CHAPTER III

EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Equipment

- Desktop computer (Pentium Dual-Core E5200, RAM 2 GB, Window 7 and Microsoft Office 2010)

3.1.2 Software

3.1.2.1 PRO/II version 9.1

The commercial simulator for simulate chemical processes.

3.1.2.2 SustainPro Program

The sustainability analysis tool on excel platform for perform sustainability analysis of process in term of safety, environmental and economic in order to make the process more sustainable.

3.1.2.3 SimaPro version 7.1

The commercial program for evaluate the environmental impacts using LCA technique.

3.1.2.4 ECON Software

The economic evaluation tool on excel platform for economic and profitability evaluation.

3.2 Experimental Procedures

3.2.1 Literature Survey

- Study and review the background of bioethanol production including their environmental impact through LCA technique.

- Study the feasibility of the potential of lignocellulosic materials in Thailand and select the best material for simulate the process. Consequently, rice straw is selected as a raw material for designing the process in this study.
- Collect the composition data of rice straw.
- Collect the information of operating condition for bioethanol production from lignocellulosic materials process.
- Study various alternative processes for improvement of the base case design in terms of energy and waste.

3.2.2 Process Simulation

- Simulate the base case process design based on rice straw as raw material from process flow diagram shown in Figure 3.1 using PRO/II 9.1 simulation program.
- Make assumptions based on the goal definition.

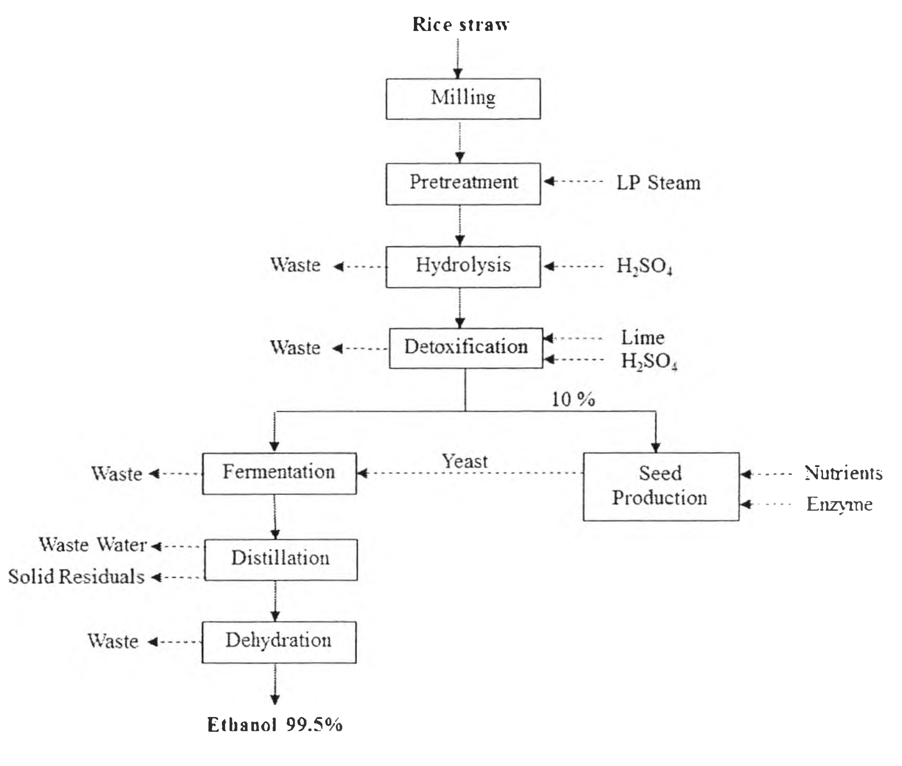

Figure 3.1 Bioethanol production process from rice straw (Binod *et al.*, 2010; NREL, 1999).

3.2.3 Sustainability Analysis

Use software named—SustainPro—(Carvalho *et al*, 2008; 2009) to generate new design alternatives which are divided into six steps as follows:

3.2.3.1 Collection of Steady-State Data

This step involves the collection of mass and energy balance data from simulation results with PRO/II 9.1.

3.2.3.2 Flowsheet Decomposition

The objective of this step is to identify all the mass and energy flow-paths in the process by decomposing into open-paths and close-paths for each compound in the process. An open-path consists of an entrance and an exit of a specific compound in the process. The closed-paths are the process recycles with respect to each compound in the process.

3.2.3.3 Calculation of Indicator Sensitivity Analysis

The objective of this step is to determine the parameters (indicators) for the sensitivity analysis.

- *Material-Value Added (MVA)*

This is calculated from the difference between the value of the component path flows outside the process boundaries and the costs in raw material consumption or feed cost as shown in Equation 3.1. Negative values for MVA indicate value lost and show that there are potentials for improving the economic efficiency. MVA is calculated in cost units per year.

$$MVA = (mass)\ (sales\ price - raw\ material\ cost) \qquad (eq.\ 3.1)$$

- *Energy and Waste Cost (EWC)*

The EWC indicator consists of two parts: EC considers the energy costs and WC the process waste costs associated with a given path, by allocating the utility consumption and waste treatment costs. They indicate the maximum theoretical saving potential for a given path. High EWC values indicate high energy consumption and waste costs that could be reduced by decreasing the path flow or the duties. EWC is calculated in cost units per year.

$$EWC = EC + WC \quad \text{(eq. 3.2)}$$

$$EC = (\text{duty})(\text{cost}) \times \frac{\text{component mass x characteristic physical property}}{\text{sum of all components (mass x characteristic physical property)}} \quad \text{(eq. 3.3)}$$

$$WC = (\text{mass})(\text{waste treatment cost}) \quad \text{(eq. 3.4)}$$

- *Reaction Quality (RQ)*

This indicator measures the effect a component path flow may have on the reactions that occur in its path. If the RQ value is positive, the path flow has a positive effect on the overall plant productivity. Negative values indicate an undesirably located component path flow in the process.

$$RQ = \frac{\text{extent of reactor x reaction parameter}}{\text{sum of desired products}} \quad \text{(eq. 3.5)}$$

- *Accumulation Factor (AF)*

AF provides a way of measuring the accumulative behavior of individual components in recycles. Note that the term ''accumulation'' is not used to mean inventory in this method. It indicates the amount of material being recycled relative to its input to the process and/or output from the process.

$$AF = \frac{\text{mass of component in recycle}}{\text{sum of component mass leaving recycle}} \quad \text{(eq. 3.6)}$$

- *Total Value Added (TVA)*

This indicator describes the economic influence a component path flow may have on the variable process costs. Negative TVA values indicate improvement potentials in the process. Still, if a path flow has a high EWC value that is compensated by a high MVA value and gave a positive TVA value it could still be possible to reduce the energy cost. TVA is calculated in cost units per year.

$$TVA = MVA - EWC \qquad \text{(eq. 3.7)}$$

- *Energy Accumulation Factor (EAF)*

The energy accumulation factor (EAF), calculates the accumulative behavior of energy in an energy cycle path flow. Since it is of interest to recycle or recover energy, these factors should be as large as possible in order to save energy. The energy accumulation factor could be calculated as:

$$EAF = \frac{\text{energy recycled}}{\text{energy leaving the recycle}} \qquad \text{(eq. 3.8)}$$

- *Total Demand Cost (TDC)*

This indicator is applied only to open-paths and traces the energy flows across the process. For each demand in the process the sum of all DC, which passes through it, are calculated. DC can be calculated using the following equation:

$$DC_{Su,d} = PE_{Su}\, EOP_{Su,d} \qquad \text{(eq. 3.9)}$$

Where, PE is the utility cost, in units of price/energy. The total cost for all the paths is expressed by:

$$TDC_d = \sum_{Su=1}^{SS} DC_{Su,d}$$

(eq. 3.10)

Where, SS is the total number of supplies (Su) with significant energy contributions corresponding to their demands (d). High values of this indicator identify the demands that consume the largest values of energy, so these are the process parts, which are more adapted to heat integration.

3.2.3.4 Calculation of Sustainability Metric

The use of the sustainability metrics follow the simple rule that the lower the value of the metric the more effective (sustainable) the process. A lower value of the metric indicates that either the impact of the process is less or the output of the process is more. The metrics calculated in this analysis are shown in Table 3.1, divided into different groups. The results report the energy used, raw material used, water consumption, and value added of this process. After alternative designs perform in SustainPro, this work would compare these new values with those of the base case design. Then, results are shown in terms of how much improvement is achieved by alternative designs.

Table 3.1 The sustainability metrics considered in SustainPro

Group	Metrics
Energy	Total Net Primary Energy Usage rate (GJ/y)
	% Total Net Primary Energy sourced from renewable
	Total Net Primary Energy Usage per Kg product (kJ/kg)
	Total Net Primary Energy Usage per unit value added (kJ/$)
Material	Total raw materials used per kg product (kg/kg)
	Total raw materials used per unit value added
	Fraction of raw materials recycled within company
	Fraction of raw materials recycled from consumers
	Hazardous raw material per kg product
Water	Net water consumed per unit mass of product (kg/kg)
	Net water consumed per unit value added
Economic	Value added ($/yr)

3.2.3.5 Calculate Safety Indices

The safety of the process is another important parameter that should be taken into account. In order to achieve the inherently safety index the value for some sub-indices need to be calculated. These sub-indices can be divided into two groups, one group, which takes into account the chemical inherent safety, and the other group that is dependent on the process inherent safety. A scale of scores for each sub-index has been defined. These scales are based on the values of some safety parameters, such as the explosiveness, the toxicity, the pressure of the process and so on.

Table 3.2 List of safety indices and their sources (Carvalho *et al.*, 2008)

Total Inherent Safety Index (ISI)			
Chemical inherent safety index, I_{ci}	**Score**	**Process inherent safety index , I_{pi}**	**Score**
Subindices for reactions hazards		Subindices for process conditions	
Heat of the main reaction, I_{rm}	0-4	Inventory, I_I	0-5
Heat of the side reactions, I_{rs}	0-4	Process temperature, I_t	0-4
Chemical Interaction, I_{int}	0-4	Process pressure, I_p	0-4
Subindices for hazardous substances		Subindices for process system	
Flammability, I_{fl}	0-4	Equipment, I_{eq}	
Explosiveness, I_{ex}	0-4	I_{ISBL}	0-4
Toxicity, I_{tox}	0-6	I_{OSBL}	0-3
Corrosivity, I_{cor}	0-2	Process structure, I_{st}	0-5
Maximum, I_{ci} score	28	Maximum, I_{pi} score	25
Maximum ISI score	**53**		

The sum of all the sub-indices scores is the inherent safety index value; this parameter has the maximum value of 53. Note that the higher is the inherent safety index value the more unsafely is the process, so the aim in all alternative designs is to try to reduce or (at least same value) as much as possible. In Table 3.2 the entire set of sub-indices, as well as the respective scales, are specified.

3.2.3.6 Generate New Design Alternatives

Alternatives are created based on operability, energy consumption, waste reduction, environmental impact, safety and cost. Alternative designs are simulated with PRO/II 9.1.

3.2.4 <u>Economic Evaluation</u>

This part can be done by using—ECON software—(Saengwirun, 2011) to evaluate the economic section which is divided into three steps as follows:

3.2.4.1 Collect the Price and Economic Information

The price of all raw material, product and utility prices are collected. Moreover, the data that related to economic is also collected for example; the inflation rate, MARR, depreciation rate and tax rate.

3.2.4.2 Unit Sizing

The data of each unit operation can be collected from PRO/II 9.1. The size of the units are calculated which up to the main parameters of that unit for instance; the area of heat exchanger can be calculated from temperature of inlet and outlet streams, overall heat transfer coefficient and duty.

3.2.4.3 Calculate Capital Cost and Operating Cost

Capital cost can be calculated from the size and operating condition of units. Capital cost is divided into two sub costs; direct cost and indirect cost. Direct cost is mainly come from the unit cost, install cost, building and yard improvement. Indirect cost is mainly construction expenses and contingency. For operating cost is the cost that has to expenses every year which have raw material and utility cost, labor cost, maintenance and operating supplies cost, and plant overhead cost.

3.2.4.4 Economic Evaluation

The profit of the project is analyzed in term of IRR, breakeven point and net present value (NPV) which up to the project life.

3.2.5 Life cycle Assessment (LCA)

The assessment is carried out in four phases consisting of:

3.2.5.1 Goal and Scope

- Identify functional unit of bioethanol production: In this study, one kilogram of bioethanol 99.5 wt% purity is used as functional unit.
- Determine system boundaries of bioethanol production (what is and is not included in this study) based on the goal definition. In this study, the selected system boundary of bioethanol production process is shown in Figure 3.2.

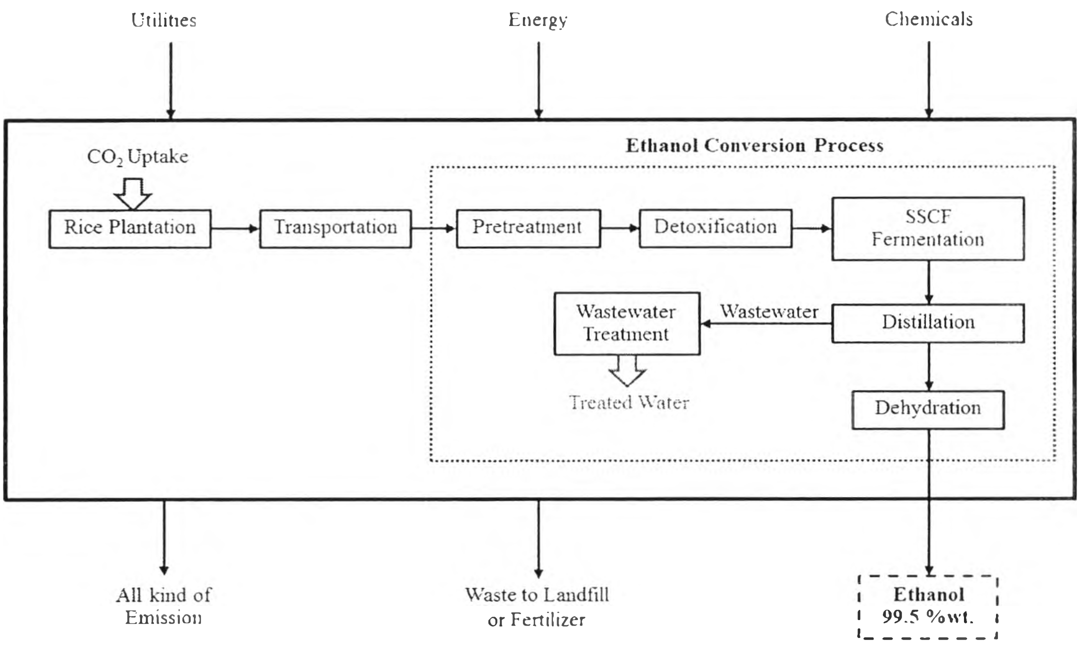

Figure 3.2 System boundary for bioethanol conversion process.

3.2.5.2 Inventory Analysis

- Collect data related to environment and technical quantities for all relevant and within the study boundaries unit processes, for example;

- Raw materials, utilities, and energy consumptions
- Air and water emissions
- Waste generations

The sources of inventory data of bioethanol conversion process are given in Table 3.3.

Table 3.3 Sources of inventory data of bioethanol conversion process

Step	Type of data	Data source
Rice plantation and transportation	2^{nd} Data	Niracharopas, 2011
Ethanol conversion	2^{nd} Data	Process simulation
Wastewater treatment	2^{nd} Data	NREL

- Quantify how much energy and raw materials are used, and how much solid, liquid and gaseous waste is generated, at each stage of the product's life.

3.2.5.3 Life Cycle Impact Assessment (LCIA)

- Calculate impact potentials based on the LCI results by using software named—SimaPro version 7.1— with CML 2 baseline 2000 method.
- Analyze and compare the impacts on human health and the environment burdens associated with raw material and energy inputs and environmental releases quantified by the inventory.

3.2.5.4 Interpretation

- Evaluate the greenhouse gas (GHG) emissions per one kilogram of ethanol for the design of bioethanol conversion process.

- Evaluate opportunities to reduce energy, material inputs, or environmental impacts at each stage of the product life-cycle.
- Analyze an improvement, in which recommendations are made based on the results of the inventory and impact stages.

3.2.6 Alternative Designs

- Generate new design alternatives using PRO/II and consider the results from sustainability analysis, economic evaluation and life cycle assessment of the base case design.
- Perform sustainability analysis of alternative designs to calculate sustainability metrics and safety indices.
- Perform economic evaluation of alternative designs to calculate the profitability.
- Perform life cycle assessment of alternative designs to evaluate environmental impact.

3.2.7 Comparison

The results between the base case and alternatives are compared to determine the improvement achieved by alternative designs. The results are given in terms of;

- Water consumption
- Sustainability metrics
- Safety indices
- Profitability
- Life cycle assessment