CHAPTER IV
RESULTS AND DISCUSSION

4.1 Rice Straw Compositions

According to the literature, the compositions of rice straw used in this report are shown in Table 4.1.

Table 4.1 Rice straw compositions (Yoswathana *et al.*, 2010)

Component	% Dry Weight Basis
Cellulose	39.50
Hemicellulose	23.00
Arabinan	3.60
Mannan	1.80
Galactan	0.40
Lignin	12.90
Ash	18.80

* Moisture content is 12 %.

4.2 Location and Capacity of Plant

4.2.1 Location of the Bioethanol Production from Rice Straw Plant

The appropriate location for the plant should be placed not only close to the available raw material sources but also not too far from ethanol distributors or refineries. In this report, the amount of rice production is used directly for indicating rice straw quantity which means the higher rice production, the more rice straw. According to Thai Rice Exporters Association (2011), Nakhonsawan province had the highest rice production in Thailand (1.8 MMton in 2009-2010 seasons). In term of the distance from plant to refinery area (in this case assume to be Rayong province), Nakhonsawan province has longer distance (400 km) compared to Suphanburi province and Nakhon Ratchasima province (the second and the fifth place of rice production respectively) which have around the same distance (300 and 315 km respectively). However, the rice production within 100 km radius (limitation area for economical transportation) of Suphanburi province was higher than Nakhon Ratchasima province (5.5 MMton and 1.9 MMton respectively). According to the previous information, the most appropriate location for places bioethanol production from rice straw plant for this report is Suphanburi province.

4.2.2 Capacity of the Bioethanol Production from Rice Straw Plant

The plant capacity was designed based on the average capacity of the existing bioethanol production plants in Thailand as seen in Table 2.6 (Chapter II). The capacity of this plant was assumed to be 200,000 L/day (around 159 ton/day) which was approximately 6.4 % of total ethanol production in Thailand. Furthermore, this capacity had to correspond to the rice straw feed available quantity in Thailand and the transportation constraint (100 km radius around the plant). At this capacity, the quantity of the rice straw was about 1.4 kton/day (0.38 MMton/year of rice) which is 6.8 % of the transportation area and 1.2 % of the total rice straw in Thailand. Note that even this research use the information based on NREL, but the chosen capacity of the plant was lower compare to the NREL plant which around 560,000 L/day (NREL, 1999). However, these data still can be used in the plant even some of them have to scale down from original data (mainly equipment sizing and economic data) because they not significantly affect to the results.

4.3 Base Case Design

4.3.1 Process Simulation of Base Case Design

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

This process design was modeled and simulated though the PRO/II 9.1, (PRO/II, 2011) as shown in Figure 4.2.

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

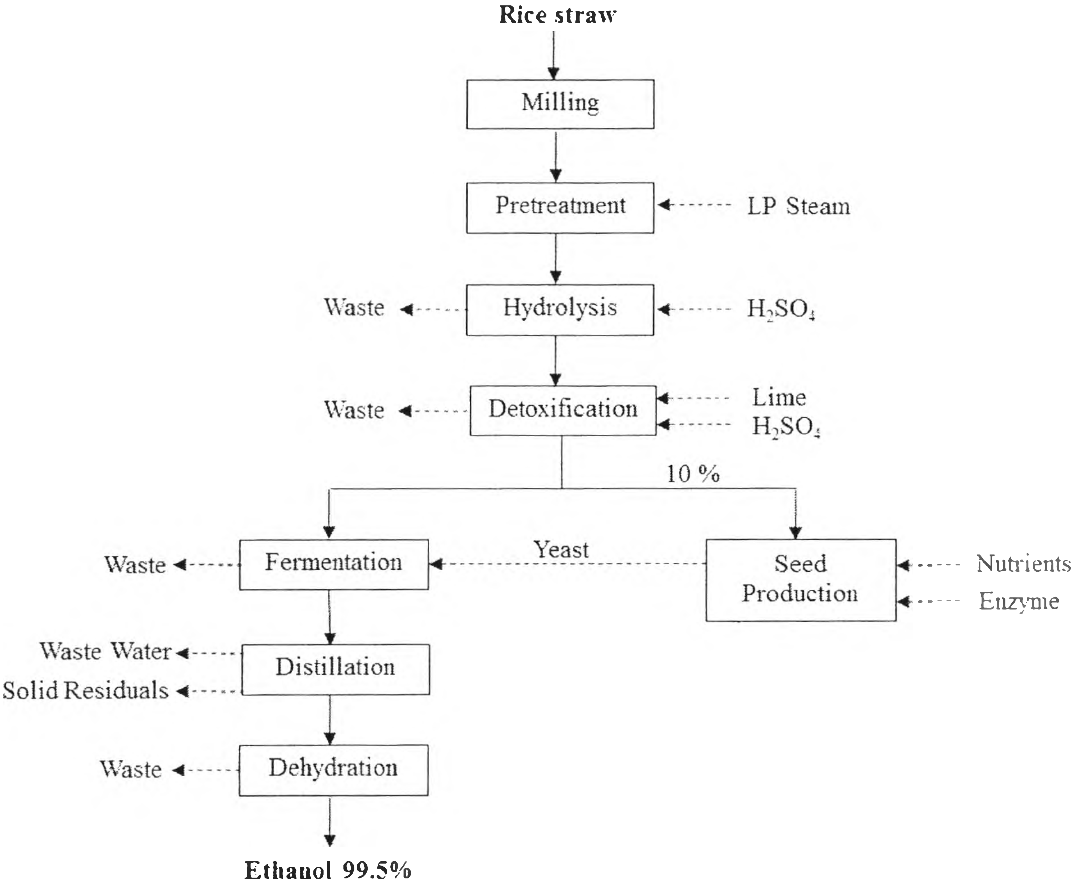

Figure 4.1 Bioethanol production process from rice straw (Binod *et al.*, 2010; NREL, 1999).

The milled rice straws are first steamed with low pressure steam in a feed (M1) to about 100 °C in order to remove non-condensable parts. After steaming, acid is added in the impregnator section of M2. Concentrated sulfuric acid is diluted with water and added to the reactor. Concentrated acid is added until the mixture (the total water, including steam and acid) in the reactor readies 1 % sulfuric acid. The reactor is brought up to temperature by direct injection of 13 atm (192 °C saturation temperature and 76 °C superheat) steam. Table C1 in Appendix C summarizes the conditions in the hydrolysis reactor. The reactions and conversions used in hydrolysis reactor are given in Table B1 in Appendix B.

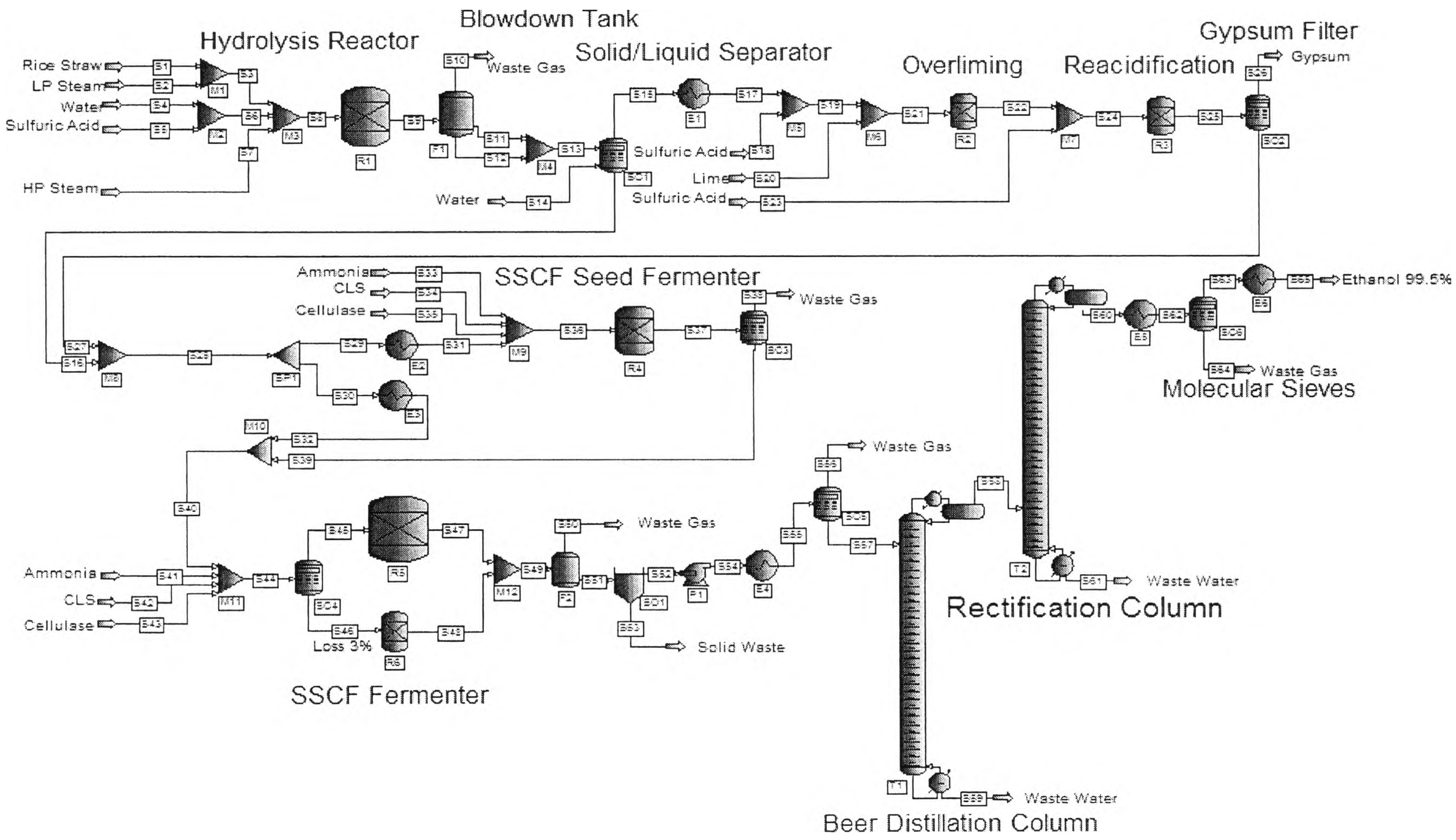

Figure 4.2 Flowsheet of the bioethanol production process from rice straw for the base case design (Binod *et al.*, 2010; NREL, 1999).

The hydrolysis reactor (R1) operates at 10 atm pressure and 180 °C. The exiting material is flash-cooled to 102 °C at 1 atm in F1. In this step, 59.9 % of the furfural and 4.2 % of HMF are removed as vapor. The hydrolyzate slurry is conveyed to a washing filter (SC1) for separation of the solids and the liquids. Water is added to wash the solids from more of the toxic materials removed. The filter can remove 99.6 % of solid from hydrolyzate slurry. The purpose of separating the liquids from the solids is to facilitate conditioning of the liquid portion to remove toxicity to the downstream fermentation. Normally, the ion exchange unit is the next part after solid and liquid separation for removing acetic acid. However, it is not necessary to use that unit in this process because acetic acid is not a significant content in the rice straw.

After solid and liquid separation, the material is overlimed. This is accomplished by heat the material to 50 °C and acidifying the liquid hydrolyzate to pH 2 by addition of sulfuric acid. Lime is then added in mixer (M6) to raise the pH to 10. In PRO/II simulation, pH is the parameter that cannot be measured, so the flowrate of lime is calculated by the ratio of main stream and lime from NREL data. Then, sulfuric acid is added again to reacidifying. The filtration is assumed to remove 100 % of the precipitated gypsum. The conditioned hydrolyzate liquid is recombined with hydrolyzate solids (which were separated in SC1) in mixer (M8) (Wooley *et al.*, 1999). Table C3 summarizes the detoxification design specifications. The reactions and conversions used in detoxification are given in Tables B2.

Detoxified hydrolyzate is split to *Zymomonas mobilis* (*Z. mobilis)* seed production and SSCF fermenters. The hydrolyzate fed to the SSCF fermenter is about 90 % by weight and the rest is fed to seed production to produce *Z. mobilis* for SSCF call “inoculum”. The seed fermenters operate at 40 °C. The incoming hydrolyzate (about 56 °C) is cooled in E2 with cooling water to 40 °C. Table C4 summarizes the seed train design specifications. The reactions and conversions used in the production SSCF seed train fermenter are given in Tables B3 and B4 (Aden *et al.*, 2002).

Then, the rest of detoxified hydrolyzate slurry is first cooled to 40 °C in E3 using cooling water and then added directly to the SSCF fermenter. In addition, inoculum from the seed fermenter at a ratio of 1/10 of the hydrolyzate is fed along with cellulose. Cellulase is fed at the rate of 2 % by weight of cellulose in hydrolyzate. Corn steep liquor is added as a nutrient at a rate of 0.25 % by weight. Table C5 summarizes the design specifications used for SSCF fermenter. The reactions and conversions used in the production SSCF fermenter are given in Tables B5 and B6.

In addition to saccharification and fermentation to ethanol, loss to other products because of contaminating organisms occurs. This is modeled as a side stream (bypassing the SSCF) that reacts to lactic acid. This allows the model to simply assign a percent loss to contamination and the conversions in Table B6 do not have to be adjusted. The loss to other products that caused by *Z. mobilis* are given in the SSCF reactions in Table B6. Table B7 shows the contamination reactions. A total of 3 % of the sugars available for fermentation are considered lost to contamination. The flash and solid separator are the units that appear in the SSCF fermenter in NREL to separate the waste from the product before fed to distillation column.

Product from the fermentation is first preheated with heat exchanger (E4). In NREL, the beer column operates in a mode to remove the CO_2 and as little ethanol as possible overhead, while removing the water in the bottoms and ethanol is removed as a vapor side draw from the column. However, it is difficult to using the side draw in PRO/II. The best way to do is using stream calculator to remove CO_2 and some of ethanol as waste gas and using column (T1) to remove the water in the bottoms. All CO_2 and only 1.5 % of the ethanol are removed here. This separation is accomplished with 32 actual trays with the feed on actual tray 4 from the top. The column T1 is operated at 1.77 atm overhead pressure. Table C6 summarizes the design specifications used for beer distillation column.

The vapor product from T1 is fed directly to T2, the rectification column. Column T2 is accomplished with 60 actual trays with the feed on actual tray 50 from the top. Most of the water is removed (63.8 %) and the ethanol mainly recovered (99.5 wt%). Table C7 summarizes the design specifications used for rectification column.

Overhead vapor from T2 is fed to the molecular sieve adsorption unit (SC6). Saturated vapor from the distillation is first heated to 100 °C which is the favorable condition in molecular sieve and fed to the unit. The product from molecular sieve is cooled by cooling water to about 40 °C for storage. Based on the yield of ethanol production of 160 L/ton dry of rice straw, this process gives the final product of 200,000 L/day with 99.5 wt% concentration of ethanol.

From Figure 4.2, in the ethanol production process from rice straw, there are 9 waste streams – S10, S26, S38, S50, S53, S56, S59, S61 and S64:

- S10 stream is waste gases that mainly are furfural, HMF and steam.
- S26 stream is gypsum waste.
- S38, S50 and S56 are flue gas streams with large amounts of carbon dioxide.
- S53 streams mainly contain solid contaminant as lignin and ash.
- S59, S61 and S64 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.

4.3.2 Sustainability Analysis of Base Case Design

4.3.2.1 Sustainability Metrics Results

SustainPro was used to analyze the sustainability of the base case design as well as new designs. This software classifies the sustainability metrics into 4 groups: energy, material, water and economic. The calculated sustainability metrics for the base case design are given in Table 4.2.

Table 4.2 Sustainability metrics results of the base case design

Metric		Base Case
Energy	Total Net Primary Energy Usage rate (GJ/y)	1,060,201
	% Total Net Primary Energy sourced from renewables	0.9992
	Total Net Primary Energy Usage per Kg product (kJ/kg)	20,002
	Total Net Primary Energy Usage per unit value added (kJ/$)	6.712
Material	Total raw materials used per kg product (kg/kg)	5.199
	Total raw materials used per unit value added	0.00174
	Fraction of raw materials recycled within company	0
	Fraction of raw materials recycled from consumers	0
	Hazardous raw material per kg product	1.768
Water	Net water consumed per unit mass of product (kg/kg)	31.45
	Net water consumed per unit value added	0.01055
Economic	Value added ($/y)	19,745,122

4.3.2.2 Indicator Results

The indicators results are related to the open paths (OP) and closed paths (CP) in the process. An OP is the course that a component makes from its entrance to its exit through an output stream. 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 386 open-paths (OP) and zero closed-paths because the process does not have any recycle streams. The mass and energy indicators were calculated. The most sensitive indicators are listed in Table 4.3.

Table 4.3 List of the most sensitive indicators for the open-paths for the base case design

Path	MVA	Prob	Path	EWC	Prob	Path	TVA	Prob
OP 380 Cellulase-S43- S53	-13,827	High	OP 38 Glucose- P R5- S59	1,250	Low	OP 380 Cellulase-S43- S53	-13,827	High
OP 383 $CASO_4$-P R2- S26	-5,224	Low	***OP 247*** ***H_2O-S14-S59***	***1,139***	***High***	OP 383 $CASO_4$-P R2- S26	-5,225	Low
OP 386 Ash-S1- S53	-2,551	High	OP 94 Ethanol- P R5- S65	1,007	Medium	***OP 247*** ***H_2O-S14-S59***	***-2,877***	***High***
OP 376 CLS-S42-S59	-2,433	High	OP 75 Arabinose-P R1-S59	799	Low	OP 386 Ash-S1-S53	-2,602	High
OP 384 $CASO_4$-P R3-S26	-2,239	Low	***OP 246*** ***H_2O-S14-S61***	***540***	***High***	OP 376 CSL-S42-S59	-2,444	High
OP 26 ***Lignin-S1-S53***	***-1,739***	***High***	***OP 279*** ***H_2O-S43-S59***	***516***	***High***	OP 384 $CASO_4$-P R3-S26	-2,239	Low
OP 247 ***H_2O-S14-S59***	***-1,738***	***High***	***OP 180*** ***H_2O-S4-S59***	***467***	***High***	***OP 26*** ***Lignin-S1-S53***	***-1,786***	***High***
OP 372 CLS-S34-S59	-1,654	High	***OP 263*** ***H_2O-S14-S59***	***463***	***High***	OP 372 CLS-S34-S59	-1,662	High
OP 379 Cellulase-S35- S53	-1,418	High	OP 62 Xylose- P R1-S59	347	Low	OP 379 Cellulase-S35- S53	-1,418	High
OP 279 ***H_2O-S43-S59***	***-841***	***High***	OP 79 Arabinose-P R1-S59	338	Low	***OP 279*** ***H_2O-S43-S59***	***-1,357***	***High***
OP 263 ***H_2O-S14-S59***	***-733***	***High***	***OP 214*** ***H_2O-S7-S59***	***273***	***High***	OP 38 Glucose-SP R5-S59	-1,250	Low
OP 314 H_2SO_4-S5-S59	-730	High	***OP 278*** ***H_2O-S43-S61***	***261***	***High***	***OP 263*** ***H_2O-S14-S59***	***-1,196***	***High***
OP 180 ***H_2O-S4-S59***	***-650***	***High***	***OP 262*** ***H_2O-S14-S61***	***228***	***High***	***OP 180*** ***H_2O-S4-S59***	***-1,117***	***High***

According to the result from Table 4.3, "Prob" means probability to improve that path. The second line of each path refers to the component and the path it follow (from starting stream to final stream). The italic bold is stand for the path that will be focused on.

From the TVA result, the highest value of indicator was OP 380 that is cellulase (enzyme) because the price as raw material is very expensive

(5 \$/kg) therefor it effects to the economic section. Considering the improvement of it, the enzyme is a difficult component to deal with as it rarely can be recovered or recycled. Actually, cellulase is impact only economic issue but not impact environmental issue of the process that much, so it will not be analyzed. Regarding the gypsum, it is the solid and also the result showed that it had low probability to improve; therefore recycling it to the process does not seem feasible. Ash is the solid that cannot handle anything with, so just leave it as the solid waste. 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. The most of indicators indicate to water which came from S4, S14 and S43 and exit at S59, S61 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 S53 which could possibly be used as energy source.

After the conclusions, 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 4.4 Scores, open-paths, indicators, components and paths in the process for the indicators chosen to further analyze as good targets for improvement

Scores	Path	Indicator	Component	Path
30	OP 180	MVA, EWC, TVA	H_2O	S4-S59
30	OP 214	MVA, EWC, TVA	H_2O	S7-S59
29	OP 246	MVA, EWC, TVA	H_2O	S14-S61
27	OP 247	MVA, EWC, TVA	H_2O	S14-S59
23	OP 262	MVA, EWC, TVA	H_2O	S14-S61
21	OP 263	MVA, EWC, TVA	H_2O	S14-S59
20	OP 279	MVA, EWC, TVA	H_2O	S43-S59
18	OP 278	MVA, EWC, TVA	H_2O	S43-S59
12	OP 26	MVA, EWC, TVA	Lignin	S1-S53

As shown in Table 4.4, water from S4 and S7 to S59 had the highest score which mean them were the top priority to improve. Furthermore, water from S14 to S59 and 61 also had high score and they affected many paths and indicators. For water from S43 had lower score than other water path which mean it was not affect the overall improvement. Furthermore, these path is the water mixed with cellulase so, it is not realistic to deal with them. 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.

4.3.2.3 Sensitivity Analysis Results

This analysis was made to the relevant streams in the selected paths in order to know the possibility to improve the indicators by variation of their variables. The variables that influencing the indicators suffering the variations of 5 %, 10 % and 15 % were analyzed. The sensitivity analysis of OP 180, OP 214, OP 246, OP 247, OP 262, OP 263 and OP 26 is shown in Tables 4.5, 4.6, 4.7, 4.8, 4.9, 4.10 and 4.11 respectively.

Table 4.5 Sensitivity analysis of OP 180 TVA

	Inlet Steam	Unit Operation								
Variable Variation (%)	S4	R1	E1	R2	R3	E3	R5	P1	E4	Reb T1
5 %	4.83 %	0.19 %	0.05 %	0.01 %	0.01 %	0.05 %	0.02 %	0.00 %	1.37 %	0.39 %
10 %	9.67 %	0.37 %	0.11 %	0.02 %	0.01 %	0.10 %	0.04 %	0.00 %	2.73 %	0.79 %
15 %	*14.54 %*	0.56 %	0.16 %	0.04 %	0.02 %	0.15 %	0.07 %	0.00 %	4.10 %	1.18 %

Table 4.6 Sensitivity analysis of OP 214 TVA

	Inlet Steam	Unit Operation								
Variable Variation (%)	S7	R1	E1	R2	R3	E3	R5	P1	E4	Reb T1
5 %	4.90 %	0.19 %	0.05 %	0.01 %	0.01 %	0.05 %	0.02 %	0.00 %	1.37 %	0.39 %
10 %	9.81 %	0.37 %	0.11 %	0.02 %	0.01 %	0.10 %	0.04 %	0.00 %	2.73 %	0.79 %
15 %	*14.73 %*	0.56 %	0.16 %	0.04 %	0.02 %	0.15 %	0.07 %	0.00 %	4.10 %	1.18 %

Table 4.7 Sensitivity analysis of OP 246 TVA

	Inlet Steam	Unit Operation								
Variable Variation (%)	S14	E1	R2	R3	E3	R5	P1	E4	Cond T1	Reb T2
5 %	3.65 %	0.00 %	0.00 %	0.00 %	0.00 %	0.00 %	0.00 %	0.05 %	0.17 %	4.68 %
10 %	7.40 %	0.00 %	0.00 %	0.00 %	0.00 %	0.00 %	0.00 %	0.10 %	0.33 %	9.35 %
15 %	*11.25 %*	0.01 %	0.00 %	0.00 %	0.01 %	0.00 %	0.00 %	0.15 %	0.50 %	14.03 %

Table 4.8 Sensitivity analysis of OP 247 TVA

	Inlet Steam	Unit Operation							
Variable Variation (%)	S14	E1	R2	R3	E3	R5	P1	E4	Reb T1
5 %	4.55 %	0.06 %	0.01 %	0.01%	0.05 %	0.02 %	0.00 %	1.42 %	0.41 %
10 %	9.14 %	0.11 %	0.03 %	0.01%	0.11 %	0.05 %	0.00 %	2.84 %	0.82 %
15 %	*13.76 %*	0.17 %	0.04 %	0.02%	0.16 %	0.07 %	0.00 %	4.26 %	1.23 %

Table 4.9 Sensitivity analysis of OP 262 TVA

	Inlet Steam	Unit Operation					
Variable Variation (%)	S14	E3	R5	P1	E4	Cond T1	Reb T2
5 %	4.43 %	0.00 %	0.00 %	0.00 %	0.05 %	0.17 %	4.68 %
10 %	8.92 %	0.00 %	0.00 %	0.00 %	0.10 %	0.33 %	9.36 %
15 %	*13.46 %*	0.01 %	0.00 %	0.00 %	0.15 %	0.50 %	14.04 %

Table 4.10 Sensitivity analysis of OP 263 TVA

	Inlet Steam	Unit Operation				
Variable Variation (%)	S14	E3	R5	P1	E4	Reb T1
5 %	4.82 %	0.05 %	0.02 %	0.00 %	1.44 %	0.41 %
10 %	9.67 %	0.11 %	0.05 %	0.00 %	2.88 %	0.83 %
15 %	*14.52 %*	0.16 %	0.07 %	0.00 %	4.32 %	1.24 %

Table 4.11 Sensitivity analysis of OP 26 TVA

	Inlet Steam	Unit Operation		
Variable Variation (%)	**S1**	**R1**	**E3**	**R5**
5 %	4.99 %	0.13 %	0.00 %	0.00 %
10 %	9.98 %	0.25 %	0.01 %	0.00 %
15 %	*14.98 %*	0.38 %	0.01 %	0.01 %

From the results shown in the tables, the approach to evaluate the sensitivity analysis performed is to focus at the sections that have the highest percentage as these are the ones with the largest impact on improving the indicators by changing of the variables. The stream S7 had the highest percentage on OP 214 (14.73 %). The stream S4 and S14 also had high percentage on OP 180 (14.54 %) and OP 263 (14.52 %) respectively. The ending stream of these paths is S59 that mean the way to design alternatives is to look at these streams and try to improve them. Regarding the path OP 26, as mention in the previous section, the best way to improve lignin is burn it as the fuel.

4.3.2.4 Safety Indices Results

This analysis using requested information regarding the component present in the process: flash point, boiling point, and toxicity. It also requires data concerning equipment: construction material, type of equipment; data related with the reaction: heat of main reaction and mass. The safety indices of the base case design of bioethanol conversion process are presented in Table 4.12.

As shown in Chapter III, the higher the score, the more unsafe is the process. If one looks at for instance the flammability, it can be seen that it took the maximum value of 4. This does not mean that the process is dangerous due to the high flammability of its components; it only means that there are in the process components that have high flammability and that in certain conditions could be dangerous. So, the conclusion to draw from this flammability result of 4 is that caution must be taken in the use of the components so that no spark accident occurs. For ISI score, it can be seen from Table 4.12 that the process was 18 from the possible maximum ISI score of 53. Hence, this bioethanol production from rice straw process was ***inherently safe***.

Table 4.12 Safety indices for the bioethanol production from rice straw process

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	Inventory, I_I	0
Heat of the side reactions, I_{rs}	0	Process temperature, I_t	2
Chemical Interaction, I_{int}	1	Process pressure, I_p	1
Subindices for hazardous substances		Subindices for process system	
Flammability, I_{fl}	4	Equipment, I_{eq}	
Explosiveness, I_{ex}	1	I_{ISBL}	2
Toxicity, I_{tox}	2	I_{OSBL}	2
Corrosivity, I_{cor}	1	Process structure, I_{st}	2
I_{ci}	**9**	I_{pi}	**9**
ISI	**18**		

The indices could be used directly as a measurement of the safety of the process, and the results can show potential targets for improving the process. However, in this study the targets for improvement aim to improve the process economically and environment while not making safety worse. Therefore, the comparison of the base case and alternatives will be further shown to confirm that the safety has improved, or that has at least maintained the same level.

4.3.3 Economic Evaluation of Base Case Design

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).

- Production rate is 66.67 ML/year (200,000 L/day)
- Annual load is 8,000 hours/year
- Working days 330 day/year

Above information is the common specification for all cases, and that therefore has been applied in all the economic evaluation calculations.

4.3.3.1 Capital Cost of Base Case Design

The outcome of the TCI (Total Capital Investment) calculations for the base case design was 63.5 MM$ 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).

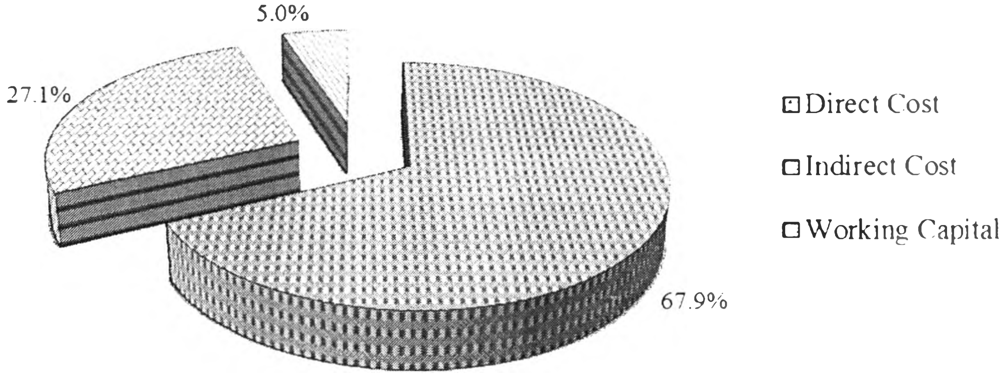

Figure 4.3 Breakdown of the total capital investment.

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

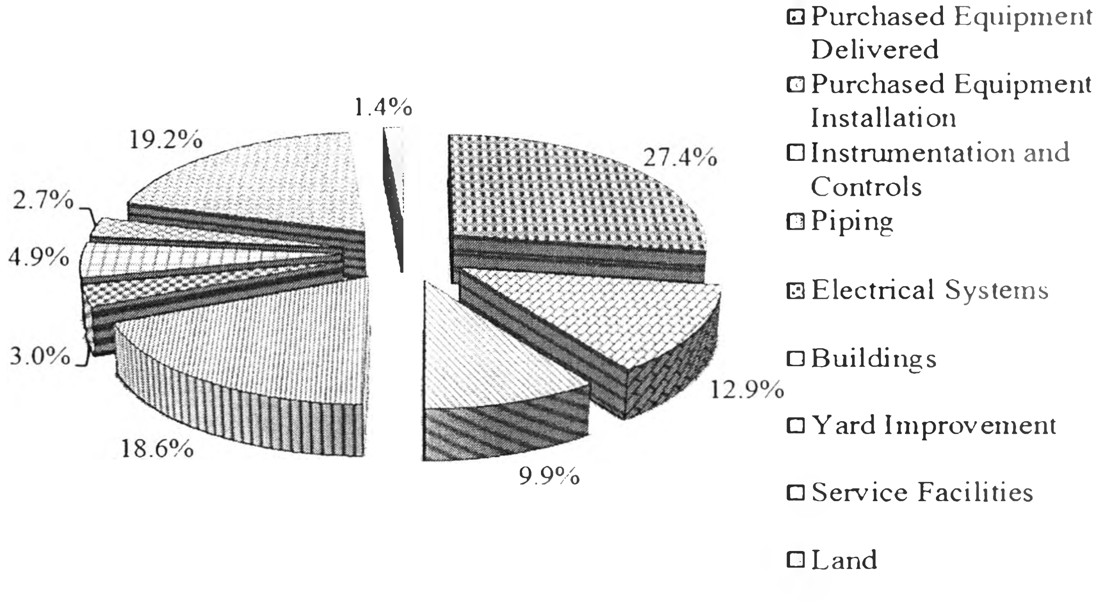

Figure 4.4 Breakdown of the direct cost.

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.

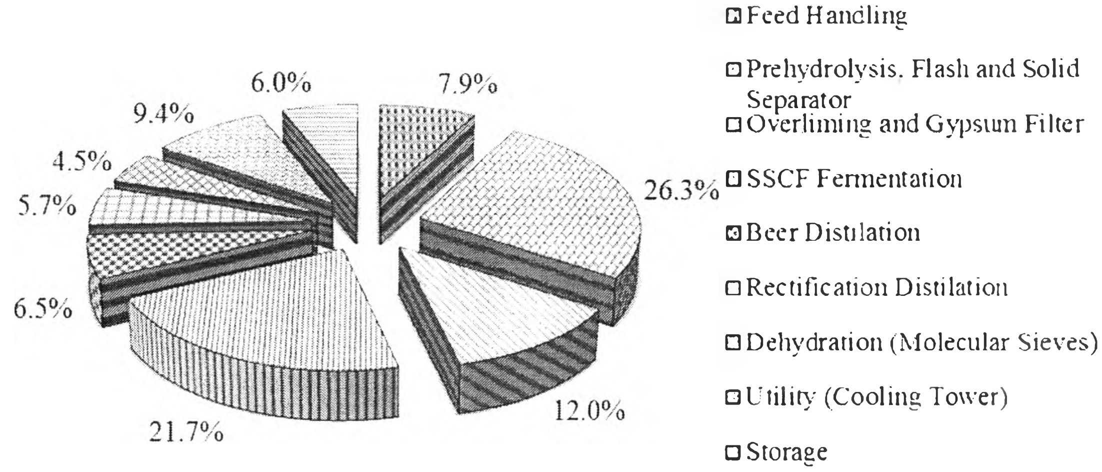

Figure 4.5 Contribution to equipment costs of each area of the process.

As shown in Figure 4.5, prehydrolysis section had the highest portion for all equipment units because the prehydrolysis reactor is very expensive unit for handle the milled rice straws and convert them to sugars which is one of the most importance process in ethanol production. 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.

4.3.3.2 Operating Cost of Base Case Design

The result of the total production cost (without depreciation) calculations for the base case design was 62.0 MM$ which has better details in Appendix E.6 and its breakdown can be seen in Figure 4.6.

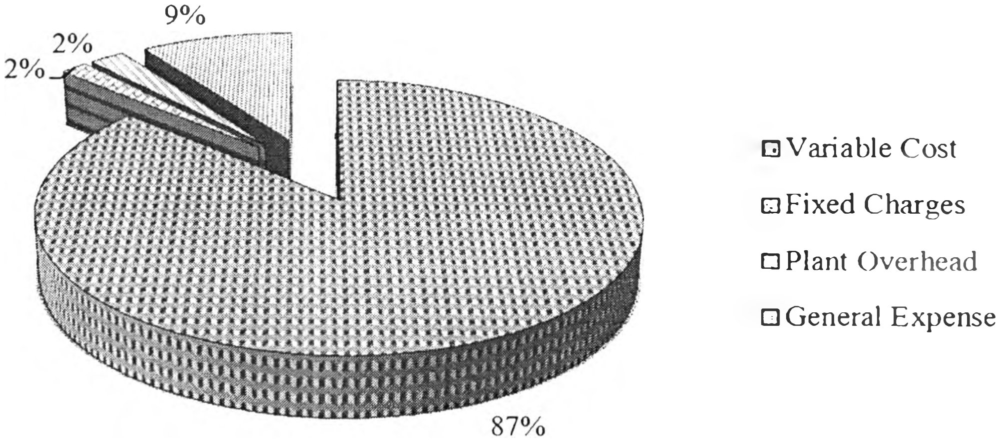

Figure 4.6 Breakdown of the total production cost.

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 0.906 $/L of ethanol (1.140 $/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.

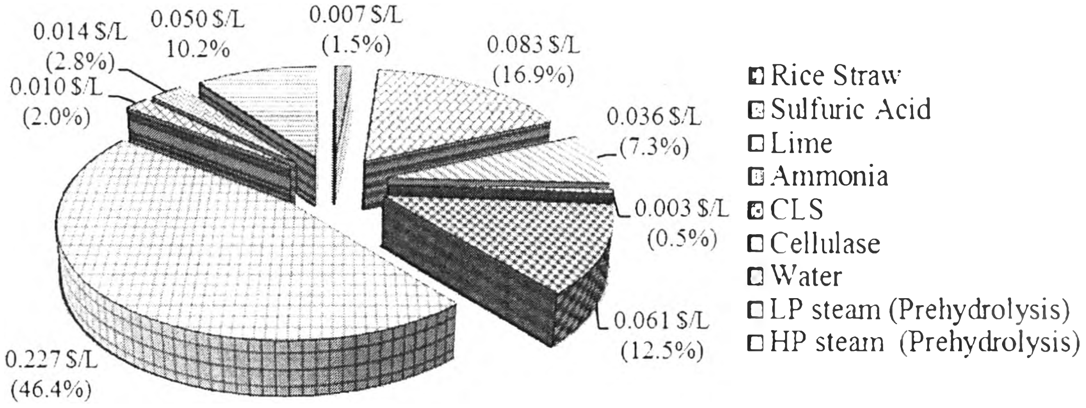

Figure 4.7 Breakdown of the contribution of raw materials for the production cost.

From Figure 4.7, it can be seen that the importance of the cellulase (enzyme) as it had the highest influence in the production cost of ethanol as mention in the previous section. Regarding the rice straw, even it is the most important feed, but it is very small portion for the production cost (1.5 %) since it is considered as the waste of rice production so the price is very cheap.

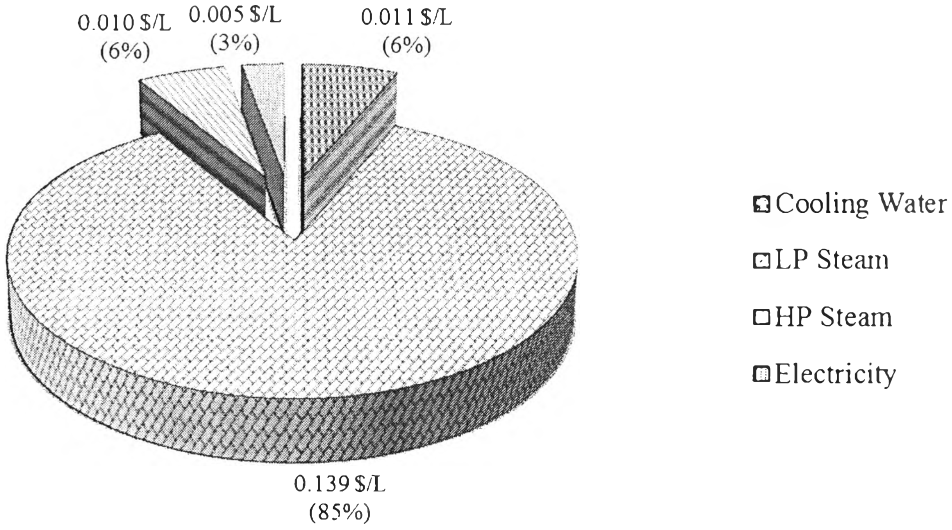

Figure 4.8 Breakdown of the contribution of utilities for the production cost.

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, 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 prehydrolysis section).

4.3.3.3 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.

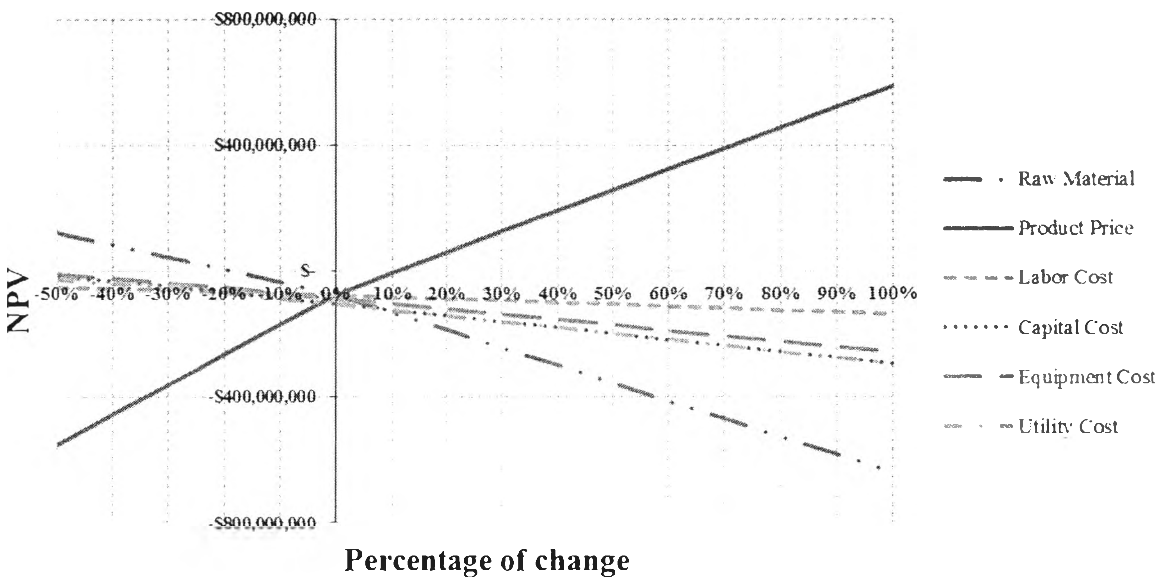

Figure 4.9 Sensitivity analysis compare to NPV.

It can be seen from Figure 4.9, the highest influence to NPV was the price of the ethanol. Also, the raw material price had high affect to the NPV which from the result in Figure 4.7, cellulase (enzyme) was the one that had the most influence to the profit.

4.3.3.4 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 (Khabibullin *et al.*, 2010).

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, 2011). 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 4.13.

Table 4.13 Profitability of the base case design

Profitability	
Not include time value of money	
Rate of Return	-13.78 %
Net Return	$-18,753,320
Include time value of money	
Continuous cash flows and discounting	
Net Present Value (NPV)	$-113,859,740
Internal Rate of Return (IRR)	N/A

According to the result, all of the parameters were in negative values which mean this project is clearly not worth to invest. Furthermore, the breakeven point did not exist in Figure 4.10. In other words, this project will never get the profit. After the process was improved, the profit should be increased.

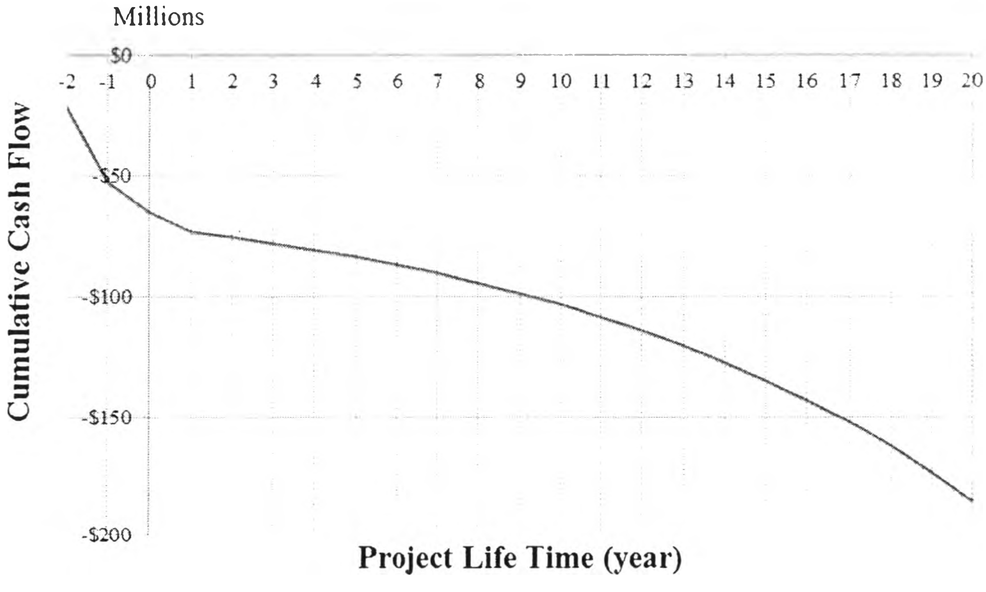

Figure 4.10 Cumulative cash flow for 20 year project of the base case design.

4.3.4 Life Cycle Assessment of Base Case Design

4.3.4.1 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.

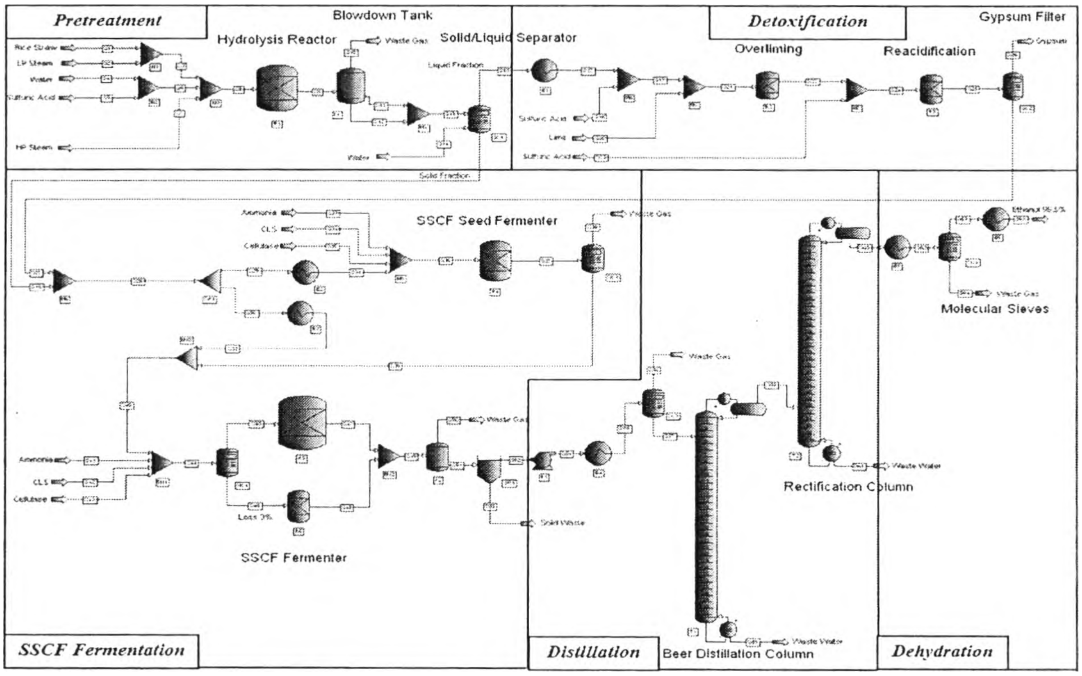

Figure 4.11 Five stage of the base case design life cycle.

For the case study, the wastewater 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 rice straw with the ethanol production process was considered. The system boundary of bioethanol production was divided into eight stages which were rice plantation, transportation, pretreatment, detoxification, SSCF fermentation, distillation, dehydration and wastewater treatment as shown in Figure 4.12. It should be noted that wastewater treatment in ethanol conversion process was not included in the economic evaluation section due to the lack of cost data and simplicity of calculations. Moreover, this stage was not the main focus, therefore this process was considered as outsource process in the life cycle.

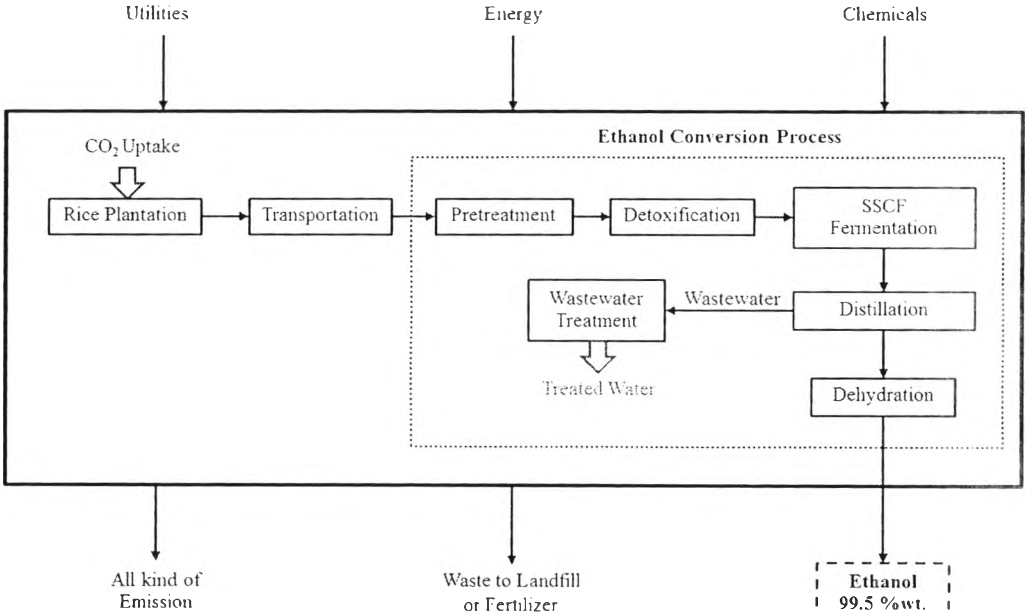

Figure 4.12 System boundary of the base case design.

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 rice for this research was assumed to be 1.1 kg CO_2/kg of rice which means that with one kilogram rice production, 1100 g carbon dioxide in the atmosphere would be absorbed (Hsu *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 4.14, 4.15, 4.16, 4.17, 4.18, 4.19, 4.20 and 4.21.

Table 4.14 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in rice plantation stage for the base case design (Niracharopas, 2011)

Input Inventory		
Type	**With Cost Allocation**	
	Amount	**Unit**
Materials/Fuels:		
Rice seed	0.0025	kg
Glyphosate	0.0013	kg
Paraquat (Bipyridylium)	0.0012	kg
Fertilizer (N)	0.0036	kg
Fertilizer (P)	0.1316	kg
Fertilizer (K)	6.58E-04	kg
Diesel	0.0029	kg
Output inventory		
Type	**Amount**	**Unit**
Products:		
Rice straw before transport	9.4016	kg
Emissions to air:		
Carbon dioxide	-7.5237	kg
Carbon monoxide	8.03E-06	kg
Nitrogen dioxide	2.87E-08	kg
Methane	5.73E-07	kg
Emissions to water:		
Wastewater	5.92E-08	m^3

Table 4.15 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in transportation (one way) stage for the base case design (Niracharopas, 2011)

Input Inventory		
Type	**Amount**	**Unit**
Materials/Fuels:		
Rice straw before transport	9.4016	kg
Diesel	0.0201	kg
Output inventory		
Type	**Amount**	**Unit**
Products:		
Rice straw	8.9315	kg
Emissions to air:		
Carbon dioxide	0.1177	kg
Carbon monoxide	0.0021	kg
Nitrogen dioxide	1.22E-04	kg
Particulate matter (PM)	3.26E-04	kg

Table 4.16 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in pretreatment stage for the base case design

Input Inventory		
Type	**Amount**	**Unit**
Materials/Fuels:		
Rice straw	8.9315	kg
Sulfuric acid	0.0859	kg
Water	12.7392	kg
Electricity/Heat:		
Steam	3.7201	kg
Output Inventory		
Type	**Amount**	**Unit**
Products:		
Output-1 from Pretreatment	12.3679	kg
Output-2 from Pretreatment	10.6388	kg
Emissions to air:		
Water	1.9642	kg
Furfural	0.0070	kg

Table 4.17 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in detoxification stage for the base case design

Input Inventory		
Type	**Amount**	**Unit**
Materials/Fuels:		
Output-1 from Pretreatment	12.3679	kg
Sulfuric acid	0.0875	kg
Calcium hydroxide (Hydrated lime)	0.1117	kg
Make up cooling water	2.6746	kg
Electricity/Heat:		
Electricity	0.0060	kWh
Output Inventory		
Type	**Amount**	**Unit**
Products:		
Output-3 from Detoxification	12.3436	kg
Waste and emissions to treatment:		
Gypsum	0.2053	kg
Biowaste to fertilizer	0.0182	kg

Table 4.18 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in SSCF fermentation stage for the base case design

Input Inventory		
Type	**Amount**	**Unit**
Materials/Fuels:		
Output-2 from Pretreatment	10.6388	kg
Output-3 from Detoxification	12.3436	kg
Ammonia	0.0056	kg
Water	2.8531	kg
Make up cooling water	5.8922	kg
Electricity/Heat:		
Electricity	0.0132	kWh
Output Inventory		
Type	**Amount**	**Unit**
Products:		
Output-4 from SSCF Fermenter	22.3392	kg
Emissions to air:		
Water	0.0144	kg
Ethanol	0.0149	kg
Carbon dioxide	0.5077	kg
Oxygen	0.0148	kg
Waste and emissions to treatment:		
Biowaste to fertilizer	1.5284	kg
Ash	1.4776	kg

Table 4.19 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in distillation stage for the base case design

Input Inventory		
Type	**Amount**	**Unit**
Materials/Fuels:		
Output-4 from SSCF Fermenter	22.3392	kg
Make up cooling water	15.2139	kg
Electricity/Heat:		
Electricity	0.0383	kWh
Steam	6.8068	kg

Table 4.19 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in distillation stage for the base case design (continue)

Output Inventory		
Type	**Amount**	**Unit**
Products:		
Output-5 from Distillation	1.0590	kg
Wastewater to WWT	20.7930	kg
Emissions to air:		
Water	0.0156	kg
Ethanol	0.0030	kg
Carbon dioxide	0.4669	kg
Oxygen	0.0014	kg

Table 4.20 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in dehydration stage for the base case design

Input Inventory		
Type	**Amount**	**Unit**
Materials/Fuels:		
Output-5 from Distillation	1.0590	kg
Make up cooling water	1.8817	kg
Electricity/Heat:		
Electricity	0.0042	kWh
Steam	0.4627	kg
Output Inventory		
Type	**Amount**	**Unit**
Products:		
Ethanol 99.5 wt%	1.0000	kg
Emissions to air:		
Water	0.0590	kg

Table 4.21 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in wastewater treatment stage for the base case design

Input Inventory		
Type	**Amount**	**Unit**
Materials/Fuels:		
Wastewater to WWT	20.7930	kg
*Water	-17.3067	kg
Electricity/Heat:		
Electricity	0.1135	kWh
Output Inventory		
Type	**Amount**	**Unit**
Products:		
Treated water	17.3067	kg
Emissions to water:		
Sulfuric acid	0.0255	kg
Acetic acid	0.0329	kg
Furfural	0.0046	kg
Ethanol	0.0172	kg
Waste and emissions to treatment:		
Biowaste to fertilizer	3.2907	kg
**Wastewater from utility	0.0334	m^3

*It gave the negative value because the treated water was recycled back to the process.

**Wastewater from steams and cooling water.

The products of each stage were considered as raw materials for the next stage, for example, rice straw before transport from the rice plantation stage was used as the raw material for transportation stage and so on. Several chemicals and substances shown in the tables did not exist in SimaPro's database: such as, the enzyme and nutrient used in the fermentation stage. However, since some chemicals and substances were present in very small amounts, they could be ignored by the cut-off rule where a cut-off level of 1 % was applied.

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 except for rice plantation stage which using cost allocation. The emission related to equipments was excluded in this research.

4.3.4.2 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 other words, the objective is to analyze and compare the environment burdens associated with raw materials used and energy inputs, and, emissions or releases as quantified by the LCI results.

After performing the life cycle inventory analysis of the base case design (bioethanol production process from rice straw) by using SimaPro 7.1, the CML 2 baseline 2000 methods were then utilized to evaluate the environmental impacts in various categories, for example, abiotic depletion, global warming potential, ozone layer depletion, human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, photochemical oxidation, acidification and eutrophication potential. The impact assessment results are shown in Table 4.22 and Figure 4.13.

Table 4.22 Environmental impact of bioethanol conversion process from rice straw per one kilogram ethanol 99.5 wt% of the base case design

Impact category	**Unit**	**Total**
Abiotic depletion	kg Sb eq	2.82E-02
Global warming (GWP100)	kg CO_2 eq	8.62E-01
Ozone layer depletion (ODP)	kg CFC-11 eq	4.93E-07
Human toxicity	kg 1,4-DB eq	1.56E+00
Fresh water aquatic ecotoxicity	kg 1,4-DB eq	1.25E+00
Marine aquatic ecotoxicity	kg 1,4-DB eq	2.89E+03
Terrestrial ecotoxicity	kg 1,4-DB eq	4.45E-02
Photochemical oxidation	kg C_2H_4	8.37E-03
Acidification	kg SO_2 eq	2.42E-02
Eutrophication	kg PO_4 eq	1.29E-02

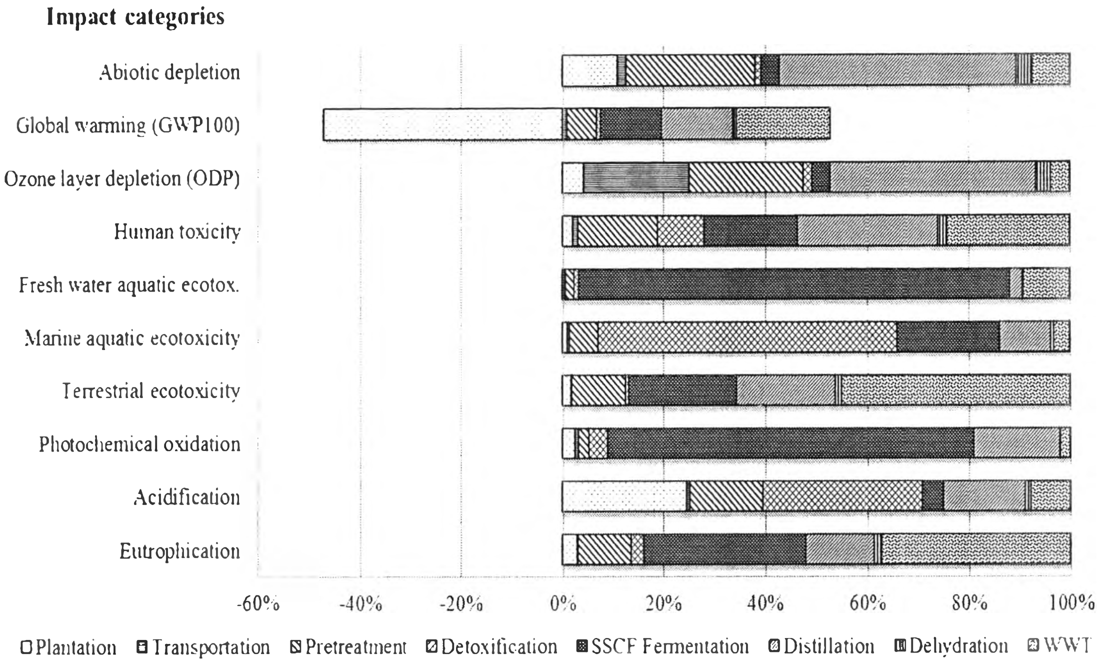

Figure 4.13 Distribution of environmental impacts classified stage by stage of the base case design.

According to Figure 4.13, rice plantation stage gave a negative of emission in global warming because rice production could uptake carbon dioxide (CO_2) which was the importance of greenhouse gas (GHG) therefore; the global warming impact was reduced. In other word, if the raw material was not biomass, the global warming for the ethanol production process will extremely high. The emission from carbon dioxide (CO_2) and carbon monoxide (CO) which came from transportation stage mainly causes ozone layer depletion. Regarding to gypsum waste from detoxification, it mainly affected to marine aquatic ecotoxicity. The huge amount of ash from rice straw that release from SSCF fermenter affected to several of impact categories, especially for flesh water aquatic ecotoxicity and photochemical oxidation which was one of the main disadvantage of rice straw as mention in the previous section. Distillation stage not only was the major cause of abiotic depletion but also the main emission in global warming because of the huge amount of steam usage. Regarding to dehydration stage, it did not cause the environmental impact much compare to other stages. The most toxic from wastewater treatment stage came from electricity and biowaste that turn into fertilizer. Now, after perform every tool, alternative designs will be generated by using all of the results from base case design.

4.4 Alternative Design Ideas

The ideas for generating new designs were based on the results of sustainability analysis, economic evaluation and life cycle assessment of base case design. There were five main alternative process ideas as follows:

- Rearrange the energy consumption in the process by using heat integration method.
- Use wastewater from beer and rectification columns (stream S59 and S61 from the base case design) as utility to exchange heat with one of the heat exchanger.
- Install the evaporator section into the process to treat wastewater from S59 and S61, and recycle treated water into the process.
- Install the membrane section into the process to treat wastewater from S59 and S61, and recycle treated water into the process.
- Generate the energy by burning lignin and other solid wastes from SSCF fermenter (stream S53).

In addition, some of 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. On the other hand, some of them could not be mixed with others, for example; evaporator and membrane water treatment. Based on this approach, the total of fifteen alternative designs was generated from different combinations of these ideas as described in Table 4.23.

The process that normally uses to treat wastewater is biogas and cogeneration process which is used as a common process in Thailand. Biogas is produced by the fermentation of organic matter in wastewater under anaerobic (having no oxygen) conditions. Then, the biogas will be burned directly as fuel or used to generate electricity. However, this idea was not included in this research because of the land use constraint of the process.

Table 4.23 Overall alternative designs

Alternative	Description
1	Base Case with ***Heat Integration***
2	Wastewater Exchange Heat as Utility
3	Wastewater Recover by Double Effect Evaporators
4	Wastewater Recover by Membranes
5	Lignin Combustion
6	Wastewater Exchange Heat as Utility + Lignin Combustion
7	Wastewater Recover by Double Effect Evaporators + Lignin Combustion
8	Wastewater Recover by Membranes + Lignin Combustion
9	Wastewater Exchange Heat as Utility with ***Heat Integration***
10	Wastewater Recover by Double Effect Evaporators with ***Heat Integration***
11	Wastewater Recover by Membranes with ***Heat Integration***
12	Lignin Combustion with ***Heat Integration***
13	Wastewater Exchange Heat as Utility + Lignin Combustion with ***Heat Integration***
14	Wastewater Recover by Evaporators + Lignin Combustion with ***Heat Integration***
15	Wastewater Recover by Membranes + Lignin Combustion with ***Heat Integration***

Next part will explain the idea of five main alternatives. After that the report will show the comparison of every alternative with the base case design in terms of water consumption, sustainability, safety indices, profitability and life cycle assessment. All of the flowsheets and the stream tables of five main idea designs were shown in Appendix D.

4.4.1 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 flowsheet, 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 two cold streams as shown in Table 4.24.

Table 4.24 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-S16	302.89	70.463	50.116	-6,163
E2	S29-S31	53.2	58.854	41.455	-926
E3	S30-S32	478.81	58.854	41.538	-8,291
E6	S63-S64	108.4	100.018	40	-6,506
Total					**-21,885**
Cold Stream					
Unit	Streams (In & Out)	FC_p (MJ/hr-°C)	Inlet Temp. (°C)	Outlet Temp. (°C)	Enthalpy (MJ/hr)
E4	S54-S55	539.23	40.193	100.463	32,499
E5	S61-S62	959.47	93.344	100	6,386
Total					**38,886**

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).

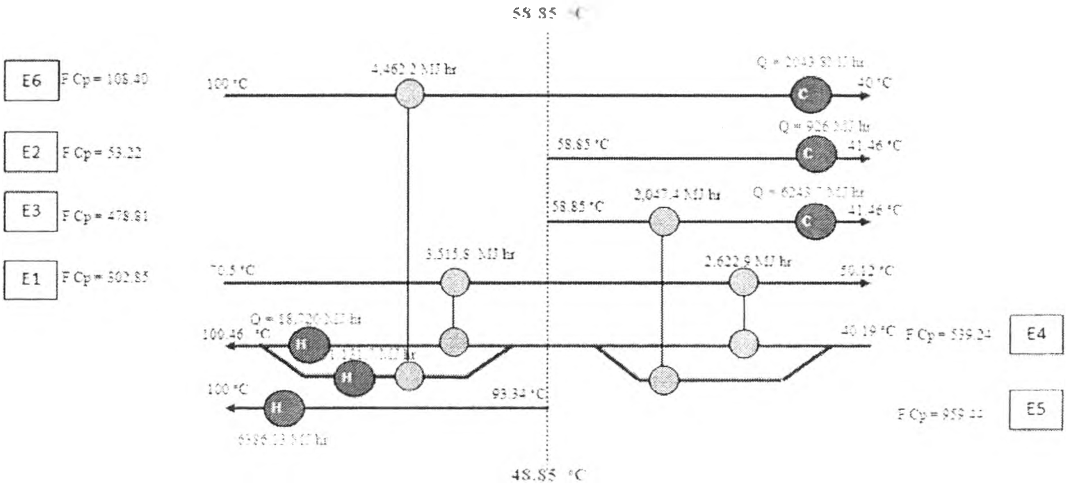

Figure 4.14 Heat exchanger network of the base case design.

The arrow from left to right (E6, E2, E3 and E1) represented to the hot streams that need to be cooled. On the contrary, the arrow from right to left (E4 and E5) 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 58.85 °C for hot side and 48.85 °C for cold side. Furthermore, there were four heat exchangers that require exchanging the heat from streams with another one which two of them were on above pinch; S63 with S54 (4.5 GJ/hr) and S15 with S54 (3.5 GJ/hr) and the other two were on below pinch; S30 with S54 (2.0 GJ/hr), and S15 with S54 (2.6 GJ/hr). As you can see, S54 need to be split either above pinch or below pinch. Therefore, the flow rate of S54 that be separated need to calculate related to the portion of FC_p. In this process, it requires three cooler and two heaters (two heaters from E4 can be merged into one heater). The final flowsheet for alternative 1 are shown in Figure 4.15. The other related alternatives (alternatives 9, 10, 11, 12, 13, 14 and 15) were used the same idea as alternative 1. They are given the flowsheets in Appendix D.

4.4.2 Wastewater Exchange Heat as Utility

This alternative was the simplest idea of new design. First of all, mix streams S59 and S61 together. The outlet temperature of this stream was around 117 °C. In case of alternative 2, the possible heat exchangers that can be exchanged with S66 were E4 and E5. If S66 exchanges with E5, the outlet temperature of S66 will be around 105 °C, which higher than inlet of E4 about 5 °C, so it cannot continue to exchange with E4 (which have higher duty than E5). Otherwise, the additional heat exchanger were required which increase capital cost, so it not the proper option. Therefore, S66 were designed to exchange with E4 (outlet temperature was around 50 °C) and leave it like that. The flowsheet for alternative 2 are shown in Figure 4.16. The other related alternatives (alternatives 2, 6, 9 and 13) were used the same idea as alternative 2. They are given the flowsheets in Appendix D.

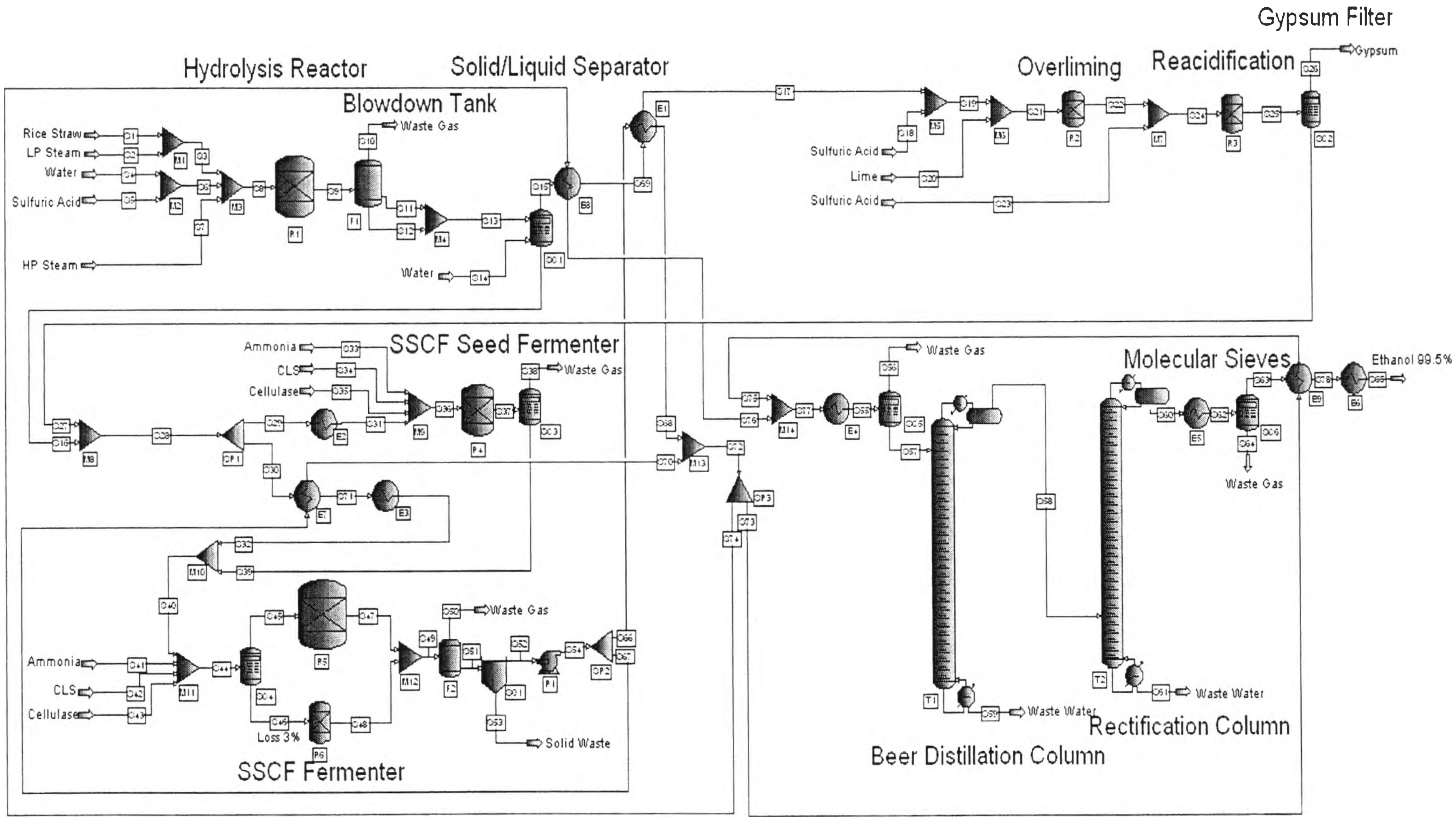

Figure 4.15 Flowsheet of the bioethanol production process from rice straw for alternative 1 design.

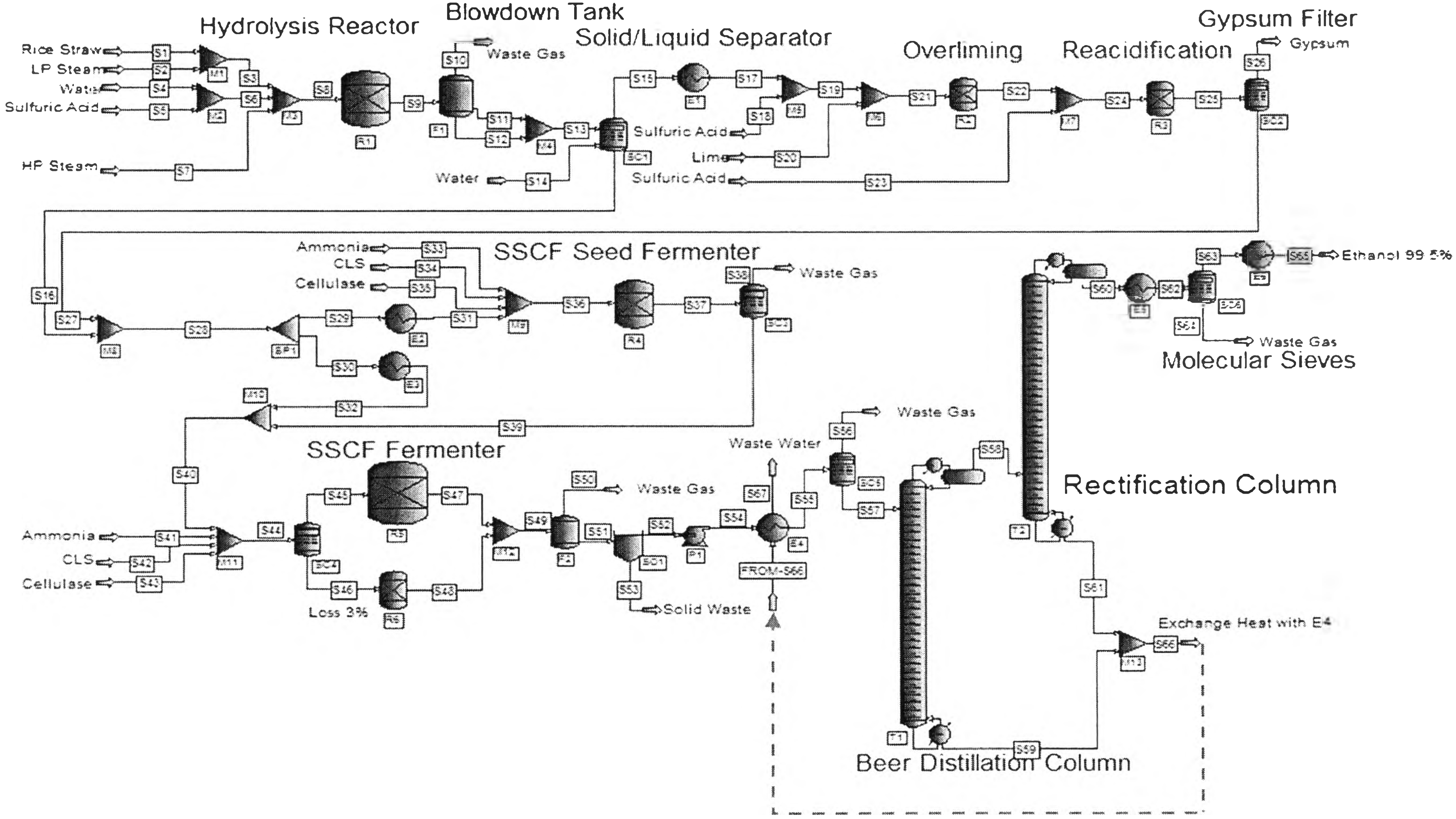

Figure 4.16 Flowsheet of the bioethanol production process from rice straw for alternative 2 design.

4.4.3 Wastewater Recover by Evaporators

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. However, recycle water had constraint of the quantity of containment that will affect to the process. In this ethanol process, the acetic acid concentration will affect the microorganism (enzyme), *Z. mobilis*, used in the fermentation step. So, this work needs to specify the upper limit of acetic acid in order to prevent enzyme inhibition.

There are many types of evaporator which call "effect". The effects indicate the number of evaporator that the operating pressure of the pervious evaporator will higher than the next one for the easier separation for instance; double effect means there are two evaporator which the operating pressure of the first one higher than the second one. Higher effect means higher number of evaporator, more capital cost but less operating cost. The effect evaporators in this report were operated below atmospheric pressure because the boiling point of the water and contaminates will drop which make the mixture easier to separate and increase the quantity of recycle water. Moreover, at this condition the duty of evaporator will reduce. However, the cost will increase because of vacuum unit cost. In this case, the vacuum unit that was chosen was air ejector because it cheaper than other ejector (www.graham-mfg.com). The key to choose number of effect in this case is cost and water recovery.

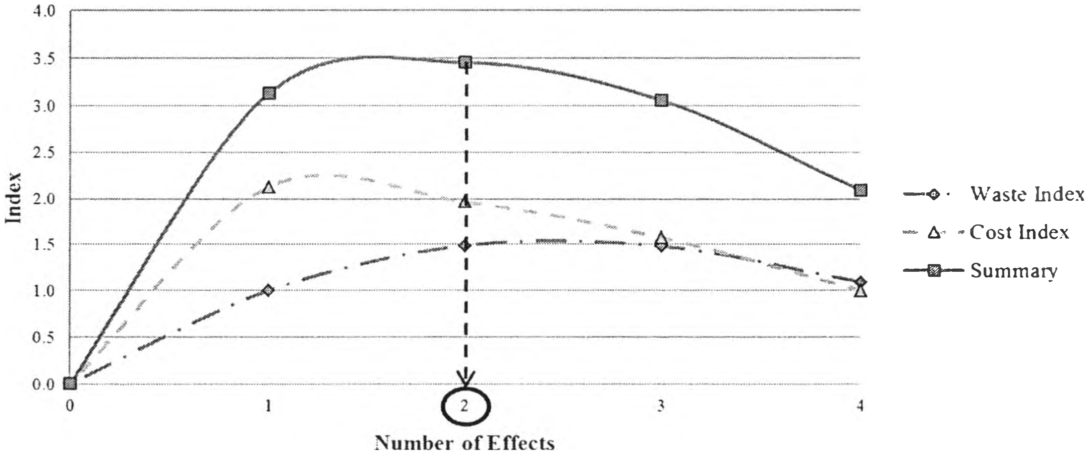

Figure 4.17 The result of comparison the effects of evaporator.

As seen from in Figure 4.17, the type of evaporator in this graph had four types of evaporator which are; single effect (one evaporator), double effect (two evaporators), triple effect (three evaporators) and quadruple effect (four evaporators). The indexes were calculated from the divide of the improve performance of each effect (compared with the base case design) with the lowest one. According to the result, the higher index means the better process. The single effect was the cheapest process for investment but worst in term of quantity of wastewater. The triple had the same quantity of wastewater as double effect but need more investment cost than double effect. So, the best chosen was double effect evaporator. The evaporators can treat wastewater around 33.7 % of the total wastewater from S59 and S61. The result of water treatment by double effect evaporators is shown below:

Table 4.25 Specification of treated water in alternative 3

Stream	**Definition**	**Max. allow conc. (ppm)**	**Contaminant conc. (ppm)**
S83	Treated water from evaporators	12,000*	9,483
S84	Treated water from evaporators	30,000*	21,508
S44	Fermenter feed (acetic acid conc.)	4,411*	1,202

*Data from NREL (Wooley *et al.*, 1999)

From Table 4.25, it shows the concentration of contaminant in recycle water and maximum concentration that the stream allow. The results shown that the concentration of recycle water was acceptable. The flowsheet for alternative 3 are shown in Figure 4.18. The other related alternatives (alternatives 7, 10 and 14) were used the same idea as alternative 3. They are given the flowsheets in Appendix D.

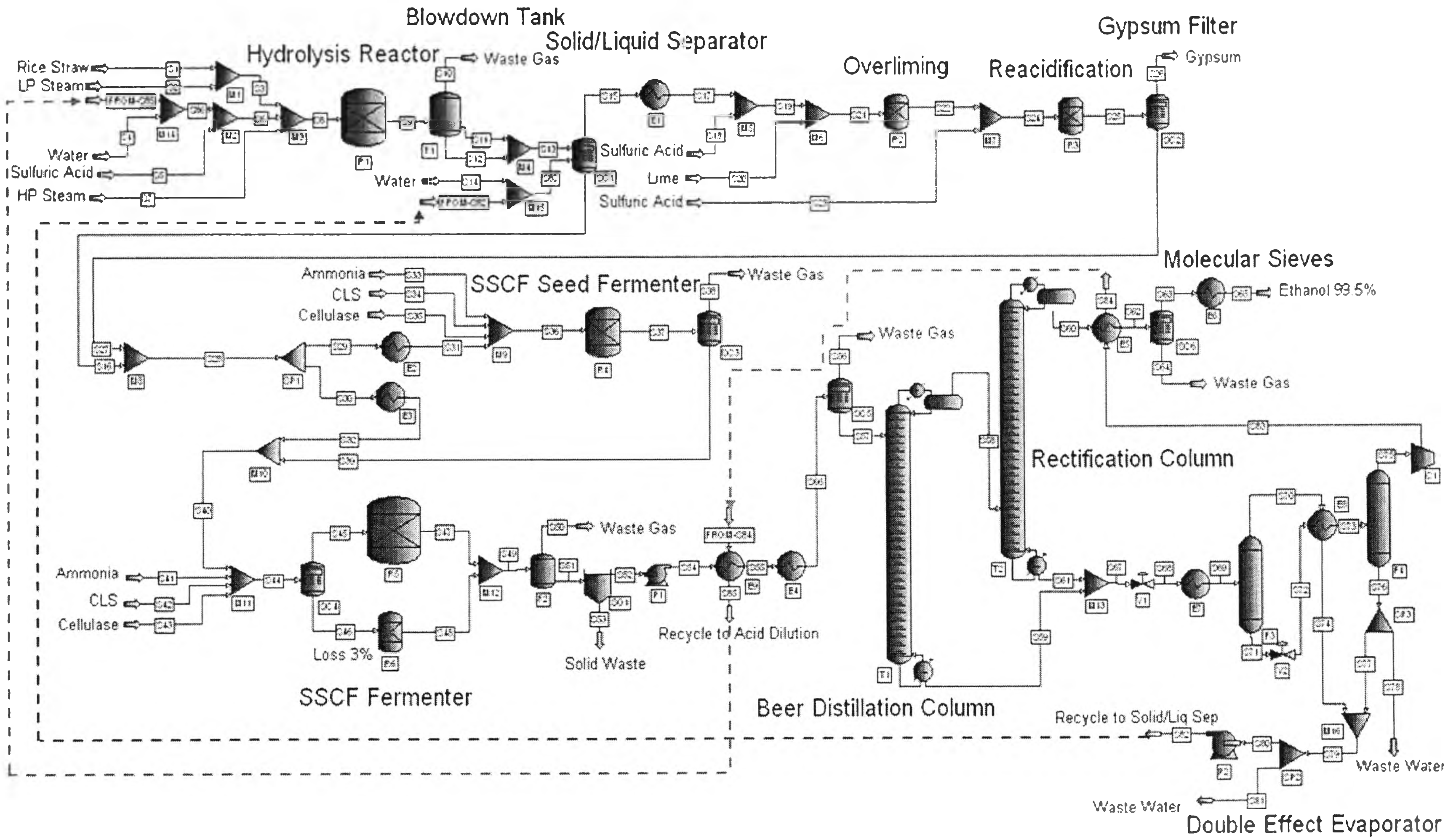

Figure 4.18 Flowsheet of the bioethanol production process from rice straw for alternative 3 design.

4.4.4 Wastewater Recover by Membranes

The idea of this alternative is the same as evaporator. Because the evaporators consume a lot of energy to treat wastewater so, the saving water will compensate with the energy consumption. Therefore, to reduce the energy consumption of evaporator, the membrane was designed to be replaced. However, the membranes have the drawback on the high install and maintain cost.

The types of membrane that were considered for this report are 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 was 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). Capital cost of membrane can be calculated by equation 4.1 (Owen *et al.*, 1995):

$$C_{mem} = c_{mem} \times Q/J \qquad \text{(eq. 4.1)}$$

Which; C_{mem} is capital investment for membrane ($)

c_{mem} is cost per area of membrane ($/m^2)

Q is volumetric flowrate of inlet water (L/hr)

J is flux (L/m^{2}hr)

If we assume that membranes have to be replaced every 10 years, the cost of replacement is around 100 $/yr per membrane area (Escobar *et al.*, 2001). The total cost of membrane and the result of water treatment by membrane are shown in Table 4.26 and Table 4.27, respectively.

Table 4.26 Total cost of membrane investment

Membrane	**MF/UF**	**RO**
Flow Rate (L/day)	3,009,985	3,009,985
Flow Rate (L/hr)	125,416	125,416
Flux (L/m^2 h)	180[a]	95[a]
Area (m^2)	696.76	1320.17
C_{mem}($/m^2)	365[a]	500[b]
Cost ($)	254,316	660,084
Total ($)	**914,400**	
Replace Membrane ($/yr)	**201,692**	

References: a. Steinwinder *et al.* (NREL), 2011
b. Baker *et al.*, 1991

Table 4.27 Specification of treated water in alternative 4

Stream	Definition	Max. allow conc. (ppm)	Contaminant conc. (ppm)
S4	Treated water from membranes	12,000*	11,419
S14	Treated water from membranes	30,000*	11,419
S44	Fermenter feed (acetic acid conc.)	4,411*	188

*Data from NREL (Wooley *et al.*, 1999)

From Table 4.27, contaminates in treating water from membrane were lower than maximum allow concentration. In addition, the acetic acid concentration of fermenter feed was acceptable. The flowsheet for alternative 4 are shown in Figure 4.19. The other related alternatives (alternatives 8, 11, and 15) were used the same idea as alternative 4. They are given the flowsheets in Appendix D.

4.4.5 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 4 are shown in Figure 4.20. The other related alternatives (alternatives 6, 7, 8, 12, 13, 14 and 15) were used the same idea as alternative 5. They are given the flowsheets in Appendix D.

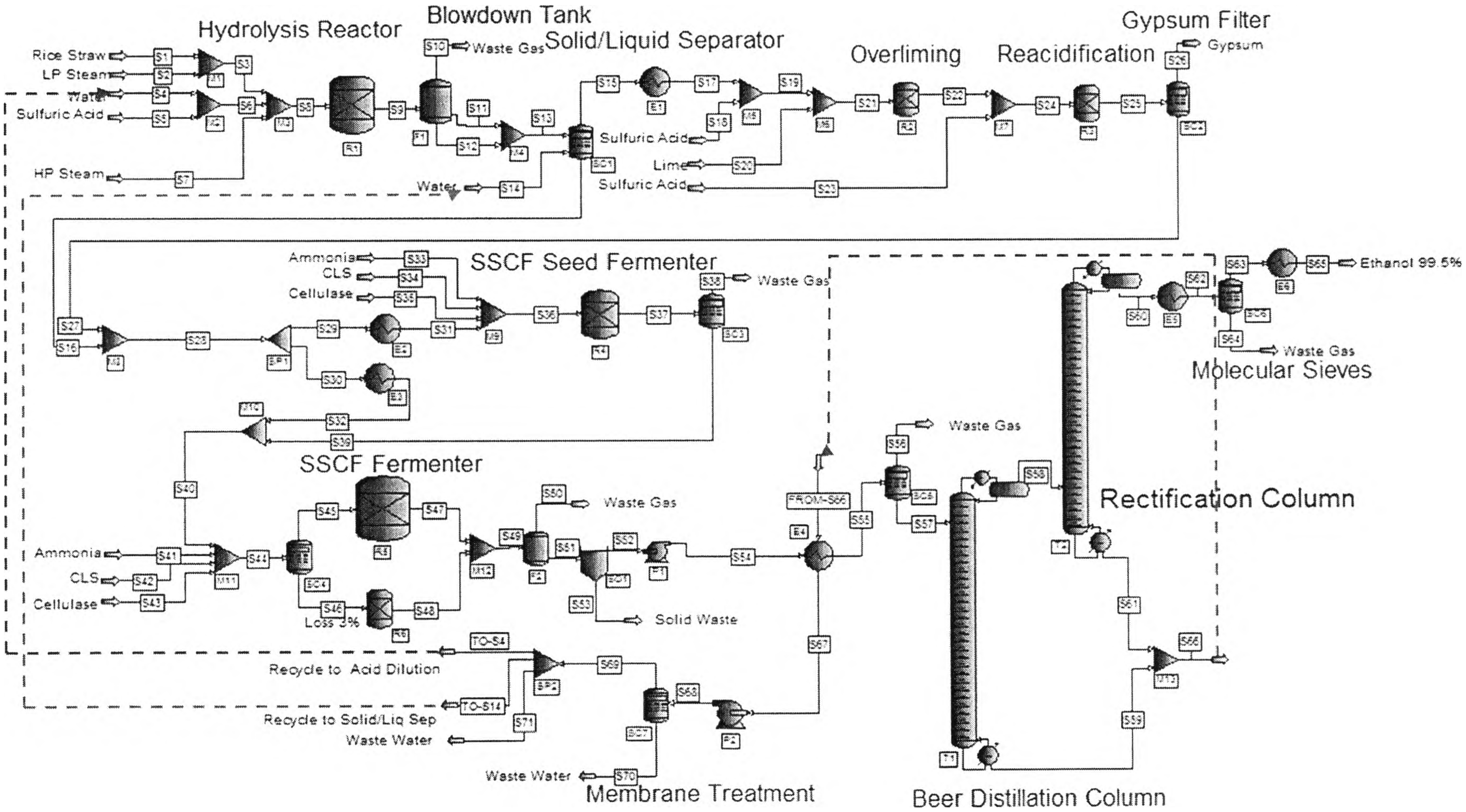

Figure 4.19 Flowsheet of the bioethanol production process from rice straw for alternative 4 design.

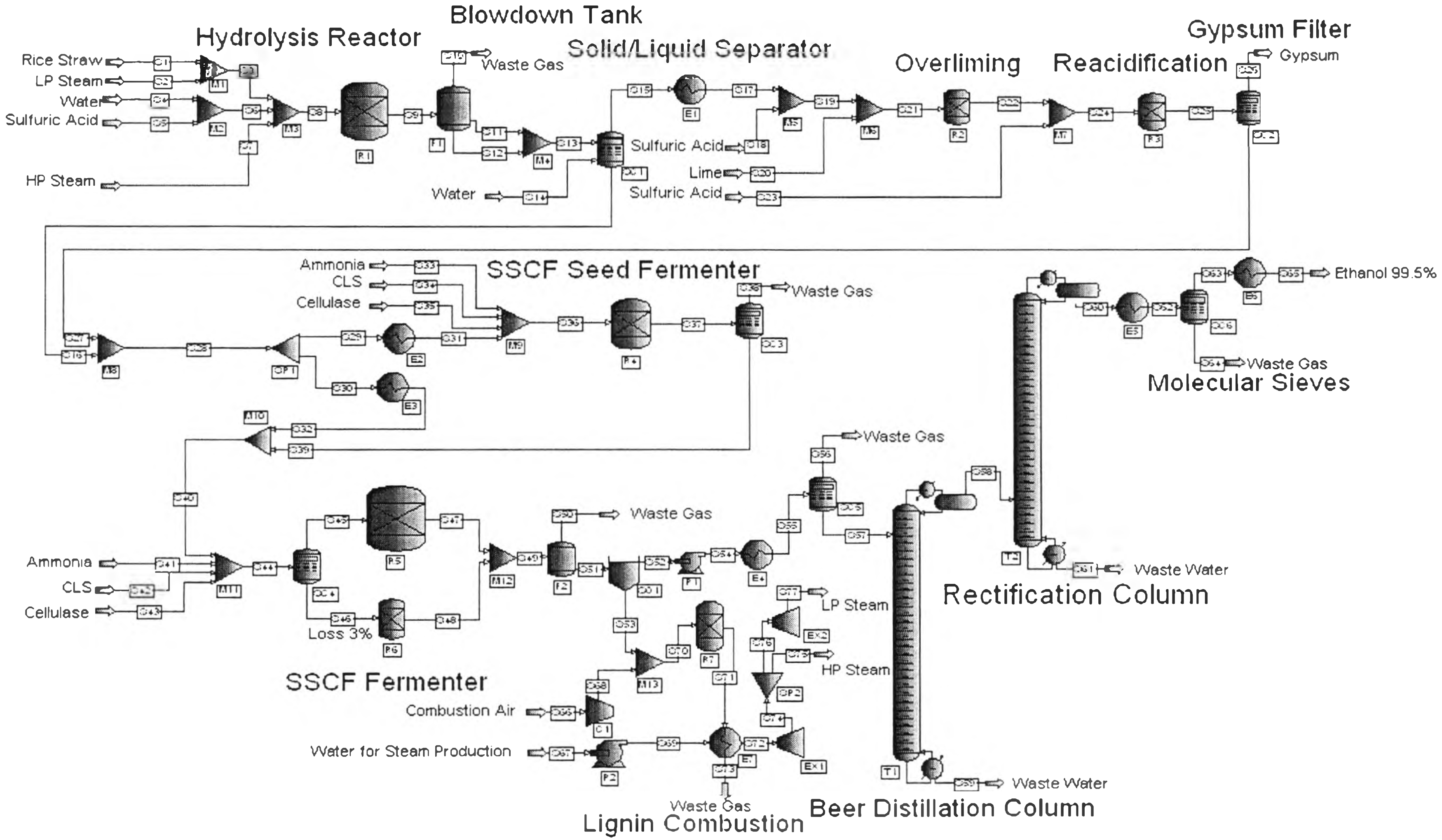

Figure 4.20 Flowsheet of the bioethanol production process from rice straw for alternative 5 design.

4.5 Comparison Between Base Case and Alternatives

4.5.1 Water Consumption

The water consumption is one of the important factors affecting the EWC indicator (from SustainPro) and the environmental impact. The comparison of water consumption between the base case design and alternatives is shown in Figure 4.21.

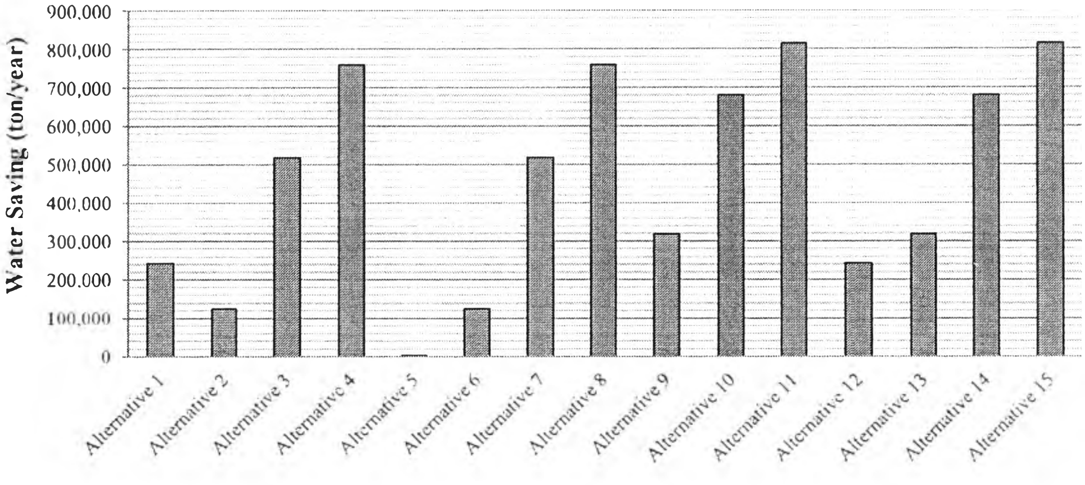

Figure 4.21 Comparison the water saving compare to the base case design.

As seen from the figure, 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. Regarding to double evaporators process designs, they reduced water consumption from recycle treated water as same as membrane but it used higher quantity of utility in the evaporator section. For heat integration designs, they can save some water because of the reduction of utility consumption from rearrange heat exchanger. Wastewater as utility designs can save water from reduce steam usage in E4. 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 11 and 15 were the best in term of water saving (35 % saving).

Table 4.28 Comparison of sustainability metrics for all of designs

Metric		Base Case	Alternative 1	Alternative 2	Alternative 3	Alternative 4	Alternative 5	Alternative 6	Alternative 7
Energy	Total Net Primary Energy Usage rate (GJ/y)	1,060,201	934,738	735,308	990,548	731,575	1,060,201	735,308	990,548
	% Total Net Primary Energy sourced from renewables	0.9992	0.9991	0.9989	0.9673	0.9940	0.9992	0.9989	0.9673
	Total Net Primary Energy Usage per Kg product (kJ/kg)	20,002	17,635	13,872	18,688	13,802	20,002	13,872	18,688
	Total Net Primary Energy Usage per unit value added (kJ/$)	6.712	5.917	4.654	4.900	3.564	4.341	3.009	3.496
Material	Total raw materials used per kg product (kg/kg)	5.199	5.199	5.199	4.872	4.945	5.199	5.199	4.872
	Total raw materials used per unit value added	0.00174	0.00174	0.00174	0.00128	0.00128	0.00113	0.00113	0.00091
	Fraction of raw materials recycled within company	0	0	0	0.005592	0.000969	0	0	0.005592
	Fraction of raw materials recycled from consumers	0	0	0	0	0	0	0	0
	Hazardous raw material per kg product	1.768	1.768	1.768	1.646	1.685	1.768	1.768	1.646
Water	Net water consumed per unit mass of product (kg/kg)	31.45	29.91	31.44	23.52	18.46	31.45	31.44	23.52
	Net water consumed per unit value added	0.01055	0.01004	0.01055	0.00617	0.00477	0.00683	0.00682	0.00440
Economic	Value added ($/y)	19,745,122	19,745,236	19,750,212	25,268,366	25,655,335	30,529,402	30,544,377	35,416,720

Metric		Alternative 8	Alternative 9	Alternative 10	Alternative 11	Alternative 12	Alternative 13	Alternative 14	Alternative 15
Energy	Total Net Primary Energy Usage rate (GJ/y)	731,575	735,214	905,741	699,761	933,679	735,214	905,741	699,761
	% Total Net Primary Energy sourced from renewables	0.9940	0.9989	0.9643	0.9937	0.9991	0.9989	0.9643	0.9937
	Total Net Primary Energy Usage per Kg product (kJ/kg)	13,802	13,871	17,088	13,202	17,615	13,871	17,088	13,202
	Total Net Primary Energy Usage per unit value added (kJ/$)	2.546	4.654	4.480	3.413	3.822	3.010	3.195	2.437
Material	Total raw materials used per kg product (kg/kg)	4.945	5.199	4.872	4.945	5.199	5.199	4.872	4.945
	Total raw materials used per unit value added	0.00091	0.00174	0.00128	0.00128	0.00113	0.00113	0.00091	0.00091
	Fraction of raw materials recycled within company	0.000969	0.000	0.009665	0.000970	0	0.000	0.009665	0.000970
	Fraction of raw materials recycled from consumers	0	0	0	0	0	0	0	0
	Hazardous raw material per kg product	1.685	1.768	1.646	1.685	1.768	1.768	1.646	1.685
Water	Net water consumed per unit mass of product (kg/kg)	18.46	29.91	22.91	18.29	29.91	29.91	22.91	18.29
	Net water consumed per unit value added	0.00341	0.01004	0.00601	0.00473	0.00649	0.00649	0.00428	0.00338
Economic	Value added ($/y)	35,913,955	19,746,018	25,269,535	25,632,202	30,533,315	30,530,259	35,440,457	35,890,434

4.5.2 Sustainability Metrics Comparison

As you can see from Table 4.28, among all alternatives studied, alternatives 11 and 15 were shown to be the most energy saving processes where approximately 34 % of the primary energy consumption could be reduced from the base case design. This result is reasonable when compared to water consumption because the reduction of primary energy (in this case LP steam and HP steam) leads to the reduction of water quantity that came from steams.

In term of raw materials consumption, alternatives 10 and 14 were shown to consume lowest raw material. This is due to the lower treating efficiency of evaporator compared to that of membrane. As a result, the amount of contaminants in wastewater from evaporator was higher than that from the membrane. Since some of these contaminants was the composition of raw materials, that why the raw material consumption in evaporator was lower than the other process.

Water consumption of sustainability metrics had the same result as actual water consumption from the previous section which alternative 11 and 15 were the most saving water quantity.

In economic aspect, alternatives 8 and 15 were the best alternatives in term of profit (35.9 MM$/year). However, these results were just calculated from operation cost (exclude capital cost) and without including time value factor, so the economic issue will analyze in detail in economic evaluation section.

4.5.3 Safety Indices Comparison

This analysis will compare the safety of the process between the base case and alternatives. The results are shown in Table 4.29.

According to the result, every design got around the same safety indices score which was 18 and 19 (out of 53). There was a little change in lignin combustion and double evaporator designs (alternatives 3, 5, 7, 10, 12, 13, 14 and 15) from I_{ISBL} indices that was the indices of equipment safety from lignin combustion and double evaporator designs. The reason was that these designs were added compressor which made the safety indices increase. However, these increases did not significant which mean that every design was still ***inherently safe***. Hence, alternative designs were approved in term of safety.

Table 4.29 Comparison of safety indices for all of designs

	Base Case	**Alternative 1**	**Alternative 2**	**Alternative 3**	**Alternative 4**	**Alternative 5**	**Alternative 6**	**Alternative 7**
Subindices for reactions hazards	Score	Score	Score	Score	Score	Score	Score	Score
Heat of the main reaction, I_{rm}	0	0	0	0	0	0	0	0
Heat of the side reactions, I_{rs}	0	0	0	0	0	0	0	0
Chemical Interaction, I_{int}	1	1	1	1	1	1	1	1
Subindices for hazardous substances								
Flammability, I_{fl}	4	4	4	4	4	4	4	4
Explosiveness, I_{ex}	1	1	1	1	1	1	1	1
Toxicity, I_{tox}	2	2	2	2	2	2	2	2
Corrosivity, I_{cor}	1	1	1	1	1	1	1	1
Chemical inherent safety index, I_{ci}	*9*	*9*	*9*	*9*	*9*	*9*	*9*	*9*
Subindices for process conditions								
Inventory, I_{i}	0	0	0	0	0	0	0	0
Process temperature, I_{t}	2	2	2	2	2	2	2	2
Process pressure, I_{p}	1	1	1	1	1	1	1	1
Subindices for process system								
I_{ISBL}	2	2	2	3	2	3	2	3
I_{OSBL}	2	2	2	2	2	2	2	2
Process structure, I_{st}	2	2	2	2	2	2	2	2
Process inherent safety index, I_{pi}	*9*	*9*	*9*	*10*	*9*	*10*	*9*	*10*
Total inherent safety index, ISI	18	18	18	19	18	19	18	19

	Alternative 8	**Alternative 9**	**Alternative 10**	**Alternative 11**	**Alternative 12**	**Alternative 13**	**Alternative 14**	**Alternative 15**
Subindices for reactions hazards	Score	Score	Score	Score	Score	Score	Score	Score
Heat of the main reaction, I_{rm}	0	0	0	0	0	0	0	0
Heat of the side reactions, I_{rs}	0	0	0	0	0	0	0	0
Chemical Interaction, I_{int}	1	1	1	1	1	1	1	1
Subindices for hazardous substances								
Flammability, I_{fl}	4	4	4	4	4	4	4	4
Explosiveness, I_{ex}	1	1	1	1	1	1	1	1
Toxicity, I_{tox}	2	2	2	2	2	2	2	2
Corrosivity, I_{cor}	1	1	1	1	1	1	1	1
Chemical inherent safety index, I_{ci}	*9*	*9*	*9*	*9*	*9*	*9*	*9*	*9*
Subindices for process conditions								
Inventory, I_{i}	0	0	0	0	0	0	0	0
Process temperature, I_{t}	2	2	2	2	2	2	2	2
Process pressure, I_{p}	1	1	1	1	1	1	1	1
Subindices for process system								
I_{ISBL}	2	2	3	2	3	3	3	3
I_{OSBL}	2	2	2	2	2	2	2	2
Process structure, I_{st}	2	2	2	2	2	2	2	2
Process inherent safety index, I_{pi}	*9*	*9*	*10*	*9*	*10*	*10*	*10*	*10*
Total inherent safety index, ISI	18	18	19	18	19	19	19	19

4.5.4 Economic Evaluation Comparison

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

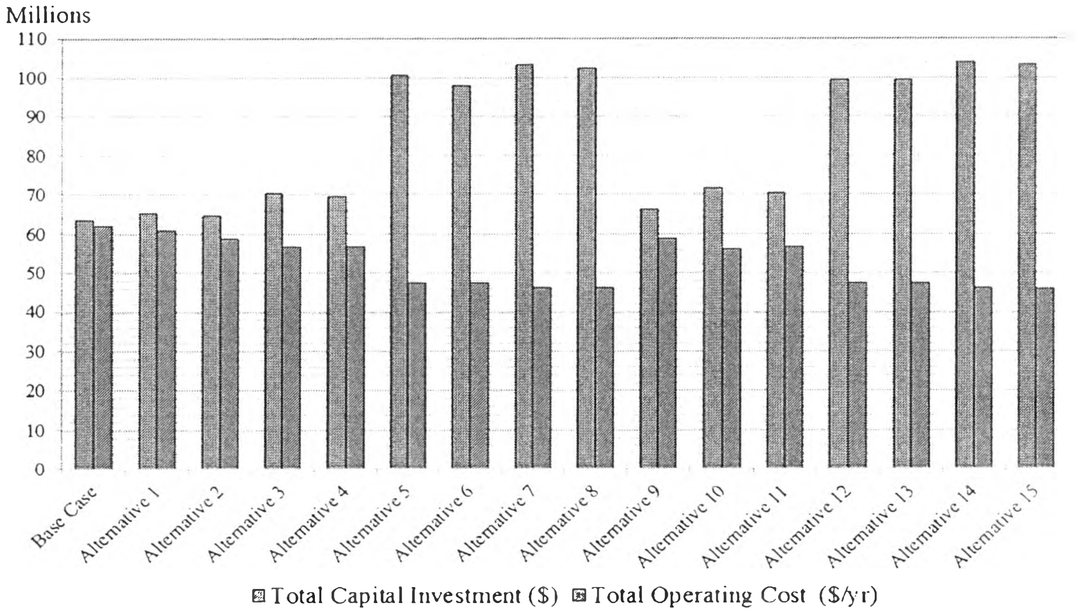

Figure 4.22 Comparison of capital cost and operating cost of each design.

As shown in Figure 4.22, heat integration designs (alternatives 1, 9, 10, 11, 12, 13, 14 and 15) required higher investment than general designs due to the addition of heat exchangers, but the operating cost was lowered because the reduction of energy consumption. Similarly, alternatives with wastewater heat exchange (alternatives 2, 6, 9 and 13) would lead to increasing capital cost due to a larger area of heat exchanger, but the operating cost was lowered. For the designs using evaporator (alternatives 3, 7, 10 and 14) and membrane (alternatives 4, 8, 11, and 15), the capital cost of these designs was increased because more unit operations were installed. However, evaporator designs had higher capital cost than membrane designs because more unit operations with high cost were needed such as compressors. 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 5, 6, 7, 8, 12, 13, 14 and 15), 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 huge amount of energy consumption so the operating cost was considerably reduced. Next, the results of economic evaluation will be considered.

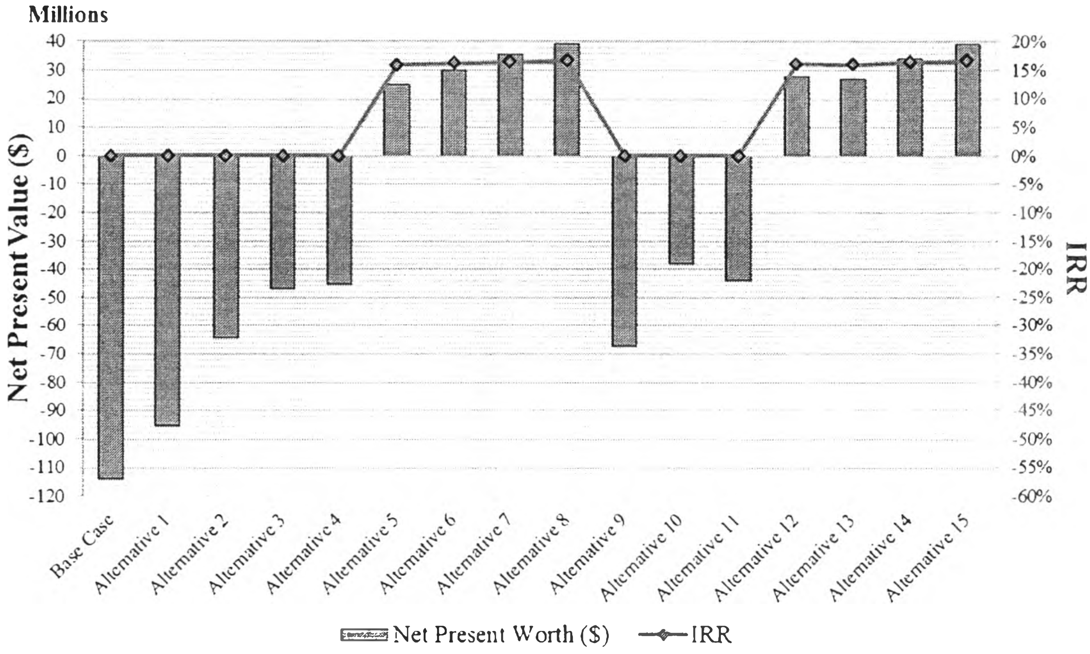

Figure 4.23 Comparison of NPV and IRR of each design for 20 years life time.

According to the results from Figure 4.23, the negative NPV or zero IRR (they did not actually equal to zero but the values could not be calculated, so they were assumed to be zero) mean those designs did not prefer to invest. In contrast, the positive NPV and positive IRR mean those designs should be considered.

Heat integration did not change significant results in term of economic because the decreasing of operating cost was compensated with the increasing of capital cost. The exchange heat of wastewater had better results than the base case design and heat integration because the saving of operating cost much more than the increasing of capital cost from the larger area of heat exchanger E4. The evaporator and membrane designs had better result compare to the other designs. However, they did not good for invest if they did not include lignin combustion in the process.

Normally, membrane designs had better NPV and IRR than evaporator designs. But for alternatives 10 and 11, the evaporator designs had the better results than the membrane designs because the original membrane design (alternative 4) was more optimized (more space to improve) than the original evaporator design (alternative 3) in term of energy. However, after install burner for lignin combustion, membrane design (alternative 15) got the better profit again. The reason is the reduction of steam usage from evaporator design (alternative 10) lead to the reduction of electricity production (the water for steam production was reduced) which mean the profit from electricity selling was cut.

Although the lignin combustion designs had high capital cost from burner as shown in Figure 4.22, all of them got both of the positive values for NPV and IRR because they sold electricity as by product and saved huge amount of steams which lead to very low operating cost.

From the result, alternatives 8 was shown to have the highest NPV of 39.8 MM$ and IRR 16.8 % for 20 years life time, followed by alternative 15 with NPV of 39.7 MM$ and IRR 16.7 % which correspond with the sustainability metrics results from Table 4.28 (in economic metric). These results were confirmed by the comparison of breakeven point results.

As you can see from Figure 4.24, the breakeven point of alternatives 8 and 15 were about 6 years. In economic point of view, alternatives 8 and 15 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 rice straw process in Thailand.

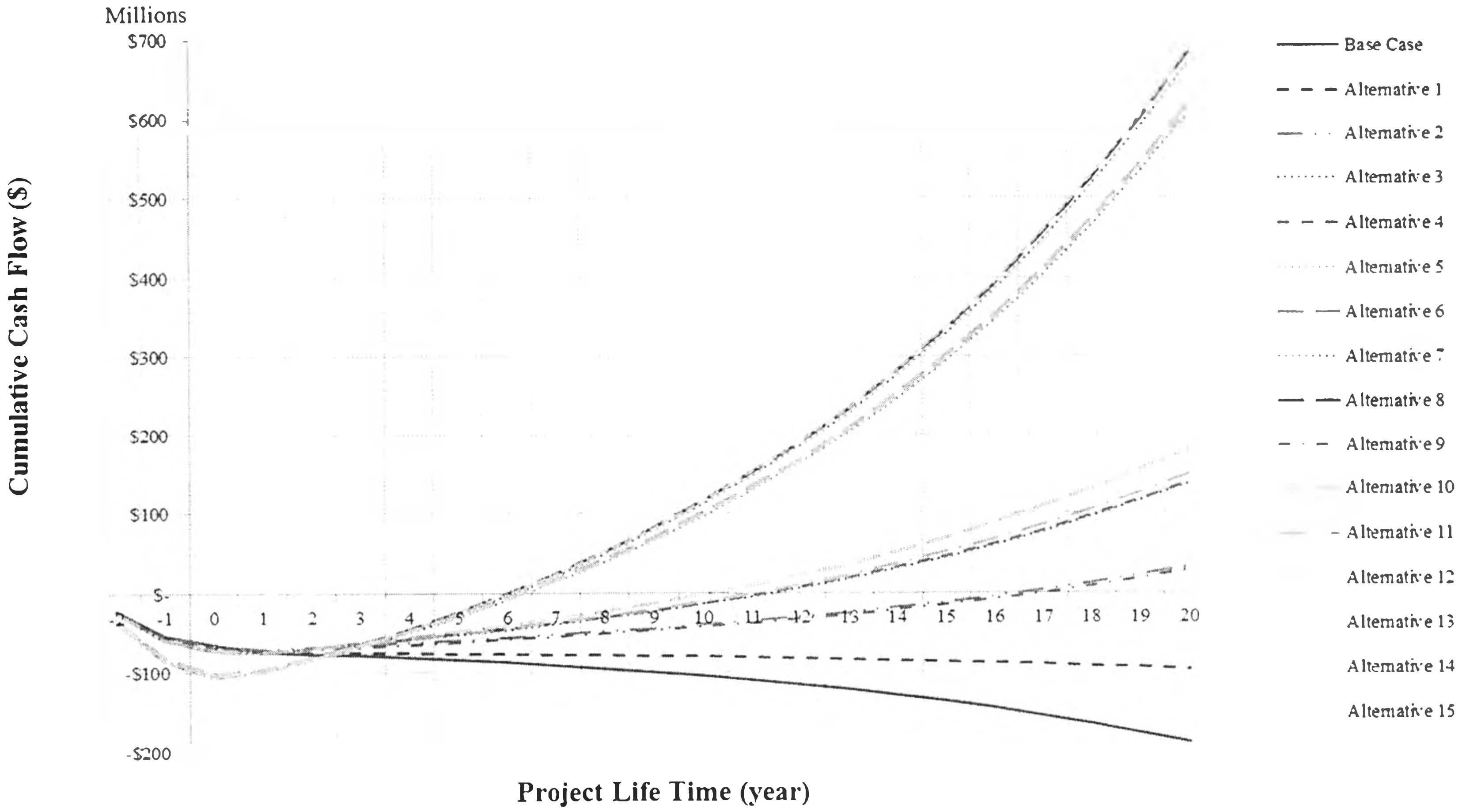

Figure 4.24 Comparison of breakeven point of each design for 20 years life time.

4.5.5 Life Cycle Assessment Comparison

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

Focusing on global warming potential (GWP as CO_2-equivalent), alternatives 8 and 15 were shown to have lowest GWP impact. They emit only 7.35 and 9.35 g CO_2 equivalent/kg bioethanol which reflects 99.2 % and 98.9 % reduction from the base case design (861.82 g CO_2 equivalent/kg bioethanol) respectively as shown in Figure 4.25. In particular, the wastewater recovery using membranes with lignin combustion (with or without heat integration) were the best design in term of global warming point of view as they had lowest GHG emission. This is due to the facts that these two designs not only reduced the steam utilization in the process which was the major contributor of GHG emissions, but also generated electricity which can compensate for their overall energy consumption.

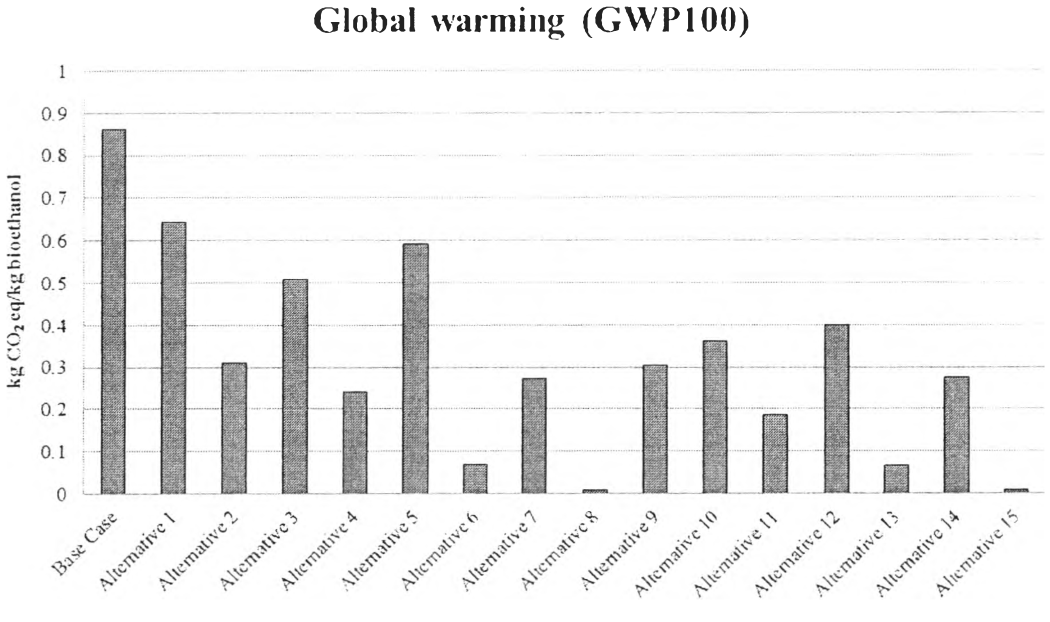

Figure 4.25 Comparison of the greenhouse effect (kg CO_2-equivalent) per one kilogram of bioethanol for each design.

For other impact categories such as abiotic depletion, global warming potential, ozone layer depletion, human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, photochemical oxidation, acidification and eutrophication potential are shown in Figures 4.26, 4.27, 4.28, 4.29, 4.30, 4.31, 4.32, 4.33 and 4.34.

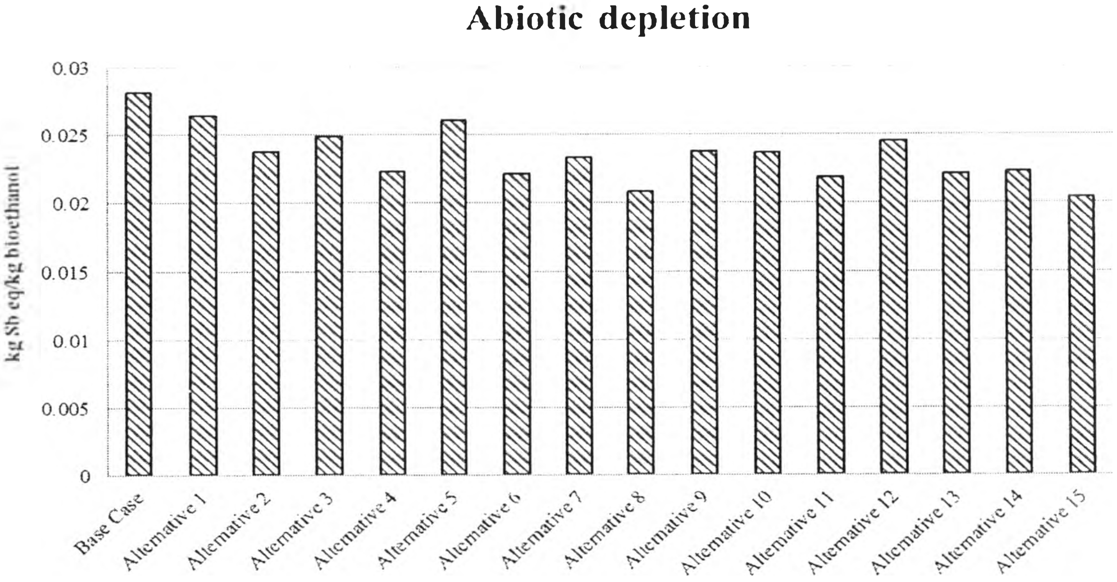

Figure 4.26 Comparison of the abiotic depletion (kg Sb-equivalent) per one kilogram of bioethanol for each design.

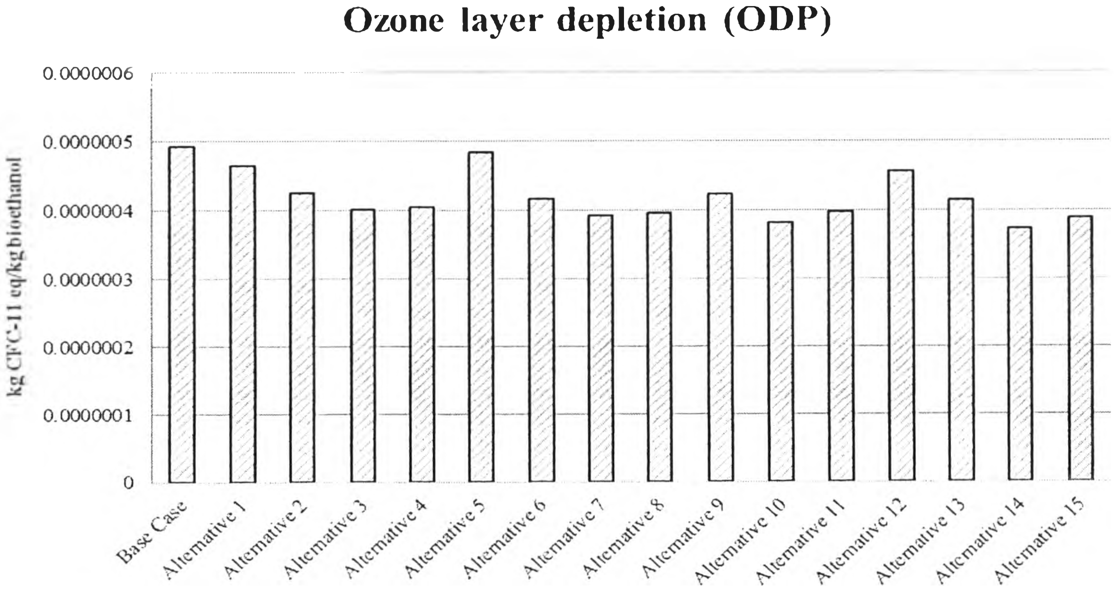

Figure 4.27 Comparison of the ozone layer depletion (kg CFC-11-equivalent) per kilogram of bioethanol for each design.

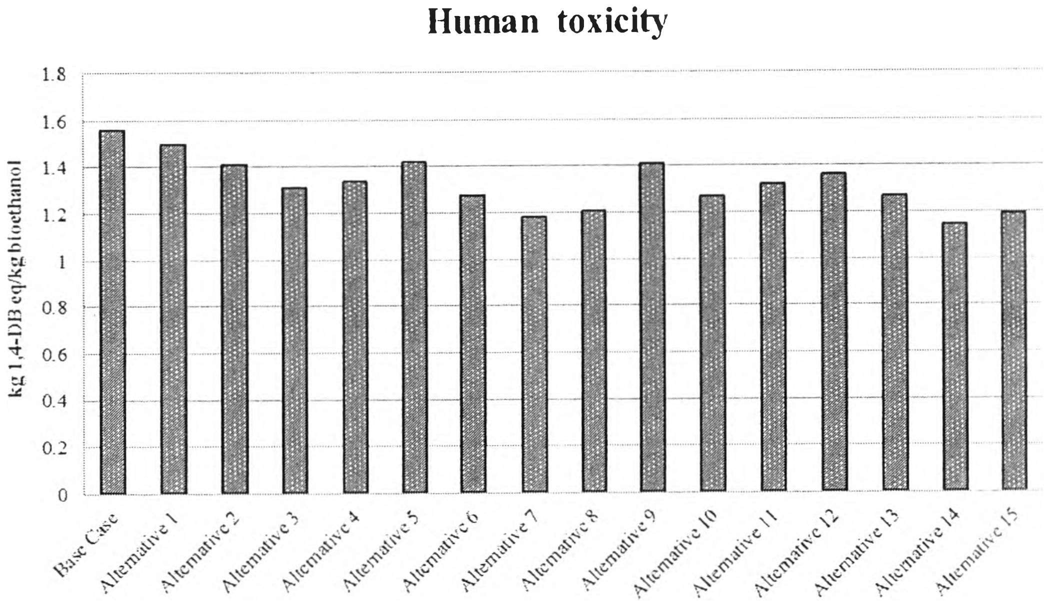

Figure 4.28 Comparison of the human toxicity (kg 1,4-DB-equivalent) per one kilogram of bioethanol for each design.

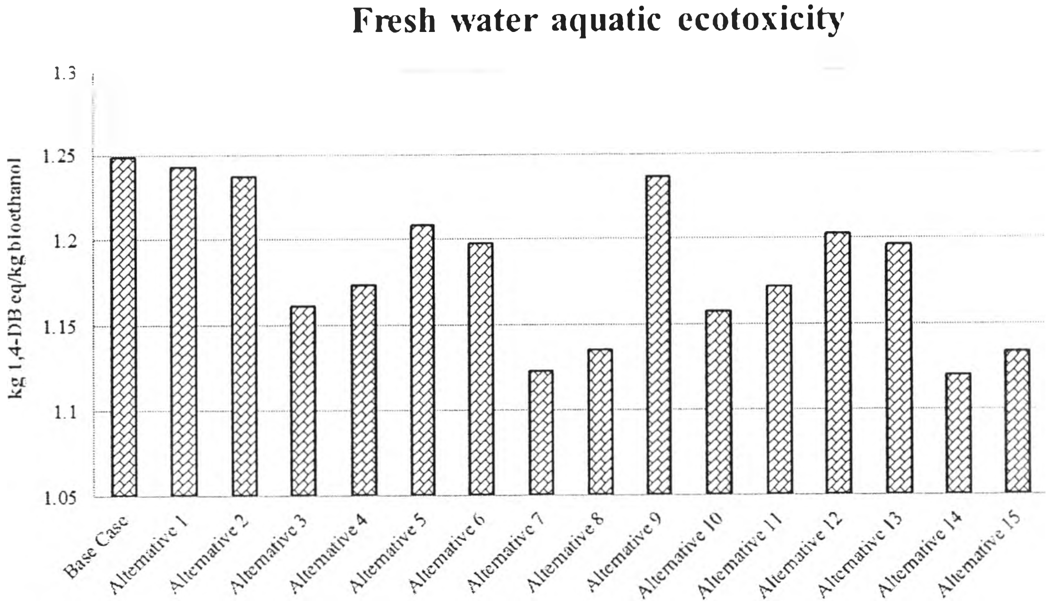

Figure 4.29 Comparison of the flesh water aquatic ecotoxicity (kg 1,4-DB-equivalent) per one kilogram of bioethanol for each design.

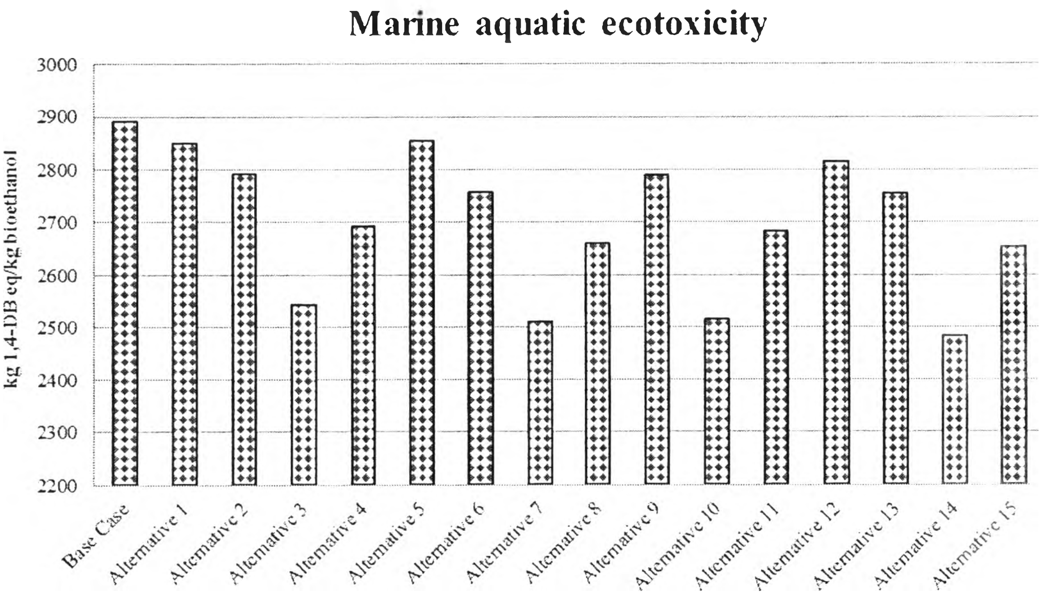

Figure 4.30 Comparison of the marine aquatic ecotoxicity (kg 1,4-DB-equivalent) per one kilogram of bioethanol for each design.

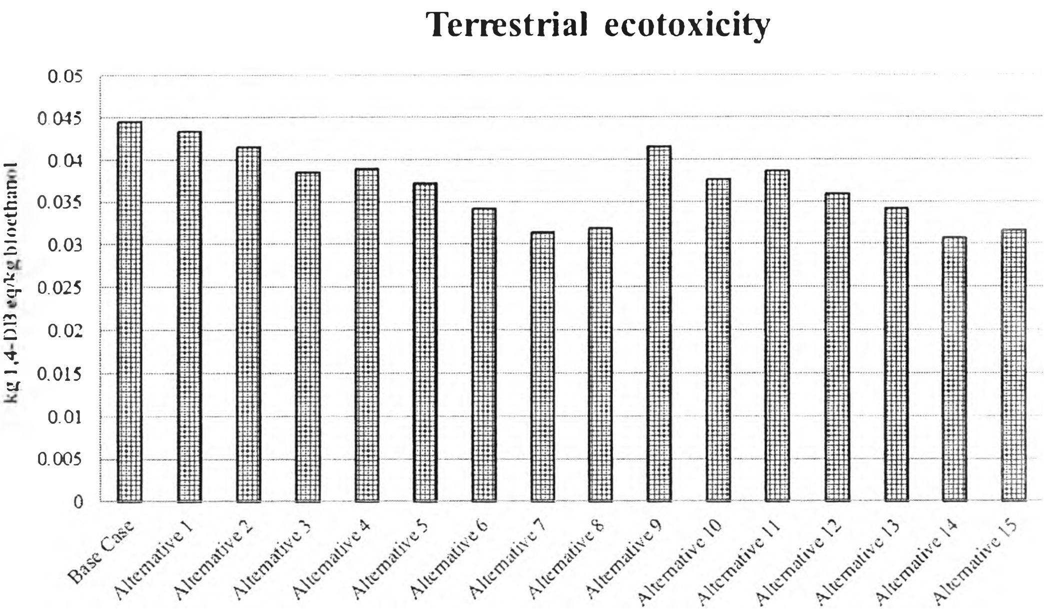

Figure 4.31 Comparison of the terrestrial ecotoxicity (kg 1,4-DB-equivalent) per one kilogram of bioethanol for each design.

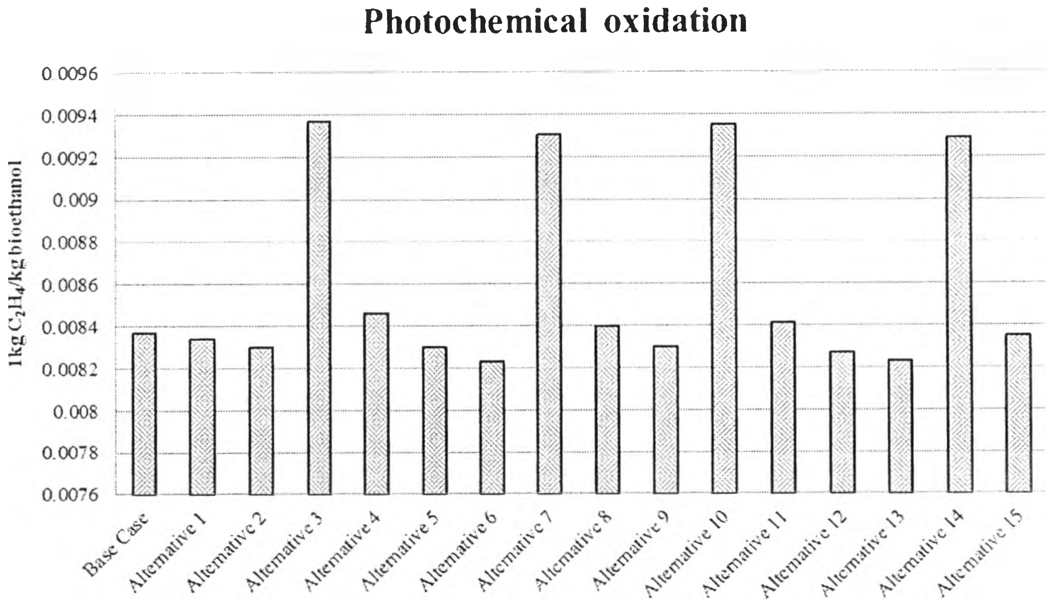

Figure 4.32 Comparison of the photochemical oxidation (kg C_2H_4) per one kilogram of bioethanol for each design.

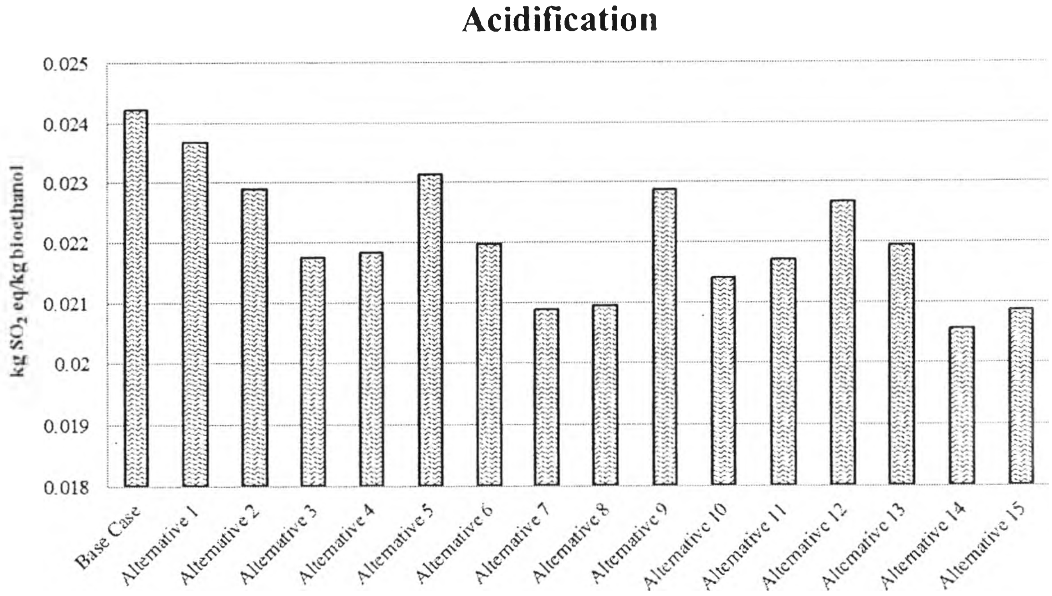

Figure 4.33 Comparison of the acidification (kg SO_2-equivalent) per one kilogram of bioethanol for each design.

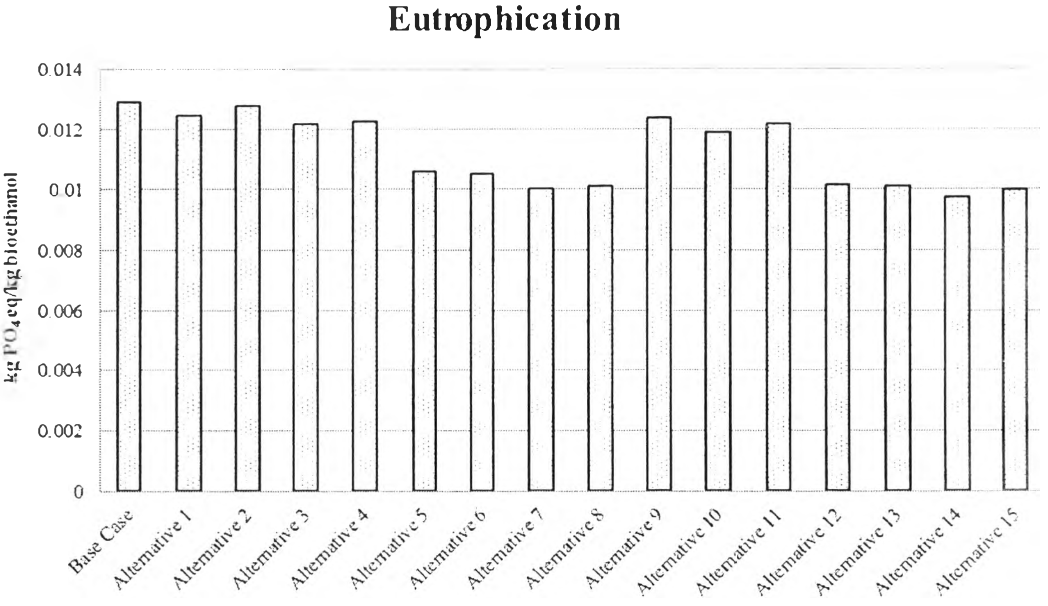

Figure 4.34 Comparison of the eutrophication (kg PO_4-equivalent) per one kilogram of bioethanol for each design.

The results from abiotic depletion, global warming potential, ozone layer depletion, human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, acidification and eutrophication potential reveal that new design alternatives were more environmental friendly. However, double evaporators and membrane designs were worse than the base case design in photochemical point of view. The reason came from these designs had recycle stream which cause the accumulation of chemical in the process therefore, the air emission contain higher quantity of these chemicals, mainly acetic acid and ethanol, which were the importance organic compound for photochemical oxidation. In photochemical oxidation, the best designs were alternatives 6 and 13.

Alternative 15 was the most environmental friendly in term of abiotic depletion with the reduction of 28 %. Alternative 14 was the best in term of ozone layer depletion, human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, acidification and eutrophication potential with the reduction of 24 %, 26.58 %, 10.30 %, 14.02 %, 30.94 %, 15.11 % and 24.31 % respectively. For overall environmental point of view, it could say that alternative 14 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 14 and 15, the other impacts of these two designs were not significantly difference. Therefore, alternative 15 would prefer for environmental issue.

4.5.6 Overall Comparison

After performing every analysis tools, the conclusion for the best design of bioethanol production process from rice straw are shown below:

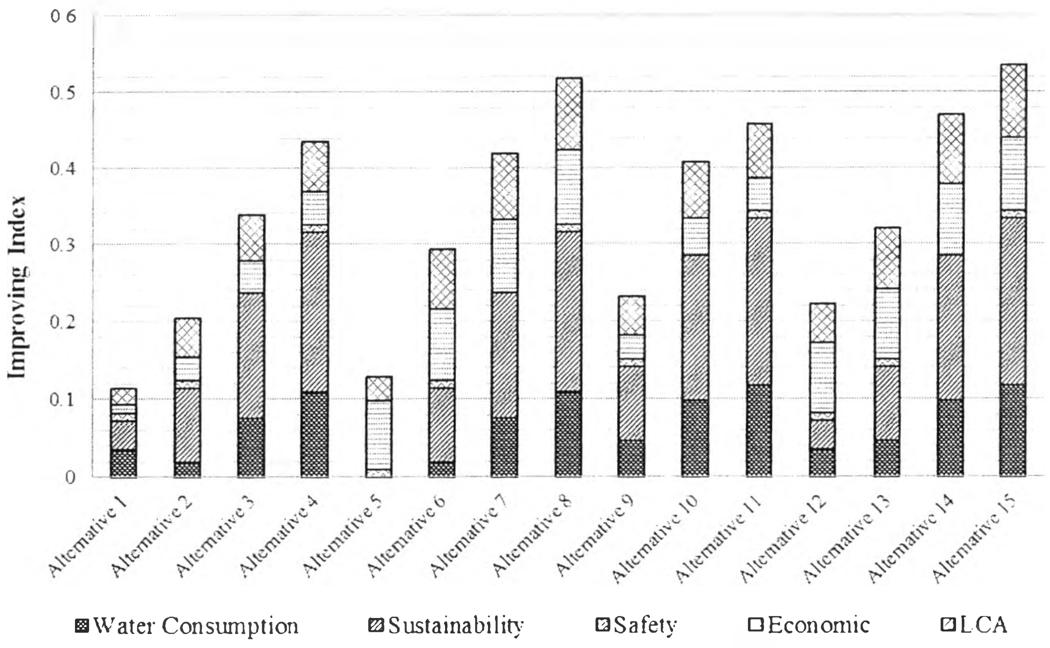

Figure 4.35 Comparison of the improving index for each of alternatives compare to the base case design.

According to the Figure 4.35, there were five parameters that were analyzed; water consumption, sustainability metric, safety, economic and LCA. Each of parameters were calculated the improving index which compare with the base case design. The higher index means the better process is. The weight of parameters was calculated related to the importance of that parameter. In other word, safety parameter for each of designs was not significantly difference compare to other parameter so; the weight of safety will be lower than the other but for sustainability metric which considering on both of energy and raw material consumption, it will weight twice as much as the other design. For more clearly view, the summary of the rank for the best design are shown in Table 4.30

Table 4.30 List of rank for the best alternative design for bioethanol production process from rice straw

Rank	Alternative	Description
1	15	Wastewater Recover by Membranes + Lignin Combustion with ***Heat Integration***
2	8	Wastewater Recover by Membranes + Lignin Combustion
3	14	Wastewater Recover by Evaporators + Lignin Combustion with ***Heat Integration***
4	11	Wastewater Recover by Membranes with ***Heat Integration***
5	4	Wastewater Recover by Membranes
6	7	Wastewater Recover by Double Effect Evaporators + Lignin Combustion
7	10	Wastewater Recover by Double Effect Evaporators with ***Heat Integration***
8	13	Wastewater Exchange Heat as Utility + Lignin Combustion with ***Heat Integration***
9	3	Wastewater Recover by Double Effect Evaporators
10	6	Wastewater Exchange Heat as Utility + Lignin Combustion
11	9	Wastewater Exchange Heat as Utility with ***Heat Integration***
12	12	Lignin Combustion with ***Heat Integration***
13	2	Wastewater Exchange Heat as Utility
14	5	Lignin Combustion
15	1	Base Case with ***Heat Integration***

As you can see from the results, they indicated that alternative 15, wastewater recovery using membranes and lignin combustion with heat integration, was shown to be the best design for bioethanol production process from rice straw because this design had the most water and energy saving and highest profit while maintaining safety awareness and environmentally friendly.