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APPENDICES

Appendix A Computer Program for Mass and Energy Balance of Pyrolyzer

Mass and Energy Balance for Pyrolysis Process (MEBPP) program was created in which it can be basic user's decision and prediction for adjustment of operating process parameters and other process conditions. The program is included basic method to calculate mass and energy balance for batch pyrolyzer by only using basic raw information of feed material. Main program automatically calculates mass and energy of various products obtained from pyrolysis process by basic chemical engineering calculation method.

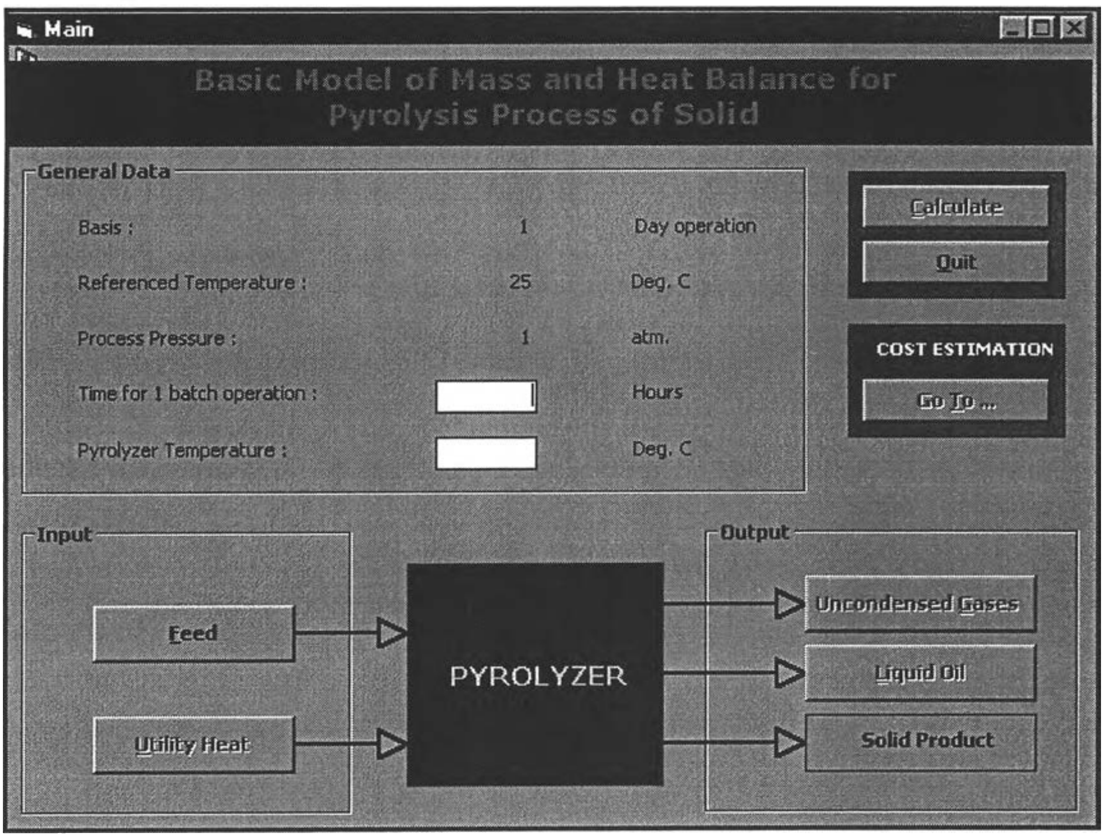

Figure A1 Main Interface.

The information corresponding to MEBPP program consists of both essential physical and chemical properties of material and process. Physical properties include input and output rate, operating temperature, feed material composition, operating time, and so on. Chemical properties are almost due to thermodynamic properties such as specific heat capacity, heating value or potential heat of feed and products, etc.

This manual presents the essential visualization component of MEBPP, as was illustrated in the following pictures. When user double click icon of MEBPP, the first window, Figure A1, is appeared.

At the first interface, calculated demand button can not be used until user add completely significant data. Begin with user have to put the basic information of process in time and pyrolyzer temperature data boxes. Then, click feed command button. Window will be changed from main interface to feed interface as is seen in Figure A2.

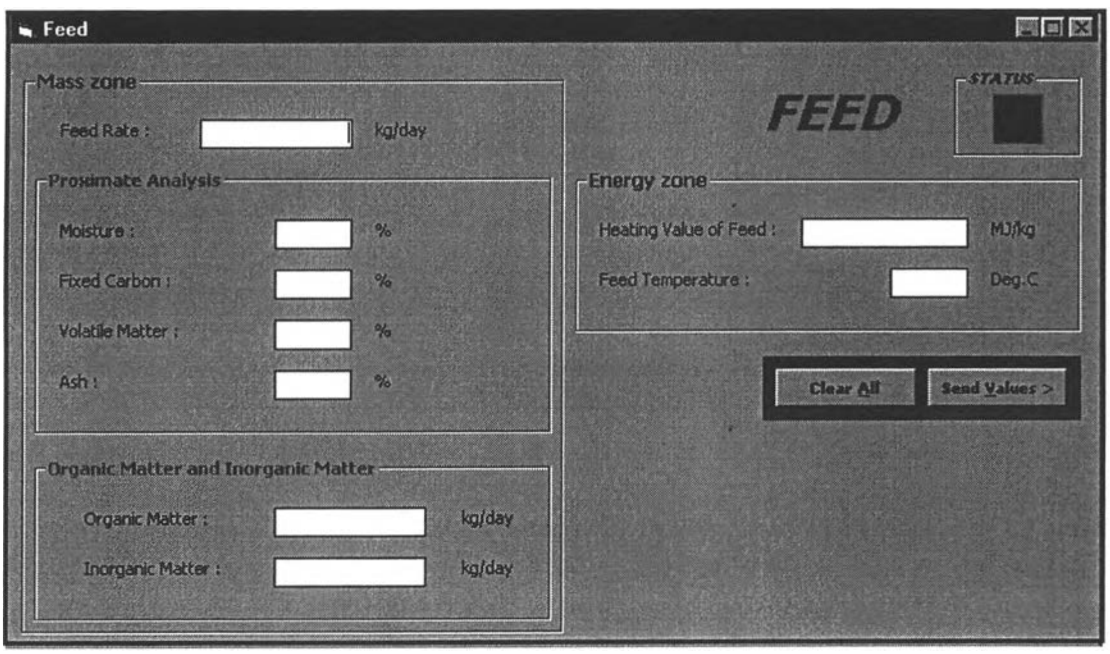

Figure A2 Feed Interface.

On feed interface, user must define all principle pilot scale informations of feed material. Only three parameters that user do not define are ash%, amount of organic matter, and amount of inorganic matter. All of these three parameters, the program is automatically calculated at the same time as user add other feed informations. Other wise, user can easily remove all data after adding completely by only clicking at clear all button.

The status color in status condition box at the right top of interface will be changed from red to green after all data are completely defined,. Clicking at send values demand button sends data. After that, the main interface will be appeared. Now, the next command button on main interface, utility heat, can be used.

Repeat the same steps with utility, uncondensed gases and liquid oil. See Figure A3, A4 ,and A5 for adding important information utility heat, uncondensed gases and liquid oil interfaces, respectively.

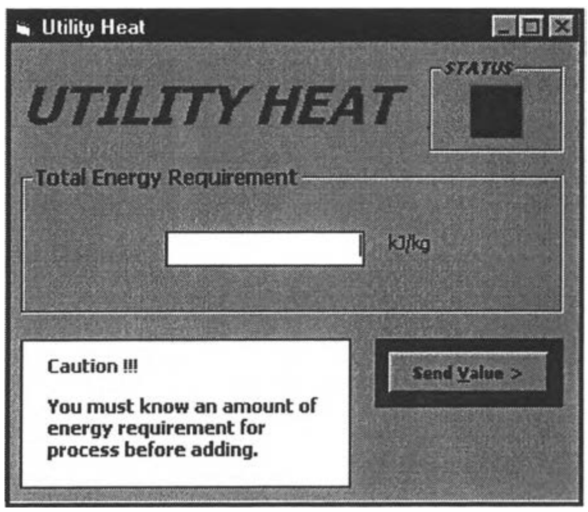

Figure A3. Utility Heat Interface.

The uncondensed gases demand button enable user to go into display gaseous products interface as is seen from Figure A4. Uncondensed gaseous products are referred to gaseous components that are unable to condense into liquid oil product and are released from the gas tube after passing the volatile gases through heat exchanger. If user know the composition (vol%) of uncondensed gaseous products, user can click at "Yes" option. Then, user can link to gaseous product composition data box to add each gas compositions. Gas compositions listed box are, here, showed only selected important gases, which are frequency found at the end of gaseous product tube. In the case of user do not know the gas composition, user can click at "No" option. The program will link to another box appeared only mean heat capacity of uncondensed gases. At here, user have to define heat capacity of uncondensed gases. In addition, user have to put uncondensed gaseous temperature and heating values or potential heat of gases as same as other.

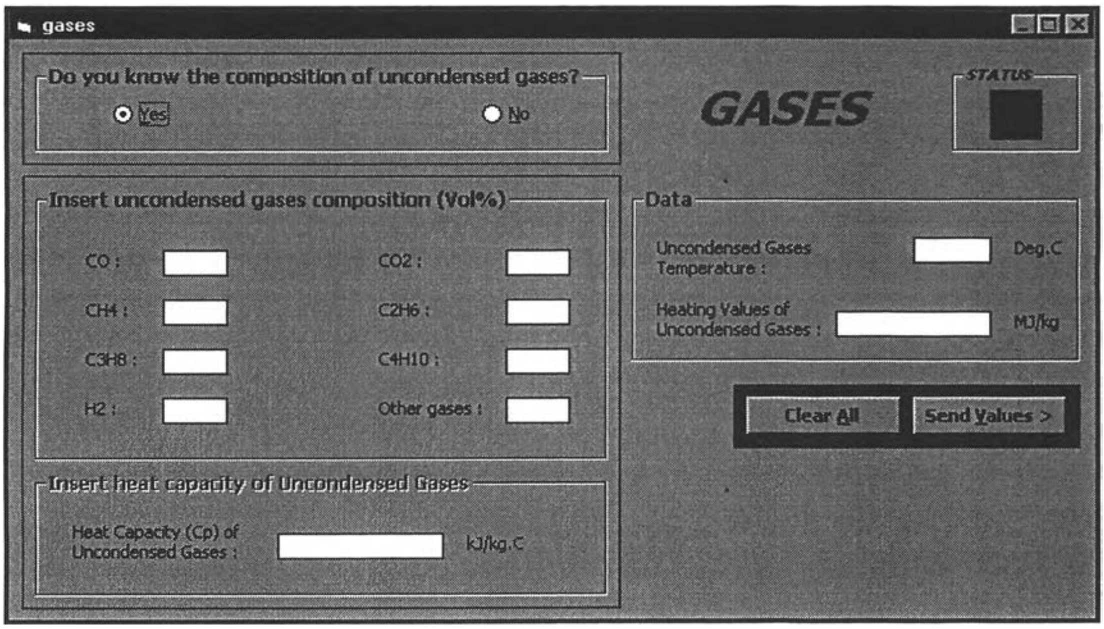

Figure A4 Uncondensed Gases Interface.

Developer would like to recommend to all user that liquid oil is the product obtained from the pyrolyzer after passing the volatile gases through heat exchanger so that liquid oil temperature should have values below pyrolyzer temperature.

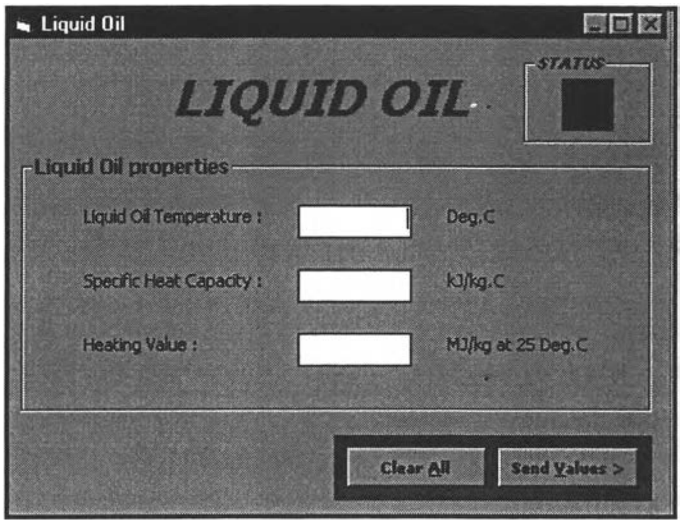

Figure A5 Liquid Oil Interface.

When all data are defined in each information interface, the calculated and cost estimation command button are appeared. User can go to see calculated results by choosing calculated command button and can enhance the cost information content by selecting cost estimation command button.

More over, if user select calculated results command button, the results page will be appeared. Summary of all calculated results are listed in results page as is shown in Figure A6.

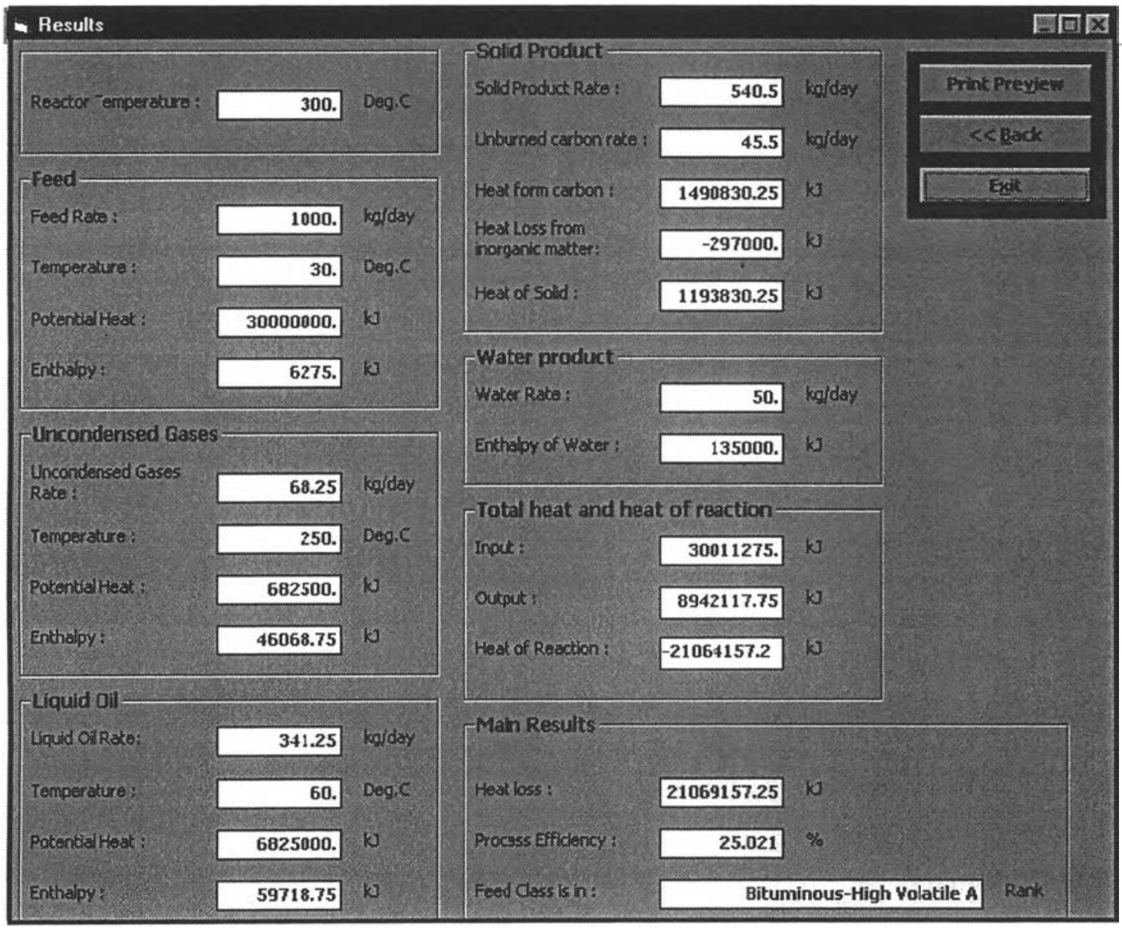

Figure A6 Calculated Results Interface.

MEBPP is able to calculate efficiency and heat of reaction of pyrolyzer when user controled pyrolyzer condition as user defined previously. Program was designed to be able to calculate and reported the rank of feed material compared with coal rank automatically. Further more, when user click print preview command button on results page the user will go to print preview page. The preview page will summarize calculated results. At this point, user can print the summarized all calculated results in table by clicking at “File” command on the left top and then choosing “Print” command. All results, then, are printed out from user’s printer. See Figure A7 for illustration of print results preview interface.

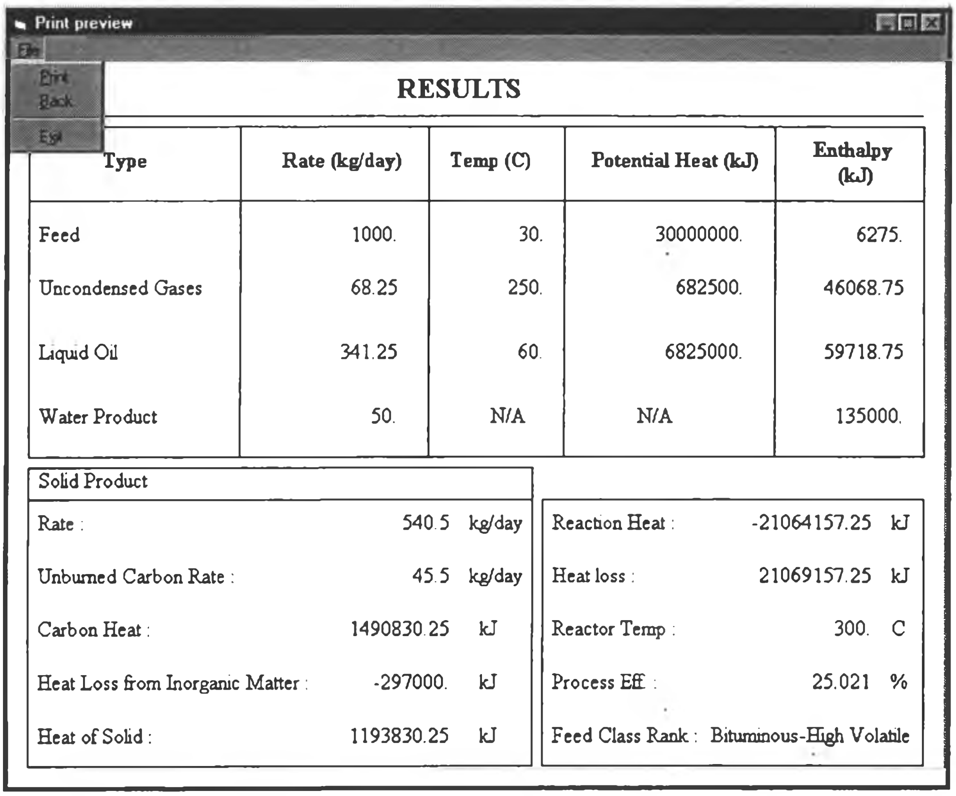

Figure A7 Results Print Preview Interface.

In the case of cost estimation command selection, the program provides selected command groups of input and output data on the cost estimation window, sees Figure A1. This function can overview basic idea in economic. The interface of cost estimation after user click on Go To command button from cost estimation dialog box on main interface is shown in Figure A8. User can select input and output concerning objective by clicking at selection buttons. The selected illustration of input and output streamlines of pyrolysis process will be showed at the middle point of window. The schematic of pyrolysis process is very helpful to select object for calculating cost of products and reactants.

It has two modes of cost estimated calculation. The first mode, if user have referenced energetic current prices of products, user must click at "Yes" option and add referenced prices at referenced energetic prices box. Cost estimation results will be shown in price unit (Baht), see Figure A9. Second mode, if user do not know current prices of referenced energetic product, user must click at "No" option. Then, cost estimated results will also be shown in energy unit (MJ), see Figure A10.

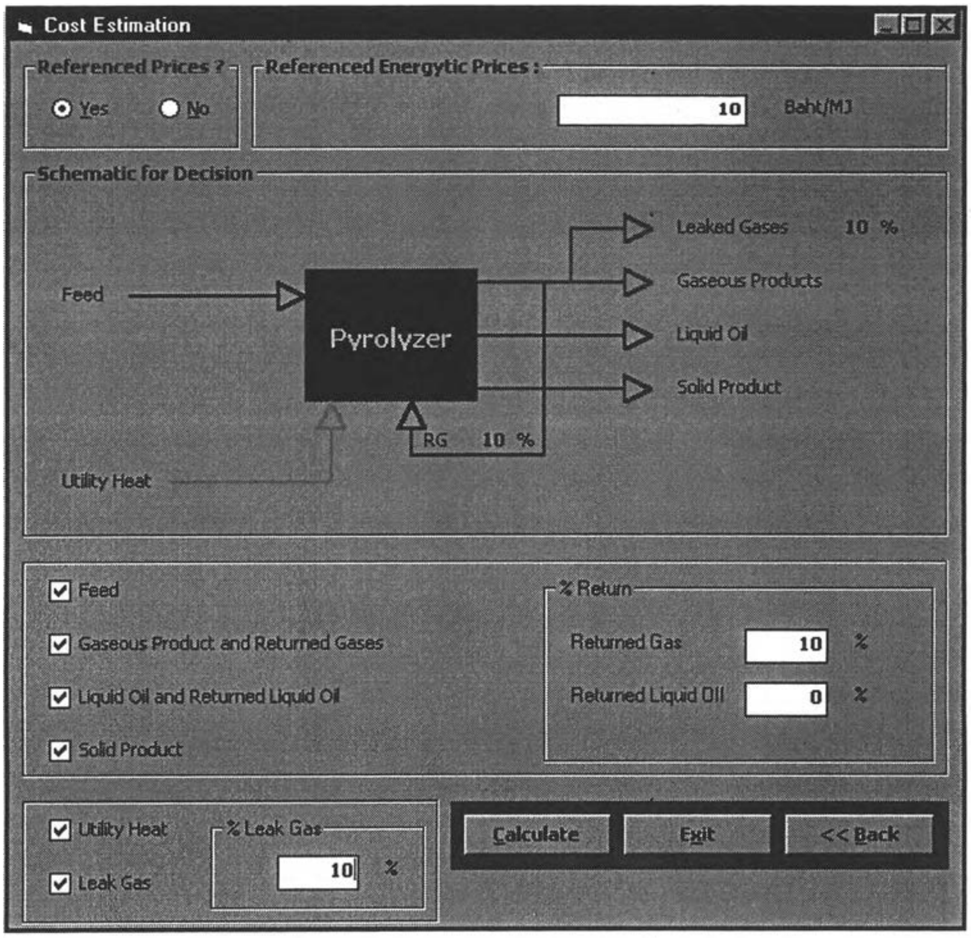

Figure A8 Cost Estimated Calculation Interface.

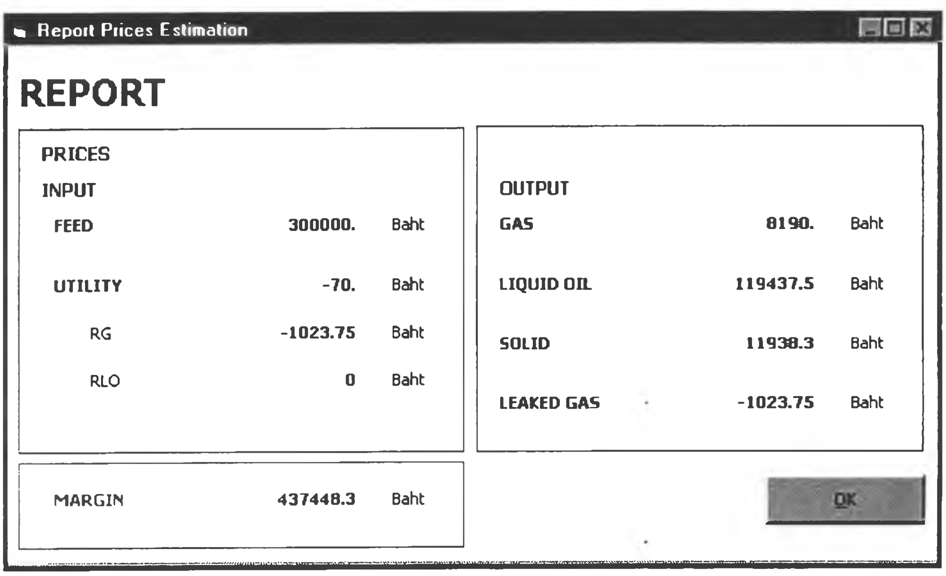

Figure A9 Prices Estimated Report Interface (the first mode).

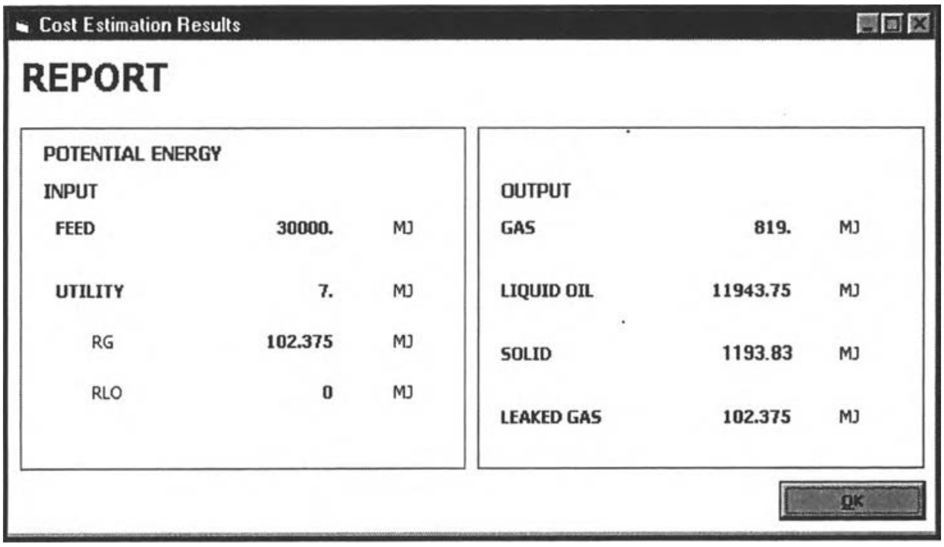

Figure A10 Energy Estimated Report Interface (the second mode).

All of this is basic guide for user to use MEBPP. This analysis is very useful for designing the suitable condition and data needed the process reach to desired operation.

Appendix B Feasibility of using chemicals for recovery valuable components from the API separator sludge

The API separator sludge is the oily sludge came from wastewater treatment site of refinery. Analysis of the API separator sludge composition showed that the API separator sludge has high quantity of light components or free oil around 10 wt%. Instead of disposing the API separator sludge directly, the idea has been created to recover valuable components before feeding to pyrolysis process. The new appropriated method was removing light components by non-ionic surfactant. This section reviewed and presented the basic idea and feasibility of using non-ionic surfactant to remove and to recover the light components from the API separator sludge.

The API separator sludge consists of solid material, water, and oil in emulsion form. The general physical properties are black, odor, and high viscosity. Pyrolysis behaviors of the API separator sludge after removing light components by non-ionic surfactant (non-ionic surfactant/the API separator sludge system) were studied by thermogravimetric analysis (TGA) at controlled heating rate of 5, 10, and $20°C \cdot min^{-1}$. All heating zones were controlled from room temperature to 700°C under N_2 gas (inert atmosphere) at flow rate of $30\ ml \cdot min^{-1}$.

TGA curves of the API separator sludge after removing the light components by non-ionic surfactant were shown in Figure B1, B2, and B3 for heating rate of 5, 10, and $20°C \cdot min^{-1}$, respectively. Weight loss of all non-ionic surfactant/the API separator sludge systems was around 30-40 % decreasing slightly from the API separator sludge (no surfactant) around 10 wt%. The maximum temperature data of the first and second pyrolysis reaction were summarized in Table B1 exhibit a completely different behavior to that the API separator sludge before and after removing light components by non-ionic surfactant. The results showed that, first reaction zone of non-ionic surfactant/the API sludge system, maximum peak temperature were shift to higher temperature compared with the API separator sludge approximately 10, 20, and 50°C for heating rate of 5, 10, and $20°C \cdot min^{-1}$, respectively.

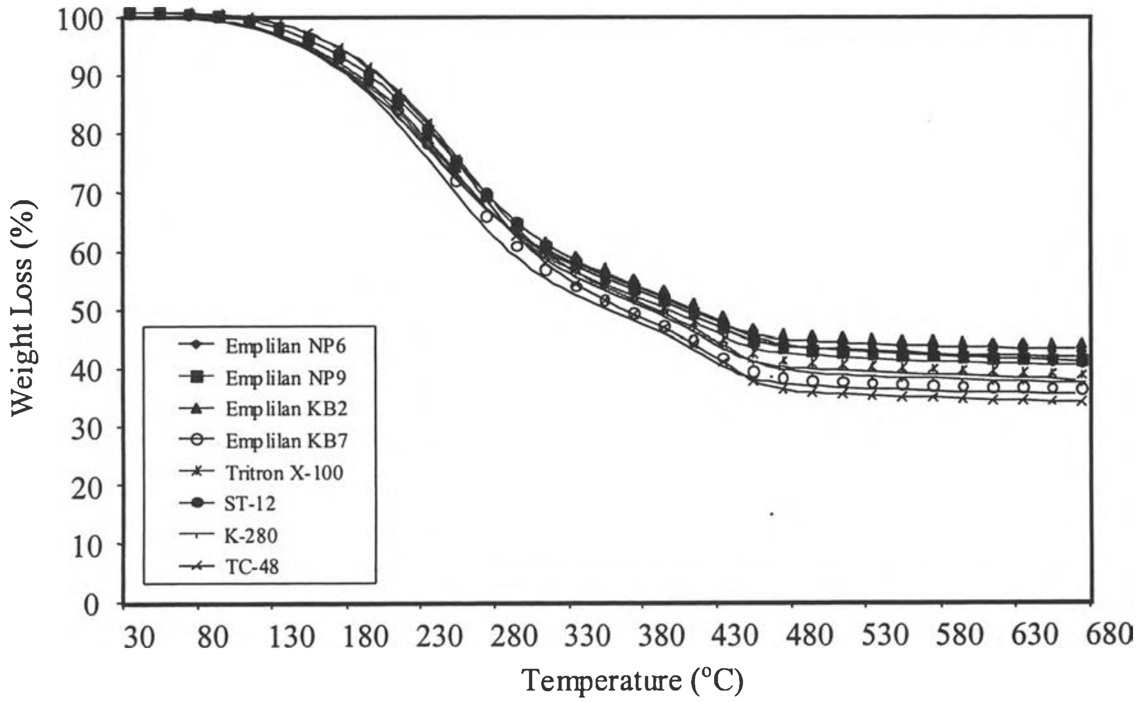

Figure B1 Thermogravimetric Analysis (TGA) curves of API separator sludge after removing light components by non-ionic surfactants at heating rate of 5 °C·min^{-1}.

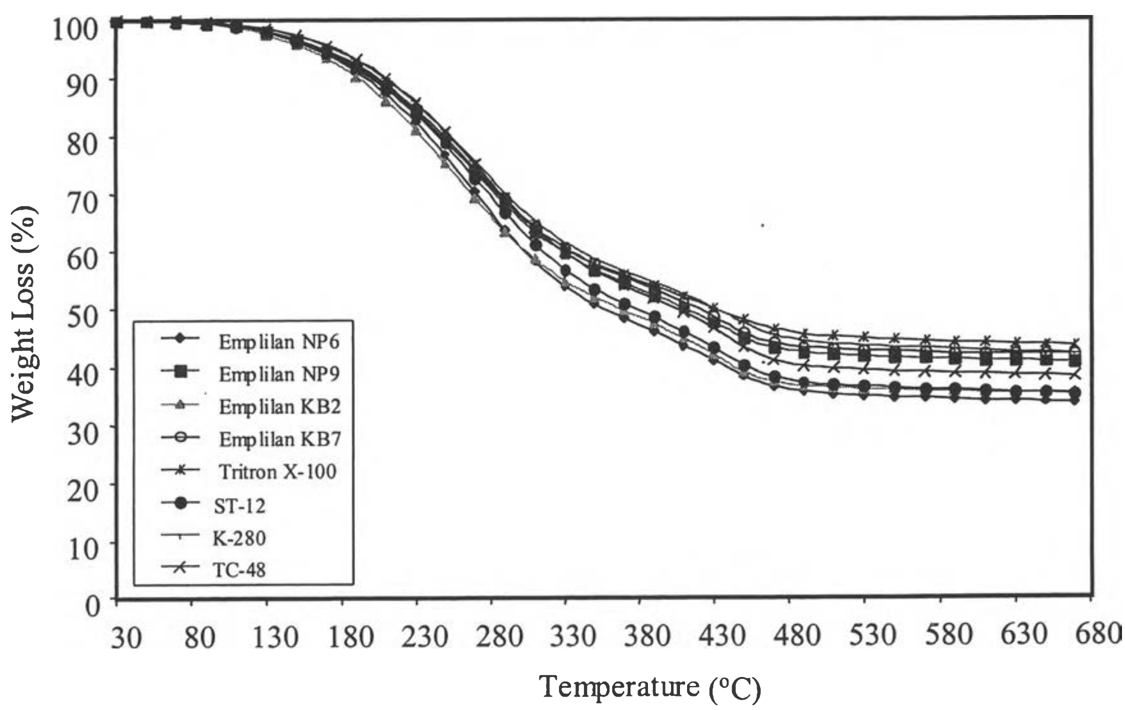

Figure B2 Thermogravimetric Analysis (TGA) curves of API separator sludge after removing light components by non-ionic surfactants at heating rate of 10 °C·min^{-1}.

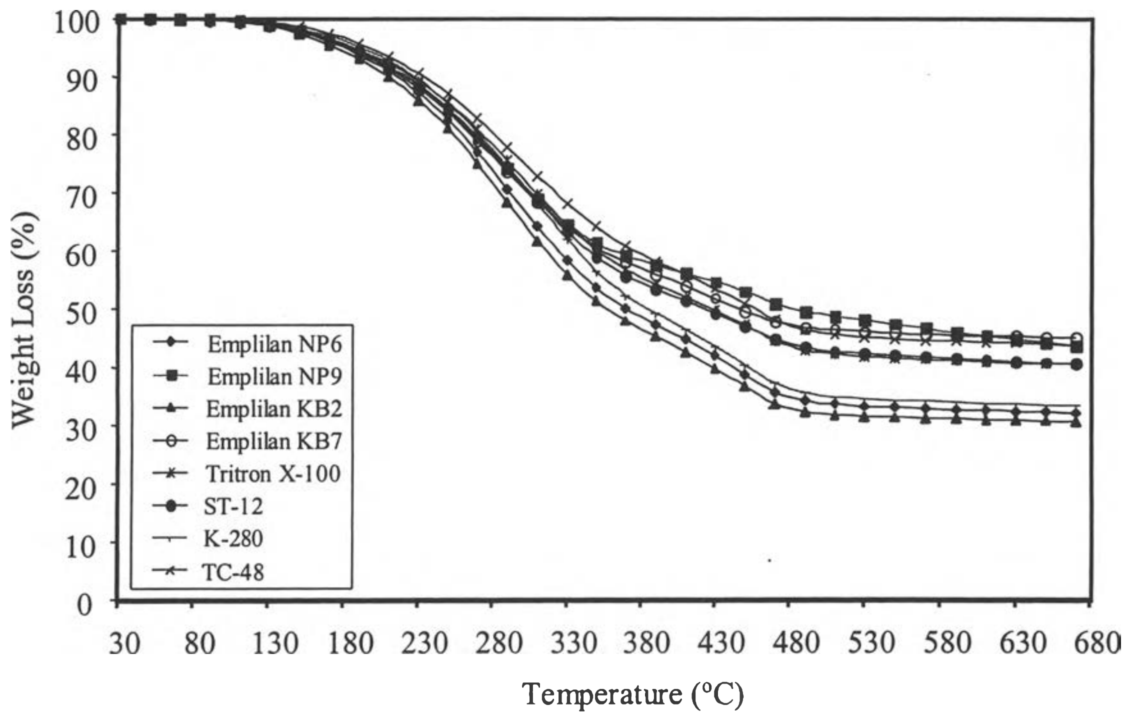

Figure B3 Thermogravimetric Analysis (TGA) curves of API separator sludge after removing light components by non-ionic surfactants at heating rate of $20\,^{\circ}C \cdot min^{-1}$.

All results can be explained that lower light components, which have light molecular weight and low boiling point, were removed from the API separator sludge matter. After removing light components by non-ionic surfactant, heavier molecular weight components and higher boiling point were remained on the API separator sludge matter so that the temperature used for pyrolysis reaction was high.

Instead of cleaning the light components by surfactant only, here, several types of chemicals were also used to study ability for removing light components. For this part, oily sludge model was created and used as the API separator sludge. The oily sludge model was mixture of sand and oil at the ratio of 50 g : 10 ml. Observation of upper phase after using several chemicals for removing oil from oily sludge model was showed in Table B2. From Table B2, Emplilan NP6 and Emplilan KB7 at 3000 ppm have higher ability to remove oil from oily sludge than other types of non-ionic surfactant around 2.5 and 11 wt%, receptively. After comparing non-ionic surfactant with detergent, in contrast, the result showed that efficiency of detergent for removing oil was higher than non-ionic surfactant. Although, the removal percentage of detergent was so high, around 53 wt%, but detergent in the practically was seldom utilized to separate oil from oily sludge because it can emit the toxic material to environment more than other types of non-ionic surfactants. Chemicals such as HCl, NaCl, methanol, and methyl acetate, which had the same concentration at 0.01 M, can also remove oil from oily sludge model, but they were not suitable for separating oil because of higher unit price.

The effects of non-ionic surfactant concentration were also studied. Two types of non-ionic surfactant, Emplilan NP6 and Emplilan KB7, were concerned at several concentrations of 5000, 7500, and 10000 ppm. The experimental conditions and results were summarized in Table B3. From Table B3, the most suitable concentration for separating oil from oily sludge model of both types of non-ionic surfactant was 5000 ppm. Amounts of removed oil were 28 wt% and 48 wt% for Emplilan NP6 and Emplilan KB7, respectively. In addition, Emplilan KB7 has higher efficiency for removing oil than Emplilan NP6 around 1.7 times. However, there were much colloidal sand particles spreading within liquid phase after using Emplilan KB7 while Emplilan NP6 had only less amount of sand particle within liquid phase and high quantity of separated oil released from oily sludge model.

Table B1 The maximum peak temperature of first and second pyrolysis reaction of non-ionic surfactant/API separator sludge system compared with the API separator sludge (no surfactant) at heating rate of 5, 10, and 20°C · min^{-1}

Maximum peak temperature of the first reaction (°C)									
Heating Rate (°C · min^{-1})	Emplilan NP6	Emplilan NP9	Emplilan KB2	Emplilan KB7	Tritron X-100	ST-12	TC-48	K-280	No Surfactant
5	246.0	241.9	242.8	242.2	260.0	254.5	250.0	253.0	230.0
10	269.0	265.9	260.8	271.1	278.5	273.6	274.3	277.7	240.0
20	293.1	291.2	291.5	288.8	297.3	298.7	297.0	308.2	250.0
Maximum peak temperature of the second reaction (°C)									
Heating Rate (°C · min^{-1})	Emplilan NP6	Emplilan NP9	Emplilan KB2	Emplilan KB7	Tritron X-100	ST-12	TC-48	K-280	No Surfactant
5	424.9	424.6	423.5	424.9	427.3	425.6	430.8	424.1	405.0
10	434.4	437.0	437.7	436.5	438.1	431.3	441.6	441.2	420.0
20	450.8	462.3	449.2	438.5	453.1	446.7	456.7	448.6	460.0

Table B2 Observation of upper phase after using several chemicals for removing oil from oily sludge model

Chemicals	Liquid phase Type A[a]	Liquid phase Type B[b]		Liquid phase Type C[c]	Amount of removed oil (ml)	% Oil removal
		High	Low			
0.01 M HCl	-	√	-	-	0.70	7.00
0.01 M NaOH	-	√	-	-	0.80	8.00
0.01 M CH_3OH	√	-	-	-	1.20	12.00
0.01 M CH_3COOCH_3	-	√	-	-	0.60	6.00
5 g/50 ml Detergent	-	-	√	-	5.30	53.00
3000 ppm NP6	√	-	-	-	0.40	4.00
3000 ppm NP9	√	-	-	-	<0.01	N/A
3000 ppm NP10	√	-	-	-	0.25	2.50
3000 ppm KB2	-	-	-	√	<0.01	N/A
3000 ppm KB7	-	-	-	√	<0.01	N/A
3000 ppm Alken 910E2X	-	-	√	-	1.10	11.00

[a]Only small oil droplet spreading

[b]Mixture of small sand particles and oil droplet spreading

[c]No small oil droplet spreading

Table B3 Experimental condition and percentage of removed oil from oily sludge model (the ratio of sand to oil was 50 g to 10 ml) by Emplilan NP6 and Emplilan KB7 at various concentrations

Non-ionic surfactant	Liquid phase Type A[a]	Liquid phase Type B[b]		Liquid phase type C[c]	Amount of removed oil (ml)	% Oil removal
		High	Low			
Emplilan NP6						
3000 ppm	√	-	-	-	0.40	4.00
5000 ppm	√	-	-	-	2.80	28.00
7500 ppm	√	-	-	-	1.70	17.00
10000 ppm	√	-	-	-	1.60	16.00
Emplilan KB7						
3000 ppm	-	-	√	-	1.10	11.00
5000 ppm	-	-	√	-	4.80	48.00
7500 ppm	-	-	√	-	4.50	45.00
10000 ppm	-	-	√	-	4.00	40.00

[a]Only small oil droplet spreading
[b]Mixture of small sand particles and oil droplet spreading
[c]No small oil droplet spreading

The removal of light component from the API separator sludge by using non-ionic surfactant was studied as an alternative to conventional treatment method. The results showed the different ability for removing light components of different chemicals.

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1. Punnaruttanakun, P., Meeyoo, V., Kalambaheti, C., Rangsunvigit, P., Rirksomboon, T., and Kitiyanan, B. (2003). Reuse of an API Separator Sludge, National Convention and Grand Exhibition on Solid Waste and Toilet Technologies, 13-15th March, Bangkok, Thailand.
2. Thipkhunthod, P., Punnaruttanakun, P., Meeyoo, C., Rangsunvigit, P., and Rirksomboon, T. (2002). Pyrolysis: an Alternative to Solid Waste Treatment, Annual Conference of The Thai Institute of Chemical Engineering and Applied Chemistry (TiChE), 8-9th November, Bangkok, Thailand.

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