CHAPTER IV
RESULTS AND DISCUSSION

4.1 Waste Composition Analysis

4.1.1 TGA Analysis

This analysis is operated at temperature 900 °C started from room temperature with heating rate 20 °C/min. As shown in Figure 4.1, the TGA analysis of the solid waste sample shows the weight lost at temperature around 200°C and rate of weight lost is increased as observed by the slope of the TGA curve, until temperature reached around 400 °C. Gómez-Siurana *et al.* (2013) has found the similar temperature range for weight lost in the sample containing glycerin and fatty acid.

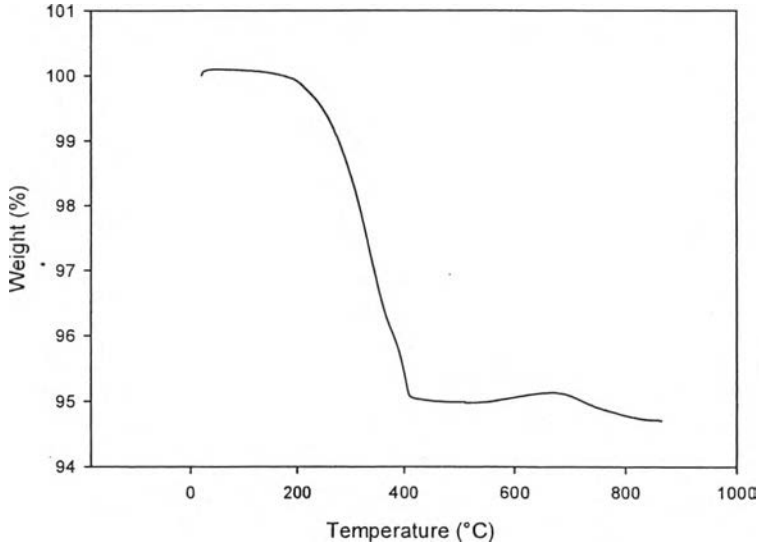

Figure 4.1 TGA analysis of solid waste sample.

4.2 Combustion of Solid Waste Sample

4.2.1 Effect of Furnace Temperature

The 10 g of solid waste sample is treated in an electrical furnace. Temperature is steadily increased until it is reached final temperature. After that the furnace temperaure is held at final temperture for 20 mins. Then treated sample is weighed to calculate weight loss and inorganic contents. Table 4.1 shows the percent recovery is around 91 - 93 % for all furnace temperature.

Table 4.1 Weight recovery of sample in each final temperature

Final Temperature (°C)	500	600	700	800	900	1000
Sample Rcovery (%wt)	93.6	93.7	93.0	93.7	91.5	92.9

The sample after treated by combustion has color depend on varied temperature. As shown in Figure 4.2, the sample from furnace temperature of 500 °C is grey-brown and the sample color is grey when the furnace temperature is 600 °C. However, it seems that organic contents are totally removed when the furnace temperature is between 700 – 800 °C, as the sample color is completely white. If the furnace temperature is increased to 900 °C and 1,000 °C, the color sample is in pink.

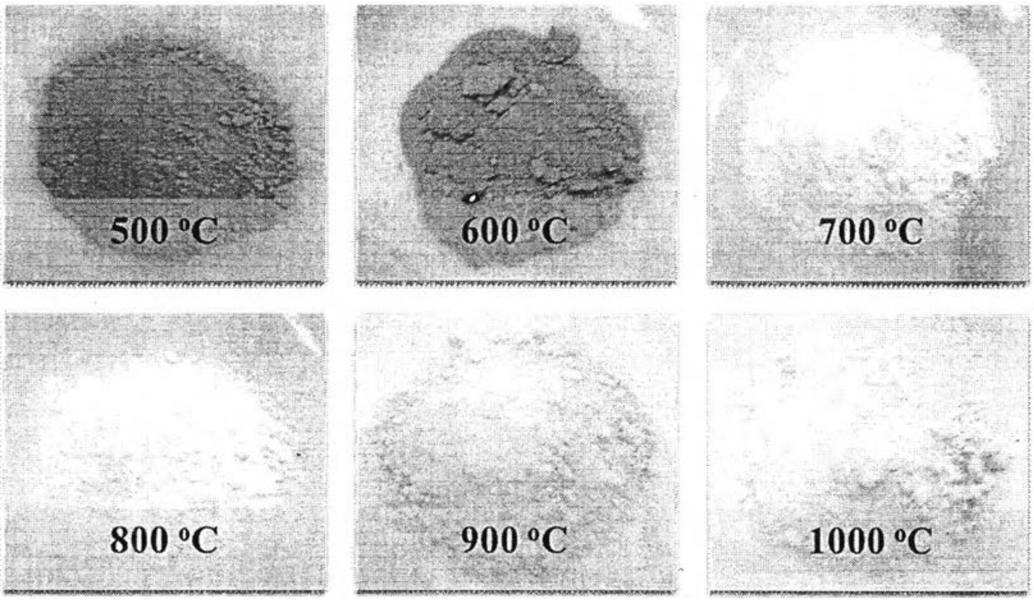

Figure 4.2 Photographs of solid waste samples after treated in furnace at different temperature.

From experimental data, it concludes that the effect of temperature and is not effect to weight of the sample. Moreover TGA analysis can confirm that no weight loss occurred anymore when temperature is increased over 400°C.

4.3 Extraction and Precipitation of Solid Waste Sample

4.3.1 Percent Recovery of Precipitated Salt

Another experiment is extraction and precipitation, after sample is soluted into solution to extract insoluble part out of the sample. Insoluble part is removed by using 110 mm filter and dried water out in oven for 10 hrs and 120 °C temperature. 99.9 % methanol or 99.9 % ethanol is added into sample solution with various ratios compare to water. They both created white aqueous solution in bottom layer and water layer is in top layer. Sample solution is left for 2 hrs, and then white aqueous solution is filtered by using 110 mm filter and kept in oven for 10 hrs to remove water. The white aqueous solution, which become white solid when dried, and insoluble part will be weighed to find percent recovery. Remaining solution from precipitation is evporated to determine the remaining salt which still dissolve in the solution.

Table 4.2 Percent recovery for extraction and precipitation

Ratio (Water:Alcohol)	5:1 (%)	5:2 (%)	5:3 (%)	5:4 (%)	5:5 (%)	5:6 (%)	5:7 (%)
99.9% Methanol	57.32	73.55	88.31	94.09	94.26	95.10	95.28
99.9% Ethanol	50.48	64.60	80.85	89.38	93.22	92.77	92.99
Recycled Ethanol	35.38	55.01	71.12	82.15	85.63	90.36	92.21

After extraction by water, the amount of soluble inorganic in 50 ml water is about 6.85 g. Then, the insoluble organic part was filtered out. After this filtration step, alcohol (methanol or ethanol) is then added to the clear aqueous solution containing soluble salts. Since adding alcohol causes the decrease of salts solubility in the aqueous solution, therefore, the salt is precipitate outs. As shown in

Table. 4.2, the percent recovery by precipitation is increased with increasing amount of alcohol. As expected, methanol is more effective in precipitation of inorganic salts compare to other in the same ratio. Because dielectric constant of methanol is higher than ethanol, so adding methanol is more effective in decreasing of salt solubility than ethanol. After filtration of salts, the ethanol in the aqueous solution is evaporated out and condensed reuse in experiment again. Recycled ethanol provides less amount of precipitated salt than 99.9 % ethanol because it contains some water. Because of azeotrope between ethanol and water, the concentration of recycled ethanol is not higher than 95.6 %. Moreover, Table 4.2 shows the effect of water : alcohol ratio on precipitation of inorganic salts.

4.4 Characterization of Treated Sample

4.4.1 XRF Analysis

Table 4.5 reports that the main compounds of treated sample are K_2O and SO_3. These compounds can count for K_2SO_4.

Table 4.3 XRF results from treated sample

Compounds	**Concentration (%wt)**			
	Combustion (700 °C/20mins)	Combustion (900 °C/20mins)	99.9 % EtOH	99.9 % MeOH
K_2O	60.04	60.20	66.99	67.50
SO_3	39.55	39.52	32.82	32.30
Other	0.41	0.28	0.19	0.20

4.4.2 XRD Analysis

The sample is analyzed by XRD to check the peak position of the experiment sample compare with standard potassium sulfate. 99.98 % purity potassium sulfate is used as reference. Figure 4.3 and Figure 4.4 show that the precipitated salt has the same XRD spectra as the potassium sulfate. This analysis confirms that treated sample from combustion and precipitated salt in this case is K_2SO_4. The high of peak refer to size of the crystal.

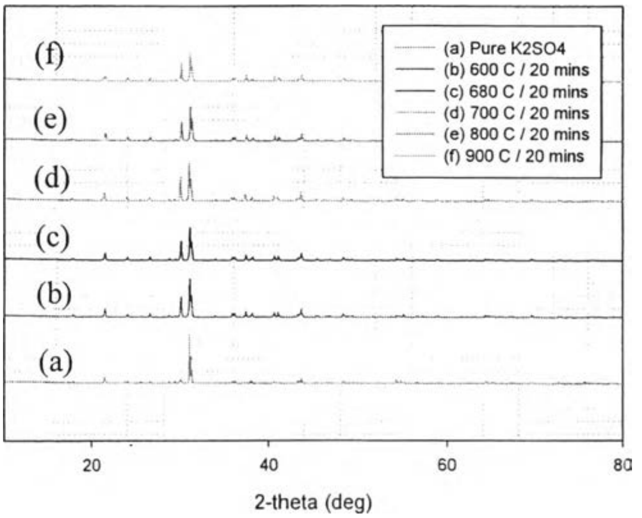

Figure 4.3 XRD analysis results from treatment in combustion. The (a) line showed the reference potassium sulfate compare to other lines which these lines are the sample from treatment in various temperatures.

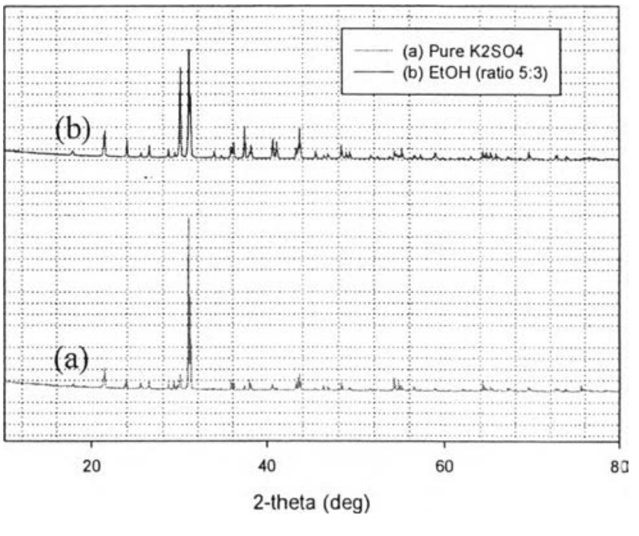

Figure 4.4 XRD result from Precipitation by using alcohol (ratio = 5:3). The (a) line is referenced potassium sulfate and (b) line is the sample from extraction and precipitation.

4.4.3 AA Analysis

To determine potassium sulfate purity by using Atomic Adsorption test, the two samples from combustion with final temperature 700 °C and 20 mins hold is dissolved in different weight to determine concentration and compare with standardize potassium sulfate solution (1000 ppm).

Standard solution is prepared by using pure 99.98 % potassium sulfate and dissolved in deionize water in various concentration, 0.5 ppm, 1.0 ppm and 1.5 ppm. After that standard curve is created to find concentration of the test samples from combustion. The samples are dissolved in deionize water in various weights. In this case, sample 1 and sample 2, are made into two solutions to determine their concentration. The result shows 99.043 % potassium sulfate purity.

4.5 Economic Evaluation

4.5.1 Combustion Process

The economic evaluation is created to compare the payback period between two experiments in commercial scale, combustion method and extraction, and precipitation method. Based on process flow diagram which shown in Figure 4.5, cost estimation of total capital investment and total production cost have been carried out. From the basis, the economic evaluations are carried out for determining of payback period. Total capital cost is calculated at minimum conditions and summarized in Table 4.4, it is approximately 41.10 million bath. The major cost is cost of purchased equipment required in the process which accounts for 40 % of total capital investment.

Table 4.4 Total capital investment for combustion process

Type	Item	Cost (Million Bath)
Fixed Capital Investment	Purchased equipment	14.56
	Purchased equipment installation	2.18
	Instrument and control (installed)	0.73
	Valve and Piping (installed)	1.09
	Electrical (installed)	0.73
	Building (include services)	1.09
	Land	7.50
	Yard improvements	0.73
	Service facilities (installed)	2.91
	Engineering and supervision	1.46
	Construction expense	1.46
	Contractor's fee	0.73
	Contingency	1.82
Working Capital		4.11
	Total	**41.10**

As shown in Table 4.5, the purchased equipment cost is based on assumption. The rotary kiln specification which can meet requirement of target production rate is 1.4 m diameter and 33 m long. The screw conveyor transports the product into warehouse and water jacket is installed to cool down the product during transportation. Wet scrubber is used to cool down temperature of flue gas and separate fly ash and CO_2 from treated flue gas. LPG station and sodium hydroxide storage tank are required for stock these utilities. Assume that LPG and sodium hydroxide storage are designed for 3 months of stock in case of lack of supply, the capacity of storages are 140 m^3 and 163 m^3 respectively.

Table 4.5 Purchased equipment costs for combustion process

Type	**Cost (Million Bath)**
Rotary kiln	5.00
Screw-conveyor with water jacket	3.50
Wet scrubber	0.10
LPG station	1.63
Sodium hydroxide storage tank	4.33
Total	**14.56**

Table 4.6 shows the total production cost per year for all operations, the major cost factor is utilities which is 30 % of total production cost. The raw material is the solid waste from biodiesel production process, so it has no cost. For combustion process, the total production cost is estimated for 12.49 million bath/yr.

Table 4.6 Total production costs for combustion process

Type	Item	Cost (Million Bath/yr)
Direct Production	Raw material	-
	Operating labor	2.98
	Direct supervisory and clerical labor	0.30
	Utilities	3.71
	Maintenance and repairs	0.74
	Operating supplies	0.07
	Laboratory charges	-
	Patents and royalties	-
Fixed Charge	Depreciation	1.46
	Local taxes	0.37
	Insurance	0.15
	Rent	-
Plant-overhead		1.23
General Expenses	Administrative costs	0.49
	Distribution and selling costs	0.49
	Research and development costs	0.49
	Financing	-
Total		**12.49**

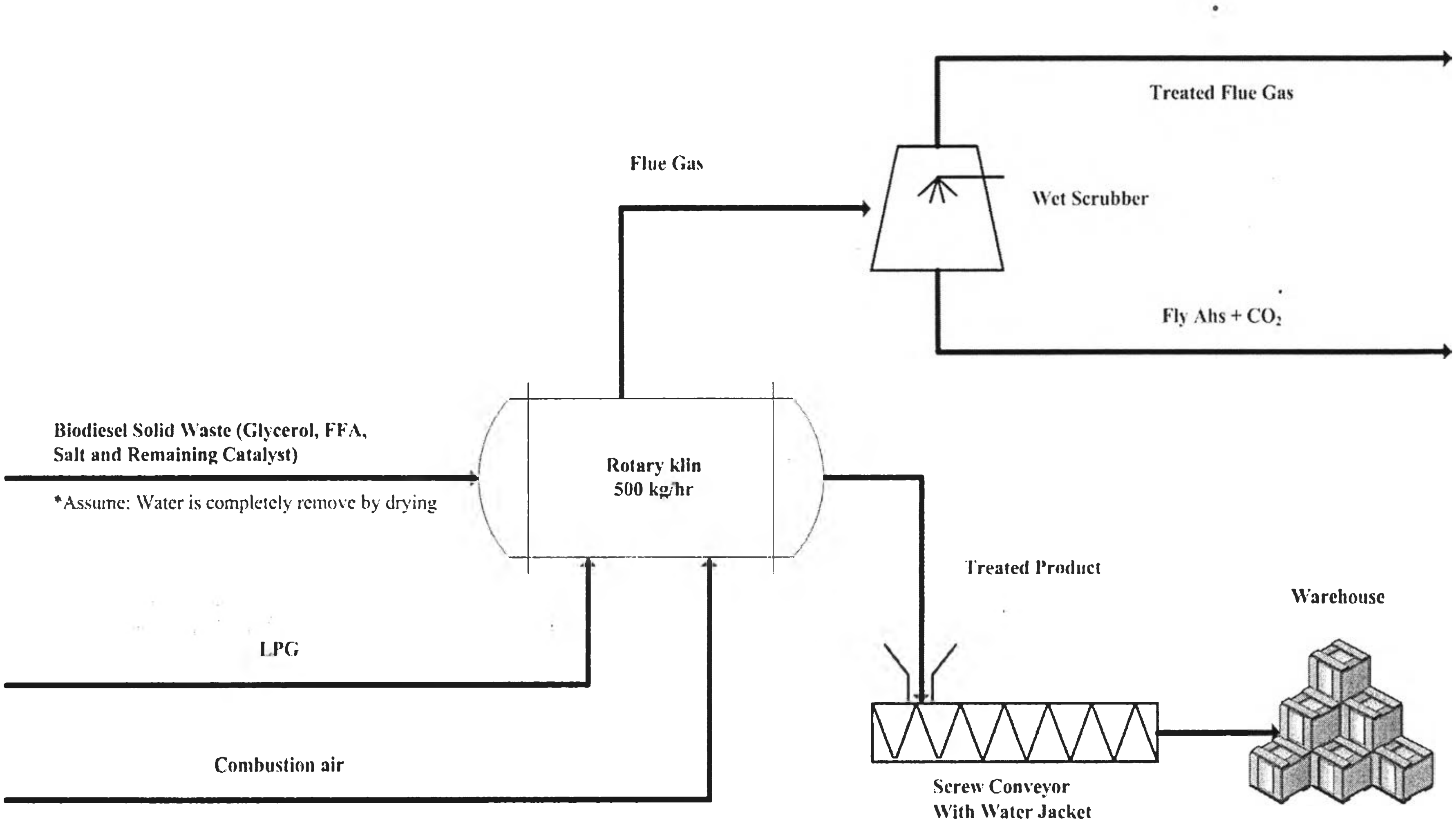

Figure 4.5 Process flow diagram of combustion.

The major cost for utilities is LPG using as fuel for rotary kiln which its cost is refered from cost of LPG on 30-Jan-2015. Electric cost is referred from the industrial rate of PEA (Provincial Electricity Authority) which is 2.61 bath/unit. The industry electric power demand is ignored in case of both process, combustion, and extraction and precipitation, are set up in the same plant. Cooling water cost is 15.55 bath per 1,000 gal, this amount of water is required to cool down the product's temperature which coming out of rotary kiln. Also sodium hydroxide and process water costs for wet scrubber are 560 bath/ton and 47.94 bath per 1,000 gal respectively. The utility cost is shown in Table 4.7.

Table 4.7 Utility cost for combustion process

Type	**Item**	**Quantity**	**Cost (Bath/year)**
Utilities	LPG	126,000 kg	2,283,120
	Electric (Purchased)	240,000 unit	627,264
	Cooling water (Well)	2,780,000 gal	43,229
	Sodium Hydroxide	1,118 ton	626,080
	Water (for sodium hydroxide solution)	2,633,400 gal	126,245
Total			**3,705,938**

4.5.2 Extraction and Precipitation Process

The process flow diagram for extraction and precipitation process is shown in Fig.4.6. Precipitator production rate is designed for 500 kg/hr. After solid waste is soluted in mixer, the insoluble part is then removed from the process by using scroll-conveyor sediment separator. At precipitator with designed production rate 500 kg/hr, ethanol is added into soluble part to extract the potassium sulfate salt. The potassium sulfate salt is separated by another scroll-conveyor sediment, dried in dryer and stored in warehouse. The solution after salt is separated is taken to distillation column for recovery amount of ethanol. To reduce the expense for ethanol, this recovered ethanol can be recycled and taken back to use in the process again.

Table 4.8 Total capital investment for extraction and precipitation process

Type	**Item**	**Cost (Million Bath)**
Fixed Capital Investment	Purchased equipment	19.83
	Purchased equipment installation	2.97
	Instrument and control (installed)	0.99
	Valve and Piping (installed)	1.49
	Electrical (installed)	0.99
	Building (include services)	1.49
	Land	7.50
	Yard improvements	0.99
	Service facilities (installed)	3.97
	Engineering and supervision	1.99
	Construction expense	1.99
	Contractor's fee	0.99
	Contingency	2.48
Working Capital		5.30
Total		**52.96**

Table 4.8 shows the estimated total capital investment for extraction and precipitation process for 52.96 million bath. The main factor for estimation is purchased equipment cost which accounts for 42 % of total capital investment. The other expenses can be determined after purchased equipment costs have been calculated. In this case, both processes assume to be created in the same area, therefore cost of land is same as the combustion process.

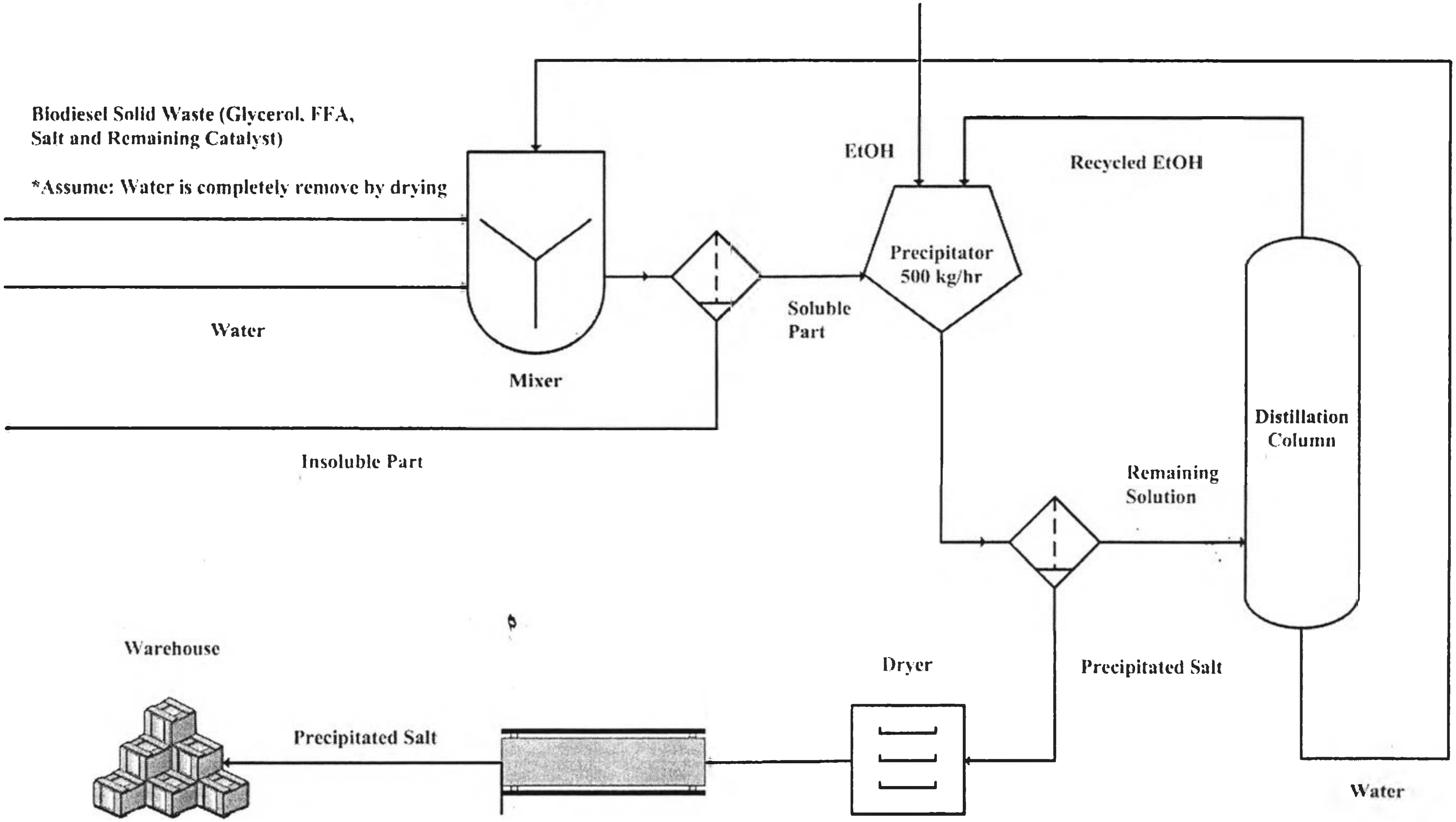

Figure 4.6 Process flow diagram of extraction and precipitation.

Total capital investment for extraction and precipitation process is more expensive than combustion process, because the equipment required for salt precipitation is expensive which shown in Table 4.9. The major cost is distillation column for ethanol recovery which accounts for 9.6 million bath. Mixing tank is designed for 0.378 m^3 capacity to solute the solid waste. There are two scroll-conveyors put into the process for solid-liquid separation. The first one is used to remove insoluble part and second conveyor is used to collect precipitated salt. Precipitator has 1.88 m^3 capacities to reach target production rate. The precipitated salt is dried and transport to store at warehouse by using belt conveyor. However, this process requires distillation column to recycle ethanol back to the process. This recycled ethanol can reduce the cost for purchasing new ethanol solution. The ethanol storage tank is designed for 5.85 m^3 capacity horizontal tank, this volume is required for 3 months of storage capacity.

Table 4.9 Purchased equipment costs for extraction and precipitation process

Type	**Cost (Million Bath)**
Mixing tank	1.90
Scroll-conveyor sediment separator (x2)	3.66
Precipitator	0.46
Distillation column	9.60
Dryer	1.23
Belt-conveyor	1.31
Ethanol storage tank	1.67
Total	**19.83**

Table 4.10 shows the total production cost for extraction and precipitation process. Due to high costs of purchased equipment and building, depreciation is the major expense which account for 35 % of total production cost. Because extraction and precipitation has more equipment than combustion process,

thus this process requires more labors than combustion process resulting in higher operating labor cost.

Table 4.10 Total production costs for extraction and precipitation process

Type	**Item**	**Cost (Million Bath/yr)**
Direct Production	Raw material	-
	Operating labor	2.98
	Direct supervisory and clerical labor	0.30
	Utilities	1.75
	Maintenance and repairs	0.95
	Operating supplies	1.17
	Laboratory charges	-
	Patents and royalties	-
Fixed Charge	Depreciation	4.77
	Local taxes	0.48
	Insurance	0.19
	Rent	-
Plant-overhead	Plant-overhead	0.58
General Expenses	Administrative costs	0.23
	Distribution and selling costs	0.23
	Research and development costs	0.23
	Financing	-
Total		**13.85**

The major cost for utilities is electric, because the equipment required for extraction and precipitation process has more number than combustion process. Process water and ethanol solution cost are 47.94 bath per 1,000 gal and 103.66

bath/gal respectively which referred from appendix E. As shown in Table 4.11, the cost for utilities approximately is 5.10 million bath/yr.

Table 4.11 Utility cost for combustion process

Type	**Item**	**Quantity**	**Cost (Bath/year)**
Utilities	Electric (Purchased)	480,000 unit	1,254,528
	Process water	4756 gal	228
	99.9% conc. ethanol	4756 gal	0.49
Total			**5,097,577**

Compare between two processes, total investment cost and total product cost for extraction and precipitation process is higher than combustion process as shown in Table 4.12. In extraction and precipitation, the expense for equipment is more expensive than combustion process resulting in higher cost of all other expenses. Thus this factor affect to depreciation cost in total product cost for extraction and precipitation process. Extraction and precipitation process spend less utility cost than combustion process, because LPG which required for combustion is expensive and it is required in large volume. Also the other utilities for cooling system such as sodium hydroxide solution and cooling water are required for cooling the product temperature. So the annual utility cost for combustion process is very high compare to extraction and precipitation process. The utility cost for extraction and precipitation process is mainly come from electricity which results from many number of equipment requiring in the process.

Table 4.12 Total investment cost and total production cost between two processes

	Combustion Process	**Extraction and Precipitation Process**
Total investment cost (million bath)	41.10	52.96
Total production cost (million bath/yr)	12.49	13.85

Table 4.13 shows the product price and payback period which calculated from cost estimation. The product price for treatment of biodiesel solid waste is 5.55 bath/kg-K_2SO_4. Assume that the treated solid waste can sell for 12, 15 and 18 bath/kg, and sell out at total production rate per year. So the payback period is 3, 2, and 2 years respectively. For extraction and precipitation, the product price is 6.16 bath/kg-K_2SO_4 and the payback period is 5, 3, and 3 years respectively.

Table 4.13 Payback period between two processes at different sale price

	Combustion Process	**Extraction and Precipitation Process**
Product price (bath/kg-K_2SO_4)	5.55	6.16
Payback period for sale price = 12 bath/kg (yr)	3	5
Payback period for sale price = 15 bath/kg (yr)	2	3
Payback period for sale price = 18 bath/kg (yr)	2	2