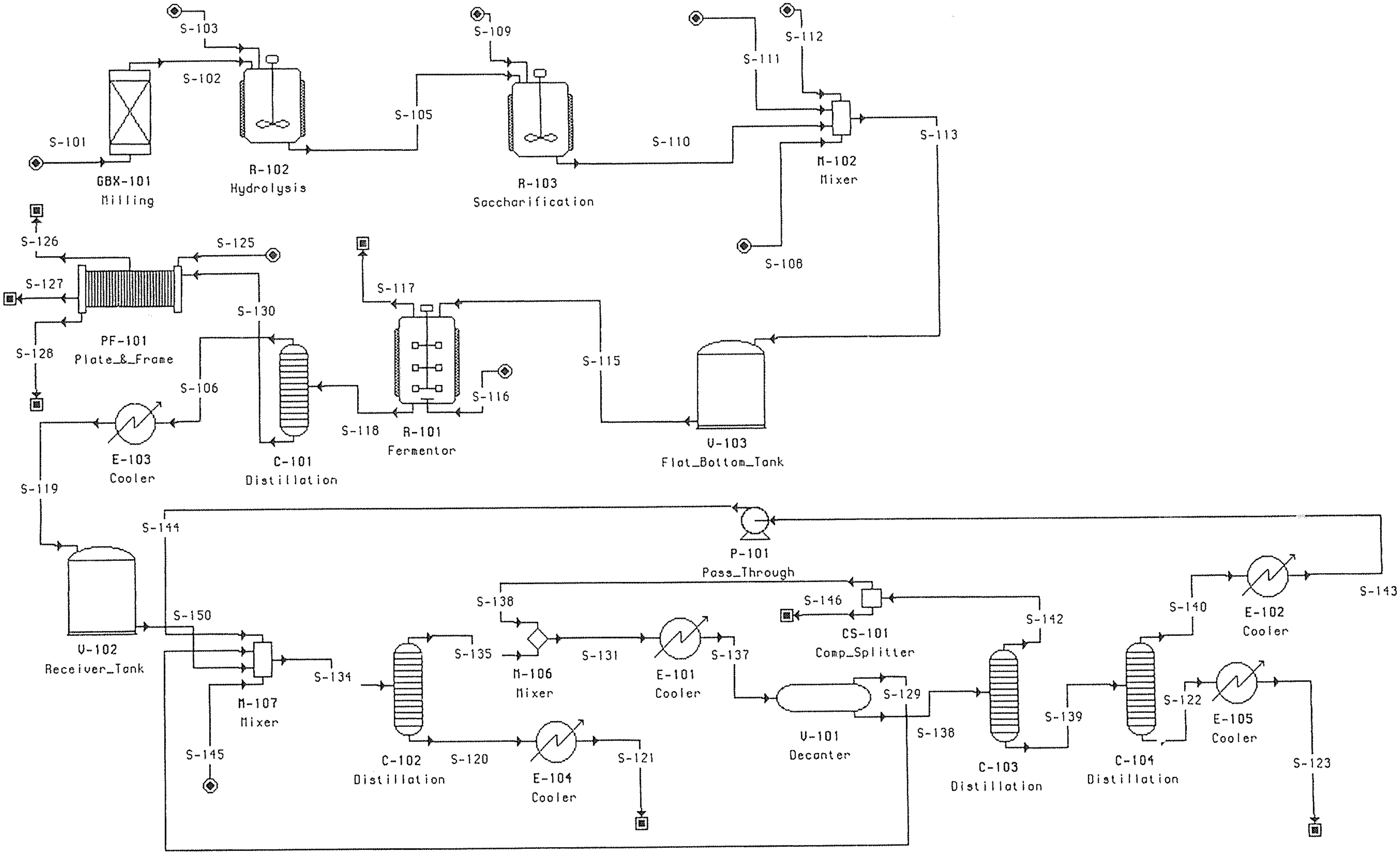

Figure 4: Flow Diagram for Ethanol Production from Corn

residue. This residue will be removed at a later stage. The combined inputs and outputs for all of the nine reactors combined is documented in Table A-2 in Appendix A.

After the corn meal has been converted to dextrin by hydrolysis, it is ready to be converted to glucose by the process of saccharification. This process requires the addition of α-amylase and glucoamylase enzymes in water a solution. These enzymes catalyze the conversion of dextrin to glucose. In the conversion process, water and dextrin combine in a 7.8:70 ratio by mass to form glucose. This reaction, represented by one reactor icon in the process flow diagram, actually requires nine reactors, each with a volume of 91.7 m^3. The reaction takes place at a temperature of 60°C and a pressure of 1.1 bar. The combined inputs and outputs for the reactors are documented in Table A-3 in Appendix A.

The next step in the process is a mixing step in which water and sulfuric acid are added to adjust the water content and the pH. Yeast and calcium oxide are also added to prepare the solution for the fermentation process. This mixing process is represented by icon M-102 in the process flow diagram. The inputs and outputs for this process can be found in Table A-4 in Appendix A.

After the mixing process, the stream is sent to a tank for storage before being sent to the fermentors. This is done because the fermentors operate in batches with down time in between batches for loading, unloading, and cleaning. This tank will have a volume of 500 m^3. This tanks is represented in the process flow diagram by icon V-103. The inputs and outputs for the storage process can be found in Table A-5 in Appendix A.

Following storage, the stream is sent to the fermentation process. The fermentors operate in batches and are staggered in such a way to maintain continuous production of ethanol. The entire fermentation operation will be treated as a continuous operation for the purposes of this study. The actual fermentation process requires eight units. These units are represented by icon R-101 in the process flow diagram. The fermentors have a volume of 569 m^3 each, and operate at 37°C and a pressure of 1.0 bar. The fermentation process converts glucose to yeast , ethanol, and carbon dioxide. The conversion is approximately

98%. The inputs and outputs for the entire fermentation operation can be found in Table A-6 in Appendix A.

After fermentation, it is necessary to concentrate the ethanol produced from approximately 6% to approximately 95%. This is accomplished by the use of a distillation column. The column will have eleven stages, a height of 4.4 m, and a diameter of 1.3 m. The top stream is 95% ethanol, and the bottom stream is made up primarily of water and corn residue. The inputs and outputs for this unit can be found in Table A-7 in Appendix A.

The next step in the process is to dry the bottom stream of the distillation tower. This material consists primarily of corn residue produced in the saccharification step and water. This material will be dewatered using a plate and frame filter. The dewatered material, after drying, can be used for animal feed and the water will be discharged. The plate and frame filter icon (PF-101) in the process flow diagram represents this dewatering process. Approximately 65% of the water is removed from the incoming stream. The inputs and outputs for the dewatering operation can be found in Table A-8 in Appendix A.

Parallel to the dewatering operation is the further processing of the ethanol. It is desired to produce anhydrous alcohol from the 95% alcohol stream. This will be accomplished with the use of three distillation towers and the addition of benzene to the stream. This will allow for near 100% separation of the alcohol-water mixture. Because this process is the same as the one used in the production of ethanol from ethylene, and the focus of this study is to compare the two processes, the process will only be considered as a whole with respect to input and output data.

Before the ethanol stream can be dehydrated, however, it first must be cooled by the use of a heat exchanger. This heat exchanger will be of the plate and frame type. Input and output data for this unit can be found in Table A-9 in Appendix A.

After cooling, the stream is sent to a receiver tank for short term storage before it is sent to the dehydration process. This tank will have a volume of 350 m^3. This tank is represented by icon V-102 on the process flow diagram. The inputs and outputs for these tanks can be found in table A-10 in Appendix A.

The first step in the dehydration process is to add approximately 4% by mass benzene to the incoming stream (Shreve and Brink, 1977). This stream, combined with several recycle streams, is sent to a distillation column (C-102). This column has twenty-five stages, a height of 10 m, and a diameter of .8 m. The bottom stream is anhydrous alcohol and the top stream is a solution of benzene, water, and a small amount of ethanol. The bottom stream is cooled using a heat exchanger (E-104) and the top stream is mixed with a recycle stream and is sent to a heat exchanger (E-101) to be cooled. The top stream is then sent to a decanter tank (V-101) to separate and recycle most of the benzene. The decanter tank has a length of 6.8 m and a diameter of 1.4 m. The benzene rich stream (S-129) is sent back to distillation column C-102. The water rich stream (S-138) is sent to a distillation column C-103 to remove the remaining benzene and a portion of the alcohol. This distillation column has twenty-six stages, a height of 10.4 m, and a diameter of .3 m. The top stream, which is rich in benzene and alcohol, is recycled to mix with the top stream from distillation column C-102. The bottom stream from C-103 is sent to a third distillation column C-104 to remove the remaining benzene and ethanol from the water. This third column has twenty-seven stages, a height of 10.8 m and a diameter of .1 m. The bottom stream, which is primarily water, is cooled in a heat exchanger (E-105) and is discharged. The top stream, which is rich in benzene and alcohol, is cooled in a heat exchanger (E-102) and recycled back to distillation column C-102. A tabulation of the material inputs and outputs for the overall process is in Table A-11 in Appendix A. The energy inputs for each unit operation in the dehydration process can be found in Table A-12, also contained in Appendix A.

3.2 Analysis

The information generated by the BioPro Designer simulation can be used to perform a life cycle inventory on the process described in the previous section. This analysis requires the use of eco-vectors, as described in Chapter two. It is important to classify each output from a process as either a product or a waste. Due to the scope of this study, it is not possible to identify environmental impacts associated with the various material and energy inputs to the different processes. The reader should note that this limits the completeness of this study. For this reason, it is necessary to modify slightly the procedure outlined in Chapter two. Inputs and waste streams will be incorporated into the eco-vector associated with each product of each process. Waste streams will be denoted with a subscript 'w'. Raw material inputs will have a component of 1.0 in the eco-vectors in place of environmental impact quantities; this is necessary as the environmental impacts are beyond the scope of this study. This also aids in the mathematics associated with the process.

The first step in the ethanol production from corn process is milling. For this process, stream S-102 is the product stream, and stream S-101 and power are the inputs. For ease of calculation, the power stream will be designated by P-101. The reader is reminded that the material components of the eco-vector are in units of kg component per kg of the stream in which they are found. In the case of energy components, the units used are BTU per BTU of the stream in which they are found. These units are used mainly for convenience of calculation. The eco-vector for the product stream can thus be calculated as follows:

$$(50974 \text{ kg/hr}) \begin{bmatrix} Corn \\ Power \end{bmatrix}_{S-102} = (50794 \text{ kg/hr}) \begin{bmatrix} 1kg \\ 0 \end{bmatrix}_{S-101}$$

$$+ (4.0 \times 10^4 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 1BTU \end{bmatrix}_{P-101} \qquad (22)$$

To solve for the corn component of the eco-vector for stream S-102, the following equation can be written:

(50974 kg/hr)(Corn) = (50794 kg/hr)(1 kg Corn/kg)

+ (4.0 x 10^4 BTU/hr)(0 kg Corn/BTU) (23)

Thus the corn component of the eco-vector can be solved for by the following equation:

$$(\text{corn}) = \left[\frac{50974 kg / hr}{50974 kg / hr}\right] \tag{24}$$

Thus the corn component of the eco-vector for stream S-102 is simply 1.0. A similar procedure can be followed for the calculation of the component associated with power. The equation is as follows:

(50974 kg/hr)(Power) = (50974 kg/hr)(0 BTU/kg)

+ (4.0 x 10^4 BTU/hr)(1 BTU/BTU) (25)

The eco-vector component for power can be solved to get .78 BTU/kg. Thus, the eco-vector associated with stream S-102 can be written as the following:

$$\begin{bmatrix} Corn \\ Power \end{bmatrix}_{S-102} = \begin{bmatrix} 1.0 \\ .78 \end{bmatrix}_{S-102}$$

This same process will be followed for each step in the process. In the interest of brevity, the initial equations and the final results will be presented; intermediate steps will not be included.

The next step in the process is hydrolysis. The inputs and outputs for this process can be found in Table A-2. Based upon the information presented, the eco-vector associated with product stream S-105 can be calculated. It is necessary to add water and heating duty components to the eco-vector. The power and heating inputs will be designated as P-102 and H-101, respectively. The eco-vector associated with stream S-105 can be calculated as follows:

$$(57841 \text{ kg/hr}) \begin{bmatrix} Corn \\ Power \\ Water \\ Heating \end{bmatrix}_{S-105} = (50974 \text{ kg/hr}) \begin{bmatrix} 1 \\ .78 \\ 0 \\ 0 \end{bmatrix}_{S-102} + (6867 \text{ kg/hr}) \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}_{S-103} +$$

$$(1.2 \text{ x } 10^6 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}_{P-102} + (1.3 \text{ x } 10^7 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}_{H-101} \qquad (26)$$

The resulting eco-vector associated with stream S-105 is the following:

$$\begin{bmatrix} Corn \\ Power \\ Water \\ Heating \end{bmatrix}_{S-105} = \begin{bmatrix} .88 \\ .69 \\ .12 \\ 237 \end{bmatrix}_{S-105} \qquad (27)$$

The next step in the process is saccharification. The inputs and outputs for this process can be found in table A-3 in Appendix A. At this point it is necessary to add three additional components to the eco-vectors; α-amylase, glucoamylase and cooling duty. The power and cooling duty inputs will be designated by P-103 and C-101, respectively. The eco-vector associated with product stream S-110 can be solved using the following equation:

$$(5.8 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} Corn \\ Power \\ Water \\ Heating \\ \alpha - amylase \\ Glucoamylase \\ Cooling \end{bmatrix}_{S-110} = (5.8 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} .88 \\ .69 \\ .12 \\ 237 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{S-105} +$$

$$(653 \text{ kg/hr}) \begin{bmatrix} 0 \\ 0 \\ .76 \\ 0 \\ .21 \\ .03 \\ 0 \end{bmatrix}_{S-109} + (1.02 \text{ x } 10^6 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{P-103} + (1.93 \text{ x } 10^7 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}_{C-101} \tag{28}$$

This equation can be solved to yield the following eco-vector associated with stream S-110:

$$\begin{bmatrix} Corn \\ Power \\ Water \\ Heating \\ \alpha - amylase \\ Glucoamylase \\ Cooling \end{bmatrix}_{S-110} = \begin{bmatrix} .87 \\ 18.1 \\ .13 \\ 234 \\ .002 \\ .0003 \\ 330 \end{bmatrix}_{S-110} \tag{29}$$

The next step in the process is a mixing step. It is now necessary to add three more components to the eco-vector; calcium oxide, sulfuric acid, and yeast. In this step, the product stream is defined to be stream S-113. The inputs and outputs for this process can be found in table A-4 in Appendix A. The following equation can be written to solve for the eco-vector associated with this stream:

$$(3.3 \text{ x } 10^5 \text{ kg/hr}) \begin{bmatrix} Corn \\ Power \\ Water \\ Heating \\ \alpha - amylase \\ Glucoamylase \\ Cooling \\ CaO \\ H_2SO_4 \\ Yeast \end{bmatrix}_{S-113} = (201 \text{ kg/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}_{S-111} +$$

$$(269 \text{ kg/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}_{S-112} + (2.8 \text{ x } 10^5 \text{ kg/hr}) \begin{bmatrix} 0 \\ 0 \\ .999 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ .01 \\ 0 \end{bmatrix}_{S-108} + (5.8 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} .87 \\ 18.1 \\ .13 \\ 234 \\ .002 \\ .0003 \\ 330 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{S-110} \tag{30}$$

The eco-vector associated with stream S-113 can be solved to get the following result:

$$\begin{bmatrix} Corn \\ Power \\ Water \\ Heating \\ \alpha - amylase \\ Glucoamylase \\ Cooling \\ CaO \\ H_2SO_4 \\ Yeast \end{bmatrix}_{S-113} = \begin{bmatrix} .15 \\ 3.14 \\ .86 \\ 40.6 \\ .0003 \\ .00005 \\ 57.3 \\ .0006 \\ .008 \\ .0008 \end{bmatrix}_{S-113} \quad (31)$$

The next step in the process is the temporary storage in the flat bottom tank. In this case, there are no chemical or physical changes to the stream. The composition and flow rate of the stream remains the same, thus allowing for the conclusion that the eco-vector associated with the stream remains the same. The inputs and outputs for this process can be found in Table 5 in Appendix A. Therefore, the eco-vector associated with stream S-113 is identical to the eco-vector associated with stream S-114, which is in turn identical to the eco-vector associated with stream S-115.

After the storage step, stream S-115 is sent to the fermentors. During this step, the product stream is defined to be stream S-118 which contains ethanol and various components. The waste stream is the carbon dioxide discharged into the atmosphere in stream S-117. It is therefore necessary to add a carbon dioxide component to the eco-vector. The power and cooling duty requirements will be designated as streams P-104 and C-102, respectively. The reader should be reminded at this point that the components of an eco-vector associated with a waste stream are negative. In many cases, a material that is introduced to a process as a raw material is later discharged to the environment as a waste. In order to account for this difference in the eco-vectors, a subscript "w" will be used for all waste streams. The inputs and outputs for this stream can be found in Table 6 in

Appendix A. The following equation can be written in order to solve for the eco-vector associated with stream S-118:

$$(3.2 \times 10^5 \text{ kg/hr}) \begin{bmatrix} Corn \\ Power \\ Water \\ Heating \\ \alpha - amylase \\ Glucoamylase \\ Cooling \\ CaO \\ H_2SO_4 \\ Yeast \\ (CO_2)_w \end{bmatrix}_{S-118} = (3.3 \times 10^5 \text{ kg/hr}) \begin{bmatrix} .15 \\ 3.14 \\ .86 \\ 40.6 \\ .0003 \\ .00005 \\ 57.3 \\ .0006 \\ .008 \\ .0008 \\ 0 \end{bmatrix}_{S-115} +$$

$$(0 \text{ kg/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{S-116} - (1.8 \times 10^4 \text{ kg/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -1 \end{bmatrix}_{S-117} + (7.9 \times 10^7 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{P-104} +$$

$$(6.5 \text{ x } 10^6 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{C-102} \qquad (32)$$

This equation can be solved for the eco-vector associated with stream S-118:

$$\begin{bmatrix} Corn \\ Power \\ Water \\ Heating \\ \alpha - amylase \\ Glucoamylase \\ Cooling \\ CaO \\ H_2SO_4 \\ Yeast \\ (CO_2)_w \end{bmatrix}_{S-118} = \begin{bmatrix} .16 \\ 251.7 \\ .91 \\ 43.0 \\ .0003 \\ .00005 \\ 81.1 \\ .0006 \\ .008 \\ .0008 \\ .06 \end{bmatrix}_{S-118} \qquad (33)$$

After the fermentation step, the product stream is sent to a distillation column to concentrate the ethanol to approximately 95%. The product stream for this process is stream S-106, which is further processed to anhydrous ethanol. The waste stream is stream S-130, which is dewatered and can be used as animal feed. This material is considered a waste stream because it cannot be reused or recycled in the ethanol manufacturing process. Because of the waste generated, it is necessary to add waste components to the eco-vectors for the appropriate materials. In addition to this, there is a power input associated with dewatering the waste product from the plate and frame filter unit PF-101. This power input will be designated as stream P-105. The heating and cooling duties associated with the distillation process will be designated as streams H-102 and C-103, respectively. The inputs and output for the distillation and dewatering processes can be found in Table 7 and Table 8 in Appendix A, respectively. The following equation can be written to solve for the eco-vector associated with stream S-106:

$$(1.9 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} Corn \\ Power \\ Water \\ Heating \\ \alpha - amylase \\ Glucoamylase \\ Cooling \\ CaO \\ H_2SO_4 \\ Yeast \\ (CO_2)w \\ (Yeast)_w \\ (Water)_w \\ (H_2SO_4)_w \\ (\alpha - amylase)_w \\ (Ethanol)_w \\ (\mathrm{Re}\,sidue)_w \\ (Glu\cos e)_w \\ (CaO)_w \\ (Glucoamylase)_w \end{bmatrix}_{S-106} = (3.2 \text{ x } 10^5 \text{ kg/hr}) \begin{bmatrix} .16 \\ 251.7 \\ .91 \\ 43.0 \\ .0003 \\ .00005 \\ 81.1 \\ .0006 \\ .008 \\ .0008 \\ .06 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{S-118} -$$

$$(3.0 \text{ x } 10^5 \text{ kg/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -.0075 \\ -.936 \\ -.01 \\ -.0005 \\ -.0013 \\ -.052 \\ -.0027 \\ -.07 \\ -.0009 \end{bmatrix}_{S-130} + (3.4 \text{ x } 10^7 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{H-102}$$

$$+ (1.2 \text{ x } 10^7 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{C-103} + (5.6 \text{ x } 10^4 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{P-105} \qquad (34)$$

This equation can be solved to get the following eco-vector associated with stream S-106:

$$\begin{bmatrix} Corn \\ Power \\ Water \\ Heating \\ \alpha-amylase \\ Glucoamylase \\ Cooling \\ CaO \\ H_2SO_4 \\ Yeast \\ (CO_2)_w \\ (Yeast)_w \\ (Water)_w \\ (H_2SO_4)_w \\ (\alpha-amylase)_w \\ (Ethanol)_w \\ (\mathrm{Re}sidue)_w \\ (Glu\cos e)_w \\ (CaO)_w \\ (Glucoamylase)_w \end{bmatrix}_{S-106} = \begin{bmatrix} 2.7 \\ 4242 \\ 15.3 \\ 2514 \\ .005 \\ .0008 \\ 2019 \\ .01 \\ .13 \\ .001 \\ 1.0 \\ .12 \\ 14.8 \\ .158 \\ .007 \\ .02 \\ .81 \\ .04 \\ .11 \\ .011 \end{bmatrix}_{S-106} \qquad (35)$$

After the first distillation process, the water and ethanol stream is cooled to be further processed to anhydrous ethanol. The cooling process is performed using a plate and frame type heat exchanger. The only input during this process is cooling duty, designated by stream C-104. The product stream is stream S-119. There are no waste streams from this process. The inputs and outputs from this process can be found in Table 9 in Appendix A. The following equation can written to solve for the eco-vector associated with stream S-119:

$$\begin{bmatrix} Corn \\ Power \\ Water \\ Heating \\ \alpha - amylase \\ Glucoamylase \\ Cooling \\ CaO \\ H_2SO_4 \\ Yeast \\ (CO_2)_w \\ (Yeast)_w \\ (Water)_w \\ (H_2SO_4)_w \\ (\alpha - amylase)_w \\ (Ethanol)_w \\ (\mathrm{Re}\,sidue)_w \\ (Glu\cos e)_w \\ (CaO)_w \\ (Glucoamylase)_w \end{bmatrix}_{S-119} = (1.9 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} 2.7 \\ 4242 \\ 15.3 \\ 2514 \\ .005 \\ .0008 \\ 2019 \\ .01 \\ .13 \\ .001 \\ 1.0 \\ .12 \\ 14.8 \\ .158 \\ .007 \\ .02 \\ .81 \\ .04 \\ .011 \\ .0009 \end{bmatrix}_{S-106} +$$

$$(5.2 \text{ x } 10^5 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{C-104} \tag{36}$$

This equation can be solved to get the following eco-vector associated with stream S-119:

$$\begin{bmatrix} Corn \\ Power \\ Water \\ Heating \\ \alpha - amylase \\ Glucoamylase \\ Cooling \\ CaO \\ H_2SO_4 \\ Yeast \\ (CO_2)_w \\ (Yeast)_w \\ (Water)_w \\ (H_2SO_4)_w \\ (\alpha - amylase)_w \\ (Ethanol)_w \\ (\mathrm{Re}\,sidue)_w \\ (Glu\cos e)_w \\ (CaO)_w \\ (Glucoamylase)_w \end{bmatrix}_{S-119} = \begin{bmatrix} 2.7 \\ 4242 \\ 15.3 \\ 2514 \\ .005 \\ .0008 \\ 2046 \\ .01 \\ .13 \\ .001 \\ 1.0 \\ .12 \\ 14.8 \\ .158 \\ .007 \\ .02 \\ .81 \\ .04 \\ .011 \\ .0009 \end{bmatrix}_{S-119} \qquad (37)$$

After the cooling process, the product stream is sent to a receiving tank (V-102) to be held until further processing into anhydrous ethanol. There are no physical or chemical changes to the stream during storage, and there are no energy inputs. The inputs and outputs for this process can be found in Table 10 in Appendix A. Thus, the eco-vector associated with stream S-150 is identical to that associated with stream S-119.

After storage, the product stream is processed into anhydrous ethanol. As previously mentioned, this process will be treated as a single step taking into account all inputs and outputs during the process. The product stream from this process is stream S-121. The waste streams are S-146 and S-123. It is necessary at this point in time to add two components to the eco-vector; benzene as a raw material and benzene as a waste. The energy input resulting from the cooling duty and heating duty will be designated as C-105 and H-103, respectively. The material and energy inputs and outputs from this process can be found in Table 11 and Table 12, respectively, in Appendix A. The following equation can be written to solve for the eco-vector associated with stream S-121:

$$(1.8 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} \mathit{Corn} \\ \mathit{Power} \\ \mathit{Water} \\ \mathit{Heating} \\ \alpha - \mathit{amylase} \\ \mathit{Glucoamylase} \\ \mathit{Cooling} \\ \mathit{CaO} \\ H_2SO_4 \\ \mathit{Yeast} \\ (CO_2)_w \\ (\mathit{Yeast})_w \\ (\mathit{Water})_w \\ (H_2SO_4)_w \\ (\alpha - \mathit{amylase})_w \\ (\mathit{Ethanol})_w \\ (\mathit{Residue})_w \\ (\mathit{Glucose})_w \\ (\mathit{CaO})_w \\ (\mathit{Glucoamylase})_w \\ \mathit{Benzene} \\ (\mathit{Benzene})_w \end{bmatrix}_{S-121} = (1.9 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} 2.7 \\ 4242 \\ 15.3 \\ 2514 \\ .005 \\ .0008 \\ 2046 \\ .01 \\ .13 \\ .001 \\ 1.0 \\ .12 \\ 14.8 \\ .158 \\ .007 \\ .02 \\ .81 \\ .04 \\ .011 \\ .0009 \\ 0 \\ 0 \end{bmatrix}_{S-150} -$$

$$(737\text{ kg/hr})\begin{bmatrix}0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\-1\\0\end{bmatrix}_{S-146}+(737\text{ kg/hr})\begin{bmatrix}0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\1\end{bmatrix}_{S-145}-(836\text{ kg/hr})\begin{bmatrix}0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\-1\\0\\0\\0\\0\\0\\0\\0\\0\\0\end{bmatrix}_{S-123}+$$

$$(1.4 \text{ x } 10^7 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{C-105} + (2.6 \text{ x } 10^7 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{H-103} \qquad (38)$$

This equation can be solved to yield the following eco-vector associated with stream S-121:

$$\begin{bmatrix} Corn \\ Power \\ Water \\ Heating \\ \alpha - amylase \\ Glucoamylase \\ Cooling \\ CaO \\ H_2SO_4 \\ Yeast \\ (CO_2)_w \\ (Yeast)_w \\ (Water)_w \\ (H_2SO_4)_w \\ (\alpha - amylase)_w \\ (Ethanol)_w \\ (\mathrm{Re}\,sidue)_w \\ (Glu\cos e)_w \\ (CaO)_w \\ (Glucoamylase)_w \\ Benzene \\ (Benzene)_w \end{bmatrix}_{S-121} = \begin{bmatrix} 2.9 \\ 4478 \\ 16.2 \\ 4098 \\ .005 \\ .0008 \\ 2937 \\ .01 \\ .14 \\ .001 \\ 1.1 \\ .13 \\ 15.7 \\ .158 \\ .007 \\ .02 \\ .86 \\ .04 \\ .011 \\ .001 \\ .04 \\ .04 \end{bmatrix}_{S-121} \qquad (39)$$

Thus, the eco-vector associated with each kilogram of anhydrous ethanol produced from the process modeled is now known.

CHAPTER 4

ANHYDROUS ETHANOL PRODUCTION FROM ETHYLENE CASE STUDY

The following chapter describes the use of BioPro Designer to model the production of ethanol from ethylene. The first section documents the modeling process and presents the data generated by the simulation program. The second section discusses this data and presents a life cycle inventory on the process. The result will be a cataloging of all inputs and outputs of the process, both energy and material, on a per kilogram of anhydrous ethanol basis.

4.1 Process Simulation

The entire flow diagram for this simulation can be found in Figure 5. The first step in the production of ethylene to anhydrous ethanol is to react water with ethylene over a catalyst as described in Section 2.4. This reaction is simulated using a well mixed reactor model. One reactor is required with a volume of 9.2 m^3. The reactor will operate at 300 °C and a pressure of 7.0 bar with an overall conversion of 95%. The incoming ethylene stream is mixed with water and an ethylene recycle stream which contains unreacted ethylene recycled from the product stream from the reactor. The mixing stream is represented by icon M-108 in the process flow diagram. The inputs and outputs for this mixing step and the reactor can be found in tables B-1 and B-2, respectively, in Appendix B.

After the reaction takes place, the product stream is cooled to separate the ethylene from the ethanol using a flash drum. The separation step is represented by icon CS-102 in the process diagram. The ethylene is recycled back to the reactor and the 95% ethanol is dehydrated using a series of distillation towers and the addition of a small amount of benzene. During the cooling and separation step a small amount of ethylene is purged from

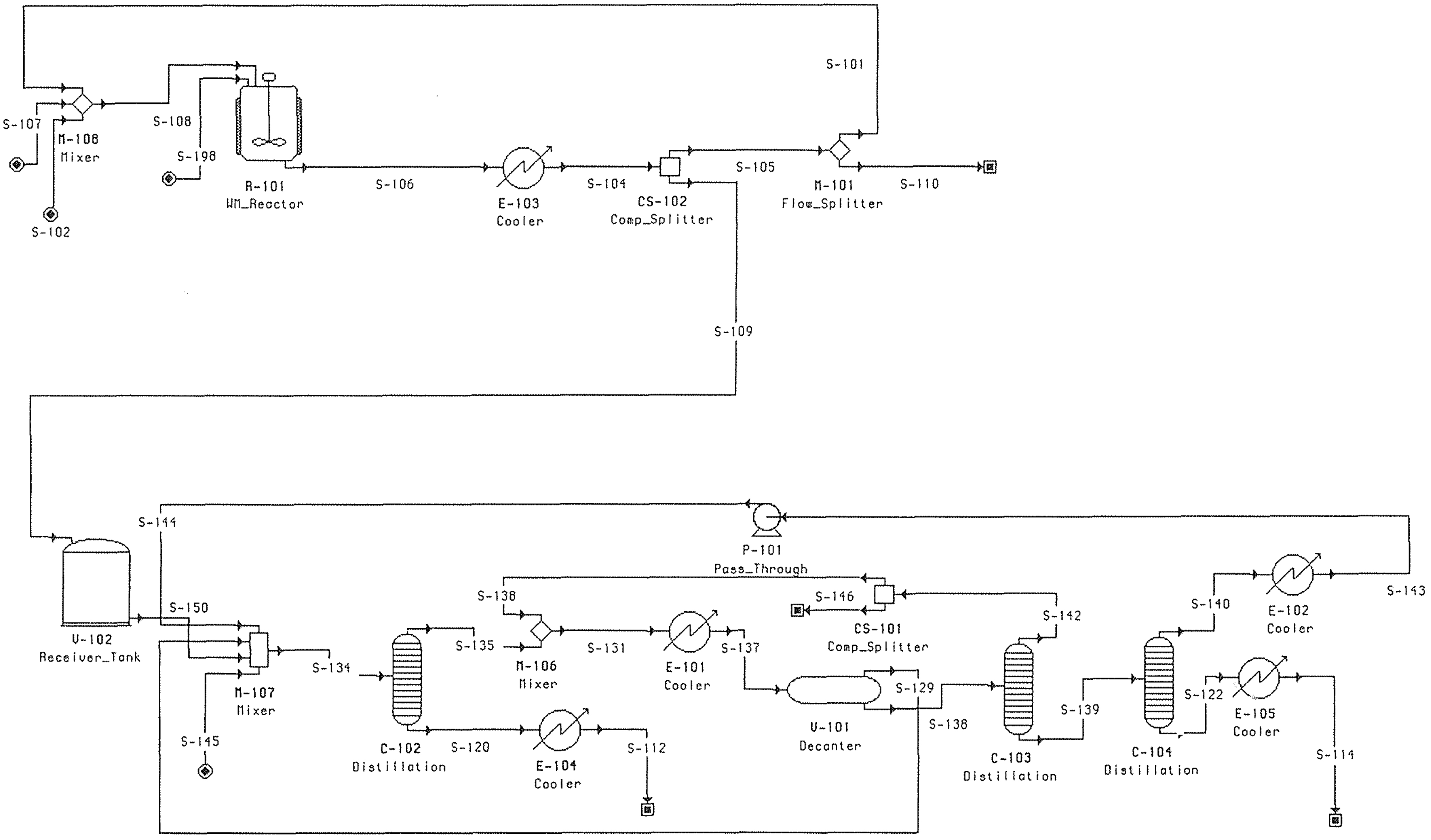

Figure 5: Flow Diagram for Ethanol Production from Ethylene

the system. This purging is represented in the process flow diagram by icon M-101. The inputs and outputs for the cooling, separation, and purging steps can be found in tables B-3, B-4, and B-5, respectively, in Appendix B.

The next step in the process is to store the 95% ethanol stream in a holding tank for further processing. It is assumed that no chemical or physical changes to the ethanol occur during this step. This holding tank, represented by unit V-102 in the process flow diagram, will have a volume of 50 m^3. The inputs and outputs for this tank can be found in table B-6 in Appendix B. After holding, the 95% ethanol stream is sent to the dehydration process.

The first step in the dehydration process is to add approximately 4% by mass benzene to the incoming ethanol/water stream (Shreve and Brink, 1977). This stream, combined with several recycle streams, is sent to a distillation column (C-102). This column has twenty-six stages, a height of 10.4 m, and a diameter of 0.8 m. The bottom stream from the column is anhydrous alcohol and the top stream is a solution of benzene, water, and a small amount of ethanol. The bottom stream is cooled using a heat exchanger and the top is mixed with a recycle stream and is sent to a heat exchanger to be cooled. It is then sent to a decanter tank to separate and recycle most of the benzene. The decanter tank has a length of 6.8 m and a diameter of 1.4 m. The benzene rich stream is sent back to distillation column C-102. The water rich stream is sent to a distillation column C-103 to remove the remaining benzene and a portion of the alcohol. This distillation column has twenty-six stages, a height of 20.2 m, and a diameter of 0.3 m. The top, which is rich in benzene and alcohol, is recycled to mix with the top stream from distillation column C-102. The bottom stream from C-103 is sent to a third distillation column C-104 to remove the remaining benzene and alcohol from the water. This column has twenty-seven stages, a height of 10.8 m, and a diameter of 0.1 m. The bottom stream, which is pure water, is cooled in a plate and frame heat exchanger (E-105) and is discharged or reused. The top stream, which is rich in benzene and alcohol, is cooled in a heat exchanger (E-102) and recycled back to distillation column C-102. This heat exchanger is a plate and frame type. A tabulation of the material inputs and outputs for the entire dehydration process is in Table B-7 in Appendix A. The energy inputs for each unit operation in the dehydration process can be found in Table B-8, also contained in Appendix B.

4.2 Analysis

The first step of the process, as described above, is to mix fresh ethylene and water with recycled ethylene from the reactor. Because this material is continuously recycled and theoretically never leaves the system as a waste, only the fresh ethylene will be considered as a component of the eco-vector. The inputs and outputs for the mixing process can be found in Table B-1 in Appendix B. The following equation can be written to solve for the eco-vector associated with Stream S-108:

$$(2.0 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} Ethylene \\ Water \end{bmatrix}_{S-108} = (1.1 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} 1 \\ 0 \end{bmatrix}_{S-107}$$

$$+ (5.6 \text{ x } 10^2 \text{ kg/hr}) \begin{bmatrix} 0 \\ 0 \end{bmatrix}_{S-101} + (8.2 \text{ x } 10^3 \text{ kg/hr}) \begin{bmatrix} 0 \\ 1 \end{bmatrix}_{S-102} \tag{40}$$

This equation can be solved to yield the following expression for the eco-vector associated with stream S-108:

$$\begin{bmatrix} Ethylene \\ Water \end{bmatrix}_{S-108} = \begin{bmatrix} .55 \\ .41 \end{bmatrix}_{S-108} \tag{41}$$

After the mixing step, the product stream is sent to a reactor that reacts ethylene and water over a catalyst to form ethanol. At this point in time it is necessary to add two components to the eco-vector; heating duty and power. The heating duty and power inputs for the reactor will be designated as streams H-104 and P-106, respectively. The inputs and outputs for this process can be found in Table B-2 in Appendix B. The following equation can be written to solve for the product stream S-106:

$$(2.0 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} Ethylene \\ Water \\ Heating \\ Power \end{bmatrix}_{S-106} = (2.0 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} .55 \\ .41 \\ 0 \\ 0 \end{bmatrix}_{S-108}$$

$$+ (0 \text{ kg/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{S-102} + (8.2 \text{ x } 10^5 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}_{H-104} + (1.4 \text{ x } 10^4 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}_{P-106} \qquad (42)$$

This equation can be solved for the eco-vector associated with stream S-106:

$$\begin{bmatrix} Ethylene \\ Water \\ Heating \\ Power \end{bmatrix}_{S-106} = \begin{bmatrix} .55 \\ .41 \\ 41 \\ .70 \end{bmatrix}_{S-106} \qquad (43)$$

The next step in the process is to cool the product stream. This is accomplished through the use of a cooler. The material inputs and outputs for this process can be found in Table B-3 in Appendix B. It is necessary at this point to add a cooling duty component to the eco-vector. The cooling duty requirements will be designated by input stream C-106. The following equation can be written to solve for the eco-vector associated with stream S-104:

$$(2.0 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} Ethylene \\ Water \\ Heating \\ Power \\ Cooling \end{bmatrix}_{S-104} = (2.0 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} .55 \\ .41 \\ 41 \\ .70 \\ 0 \end{bmatrix}_{S-106}$$

$$+ (1.8 \text{ x } 10^5 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}_{C-106} \tag{44}$$

This equation can be solved to yield the following:

$$\begin{bmatrix} Ethylene \\ Water \\ Heating \\ Power \\ Cooling \end{bmatrix}_{S-104} = \begin{bmatrix} .55 \\ .41 \\ 41 \\ .70 \\ 9.0 \end{bmatrix}_{S-104} \tag{45}$$

After the cooling process, the product stream is split into two separate streams; the ethylene is in the vapor phase and the ethanol/water mixture is in the liquid phase. The inputs and outputs for this separation process can be found in Table B-4 in Appendix B. After the ethylene is separated, part of it is recycled and mixed with the fresh ethylene feed, and part of it is purged and discharged as a waste. The inputs and outputs for this purging process can be found in Table B-5 in Appendix B. Because only inputs and outputs from the process are of interest for this study, the separation and purging process will be treated as a whole. Also, as previously mentioned, the recycle stream will not have any components in its eco-vector because it theoretically never leaves the process. Thus, the input for the combined separation/purging process is stream S-104, the product stream is stream S-109, and the waste stream is stream S-110. At this point it is necessary to add ethylene waste to the eco-vector. The reader is reminded that waste materials are denoted with a subscript "w" to differentiate them from raw materials. Thus, after all these assumptions are made, the following equation can be written to solve for the eco-vector associated with stream S-109:

$$(1.9 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} Ethylene \\ Water \\ Heating \\ Power \\ Cooling \\ (Ethylene)_w \end{bmatrix}_{S-109} = (2.0 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} .55 \\ .41 \\ 41 \\ .70 \\ 9.0 \\ 0 \end{bmatrix}_{S-104} - (30 \text{ kg/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -1 \end{bmatrix}_{S-110} \qquad (46)$$

This equation can be solved to get the following eco-vector associated with stream S-109:

$$\begin{bmatrix} Ethylene \\ Water \\ Heating \\ Power \\ Cooling \\ (Ethylene)_w \end{bmatrix}_{S-109} = \begin{bmatrix} .58 \\ .43 \\ 43 \\ .74 \\ 9.5 \\ .0016 \end{bmatrix}_{S-109} \qquad (47)$$

The next step in the process is to take this ethanol/water stream and store it in a receiver tank before further processing into anhydrous ethanol. This storage process will not alter the stream in any way; thus it can be assumed that the eco-vector associated with stream S-150 is identical to the one associated with stream S-109. The inputs and outputs associated with this step can be found in Table B-6 in Appendix B.

After storage, the ethanol/water stream is processed into anhydrous ethanol. As mentioned in the previous chapter, this process will be treated as a whole. The product of this process is stream S-112. and the wastes are streams S-146 and S-114. The material inputs and outputs can be found in Table B-7 in Appendix B. It is necessary at this point to add three material components to the eco-vector; benzene as a raw material, benzene as a waste material, and water as a waste material. The energy inputs and outputs associated with the dehydration process can be found in Table B-8 in Appendix B. The heating and cooling duty inputs for this process will be designated as streams H-105 and C-107, respectively. Thus, the following equation can be written to solve for the eco-vector associated with stream S-112:

$$(1.8 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} Ethylene \\ Water \\ Heating \\ Power \\ Cooling \\ (Ethylene)_w \\ Benzene \\ (Benzene)_w \\ (Water)_w \end{bmatrix}_{S-112} = (1.9 \text{ x } 10^4 \text{ kg/hr}) \begin{bmatrix} .58 \\ .43 \\ 43 \\ .74 \\ 9.5 \\ .0016 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{S-150} -$$

$$(7.6 \text{ x } 10^2 \text{ kg/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -1 \\ 0 \end{bmatrix}_{S-146} - (9.9 \text{ x } 10^2 \text{ kg/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -1 \end{bmatrix}_{S-114} + (7.6 \text{ x } 10^2 \text{ kg/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}_{S-145} +$$

$$(2.6 \text{ x } 10^7 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{H-105} + (1.4 \text{ x } 10^7 \text{ BTU/hr}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}_{C-107} \qquad (48)$$

This equation can be solved to yield the following expression for the eco-vector associated with stream S-112:

$$\begin{bmatrix} Ethylene \\ Water \\ Heating \\ Power \\ Cooling \\ (Ethylene)_w \\ Benzene \\ (Benzene)_w \\ (Water)_w \end{bmatrix}_{S-112} = \begin{bmatrix} .61 \\ .45 \\ 1490 \\ .78 \\ 788 \\ .0017 \\ .04 \\ .04 \\ .06 \end{bmatrix}_{S-112} \qquad (49)$$

Thus, equation (49) gives the eco-vector associated with the anhydrous ethanol stream S-112.

CHAPTER 5

DISCUSSION

The previous two chapters have described the process of generating the eco-vector associated with production of anhydrous ethanol from corn and from ethylene, respectively. This is the first step in the life cycle analysis methodology. The next step in this methodology is to take this information and assess the impact on the environment from each component of the eco-vector. The sum of these environmental impacts yields the total environmental impact of the final product, thus allowing the two processes to be directly compared. This step is referred to as life cycle impact analysis.

At the present time, information permitting a life cycle impact analysis of the two processes considered in this study is unavailable. For purposes of illustration, Figures 6-8 graph the raw material inputs, energy inputs, and emissions, respectively, for the anhydrous ethanol production from corn process. Figures 9-11 graph these same quantities for the anhydrous ethanol production from ethylene process.

Although the raw material inputs and emissions cannot be directly compared, one can draw some general conclusions about the energy requirements for each process. Upon comparison of the cooling duties required for each process, for example, it is found that the ethanol production from corn process requires approximately 2937 BTU/kg anhydrous ethanol produced, as opposed to 788 BTU/kg for the ethanol production from ethylene process. Similarly, the heating duties and power for the ethanol production from corn process are found to be 4098 BTU/kg and 4478 BTU/kg, respectively, as opposed to 1490 BTU/kg and .78 BTU/kg for ethanol production from ethylene. Overall, the ethanol production from corn requires 11513 BTU per kg of anhydrous ethanol produced. The ethanol production from ethylene, requires 2279 BTU per kg of anhydrous ethanol produced. Assuming the energy used is produced in the same manner, thus having the same environmental impact, one can conclude that the ethanol production from ethylene has less impact on the environment than ethanol production from corn, with respect to energy.

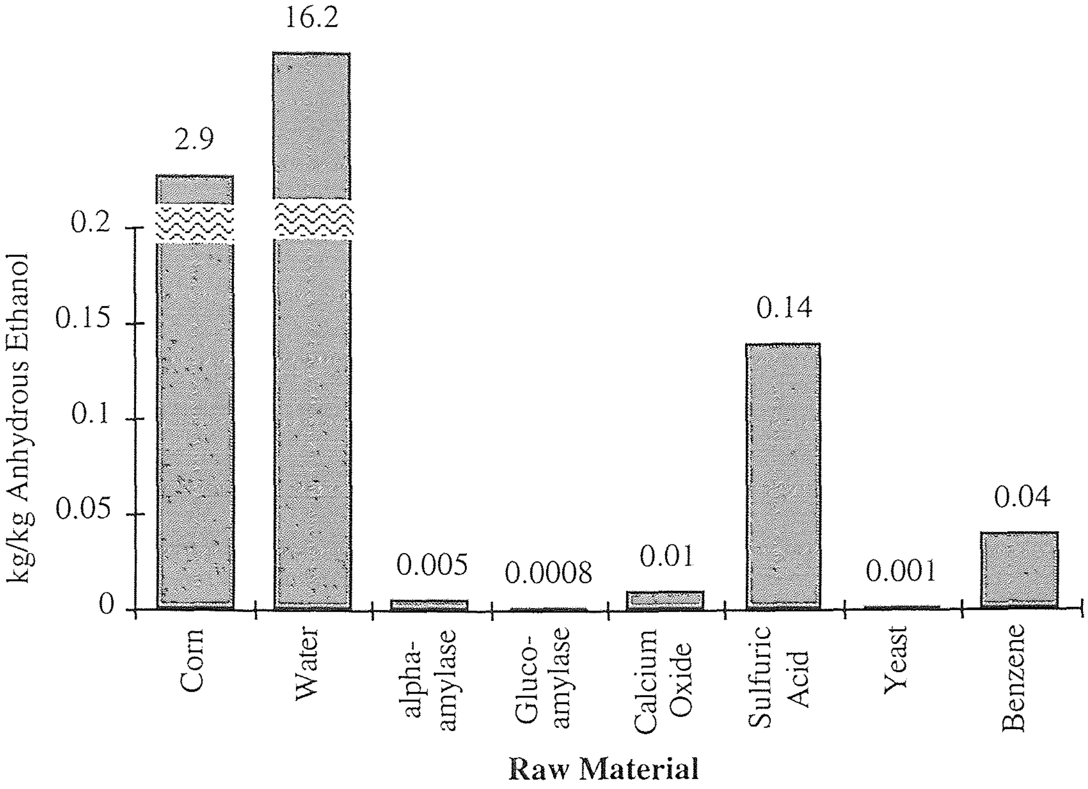

Figure 6: Raw Material Inputs for Anhydrous Ethanol Production from Corn

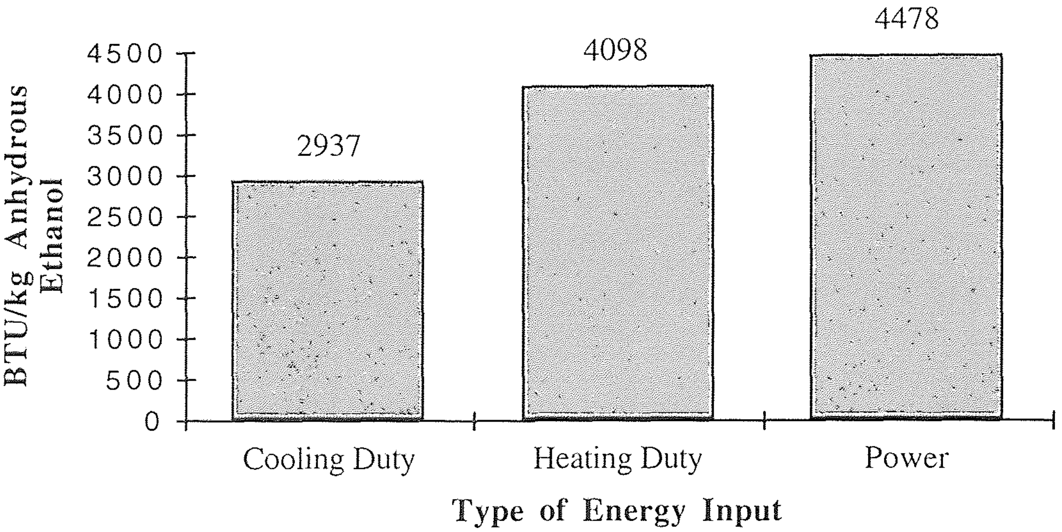

Figure 7: Energy Inputs for Anhydrous Ethanol Production from Corn

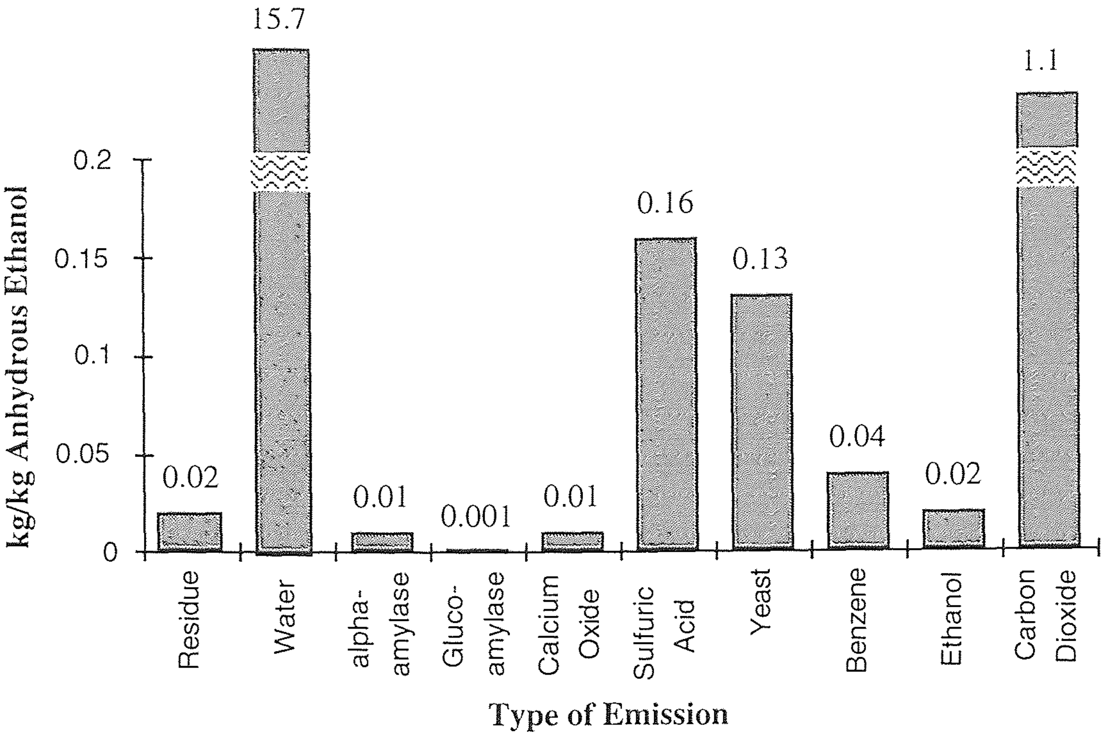

Figure 8: Emissions from Anhydrous Ethanol Production from Corn

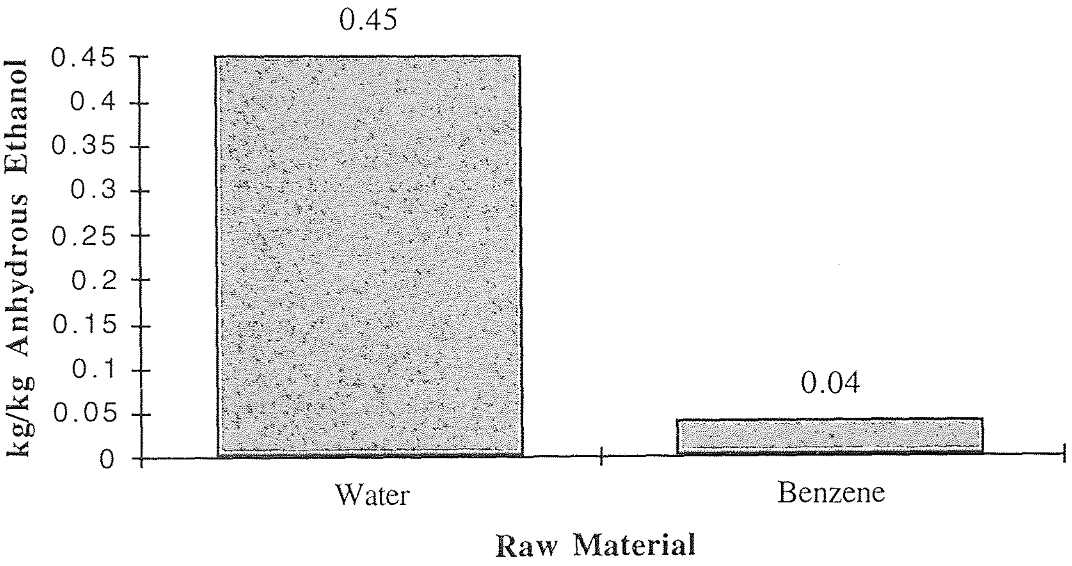

Figure 9: Raw Material Inputs for Anhydrous Ethanol Production from Ethylene

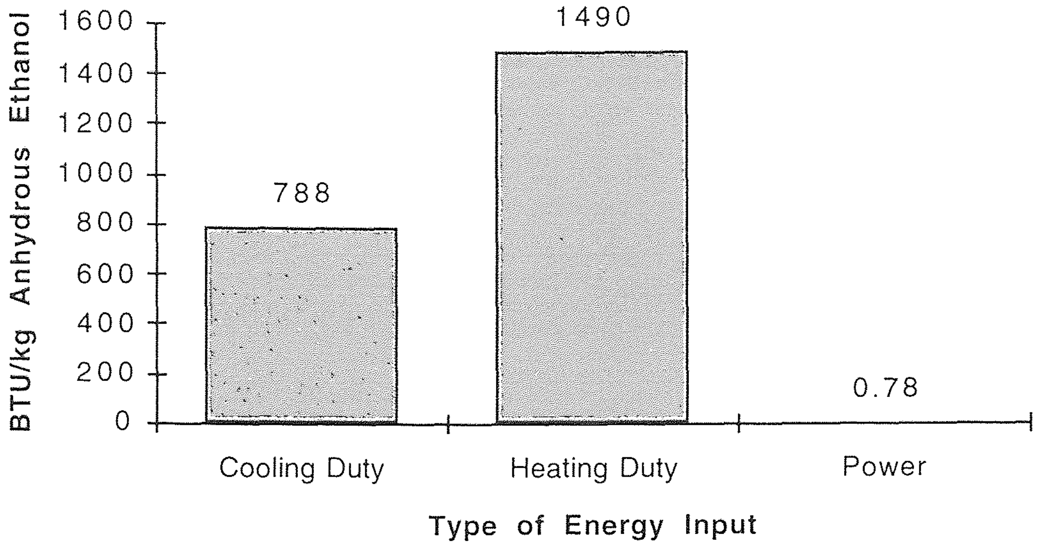

Figure 10: Energy Inputs for Anhydrous Ethanol Production from Ethylene

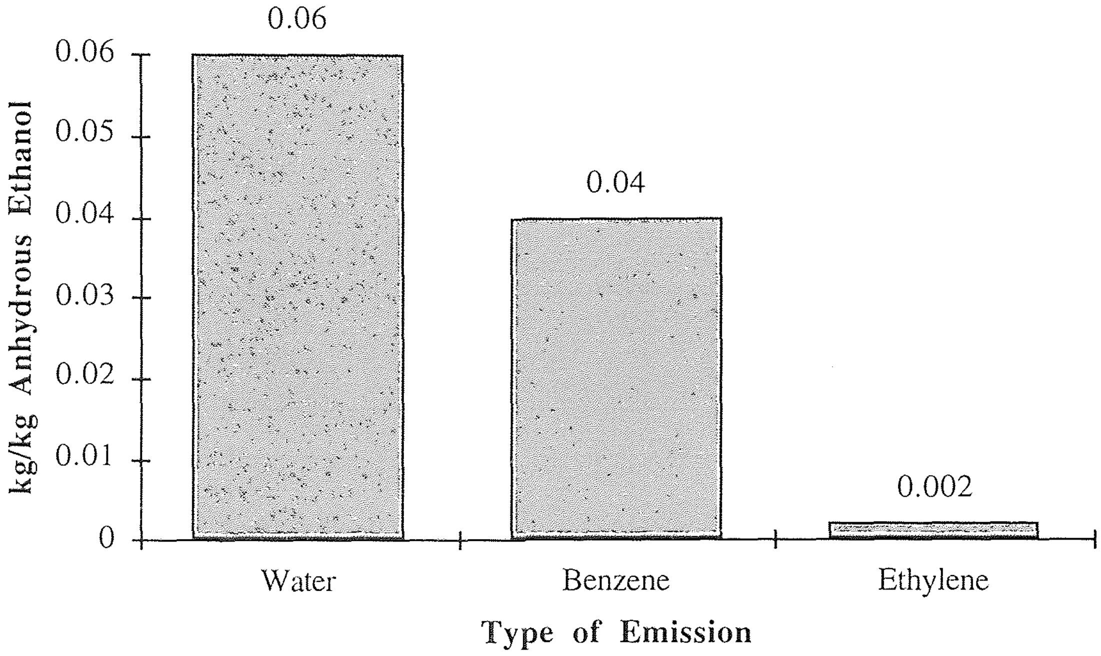

Figure 11: Emissions from Anhydrous Ethanol Production from Ethylene

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

This project has demonstrated the use of Life Cycle Analysis Methodology to analyze two methods of anhydrous ethanol production. The processes were modeled using BioPro Designer, a computer simulation program developed by Dr. Demetri Petrides of the New Jersey Institute of Technology. The information generated by this program was utilized to create eco-vectors associated with each step of the processes. These eco-vectors are an indication of the environmental "charge" associated with each step of the process. The result is an eco-vector for the final product. The eco-vector associated with anhydrous ethanol production from corn can be found in equation (39) in chapter three. The eco-vector associated with anhydrous ethanol production from ethylene can be found in equation (49) in chapter four. For the convenience of the reader, the information found in the eco-vectors associated with each process has been summarized in Chapter five.

6.2 Recommendations and Future Work

This study represents the first stage in the Life Cycle Analysis methodology, referred to as Life Cycle Inventory Analysis. The next step is to take the information generated during the Life Cycle Inventory Analysis step and assess the impact to the environment, or environmental loading, associated with each component of the eco-vector. This assessment, as mentioned in chapter two, should address ecological and human health considerations. Currently, there is no agreed on method to perform this assessment. Once this assessment is complete, both processes for ethanol could be compared in order to determine which one has a higher environmental load. After this step of the Life Cycle Analysis methodology is completed, the third step in the methodology can be performed.

As explained in Chapter two, this final step is called Life Cycle Improvement Analysis, where the processes are analyzed to determine ways to reduce the environmental load of the process. This can be done by analyzing the eco-vector associated with each step in the process. This last step can be a valuable tool for pollution prevention and waste minimization efforts.

APPENDIX A

STREAM REPORTS FROM BIOPRO DESIGNER SIMULATION FOR ANHYDROUS ETHANOL PRODUCTION FROM CORN

Table A-1: Inputs and Output Streams for Milling Process (GBX-101)

	STREAM S-101	**STREAM S-102**	**ENERGY (BTU/hr)**
Corn (kg/hr)	5.1×10^4	5.1×10^4	0
Cornmeal (kg/hr)	0	0	0
Power (BTU/hr)	0	0	4.0×10^4

Table A-2: Inputs and Outputs for Hydrolysis (R-102)

	STREAM S-102	**STREAM S-103**	**STREAM S-105**	**ENERGY (BTU/hr)**
Cornmeal (kg/hr)	5.1×10^4		0	0
Water (kg/hr)	0	6.9×10^3	6.9×10^3	0
Corn Residue (kg/hr)	0	0	1.5×10^4	0
Heating Duty (BTU/hr)	0	0	0	1.34×10^7
Power (BTU/hr)	0	0	0	1.18×10^6
Dextrin (kg/hr)	0	0	3.6×10^4	0

Table A-3: Inputs and Outputs for Saccharification (R-103)

	STREAM S-105	**STREAM S-109**	**STREAM S-110**	**ENERGY (BTU/hr)**
Glucoamylase (kg/hr)	0	17.4	17.4	0
α-amylase (kg/hr)	0	1.4×10^2	1.4×10^2	0
Water (kg/hr)	6.9×10^3	5.0×10^2	3.3×10^3	0
Cooling Duty (BTU/hr)	0	0	0	1.9×10^7
Corn Residue (kg/hr)	1.5×10^4	0	1.5×10^4	0
Power (BTU/hr)	0	0	0	1.0×10^6
Glucose (kg/hr)	0	0	4.0×10^4	0
Dextrin (kg/hr)	3.6×10^4	0	0	0

Table A-4: Inputs and Outputs for Mixer (M-102)

	STREAM S-111	**STREAM S-112**	**STREAM S-110**	**STREAM S-108**	**STREAM S-113**
Glucoamylase (kg/hr)	0	0	17.4	0	17.4
α-amylase (kg/hr)	0	0	1.4×10^2	0	1.4×10^2
Water (kg/hr)	0	0	3.4×10^3	2.8×10^5	2.8×10^5
Yeast (kg/hr)	0	2.7×10^2	0	0	2.7×10^2
Sulfuric Acid (kg/hr)	0	0	0	31	31
Calcium Oxide (kg/hr)	2.0×10^2	0	0	0	2.0×10^2
Corn Residue (kg/hr)	0	0	1.5×10^4	0	1.5×10^4
Glucose (kg/hr)	0	0	4.0×10^4	0	4.0×10^4

Table A-5: Inputs and Outputs for Storage (V-103)

	STREAM S-115	STREAM S-113
Glucoamylase (kg/hr)	17.4	17.4
α-amylase (kg/hr)	1.4×10^2	1.4×10^2
Water (kg/hr)	2.8×10^5	2.8×10^5
Yeast (kg/hr)	2.7×10^2	2.7×10^2
Sulfuric Acid (kg/hr)	31	31
Calcium Oxide (kg/hr)	2.0×10^2	2.0×10^2
Corn Residue (kg/hr)	1.5×10^4	1.5×10^4
Glucose (kg/hr)	4.0×10^4	4.0×10^4

Table A-6: Inputs and Outputs for Fermentation (R-101)

	STREAM S-115	STREAM S-116	STREAM S-117	STREAM S-118	ENERGY (BTU/hr)
Glucoamylase (kg/hr)	17.4	0	0	17.4	0
α-amylase (kg/hr)	138	0	0	1.4 x 10^2	0
Water (kg/hr)	2.8 x 10^5	0	0	2.8 x 10^5	0
Cooling Duty (BTU/hr)	0	0	0	0	6.49 x 10^6
Yeast (kg/hr)	269	0	0	2.2 x 10^3	0
Carbon Dioxide (kg/hr)	0	0	1.8.x 10^4	0	0
Ethanol (kg/hr)	0	0	0	1.9 x 10^4	0
Sulfuric Acid (kg/hr)	31	0	0	31	0
Calcium Oxide (kg/hr)	201	0	0	201	0
Corn Residue (kg/hr)	1.5 x 10^4	0	0	1.5 x 10^4	0
Power (BTU/hr)	0	0	0	0	7.9 x 10^7
Glucose (kg/hr)	4.0 x 10^4	0	0	4.0 x 10^4	0

Table A-7: Inputs and Outputs for Distillation Column (C-101)

	STREAM S-118	**STREAM S-106**	**STREAM S-130**	**ENERGY (BTU/hr)**
Glucoamylase (kg/hr)	17.4	0	17.4	0
α-amylase (kg/hr)	1.4 x 10^2	0	1.4 x 10^2	0
Water (kg/hr)	2.8 x 10^5	8.4 x 10^2	2.8 x 10^5	0
Cooling Duty (BTU/hr)	0	0	0	1.2 x 10^7
Yeast (kg/hr)	2.2 x 10^3	0	2.2 x 10^3	0
Carbon Dioxide (kg/hr)	0	0	0	0
Ethanol (kg/hr)	1.9 x 10^4	1.8 x 10^4	3.7 x 10^2	0
Sulfuric Acid (kg/hr)	31	0	31	0
Calcium Oxide (kg/hr)	201	0	201	0
Corn Residue (kg/hr)	1.5 x 10^4	0	1.5 x 10^4	0
Heating Duty (BTU/hr)	0	0	0	3.4 x 10^7
Glucose (kg/hr)	4.0 x 10^4	0	0	0

Table A-8: Inputs and Outputs for Plate and Frame Filter (PF-101)

	STREAM S-125	STREAM S-126	STREAM S-130	STREAM S-127	STREAM S-128	ENERGY (BTU/hr)
Glucoamylase (kg/hr)	0	0.348	17.4	17.1	0	0
α-amylase (kg/hr)	0	2.76	1.4×10^2	1.4×10^2	0	0
Water (kg/hr)	0	5.6×10^3	2.8×10^5	2.7×10^5	0	0
Yeast (kg/hr)	0	1.1×10^3	2.2×10^3	1.1×10^3	0	0
Ethanol (kg/hr)	0	7.5	3.7×10^2	3.7×10^2	0	0
Sulfuric Acid (kg/hr)	0	.62	31	31	0	0
Calcium Oxide (kg/hr)	0	2.0×10^2	2.0×10^2	2	0	0
Corn Residue (kg/hr)	0	1.5×10^4	1.5×10^4	1.5×10^3	0	0
Power (BTU/hr)	0	0	0		0	3.4×10^7
Glucose (kg/hr)	0	7.9×10^2	0	7.9	0	0

Table A-9: Inputs and Outputs for Heat Exchanger (E-103)

	STREAM S-106	**STREAM S-119**	**ENERGY (BTU/hr)**
Water (kg/hr)	8.4 x 10^2	8.4 x 10^2	0
Ethanol (kg/hr)	1.8 x 10^4	1.8 x 10^4	0
Cooling Duty (BTU/hr)	0	0	5.23 x 10^5

Table A-10: Material Inputs and Outputs for Receiver Tank (V-102)

	STREAM S-150	**STREAM S-119**
Water (kg/hr)	8.4 x 10^2	8.4 x 10^2
Ethanol (kg/hr)	1.8 x 10^4	1.8 x 10^4

Table A-11: Material Inputs and Outputs for Ethanol Dehydration

	STREAM S-150	**STREAM S-145**	**STREAM S-121**	**STREAM S-123**	**STREAM S-146**
Water (kg/hr)	8.4×10^2	0	0	8.4×10^2	0
Ethanol (kg/hr)	1.8×10^4	0	1.8×10^4	0	0
Benzene (kg/hr)	0	7.4×10^2	0	0	7.4×10^2

Table A-12: Energy Inputs for Alcohol Dehydration Process

	C-102	**E-101**	**E-104**	**C-103**	**C-104**	**E-102**	**E-105**
Cooling (BTU/hr)	4.7×10^7	2.1×10^5	7.0×10^5	3.3×10^6	4.1×10^6	2.0×10^3	2.5×10^5
Heating (BTU/hr)	1.5×10^7	0	0	5.2×10^6	4.2×10^6	0	0

APPENDIX B

STREAM REPORTS FROM BIOPRO DESIGNER SIMULATION FOR ANHYDROUS ETHANOL PRODUCTION FROM ETHYLENE

Table B-1: Inputs and Output Streams for Mixer (M-108)

	STREAM S-107	STREAM S-101	STREAM S-102	STREAM S-108
Ethylene (kg/hr)	1.1×10^4	5.6×10^2	0	1.2×10^4
Water (kg/hr)			8.2×10^3	8.2×10^3

Table B-2: Inputs and Outputs for Reactor (R-101)

	STREAM S-108	STREAM S-198	STREAM S-106	ENERGY
Water (kg/hr)	8.2×10^3	0	9.9×10^2	0
Ethylene (kg/hr)	1.2×10^4	0	5.9×10^2	0
Heating (BTU/hr)	0	0	0	8.2×10^5
Power (BTU/hr)	0	0	0	1.4×10^4
Ethanol (kg/hr)	0	0	1.8×10^4	0

Table B-3: Inputs and Outputs for Cooler (E-103)

	STREAM S-106	**STREAM S-104**	**ENERGY**
Water (kg/hr)	9.9×10^2	9.9×10^2	0
Ethylene (kg/hr)	5.9×10^2	5.9×10^2	0
Cooling (BTU/hr)	0	0	1.8×10^5
Ethanol (kg/hr)	1.8×10^4	1.8×10^4	0

Table B-4: Inputs and Outputs for Separator (CS-102)

	STREAM S-104	**STREAM S-105**	**STREAM S-109**
Water (kg/hr)	9.9×10^2	0	9.9×10^2
Ethylene (kg/hr)	5.9×10^2	5.9×10^2	0
Ethanol (kg/hr)	1.8×10^4	0	1.8×10^4

Table B-5: Inputs and Outputs for Purging Process (M-101)

	STREAM S-105	**STREAM S-101**	**STREAM S-110**
Ethylene (kg/hr)	5.9×10^2	5.6×10^2	30

Table B-6: Inputs and Outputs for Receiver Tank (V-102)

	STREAM S-109	**STREAM S-150**
Water (kg/hr)	9.9×10^2	9.9×10^2
Ethanol (kg/hr)	1.8×10^4	1.8×10^4

Table B-7: Material Inputs and Outputs for Ethanol Dehydration

	STREAM S-150	**STREAM S-145**	**STREAM S-112**	**STREAM S-114**	**STREAM S-146**
Water (kg/hr)	9.9×10^2	0	0	9.9×10^2	0
Ethyl Alcohol (kg/hr)	1.8×10^4	0	1.8×10^4	0	0
Benzene (kg/hr)	0	7.6×10^2	0	0	7.6×10^2

Table B-8: Energy Inputs for Ethanol Dehydration Process

	C-102	**E-101**	**E-104**	**C-103**	**C-104**	**E-102**	**E-105**
Cooling (BTU/hr)	4.8×10^6	1.7×10^5	3.5×10^5	3.8×10^6	4.7×10^6	1.9×10^3	2.9×10^5
Heating (BTU/hr)	1.6×10^7	0	0	5.6×10^6	4.8×10^6	0	0

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