CHAPTER IV
RESULTS AND DISCUSSION

4.1 Base Case Design

4.1.1 Process Simulation of Base Case Design

A typical ethanol production based on the current ethanol manufacturing process, as shown in Figure 4.1 was selected as the base case design.

Lists of components, process conditions, reactions and process flow sheet are given in Appendix A, B, C and D, respectively.

This process design was modeled and simulated though the use of PRO/II 9.1, (PRO/II, 2011) process simulator as shown in Figure 4.2. Process contains 67 streams and 39 unit operations. The capacity of this plant is 150,000 L/day or around 50 ML/year. Cassava rhizome is milled into small pieces and then sent to the pretreatment area. After that, concentrated sulfuric acid is added to the hydrolysis reactor to convert cellulose and Hemicellulose into C6 and C5 sugars. The hydrolyzate is then sent to detoxification part to remove contaminate composition such as furfural and HMF. Then, the detoxified hydrolyzate is split to yeast seed production for 10 % and the other rest is sent to the fermenter by yeast from seed production. Finally, they are passed through ethanol recovery section, which are distillation, and dehydration, to achieve the final product which is ethanol with 99.5 % purity.

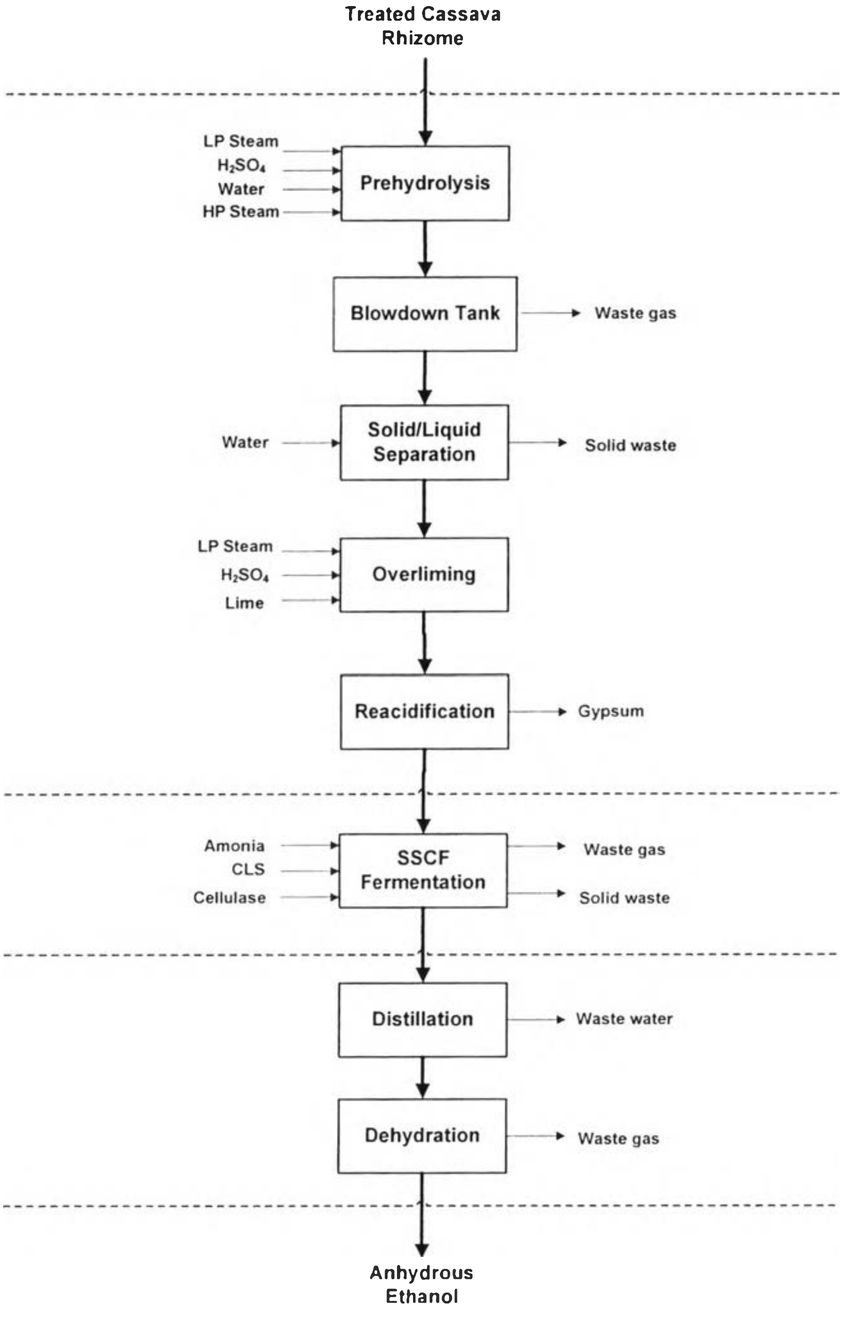

Figure 4.1 Base case process flow sheet and unit operations for bioethanol production process from cassava rhizome.

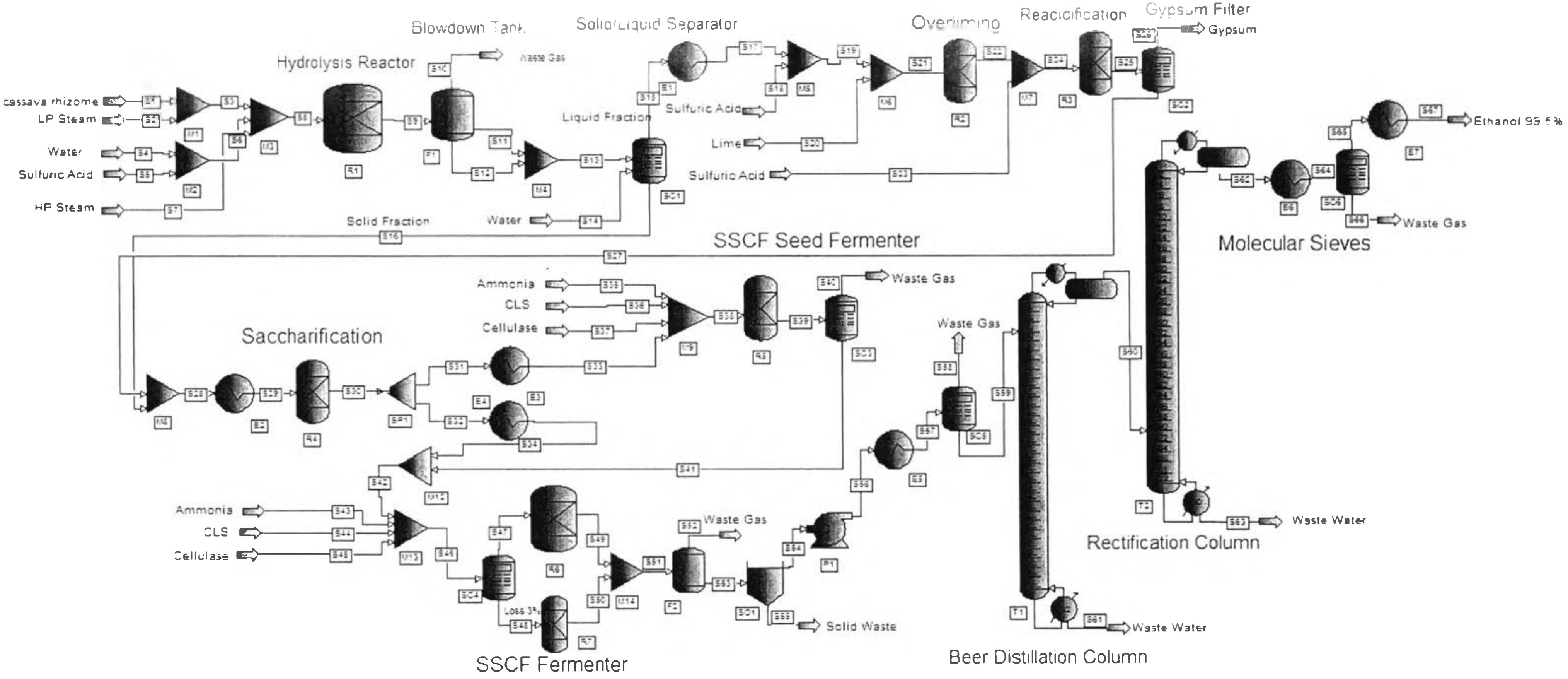

Figure 4.2 Flowsheet of the bioethanol production process from cassava rhizome for base case design implemented in PRO/II

The feedstock, in this case cassava rhizome, is delivered to the feed handling area for size reduction and storage. The washed, shredded cassava rhizome is fed to pretreatment and first steamed with low-pressure steam in a presteamer (M1) to about 100°C in order to removes non-condensables that can take up space in the reactor and solubilize some of the lignin in the feedstock and expose the cellulose for subsequent enzymatic hydrolysis. After the cassava rhizome is steamed, acid is added to the reactor. Concentrated sulfuric acid is diluted until the mixture (the total water, including steam and acid) in the reactor is 1.1% sulfuric acid (M2). The reactor is brought up to temperature by direct injection of 13 atm (192°C saturation temperature and 76°C superheat) steam.

The pretreatment reactor (R1) operates at 12.1 atm (177 psia) pressure and 190°C. The exiting material from the pretreatment reactor is flash cooled to 1 atm (14.7 psia) in F1. In this flash, 7.8% of the acetic acid and 61% of the furfural and HMF are removed as vapor. The hydrolyzate slurry with 21% insoluble solids is conveyed to a filter (SC1) for separate the solids and the liquids. The liquids are separated from the solids to facilitate conditioning of the liquid portion to reduce toxicity of the stream to downstream fermentation.

After the separation step, the material is overlimed. Lime is added in reactor R2 to raise the pH to 10. The filtration is assumed to remove 99.5% of the precipitated gypsum and the solids are assumed to contain 20% liquid. After the gypsum is filtered, the conditioned hydrolyzate liquid is recombined with hydrolyzate solids (which were separated in SC1) in mixer (M8).

Detoxified and diluted hydrolyzate fed to the saccharification vessels is about 20% total solids (soluble and insoluble solids) including the dilution that will occur when the cellulase stream is mixed in. The enzyme loading is determined by the amount of cellulose present in the hydrolyzate and the target hydrolysis conversion level with the combined residence time of the saccharification reactor (R4) and the fermenters. A heat exchanger (E2) is used to heat the 51°C hydrolyzate slurry exiting the re-acidification reactor (R3) to 65°C, the saccharification temperature, using low-pressure steam. The saccharified slurry contains 38.2% sugars including 15.6% glucose and 22.6% xylose.

Saccharified slurry is cooled (E3, E4) to 41°C and a portion is sent to the seed production area. The total amount of saccharified slurry split off to seed production is 10%. The required inoculum volume has been experimentally determined to be 10%, both for the *Zymomonas mobilis* (*Z. mobilis)* seed train and the production train. Inaddition, inoculum from the seed train at a ratio of 1/10th of the hydrolyzate is fed along with corn steep liquor, added as a nutrient at a rate of 0.25% , and Diammonium Phosphate (DAP), added as a nutrient at a rate of 0.33 g/L. The reactions and conversions used in the production SSCF fermenter are given in Tables B3, B4 and B5.

In addition to fermenting sugars to ethanol, sugars are converted to other products because of the presence of contaminating organisms. A total of 3% of the sugars available for fermentation are assumed lost to contamination. This is modeled as a side stream (bypassing fermentation) where sugars are reacted to form lactic acid. This allows the model to simply assign a percent loss to contamination and the conversions in the fermentor model do not have to be adjusted. The loss to other products that caused by *Z. mobilis* are given in the SSCF contamination loss reactions in Table B6.

Product from the fermentation is first preheated with heat exchanger (E5). The beer column (T1) operates in a mode to remove the CO_2 and as little ethanol as possible overhead, while removing about 90% of the water to the bottoms. The ethanol is removed as a vapor side draw from the column and fed directly to the rectification column (T2). This separation is accomplished with 32 actual trays with the feed entering on the fourth tray from the top. Both columns (T1 and T2) are operated below 2 atm. (30 psia.) overhead pressure. Table C7 summarizes the design specifications used for beer distillation column.

The vapor side draw from T1 is fed directly to T2, the rectification column. This column uses 60 actual trays with the feed on actual tray 50 from the top. The required reflux ratio is 3.2:1 to obtain a vapor overhead mixture of 93.9% w/w ethanol and a bottoms composition of 0.06% w/w ethanol. Only 0.2% of the ethanol from fermentation is lost in the bottoms. The composition of 6.1% water in the feed to the adsorption column.

Overhead vapor from T2 is fed to the molecular sieve adsorption unit (SC6). Saturated vapor from the distillation is first superheated and fed to one of two adsorption columns. The adsorption column removes 95% of the water and a small portion of ethanol. The 99.5% pure ethanol vapor is cooled by heat exchange against regenerate condensate and finally condensed and pumped to storage.

From Figure 4.2, in the ethanol production process from cassava rhizome, there are 9 waste streams S10, S26, S40, S52, S55, S58, S61, S63 and S66:

- S10 stream is waste gases that mainly are furfural, HMF and steam.
- S26 stream is gypsum waste.
- S40, S52 and S58 are flue gas streams with large amounts of CO_2
- S55 streams mainly contain solid contaminant as lignin and ash.
- S61, S63 and S66 streams contain mainly water.

In order to make the base case design more sustainable, sustainability analysis is performed to generate new design alternatives as can be seen in next section.

4.1.2 Sustainability Analysis of Base Case Design

4.1.2.1 Sustainability Results

SustainPro was used to analyze relevant indicators in sustainability results of the base case design as well as new designs. This software classifies the sustainability results into 3 groups: energy, material, and water. The calculated sustainability results for the base case design are given in 4.1.

Table 4.1 Sustainability results of the base case design

Results		**Base Case**
Energy	Total Net Primary Energy Usage rate (GJ/y)	492,628.061
	% Total Net Primary Energy sourced from renewables	1.000
	Total Net Primary Energy Usage per Kg product (kJ/kg)	12,528.610
Material	Total raw materials used per kg product (kg/kg)	7.686
	Fraction of raw materials recycled within company	0.000
	Fraction of raw materials recycled from consumers	0.000
	Hazardous raw material per kg product	0.128
Water	Net water consumed per unit mass of product (kg/kg)	4.392
	Net water consumed per unit value added	0.053

4.1.2.2 Indicator Results

The indicators in terms of open paths (OP) and closed paths (CP), Open paths (OP) are paths taken by the compounds present in the system as they enter and leave the process, closed paths (CP) follow similar concept as the OP, but are obviously circular paths in the process by recycling. The SustainPro decomposed the base case flowsheet into 333 open-paths (OP) and zero closed-paths because the process does not have any recycle streams. The significant sensitive indicators are listed in Table 4.2.

Table 4.2 List of the significant sensitive indicators for the open-paths for the base case design

Path	MVA	Probability	Path	EWC	Probability	Path	TVA	Probability
OP 322 CSL S44-S61	-553.4118378	High	OP 67 Ethanol P R6-S67	795.4947197	Medium	OP 322 CSL S44-S61	-553.4208932	High
OP 206 **Water S14-S52**	-505.9690824	High	OP 43 Xylose P R1-S61	270.9546434	Low	**OP 206** **Water S14-S52**	-505.9691713	High
OP 15 **Lignin S1-S55**	-440.496763	High	OP 50 Xylose P R1-S61	145.3521029	Low	**OP 15** **Lignin S1-S55**	-473.1252671	High
OP 318 CSL S36-S61	-376.3200497	High	OP 35 Glucose P R4-S61	102.8091235	Low	OP 318 CSL S36-S61	-376.3262316	High
OP 326 Cellulase S45-S55	-299.59441	High	OP 62 Ethanol P R5-S67	74.91539847	Medium	OP 326 Cellulase S45-S55	-299.6223494	High
OP 222 **Water S14-S52**	-134.4981105	High	OP 44 Xylose P R1-R R6	42.21961989	Low	OP 43 Xylose P R1-S61	-270.9546434	Low
OP 139 **Water S4-S52**	-127.3436715	High	**OP 15** **Lignin S1-S55**	32.62850409	High	OP 50 Xylose P R1-S61	-145.3521029	Low
OP 173 **Water S7-S52**	-80.76308145	High	OP 36 Glucose P R4-R R6	32.08323439	Low	**OP 222** **Water S14-S52**	-134.4981226	High
OP 211 **Water S14-S61**	-67.58765465	High	**OP 209** **Water S14-S66**	18.34001626	High	**OP 139** **Water S4-S52**	-127.3436938	High
OP 199 **Water S14-S52**	-56.19067756	High	OP 51 Xylose P R1-R R6	17.47142581	Low	OP 35 Glucose P R4-S61	-102.8091235	Low
OP 14 **Lignin S1-S55**	-48.94408477	High	OP 21 Glucose P R1- S61	6.855880046	Low	**OP 173** **Water S7-S52**	-80.76309563	High
OP 10 Hemicellulose S1-S55	-40.23479393	High	**OP 14** **Lignin S1-S55**	5.681171501	High	**OP 211** **Water S14-S61**	-68.47169286	High
OP 155 **Water S4-S52**	-33.85084939	High	OP 39 Xylose P R1-S61	5.423236758	Low	**OP 199** **Water S14-S52**	-56.19069028	High
OP 325 Cellulase S37-S55	-29.959441	High	OP 6 Cellulose S1-R R4	5.184746278	Low	**OP 14** **Lignin S1-S55**	-54.62525628	High
OP 189 **Water S7-S52**	-21.46866722	High	**OP 225** **Water S14-S66**	4.875166492	High	OP 44 Xylose P R1-R R6	-42.21961989	Low
OP 106 **Water S2-S52**	-20.10741065	High	**OP 142** **Water S4-S66**	4.615865054	High	OP 10 Hemicellulose S1-S55	-41.13323471	High
OP 227 **Water S14-S61**	-17.96633858	High	OP 42 Xylose P R1-R R5	4.439379577	Low	**OP 155** **Water S4-S52**	-33.85085242	High
OP 144 **Water S4-S61**	-17.0106443	High	OP 34 Glucose P R4-R R5	3.340191109	Low	OP 36 Glucose P R4-R R6	-32.08323439	Low

As shown in Table 4.2, path is the course that a component makes from its entrance to its exit through an output stream. The second line of each path identifies to the component and the path it follow (from starting stream to final stream). probability means probability to improve that path. According to MVA and TVA result, if the score had high negative value which mean them ware the top priority to improve by increasing value to be positive. For EWC, if the score had high value which mean them ware the top priority to improve by reducing value to be zero. The bold text is stand for the path that will be focused on.

From the TVA result, the highest value of indicator was OP 322 that is Corn steep liquor (CSL) because the price as raw material is very expensive (0.800 $/kg) therefore it effects to the economic section. Considering the improvement of it, corn steep liquor (CSL) is the water with nutrients that serve as a nutrient source in the seed train and SSCF, so it is not seem reasonable to be separating and recycling to the process. Cellulase is enzyme which used in saccharification and co-fermantation process. As the same reason with corn steep liquor (CSL), cellulase is impact only economic issue but not impact environmental issue of the process that much, so it will not be analyzed.The most of indicators indicate to water which came from S4, S7 and S14 and exit at S52, S61 and S66 which is reasonable because these streams have very high flow rate of water and contaminants therefore they were one of the targets to improve. Regarding the sugars, they can be recycled along with the water. Moreover, lignin was another target for potential improvement as there was huge amount of it in S55 which could possibly be used as energy source.

After the consideration, it was decided to focus on the analysis of water and lignin. Using the Indicators Sensitivity Analysis Algorithm (ISA) in SustainPro, the OPs that are intended to analyze are evaluated and given scores to the ones with the highest potential for improvement, and these results are displayed below:

Table 4.3 Open-paths, components, paths, indicators and scores in the process for the indicators chosen to further analyze as good targets for improvement

Path	Component	Path	Indicator	Scores
OP 142	H_2O	S4-S66	MVA, EWC, TVA	34
OP 211	H_2O	S14-S61	MVA, EWC, TVA	33
OP 144	H_2O	S4-S61	MVA, EWC, TVA	32
OP 225	H_2O	S14-S66	MVA, EWC, TVA	29
OP 227	H_2O	S14-S61	MVA, EWC, TVA	24
OP 199	H_2O	S14-S52	MVA, EWC, TVA	22
OP 206	H_2O	S14-S52	MVA, EWC, TVA	20
OP 173	H_2O	S7-S52	MVA, EWC, TVA	18
OP 139	H_2O	S4-S52	MVA, EWC, TVA	18
OP 106	H_2O	S2-S52	MVA, EWC, TVA	18
OP 15	Lignin	S1-S55	MVA, EWC, TVA	14
OP 14	Lignin	S1-S55	MVA, EWC, TVA	14
OP 189	H_2O	S7-S52	MVA, EWC, TVA	12
OP 155	H_2O	S4-S52	MVA, EWC, TVA	12
OP 222	H_2O	S14-S52	MVA, EWC, TVA	10

As shown in Table 4.3, water from S4 and S14 to S61 and S66 had the highest score which mean them were the top priority to improve. Furthermore, water from S14 to S52 also had high score and they affected many paths and indicators. For water from S2 and S7 had lower score than other water path which mean it was not affect the overall improvement. The lignin also had low score because of the price of it compare to water. Nevertheless, it does not mean it is not importance when considering the quantity of it as the waste which is huge. To consider these streams in tern of sensitivity, next section will show the variation of indicator when they are influenced by the change of variables of these path.

4.1.3 Economic Evaluation of Base Case Design

Since the implementation of the final design will most likely be based on economic factors, assuming all other issues have been found acceptable, every feasible and sustainable design alternative also needs an economic analysis.

According to the methods of economic evaluation by SustainPro, the indicators MVA and TVA can said that whether the economic sustainability of the process was improved or not. However, it does not take the investment of the process in account. From this reason, this section of the report serves as extra information of economic issue for the base case design which was calculated by using ECON software (Saengwirun, 2011).

This process design was modeled and simulated by the PRO/II 9.1 as mention before. The capacity of this plant is 150,000 L/day or around 50 ML/year, plant operate 330 days/year and annual load is approximately 8,000 hours/year.

4.1.3.1 Capital Cost of Base Case Design

The outcome of the Total Capital Investment (TCI) calculations for the base case design was 82.9 MM$. The greatest share of 71.1 % was from direct cost section, followed by indirect cost section and working capital section shared 28.5 % and 0.4 % respectively which is better explained in Appendix E.5 and its breakdown can be seen in Figure 4.3. For this research, capital cost including building, yard improvement and service facilities, and land (Outside Battery Limits, OSBL).

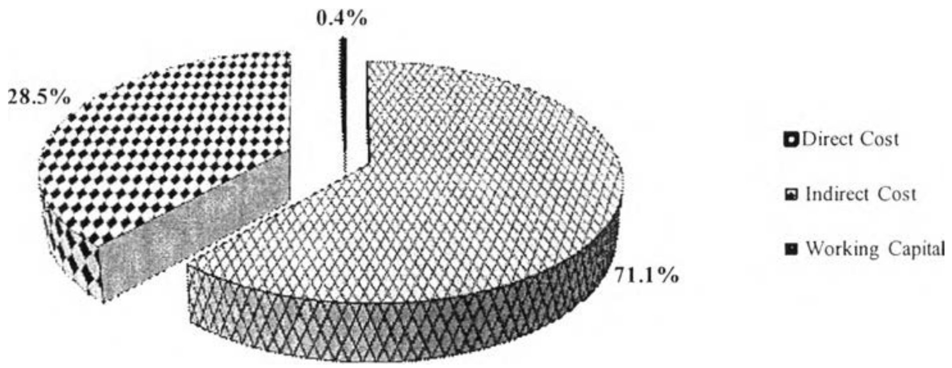

Figure 4.3 Breakdown of the total capital investment.

The direct costs are clearly what takes the largest piece, thus it is interesting to see what constitutes the direct costs.

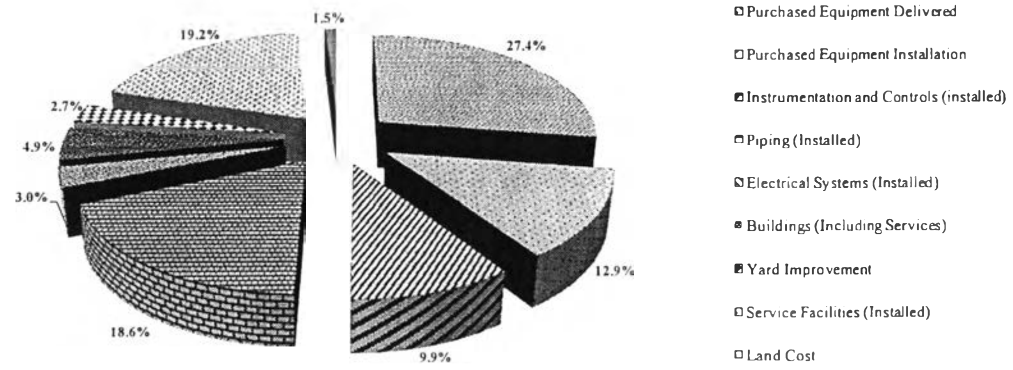

Figure 4.4 Breakdown of the direct cost.

As can be seen from Figure 4.4, the equipment costs (purchased equipment delivered) had the largest weight on the direct costs, hence is what the most influences the TCI. Appendix E.4 summarizes sizing and purchase cost of each equipment. Next is the equipment costs breakdown to gain further insight.

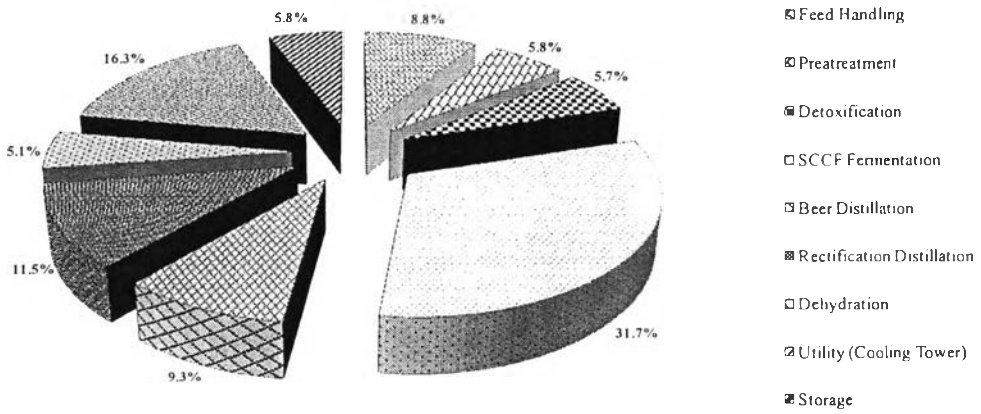

Figure 4.5 Contribution to equipment costs of each area of the process.

As shown in Figure 4.5, SSCF fermentation section had the highest portion for all equipment units because SSCF fermentation are largest area of process in ethanol production plant which shared 31.7 %, followed by utility, rectification distillation, beer distillation, feed handling, pretreatment, storage, detoxification and dehydration section shared 16.3 %, 11.5 %, 9.3 %, 8.8 %, 5.8 %, 5.8 %, 5.7 % and 5.1 %, respectively. The improvement of alternative process have to also consider cost of the equipment because if the environmental impacts and utilities are reduce but the increasing of equipment cost is very huge, that process is still not realistic. The importance thing is to balance these factors to optimum point.

4.1.3.2 Operating Cost of Base Case Design

The result of the total production cost (without depreciation) calculations for the base case design was 25.6 MM$. The greatest share of 71.9 % was from variable cost section, followed by general expense section, plant overhead section and fixed charges section shared 11.1 % , 9.3 % and 7.7 % respectively which has better details in Appendix E.6. The breakdown of the total product cost can be seen in Figure 4.6.

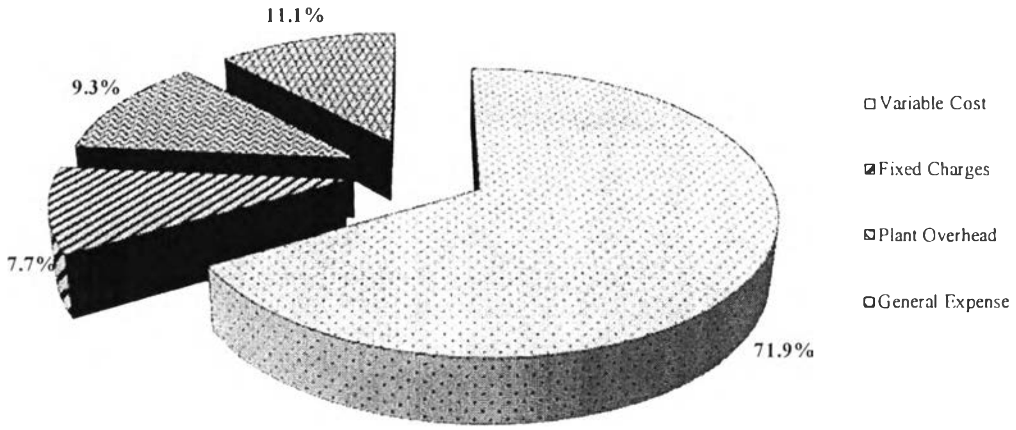

Figure 4.6 Breakdown of the total production cost.

As shown in Figure 4.6, the variable cost was the highest portion for total production cost which mainly came from raw materials and utility cost. Therefore, our first interesting aspect for operating cost of the base case design was to show each of raw material and utility prices compared to production capacity to see which were the ones with a larger weight on 0.69 \$/L of ethanol (0.874 \$/kg), and these results are presented in Figure 4.7 and Figure 4.8, respectively. Appendix E.2 and E.3 summarizes raw materials, product and utility annual price, respectively.

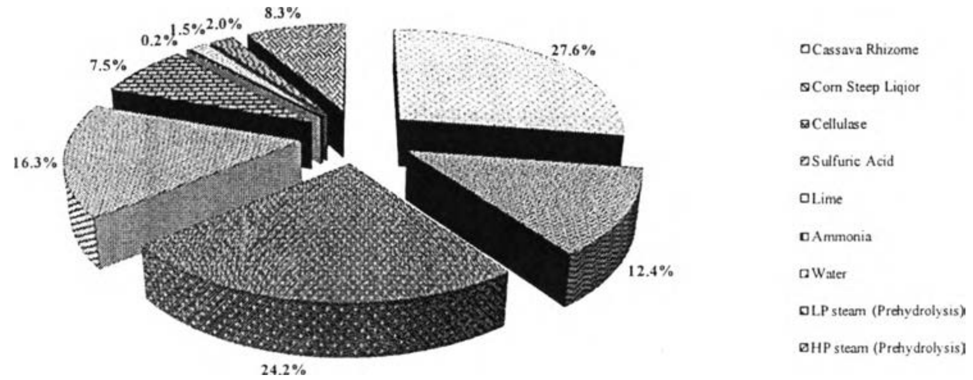

Figure 4.7 Breakdown of the contribution of raw materials for the production cost.

From Figure 4.7, the raw material was the highest portion for the variable cost which mainly came from cassava rhizome and cellulase cost. Regarding the cassava rhizome, even it is very large portion for the production cost in term of raw materials, but it is the most important feed and its the quantity had the influence in the quantity of ethanol directly, since it is considered as the waste of cassava production so the price is very cheap. Thus, next interesting raw material is cellulase (enzyme) as it had the high influence in the production cost of ethanol as mention in the previous section. Although, the process required less the quantity of it, but the price is very expensive.

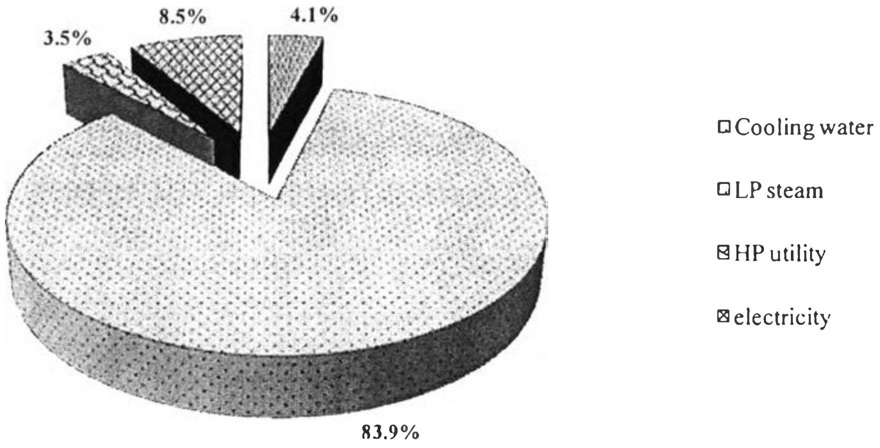

Figure 4.8 Breakdown of the contribution of utilities for the production cost.

From Figure 4.8, low pressure stream had the highest influence in the production cost of ethanol because it was mainly consumed in distillation sections (heat exchanger E4 and E5, reboiler of beer and rectification) which had very high duty (LP steam and HP steam in this utility cost do not include the one from pretreatment section).

4.1.3.3 Economic Sensitivity Analysis of Base Case Design

The economic sensitivity analysis will be made to the raw materials, product price, labor cost, capital cost, equipment cost and utilities cost.

It can be seen from Figure 4.9, the highest influence to NPV was the price of the ethanol. Also, the equipment cost had high effect on the NPV which from the result shown in Figure 4.5, SCCF fermentation section was the one that had the most influence to the profit.

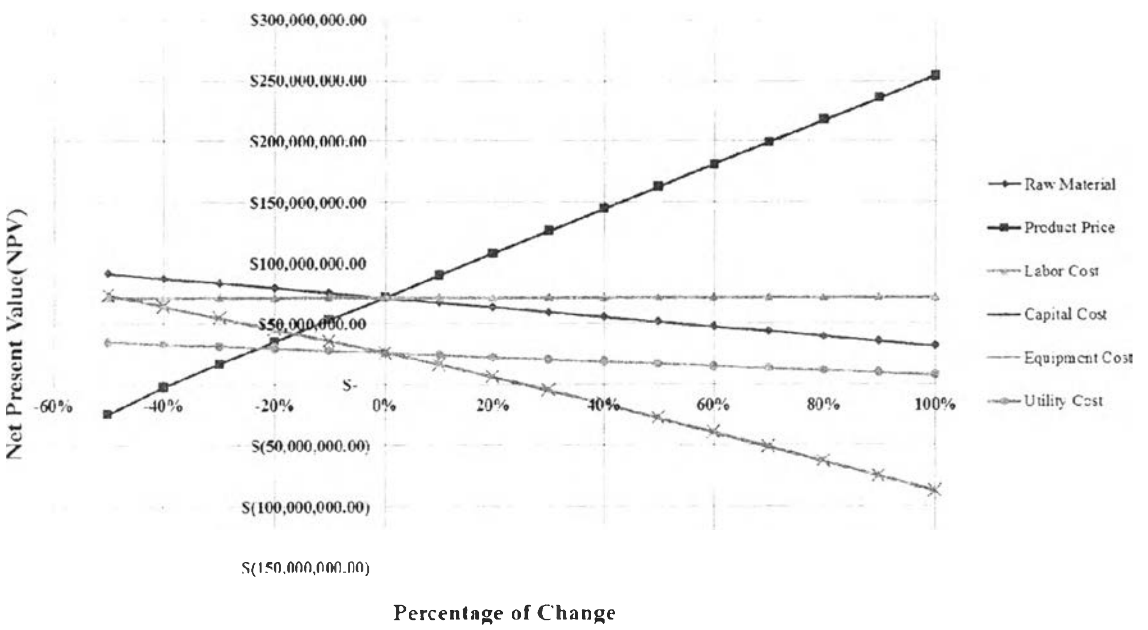

Figure 4.9 Sensitivity analysis compare to NPV.

4.1.3.4 Profitability of Base Case Design

Profitability is the measure of the amount of profit that can be obtained from a given situation. It is as common denominator for all business activities. The determination and analysis of profits obtainable from the investment of capital and the choice of the best investment among various alternatives are major goals of the investment analysis

For this work, the life time of the project was assumed to be 20 years. The MARR (Minimum Acceptable Rate of Return) was fixed to be 15 %. The depreciation for the plant is estimated to be at 20 year by MACRS method. The income tax rate that has to be paid to the government is assumed to be at 30 % (RD, 2013). According to the price of ethanol will increasing in the future the inflation was set. The inflation rate of construction, product and total product cost were assumed to be 2 %, 10 % and 10 % respectively. The inflation rate of product was set by the real increasing price data in the previous year (EPPO, 2011) and the other rest was set by using the product price as reference. The summary of investment analysis for the base cases design is shown in Table 4.4.

Table 4.4 Profitability of the base case design

Profitability		
not include time value of money		
Rate of Return		10.13%
Pay Back Period		6.58
Net Return	$	4,165,854.72
include time value of money		
Annual End of Year cash flows and discounting		
Net Present Worth	$	39,586,633.00
DCFR	$	0.30
Continuous cash flows and discounting		
Net Present Worth	$	42,496,587.41
DCFR	$	0.14

According to the result, all of the parameters were in high positive values which mean this project is clearly good for investment. Moreover, the breakeven pointed that the project will get much the profit for long period as shown in Figure 4.10. Although, It seems like the best process which attracted to invest in term of economic. But, the average expectable environment is not good enough. After the process was improved, the profit and quality of environment should be increased concurrently.

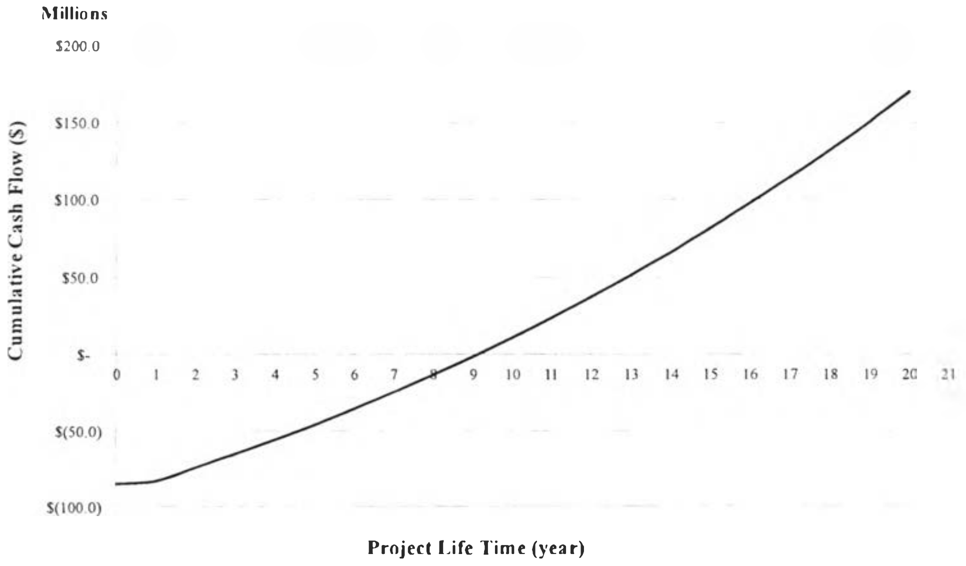

Figure 4.10 Cumulative cash flow for 20 year project of the base case design.

4.1.4 Life Cycle Assessment of Base Case Design

4.1.4.1 System Boundary and Life Cycle Inventory of Base Case Design

Life cycle inventory (LCI) is a process to quantify all inputs (raw materials used and energy consumed) and environmental releases (all kind of emissions including waste) associated with each stage of the process life cycle. In this research, the base case design of the bioethanol conversion process was divided into five stages: pretreatment, detoxification, SSCF fermentation, distillation and dehydration as shown in Figure 4.11.

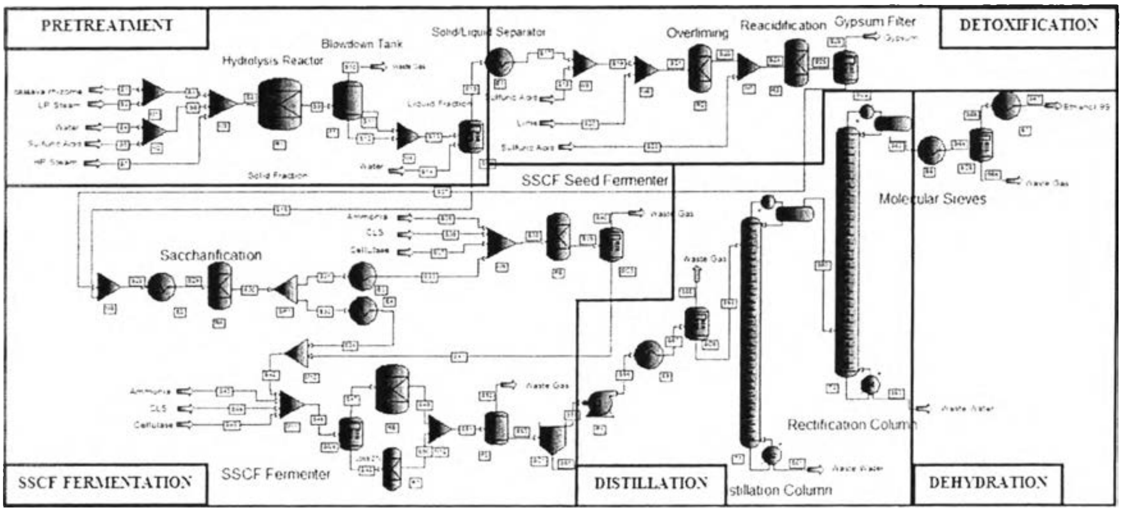

Figure 4.11 Five stage of the base case design life cycle.

For the case study, the waste water from the plant has been designed to be treated in wastewater treatment. The treated water was assumes to be recycled back to the plant. In reality, wastewater treatment should be included in the plant but that not the main objective for the research so, it was assume to be an outsource treatment and used as an idea for the overview for commercial plant.

In order to perform the life cycle assessment consistently, integration of plantation and transportation of cassava rhizome with the ethanol production process was considered. So, the system boundary of bioethanol production was divided into eight stages which were cassava plantation, transportation, pretreatment, detoxification, SSCF fermentation, distillation, dehydration and wastewater treatment as shown in Figure 4.12. Note that wastewater treatment in ethanol conversion process was not included in the economic evaluation section. The reasons came from the lack of cost data and also too complicate to calculate. Moreover, this stage was not the main issue to focus, Therefore, this process was considered as outsource process in the life cycle.

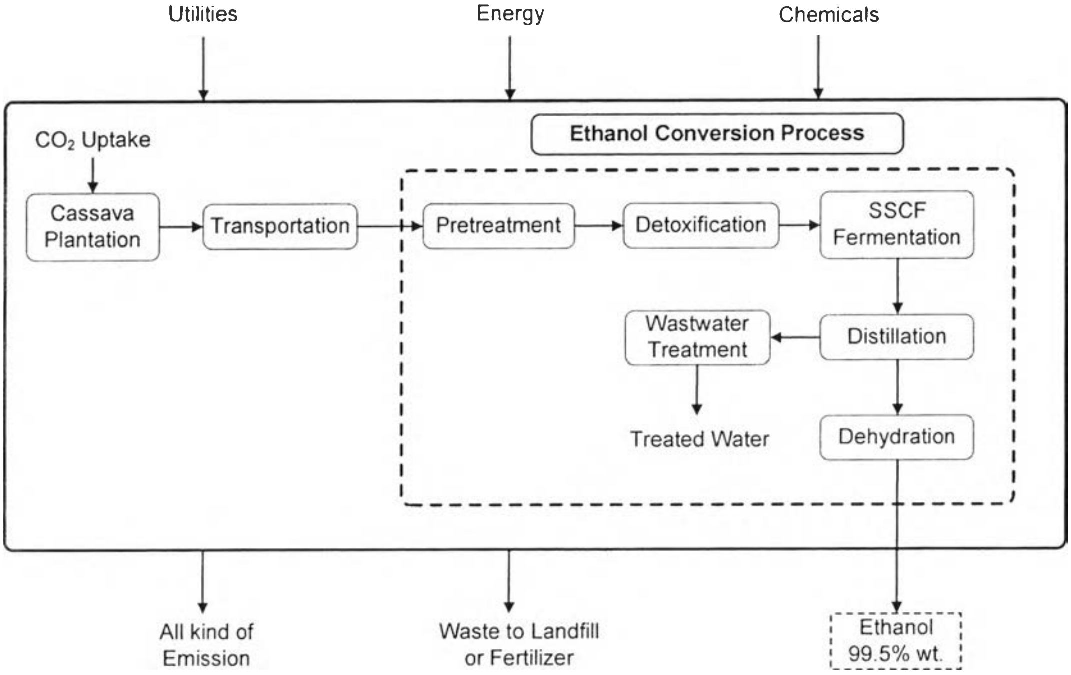

Figure 4.12 System boundary of the base case design.

The basis of one kilogram of 99.5 wt% ethanol was set as a functional unit for the inventory analysis. Carbon dioxide (CO_2) uptake of cassava for this research was assumed to be 0.09 kg CO_2/kg of cassava root that as every kilogram of cassava root production would be absorb 90 gram carbon dioxide from atmosphere (Klongsiri *et al.*, 2009). The inventory analysis of the process life cycle is presented stage by stage. Details of input and output inventory data for each stage are presented in Tables 4.5, 4.6, 4.7, 4.8, 4.9, 4.10, 4.11 and 4.12.

Table 4.5 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in cassava plantation stage for the base case design (Khongsiri, S. (2009).

Inventory of cassava roots plantation					
Input			**Output**		
Type	**Quantity**	**Unit**	**Type**	**Quantity**	**Unit**
Raw material			**Products**		
Cassava stems	3.3920	piece	Cassava root	9.8319	kg
Cassava peel	10.5792	kg	Cassava Leaves	2.2912	kg
Chicken manure	25.3664	kg	Cassava Rhizome	3.1660	kg
N-fertilizer	0.0123	kg	Cassava stems	8.5734	piece
P-fertilizer	0.0069	kg			
K-fertilizer	0.0131	kg	**Air emissions**		
Alachlor	0.0009	kg	Carbon dioxide	-0.8013	kg
Paraquat	0.0015	kg	Nitrogen oxide	0.0017	kg
Glyphosate	0.0029	kg	Sulfur dioxide	0.0001	kg
Zinc	0.0008	kg	Nitrous oxide	0.0004	kg
			Ammonia	0.0026	kg
Fuel			Volatile organic compound	0.0006	kg
Diesel	0.0243	kg			

Table 4.6 Results of the inventory analysis of cassava rhizome per one kilogram ethanol 99.5 wt% production in transportation (one way) stage for the base case design (Niracharopas, 2011).

Inventory of cassava rhizome transportation					
Input			**Output**		
Type	**Quantity**	**Unit**	**Type**	**Quantity**	**Unit**
Raw material			**Products**		
Cassava Rhizome	3.1660	kg	Cassava Rhizome	3.1660	kg
Fuel			**Air emissions**		
Diesel	0.0135	kg	Carbon dioxide	0.0786	kg
			Carbon monoxide	0.0014	kg
			Nitrogen oxide	0.0001	kg
			Particulate matter (PM)	0.0002	kg

Table 4.7 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in pretreatment stage for the base case design.

Inventory of pretreatment					
Input			Output		
Type	Quantity	Unit	Type	Quantity	Unit
Raw material			**Products**		
Cassava Rhizome	3.1660	kg	Pretreated Output-1	3.9931	kg
Sulfuric acid	0.0200	kg	Pretreated Output-2	3.0843	kg
Water	3.5995	kg			
			Air emissions		
Electricity/Heat			Water	0.4777	kg
Steam	1.2078	kg	Furfural	0.0234	kg

Table 4.8 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in detoxification stage for the base case design.

Inventory of detoxification					
Input			Output		
Type	Quantity	Unit	Type	Quantity	Unit
Raw material			**Products**		
Pretreated Output-1	3.9931	kg	Detoxificated Output	3.9882	kg
Sulfuric acid	0.0320	kg			
Lime	0.0361	kg	**Air emissions/Waste**		
Make up cooling water	0.6205	kg	Gypsum	0.0664	kg
			Bio waste	0.0066	kg
Electricity/Heat					
Electricity	0.0025	kW			

Table 4.9 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in SSCF fermentation stage for the base case design.

Inventory of SSCF fermentation					
Input			**Output**		
Type	**Quantity**	**Unit**	**Type**	**Quantity**	**Unit**
Raw material			**Products**		
Pretreated Output-2	3.0843	kg	SSCF Fermented Output	5.1801	kg
Detoxificated Output	3.9882	kg			
Ammonia	0.0007	kg	**Air emissions**		
Water	0.0076	kg	Water	0.0267	kg
Make up cooling water	1.7085	kg	Ethanol	0.0596	kg
			Carbon dioxide	0.9100	kg
Electricity/Heat			Oxygen	0.0018	kg
Electricity	0.0068	kW	Acetic acid	0.00003	kg
			Furfural	0.00044	kg
			Waste		
			Bio waste	0.8168	kg
			Ash	0.1165	kg

Table 4.10 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in distillation stage for the base case design.

Inventory of distillation					
Input			**Output**		
Type	**Quantity**	**Unit**	**Type**	**Quantity**	**Unit**
Raw material			**Products**		
SSCF Fermented Output	5.1801	kg	Distillated Output	1.0636	kg
Make up cooling water	11.0086	kg	Waste Water from distillator	3.9898	kg
Electricity/Heat			**Air emissions**		
Electricity	0.0451	kW	Water	0.0033	kg
Steam	3.2557	kg	Ethanol	0.0031	kg
			Carbon dioxide	0.1202	kg
			Oxygen	0.00002	kg

Table 4.11 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in dehydration stage for the base case design.

Inventory of dehydration					
Input			Output		
Type	Quantity	Unit	Type	Quantity	Unit
Raw material			**Products**		
Distillated Output	1.0636	kg	Ethanol 99.5% wt.	1.0000	kg
Make up cooling water	2.7900	kg			
Electricity/Heat			**Air emissions**		
Electricity	0.0111	kW	Water	0.0636	kg

Table 4.12 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in wastewater treatment stage for the base case design.

Inventory of waste water treatment					
Input			Output		
Type	Quantity	Unit	Type	Quantity	Unit
Raw material			**Products**		
Waste Water from distillator	3.9898	kg	Treated water	3.6223	kg
Electricity/Heat			**Water emissions**		
Electricity	0.1416	kW	Sulfuric acid	0.0042	kg
			Acetic acid	0.0035	kg
			Furfural	0.0249	kg
			Ethanol	0.0173	kg
			Waste		
			Biowaste	0.3177	kg

The products of each stage were considered as raw materials for the next stage, for example, pretreated output from the pretreatment stage was used as the raw material for detoxification stage and so on. In this analysis, the amount of make-up water for cooling water was also considered in the boundary. For biowaste (cellulose, hemicellulose and sugar) from the process, it was assumed to turn into fertilizer. Allocation method of all stage using mass allocation. The emission related to equipments was excluded in this research.

4.1.4.2 Life Cycle Impact Assessment of Base Case Design

Life cycle impact assessment (LCIA) is used to evaluate the contribution of the process to the different environmental impact categories. In order to verify that the environmental impacts of the proposed design alternatives are lower, it is necessary to generate and compare the feasible design alternatives according to an established set of performance criteria. Design alternatives can be generated by identifying and quantifying energy and materials used and wastes released to the environment in terms of GHG emissions and fossil resource depletion to acidification and toxicity.

After performing the life cycle inventory analysis of the base case design (bioethanol production process from cassava rhizome) by using SimaPro 7.1, the CML 2 baseline 2000 methods were then utilized to evaluate the environmental impacts in various categories. The impact assessment results are shown in Table 4.13 and Figure 4.13.

Table 4.13 Environmental impact of bioethanol conversion process from cassava rhizome per a kilogram ethanol 99.5 wt% of the base case design

Impact category	Unit	Total
Abiotic depletion	kg Sb eq	8.54E-03
Global warming (GWP100)	kg CO_2 eq	1.68E+00
Ozone layer depletion (ODP)	kg CFC-11 eq	1.11E-07
Human toxicity	kg 1,4-DB eq	3.05E+00
Fresh water aquatic ecotox.	kg 1,4-DB eq	1.11E+01
Marine aquatic ecotoxicity	kg 1,4-DB eq	9.89E+03
Terrestrial ecotoxicity	kg 1,4-DB eq	5.09E-03
Photochemical oxidation	kg C_2H_4	1.91E-02
Acidification	kg SO_2 eq	5.64E-03
Eutrophication	kg PO_4 eq	1.78E-03

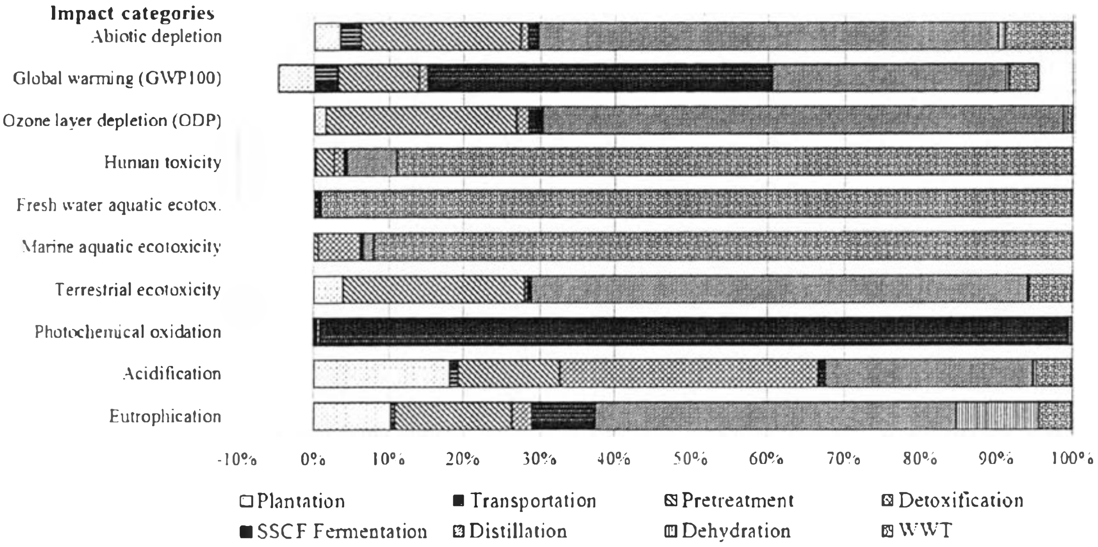

Figure 4.13 Distribution of environmental impacts classified stage by stage of the base case design.

According to Figure 4.13, cassava plantation stage gives a negative of emission in global warming (GWP100) because cassava production could uptake CO_2 which influences the greenhouse gas (GHG) emission, thereby reducing the global warming impact. Conversely, if the raw material was not plant and so is unable to uptake CO_2, the global warming for the ethanol production process will become much higher. The emission of CO_2 and CO actually comes from the SSCF fermentation and distillation stage. Although, Plant stage gives a negative of emission in global warming but also the cause of acidification and eutrophication because of the amount of fertilizer usage. The huge amount of solidwaste and ash from cassava rhizome that release from SSCF fermenter affected to photochemical oxidation. The gypsum waste from detoxification is found to affect the acidification. The distillation stage is the major cause of terrestrial ecotoxicity and eutrophication because of the large biowaste. Moreover, the huge amount of utility usage in this stage also effected to ozone layer depletion, abiotic depletion and global warming. The dehydration stage does not cause significant environmental impact, compared to other stages. The most toxic from wastewater treatment stage coming from electricity generation releases toxic materials and some biowaste from the wastewater turn into fertilizer which was found to mainly affect the water aquatic ecotox, marine aquatic ecotoxicity and human toxicity. Now, after perform every tool, alternative designs will be generated by using all of the results from base case design.

4.2 Alternative Design Ideas

The results of sustainability analysis of base case. There were three main alternative process design ideas as follows:

- Rearrange the energy consumption in the process by using heat integration method.
- Install the membrane section into the process to treat water from S61 and S63, and recycle treated water into the process.
- Generate the energy by burn lignin and other solid wastes from SSCF fermenter (stream S55).

In addition, these alternatives could be mixed with another. For instance, after rearrange heat exchanger, the lignin combustion could be also installed in the process as well. Based on this approach, the total of seven alternative designs was generated from different combinations of these ideas as described in Table 4.14.

Table 4.14 Overall alternative designs

Alternative	Description
1	Base Case with Heat Integration
2	Waste Water Recover by Membranes
3	Lignin Combustion
4	Waste Water Recover by Membranes + Lignin Combustion
5	Waste Water Recover by Membranes with Heat integrate
6	Lignin Combustion with Heat integrate
7	Waste Water Recover by Membranes + Lignin Combustion with Heat integrate

Next part will explain the idea of three main alternatives. After that the report will show the comparison of every alternative with the base case design in terms of water consumption, sustainability, profitability and life cycle assessment. All of the flow sheets and the stream tables of three main idea designs were shown in Appendix D. For the other stream tables, they appear in attached CD.

4.2.1 Base Case with Heat Integration

These alternatives mainly focused on the reduction of energy usage in the process by rearrangement of heat exchanger which also can be reducing the operating cost in economic issue. However, the drawback of this process is the higher area of heat exchanger lead to increasing of capital cost. So, the optimization between the reduction of operating cost (and environmental issue) and the increasing of capital cost is required.

This section will use alternative 1 as the example to explain the other related alternatives. According to the base case flow sheet, there were some of heat exchangers that could be exchanged heat with the others. In order to do that, the source and sink (hot and cold stream) information have to be collected. There were four hot streams and three cold streams as shown in Table 4.15.

Table 4.15 Hot and cold streams in each heat exchanger from the base case design

Hot Stream					
Unit	Streams (In & Out)	FC_p (MJ/hr-°C)	Inlet Temp. (°C)	Outlet Temp. (°C)	Enthalpy (MJ/hr)
E1	S15-S17	67.88	62.66	50.00	-859.30
E3	S31-S33	10.03	65.00	41.56	-235.20
E4	S32-S34	90.31	65.00	40.86	-2180.00
E7	S65-S67	80.65	100.02	40.00	-4840.40
Total					**-8115.90**
Cold Stream					
Unit	Streams (In & Out)	FC_p (MJ/hr-°C)	Inlet Temp. (°C)	Outlet Temp. (°C)	Enthalpy (MJ/hr)
E2	S28-S29	102.44	54.14	65.00	1113.00
E5	S56-S57	95.81	41.24	100.51	5678.50
E6	S62-S64	721.61	93.34	100.00	4805.90
Total					**11597.40**

According to above information, heat integration can be done by using pinch analysis method to generate heat exchanger network as shown in Figure 4.14. The assumption of temperature difference (ΔT_{min}) for this research is 10 °C (which will use this value for every alternative).

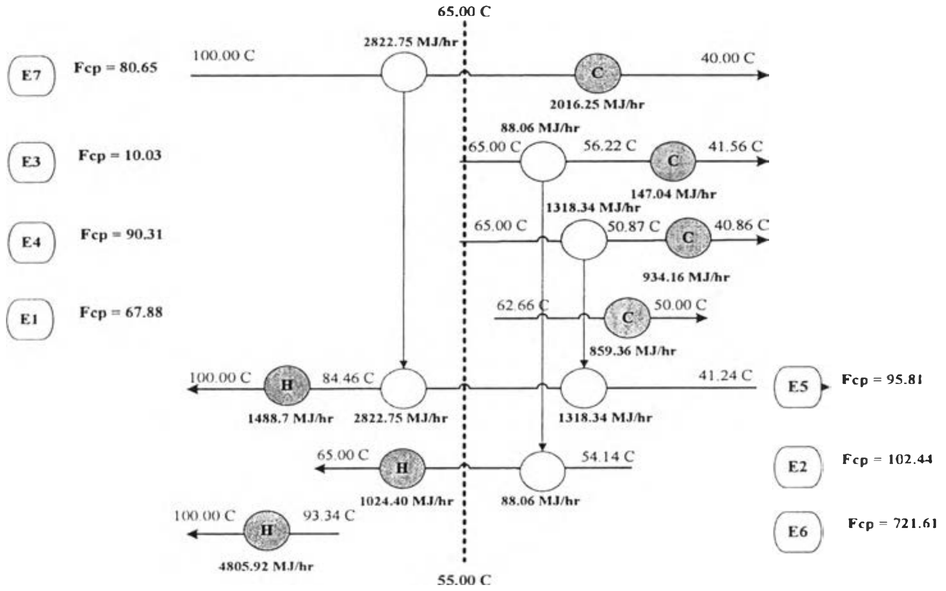

Figure 4.14 Heat exchanger network of the base case design.

The arrow from left to right (E7, E3, E4 and E1) represented to the hot streams that need to be cooled. On the contrary, the arrow from right to left (E5, E2 and E6) represented to the cold streams that need to be heated up. The circles with connected line refer to the heat exchanger. The circles with "C" and "H" refer to cooler and heater respectively. The result showed that base case design had pinch temperatures at 65.00 °C for hot side and 55.00 °C for cold side. Furthermore, there were three heat exchangers that require exchanging the heat from streams with another one which one of them was on above pinch; S56 with S65 (2.8 GJ/hr) and the other two were on below pinch; S31 with S28 (0.1 GJ/hr), and S32 with S56 (1.3 GJ/hr). In this process, it requires four cooler and three heaters. The final flowsheet for alternative 1 are shown in Figure 4.15. The other related alternatives (alternatives 5, 6, and 7) were used the same idea as alternative 1. They are given the flowsheets in Appendix D and the stream tables in attached CD.

4.2.2 Wastewater Recover by Membrane

These alternative ideas were to use wastewater and recycle it in order to reduce water consumption which make process more sustainable and reduce the operating cost.

The type of membrane that be chosen for this report had two series of membranes;

- MF/UF Membranes (Microfiltration and Ultrafitration) use for remove total suspended solids.
- RO Membranes (Reverse Osmosis) use for remove sugar and acid.

According to Pearce (2007), "Prior to the introduction of membrane filtration, the application of RO in wastewater reuse was restricted due to fouling problems. However, MF/UF provides an excellent feed quality for further treatment, and this technological advance, combined with the market requirements, has led to the rapid rise in wastewater reuse schemes." Pearce said this mean that "MF/UF uses a sieving mechanism, which provides an absolute barrier to particles above the size of the MF/UF membrane pores, and thus can provide a much better RO feed."

The reason that this research chooses RO membrane is related with the journal from Pearce which said "RO has emerged as the most suitable technology for addressing water needs in most areas, since it is a flexible cost effective technology with a mainly good track record. Two important trends have emerged in the last 15 years of RO development. Firstly, RO membrane performance has improved markedly, and secondly, prices have reduced sharply as markets have expanded and projects have become larger. Now, the RO option is often cost competitive, and provides an independent flexible option to a project developer. Recently significant improvements have been made in system design and energy recovery, enhancing the RO option even further." Moreover, the required concentration of contaminate in the treat water is very low. Therefore, it would be more suitable to use the RO which has high efficiency to remove the contaminant. However, NF membrane (Nanofiltration membrane) can also be used when consider on the efficiency and cost of the membrane. In other word, if the process is less concern on concentration of contaminants, NF would be the better option to reduce the cost.

The operating condition for membrane is 50-55 °C and 21 atm (Pearce, 2007). Membranes can recover water around 80 % and remove contaminant around 95 % (Koyuncu *et al.*, 2001). The flowsheet for alternative 2 are shown in Figure 4.16. The other related alternatives (alternatives 4, 5, and 7) were used the same idea as alternative 2. They are given the flowsheets in Appendix D and the stream tables in attached CD.

4.2.3 Lignin Combustion

For this process, the process will install the combustion chamber and steam generator. The propose of this alternative is to burn solid waste (mainly lignin) and use the heat from combustion to generate steam (LP steam and HP steam) that can be compensated with steam that use in the process. Moreover, the electricity that was generated from turbine can be sold as one of the product. The flowsheet for alternative 3 are shown in Figure 4.17. The other related alternatives (alternatives 4, 6 and 7) were used the same idea as alternative 3. They are given the flowsheets in Appendix D and the stream tables in attached CD.

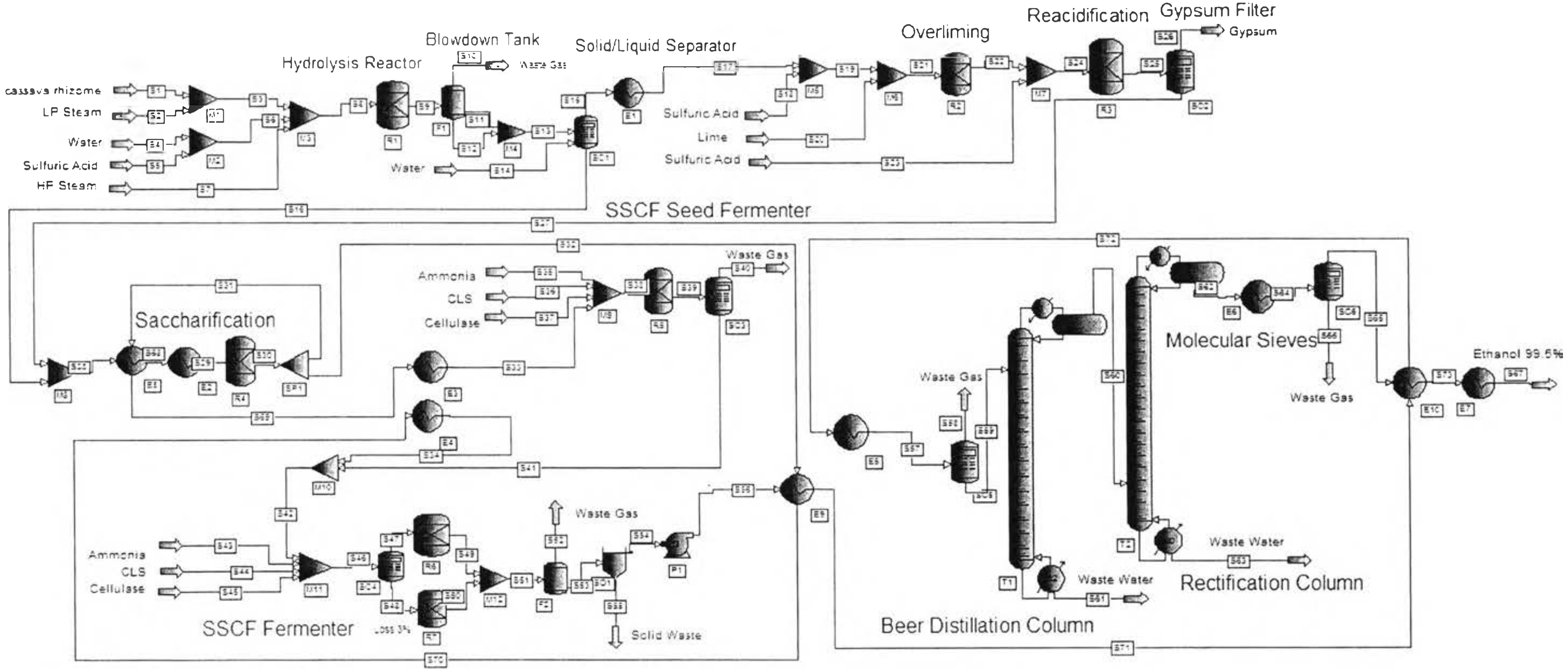

Figure 4.15 Flowsheet of the bioethanol production process from cassava rhizome for alternative 1 design.

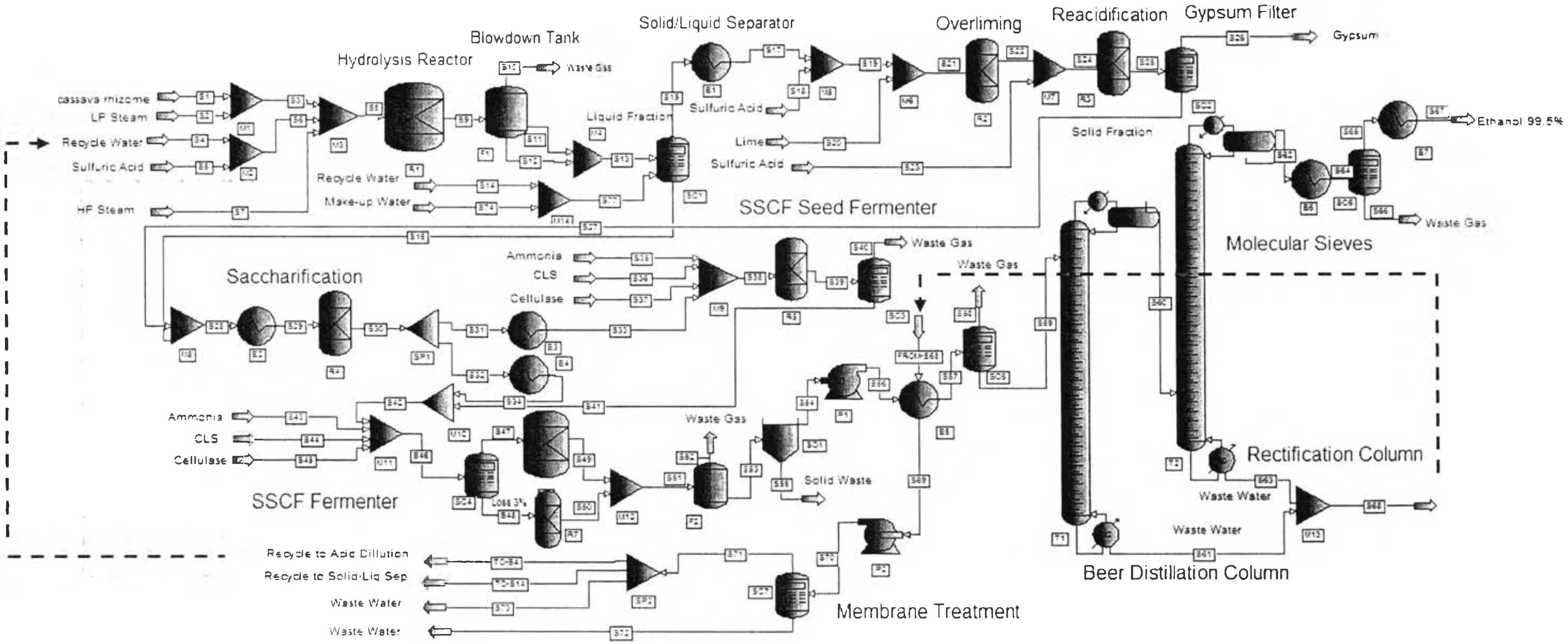

Figure 4.16 Flowsheet of the bioethanol production process from cassava rhizome for alternative 2 design.

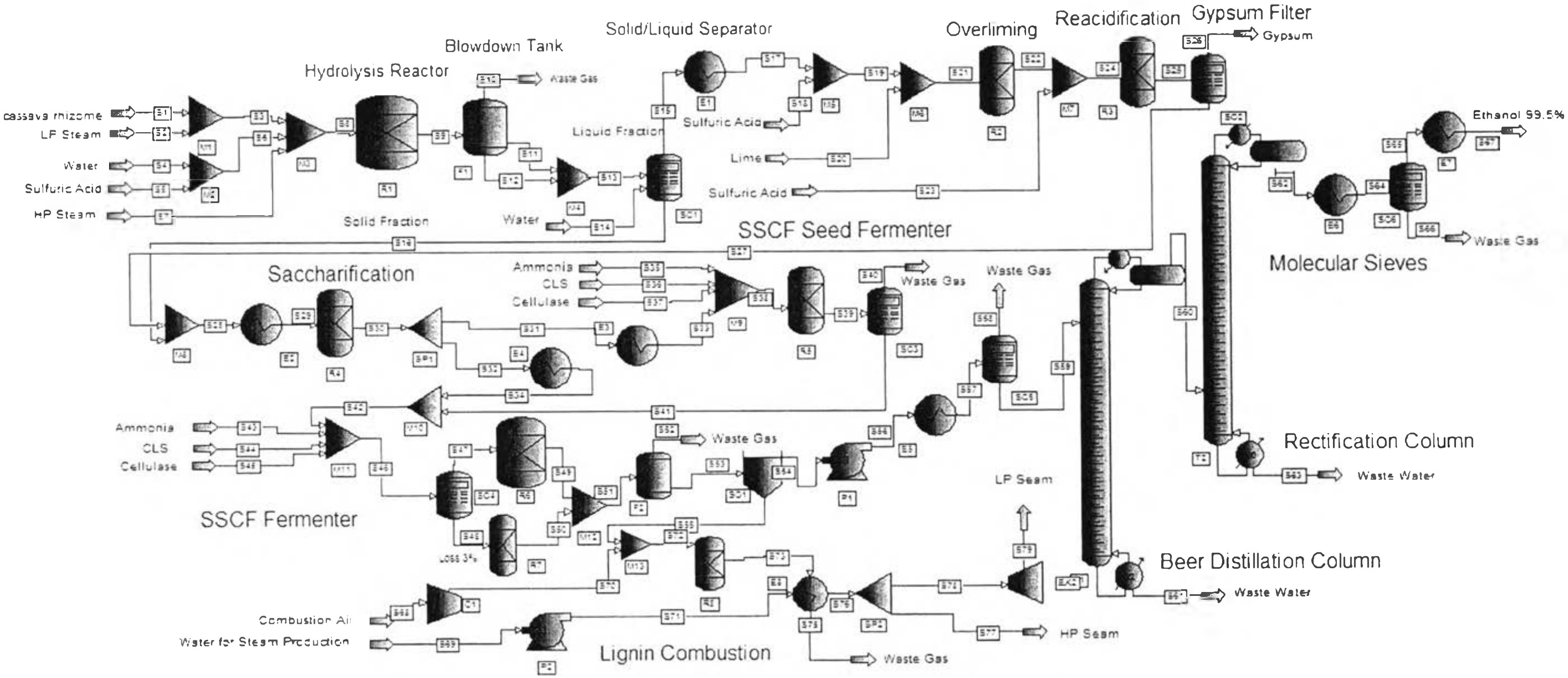

Figure 4.17 Flowsheet of the bioethanol production process from cassava rhizome for alternative 3 design.

4.3 Comparison Between Base Case and Alternatives

4.3.1 Water Consumption

The water consumption is one of the important factors affecting the EWC indicator (SustainPro) and the environmental impact. The comparison of water consumption between the base case design and alternatives is shown in Figure 4.18.

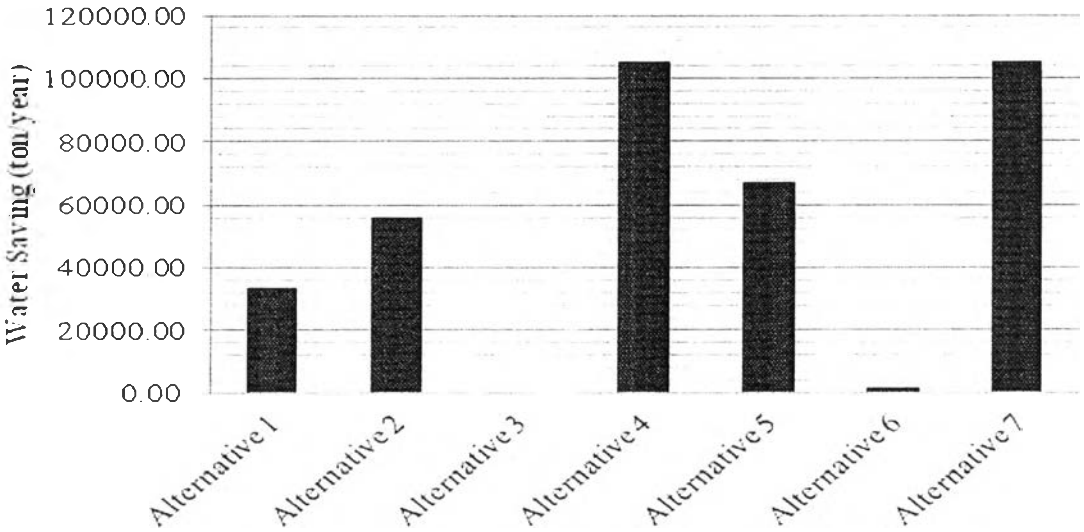

Figure 4.18 Comparison the water saving compare to the base case design.

As seen from Figure 4.18, the water consumption from the membrane process designs were the lowest (the most saving) which reasonable because these process were recycle the water and consume less utility compare to the other because not only the utility consumption, especially steams, was dramatically reduced but also the huge amount of wastewater was treated and recycle back to the process. For heat integration designs, they can save some water because of the reduction of utility consumption from rearrange heat exchanger. However, lignin combustion designs did not save any water because the designs focus only to use solid waste as fuel. The final result was that alternatives 4 and 7 shown the best in term of water saving (60 % saving).

4.3.2 Economic Evaluation Comparison

First of all, the comparison of capital cost and operating cost of each design is considered as shown below;

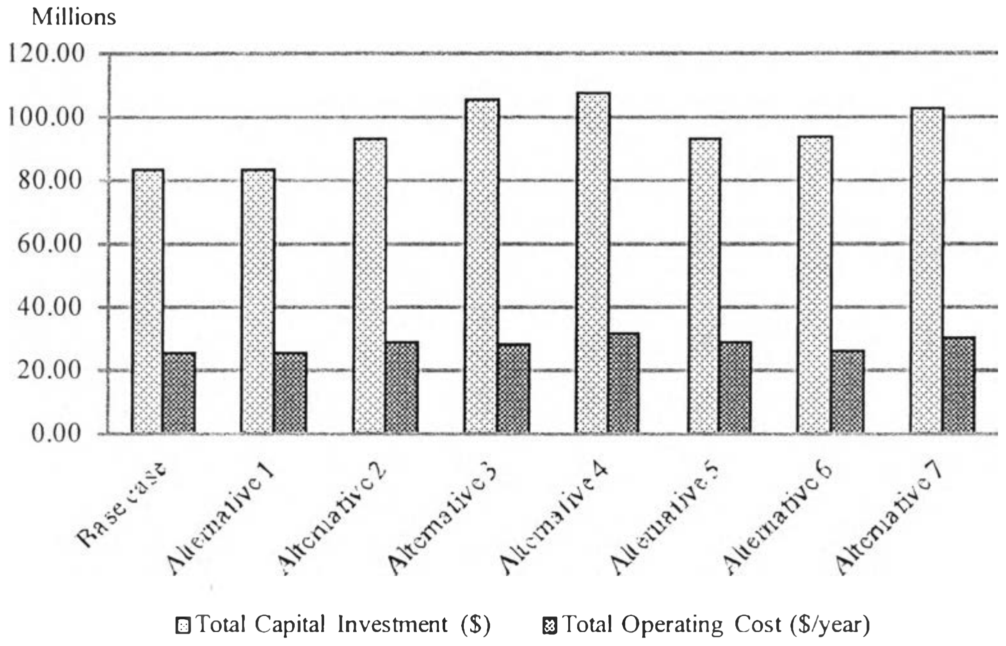

Figure 4.19 Comparison of capital cost and operating cost of each design.

As shown in Figure 4.19, heat integration designs (alternatives 1, 5, 6 and 7) required higher investment than base case designs due to the addition of heat exchangers, but the operating cost was lowered because the reduction of energy consumption. Similarly, alternatives with membrane (alternatives 2, 4, 5 and 7), the capital cost of these designs was increased because more unit operations were installed. This could be compensated by lower operating cost of these designs as a result of recycle of water and some raw materials. For lignin combustion processes (alternatives 3, 4, 6 and 7), these designs led to a significant increase of the investment cost because the combustor and generator units were very expensive. However, because of the electricity and steam generators, the designs with lignin combustion process can reduce the much amount of energy consumption so the operating cost was reduced. Next, the results of economic evaluation will be considered.

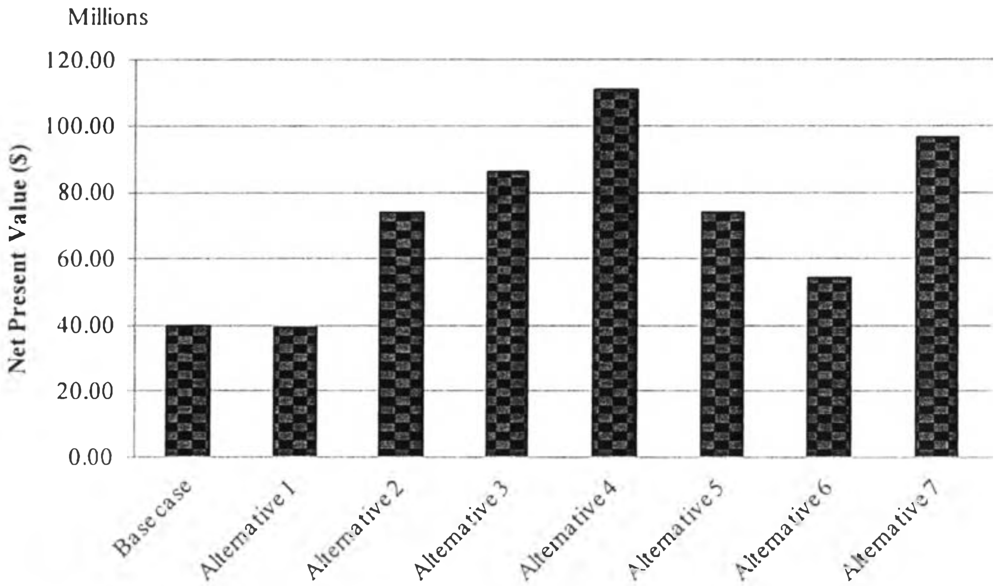

Figure 4.20 Comparison of NPV of each design for 20 years life time.

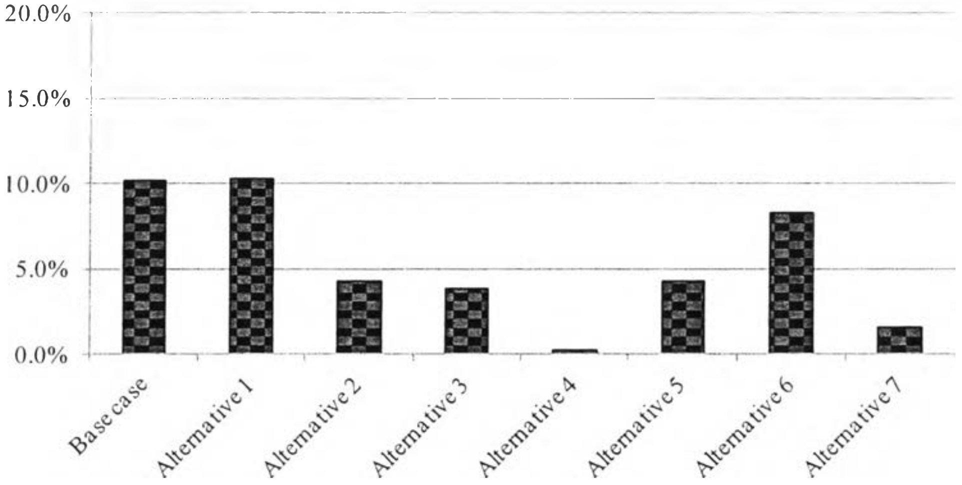

Figure 4.21 Comparison of IRR of each design for 20 years life time.

According to the results from Figure 4.20 and 4.21, the high positive NPV or IRR mean those designs was prefered for investment. Heat integration design had worst result in term of economic compare to the other designs because of the increasing both of capital cost and operating cost from addition of heat exchanger. The membrane designs was shown to significantly the results in term of economic because the saving of operating cost is much more than the increasing of capital cost from reduction of energy usage in the process by recycle water back to process. Although the lignin combustion designs had high capital cost from burner as shown in Figure 4.19, all of them got both of the high positive values for NPV and IRR because they could sell electricity as by product and saved huge amount of steams which lead to very low operating cost.

From the result, alternatives 4 was shown to have the highest NPV of 110.4 MM$ and IRR 0.13 % for 20 years life time, followed by alternative 7 with NPV of 96.4 MM$ and IRR 1.0 %.

As you can see from Figure 4.22, the breakeven point of alternatives 4 and 7 were about 15 years. In economic point of view, alternatives 4 and 7 were the best alternatives to invest. Next section will consider on LCA analysis which is the last tool to choose the best design for ethanol production from cassava rhizome process in Thailand.

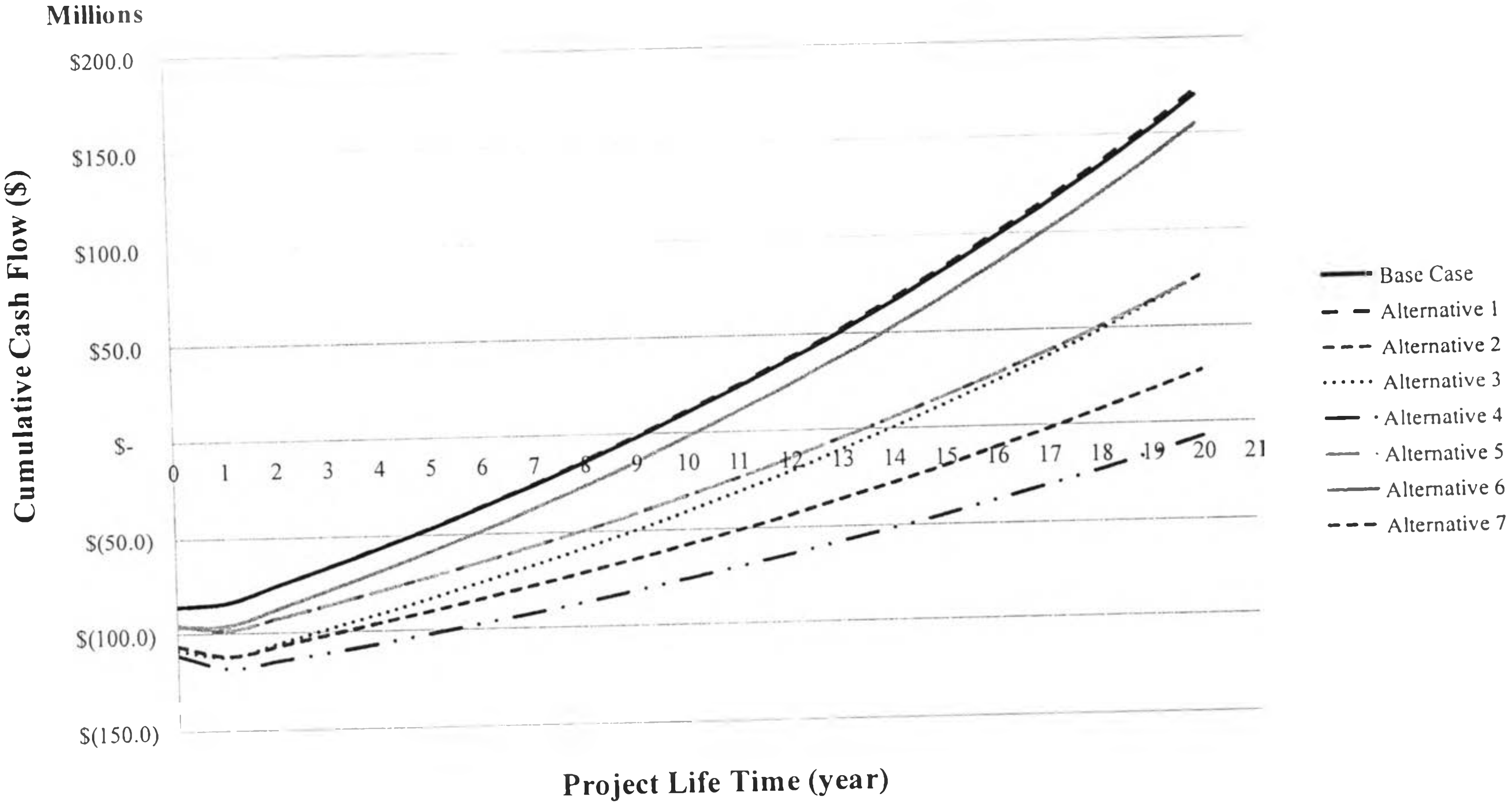

Figure 4.22 Comparison of breakeven point of each design for 20 years life time.

4.3.3 Life Cycle Assessment Comparison

After performing the life cycle impact assessment to evaluate environmental impacts, alternatives design were compared to the base case design. Details of system boundary and environmental impact for alternative designs are given in Appendix F. For LCIA data of alternative designs, they are included in attached CD.

Focusing on global warming potential (GWP as CO_2-equivalent), alternatives 2 and 5 were shown to have lowest GWP impact. They show emission of only 2.04 and 2.05 kg CO_2 equivalent/kg bioethanol which reflects 15.7 % and 15.1 % reduction from the base case design (2.42 kg CO_2 equivalent/kg bioethanol) respectively as shown in Figure 4.23. In particular, the wastewater recovery using membranes with heat integrate (alternative 5) was the best design in term of global warming point of view as it had lowest GHG emission. This is due to the facts that this design not only reduced GHG emissions, but also reduced of energy usage in the process by rearrangement of heat exchanger.

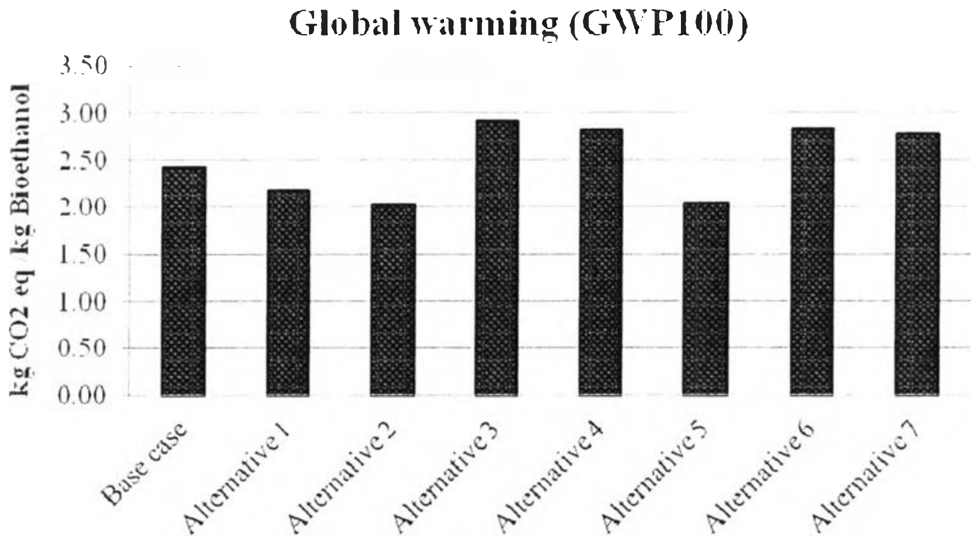

Figure 4.23 Comparison of the greenhouse effect (kg CO_2-equivalent) per one kilogram of bioethanol for each design.

For other impact categories such as abiotic depletion, ozone layer depletion, human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, photochemical oxidation, acidification and eutrophication potential are shown in Figures 4.24, 4.25, 4.26, 4.27, 4.28, 4.29, 4.30, 4.31 and 4.32, respectively.

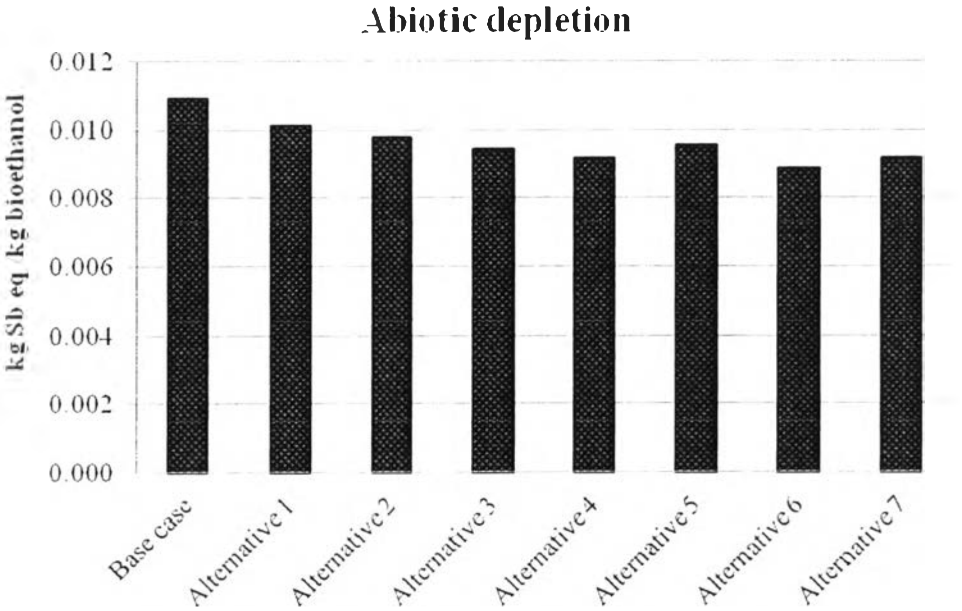

Figure 4.24 Comparison of the abiotic depletion (kg Sb-equivalent) per one kilogram of bioethanol for each design.

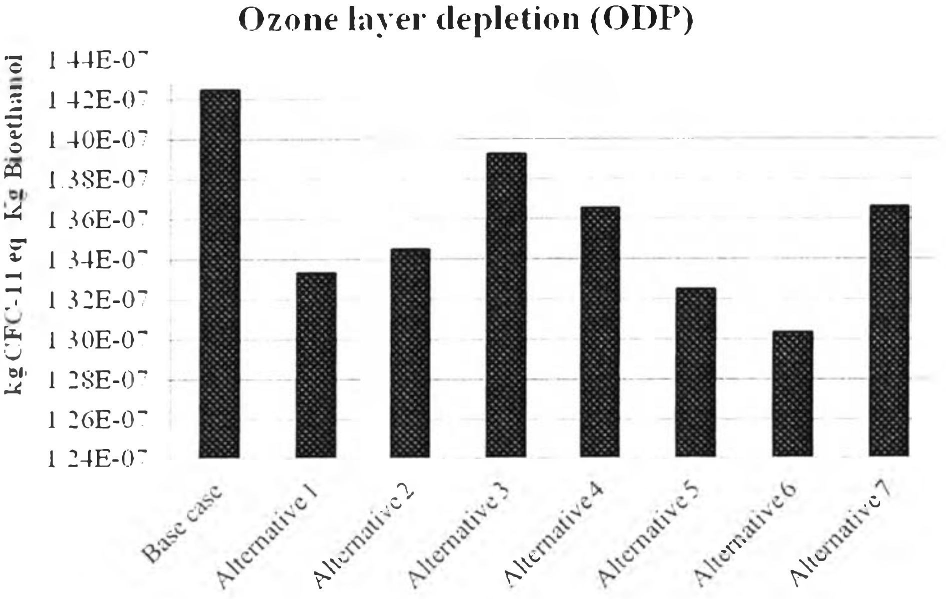

Figure 4.25 Comparison of the ozone layer depletion (kg CFC-11-equivalent) per kilogram of bioethanol for each design.

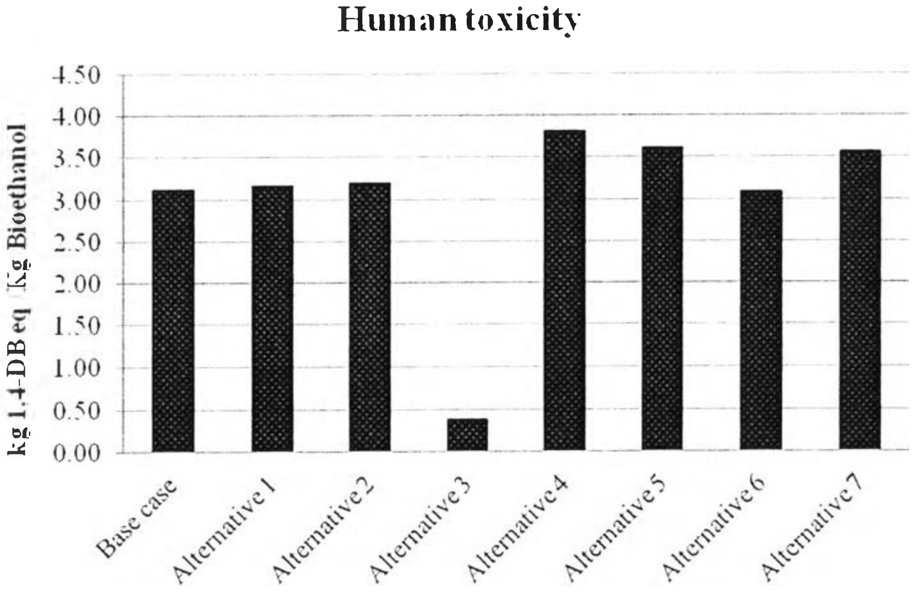

Figure 4.26 Comparison of the human toxicity (kg 1,4-DB-equivalent) per one kilogram of bioethanol for each design.

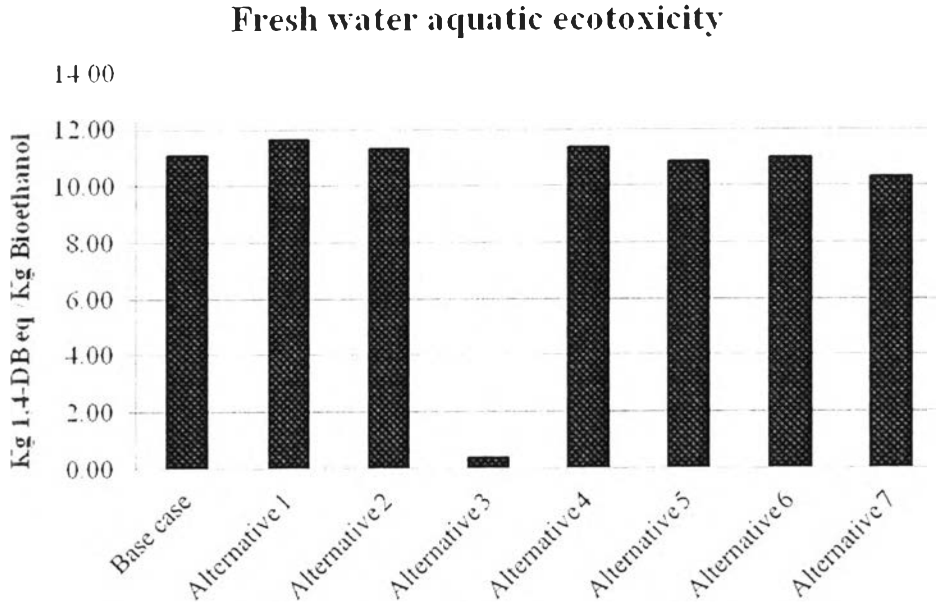

Figure 4.27 Comparison of the flesh water aquatic ecotoxicity (kg 1,4-DB-equivalent) per one kilogram of bioethanol for each design.

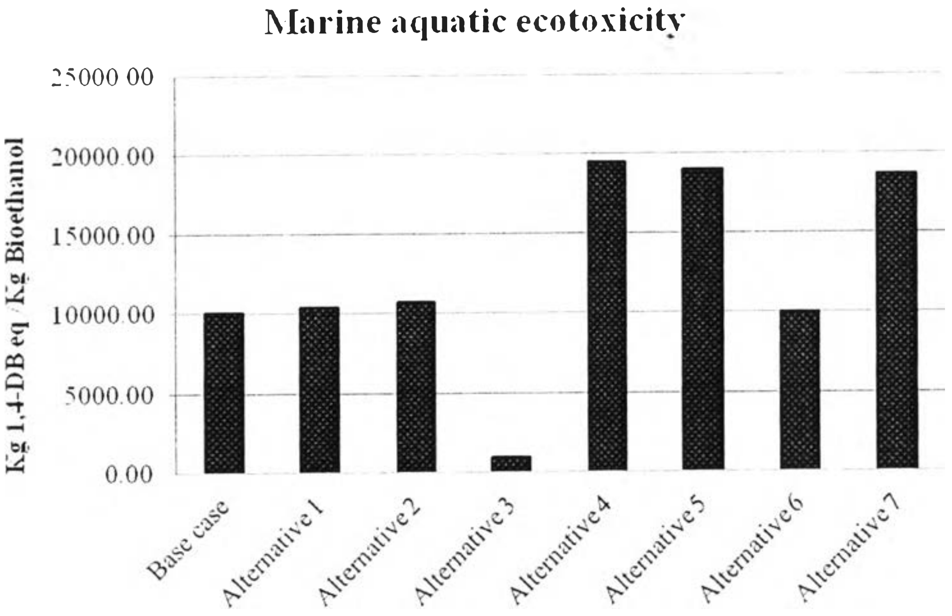

Figure 4.28 Comparison of the marine aquatic ecotoxicity (kg 1,4-DB-equivalent) per one kilogram of bioethanol for each design.

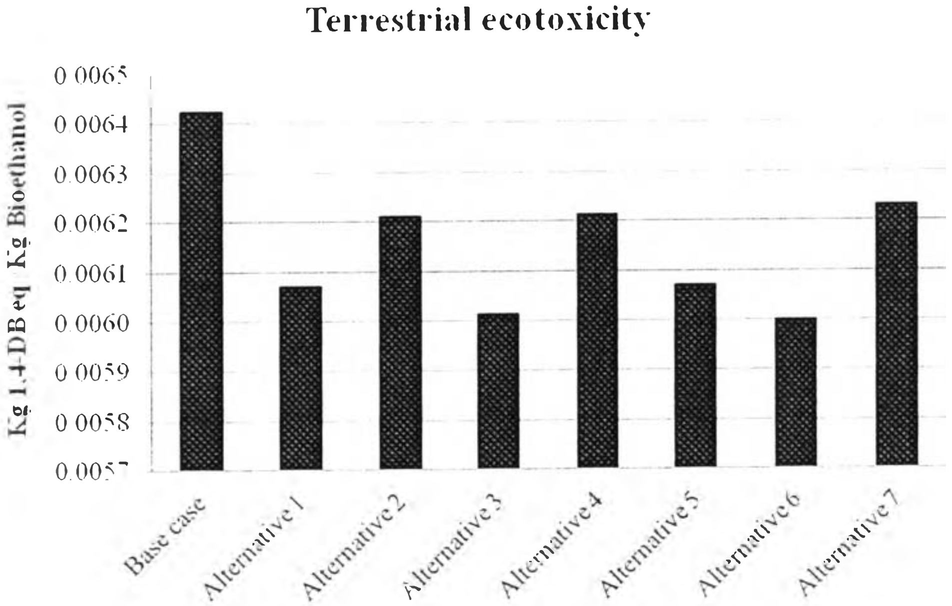

Figure 4.29 Comparison of the terrestrial ecotoxicity (kg 1,4-DB-equivalent) per one kilogram of bioethanol for each design.

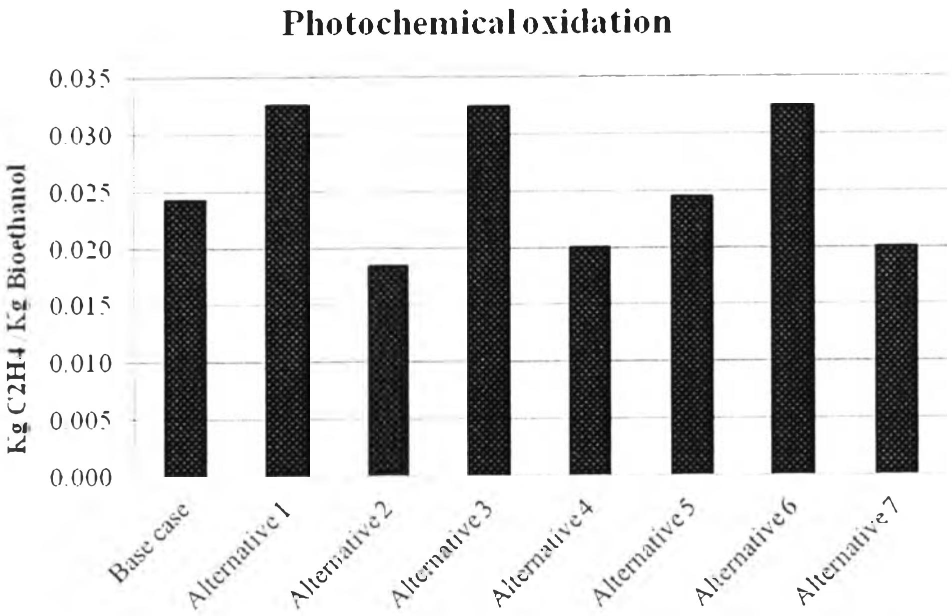

Figure 4.30 Comparison of the photochemical oxidation (kg C_2H_4) per one kilogram of bioethanol for each design.

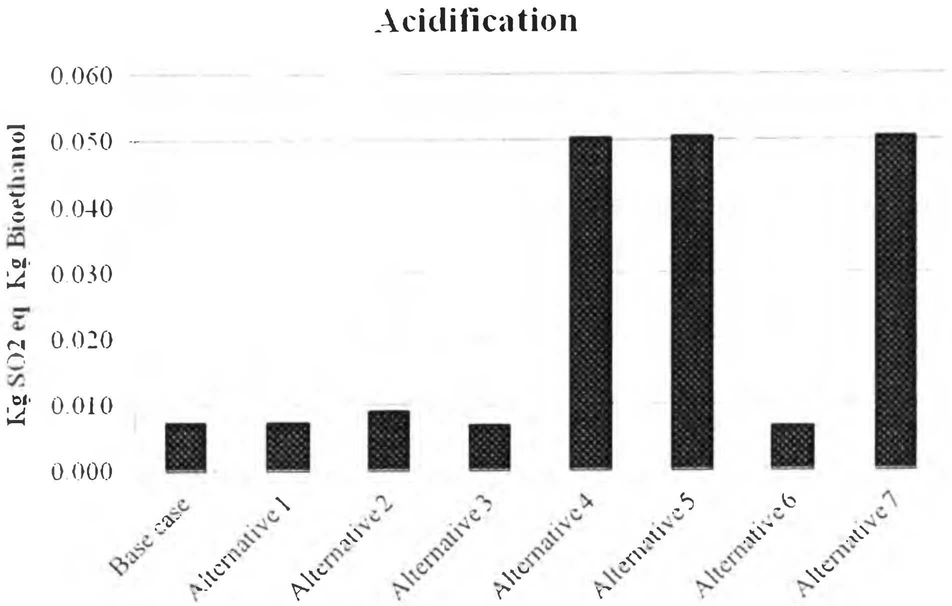

Figure 4.31 Comparison of the acidification (kg SO_2-equivalent) per one kilogram of bioethanol for each design.

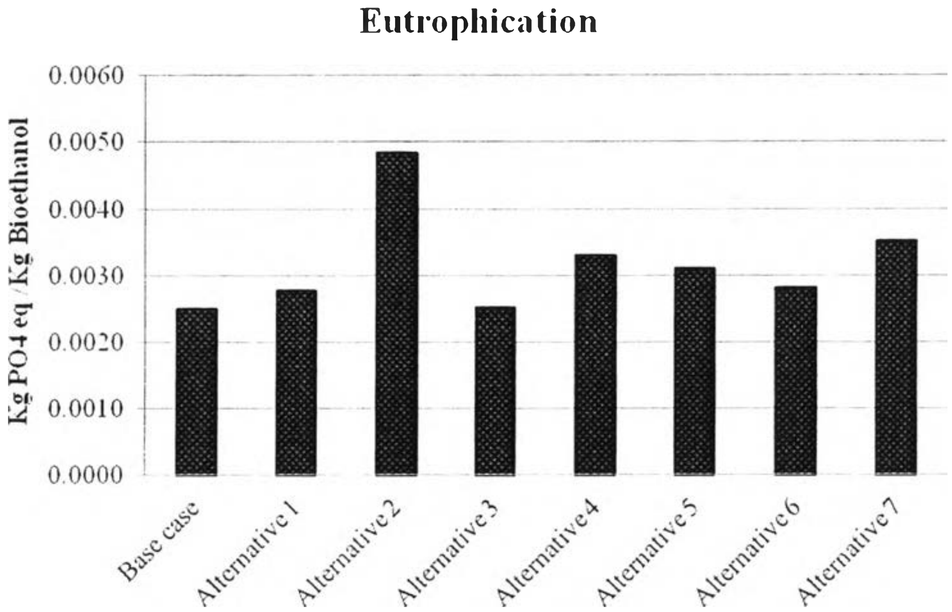

Figure 4.32 Comparison of the eutrophication (kg PO_4-equivalent) per one kilogram of bioethanol for each design.

The results from abiotic depletion, ozone layer depletion and terrestrial ecotoxicity that new design alternatives were more environmental friendly. For others impact, human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, acidification and eutrophication potential reveal that new design alternatives were nearby base case design.

Alternative 5 was the most environmental friendly in term of global warming with the reduction of 15.1 %. Alternative 3 was the best in term of abiotic depletion, ozone layer depletion, human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, acidification and eutrophication potential with the reduction of 13.2 %, 2.3 %, 88.2 %, 96.7 %, 90.8 %, 6.4, 5.3 % and 1.2 % respectively. For overall environmental point of view, it could say that alternative 3 was the best design in term of environment. However, this research focus mainly on global warming from greenhouse gases (GHG) which this alternative was not good enough on this impact. Furthermore, comparing between alternative 3 and 5, the other impacts of these two designs were not significantly difference. Therefore, alternative 5 would be prefered for environmental aspect.

4.3.4 Overall Comparison

After performing every analysis tools, the conclusion for the best design of bioethanol production process from cassava rhizome are shown below.

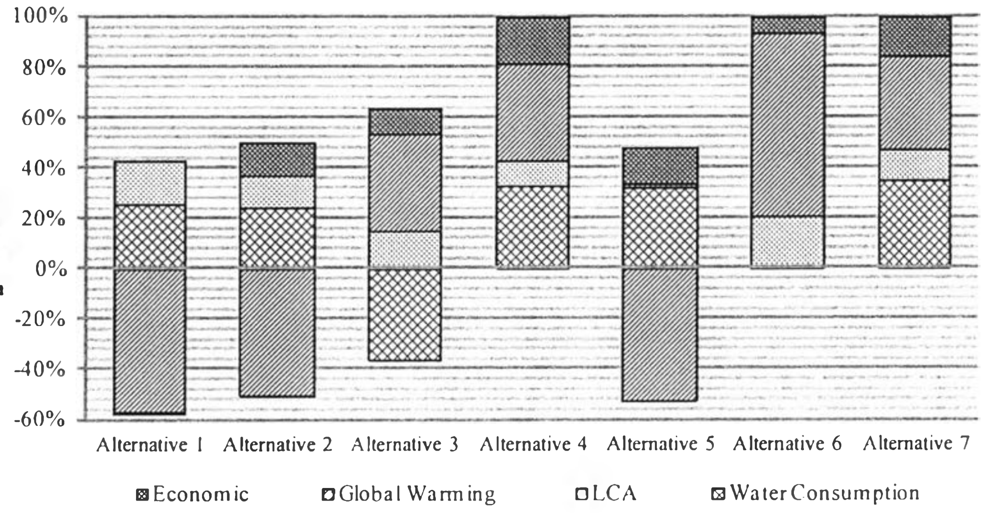

Figure 4.33 Comparison of the improving index for each of alternatives compare to the base case design.

According to Figure 4.33, there were four parameters that were analyzed; economic, global warming, LCA and water consumption. Each of parameters were calculated the improving index which compare with the base case design. The higher positive index means the better process is in term of that parameter. On the other hand, negative index means the worse process is. For more clearly view, the summary of the rank for the best design are shown in Table 4.16.

Table 4.16 List of rank for the best alternative design for bioethanol production process from cassava rhizome

Rank	Alternative	Description
1	4	Waste Water Recover by Membranes + Lignin Combustion
2	7	Waste Water Recover by Membranes + Lignin Combustion with Heat integrate
3	6	Lignin Combustion with Heat integrate
4	3	Lignin Combustion
5	5	Waste Water Recover by Membranes with Heat integrate
6	2	Waste Water Recover by Membranes
7	1	Base Case with Heat Integration

As you can see from the results, they indicated that alternative 4, waste water recovery using membranes and lignin combustion, was shown to be the best design for bioethanol production process from cassava rhizome because this design had the most water and energy saving and highest profit environmentally friendly.