CHAPTER IV
RESULTS AND DISCUSSION

4.1 Process Simulation and Sustainability Analysis

4.1.1 Base Case Design

4.1.1 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.

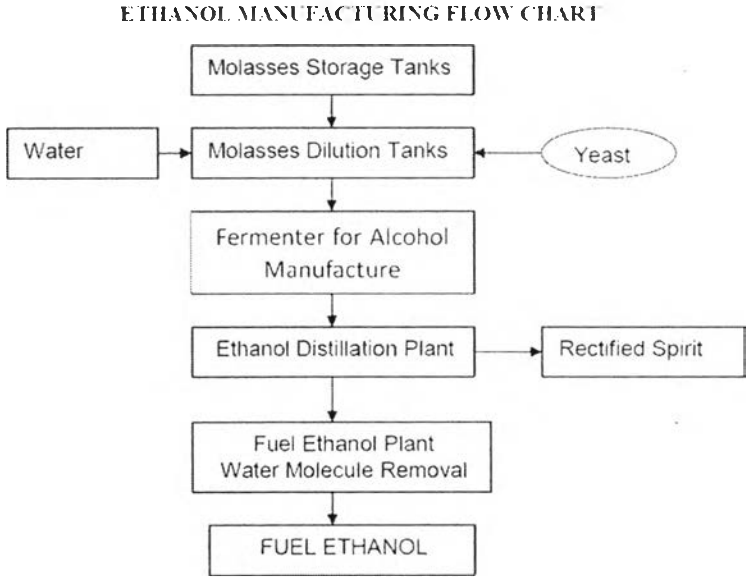

Figure 4.1 Ethanol manufacturing process.

This process design was modeled and simulated though the PRO/II 8.2, (PRO/II, 2006) process simulator, as shown in Figure 4.2.

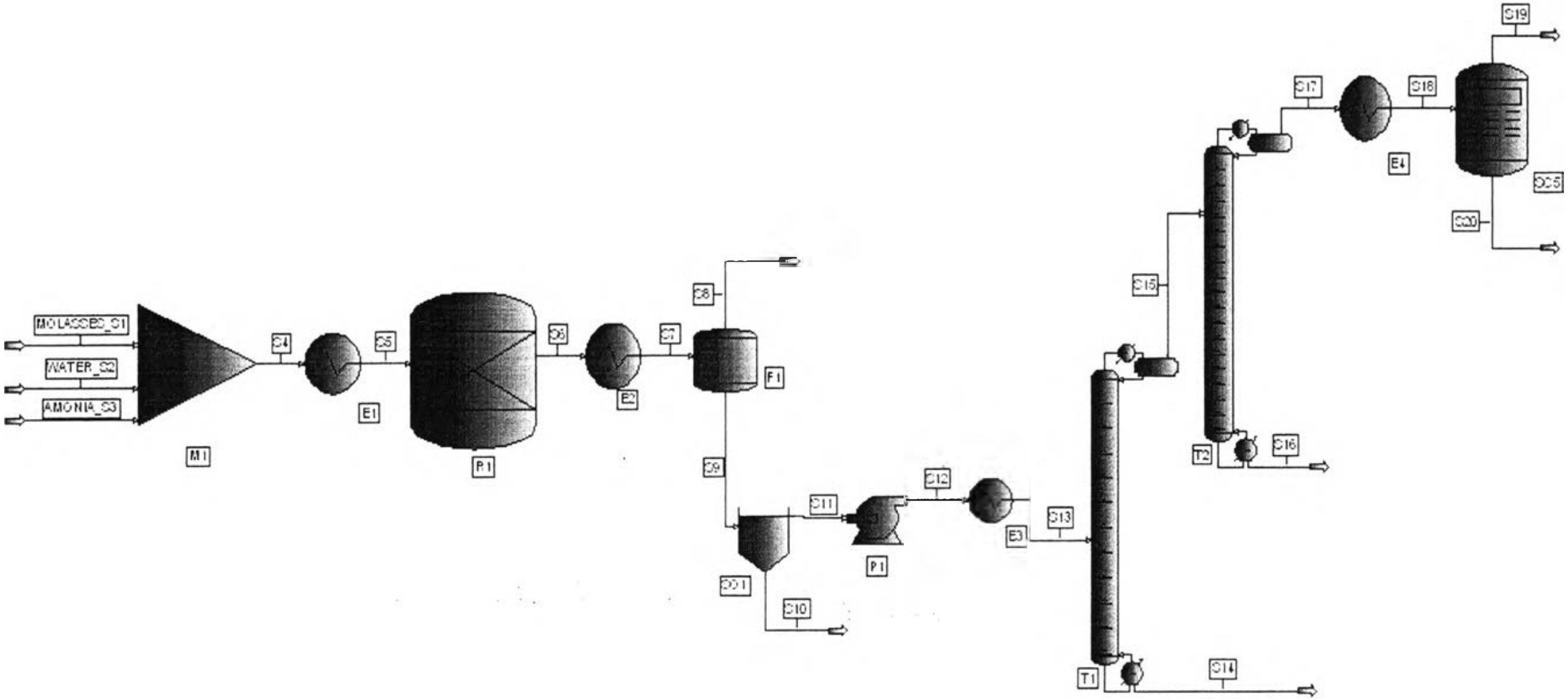

Figure 4.2 Bioethanol Conversion Process Flowsheet Implemented in PRO/II.

Lists of components, reactions, and mass flow rate that take place in the process are given in Appendix A, D and E, respectively. As substrate for bio-ethanol conversion, molasses available in Thailand was considered. The main components of the molasses feed are sugar (sucrose and glucose), so this process should be less complicated than bio-ethanol from other types of biomass such as cassava or lignocellulosic materials, where pretreatment of the substrate is necessary. The process is starting from dilution of molasses with water and then sent directly to the fermentation tank without pretreatment and hydrolysis steps. In this stage, two different operations are taking place – saccharification of the remaining cellulose to glucose, and also the fermentation of the resulting glucose and other sugars to ethanol using micro the organism, *Zymomonas mobilis*, as the enzyme. After this step, ethanol produced from molasses is sent to the recovery stage, which consists of flash drum, solid separator, distillation and membrane separator. The mixture is purified to ethanol fuel grade 99.5 wt% with the production capacity of 100 kilograms per hour.

From Figure 4.2 ethanol production process, there are 5 waste streams - S8, S10, S14, S16, and S20:

- S8 is flue gas stream with large amounts of carbon dioxide.
- S10 stream contains mainly unconverted cellulose and ash.
- S14 stream mainly contains water and some contaminant as unconverted glucose
- S16 and S20 streams contain mainly water.

In order to make the base case design more sustainable, sustainability analysis is performed to generate new design alternatives.

4.1.1.2 Sustainability Analysis

4.1.1.2.1 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 4.1.

Table 4.1 Sustainability metrics results of base case design

Metric	Base case
Energy	
Total Net Primary Energy Usage rate (GJ/y)	84086.611
% Total Net Primary Energy sourced from renewable	0.998
Total Net Primary Energy Usage per Kg product (kJ/kg)	82134.980
Total Net Primary Energy Usage per unit value added (kJ/$)	27.479
Material	
Total raw materials used per kg product (kg/kg)	13.410
Total raw materials used per unit value added	0.004
Fraction of raw materials recycled within company	0.000
Fraction of raw materials recycled from consumers	0.000
Hazardous raw material per kg product	0.340
Water	
Net water consumed per unit mass of product (kg/kg)	228.514
Net water consumed per unit value added	0.076
Economic	
Value added ($/y)	424997.673

Nguyen *et al.* (2008) studied a full chain energy analysis of fuel ethanol from cane molasses in Thailand. This research found that the energy consumption of bioethanol production from molasses was 23.159 MJ/Kg ethanol (data from MoE factory in Thailand), which is less than the value obtained in this work, because internal energy sources of Nguyen's work such as steam and electricity which produce from biogas and cogeneration was not taken into account. For SustainPro program, all steam and electricity required for the process were taken into account, even they came from the internal sources. Those utilities were the important part of energy consumption of recovery section which consisted of pump and distillation columns. That is the reason of the difference between Lan's work and this research.

4.1.1.2.2 Indicator Results

The SustainPro software decomposed the base case flowsheet into 41 open-paths (OP) and zero closed-paths since the process does not have any recycle streams. The mass and energy indicators were calculated. The most sensitive indicators are listed in Table 4.2.

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

Path	MVA	Probability	Path	EWC	Probability	Path	TVA	Probability
OP 24	-100.301	High	OP 10	290.731		OP 10	-293.720	
OP 13	-17.859	High	OP 13	247.822	High	OP 13	-265.681	High
OP 11	-4.622		OP 11	69.096		OP 24	-104.526	High
OP 10	-2.989		OP 2	30.451	Medium	OP 11	-73.718	
OP 23	-0.965	High	OP 5	21.154		OP 5	-21.371	
OP 28	-0.873	Low	OP 9	10.079		OP 9	-10.171	
OP 33	-0.725	Low	OP 20	9.672		OP 20	-9.672	
OP 6	-0.336		OP 6	5.027		OP 6	-5.364	
OP 31	-0.261	High	OP 24	4.224	High	OP 23	-0.966	High
OP 5	-0.217		OP 4	0.733		OP 28	-0.958	Low
OP 27	-0.185	Low	OP 15	0.359	Low	OP 4	-0.740	
OP 1	-0.141	High	OP 14	0.284	Low	OP 33	-0.725	Low
OP 29	-0.115	Low	OP 34	0.224	High	OP 15	-0.359	Low
OP 9	-0.092		OP 40	0.222	High	OP 14	-0.284	Low
OP 26	-0.048	High	OP 41	0.206	High	OP 31	-0.277	High
OP 30	-0.027	Low	OP 39	0.171	High	OP 34	-0.224	High
OP 4	-0.007		OP 38	0.155	High	OP 27	-0.199	Low

The indicators are listed in the order of their values, the higher the value the higher the priority (high value at the top and low value at the bottom). The table also indicates the corresponding paths where process improvements could be implemented. For MVA or TVA, they indicate the potential to improve the process by making them less negative through design changes. On the other hand, positive values of the EWC 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. For base case design, we can observe the sensitive indicators and the corresponding open-paths that have high potentials for improvement and for which materials we can increase their added value.

From the results shown in Table 4.2, open path OP 10, OP11, OP 13, OP 23, OP24, and OP 31 are selected based on the high value of TVA and high possible path for improvement in each indicator. The details of those potential paths are given in Table 4.3.

Table 4.3 Details of high potential paths for improvement

Path	Component	Starting stream/unit	Ending stream/unit
OP 10	WATER	WATER_S2	S16
OP 11	WATER	WATER_S2	S14
OP 13	C6 (Glucose)	MOLASSES_S1	S14
OP 23	NH3(Ammonia)	MOLASSES_S1	S8
OP 24	NH3(Ammonia)	MOLASSES_S1	S20
OP 31	CELLULOSE	MOLASSES_S1	S10

According to Table 4.3, it can be seen that the open-paths with high potential for improvement involve water (open path 10 and open path 11), glucose (open path13), ammonia (open path 23 and open path 24), and cellulose (open path 31). Based on this information, we chose only OP 10, OP11, OP 13, and OP 31 paths for further improvement. The paths involved ammonia (OP23 and OP 24) are not included because OP 23 contained ammonia in gas phase which is difficult to recover.. For OP 24, the result shows the large amount of ammonia because the assumption was made that nitrogen compound in molasses was only ammonia. However, the actual input of ammonia is only 0.1% of total amount of input in order to use as nitrogen source for growth factor. For those reasons, we can generate 4 new design alternatives. For the first alternative, recycle of water and glucose need to be considered because it will reduce raw material usage. For another alternative, conversion of unconverted cellulose is interesting, as it will increase the value added. Then, alternatives 2, 3, and 4 are created corresponding to combustion of unconverted cellulose, pyrolysis of unconverted cellulose to produce bio-oil, and hydroxymethyl furfural (HMF) production with the unconverted cellulose, as shown in Figure 4.3.

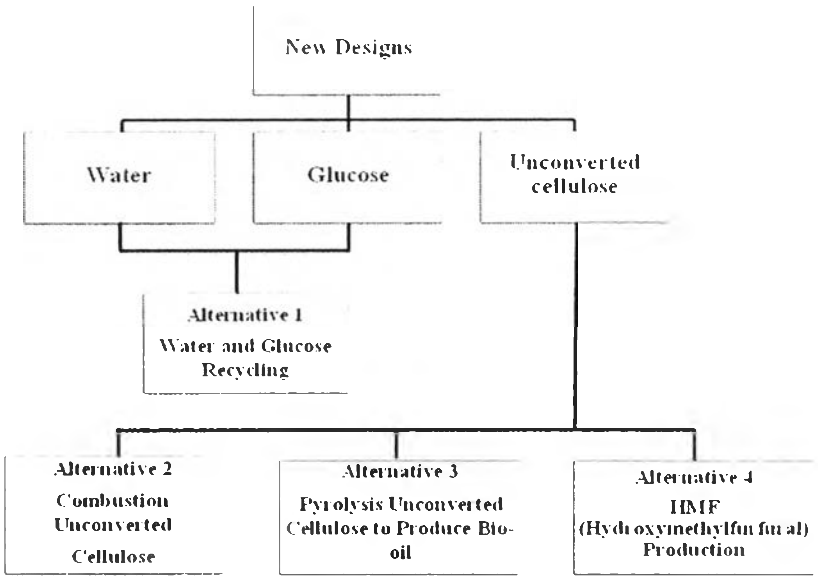

Figure 4.3 The new design alternatives.

We can focus on the components involved in the corresponding (potential) open-paths, starting with water that is released from streams S14 and S16 (OP11 and OP10). Normally, waste water from the ethanol production process is used to produce biogas which can generate electricity. In this case, the value of the wastewater is around 0.00136 USD per kilogram of waste water (to generate electricity from biogas). But SustainPro results show that waste water has a potential for improvement. Consequently, alternative 1 has been generated by adding a recycle stream. In addition, the glucose (OP 13) that does not convert to ethanol can be recycled back to the system by using water (OP 10 and OP 11) as a carrier.

Next target for improvement is unconverted cellulose. Since the manufacturing process needs fuel to heat, cellulose is a good material able to combust and generates the heat very well. So, alternative 2 is the combustion of unconverted cellulose in order to recover the heat.

4.1.2 Alternative 1 (Water and Glucose Recycling)

4.1.2.1 Process Simulation of Alternative 1

The design alternative 1 was obtained for improvement of open path 10, 11, and 13 as shown in Figure 4.4. According to this figure, stream 23 mainly contains glucose which is a raw material. Stream S25, water, a main component, has some contaminants of acetic acid which affect the micro organism (enzyme), *Zymomonas mobilis*, used in the fermentation step. So, this work needs to specify the upper limit of acetic acid in order to prevent enzyme inhibition.

Table 4.4 Limitation of acetic acid in ethanol production process with recycle stream to prevent enzyme inhibition

Limitation of acitric acid		**NREL process**	**My process**
Acetic acid	KG-MOL/HR	16.685	0.040
Std liq rate	LIT/HR	328883.000	1762.769
Concentration of acid	MOL/LIT	0.0507	0.023

*NREL process produce ethanol 18,557 kg/ hr
*My process produce ethanol 153 kg/hr

From Table 4.4, NREL process (ethanol production process from lignocellulosic biomass) has a concentration of acetic acid higher than that of design alternative 1 (ethanol production process from molasses with recycle stream). So, design alternative 1 is acceptable. Next step is to perform Sustainability Analysis.

4.1.2.2 Sustainability Analysis

4.1.2.2.1 Sustainability Metrics Results

After this process is analyzed based on Sustainability Metric, the results are divided into 4 groups: energy, material, water, and economic as given in Table 4.5.

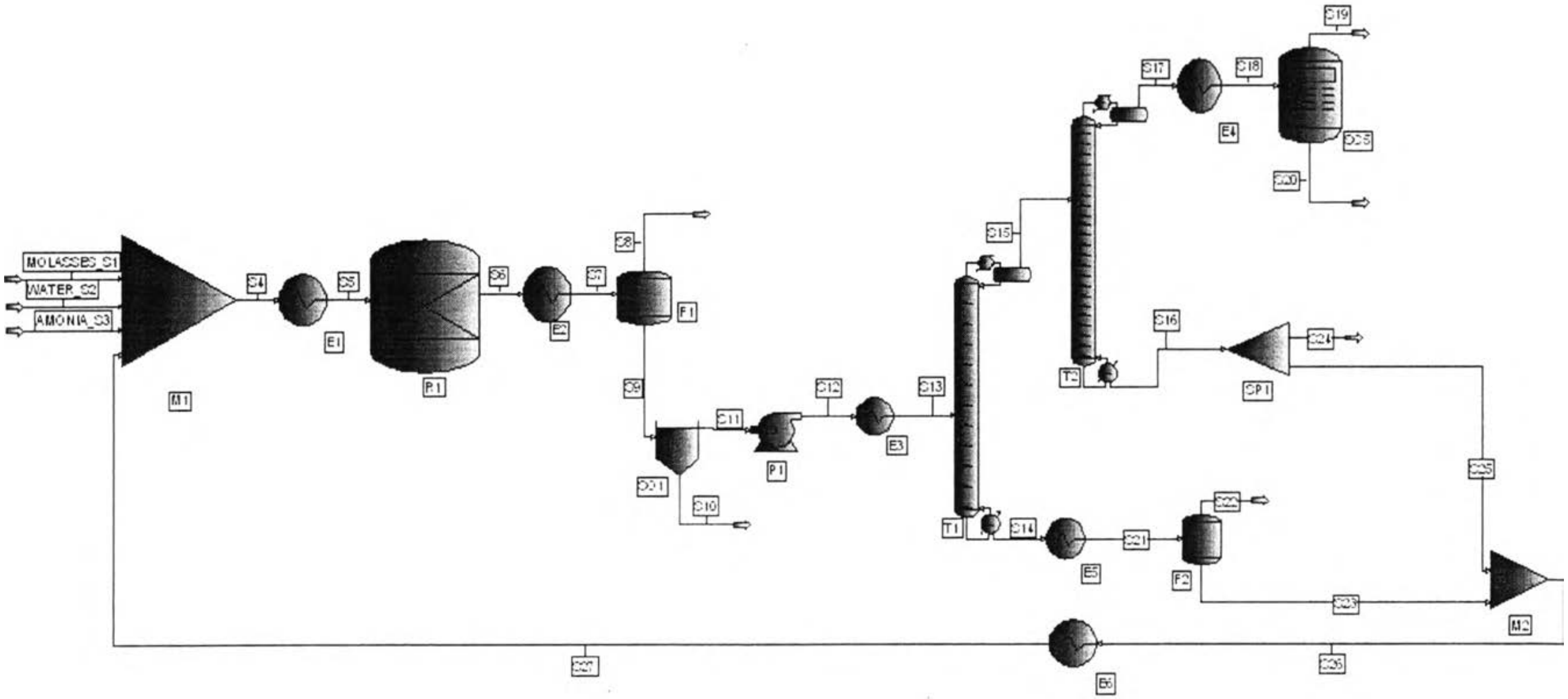

Figure 4.4 The main operations of the bio-ethanol process from molasses for Alternative 1 (Water and Glucose Recycling).

Table 4.5 Sustainability metrics results of alternative1 (ethanol production process from molasses with recycle stream)

Metric	Base case	Alternative 1	% Change
Energy			
Total Net Primary Energy Usage rate (GJ/y)	84086.611	113064.415	34.462
% Total Net Primary Energy sourced from renewables	0.998	0.998	0.055
Total Net Primary Energy Usage per Kg product (kJ/kg)	82134.980	102297.809	24.548
Total Net Primary Energy Usage per unit value added (kJ/$)	27.479	31.620	15.067
Material			
Total raw materials used per kg product (kg/kg)	13.410	8.700	-35.125
Total raw materials used per unit value added	0.004	0.003	-40.064
Fraction of raw materials recycled within company	0.000	0.424	0.000
Fraction of raw materials recycled from consumers	0.000	0.000	0.000
Hazardous raw material per kg product	0.340	0.315	-7.373
Water			
Net water consumed per unit mass of product (kg/kg)	228.514	262.126	14.709
Net water consumed per unit value added	0.076	0.081	5.976
Economic			
Value added ($/y)	424997.673	496632.751	16.855

From Table 4.5, focusing on the economic terms, it can be seen that design alternative 1 can increase value added by around 17 % compared to the base case design.

4.1.2.2.2 Indicator Results

The most sensitive indicators are calculated in term of mass and energy as seen in Table 4.6. In design alternative 1, some components are recycled back to the system, so only mass added value has been improved.

Table 4.6 List of the most sensitive indicators for the open-paths for alternative1 (ethanol production process from molasses with recycle stream)

Path	MVA	Probability	Path	EWC	Probability	Path	TVA	Probability
OP 24	-100.0387	High	OP 11	151.3394		OP 11	-155.6680	
OP 11	-4.3286		OP 2	23.4183	Medium	OP 24	-102.8299	High
OP 23	-1.2017	High	OP 6	18.6026		OP 6	-19.1347	
OP 28	-0.8725	Low	OP 10	8.3896		OP 10	-8.5129	
OP 33	-0.7831	Low	OP 20	7.3793		OP 20	-7.3793	
OP 6	-0.5321		OP 9	6.8959		OP 9	-6.9825	
OP 31	-0.2609	High	OP 24	2.7912	High	OP 13	-1.3288	High
OP 27	-0.2001	Low	OP 13	1.2315	High	OP 28	-1.2570	Low
OP 1	-0.1898	High	OP 5	1.0313		OP 23	-1.2023	High
OP 29	-0.1241	Low	OP 40	0.9937	High	OP 5	-1.0464	
OP 10	-0.1233		OP 41	0.8917	High	OP 40	-0.9408	High
OP 13	-0.0972	High	OP 4	0.8476		OP 4	-0.8583	
OP 9	-0.0866		OP 39	0.7719	High	OP 41	-0.8289	High
OP 26	-0.0481	High	OP 38	0.7079	High	OP 33	-0.7832	Low
OP 30	-0.0295	Low	OP 37	0.5828	High	OP 39	-0.7336	High
OP 5	-0.0152		OP 14	0.5759	Low	OP 38	-0.6783	High
OP 4	-0.0106		OP 15	0.5591	Low	OP 14	-0.5759	Low

For design alternative 1, not only the value added was increased but also the process was improved by making MVA less negative than base case design, as seen in Table 4.7.

Table 4.7 Comparison of MVA of the base case and design alternative 1

Path	Component	Starting stream/unit	Ending stream/unit	MVA of Base Case	MVA of Alternative 1
OP 10	WATER	WATER_S2	S16	-2.989	-0.1232
OP 11	WATER	WATER_S2	S14	-4.622	-4.3286
OP 13	C6 (Glucose)	MOLASSES_S1	S14	-17.859	-0.0972

The next attempt at improving the base case design is how to utilize the unconverted cellulose that gives high value added and can improve MVA, EWC, and TVA. Since the manufacturing process needs fuel to heat, cellulose is a good material able to combust and generates the heat very well. So, alternative 2 is the combustion of unconverted cellulose in order to recover the heat.

4.1.3 Alternative 2 (The Combustion of Unconverted Cellulose)

4.1.3.1 Process Simulation of Alternative 2

Alternative 2 uses model simulation of the base case design as a reference. Because it is not necessary to combust unconverted cellulose in ProII. The SustainPro software can calculate the combustion of unconverted cellulose by identification of cellulose as fuel. Important data is heat of combustion needed as input to the software so that the heat from the combustion can be recovered to generate steam. So, the Sustainability Analysis results are discussed in the next section.

4.1.3.2 Sustainability Analysis

4.1.3.2.1 Sustainability Metrics Results

SustainPro was used to analyze the sustainability of this design alternative. This program classifies the metrics into 4 groups: energy, material, water, and economic which are given in Table 4.8.

Table 4.8 Sustainability metrics results of design alternative 2 (The Combustion of Unconverted Cellulose)

Metric	Base case	Alternative 2	% Change
Energy			
Total Net Primary Energy Usage rate (GJ/y)	84086.611	84086.611	0.000
% Total Net Primary Energy sourced from renewable	0.998	0.998	0.000
Total Net Primary Energy Usage per Kg product (kJ/kg)	82134.980	82134.980	0.000
Total Net Primary Energy Usage per unit value added (kJ/$)	27.479	26.456	-3.725
Material			
Total raw materials used per kg product (kg/kg)	13.410	13.410	0.000
Total raw materials used per unit value added	0.004	0.004	-3.725
Fraction of raw materials recycled within company	0.000	0.000	0.000
Fraction of raw materials recycled from consumers	0.000	0.000	0.000
Hazardous raw material per kg product	0.340	0.340	0.000
Water			
Net water consumed per unit mass of product (kg/kg)	228.514	228.514	0.000
Net water consumed per unit value added	0.076	0.074	-3.725
Economic			
Value added ($/y)	424997.673	441442.097	3.869

When fuel is generated by combustion of unconverted cellulose, it can save energy usage by around 3.7 % and additional profit of around 3.9 % compared to the base case design corresponding to Table 4.8.

4.1.3.2.2 Indicator Results

The most sensitive indicators are calculated in terms of mass and energy as seen in Table 4.9 for design alternative 2, which focused on the combustion of unconverted cellulose

Table 4.9 List of the most sensitive indicators for the open-paths for alternative 2

Path	MVA	Probability	Path	EWC	Probability	Path	TVA	Probability
OP 24	-100.3014	High	OP 10	290.7307		OP 10	-293.7197	
OP 13	-17.8589	High	OP 13	247.8217	High	OP 13	-265.6806	High
OP 11	-4.6220		OP 11	69.0958		OP 24	-104.5259	High
OP 10	-2.9890		OP 2	30.4513	Medium	OP 11	-73.7177	
OP 23	-0.9652	High	OP 5	21.1535		OP 5	-21.3710	
OP 28	-0.8725	Low	OP 9	10.0790		OP 9	-10.1714	
OP 33	-0.3434	Low	OP 20	9.6725		OP 20	-9.6725	
OP 6	-0.3363		OP 6	5.0274		OP 6	-5.3637	
OP 5	-0.2175		OP 24	4.2245	High	OP 23	-0.9655	High
OP 27	-0.1853	Low	OP 4	0.7333		OP 28	-0.9578	Low
OP 1	-0.1410	High	OP 15	0.3590	Low	OP 4	-0.7401	
OP 29	-0.1149	Low	OP 14	0.2841	Low	OP 15	-0.3590	Low
OP 9	-0.0924		OP 34	0.2241	High	OP 33	-0.3435	Low
OP 26	-0.0482	High	OP 40	0.2224	High	OP 14	-0.2841	Low
OP 30	-0.0273	Low	OP 41	0.2055	High	OP 27	-0.1990	Low
OP 4	-0.0067		OP 39	0.1714	High	OP 40	-0.1695	High

In addition, it can improve the process by making MVA (OP 31) more positive as shown in Table 4.10. Thus, the combustion of unconverted cellulose increases mass value added rather than releasing it to the environment.

Table 4.10 Comparison of MVA of the base case and alternative 2

Path	Component	Starting stream/unit	Ending stream/unit	MVA of Base Case	MVA of Alternative 2
OP 31	CELLULOSE	MOLASSES_S1	S10	-0.2608	2.0940

4.1.4 Alternative 3 (Production of Bio-oil from Unconverted Cellulose)

4.1.4.1 Process Simulation of Alternative 3

Pyrolysis is another option to convert unconverted biomass to more valuable products. In design alternative 3, the pyrolysis process was introduced to the base case process and followed by stream 10 containing unconverted cellulose. In this case, a bubbling fluidized bed reactor was considered. A bubbling bed operate in an adiabatic regime with all the process heat is supplied by the preheated fluidizing gas, which in many instances are recycled pyrolysis gas (Ringer *et al.*, 2006). This process was needed to integrate the combustion of char and gas byproducts in order to provide the necessary heat requirement as shown in Figure 4.5.

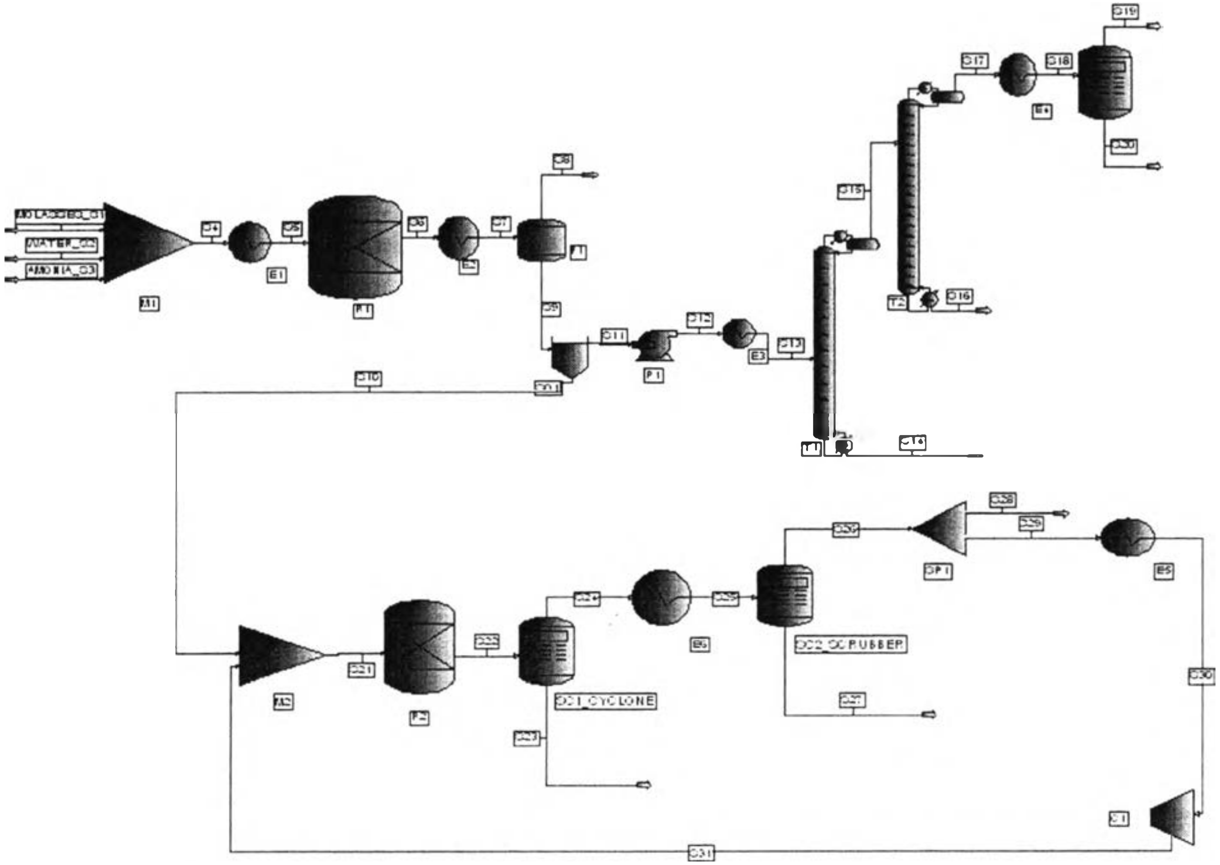

Figure 4.5 The main operations of the bio-ethanol process from molasses for Alternative 3 (Production of Bio-oil from Unconverted Cellulose).

Bio-oil can substitute for fossil fuels to generate heat, power and chemicals. Short-term applications are boilers and furnaces, whereas turbines and diesel engines may become available on the somewhat longer term applications. Upgrading of the bio-oil to a transportation fuel is technically feasible, but needs further development. Fischer-Tropsch fuels can be derived from the bio-oil through synthesis gas processes. Furthermore, there is a wide range of chemicals that can be extracted or derived from the bio-oil. A general overview is depicted below.

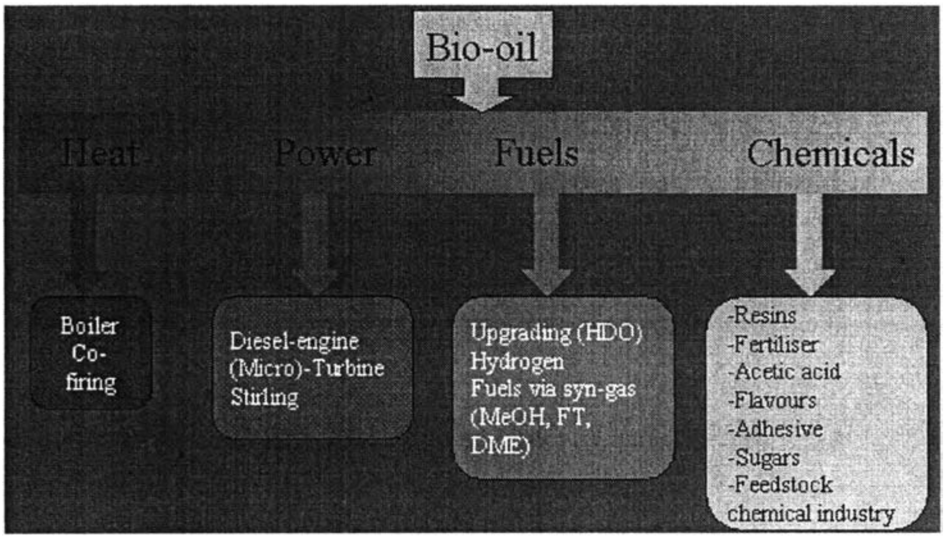

Figure 4.6 General overview of Pyrolysis oil applications (www.btgworld.com).

Table 4.11 Comparison between bio-oil from simulation and bio-oil from reference

Component	My Bio-oil	*Bio-oil Ref.	% change
ACETALD	0.002	0.002	0.20
HAA	0.060	0.060	0.09
ACETONE	0.027	0.027	0.13
HA	0.028	0.028	0.02
PA	0.002	0.002	0.01
FURFURAL	0.010	0.010	0.00
FUROH	0.012	0.012	-0.05
HMF	0.021	0.021	-2.13
LG	0.824	0.824	0.04
HEXANE	0.002	0.002	0.00
C9ester	0.007	0.007	-0.12
MANNOSE	0.006	0.006	0.08
total	1.000	1.000	

*Bio-oil Ref. (source: Shen and Gu, 2009).

Shen and Gu (2009) investigated the mechanisms of the cellulose pyrolysis. The mechanism (see appendix B) that they had studied has been used as a reference in this work. According to design alternative 3, the results from simulation were compared with those from the Shin and Gu reference. According to Table 4.11, the components calculated by each method were found to be very similar and therefore, the simulation was considered acceptable.

The next section, the Sustainability Analysis results are discussed.

4.1.4.2 Sustainability Analysis

4.1.4.2.1 Sustainability Metrics Results

This design alternative 3 was analyzed in Sustainability Metric section of SustainPro, the results are divided into 4 groups: energy, material, water, and economic as shown in Table 4.12.

Table 4.12 Sustainability metrics results of alternative 3 (Production of Bio-oil from Unconverted Cellulose)

Metric	Base case	Alternative 3	% Change
Energy			
Total Net Primary Energy Usage rate (GJ/y)	84086.611	85920.048	2.180
% Total Net Primary Energy sourced from renewable	0.998	0.996	-0.186
Total Net Primary Energy Usage per Kg product (kJ/kg)	82134.980	83924.307	2.179
Total Net Primary Energy Usage per unit value added (kJ/$)	27.479	26.546	-3.398
Material			
Total raw materials used per kg product (kg/kg)	13.410	13.410	-0.002
Total raw materials used per unit value added	0.004	0.004	-5.459
Fraction of raw materials recycled within company	0.000	0.000	0.000
Fraction of raw materials recycled from consumers	0.000	0.000	0.000
Hazardous raw material per kg product	0.340	0.174	-48.800
Water			
Net water consumed per unit mass of product (kg/kg)	228.514	232.550	1.766
Net water consumed per unit value added	0.076	0.074	-3.787
Economic			
Value added ($/y)	424997.673	449537.460	5.774

Because this process generated the heat from the combustion of char and gas products, it can reduce energy usage by around 3% and can get additional profit by around 6 % higher than those of the base case design (see to Table 4.12).

This work focuses on how much value added is increased by using unconverted cellulose as raw material. So we were not interested in Indicator Results. Next step, unconverted cellulose utilize as raw material of production of Hydroxymethyl furfural (HMF)

4.1.5 Alternative 4 (Production of Hydroxymethyl Furfural from Unconverted Cellulose)

4.1.5.1 Process Simulation of Alternative 4

The ability to use cellulosic biomass as feedstock for the large-scale production of liquid fuels and chemicals depends critically on the development of effective low temperature processes. One promising biomass-derived platform chemical is 5-hydroxymethylfurfural (HMF), which is suitable for alternative polymers or for liquid bio-fuels. While HMF can currently be made from fructose and glucose, the ability to synthesize HMF directly from raw natural cellulose would remove a major barrier to the development of a sustainable HMF platform. According to base case, ethanol conversion process releases solid waste to the environment, but unconverted cellulose is included in the solid stream. The objective is to use this solid waste. This design alternative 4 therefore selects the production of Hydroxymethyl furfural (HMF) from unconverted cellulose.

HMF has an aromatic-type ring structure and active functional groups on two sides. This compound has been identified as an important intermediate. It is a flexible intermediate because a variety of target molecules can be synthesized from it, such as, specialty chemicals in the agricultural, consumer, and pharmaceutical industries. The intermediate component can form thermal resistant polymers, fuel additives, and liquid fuel.

Alternative 4, production of HMF from waste cellulose uses Methyl isobutyl ketone (MIBK) as solvent and Titanium dioxide ($TiO2$) as catalyst (McNeff *et. al.*, 2010). The preheater was used to bring a mixture to the target temperature and fed into reactor. After that, product solution will pass through the recovery section and recycle solvent section. From process simulation, purity of HMF is found to be 99.57%, corresponding to process flowsheet shown in Figure 4.7.

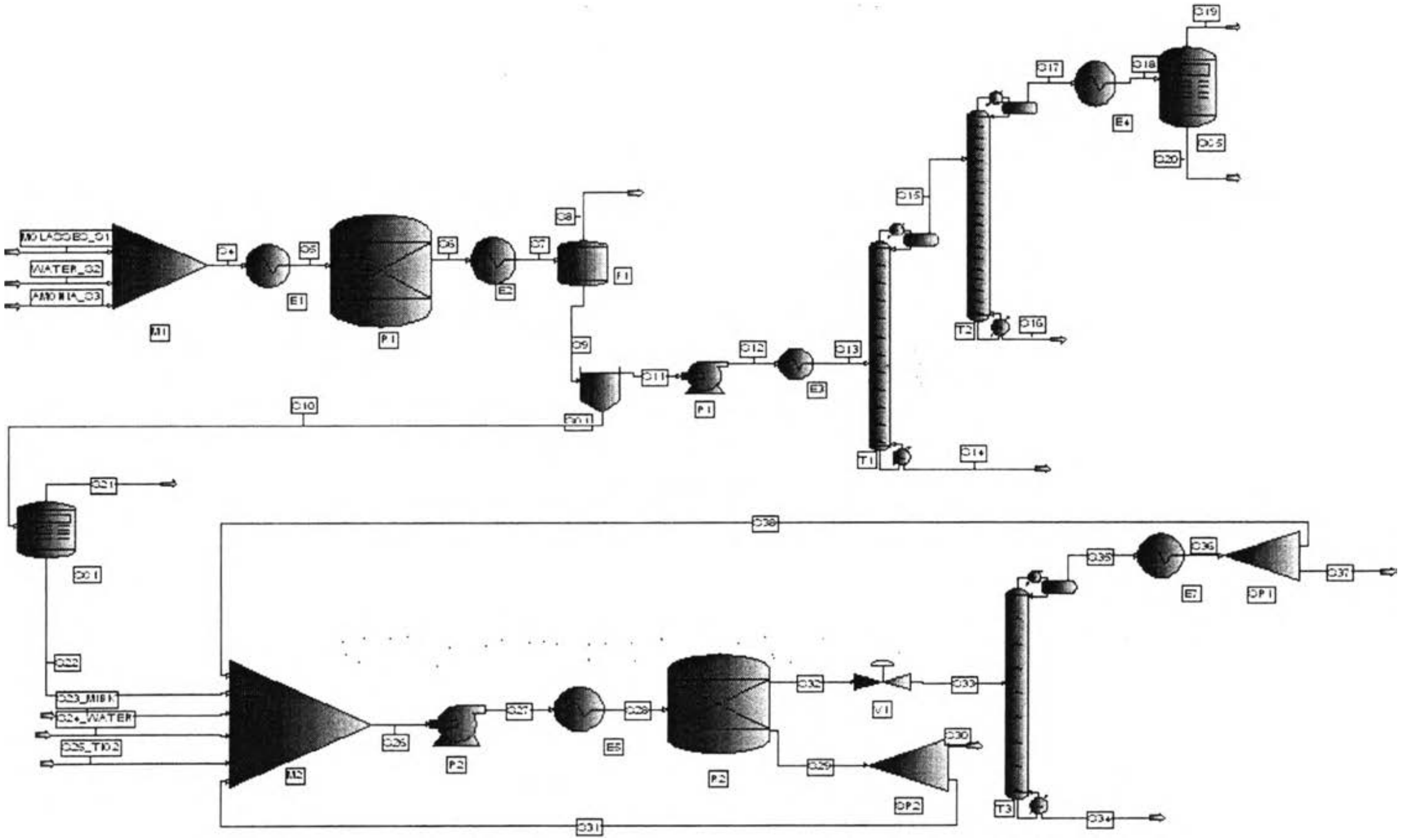

Figure 4.7 The main operations of the bio-ethanol process from molasses for alternative 4 (Production of Hydroxymethyl Furfural from Unconverted Cellulose).

4.1.5.2 Sustainability Analysis

Sustainability Metrics Results - for this design alternative, sustainability analysis was performed and the result are given in terms of energy, material, water, and economic metrics, as shown in Table 4.13.

Table 4.13 Sustainability metrics results of alternative 4 (Production of Hydroxymethyl Furfural from Unconverted Cellulose)

Metric	Base case	Alternative 4	% change
Energy			
Total Net Primary Energy Usage rate (GJ/y)	84086.611	91525.705	8.847
% Total Net Primary Energy sourced from renewables	0.998	0.998	0.000
Total Net Primary Energy Usage per Kg product (kJ/kg)	82134.980	87602.346	6.657
Total Net Primary Energy Usage per unit value added (kJ/$)	27.479	27.464	-0.055
Material			
Total raw materials used per kg product (kg/kg)	13.410	13.243	-1.245
Total raw materials used per unit value added	0.004	0.004	-7.459
Fraction of raw materials recycled within company	0.000	0.130	0.000
Fraction of raw materials recycled from consumers	0.000	0.000	0.000
Hazardous raw material per kg product	0.340	0.333	-2.114
Water			
Net water consumed per unit mass of product (kg/kg)	228.514	250.227	9.502
Net water consumed per unit value added	0.076	0.078	2.612
Economic			
Value added ($/y)	424997.673	462849.922	8.906

This process was developed in order to produce the important intermediate compound to form polymers and fuel additives. Those components are high valued products. So alternative 4 gives increased profit by around 9 %, compared to the base case (see Table 4.13).

The above improvement results were obtained through SustainPro where the objective was to enhance the process economically and make it more sustainable. Also, each case study need to focus on the environmental impact, as well. So, life cycle assessment (LCA) was applied to consider greenhouse gases emissions.

4.2 Life Cycle Assessment (LCA)

4.2.1 Base Case Design

4.2.1.1 System Boundary and Life Cycle Inventory of Base Case Process

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 two stages: a fermentation stage and a recovery stage. as shown in Figure 4.8.

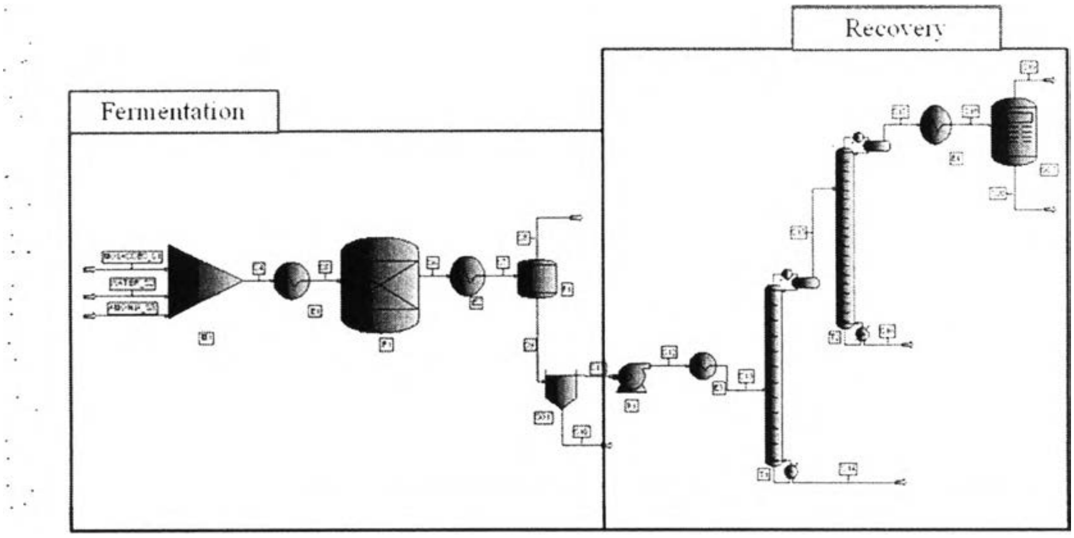

Figure 4.8 Two stages of base case process life cycle.

For the case study, the wastewater from the plant has been designed to produce steam and electricity through biogas and cogeneration system to supply energy to the system. An 85% efficiency of cogeneration was assumed to this analysis (58.73% efficiency of biogas is used to generate steam, 26.27% efficiency of biogas go to electricity production). The products from this section, electricity and steam, were considered to compensate the overall energy consumption in the process. In order to perform the life cycle assessment consistently, integration of farming of sugarcane with the ethanol production process was considered. So, the system boundary of bioethanol production was divided for the two sections, farming and ethanol conversion process, into five stages: sugarcane plantation, sugarcane milling, fermentation, recovery, and biogas and cogeneration, as shown in Figure 4.9.

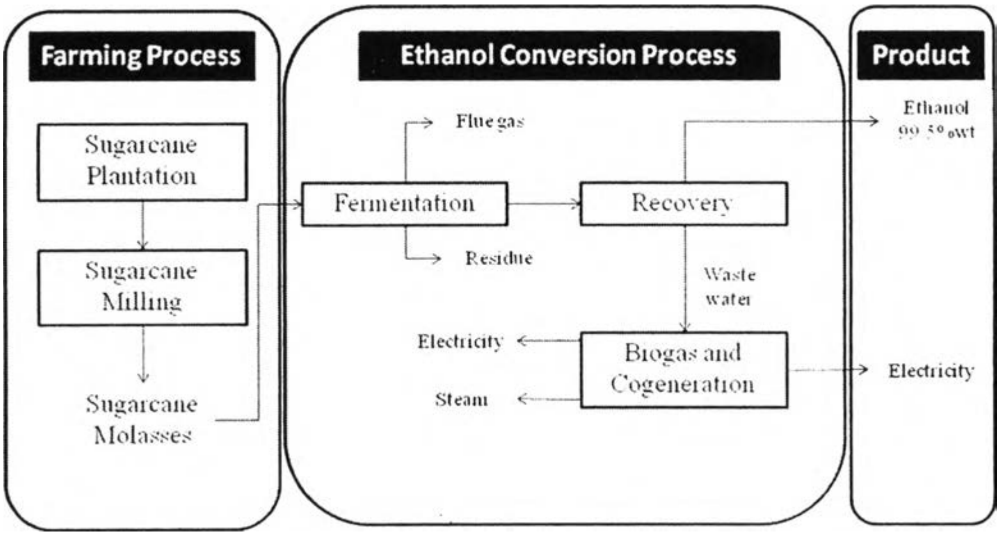

Figure 4.9 System boundary of bioethanol production process.

The basis of one kilogram of 99.5wt% ethanol was set as a functional unit for the inventory analysis. In this analysis, the amount of cooling water was neglected because normal water was used to cool the unit and it could be recycled back to the system (process section). Assumption for the simulation, the energy supplied (steam and electricity) to the process came from a bagasse boiler located in the sugarcane milling area. Bagasse, the fiber left after sugar cane juice is extracted, is burned in boilers to produce steam and electricity for the operation of sugar mills. In just some season, bagasse may not be able to come enough for power production. Some kinds of agricultural residue such as rice or wood husk are burned as a supplemental fuel in sugar milling to save fossil energy. Anyway, that ratio of bagasse weight to the agricultural residues is not much and the assumption is that all agricultural residues used is from 100% bagasse. But if the electricity produced in excess of sugarcane milling process demand will be sold to the grid. By using this energy from biomass (sugarcane bagasse), carbon dioxide (CO_2) released can be subtracted because sugarcane, as it is naturally grown, absorbs CO_2 and therefore, the net amount of CO_2 added to the atmosphere from used biomass energy is reduced, as long as sugarcanes are replanted. Also, CO_2 produced from fermentation of bioethanol production was not considered to be a 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 for each stage are presented in Tables 4.14, 4.15, 4.16, 4.17, and 4.18.

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

Input Inventory				**Output Inventory**		
Type	**Amount**	**Unit**		**Type**	**Amount**	**Unit**
Fuel:				***Product***		
Diesel	1.50E-02	kg		Sugarcane	14.988	kg
Chemical:						
Fertilizer (N)	2.22E-02	kg				
Fertilizer (P)	1.04E-02	kg				
Fertilizer (K)	9.23E-03	kg				
Paraquat (Bipyridylium)	1.61E-04	kg				
Glyphosate	2.57E-05	kg				
Atrazine	5.62E-04	kg				
Ametryne	4.01E-04	kg				
2,4-D	1.61E-04	kg				

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

Input Inventory			**Output Inventory**		
Type	**Amount**	**Unit**	**Type**	**Amount**	**Unit**
Raw material:			***Product***		
Sugarcane plant	14.988	kg	Molasses	3.564	kg
Energy:			***Avoid Product***		
Production of Electricity & Steam Bagasse mainly & other	4.172	kg	Electricity	0.406	kWh
-Electricity from bagasse	0.260	kWh			
-Steam from bagasse	6.739	kg			
Chemical:					
Lime	3.16E-02	kg			
Sodium chloride	1.18E-02	kg			
Hydrochloric acid	6.74E-06	kg			
SiO2	3.47E-05	kg			
Biocide	5.49E-05	kg			
Aluminium sulfate	5.59E-05	kg			
Caustic soda flake	1.73E-05	kg			
Flocculants (Iron sulphate)	5.78E-04	kg			
Miscellaneous	8.57E-05	kg			

Table 4.16 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***		
Molasses	3.564	Kg	Output-1 From fermentation stage	12.612	Kg
Water	9.846	Kg			
Ammonia	7.75E-05	Kg	***Final waste flow***		
			Residues	0.462	Kg
Utilities			***Emission to Air***		
Steam	0.106	Kg	Ethanol	1.25E-03	Kg
			Water	1.57E-03	Kg
			Acetic acid	1.08E-06	Kg
			Carbondioxide	3.32E-01	Kg
			Oxygen	4.78E-04	Kg
			Ammonia	1.53E-03	Kg

Table 4.17 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-1 From fermentation stage	12.612	kg		Ethanol 99.5 wt%	1.000	kg
Energy						
Steam	12.621	kg		***Liquid waste***		
Electricity	0.048	kW		Waste water	11.612	kg

Table 4.18 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	11.612	Kg		Steam	2.325	Kg
				Electricity	0.625	KWh
				Emission to air		
				Nitrogen oxides	1.13E-04	kg
				Carbon monoxide, biogenic	3.60E-04	kg
				Methane, biogenic	1.73E-04	kg
				NMVOC	1.50E-05	kg
				Dinitrogen monoxide	1.88E-05	kg
				Sulfur dioxide	1.58E-04	kg
				Platinum	5.26E-11	kg
				Heat, waste	6.657	MJ
				Used mineral oil, to waste inceneration	6.20E-05	kg

The products of each stage were considered as raw materials for the next stage, for example, sugarcane from the sugarcane plantation stage was used as the raw material for sugarcane milling stage and so on. Several chemicals and substances shown in the tables did not exist in SimaPro's database: such as, the enzyme used in the fermentation stage and chemical species in the sugarcane milling stage (Miscellaneous). 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.

4.2.1.2 Life Cycle Impact Assessment of Base Case Process

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 sugarcane molasses) by using SimaPro 7.0, the CML 2 baseline 2000 methods were then utilized to evaluate the environmental impacts in various categories, for example, global warming potential, ozone layer depletion, acidification, eutrophication potential, and energy resources. The impact assessment results are shown in Table 4.19 and Figure 4.10 where the impact of only global warming potential (GWP) is highlighted.

Table 4.19 Environmental impact of bioethanol conversion process per one kilogram ethanol 99.5 wt% (base case design)

Impact category	**Unit**	**Total**
abiotic depletion	kg Sb eq	-4.26E-03
global warming (GWP100)	kg CO2 eq	-2.22E-01
ozone layer depletion (ODP)	kg CFC-11 eq	1.35E-08
human toxicity	kg 1,4-DB eq	1.62E+00
fresh water aquatic ecotox.	kg 1,4-DB eq	1.26E-01
marine aquatic ecotoxicity	kg 1,4-DB eq	5.59E+01
terrestrial ecotoxicity	kg 1,4-DB eq	5.64E-02
photochemical oxidation	kg C2H4	5.31E-03
Acidification	kg SO2 eq	3.85E-03
Eutrophication	kg PO4--- eq	1.13E-03

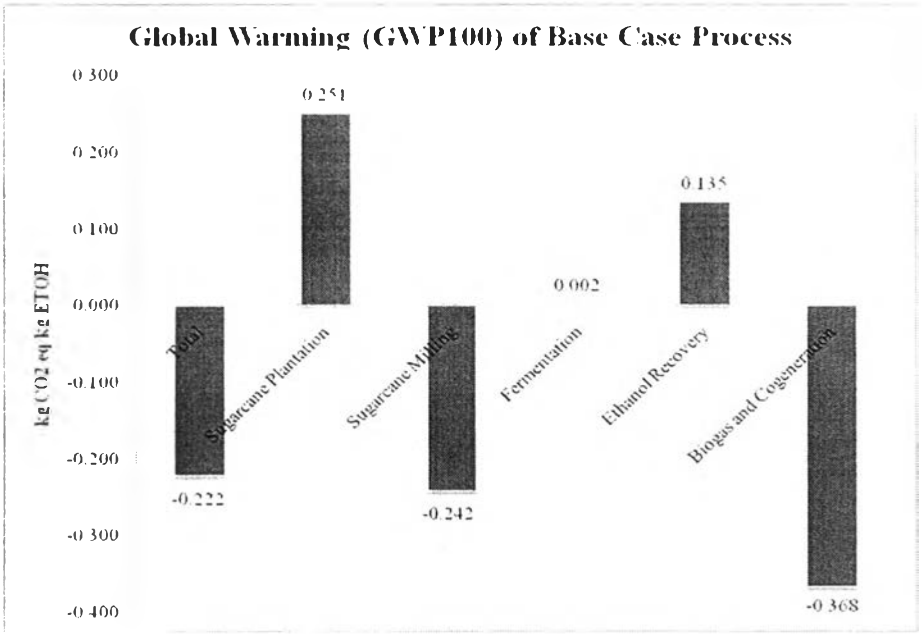

Figure 4.10 Distribution of global warming classified stage by stage (base case design).

For the results of Figure 10, the sugarcane milling stage and the biogas and cogeneration stage were considered to generate some electricity. After remunerating, the remaining electricity could be sold as commercial electricity in Thailand; resulting in a reduction of the green house gases emission from electricity production. The results (see Fig 4.10) showed that CO_2 emission was mainly caused by the high energy consumption in the recovery stage, and fossil fuel (diesel) and chemical substance (fertilizer) usage in the sugarcane plantation stage.

4.2.2 Alternative 1 (Water and Glucose Recycling)

4.2.2.1 System Boundary and Life Cycle Inventory of Alternative 1

For this alternative 1, five stages of the inventory analysis were considered: sugarcane plantation, sugarcane milling, fermentation, recovery, and biogas and cogeneration. Farming process (sugarcane plantation and sugarcane milling) remains the same as base case process, which has been discussed above. From now on, the case study would focus only on the bioethanol conversion process (fermentation, ethanol recovery, and biogas and cogeneration stages). In alternative

1, recycle of glucose and water need energy to separate glucose from waste-water, which is different from the base case as shown in Figures 4.11 and 4.12.

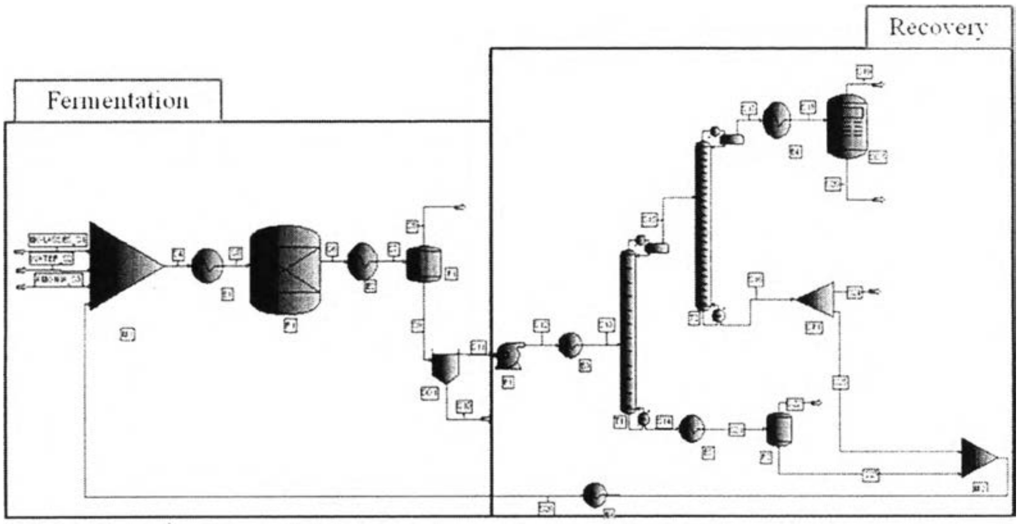

Figure 4.11 Two stages of base case process life cycle of alternative 1.

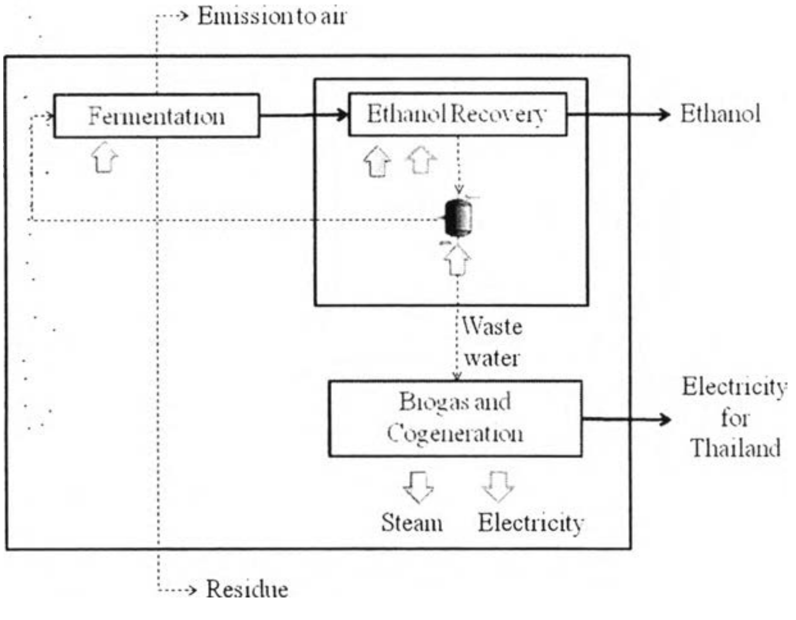

Figure 4.12 System boundary of bioethanol conversion process (alternative 1).

The inventory analysis of the process life cycle is presented stage by stage. Details of input and output inventory data of each stage are given in Appendix F.

4.2.2.2 Life Cycle Impact Assessment of Alternative 1

The life cycle impact assessment (LCIA) was performed to evaluate environmental impacts of the new design alternatives for various impact categories and compared to the base case. For this case, as water was recycled back to the system, it would reduce the steam and electricity production from waste-water. However, as recycling glucose would create more ethanol production, the basis of one kilogram of ethanol as a functional unit would therefore give the energy consumption to be less than the base case for each stage. The exception was the ethanol recovery section, where the purification of glucose took place (the higher the energy consumption the higher green house gases emission). The impact assessments for alternative 1 are shown in Table 4.20

Table 4.20 Environmental impact of bioethanol conversion process per one kilogram ethanol 99.5 wt% (alternative 1)

Impact category	**Unit**	**Total**
abiotic depletion	kg Sb eq	-2.21E-03
global warming (GWP100)	kg CO2 eq	2.67E-02
ozone layer depletion (ODP)	kg CFC-11 eq	2.05E-08
human toxicity	kg 1,4-DB eq	2.71E+00
fresh water aquatic ecotox.	kg 1,4-DB eq	2.09E-01
marine aquatic ecotoxicity	kg 1,4-DB eq	8.86E+01
terrestrial ecotoxicity	kg 1,4-DB eq	9.43E-02
photochemical oxidation	kg C2H4	8.67E-03
Acidification	kg SO2 eq	5.85E-03
eutrophication	kg PO4--- eq	1.69E-03

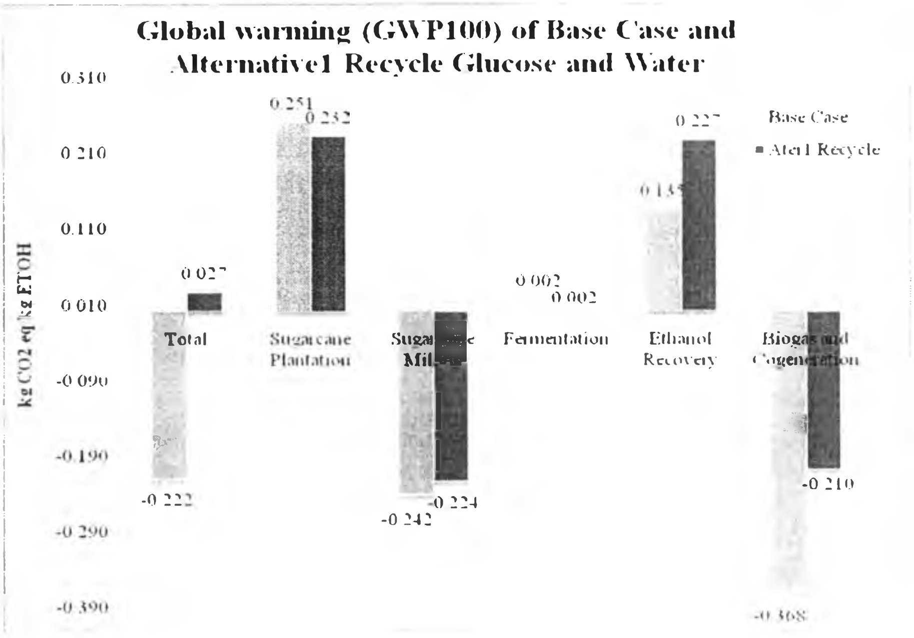

Figure 4.13 Distribution of global warming classified stage by stage (alternative 1).

As shown by Figure 4.13, the total green house gas emissions for alternative 1 increased because there was higher energy consumption in the recovery stage, and less electricity production in the biogas and cogeneration stage than the base case design of the process.

4.2.3 Alternative 2 (The Combustion of Unconverted Cellulose)

4.2.3.1 System Boundary and Life Cycle Inventory of Alternative 2

Alternative 2 considers combustion of unconverted cellulose to generate heat and therefore, heat can be reused by the process. But it was inadequate because it caused a solid residue of around 16 wt% of molasses (12% was ash and the rest was cellulose). So, another heat sources that should be supplied came from bagasses cogeneration (data base available in SimaPro). The system boundary for Alternative 2 is shown in Figure 4.14.

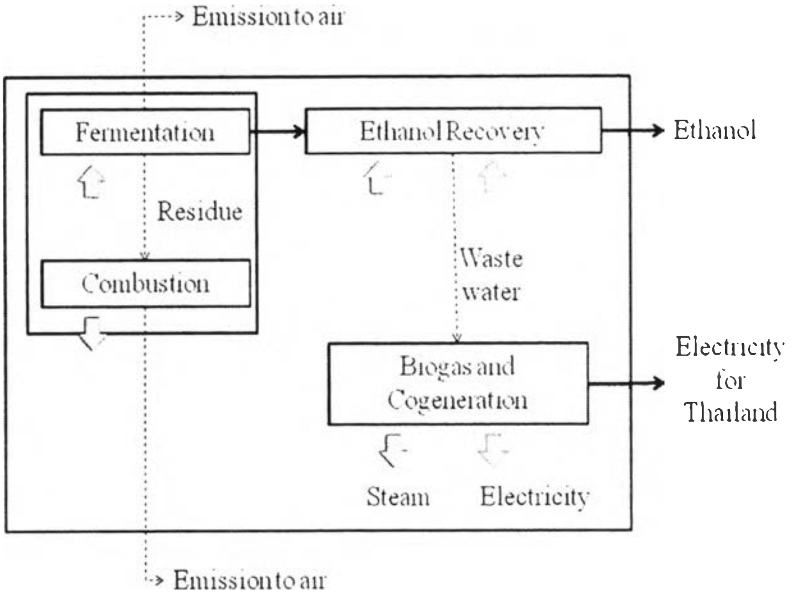

Figure 4.14 System boundary of bioethanol conversion process (alternative 2).

4.2.3.2 Life Cycle Impact Assessment of Alternative 2

Details of input and output inventory data of each stage are presented in Appendix F. The impact assessment results corresponding to the life cycle inventory analysis of bioethanol production process for alternative 2 are given in Table 4.21.

Table 4.21 Environmental impact of bioethanol conversion process per one kilogram ethanol 99.5 wt% (alternative 2)

Impact category	**Unit**	**Total**
abiotic depletion	kg Sb eq	-4.37E-03
global warming (GWP100)	kg CO2 eq	-2.45E-01
ozone layer depletion (ODP)	kg CFC-11 eq	1.19E-08
human toxicity	kg 1,4-DB eq	1.38E+00
fresh water aquatic ecotox.	kg 1,4-DB eq	1.07E-01
marine aquatic ecotoxicity	kg 1,4-DB eq	4.84E+01
terrestrial ecotoxicity	kg 1,4-DB eq	4.78E-02
photochemical oxidation	kg C2H4	4.57E-03
acidification	kg SO2 eq	3.56E-03
eutrophication	kg PO4--- eq	1.03E-03

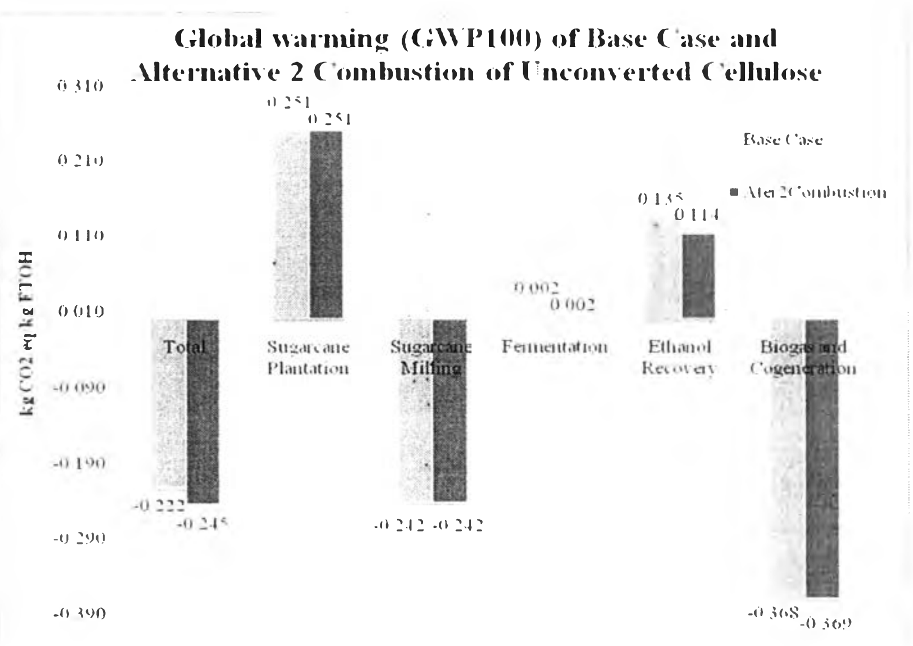

Figure 4.15 Distribution of global warming classified stage by stage (alternative 2).

According to Figure 15, the results show that total green house gases emission for alternative 2 is less than the base case by around 10%. The main reason was the heat recovered from combustion process can be further used in the ethanol recovery stage.

4.2.4 Alternative 3 (Production of Bio-oil from Unconverted Cellulose)

4.2.4.1 System Boundary and Life Cycle Inventory of Alternative 3

When the pyrolysis process is introduced to the base case, it would create several products such as flue gas, char and bio-oil. These were utilized as follows.

- Flue gas: -Some of them recycled back to the pyrolysis process to use as carrier gas
  -The rest of flue gas was sent to combustion to recover heat
- Char: - They could combust to recover heat.
- Bio-oil: -This product could replace production of fuel oil to be used in boilers and furnaces because its specification did not match the commercial product for sale.

This process design was verified through process simulation (using the ProII/8.2 software). It was divided into three stages, as shown in Figure 4.16

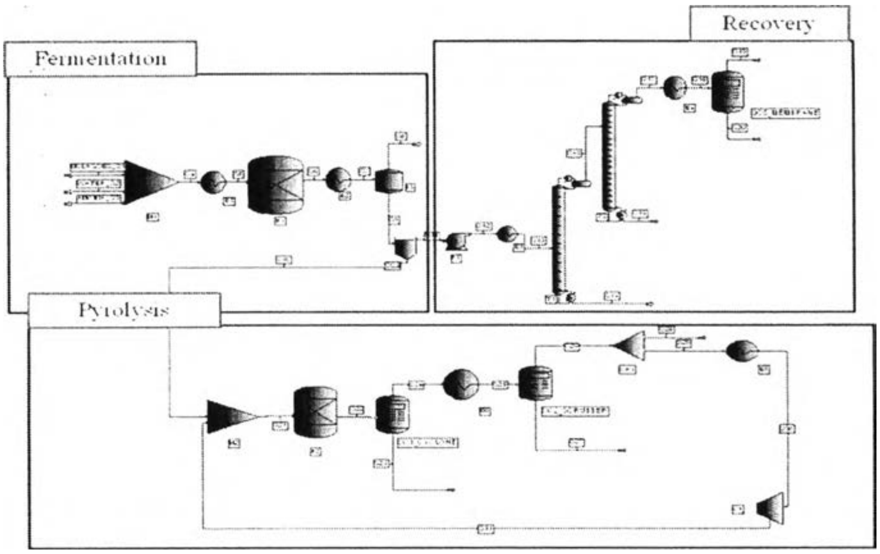

Figure 4.16 Three stages of base case process life cycle of alternative 3.

After integrating ethanol conversion process, the system boundary was set up as shown in Figure 4.17

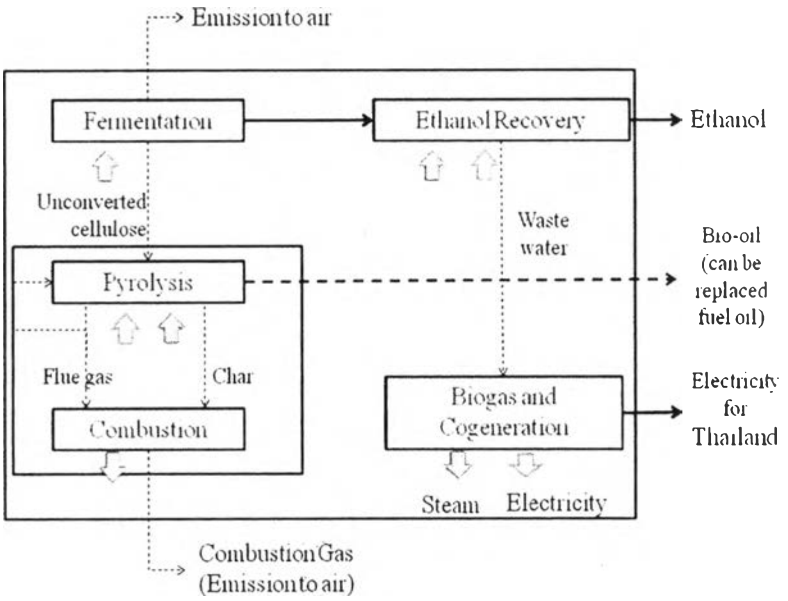

Figure 4.17 System boundary of bioethanol conversion process (alternative 3).

According to Figure 4.17, there were two products that could be sold (not including electricity, because it can be further utilize in the process which was set as avoid product). Biooil and ethanol need to specify heat content when they sell. They came from fermentation stage which is output-1 from fermentation stream and solid residue stream. At this point, the mass allocation is done as given in Table 4.22.

Table 4.22 Partitioning fraction between output-1 from fermentation stage and solid residue allocation (alternative 3)

Scenario	**Enthalpy MJ/hr**	**Allocation (%)**
Output-1 From fermentation stage	76.00	96.20
Solid Residue (unconverted cellulose)	3.00	3.80
Total	79.00	100.00

Details of the stage by stage life cycle inventory analysis of the alternative 3 are given in Appendix F.

4.2.4.2 Life Cycle Impact Assessment of Alternative 3

The life cycle impact assessment (LCIA) was performed to evaluate environmental impacts for the various impact categories. Details of LCIA are given in Table 4.23. Focusing on global warming potential (GWP as CO_2-equivalent), alternative 3 was compared to the base case design as shown in Figure 4.18.

Table 4.23 Environmental impact of bioethanol conversion process per one kilogram ethanol 99.5 wt% (alternative 3)

Impact category	**Unit**	**Total**
abiotic depletion	kg Sb eq	-4.81E-03
global warming (GWP100)	kg CO2 eq	-2.34E-01
ozone layer depletion (ODP)	kg CFC-11 eq	-1.17E-07
human toxicity	kg 1,4-DB eq	1.63E+00
fresh water aquatic ecotox.	kg 1,4-DB eq	1.24E-01
marine aquatic ecotoxicity	kg 1,4-DB eq	4.06E+01
terrestrial ecotoxicity	kg 1,4-DB eq	5.73E-02
photochemical oxidation	kg C2H4	5.37E-03
acidification	kg SO2 eq	3.69E-03
eutrophication	kg PO4--- eq	1.11E-03

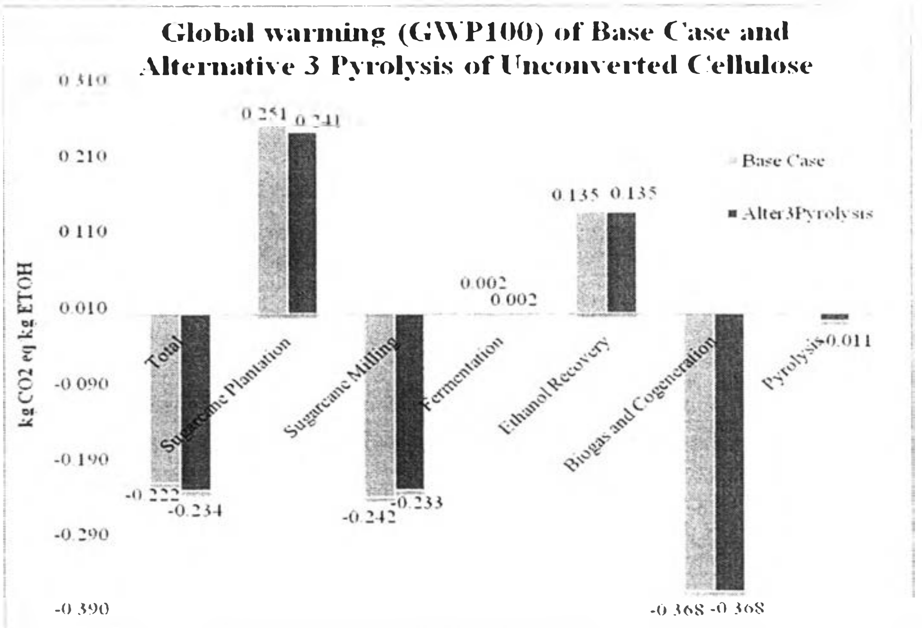

Figure 4.18 Distribution of global warming classified stage by stage (alternative 3).

Because of allocation, generating utility of pyrolysis process, and replacement of fuel oil by pyrolysis oil, the total green house gases emission of alternative 3 was less than base case by around 5% (see Figure 4.18).

4.2.5 Alternative 4 (Production of Hydroxymethyl Furfural from Unconverted Cellulose)

4.2.5.1 System Boundary and Life Cycle Inventory of Alternative 4

In alternative 4, Hydroxymethyl furfural (HMF) is produced from unconverted cellulose. HMF, which is derived from cellulose, is a potential "carbon-neutral" feedstock for fuels and chemicals. HMF could be converted to 2,5-dimethylfuran (DMF), which is a liquid biofuel that has an energy density 40% greater than ethanol, making it comparable to gasoline. Oxidation of HMF also gives 2,5-furandicarboxylic acid, which has been proposed as a replacement terephthalic acid for the production of plastics (Huber, 2006). For alternative 4, HMF was considered to replace terephthalic acid production. Heat and electricity were important utilities for production of HMF. Raw materials which needed to input were water and Methyl isobutyl ketone (MIBK). Disposal; solvent mixture was vented before recycling back to the system. Three stages of process are shown in Figure 4.19. And system boundary of bioethanol conversion process is set as shown in Figure 4.20.

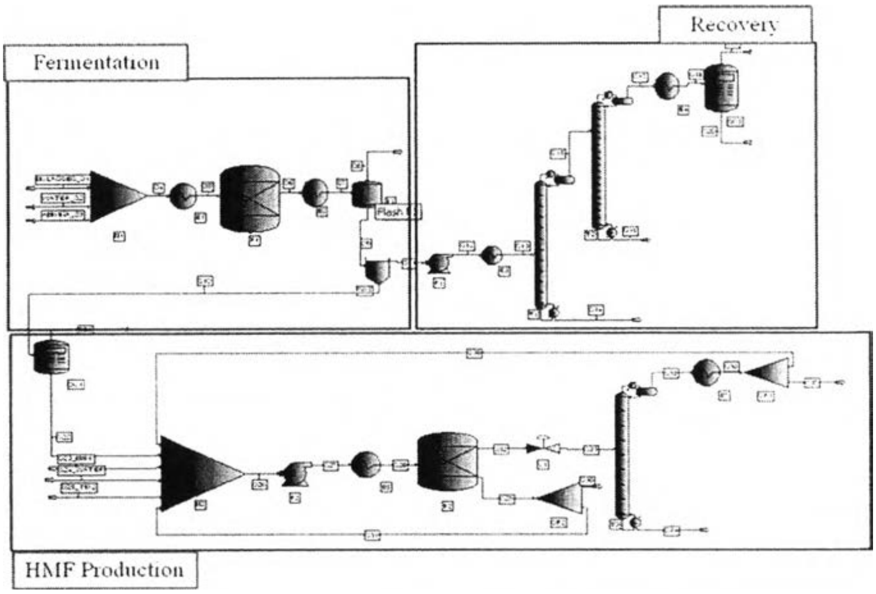

Figure 4.19 Three stages of base case process life cycle of alternative 4.

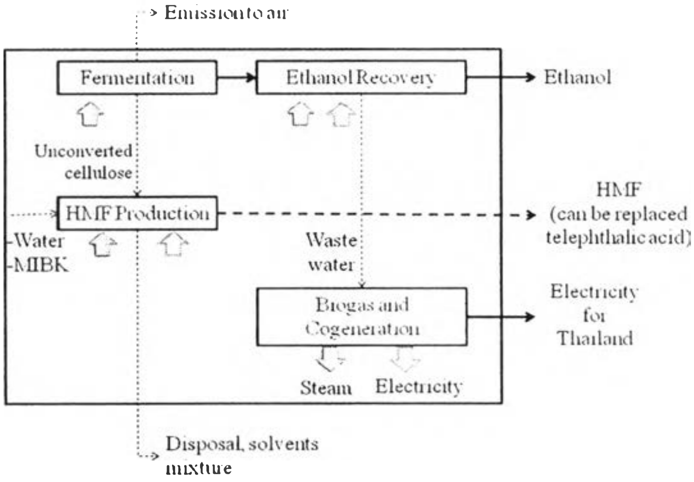

Figure 4.20 System boundary of bioethanol conversion process (alternative 4).

With alternative 4, this process generates two products – ethanol and HMF, which could be sold as chemical products. They are the output from the fermentation stage but different stream. At this point was necessary to allocate by using product yield and product price. Table 4.24 gives the percent allocations.

Table 4.24 Partitioning fraction between output-1 from fermentation stage and solid residue allocation (alternative 4)

Scenario	Allocation (%)
Output-1 from fermentation stage (Ethanol)	92.67
Solid residue (HMF)	7.33
Total	100

The details of the life cycle inventory analysis of the new design alternatives are shown in Appendix F.

4.2.5.2 Life Cycle Impact Assessment of Alternative 4

After performing the life cycle inventory analysis for design alternative 4, the impact assessment results for various categories such as abiotic depletion, global warming (GWP100), and ozone layer depletion (ODP) were calculated (see Table 4.25).

Table 4.25 Environmental impact of bioethanol conversion process per one kilogram ethanol 99.5 wt% (alternative 4)

Impact category	Unit	Total
abiotic depletion	kg Sb eq	2.25E-04
global warming (GWP100)	kg CO2 eq	2.82E-01
ozone layer depletion (ODP)	kg CFC-11 eq	2.20E-08
human toxicity	kg 1,4-DB eq	1.74E+00
fresh water aquatic ecotox.	kg 1,4-DB eq	1.44E-01
marine aquatic ecotoxicity	kg 1,4-DB eq	1.13E+02
terrestrial ecotoxicity	kg 1,4-DB eq	5.94E-02
photochemical oxidation	kg C2H4	6.22E-03
acidification	kg SO2 eq	5.42E-03
eutrophication	kg PO4--- eq	2.51E-03

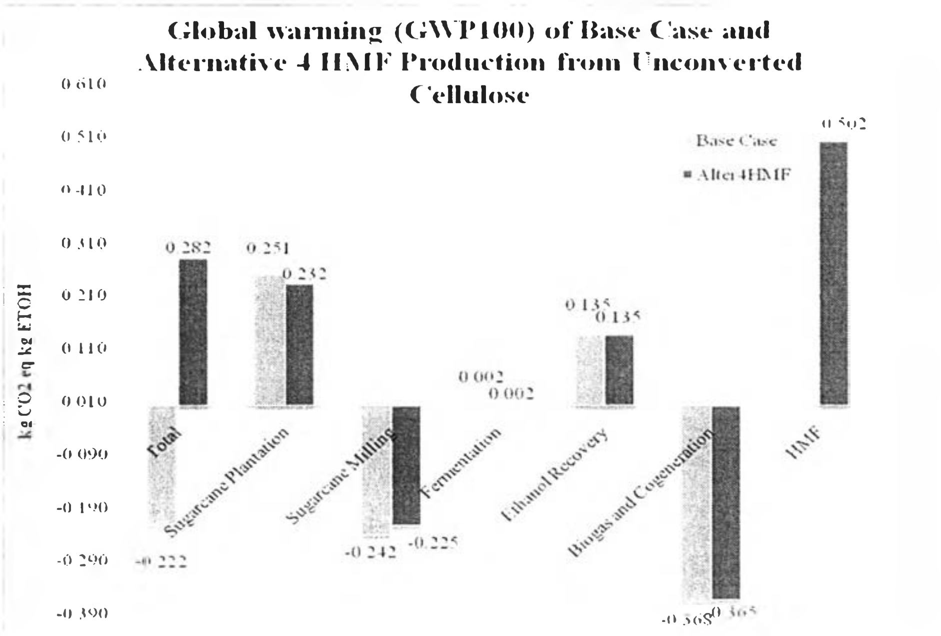

Figure 4.21 Distribution of global warming classified stage by stage (alternative 4).

From Figure 4.21, it can be noted that alternative 4 releases higher green house gases than the base case design. The main reason for this is the added HMF production stage. While 70 % carbon dioxide equivalent of HMF production came from MIBK production that used as solvent in the process. Another 30 % went to dispose of solvents mixture.

4.3 Comparison between Base Case and Alternatives

4.3.1 Sustainability Analysis

Sustainability metrics was used for this analysis and these were calculated by using the SustainPro software. These analyses were used for comparing the sustainability of different design alternatives through 4 groups of metrics: energy, material, water, and economic, as given in Table 4.26.

Table 4.26 Comparison of sustainability metrics between the base case and alternatives

Metric	Base case	Alternative1	Alternative2	Alternative 3	Alternative 4
Energy					
Total Net Primary Energy Usage rate (GJ/y)	8.41E+04	1.13E+05	8.41E+04	8.59E+04	9.15E+04
% Total Net Primary Energy sourced from renewables	9.98E-01	9.98E-01	9.98E-01	9.96E-01	9.98E-01
Total Net Primary Energy Usage per Kg product (kJ/kg)	8.21E+04	1.02E+05	8.21E+04	8.39E+04	8.76E+04
Total Net Primary Energy Usage per unit value added (kJ/$)	2.75E+01	3.16E+01	2.65E+01	2.65E+01	2.75E+01
Material					
Total raw materials used per kg product (kg/kg)	1.34E+01	8.70E+00	1.34E+01	1.34E+01	1.32E+01
Total raw materials used per unit value added	4.49E-03	2.69E-03	4.32E-03	4.24E-03	4.15E-03
Fraction of raw materials recycled within company	0.00E+00	4.24E-01	0.00E+00	0.00E+00	1.30E-01
Fraction of raw materials recycled from consumers	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Hazardous raw material per kg product	3.40E-01	3.15E-01	3.40E-01	1.74E-01	3.33E-01
Water					
Net water consumed per unit mass of product (kg/kg)	2.29E+02	2.62E+02	2.29E+02	2.33E+02	2.50E+02
Net water consumed per unit value added	7.65E-02	8.10E-02	7.36E-02	7.36E-02	7.84E-02
Economic					
Value added ($/y)	4.25E+05	4.97E+05	4.41E+05	4.50E+05	4.63E+05

It can be seen that the sustainability metrics of the new design alternatives have improved significantly in economic aspects; the increased value added means more profitable processes. In terms of energy usage, new design alternatives are better since energy was generated by the process itself. In terms of material and water consumption, the metrics from the new design alternatives almost maintained the same value compared to the base case.

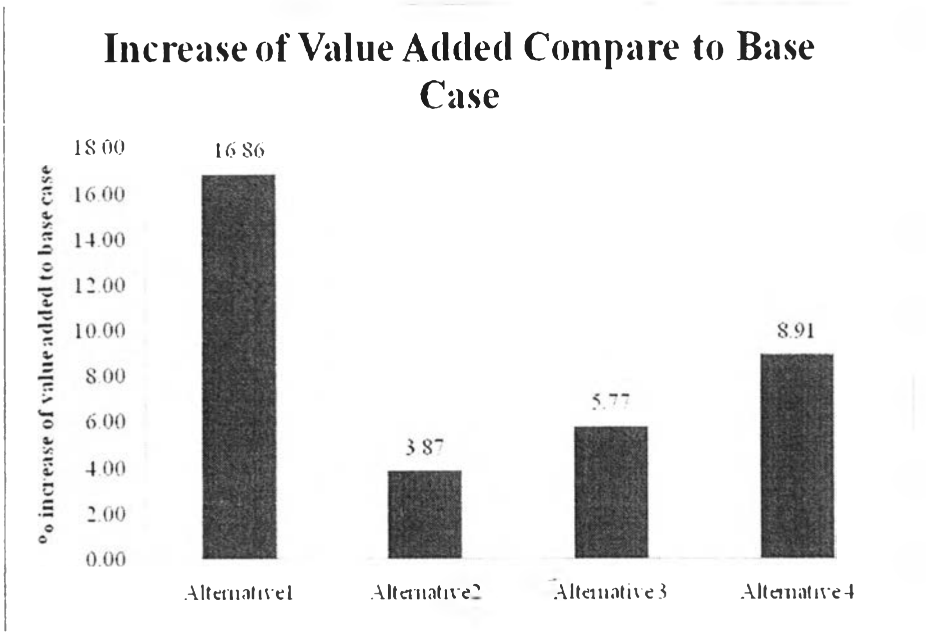

Figure 4.22 Comparison of economic item between the base case and alternatives.

Focusing on the economic terms, value added of alternative 1 (recycle glucose and water) increased by 17 % compared to the base case design, which is the highest of economic value compared to the other alternative designs according to Figure 4.22.

4.3.2 Life Cycle Assessment

After performing the life cycle impact assessment to evaluate environmental impacts, the new design alternatives were compared to the base case. Details of LCIA are given in Appendix G.

Focusing on global warming potential (GWP as kg CO_2-equivalent), Alternative 2 has shown to be the lowest greenhouse gas (GHG) emission followed by Alternative 3 as shown in Figures 4.23. Because of these two alternatives generate other heat sources to compensate for their overall energy consumptions.

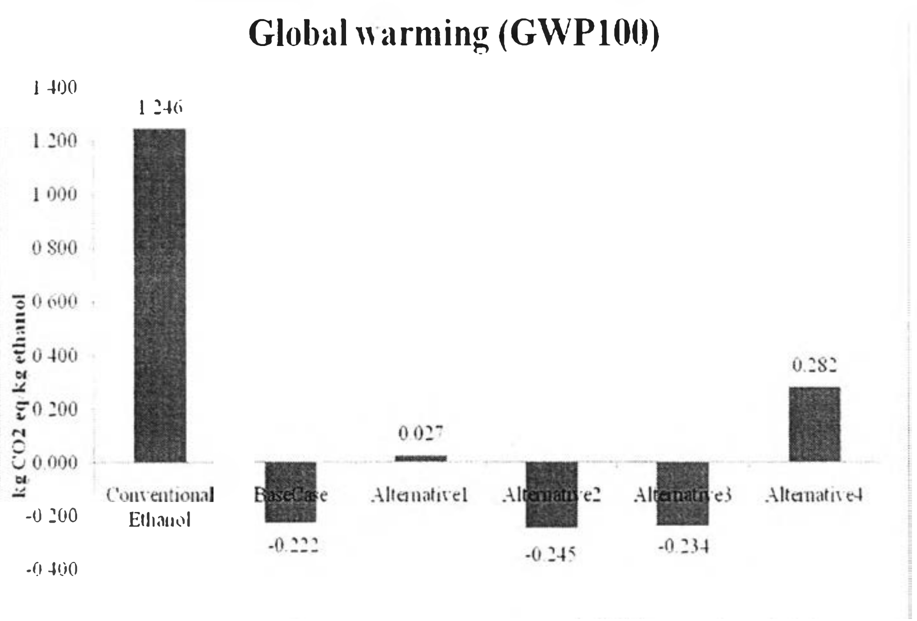

Figure 4.23 Comparison of the greenhouse effect (gCO2-equivalent) generated from bioethanol conversion process between the base case and alternatives per kilogram of bioethanol.

Figure 4.24 illustrates the comparison between the base case and all alternatives studied. Comparing to the base case design, the results show that Alternative 1 yields the highest economic value added but the environmental impact also increases. In contrast, Alternative 2 not only increases the economic value added but also lowers the environmental impact due to the overall reduction in energy used in the process. When compromising the two effects (economic value added and environmental impact), the alternative 2 has been shown to be the best alternative. It is important to note that the capital cost and investment were not taken into account in the economic value added calculations presented in this work. If they were calculated, the capital cost of this alternative 2 should also be the lowest among the other alternatives.

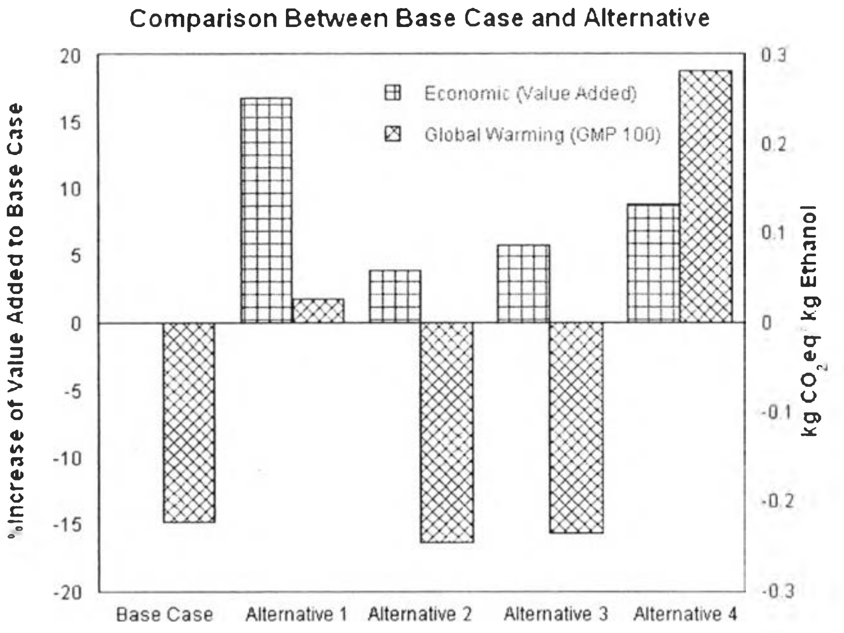

Figure 4.24 Comparison between base case and alternatives both in economical and environmental terms.