CHAPTER IV
RESULTS AND DISCUSSION

4.1 Base Case Design

4.1.1 Process Simulation of Base Case Design

4.1.1.1 TRE Design

TRE process was used as a model of this design. The process is designed to produce ethanol 99.5 wt% from sugarcane bagasse with the production capacity of 120,000 liters/day. The main operations of TRE process are shown in Figure 4.1.

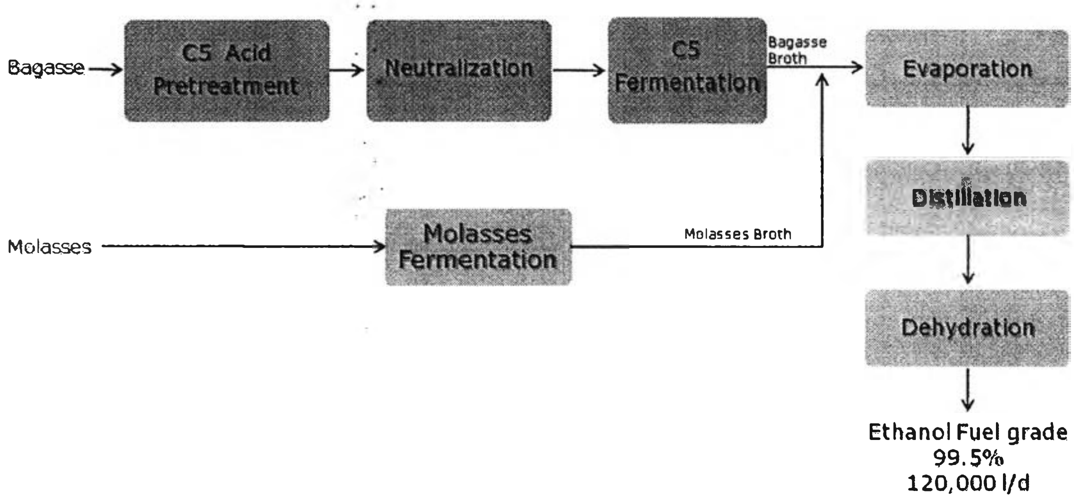

Figure 4.1 The main operations of TRE process.

TRE process was modeled on a continuous basis by process simulator, PRO/II 8.2, (PRO/II, 2006) as shown in Appendix C. Lists of components and reactions that take place in the process are shown in Appendix A and B, respectively. The process starting from sugarcane bagasse being conveyed to the C5-pretreatment area of the process. The feedstock is treated with dilute sulphuric acid at 162 ℃ in order to liberate hemicellulose and other compounds. Hemicellulose is then converted to C5-sugar, xylose. Afterwards the process stream is sent to a blowdown tank to remove inhibitors and water, followed by the insoluble solid liquid separation to separate and remove the insoluble solid fraction out. The liquid fraction is fed to overliming, neutralization and gypsum filter to further remove inhibitors. The inhibitors are liberated in the pretreatment and toxic to the fermentation microorganisms. These compounds are removed in this area. The detoxified stream is then fed to fermentation using microorganism, *KO11*, to convert xylose to ethanol. After this step, the ethanol from the bagasse broth is mixed with the ethanol from the molasses broth and sent to product recovery area. The composition in molasses broth was calculated according the data available from TRE, however, the calculation has only the mixture of water and ethanol reached the target concentration without any contamination. The product recovery stage consists of evaporation, distillation and molecular sieve adsorption. In this recovery section, the plant data are not available, therefore, the data were simulated according to Kramer (1981) and Morales *et al.* (2009) study. The mixed broth is finally purified to ethanol fuel grade 99.5 wt%.

However, TRE process converts hemicelluloses to ethanol only while cellulose is separated and sent to boiler to generate steam electricity. Since cellulose is the major component in bagasse (accounting for around 44% while hemicelluloses only accounts for around 27%) and, as cellulose can be converted to C6-sugar, glucose, with the high conversion. Therefore, the cellulose conversion step was added as applied by Morales *et al.* (2009) to the TRE design.

4.1.1.2 Base Case Design

Base case design was simulated for the TRE process converting hemicelluloses with the addition of the cellulose conversion process as shown in Appendix C. Starting from the pretreatment stage, sugarcane bagasse is treated with dilute sulphuric acid to hydrolyze hemicellulose and other compounds. Hemicellulose is then converted to C5-sugar, xylose. After that the process stream is fed to a blowdown tank to remove inhibitors and water, followed by a neutralization stage, the solid liquid separation to separate and remove the insoluble solid fraction. The liquid fraction is fed to overliming, neutralization and gypsum filter to further remove inhibitors which are toxic to the fermentation microorganisms. The previously separated stream with the insoluble solid is then mixed again with the detoxified stream and then fed to fermentation stage. In this stage, two different operations are occurring: saccharification of the remaining cellulose to glucose, and also the fermentation of the resulting glucose and other sugars (from the dilute acid pretreatment of hemicellulose) to ethanol using microorganism, *Zymomonas mobilis*. After this step, the ethanol from the bagasse broth is mixed with the ethanol from the molasses broth and sent to the product recovery stage, which consists of quadruple effect evaporation, distillation and molecular sieve adsorption. The mixed broth is purified to ethanol fuel grade 99.5 wt%.

This advanced design was used as the base case design to perform sustainability analysis and life cycle assessment. The stream summary with mass flow, energy flow and conditions regarding all components in all streams of the process is shown in Appendix D.

4.1.2 Sustainability Analysis

4.1.2.1 Indicator Results

SustainPro was used to analyze the sustainability of the design. The program decomposed base case flowsheet into 2896 open-paths (OP) and 84 close-paths (C). The mass and energy indicators were calculated. The most sensitive indicators are listed in Table 4.1 and Table 4.2.

Table 4.1 List of the most sensitive indicators for the open-paths

Path	MVA	Probability	Path	EWC	Probability	Path	TVA	Probability
OP 2680	**-229.1**	High	**OP 2258**	**256.7**	Low	**OP 554**	**-332.0**	High
OP 554	**-78.6**	High	**OP 554**	**253.4**	High	**OP 2258**	**-256.7**	Low
OP 555	**-72.7**	High	**OP 2782**	**195.2**	High	**OP 2680**	**-230.5**	High
OP 2667	**-21.8**	High	**OP 555**	**83.5**	High	**OP 2782**	**-216.8**	High
OP 2782	**-21.6**	High	**OP 2254**	**75.1**	High	**OP 555**	**-156.2**	High
OP 2254	-12.1	High	OP 2245	44.8	Low	OP 2254	-87.3	High
OP 2265	-7.6	High	OP 770	42.0	Low	OP 2245	-44.8	Low
OP 515	-4.9	High	OP 2769	39.3	High	OP 770	-42.0	Low
OP 516	-4.6	High	OP 515	25.2	High	OP 2769	-41.7	High
OP 488	-3.7	High	OP 2406	24.4	Low	OP 515	-30.1	High

Table 4.2 List of most sensitive indicators for the close-paths

Path	EWC	Probability	Path	AF	Probability
C58	282.1	Check AF	C65	0.5	Low
C2	4.5	Check AF	C58	0.5	High
C30	0.5	Check AF	C37	0.5	Low
C64	0.2	Check AF	C9	0.5	Low
C57	0.1	High	C64	0.4	High

The most sensitive indicators listed in Tables 4.1 and 4.2 have different meaning. For example, negative values of MVA or TVA indicate the potential to improve the process by making them positive through design changes. Positive values of the EWC, on the other hand, indicate that too much energy is being used (or wasted) and there is a potential to improve the process by reducing these values through design changes. In open-path, the top five values in each indicator are in bold, OP 554, OP 555, OP 2254, OP 2258, OP 2667, OP 2680, and OP 2782. In close-paths, C 58 and C 2 are the two highest values for EWC. C 65 and C 58 rank on top values for AF. The details of those potential paths are shown in Table 4.3. At this point it was necessary to make the judgment regarding the question to which path and indicator can provide the best improvement.

Table 4.3 Details of high potential paths for improvement

Path	Component	Starting stream/unit	Ending stream/unit
OP 554	WATER	S-66	S-72
OP 555	WATER	S-66	S-78
OP 2254	CELLULOS	S-01	S-72
OP 2258	CELLULOS	S-01	R5
OP 2667	CELLULAC	S-40	S-72
OP 2680	CELLULAC	S-55	S-72
OP 2782	LIGNIN	S-01	S-72
C2	WATER	S-69	S-75
C58	WATER	S-71	S-73
C65	ACETIC ACID	S-71	S-73

Focus on the component from potential paths, starting with cellulose, their paths and streams involve with plenty of soluble and insoluble solid matter, therefore, recycling it to the process does not seem feasible. Cellulac (*cellulase*), a class of enzyme, which is rarely separated in order to recycle or recover back to the process, therefore, it will not be further analyzed. Lignin is an unwanted compound in the process, and is one of interesting targets for improvement because it enters and exits the process unchanged. Separating it before entering the process has the possibility to reduce flows and a consequence the required volume for the equipment. If the flows are reduced, the energy consumption will also be decreased. However, in term of the new design alternatives to implement in PRO/II, this was decided not to be considered. Acetic acid is a compound generated in just a small portion from fermentation section of the process, thus it was not considered. The component that has been massively used and has high potential for improvement paths is water. Therefore, the paths related to water (OP 554, OP 555, C58, and C2) were selected for further analysis.

After the previous selection, the sensitivity analysis was performed to pursue the analysis of the paths related to water in EWC. The scores from the sensitivity analysis from SustainPro were analyzed and given scores to open paths and close paths with the high potential for improvement as shown in Table 4.4.

Table 4.4 Scores from the indicators sensitivity analysis algorithm

Path	Indicator	Score
OP 554	EWC	27
OP 555	EWC	26
C2	EWC	12
C58	EWC	16

From Table 4.4, the score in open paths, OP 554 is slightly higher than OP 555. In close paths, the score from C58 is higher than from C2.

4.1.2.2 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 554, OP 555, C2, and C58 is shown in Tables 4.5, 4.6, 4.7, and 4.8, respectively.

Table 4.5 Sensitivity analysis of OP 554

	Deviation (%)					
Variation (%)	S-66	F2	F3	F4	F5	E6
5%	3.28%	0.07%	0.00%	0.01%	4.29%	0.63%
10%	6.69%	0.13%	0.00%	0.01%	8.59%	1.27%
15%	10.22%	0.20%	0.00%	0.02%	12.88%	1.90%

Table 4.6 Sensitivity analysis of OP 555

	Deviation (%)				
Variation (%	S-66	F2	E6	C1	Reb T1
5%	1.87%	0.19%	1.78%	0.04%	2.99%
10%	3.86%	0.37%	3.56%	0.08%	5.99%
15%	5.96%	0.56%	5.34%	0.12%	8.98%

Table 4.7 Sensitivity analysis of C2

	Deviation (%)		
Variation (%	F2	F3	Flow C2
5%	4.89%	0.11%	3.53%
10%	9.77%	0.23%	7.17%
15%	14.66%	0.34%	10.92%

Table 4.8 Sensitivity analysis of C58

	Deviation (%)		
Variation (%)	F4	F5	Flow C58
5%	0.01%	4.99%	2.86%
10%	0.01%	9.99%	5.85%
15%	0.02%	14.98%	8.98%

From the results shown in the above tables, the way to evaluate the sensitivity analysis performed by SustainPro is to look at which sections have the highest percentage. The evaporator F5 has the highest percentage on OP 554 and C58 while the evaporator F2 has the highest percentage on C2, the reboiler T1 has the highest percentage on OP 555. Those high percentages are the ones having the large impact on improving the indicators by changing the variable. The way to design alternatives is to look at those units and try to improve them.

Based on these indicator results, it can be summarized that there is a room for improvement through the paths with respect to EWC. For the selected paths and the indicator sensitivity analysis, it was determined that the paths related to water (OP 555, OP 554 and C58), which pass through the recovery area, have high potential for improvement in terms of EWC. The sensitivity analysis also determined that the design of the quadruple effect evaporator and the distillation column could also be improved.

4.1.2.3 Sustainability Metrics Results

SustainPro classifies their metrics into 4 groups: energy, material, water, and economic. The sustainability metrics of base case design are shown in Table 4.9.

Table 4.9 Sustainability metrics results of base case design

Energy	Total Net Primary Energy Usage rate (GJ/y)	1.67.E+06
	% Total Net Primary Energy sourced from renewables	1.00
	Total Net Primary Energy Usage per Kg product (kJ/kg)	47815.07
	Total Net Primary Energy Usage per unit value added (kJ/$)	7.71
Material	Total raw materials used per kg product (kg/kg)	14.24
	Total raw materials used per unit value added	0.00
	Fraction of raw materials recycled within company	1.35
	Fraction of raw materials recycled from consumers	0.00
	Hazardous raw material per kg product	0.86
Water	Net water consumed per unit mass of product (kg/kg)	144.66
	Net water consumed per unit value added	0.02
Economic	Value added	2.71.E+07

However, the more interesting of the results is to compare it between base case and alternatives. The further comparison of metrics is shown in Table 4.26 in section 4.3.2.2.

4.1.2.4 WAR Algorithm Results

Waste reduction (WAR) algorithm is the environmental metrics considered in sustainability metrics, but it was needed to calculate by using integrated computer aided system (ICAS) software. The results are shown in Table 4.10.

Table 4.10 WAR algorithm results of base case design obtained through ICAS

	Stream No	HTPE	ATP	TTP	GWP	ODP	PCOP	AP
Input	S-01	0	0	0	0	0	0	0
	S-02	0	0	0	0	0	0	0
	S-04	0	0	0	0	0	0	0
	S-05	78	5	44	0	0	0	0
	S-07	0	0	0	0	0	0	0
	S-14	0	0	0	0	0	0	0
	S-20	29	33	71	0	0	0	0
	S-22	145	8	81	0	0	0	0
	S-26	566	33	316	0	0	0	0
	S-39	0	0	1	0	0	0	2
	S-53	0	1	7	0	0	0	12
	Input summary	819	80	519	0	0	0	14
Output	S-10	5	9	1763	0	0	0	0
	S-30	98	5	723	0	0	0	0
	S-64	1	1079	29	9	0	266	0
	S-72	25	4	63	0	0	7	0
	S-78	3	5	544	0	0	0	0
	S-81	2	34	546	0	0	0	0
	S-83	5	2	1680	0	0	18571	0
	Output summary	139	1139	5348	9	0	18843	0
	Impact generated	**-679**	**1059**	**4830**	9	**0**	**18843**	**-14**

As it was stated in previous section, the lower the value, the more environmental friendly it is. The results between base case and alternatives are compared in this study (Table 4.27 in section 4.3.2.3).

4.1.2.5 Safety Indices Results

This analysis was performed in SustainPro 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 base case design of bioethanol conversion process are presented in Table 4.11.

Table 4.11 Safety indices for the bioethanol conversion process

Chemical inherent safety index,Ici	**Score**	**Process inherent safety index,Ipi**	**Score**
Subindices for reactions hazards		**Subindices for process conditions**	
Heat of the main reaction,Irm	0	Inventory,Ii	4
Heat of the side reactions,Irs	3	Process temperature,It	2
Chemical Interaction,Iint	2	Process pressure,Ip	1
Subindices for hazardous substances		**Subindices for process system**	
Flammability,Ifl	4	Equipment,Ieq	
Explosiveness,Iex	1	Isbl	3
Toxicity,Itox	2	Osbl	2
Corrosivity,Icor	0	Process structure,Ist	2
Ici	**12**	**Ipi**	**14**
ISI	**26**		

From the possible maximum score of 53 as shown in Chapter 2, it can be seen from Table 4.11 that the process ISI is 26. Hence, this bioethanol conversion process is inherently safe. 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 given by SustainPro aim to improve the process economically while not making safety worse. Therefore, the comparison of base case design and alternatives will be further shown to confirm that the safety has improved, or that has at least maintained the same.

4.1.3 Life cycle assessment

4.1.3.1 Life Cycle Inventory of Bioethanol Conversion Process

A 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 generation—associated with each stage of process life cycle. In this research, the base case design of bioethanol conversion process was divided into four stages: pretreatment, neutralization, fermentation, and recovery as shown in Figure 4.2.

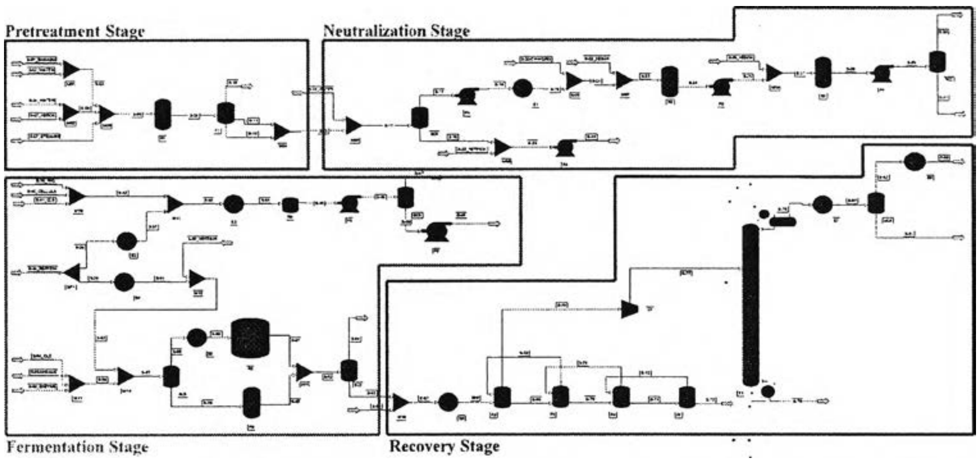

Figure 4.2 Four stages of process life cycle.

According to TRE's project, the wastewater from the plant has been designed to produce steam and electricity through biogas and cogeneration system to supply energy to the system. In order to perform the life cycle assessment with the data available from the plant, this biogas and cogeneration stage was also included in this study. The system boundary of bioethanol conversion process is shown in Figure 4.3.

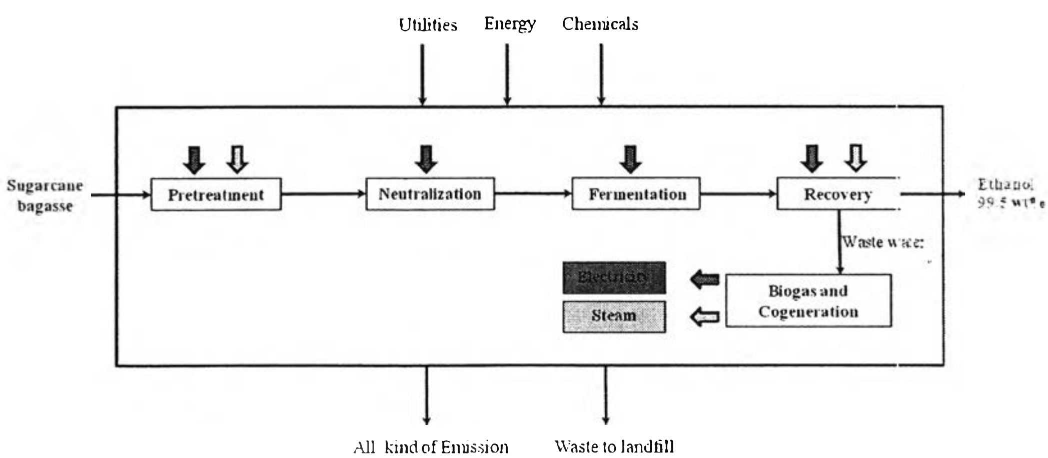

Figure 4.3 System boundary of bioethanol conversion process.

The inventory data of each stage on a basis of one kilogram of 99.5 wt% ethanol as the functional unit were obtained directly from process simulator, PRO/II. In this analysis, the amount of cooling water is neglected since TRE use normal water to cool there unit and it can recycle back to the system. No make-up water added was assumed because the cold outlet temperature is 50 °C in the process. In the actual operation, the energy supplied (steam and electricity) to TRE process comes from a bagasse boiler located in the sugar mill area. By using this energy from biomass (sugarcane bagasse), carbon dioxide (CO_2) released can be omitted because sugarcane absorbs CO_2 as it is naturally grown and, the net amount of CO_2 added to the atmosphere from biomass energy use can be reduced through using biomass as long as sugarcane are replanted. Also, CO_2 produced from fermentation of bioethanol production is not considered to be greenhouse gas emission because of the utilization of renewable source as raw material for this process. The inventory analysis of the process life cycle is presented stage by stage. Details of input and output inventory data of each stage are presented in Tables 4.12, 4.13, 4.14, 4.15, and 4.17.

Table 4.12 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in pretreatment stage

Input Inventory				Output Inventory		
Type	Amount	Unit		Type	Amount	Unit
Material				*Product*		
Sulphuric acid	0.0037	Kg		Output-1 from Pretreatment Stage	12.8128	Kg
Utilities				*Emission to Air*		
Water	3.1275	Kg		Water	2.2735	Kg
				Furfural	0.0046	Kg
Energy						
Steam	12.6892	Kg				

Table 4.13 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in neutralization stage

Input Inventory				Output Inventory		
Type	Amount	Unit		Type	Amount	Unit
Material				***Product***		
Output-1 from Pretreatment Stage	12.8128	Kg		Output-2 from Neutralization Stage	19.5563	Kg
Sulphuric acid	0.0336	Kg				
Calcium hydroxide	0.0273	Kg		***Solid Waste***		
				Gypsum	0.0502	Kg
Utilities				Glucose	0.0002	
Water	6.8915	Kg		Xylose	0.0019	
				Arabinose	0.0001	
Energy				Cellulose	0.1471	
Electricity	0.0002	KWh		Hemicellulose	0.0086	
				Arabinan	0.0007	
				Mannan	0.0001	

Table 4.14 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in fermentation stage

Input Inventory				Output Inventory		
Type	Amount	Unit		Type	Amount	Unit
Material				***Product***		
Output-2 from neutralization stage	19.5563	Kg		Output-3 from fermentation stage	20.1403	Kg
Ammonia	0.0006	Kg				
Cellulase	0.0025	Kg		***Emission to Air***		
Corn steep liquor	0.0665	Kg		Water	0.0148	Kg
Zymomonas Mobilis	0.0262	Kg		Ethanol	0.0165	Kg
				Carbondioxide	0.9435	Kg
Utilities				Oxygen	0.0010	Kg
Water	1.4639	Kg				
Energy						
Electricity	0.00002	KWh				

The products of each stage were considered as raw materials for the next stage, for example, Output-1 from pretreatment stage was used as a material for neutralization stage. In neutralization and fermentation stage, several chemicals and substances shown in these two tables do not exist in SimaPro's database: calcium hydroxide, corn steep liquor, enzyme (cellulase and zymomona mobilis), sugar (glucose, xylose, arabinose, and mannose), and cellulosic compound (cellulose, hemicelluloses, arabinose, and mannose). However, these chemicals and substances are presented in a very small amount and could be omitted by the cut-off rule when a cut-off level of 1% was applied.

Table 4.15 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in recovery stage

Input Inventory				Output Inventory		
Type	**Amount**	**Unit**		**Type**	**Amount**	**Unit**
Material				***Product***		
Output-3 from fermentation stage	20.1403	Kg		Ethanol 99.5 wt%	1.0000	Kg
Energy						
Electricity	0.0091	KWh		***Liquid waste***		
Steam	13.4970	Kg		Waste water	19.0751	Kg

After fermentation stage, the process steam Output-3 from fermentation stage as bagasse broth is mixed inline with molasses broth stream as shown in Figure 4.1. The mixed broth is then fed to the recovery stage. At this point, the allocation of mixed broth is done with two options: mass allocation (MA), and Waste removed allocation (WrA) in this stage between bagasse broth and molasse broth. The comparison between these two allocation methods is shown in Table 4.16.

Table 4.16 Partitioning fraction between mass and water removed allocation

Scenario	Mass(feed) allocation		Waste removed allocation	
	Kg/hr	MA	Kg/hr	WrA
Bagasse broth	14735	24.73%	14003	25.36%
Molasse broth	44850	75.27%	41213	74.64%
Total	59585	100%	55216	100.00%

The results from these two allocation methods show only a slight difference, which means that both methods can be applied to this assessment. However, MA has a disadvantage on the difference in the percentage of ethanol between bagasse broth (6 wt%) and molasse broth (10 wt%). Since the target of the recovery stage is to remove water mainly in order to reach 99.5 wt% ethanol purity, therefore, WrA seems to be more resonable. The percentage of 25.36 was allocated to total mass in the mixed broth in order to get the energy consumption and amount of wastewater weighted to bagasse broth. The next concerning issue is the allocation of the final product. However, since this stage generates only ethanol 99.5 wt% and wastewater, therefore, 100% allocation was weighted to bioethanol.

Up to this point, after four stages of bioethanol conversion process, ethanol 99.5 wt% was obtained as the final product. Biogas and cogeneration stage was employed to convert wastewater to electricity and steam supplied to the plant. An 85% efficiency of cogeneration was assumed to this analysis. Details of input and output inventory data of biogas and cogeneration stage are shown in Table 4.17.

Table 4.17 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in biogas and cogeneration stage

Input Inventory				Output Inventory		
Type	Amount	Unit		Type	Amount	Unit
Material				*Product*		
Waste water	19.0751	Kg		Steam	3.6617	Kg
				Electricity	0.9700	KWh
				Emission to air		
				Nitrogen oxides	1.75E-04	Kg
				Carbon monoxide	5.59E-04	Kg
				Methane, biogenic	2.68E-04	Kg
				NMVOC	2.33E-05	Kg
				Dinitrogen monoxide	2.91E-05	Kg
				Sulfur dioxide	2.45E-04	Kg
				Platinum	8.16E-11	Kg
				Heat, waste	1.03E+01	MJ
				Used mineral oil, to waste inceneration	3.50E-04	Kg

It should be noted that the inventory for this stage was obtained according to the data available from TRE and Ecoinvent database. The products from this stage, electricity and steam, were considered to compensate the overall energy consumption in the process.

4.1.3.2 Life cycle energy analysis

A life cycle energy analysis (LCEA) is an approach in which all energy inputs to a product are accounted to the entire production system of bioethanol conversion process. In this research, after performing the life cycle inventory analysis of the bioethanol conversion process, the life cycle energy efficiency was studied in term of and Net Energy Ratio (NER) which refer to the ratio between total energy required to complete the process life cycle and the amount of energy contained in the products. The NER of base case design is estimated to be 0.83. The NER of the base case is compared to NERs of the alternatives and discussed in section 4.3.3.

4.1.3.3 Life cycle impact assessment

A life cycle impact assessment (LCIA) is used to evaluate of the contribution to environmental impact categories. In other words, this phase is to analyze and compare the environment burdens associated with raw material use and energy inputs and emissions releases as quantified by the LCI results.

After performing the life cycle inventory analysis of the base case design of bioethanol conversion process from sugarcane bagasse using SimaPro 7.0, the CML 2 baseline 2000 and Eco-indicator 95 methods were then utilized to evaluate the environmental impacts in various categories such as global warming potential, ozone layer depletion, acidification, eutrophication potential, and energy resources. The impact assessment results are shown in Tables 4.18 and 4.19.

Table 4.18 Environmental impact of bioethanol conversion process per one kilogram ethanol 99.5 wt%

Impact category	Unit	Total
Abiotic depletion	kg Sb eq	1.23E-04
Acidification	kg SO2 eq	2.99E-03
Eutrophication	kg PO4--- eq	4.71E-04
Global warming (GWP100)	kg CO2 eq	7.97E-02
Ozone layer depletion (ODP)	kg CFC-11 eq	2.18E-09
Human toxicity	kg 1,4-DB eq	3.15E-02
Fresh water aquatic ecotox.	kg 1,4-DB eq	1.56E-03
Marine aquatic ecotoxicity	kg 1,4-DB eq	2.68E+00
Terrestrial ecotoxicity	kg 1,4-DB eq	7.42E-05
Photochemical oxidation	kg C2H4	7.02E-03
Energy resources	MJ LHV	5.44E-01

Table 4.19 Environmental impact of bioethanol conversion process per one megajoule ethanol 99.5 wt%.

Impact category	Unit	Total
Abiotic depletion	kg Sb eq	4.63E-06
Acidification	kg SO2 eq	1.04E-04
Eutrophication	kg PO4--- eq	1.67E-05
Global warming (GWP100)	kg CO2 eq	2.39E-03
Ozone layer depletion (ODP)	kg CFC-11 eq	8.23E-11
Human toxicity	kg 1,4-DB eq	1.18E-03
Fresh water aquatic ecotox.	kg 1,4-DB eq	5.93E-05
Marine aquatic ecotoxicity	kg 1,4-DB eq	1.01E-01
Terrestrial ecotoxicity	kg 1,4-DB eq	2.80E-06
Photochemical oxidation	kg C2H4	2.59E-04
Energy resources	MJ LHV	2.05E-02

The LCIA results of the base case and alternatives are compared and discussed in section 4.3.3. The results based on both functional units, one kilogram and one megajoule of ethanol show the same trend. From the emissions distributed from all stages of the entire process, the distribution of impact is shown in Figure 4.4.

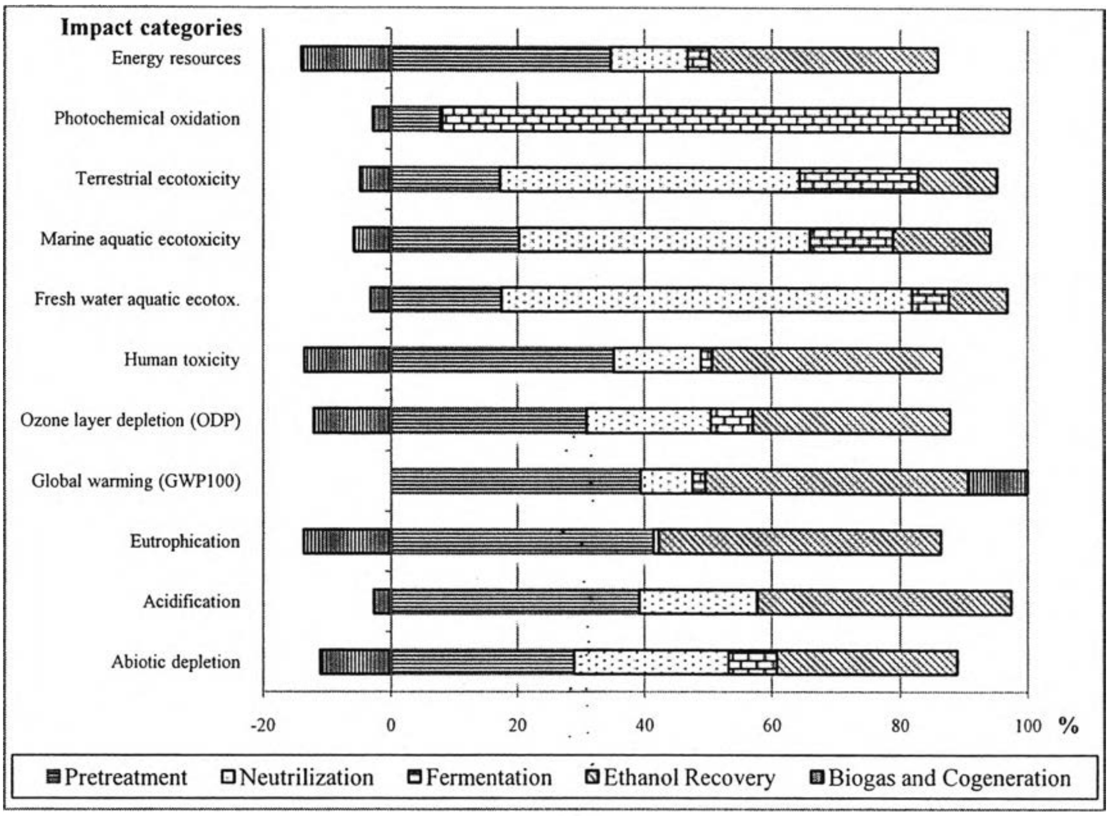

Figure 4.4 Distribution of environmental impacts classified stage by stage.

For all impact categories except global warming, the biogas and cogeneration stage gives a negative of emission because the electricity and steam generated from wastewater treatment in this stage can compensate the overall energy consumption. The lower the energy consumption, the lower is the emission and impact of the process. In the case of global warming (GWP), carbon dioxide released from burning biogas is much higher than the compensation of electricity and steam generated. Hence, there is no negative emission on GWP. The results show that CO_2 emission is mainly caused by the high energy consumption in recovery stage (41%), and pretreatment stage (39%) of the process.

4.2 Generation of design alternatives

4.2.1 Process aspect

The idea for generating new design alternatives comes from the results from sustainability analysis. The indicator results show that the recovery stage has high potential for improvement according to OP 554, OP 555, and C58. The sensitivity analysis from selected path shows that evaporator F2 and F5, and reboiler's column T1 has large impact for improving the indicators by changing the variables. In response to this, the new design alternative was projected to reduce the heating duties of unit operations in the recovery area, as the heating duty has a strong influence on the environmental impact. The lower the duty, the lower the energy consumed. If the energy consumption is decreased, the EWC indicator will also decrease, leading to a more sustainable and economical process. Then, the life cycle assessment is to be further verified for environmental impacts. Identifying the possibilities for reduction of EWC in OP 554, OP 555 and C58 of base case design was done by focusing on the possibilities for reduction of the heating duties of units present in the selected paths.

Three design alternatives were generated and classified into two platforms, the evaporator platform—TRE use evaporator at to recover ethanol from impurities—, and the distillation platform—change evaporators to a distillation column—. All designs were aimed to meet the purity of 90.00 wt% before being sent to molecular sieve adsorption unit.

4.2.1.1 Evaporator Platform

This platform was simulated based on the real operation in TRE (using quadruple effect evaporator). The condition of each unit was obtained from Kramer (1981). The specification of product was adapted from the actual plant data. The hot spot of the new design was focused on evaporator F2 and F5. The conditions given by Kramer are operating under ultra-high vacuum condition. The first attempt was to change from that high vacuum condition to a mild vacuum condition. Alternative-1 was designed by this attempt. The process flowsheet implemented in PRO/II of Alternative-1 is the same as base case design as shown in Appendix C because it was just a change the operating condition. The difference of vacuum pressure between base case and Alternative-1 is shown in Table 4.20. The results show that Alternative-1 has the insignificant heat duty reduction compared to the base case.

Table 4.20 Comparison of operating condition and duty between the base case and Alternative-1

Unit	Pressure (atm)		Duty (GJ/hr)	
	Base case	Alternative-1	Base case	Alternative-1
F2	0.87	0.95	1.46	1.42
F3	0.50	0.90	-1.39	0.16
F4	0.13	0.85	-5.37	1.12
F5	0.12	0.80	64.87	62.24
Total heat duty			66.33	64.94

The next attempt was to change quadruple effect evaporator to triple effect. The duty in F5 was the highest because it operated at the highest vacuum condition, therefore getting rid of F5 while maintaining the product specification could lower down the overall evaporation duty. Alternative-2 was designed by this attempt as shown in Appendix C. The comparison of duty between base case and Alternative-2 is shown in Table 4.21. The results show that although Alternative-2 has higher heat duty reduction than Alternative-1, but it still has a slight heat duty reduction compared to the base case.

Table 4.21 Comparison of duty between the base case and Alternative-2

Unit	Duty	
	Base case	Alternative-2
F2	1.46	1.43
F3	-1.39	-1.23
F4	-5.37	59.12
F5	64.87	
Total Heat duty	66.33	60.55

The next attempt was to add an evaporator, F6, before distillation to reduce the flowrate. The lower flowrate pass through the column can lead to reducing the heat duty itself. Alternative-3 was designed by this attempt as shown in Appendix C. The comparison of duty between base case and Alternative-3 is shown in Table 4.22. The results show that although Alternative-3 can reduce the heat duty in distillation column but the heat duty in quadruple effect evaporator was increased. Because the water removed from a new evaporator need to recycle back to F1 to recover a portion of ethanol which was lost from a new evaporation, therefore, the total heat duty in Alternative-3 has higher than the base case.

Table 4.22 Comparison of duty between the base case and Alternative-3

Unit	**Duty**	
	Base case	**Alternative-3**
F2	1.46	-11.25
F3	-1.39	-1.88
F4	-5.37	-7.81
F5	64.87	78.80
F6		-12.50
T1-Reboiler	6.64	5.36
T1-Condenser	-64.48	-50.70
Total Heat duty	72.97	84.16

4.2.1.2 Distillation Platform

Changing platform means replacing the quadruple effect evaporator by a beer distillation column. A two distillation column is a conventional process, the first column (beer column) is used to remove the dissolved CO_2 and most of the water, and the second distillation column is used to purify the ethanol to near azeotropic composition. The new design was simulated based on Morales *et al.* (2009). This is assigned as Alternatives-4 as shown in Appendix C. The comparison of duty between four evaporators from base case and beer column T1 from Alternative-4 is shown in Table 4.23.

Table 4.23 Comparison of duty between the base case and Alternative-4

Unit	Duty (GJ/hr)	
	Base case	Alternative-4
F2	1.4625	
F3	-1.3866	
F4	-5.3688	
F5	64.8658	
Reboiler T1		19.1478
Reboiler T2	6.6437	2.5706
Total heat duty	72.9720	21.7184

It can be seen from the table that Alternativs-4 has a significant reduction in energy consumption. The total heating duty in the recovery stage was reduced by 60% (from 72.97 to 21.72 gigajoules/hr). In process aspect, Alternative-4 seems to be the best option. However, for this alternative, the new investment will need to be made. This result can provide guidance in terms of deciding whether for the recovery technology, use of the beer distillation instead of the quadruple effect evaporator would result in a more sustainable process.

4.2.2 Energy Efficiency Aspect

The target of this aspect is to use less energy to provide the same level of energy service. In other words, reducing energy consumption and eliminating energy wastage are considered in order to utilize it efficiently. This attempt can be done by identifying the possibility of reducing TVA in OP 554 and OP555 of base case design and then focusing the possibility to reduce the duty of units along those paths pass through. Therefore, the heat integration was applied to Alternative-4—the best design from process aspect—.

4.2.2.1 Heat Integration

There are four hot streams and two cold streams in Alternative-4. In addition, the waste streams from both distillation column T1 and T2 have high potential to supply heat to the system because of their high flowrates and temperatures. The two hot waste streams were projected to be 40.15 °C at the outlet. The properties of those streams are shown in Tables 4.24-4.25, and Figure 4.5.

Table 4.24 Properties of hot and cold stream in Alternative-4

Stream	T_{Hot} (°C)	T_{Cold} (°C)	Q (KW)
H1 S-18--S-19	72.25	50.00	181
H2 S-36—S-37	59.83	30.00	43
H3 S-38—S-51	59.83	30.00	388
H4 S-77—S-78	99.99	32.00	1201
C1 S-68--S-69	100.00	29.94	4674
C2 S-74—S-75	95.00	78.71	31

Table 4.25 Properties of potential heat supplied in Alternative-4

Stream	T_{Hot} (°C)	T_{Cold} (°C)	Q (KW)
H5 S-71	120.73	40.15	4698
H6 S-73	100.02	40.15	285

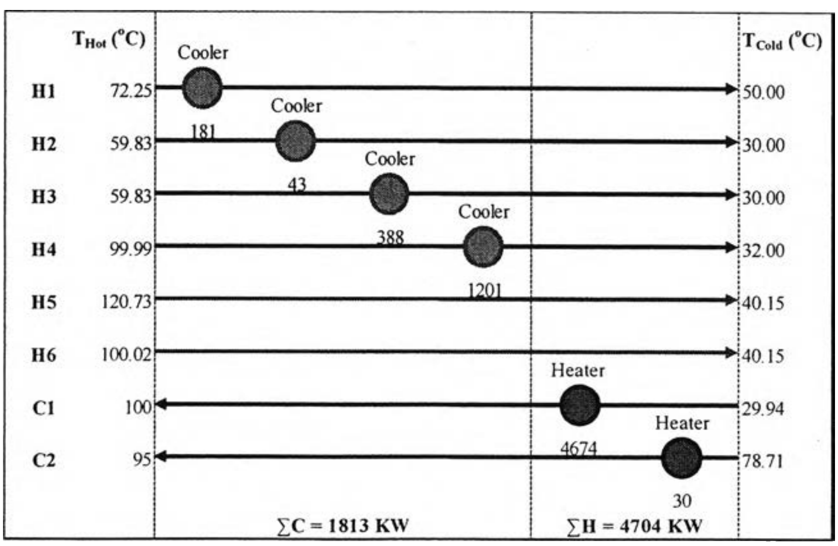

Figure 4.5 Grid diagram of hot and cold stream in Alternative-4.

All of the stream data above was sent to an optimization tool, GAMS, to calculate the possibility to do heat integration. The data were added to GAMS and the results are shown in Appendix E. The matching between hot and cold stream was done. The results from GAMS reported that the potential hot stream H5 can be matched with cold stream C1 to supply the heat, and potential hot stream H6 can be matched with cold stream C2, as shown in Figure 4.6.

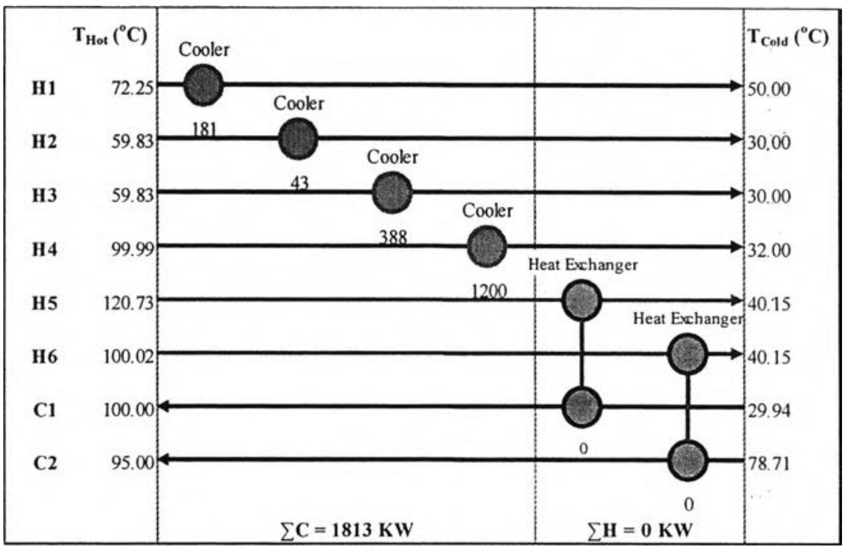

Figure 4.6 Grid diagram of hot and cold stream in Alternative-5.

From Figures 4.5 and 4.6, it can be seen that after performing heat integration of Alternative-4 as suggested by GAMS, the total heat duty of new design (Alternative-5) was decreased from 4704 KW to 0 KW while the total cooling duty was the same as before. The integration between potential streams and cold streams can reduce the heat duty, while other hot steams were not used because there are only two cold streams in this process. The new design, Alternative-5, is achieved through the heat integration as shown in details in Appendix E.

4.3 Comparison between base case and alternatives

4.3.1 Energy Consumption

The energy consumption is one of the important factors affecting the EWC indicator and the environmental impact. In this study, the major hot spot for improvement is heat duty, which is related to the high values of EWC in OP 554 and OP 555 (given by SustainPro) and the CO_2 emission as indicated by life cycle assessment. The comparison of energy consumption between base case design and alternatives is shown in Table 4.26.

Table 4.26 Comparison of total energy consumption between the base case and alternatives

Design	Heating Duty (GJ/hr)	Cooling Duty (GJ/hr)
Base Case	167	92
Alternative-1	165	85
Alternative-2	161	87
Alternative-3	178	105
Alternative-4	117	33
Alternative-5	101	33

As seen from the table, the heating duties of almost all new design alternatives are less than base case design. The heating duty for Alternative-5 from energy efficiency aspect is 101 gigajoule per hour, that is, a 40 % reduction compared to the base case design. The reduction in cooling duty observed also shows the improvements for alternatives.

In case of Alternative-3, the total energy consumption is higher than the base case design due to higher heating and cooling duty in quadruple effect evaporator resulting from the higher flowrate pass through its unit.

4.3.2 Sustainability Analysis

4.3.2.1 Indicators

All of the indicators for the paths OP 554 and OP 555 were compared for the base case design and the alternatives as shown in Tables 4.27 and 4.28, respectively. Since two of the new design alternatives has no close path referring to C2 and C58, the comparison of those close paths between base case and alternatives were not considered.

Table 4.27 Comparison of indicators of alternatives corresponding to the same OP 554 of the base case design

Path	MVA	EWC	TVA
OP 554-Base Case H2O-(S-66)-(S-72)-Evaporator	-78.60	253.38	-331.98
OP 554-New-Alternative-1 H2O-(S-66)-(S-72)-Evaporator	-78.60	247.03	-325.63
OP 554-New-Alternative-2 H2O-(S-66)-(S-71)-Evaporator	-78.46	233.19	-311.65
OP 554-New-Alternative-3 H2O-(S-66)-(S-72)-Evaporator	-94.43	309.30	-403.73
OP 187-New-Alternative-4 H2O-(S-66)-(S-71)-1st Column	-139.74	197.60	-337.33
OP 247-New-Alternative-5 H2O-(S-66)-(S-79)-1st Column	-139.74	130.81	-270.54

Table 4.28 Comparison of indicators of alternatives corresponding to the same OP 555 of the base case design

Path	MVA	EWC	TVA
OP 555-Base Case H2O-(S-66)-(S-78)-2nd Column	-72.72	83.46	-156.18
OP 555-New-Alternative-1 H2O-(S-66)-(S-78)-2nd Column	-72.71	81.07	-153.79
OP 555-New-Alternative-2 H2O-(S-66)-(S-78)-2nd Column	-72.72	84.96	-157.67
OP 555-New-Alternative-3 H2O-(S-66)-(S-78)-2nd Column	-56.72	65.53	-122.25
OP 188-New-Alternative-4 H2O-(S-66)-(S-73)-2nd Column	-11.54	24.87	-36.42
OP 248-New-Alternative-5 H2O-(S-66)-(S-80)---2nd Column	-11.54	19.36	-30.90

As mentioned earlier (Figure 2.15), the closer to zero the indicators, the better for the process. It can be seen that TVA for almost all alternatives have improved considerably. In OP 554, MVA has increased in Alternative-4 and Alternative-5 from distillation platform because of the use of a beer distillation column where water is mainly removed. Therefore, the mass out from this path is much higher than those from evaporator platform caused by the high value in the MVA. However, EWC for almost all alternatives has improved significantly and compensated for the MVA value giving the improvement in all alternatives in TVA. In OP 555, all indicators belonging to alternatives from distillation platform have improved considerably. In both open paths, Alternative-5 has the highest improvement due to the lowest energy consumption.

In case of Alternative-3, all indicators in OP 555 are slightly improved as a result of the lower heat duty in distillation column. However, the indicators in OP 554 are worse because of the higher flowrate leading to the higher heat duty in quadruple effect evaporator compared to the base case.

4.3.2.2 Sustainability Metrics

Sustainability metrics calculated using SustainPro were used for comparing the sustainability of different designs through 4 groups of metrics: energy, material, water, and economic, as shown in Table 4.29.

It can be seen that the sustainability metrics of the new design alternatives (except Alternative-3) have improved significantly in almost all metric items compared to the base case, whilst for some remained the same. In energy and water consumption, the new designs have been proved to be considerably better. In economic aspect, the increased value added means the more profitable processes. In material aspect, the metrics from the new design alternatives almost maintained the same value compared to the base case.

In case of Alternative-3, the metrics are worse than the base case and other alternatives, especially in energy group from the higher energy consumption.

Table 4.29 Comparison of sustainability metrics between the base case and alternatives

		BC	A-1	A-2	A-3	A-4	A-5
Energy	Total Net Primary Energy Usage rate (GJ/y)	1.67.E+06	1.65.E+06	1.62.E+06	1.78.E+06	1.18.E+06	1.01.E+06
	% Total Net Primary Energy sourced from renewables	1.00	1.00	1.00	1.00	1.00	1.00
	Total Net Primary Energy Usage per Kg product (kJ/kg)	47815.07	47355.42	46313.78	51009.30	33835.02	28991.00
	Total Net Primary Energy Usage per unit value added (kJ/$)	7.71	7.63	7.46	8.22	5.45	4.68
Material	Total raw materials used per kg product (kg/kg)	14.24	14.25	14.27	14.24	14.31	14.23
	Total raw materials used per unit value added	0.00	0.00	0.00	0.00	0.00	0.00
	Fraction of raw materials recycled within company	1.35	1.35	0.90	1.71	0.00	1.35
	Fraction of raw materials recycled from consumers	0.00	0.00	0.00	0.00	0.00	0.00
	Hazardous raw material per kg product	0.86	0.86	0.86	0.86	0.85	0.86
Water	Net water consumed per unit mass of product (kg/kg)	144.66	126.99	128.50	147.24	43.90	43.90
	Net water consumed per unit value added	0.02	0.02	0.02	0.02	0.01	0.01
Economic	Value added ($/yr)	2.57.E+07	2.57.E+07	2.57.E+07	2.56.E+07	2.61.E+07	2.62.E+07

4.3.2.3 WAR Algorithm

All alternatives both in process and energy efficiency aspects had been performed the WAR algorithm using ICAS to compare the impacts generated in the entire manufacturing process with the base case design. The comparison of impacts generated is shown in Table 4.30.

Table 4.30 Comparison of WAR algorithm between the base case and alternatives

	HTPE	ATP	TTP	GWP	ODP	PCOP	AP
Base Case	-679	1059	4830	9	0	18843	-14.05
Alternative-1	-679	1059	4822	9	0	18815	-14.05
Alternative-2	-679	1059	4829	9	0	18890	-14.05
Alternative-3	-679	1059	4824	9		18841	-14.05
Alternative-4	-679	1059	4831	9	0	18849	-14.05
Alternative-5	-679	1059	4826	9	0	18848	-14.05

A negative value shown the effect of the corresponding property to the environment has improved. On the other hand, a positive value means the effect of the corresponding to the environment has become worse. From the table, the impact generated between the base case and alternatives are nearly the same. There is not much change in HTPE, ATP, GWP, ODP and AP, indicating that the new designs are able to reduce the energy consumption without harming the environment more than the base case.

4.3.2.4 Safety Indices

The safety of the process is one of the important issues in SustainPro which is intended to confirm proper working as well as creating new more profitable design alternatives without harming the environment. Safety indices results of Alternative-1, Alternative-2, and Alternatives-3 are exactly the same ISI of 26 as that of the base case design (shown in Table 4.11) whereas, for Altenative-4 and Alternative-5, ISI are 25 as shown in Table 4.31.

Table 4.31 Safety indices of Alternative 4 and 5

Chemical inherent safety index,Ici	Score	Process inherent safety index,Ipi	Score
Subindices for reactions hazards		**Subindices for process conditions**	
Heat of the main reaction,Irm	0	Inventory,Ii	4
Heat of the side reactions,Irs	3	Process temperature,It	2
Chemical Interaction,Iint	2	Process pressure,Ip	1
Subindices for hazardous substances		**Subindices for process system**	
Flammability,Ifl	4	Equipment,Ieq	
Explosiveness,Iex	1	Isbl	2
Toxicity,Itox	2	Osbl	2
Corrosivity,Icor	0	Process structure,Ist	2
Ici	**12**	**Ipi**	**13**
ISI	**25**		

The safety improvement in Alternative-3 and Alternative-4 is that both designs do not have a compressor in the process compared with the base case, Alternative-1, Alternative-2, and Alternative-3 resulted in subindices for process system Isbl. Therefore, it can be concluded that in term of safety, Alternative-1, Alternative-2, and Alternative-3 did make safety issue neither better nor worse, while Alternative-4 and Alternative-5 made it better compared to the base case.

4.3.3 Life Cycle Assessment

The details of the life cycle inventory analysis of the new design alternatives are shown in Appendix F. The life cycle energy analysis was made to evaluate the energy efficiency of the new design alternatives in term of net energy ratio (NER). The comparison of energy efficiency in term of NER between the base case and 4 new design alternatives is shown in Figure 4.7.

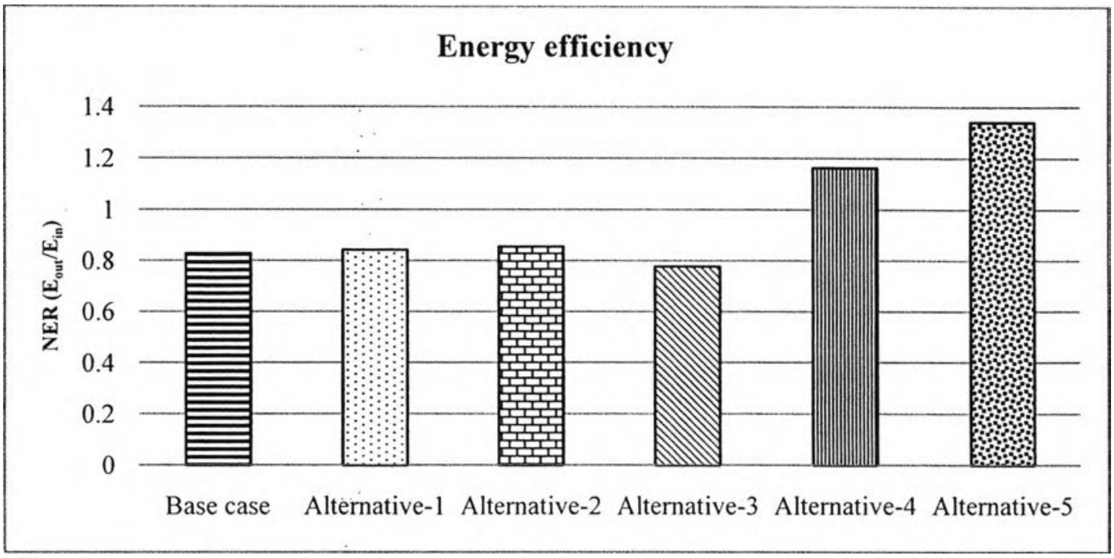

Figure 4.7 Comparison of net energy ratio from bioethanol conversion process between the base case and alternatives.

The results show that all new design alternatives are more energy efficient than the base case, except Alternative-3. It also indicates that from energy efficiency aspect Alternative-5 is the best design with the NER 1.34, that is 62% higher than the base case design (0.83).

The life cycle impact assessment (LCIA) was performed to evaluate environmental impacts of the new design alternatives for various impact categories and compare to the base case. Details of LCIA are shown in Appendix G.

Focusing on global warming potential (GWP as CO_2-equivalent), Alternative-5 has the lowest greenhouse gas (GHG) emission as shown in Figures 4.8, and 4.9.

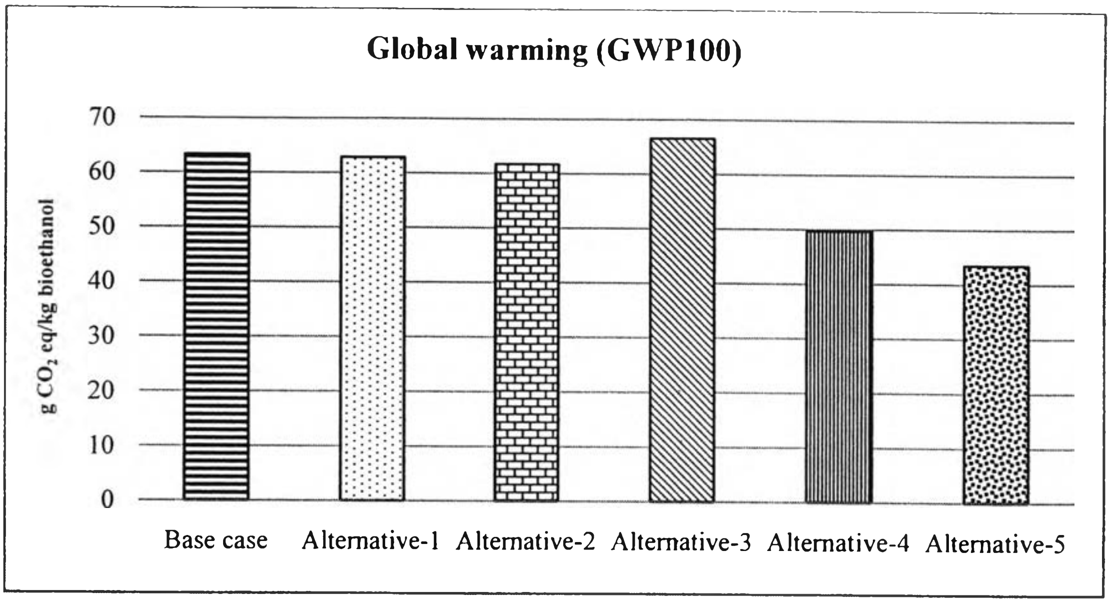

Figure 4.8 Comparison of the greenhouse effect (gCO_2-equivalent) generated from bioethanol conversion process between the base case and alternatives per kilogram of bioethanol.

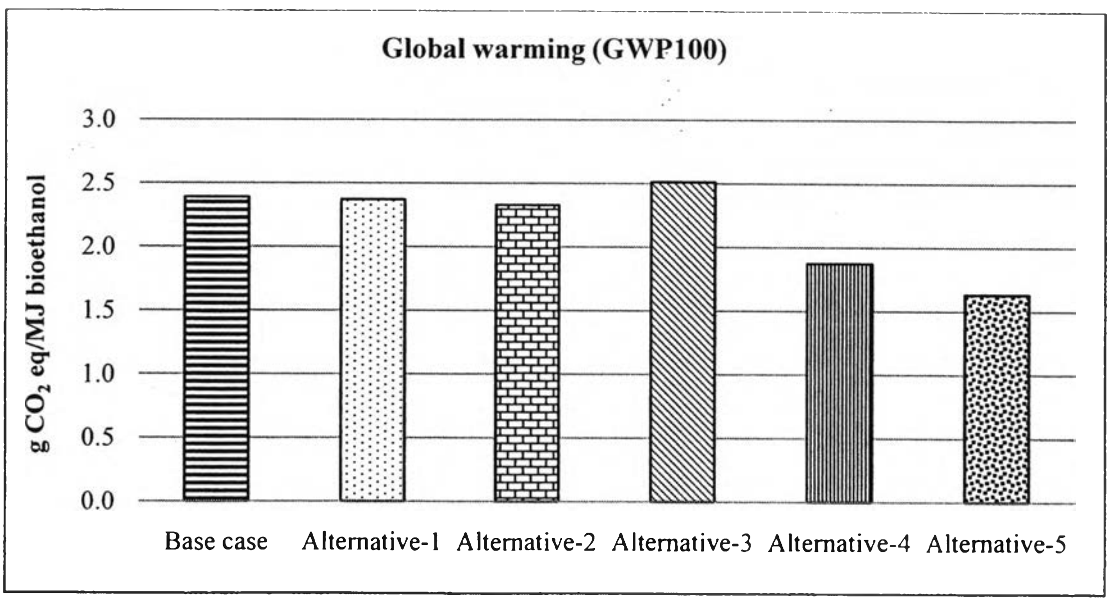

Figure 4.9 Comparison of the greenhouse effect (gCO_2-equivalent) generated from bioethanol conversion process between the base case and alternatives per megajoule of bioethanol.

Alternative-5 has been shown to emit only 43 g CO_2 equivalent/kg ethanol, which reflects 32% reduction from the base case design (63 g CO_2 equivalent/kg ethanol). The reduction of greenhouse gas emission comes from less energy consumption compared with the base case design. This is attributed to the lower steam consumption in the recovery stage where the heat duty was decreased.

For other impact categories such as acidification, eutrophication, and energy resources, the impacts observed in Alternative-1, Alternative-2, Alternative-4, and Alternative-5 are lower than base case design as shown in Figures 4.10, 4.11, 4.12, 4.13, 4.14, and 4.15.

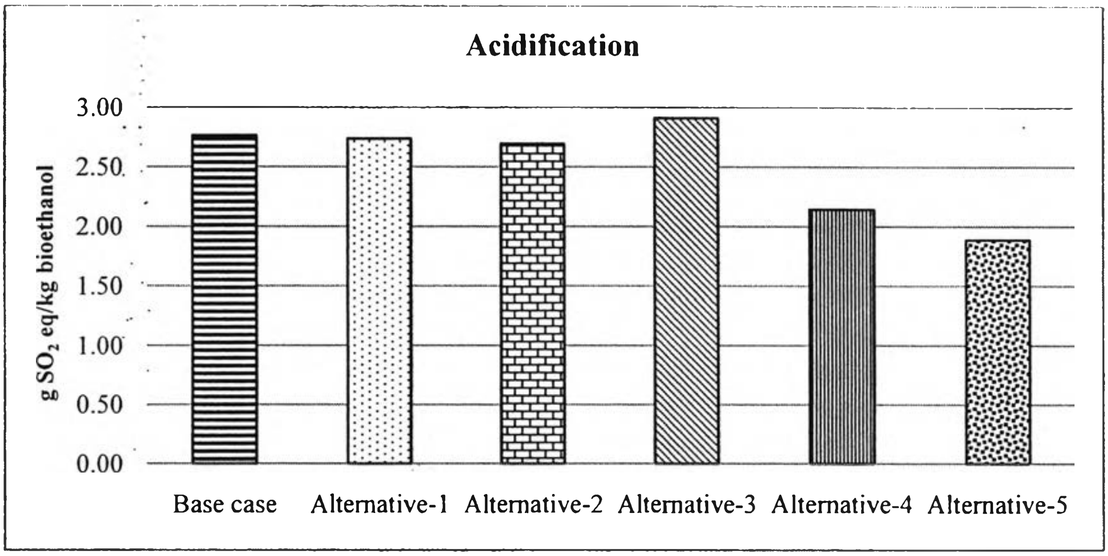

Figure 4.10 Comparison of the acidification (gSO_2-equivalent) generated from bioethanol conversion process between the base case and alternatives per kilogram of bioethanol.

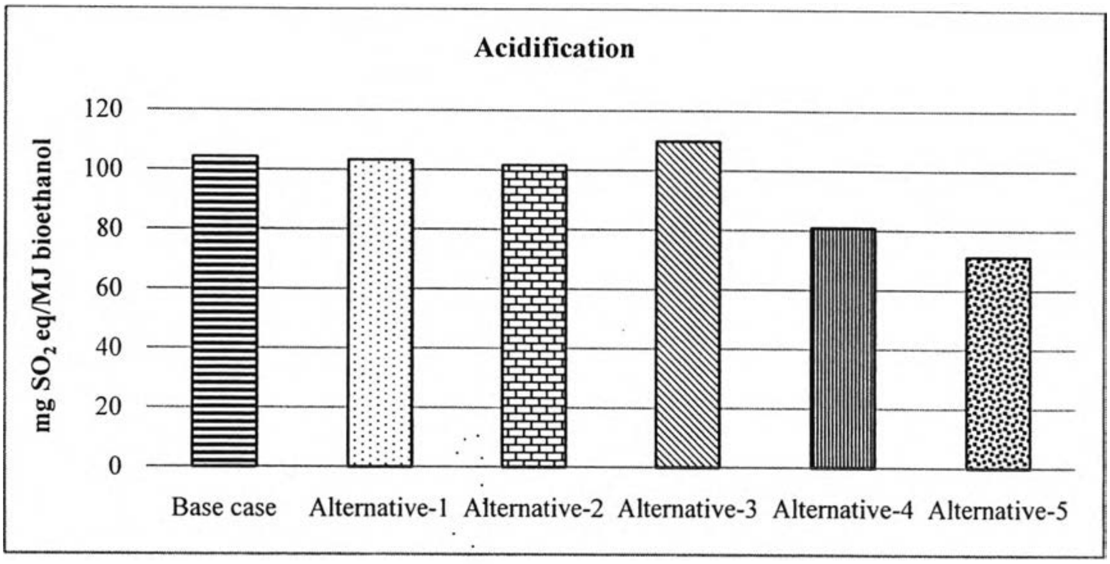

Figure 4.11 Comparison of the acidification (mgSO$_2$-equivalent) generated from bioethanol conversion process between the base case and alternatives per megajoule of bioethanol.

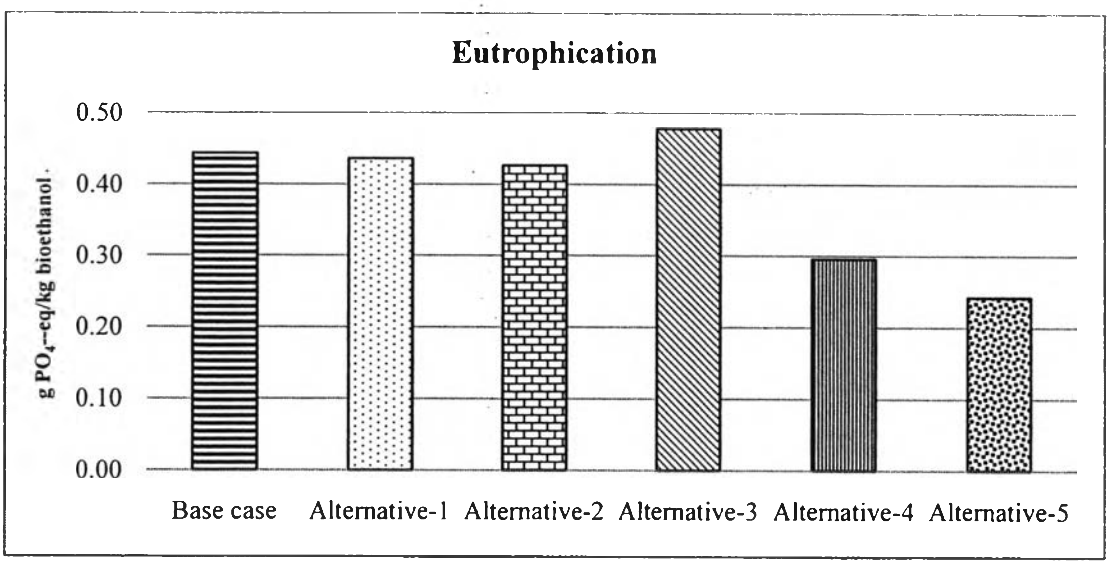

Figure 4.12 Comparison of the eutrophication (gPO$_4$--equivalent) generated from bioethanol conversion process between the base case and alternatives per kilogram of bioethanol.

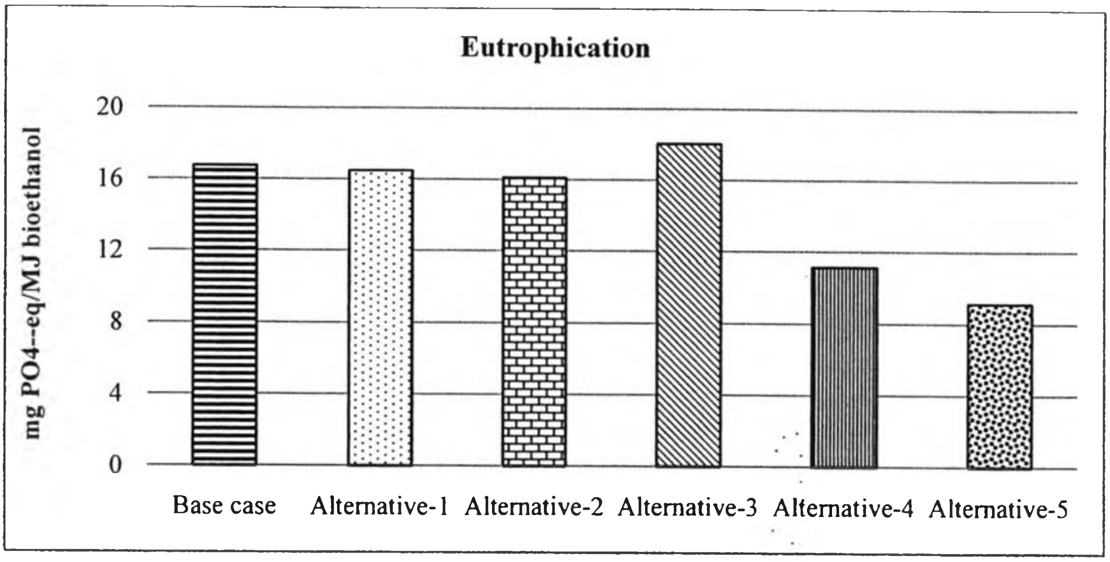

Figure 4.13 Comparison of the eutrophication (mgPO_4--equivalent) generated from bioethanol conversion process between the base case and alternatives per megajoule of bioethanol.

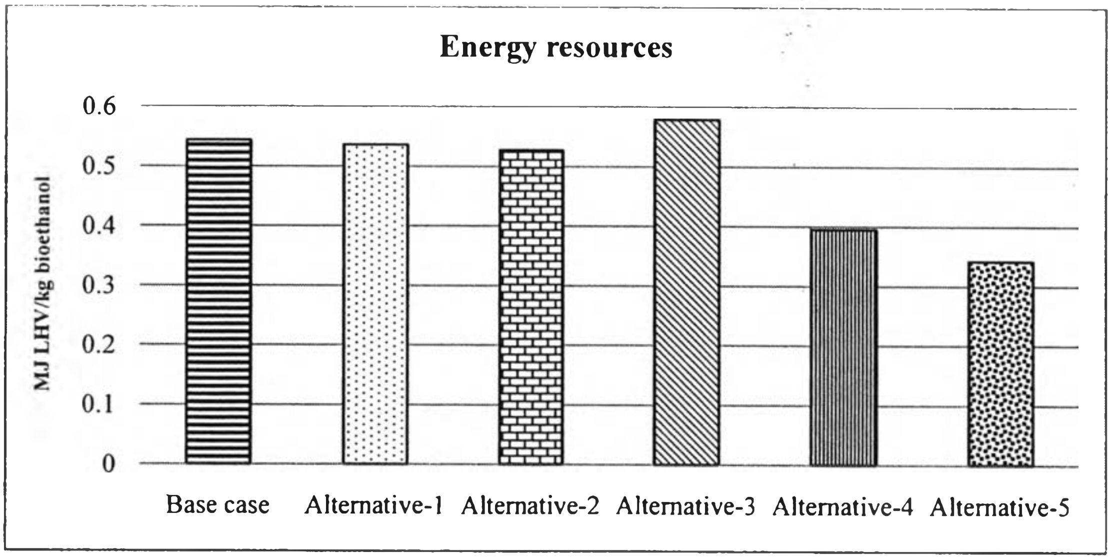

Figure 4.14 Comparison of the energy resources (MJ LHV) from bioethanol conversion process between the base case and alternatives per kilogram of bioethanol.

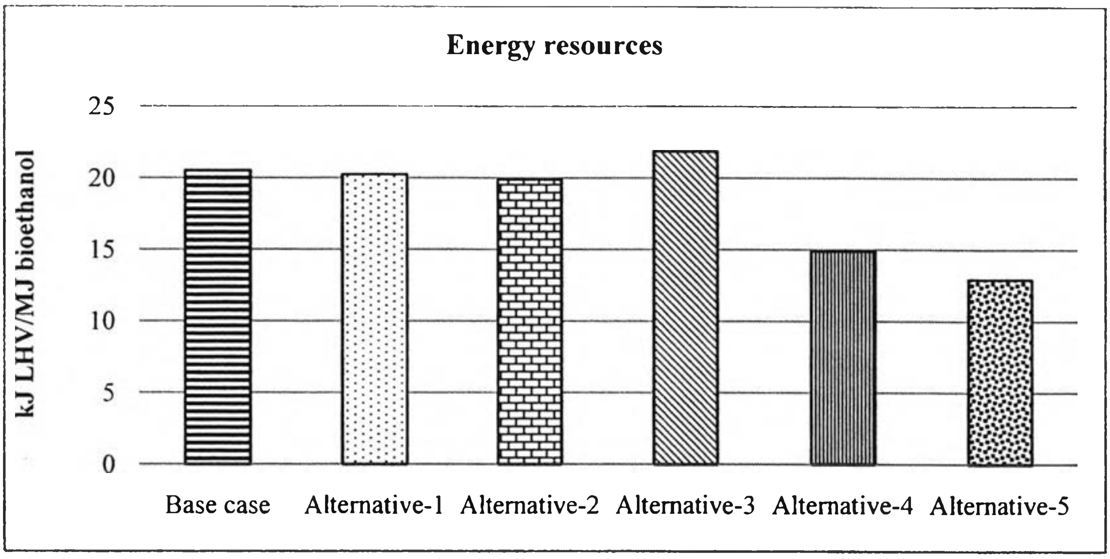

Figure 4.15 Comparison of the energy resources (kJ LHV) from bioethanol conversion process between the base case and alternatives per megajoule of bioethanol.

The results from acidification, eutrophication, and energy resources reveal that the new design alternatives (except Alternative-3) are more environmental friendly, and Alternative-5 is the most environmental friendly with the reduction of 32% in acidification, 45% in eutrophication, and 37% in energy resources compared to the base case design. The reduction of all impact categories is mainly through the lower energy consumption in the recovery stage.

From the four examples of impact categories above, it can be summarized that Alternative-1, Alternative-2, Alternative-4, and Alternative-5 are more environmental friendly than the base case design. Among alternatives studied, the emission from the new design on distillation platform (Alternative 4 and 5) is much lower than those of evaporator platform (Alternative 1, 2, and 3), and the one on energy efficiency aspect (Alternative-4) releases the emission less than those of the process aspect (Alternative 1, 2, 3, and 4).