CHAPTER IV
RESULTS AND DISCUSSION

4.1 Data Collection

The general properties of the components were collected from literature such as handbooks (for example, Perry's Chemical Engineers' Handbook), textbooks (Biorefineries-Industrial Process and Products, Volume 2), the internet (ScienceDirect, Wikipedia), and mainly from existing biodiesel plants, and the PRO/II database with rapeseed oil as raw material, or ICAS's prediction tool (Table 4.2).

In this study, the type of raw material, palm oil, used in this plant has the composition as listed in Table 4.1.

Table 4.1 Palm oil composition in Thailand

Palm Oils Composition in Thailand				
	C12	C14	C16	C18	C20
Name		Myristate	Palmitrate	Stearate	
%wt	0.2	1.2	62	35	1.6

Source: Veerasuwan Co., Ltd (Thailand).

Table 4.2 The general properties of components used in the process

	General Properties of Components														
Properties	Triglyceride			Methyl Palmitrate			Methyl Stearate			Mono_Glyceride			Di_Glyceride		
	ProII	Ref.	ProPred ICAS	ProII	Ref.	ProPred ICAS	ProII	Ref.	ProPred ICAS	ProII	Ref.	ProPred	ProII	Ref.	ProPred ICAS
Tm (K)			419.85		303.15	287.17	292.12	291.15	282.56			474.90			659.27
Tb (K)			852.22			586.77	609.13	716.15	608.44			685.35			785.22
Tc (K)			1039.12			760.30	789.37		782.24			1138.77			1922.41
Pc (bar)			7.27			14.18	13.23		13.04			10.84			4.25
Vc (cm3/mol)			3289.67			1009.18	1125.50		1127.21			1269.50			2284.50
Zc			0.28			0.23	0.23		0.23			0.15			0.06
Gf (297K) kJ/mol			-482.12			-222.71	-49.50		-201.27			-460.51			-482.50
Hf (298K) kJ/mol			-2191.96			-714.39	-527.61		-754.10			-1103.79			-1640.36
d (25 C) (kg/liter)		0.92					0.90	0.88							

PRO/II: data collected from the database of the PRO/II software.

Ref.: data referenced from several sources, such as handbooks, internet, textbooks, etc.

ProPred: data collected from ICAS's prediction tool.

Since the prediction properties of components in existing processes can be obtained through ICAS; it is necessary to build the database in PRO/II.

4.2 Data Analysis (ICAS work)

4.2.1 Constructing the Chemical Structures of Process Components in ICAS

By using the ICAS prediction tool, the approximate temperature–dependant property predictions of various components in the process required by PRO/II can be found.

In this project, the structures of five components that are not in the database of PRO/II were built. These structures are given below (Figure 4.1-4.5).
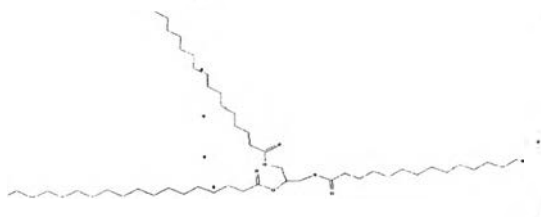
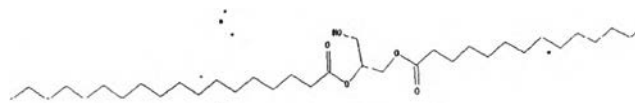**Figure 4.1** Structure of Triglyceride: $C_{53}H_{102}O_6$

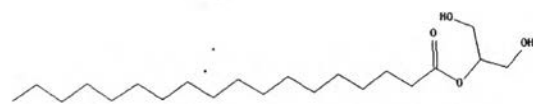**Figure 4.2** Structure of Diglyceride: $C_{37}H_{72}O_5$

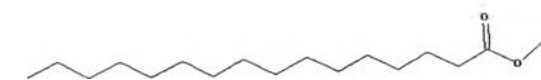**Figure 4.3** Structure of Monoglyceride: $C_{37}H_{72}O_5$

Figure 4.4 Structure of Methyl Palmitrate: $C_{17}H_{34}O_2$.
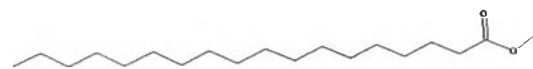
Figure 4.5 Structure of Methyl Stearate: $C_{19}H_{38}O_2$.

4.2.2 Constructing the Database in PRO/II by Using the Results Collected from ICAS

After constructing the structures and running the ICAS software, the thermophysical properties, such as fixed properties or temperature dependence (correlation coefficients of vapor pressure, enthalpy, enthalpy of vaporization, density, viscosity, thermal conductivity) can be found and listed below.

1. Vapor Pressure

Definition and units: Vapor pressure is the pressure of a vapor in equilibrium with its non-vapor phase. The higher the vapor pressure of a material at a given temperature, the lower the boiling point. At the boiling temperature, the vapor pressure becomes sufficient to overcome atmospheric pressure and lift the liquid to form bubbles inside the bulk of the substance. Vapor pressure is one of the most important basic thermodynamic properties affecting liquids and vapors. All the correlation coefficients and equation forms in the range of working temperature are given in Table 4.3 for the different compounds present in the process. The most common unit for vapor pressure is the torr. 1 torr = 1 mm Hg.

Table 4.3 Vapor pressure correlation of components, from ICAS

Vapor pressure correlations from ICAS (bar)							
Compounds	C_1	C_2	C_3	C_4	C_5	Min T(K)	Max T(K)	Equation
Triglyceride								$\ln(\text{Pvp}) = C_1 + \dfrac{C_2}{C_3+T} + C_4T + C_5T^2$
	6.0	-2832.7	-162.4	0.0	0.0	400	700	
Methyl Stearate								$\ln(\text{Pvp}) = C_1 + \dfrac{C_2}{C_3+T} + C_4T + C_5T^2$
	-82.8	-4773.8	23.2	0.0	2.0	330	650	
Methyl Palmitrate								$\ln(\text{Pvp}) = C_1 + \dfrac{C_2}{C_3+T} + C_4T + C_5T^2$
	115.6	-13762.0	-13.6	0.0	2.0	330	650	
Monoglyceride								$\ln(\text{Pvp}) = C_1 + \dfrac{C_2}{C_3+T} + C_4T + C_5T^2$
	7.9	-3802.4	-153.6	0.0	0.0	450	700	
Diglyceride								$\ln(\text{Pvp}) = C_1 + \dfrac{C_2}{C_3+T} + C_4T + C_5T^2$
	7.9	-2568.5	-270.4	0.0	0.0	600	700	

Comments for Table 4.3

➢ The data are not available from literature, so the vapor pressure of components has to be predicted.

➢ The properties are predicted using the ICAS tool. Based on these predictions, the effect of increase of temperature on vapor pressure (Figure 4.6) is shown to be that the vapor pressure of all components increases with increase of temperature.
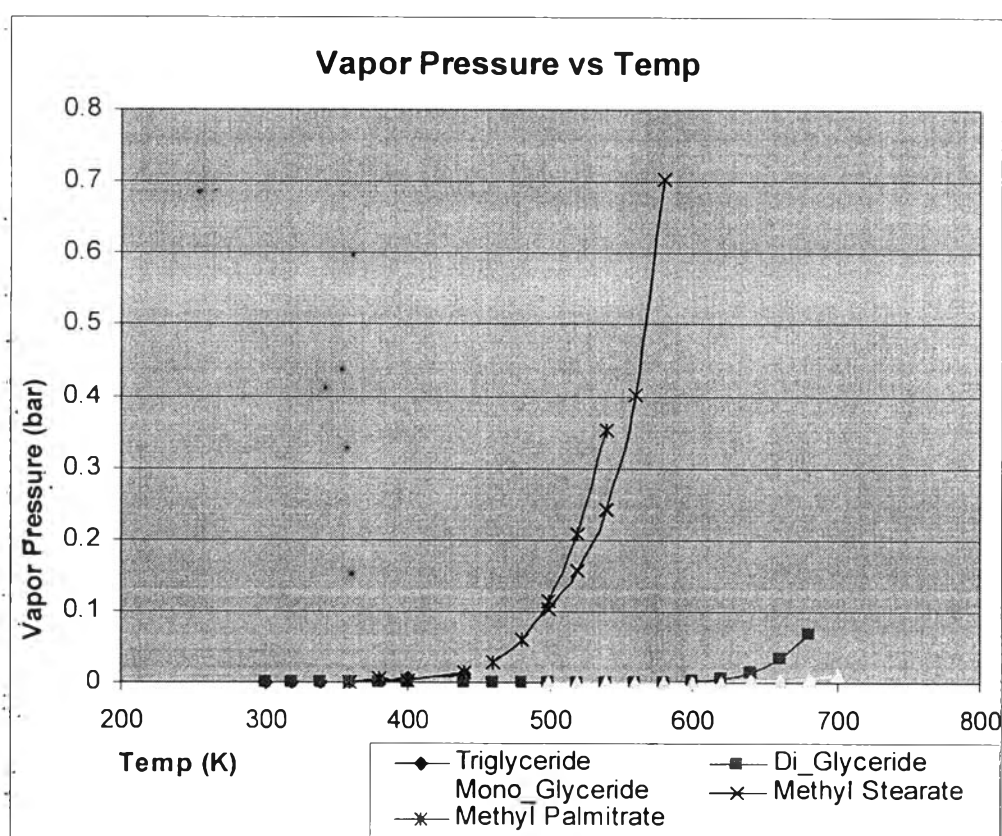

Figure 4.6 Vapor pressure of components as a function of temperature by the ICAS's prediction tool.

2. Enthalpy of Vaporization

Definition and units: The enthalpy of vaporization is defined as the difference between the enthalpies per unit mole or mass of saturated vapor and liquid of a pure component. It is measured at the boiling point of the component, although tabulated values are usually corrected to 298K and the correction usually is small.

The most popular units used are kJ/mol, although kJ/kg, kcal/mol, cal/g, and Btu/lb, among others, are also possible.

Table 4.4 Enthalpy of vaporization correlations of components, from ICAS

Enthalpy of Vaporization from ICAS (KJ/mol)							
Compounds	C_1	C_2	C_3	C_4	Min T(K)	Max T(K)	Equation
Triglyceride	152.67	-0.13	0.00	0.00	330	800	$\mathrm{Pr}\,op = \sum_{i=1}^{n} C_i T^{i-1}$
Methyl Stearate	145.98	1.21	-1.23	0.53	312	650	$\ln(\mathrm{Pr}op) = C_1(1-Tr)^X$ Where $X = C_2 + C_3 Tr + C_4 Tr^2$
Methyl Palmitrate	101.93	0.60	-0.13	-0.06	300	600	$\mathrm{Pr}\,op = \sum_{i=1}^{n} C_i T^{i-1}$
Monoglyceride	194.29	-0.18	0.00	0.00	450	700	$\mathrm{Pr}\,op = \sum_{i=1}^{n} C_i T^{i-1}$
Diglyceride	439.73	-1.12	0.00	0.00	300	700	$\mathrm{Pr}\,op = \sum_{i=1}^{n} C_i T^{i-1}$

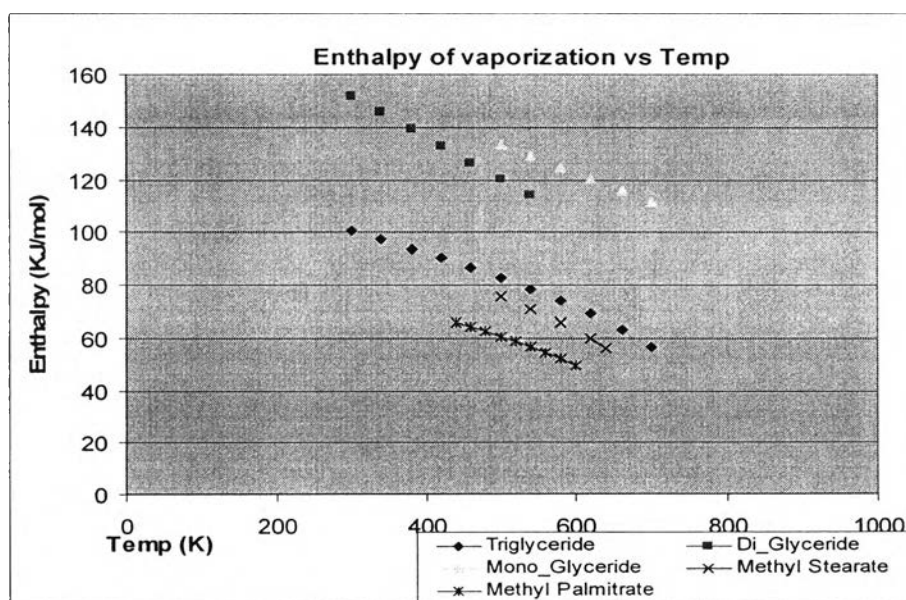Figure 4.7 shows that the enthalpy of vaporization of all the components decreases with increase of temperature.

Figure 4.7 Enthalpy of vaporization of components as a function of temperature by the ICAS prediction tool.

3. Ideal Gas Enthalpy

Definition: Ideal Gas Enthapy is a thermodynamic function of a system, equivalent to the sum of the internal energy of the system and the product of its volume multiplied by the pressure exerted on it by its surroundings:

$$H = U + pV \tag{4.1}$$

where

H = enthalpy, U = internal energy, p = pressure, V = volume

Enthalpy is a state function, i.e. its value is the same for a given set of system conditions regardless of the path taken to reach the set of conditions. Enthalpy is evaluated relative to a reference state, usually the ideal gas state.

Vapor enthalpy is the enthalpy of the vapor portion of a system and is usually determined by expressions derived from the equations of state.

·In this project, the enthalpy of vapor and liquid could not be derived directly from ICAS, so it is calculated by equation (4.2). The enthalpy of an ideal gas at any temperature, T is:

$$h_T - h_{273} = \int_{T_{273}}^{T} C_p \, dT \tag{4.2}$$

where

T_0: is a reference temperature of 25°C,

C_p: Heat capacity, collected from ICAS.

The situation is simplest if specific heat is constant, that is, no temperature dependence. It is then possible to integrate the above equation directly to:

$$h_T - h_{273} = C_p (T - 273) \tag{4.3}$$

So the enthalpy of ideal gas at any temperature can be easily calculated from the result of ICAS. After getting the enthalpy, it can be put in Excel and find the correlation coefficient and equation forms. The result obtained can then be transferred to PRO/II.

Ideal gas correlation coefficients and the equation forms used for different components with a range of temperatures in the process are shown in Table 4.5.

Table 4.5 Ideal gas enthalpy correlation coefficients and equation forms of components, from ICAS

Ideal Gas Enthalpy of Components from ICAS (kJ/kgmol)						
Compounds	C_1	C_2	C_3	C_4	Min T(K)	Max T(K)	Equation
Triglyceride	-1e+6	3353.7	0.00	0.00	330	800	$\Pr op = \sum_{i=1}^{n} C_i T^{i-1}$
Methyl Stearate	-350262	1003.8	0.00	0.00	312	650	$\Pr op = \sum_{i=1}^{n} C_i T^{i-1}$
Methyl Palmitrate	-218006	720.2	0.00	0.00	300	600	$\Pr op = \sum_{i=1}^{n} C_i T^{i-1}$
Monoglyceride	-417122	1179.5	0.00	0.00	450	700	$\Pr op = \sum_{i=1}^{n} C_i T^{i-1}$
Diglyceride	853619	2228.1	0.00	0.00	300	700	$\Pr op = \sum_{i=1}^{n} C_i T^{i-1}$

Figure 4.8 is an example of how to find the correlation coefficients and equation form of ideal gas enthalpy in Excel. It shows that with the increase in temperature, ideal gas enthalpy also increases as a result.
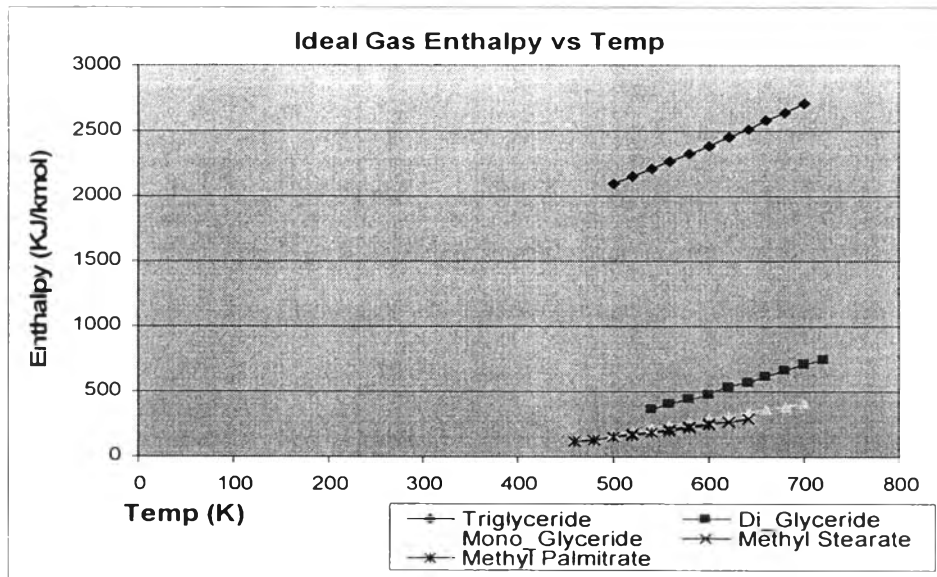
Figure 4.8 Ideal gas enthalpy components as a function of temperature by the ICAS prediction tool.

4. Liquid Enthalpy

Repeating the above procedure with ideal gas enthalpy, the liquid enthalpy correlation coefficients and the equation forms used for different components can be obtained. The results are shown in Table 4.6.

Table 4.6 Liquid enthalpy correlation coefficients and equation forms of components, from ICAS

Liquid Enthalpy of Components from ICAS (kJ/kgmol)						
Compounds	C_1	C_2	C_3	C_4	Min T(K)	Max T(K)	Equation
Triglyceride	5.53e+5	3353.7	0.00	0.00	330	800	$\Pr op = \sum_{i=1}^{n} C_i T^{i-1}$
Methyl Stearate	-2.77e+5	941.5	0.00	0.00	312	650	$\Pr op = \sum_{i=1}^{n} C_i T^{i-1}$
Methyl Palmitrate	-2.32e+5	779.70	0.00	0.00	300	600	$\Pr op = \sum_{i=1}^{n} C_i T^{i-1}$
Monoglyceride	-3.24e+5	1099.1	0.00	0.00	450	700	$\Pr op = \sum_{i=1}^{n} C_i T^{i-1}$
Diglyceride	1.69e+5	-1408.8	2.88	0.00	300	700	$\Pr op = \sum_{i=1}^{n} C_i T^{i-1}$

5. Density

Definition and units: Density is mass, *m,* per unit volume, *V.*

In SI Units: ρ (rho) is the density of the substance, measured in kg.m^{-3}

Density prediction with temperature range by using correlations is shown in the Table 4.7.

Table 4.7 Liquid density correlation coefficients and equation forms of components, from ICAS

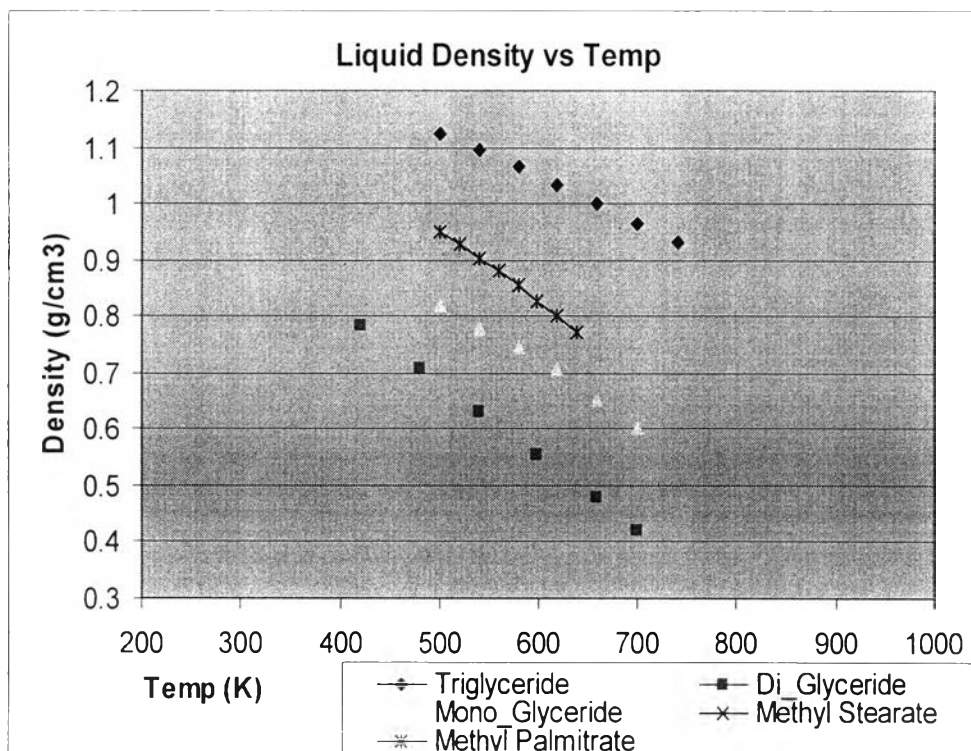| Liquid Density of Components from ICAS (g/cm^3)							
Compounds	C_1	C_2	C_3	C_4	Min T(K)	Max T(K)	Equation
Triglyceride	5.53e+5	3353.7	0.0	0.0	330	800	$\mathrm{Pr}\ op = C_1 / C_2^X$ Where $X = 1 + (1 - T / C_3)^{C_4}$
Methyl Stearate	-2.77e+5	941.5	0.0	0.0	312	650	$\mathrm{Pr}\ op = C_1 / C_2^X$ Where $X = 1 + (1 - T / C_3)^{C_4}$
Methyl Palmitrate	-2.32e+5	779.70	0.0	0.0	300	600	$\mathrm{Pr}\ op = C_1 / C_2^X$ Where $X = 1 + (1 - T / C_3)^{C_4}$
Monoglyceride	-3.24e+5	1099.1	0.0	0.0	450	700	$\mathrm{Pr}\ op = C_1 / C_2^X$ Where $X = 1 + (1 - T / C_3)^{C_4}$
Diglyceride	1.69e+5	-1408.8	2.9	0.0	300	700	$\mathrm{Pr}\ op = C_1 / C_2^X$ Where $X = 1 + (1 - T / C_3)^{C_4}$

Figure 4.9 Liquid density of components as a function of temperature by the ICAS prediction tool.

Figure 4.9 shows that with an increase in temperature, the liquid density will be decreased as a result, and the curves of Methyl Stearate and Methyl Palmitrate are overlapped. This means that the density of Methyl Stearate and Methyl Palmitrate are the same in this temperature range.

6. Viscosity

Definition and Units: Viscosity is a measure of the resistance of a fluid to deform under shear stress. It is commonly perceived as "thickness", or resistance to flow. Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. Thus, water and methanol are "thin", having a lower viscosity, while Palm oil and Methyl Stearate are "thick" having a higher viscosity. All real fluids (except superfluids) have some resistance to shear stress, but a fluid which has no resistance to shear stress is known as an ideal fluid.

The absolute viscosity (μ) is also known as the *dynamic viscosity*, and is often shortened to simply *viscosity*. The equation can be expressed in terms of shear stress; $\tau = F/A = \mu(u/y)$. The rate of shear deformation is u / y and can also be written as a shear velocity, du/dy. Hence, through this method, the relation between the shear stress and the velocity gradient can be obtained.

The SI system unit of dynamic viscosity is the pascal-second (Pa·s), which is identical to $1 \; k{\cdot}m^{-1}{\cdot}s^{-1}$. If a fluid with a viscosity of one Pa·s is placed between two plates, and one plate is pushed sideways with a shear stress of one pascal, it moves a distance equal to the thickness of the layer between the plates in one second.

The centimetre-gram-second system (CGS) physical unit for dynamic viscosity is the *poise*. It is more commonly expressed, particularly in ASTM standards, as *centipoise* (cP).

$$1 \; P = 1 \; g{\cdot}cm^{-1}{\cdot}s^{-1}$$

The relation between Poise and Pascal-second is:

$$10 \; P = 1 \; kg{\cdot}m^{-1}{\cdot}s^{-1} = 1 \; Pa{\cdot}s$$

$$1 \; cP = 0.001 \; Pa{\cdot}s = 1 \; mPa{\cdot}s$$

For vapor phase

Table 4.8 Vapor viscosity correlation coefficients and equation forms of components, from ICAS

Vapor Viscosity of Components from ICAS (Cp)						
Compounds	C_1	C_2	C_3	C_4	Min T(K)	Max T(K)	Equation
Triglyceride	-14.3	6883.2	0.0	0.0	600	900	$\ln(\text{Pro}p) = C_1 + \dfrac{C_2}{T} + C_3 \ln T + C_4 T^2$
Methyl Stearate	-6.2	2489.2	0.0	0.0	600	650	$\ln(\text{Pro}p) = C_1 + \dfrac{C_2}{T} + C_3 \ln T + C_4 T^2$
Methyl Palmitrate	-5.9	2301.0	0.0	0.0	500	700	$\ln(\text{Pro}p) = C_1 + \dfrac{C_2}{T} + C_3 \ln T + C_4 T^2$
Monoglyceride	-13.6	6153.9	0.0	0.0	600	900	$\ln(\text{Pro}p) = C_1 + \dfrac{C_2}{T} + C_3 \ln T + C_4 T^2$
Diglyceride	-13.8	6517.3	0.0	0.0	600	900	$\ln(\text{Pro}p) = C_1 + \dfrac{C_2}{T} + C_3 \ln T + C_4 T^2$

For liquid phase

Table 4.9 Liquid viscosity correlation coefficients and equation forms of components, from ICAS

Liquid Viscosity of Components from ICAS (Cp)						
Compounds	C_1	C_2	C_3	C_4	Min T(K)	Max T(K)	Equation
Triglyceride	-14.30	6883.15	0.00	0.00	400	500	$\ln(\text{P}v\text{p}) = C_1 + \dfrac{C_2}{T} + C_3 \ln T + C_4 T^2$
Methyl Stearate	-6.18	2489.19	0.00	0.00	300	650	$\ln(\text{P}v\text{p}) = C_1 + \dfrac{C_2}{T} + C_3 \ln T + C_4 T^2$
Methyl Palmitrate	-5.88	2300.8	0.00	0.00	300	600	$\ln(\text{P}v\text{p}) = C_1 + \dfrac{C_2}{T} + C_3 \ln T + C_4 T^2$
Monoglyceride	-13.61	6154.19	0.00	0.00	300	600	$\ln(\text{P}v\text{p}) = C_1 + \dfrac{C_2}{T} + C_3 \ln T + C_4 T^2$
Diglyceride	-13.84	6502.46	0.00	0.00	600	700	$\ln(\text{P}v\text{p}) = C_1 + \dfrac{C_2}{T} + C_3 \ln T + C_4 T^2$

It is easily realized that the equations for liquid viscosity and vapor viscosity are the same.
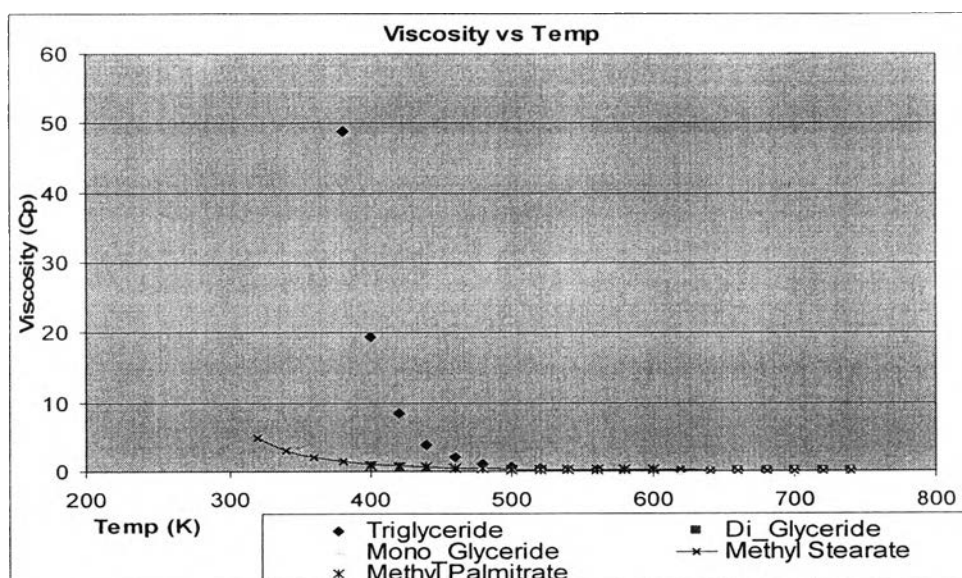

Figure 4.10 Viscosity of components as a function of temperature by the ICAS prediction tool.

Figure 4.10 shows that the viscosity of components decreases very quickly at melting point.

7. Thermal Conductivity

Definition and Units: Thermal conductivity (k) is the intensive property of a material that indicates its ability to conduct heat. It is used primarily in Fourier's Law for heat conduction.

The most popular units are SI, W/(m*K) and Imperial units, (btu*ft)/(hr*(ft^2)*F). To convert between the two, the relation 1 (btu*ft)/(hr*(ft^2)*F) = 1.73 W/(m*K) is used.

The thermal conductivity of various components present in the biodiesel plant is predicted by the correlation coefficients and equation form from the ICAS prediction tool (shown in Table 4.10 below).

For liquid phase

Table 4.10 Liquid conductivity correlation coefficients and equation forms of components, from ICAS

Liquid Conductivity of Components from ICAS (W/m*K)						
Compounds	C_1	C_2	C_3	C_4	Min T(K)	Max T(K)	Equation
Triglyceride	0.1	0.9	-0.7	0.5	400	500	$Prop=C_1(1-Tr)^{(C_2+C_3Tr+C_4Tr^2)}$
Methyl Stearate	0.2	0.0	0.0	0.0	312	650	$Prop=\sum_{i=1}^{n} C_1 T^{-1}$
Methyl Palmitrate	0.1	0.0	0.0	0.0	300	600	$Prop=\sum_{i=1}^{n} C_1 T^{-1}$
Monoglyceride	0.2	0.9	-0.7	0.4	312	600	$Prop=C_1(1-Tr)^{(C_2+C_3Tr+C_4Tr^2)}$
Diglyceride	1e+4	112.29	-336.3	313.4	400	700	$Prop=C_1(1-Tr)^{(C_2+C_3Tr+C_4Tr^2)}$
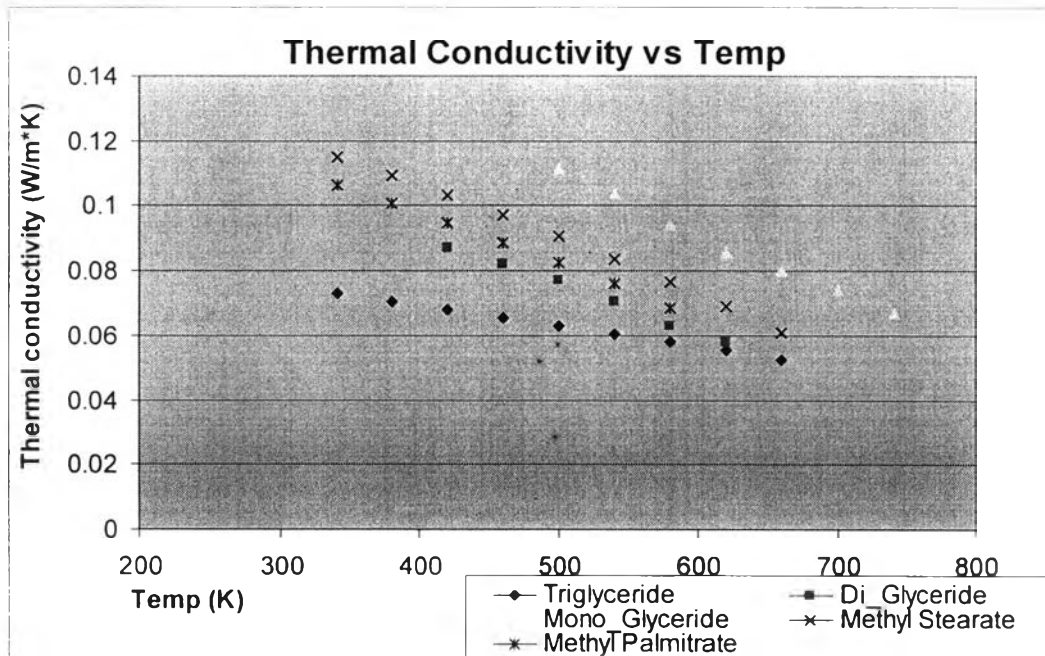
Figure 4.11 Thermal conductivity of components as a function of temperature by the ICAS prediction tool.

Figure 4.11 shows that with the increase in temperature, thermal conductivity will be decreased as a result.

8. Surface Tension

Definition and units: Surface Tension is the force occurring on a liquid-gas interface resulting in a thin film on the surface. It can be quantified as the force acting on the interface per unit length of the film at equilibrium state, which also equals the energy required to increase the surface area of the liquid by a unit amount (the surface energy). This force tends to minimize the area of the surface, thus explaining why drops and bubbles are spherical.

SI units of surface tension: N/m

Because ICAS does not support to find the correlation coefficients and equation form from, so it has been left out in PRO/II.

4.3 Data Processing (PRO/II Work)

4.3.1 Mass Calculation for Process

4.3.1.1 Step 01

The database of components is built for Triglyceride, Diglyceride, Monoglyceride, and Methyl Esters in PRO/II. All of the thermal-physical properties are filled manually with the data collected from ICAS, including fixed properties (molecular weight, density, critical properties, heat of formation, etc.) or temperature dependent (vapor pressure, enthalpy, density, viscosity, etc.) (Figure 4.12).

Figure 4.12 Captured screen of the PRO/II component properties window.

4.3.1.2 Step 02: Building the Simplest Process to Match Mass Balance

In this step, the simplest process flowsheet of the biodiesel plant is built (Figure 4.13) to calculate the mass balance of process.
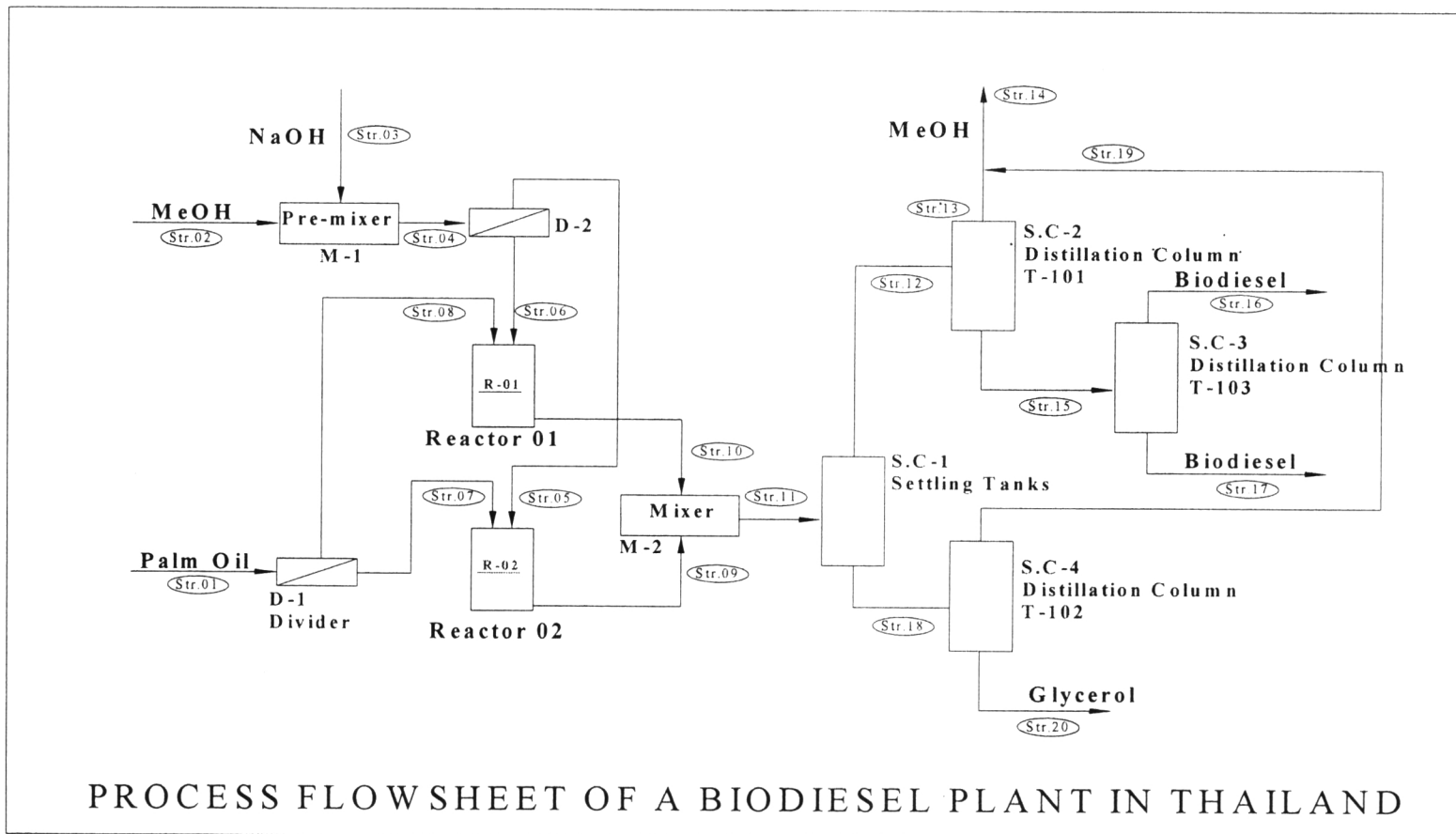
Figure 4.13 Process flowsheet of a biodiesel plant in Thailand.

Str.01: Stream01   D-1: Divider 01   M-1: Mixer 01   R-01: Reactor 01   SC-1: Stream Calculator 01

The real reactions occur in the reactors.

The transesterification of palm oils with methanol has long been the preferred method for producing biodiesel. During the reaction, triglyceride reacts with methanol in the presence of a catalyst (NaOH) to produce methyl esters and glycerol. The overall reaction scheme is shown below:

$$
\begin{array}{l}
H_2C-OCOR' \\
HC-OCOR'' \\
H_2C-OCOR''
\end{array}
+ 3\ ROH
\xrightleftharpoons{catalyst}
\begin{array}{l}
ROCOR' \\
+ \\
ROCOR'' \\
+ \\
ROCOR''
\end{array}
+
\begin{array}{l}
H_2C-OH \\
HC-OH \\
H_2C-OH
\end{array}
$$

triglyceride   alcohol   mixture of alkyl   glycerol
                                                         esters
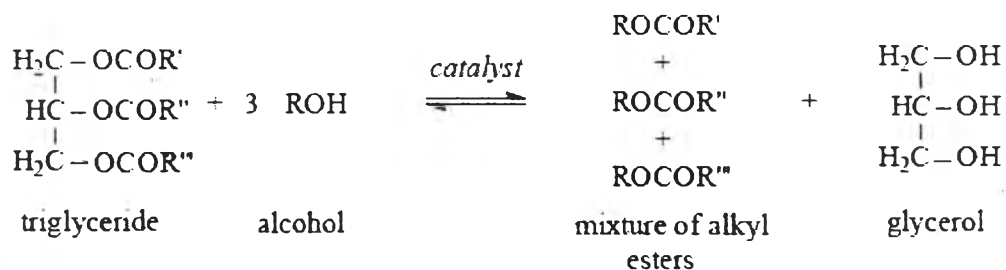
where

Triglyceride: the main composition of palm oils

Alcohol: methanol

Mixture of alkyl esters: biodiesel

The overall reaction is normally a sequence of three consecutive steps, which are reversible reactions. In the first step, diglycerides are obtained from triglycerides, monoglycerides are produced from diglycerides, and in the last step, glycerol is obtained from monoglycerides. In all of these reactions, esters are produced

Triglycerides + Methanol $\longrightarrow$ Methyl Esters + Diglycerides

Diglycerides + Methanol $\longrightarrow$ Methyl Esters + Monoglycerides

Monoglycerides + Methanol $\longrightarrow$ Methyl Esters + Glycerol
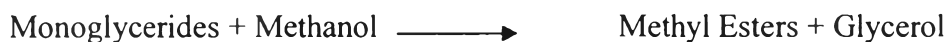
The stream outlets from the reactors contain: Methyl Esters, Glycerol, and Glycerides (monoglyceride, diglyceride, and triglyceride).

Average Stoichiometry = Triglyceride : Methanol = 1:3. However, an excess of methanol is usually more appropriate to improve the reaction towards the desired

product. In this present study, to get reaction conversion of about 95%, the molar ratio of methanol : triglyceride is 5:1.

A summary of the operation parameters of units in the process is shown in Table 4.11.

Table 4.11 Operation parameters of each unit in biodiesel process

Table of Operations	
Reactors 01 and 02	Stoichiometer Coefficient = Triglyceride : Methanol = 1:3 Key Component = Triglyceride Conversion = 95%
Divider 01	Divide fraction (in mass) S7:S8 = 1:1
Divider 02	Divide fraction (in mass) S5:S6 = 1:1
Mixer 01	
Mixer 02	
Stream Calculator 01 (Settling Tanks)	Recovery factor of Triglyceride = 90% (Top) Recovery factor of Methanol = 80% (Top) Recovery factor of Methyl Esters = 98% (Top) Recovery factor of Glycerine = 99% (Bottom) Recovery factor of Diglyceride = 90% (Top) Recovery factor of Monoglyceride = 90% (Top)
Stream Calculator 03 (Distillation Column T-103)	Recovery factor of Triglyceride = 90% (Bottom) Recovery factor of Methanol = 99% (Top) Recovery factor of Methyl Esters = 90% (Top) Recovery factor of Glycerine = 99% (Top) Recovery factor of Diglyceride = 90% (Bottom) Recovery factor of Monoglyceride = 90% (Bottom)
Stream Calculator 02 (Distillation Column T-101)	Recovery factor of Triglyceride = 100% (Bottom) Recovery factor of Methanol = 99% (Top) Recovery factor of Methyl Esters = 100% (Bottom) Recovery factor of Glycerine = 100% (Bottom) Recovery factor of Diglyceride = 100% (Bottom) Recovery factor of Monoglyceride = 100% (Bottom)
Stream Calculator 04 (Distillation Column T-102)	Recovery factor of Triglyceride = 99% (Bottom) Recovery factor of Methanol = 99% (Top) Recovery factor of Methyl Esters = 99% (Bottom) Recovery factor of Glycerine = 99% (Bottom) Recovery factor of Diglyceride = 99% (Bottom) Recovery factor of Monoyceride = 99% (Bottom)

The calculation of the mass balance for each stream in the process, which is shown in Table 4.12, will be compared with the data collected from the real biodiesel plant (Table 4.13 below).

Table 4.12 Mass balance table by PRO/II

Information Table of Flowsheet Process (in Batch)

Streams / Variables	1	2	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Triglyceride kmol/h	8.60	0.00	0.00	0.00	0.00	4.30	4.30	0.22	0.22	0.43	0.30	0.00	0.00	0.30	0.03	0.27	0.13	0.00	0.13
Methanol kmol/h	0.00	41.09	41.09	20.55	20.55	0.00	0.00	8.49	8.49	16.97	13.58	13.58	16.97	0.00	0.00	0.00	3.39	3.39	0.00
Methyl Ester's kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	12.06	12.06	24.12	23.64	0.00	0.00	23.64	22.93	0.71	0.48	0.00	0.48
Glycerol kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.96	3.96	7.91	0.08	0.00	0.00	0.08	0.08	0.00	7.83	0.00	7.83
Monoglyceride kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.06	0.13	0.09	0.00	0.00	0.09	0.06	0.03	0.04	0.00	0.04
Diglyceride kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.06	0.13	0.09	0.00	0.00	0.09	0.06	0.03	0.04	0.00	0.04
Phase	L	L	L	L	L	L	L	L	L	L	L	V	V	L	V	L	L	V	L
Temp.(C)	55.00	60.00	60.00	60.00	60.00	55.00	55.00	60.00	60.00	60.00									
Pres.(atm)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00									
Density (kg/l)	0.92	0.79	0.79	0.79	0.79	0.92	0.92	0.90	0.90	0.90									
Mass (kg/h)	7666.60	1316.70	1316.70	658.35	658.35	3833.30	3833.30	4491.65	4491.65	8983.30									
Flowrate Liters/h	8333.30	1666.70	1666.70	833.35	833.35	4166.65	4166.65	4990.72	4990.72	9981.44									

Table 4.13 Mass balance table by data collected from the biodiesel plant

Plant data - Information Table of Flowsheet Process (in Batch)																			
Streams / Variables	1	2	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Triglyceride kmol/h	8.60	0.00	0.00	0.00	0.00	4.30	4.30	0.44	0.44	0.88	0.31	0.00	0.00	0.313	0.09	0.23	0.58	0.00	0.58
Methanol kmol/h	0.00	41.09	41.09	20.55	20.55	0.00	0.00	8.62	8.62	17.24	13.79	13.79	17.24	0.00	0.00	0.00	3.45	3.45	0.00
Methyl Esters kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	11.90	11.90	23.80	23.32	0.00	0.00	23.32	13.99	9.33	0.48	0.00	0.48
Glycerol kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.93	3.93	7.85	0.08	0.00	0.00	0.08	0.08	0.00	7.77	0.00	7.77
Monoglyceride kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	*NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Diglyceride kmol/h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Phase	L	L	L	L	L	L	L	L	L	L	L	V	V	L	V	L	L	V	L
Temp.(C)	55.00	60.00	60.00	60.00	60.00	55.00	55.00	60.00	60.00	60.00									
Pres.(atm)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00									
Density (kg/l)	0.92	0.79	0.79	0.79	0.79	0.92	0.92	0.90	0.90	0.90									
Mass (kg/h)	7666.60	1316.70	1316.70	658.35	658.35	3833.30	3833.30	4491.65	4491.65	8983.30									
Flowrate Liters/h	8333.30	1666.70	1666.70	833.35	833.35	4166.65	4166.65	4990.72	4990.72	9981.44									

*NA: Not available data

The mass balance of each stream in the process flowsheets (Tables 4.12) is close to ones obtained from plant data (Table 4.13) i.e. the maximum difference is approximately 2%. While the compositions in streams 12 through 20 have a larger variation (5%).

After obtaining the mass balance by simple calculation, reactor design by PRO/II is performed. Since PRO/II allows only one reaction per reactor, three reactors must be defined in order to construct three reactions (Figure 4.14).
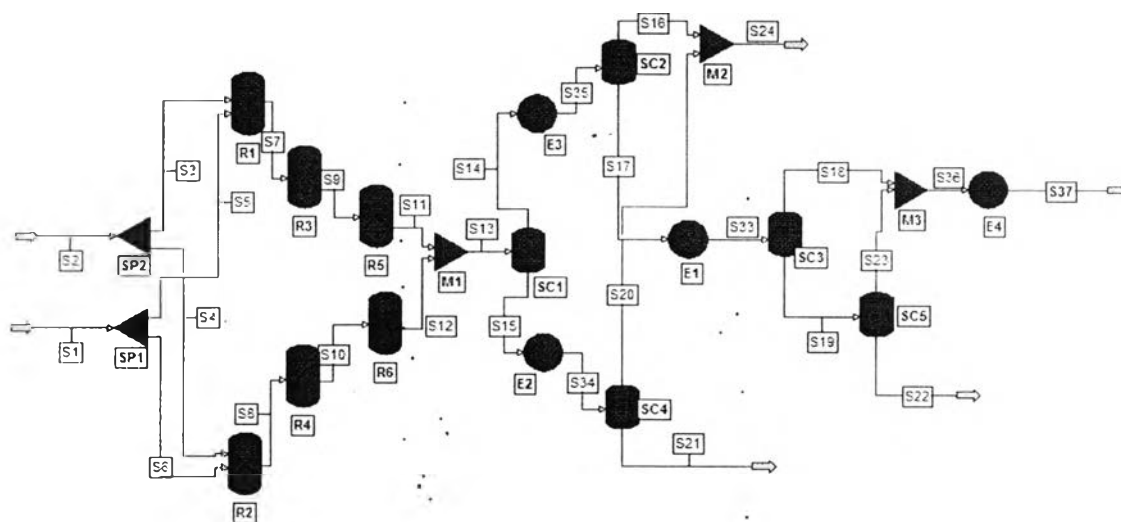

Figure 4.14 The process flowsheet of a biodiesel plant in Thailand.

4.3.2 Energy Balance for the Process

Temperature and pressure are set for each stream. The PRO/II simulation result is located in Appendix A.

4.4 General Heat Analysis for Each Unit in the Process

4.4.1 The Energy Intensive Unit in Process

In this section, the energy balance of each unit is calculated and shown in the Table 4.14.

Table 4.14 The simple analysis for heat addition or removal of each unit

Heat Analysis for Each Unit in Process					
1	2	3	4	5	6
Unit (j)	Qj (MMBTU/hr)	Real Unit	Name in company flowsheet	Heat addition or removal	How to add or remove
R1	0.090	Reactor	Reactor: R-101A	Add	Hot oil
R2	0.090	Reactor	Reactor: R-101B	Add	Hot oil
SC1	-0.095	Flash tanks	D - 103A-L 14 Tanks	Remove	Cooling water
SC2&E1	2.870	Vacuum Distillation Column	T - 101	Add	Hot oil
SC3,SC5&E3	2.830	Vacuum Distillation Column	T - 103	Add	Hot oil
SC4&E2	0.670	Vacuum Distillation Column	T - 102	Add	Hot oil
E4	-0.630	Heat Exchanger	E-108A/B	Remove	Cooling water
E5	-2.800	Heat Exchanger	E-105A-E	Remove	Cooling water
E6	-0.860	Heat Exchanger		Remove	Cooling water
Total Heat Add	6.550				
Total Heat Removal	-4.385				

> The column 1 of the table (4.14) shows the symbol of operation units in the process.

> The column 2 was heat demand/supply calculated by the following equation:

$$Qj = \Sigma \Delta H_{stream\ out} - \Sigma \Delta H_{stream\ in} \qquad (4.5)$$

where

> $\Delta H_{stream\ out}$ and $\Delta H_{stream\ in}$ of each unit are collected from the PROII file.

> Columns 3 and 4 are description of units.

> Columns 5 and 6 describe whether to add or remove heat for the units and the heat addition or removal medium.

From the information in this table, the unit that is necessary to add or remove heat will be identified. However, a stream calculator was used instead of a distillation column. In principle, the stream calculator just shows the overall energy supply for the unit; it does not show the detail for the reboiler and condenser.

The comparison between energy consumption of the simulated result and the real plant is shown in Table 4.15. This is really an important comparison, because it is a good way to check the prediction properties predicted by the ICAS tool in the previous section.

Table 4.15 The difference between calculating utilities and real plant utilities

Heat Analysis for Each Unit in Process							
1	2a	2b	2c	3	4	5	6
Unit (j)	Qj (MMBTU/hr) PROII	Qj (MMBTU/hr) Plant	Q loss in the plant (MMBTU/hr)	Real Unit	Name in company flowsheet	Heat addition or removal	Heating/Cooling medium
R1	0.090	0.120	0.030	Reactor	Reactor: R-101A	Add	Hot oil
R2	0.090	0.120	0.030	Reactor	Reactor: R-101B	Add	Hot oil
SC1	-0.095	0.000		Flash tanks	D - 103A-L 14 Tanks	Remove	Cooling water
SC2&E1	2.870	3.240	0.370	Vacuum Distillation Column	T - 101	Add	Hot oil
SC3,SC5&E3	2.830	3.479	0.649	Vacuum Distillation Column	T - 103	Add	Hot oil
SC4&E2	0.670	0.817	0.147	Vacuum Distillation Column	T - 102	Add	Hot oil
E4	-0.630	-0.788	-0.158	Heat Exchanger	E-108A/B	Remove	Cooling water
E5	-2.800	-3.250	-0.350	Heat Exchanger	E-105A-E	Remove	Cooling water
E6	-0.860	-1.012	-0.152	Heat Exchanger		Remove	Cooling water
Total Heat Add	6.550	7.776	1.226				
Total Heat Removal	-4.385	-5.050	-0.660				

Data in column 2a and 2b shown that the utilities duty (MMBTU/hr) from the PRO/II result (existing plant) is higher than the data collected from plant because the heat loss is around 20-30% in this biodiesel process. In this present study, it found the most energy consuming units are T-103 and T-101. However, the detailed analysis of the energy consumption of distillation columns T-103 and T-101 will be shown in the next section.

The direct cost and percentage cost of each unit in the process is calculated and shown in Table 4.16.

Table 4.16 The direct cost and percentage cost analysis of each unit in the process

						Heat Analysis for Each Unit in Process						
1	2	3	4	5	6	7	8	9	10	11	12	13
										Heating/Cooling Medium		
Unit (j)	Qj (MMBTU/hr)	Real Unit	Name in company flowsheet	Heat add or removal	How to add or remove	Details	Effitiency Heat Transfer	Average Cp(BTU/kg.K)	Price (USD/Kg)	Flowrate (Kg/hr)	Price (USD) of Heating/Cooling	Percentage of Cost
R1	0.090	Reactor	Reactor: R-101A	Add	Hot oil	Cool Stream: 30^0C up to 64^0C Hot Stream: 180^0C down to 100^0C	100%	2.23	1.1	504.98	555.48	1.89
R2	0.090	Reactor	Reactor: R-101B	Add	Hot oil	Cool Stream: 30^0C up to 64^0C Hot Stream: 180^0C down to 100^0C	100%	2.23	1.1	504.98	555.48	1.89
SC1	0.000	Flash tanks	D - 103A-L 14 Tanks	No	No							
SC2&E1	2.870	Vacuum Distillation Column	T - 101	Add	Hot oil	Cool Stream: 60^0C up to 117^0C Hot Stream: 290^0C down to 120^0C	100%	2.56	1.82	6595.70	12004.17	40.87
SC3,SC5&E3	2.830	Vacuum Distillation Column	T - 103	Add	Hot oil	Cool Stream:117^0C up to 274^0C Hot Stream: 290^0C down to 140^0C	100%	2.56	1.82	7370.94	13415.12	45.68
SC4&E2	0.670	Vacuum Distillation Column	T - 102	Add	Hot oil	Ethanol recovery Hot Stream: 290^0C down to 120^0C	100%	2.56	1.82	1539.76	2802.37	9.54
E4	-0.630	Heat Exchanger	E-108A/B	Remove	Cooling water	Cooling down methanol Hot Stream: 89^0C down to 60^0C Cool Stream: 30^0C up to 60^0C	100%	3.97	0.001	5286.85	5.29	0.02
E5	-2.800	Heat Exchanger	E-105A-E	Remove	Cooling water	Cooling down top product Hot Stream: 250^0C down to 60^0C Cool Stream: 30^0C up to 60^0C	100%	3.97	0.001	23497.11	23.50	0.08
E6	-0.860	Heat Exchanger	E-105A-E	Remove	Cooling water	Cooling down bottom product Hot Stream: 275^0C down to 60^0C Cool Stream: 30^0C up to 60^0C	100%	3.97	0.001	7216.97	7.22	0.02
Total Heat Add	6.550									16516.37		
Total Heat Removal	-4.290									36000.93		
Total cost											29368.62	100.00

In Table 4.16 some other columns were added to calculate the operating cost for each unit:

> Column 8 is the efficiency of heat transfer; in this section, we chose efficiency equal to 100% (no energy loss) for all cases.

> Column 9 shows the average heat capacity of hot oil or cooling water in temperature working rank.

> Column 10 shows the price in USD of a liter of hot oil or cooling water used in the process.

> Column 11 shows the flow rate request for units; it can be calculated from the following equation:

$$F_{oil \; or \; water} = Q_{add \; or \; remove}/(C_p * \Delta T) \tag{4.6}$$

> Column 12 shows the estimated direct cost for each units; it can be calculated from the following equation:

$$Cost = Flow \; rate * Price \tag{4.7}$$

> Column 13 shows the percentage of direct cost on each unit to find the operation that costs the most in terms of percentage of cost. The next step is to analyze and optimize for this unit first, then try for the second highest, and so on.

It is easy to realize from column 12 that distillation columns T-101 and T-103 are the most energy consuming units in the process. They took above 40% of direct cost of whole units. The rigorous designs of T-101 and T-103 are required for improving the energy efficiency and product specification.

4.4.2 Specific Heat Analysis for T-103 and T-101

In this section, the target of project will be set for analyzing the most costly operating units in terms of percentage of total cost.

Table 4.16 shows that

> Distillation column T-103 (including preheat E3) took about 46% of the direct cost.

> Distillation column T-101 (including preheat E1) took about 41% of the direct cost.

The total cost for the these two units are about 87% of the direct cost. The operating cost of two columns can be reduced about 10% for both column or 8.7% of total operating cost by using Optimizer in PRO/II.

4.4.2.1   Analyzing Design and Cost of T-103

By analyzing the condenser and reboiler heat duty in the distillation column, as shown below (Figure 4.15), the various sources of heat necessary for the column can be analyzed.
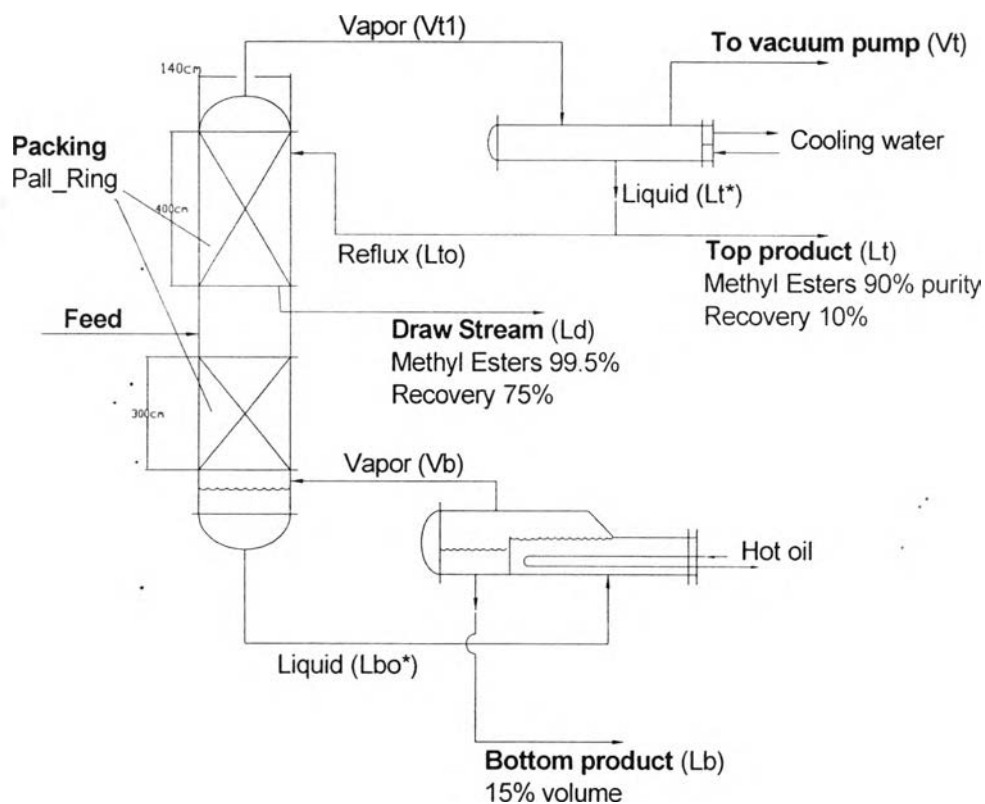

Figure 4.15 Material-balance diagram for continuous vacuum column T-103.

After that, the heat duty for each section as a function of reflux ratio of column can be calculated, as shown in Table 4.17. (See Appendix B for the detailed calculation).

Table 4.17 Relationship between reflux ratios, heat duty of condenser and reboiler-T103

Relationship between reflux ratios-T103				
Reflux Ratio (L/D) Condenser	4	6	8	10
Heat condensation (MMBTU/hr)	1.69	2.37	3.04	3.72
Heat vaporization (MMBTU/hr)	0.00	0.54	1.21	1.89
Reflux Ratio Reboiler	0.00	2.28	5.16	8.03

4.4.2.2   Analyzing Design and Cost of T-101

Similar calculation as for T-101.

Table 4.18 Relationship between reflux ratios, heat duty of condenser, reboiler-T101

Relationship between reflux ratios-T101				
Reflux Ratio (L/D) Condenser	0	2	4	6
Heat condensation (MMBTU/hr)	0.46	1.39	2.32	3.25
Heat vaporization (MMBTU/hr)	1.41	2.34	3.27	4.20
Reflux Ratio Reboiler	0.06	0.10	0.13	0.17

4.5 Rigorous Design and Optimization for T-103 and T-101

4.5.1 Distillation Column T-103

The target of this work is satisfaction of the objective functions:

1.   Set the product recovery (85%) for distillation column T-103, this number was optimized in laboratory.

2.   Minimize the utilities costs supply for this column by using Optimizer in PRO/II

In the first step, the specification of product was setup for the column T-103 in PRO/II to get the product recovery (B100) is 85%. PRO/II result gave the design parameters to compare with the base case in the table below (Table 4.19):

Hot utility cost: 16.3 USD/10^6 BTU/hr

Cold utility cost: 5 USD/10^6 BTU/hr

Table 4.19 Data comparison between base case and result from PRO/II (Case02) of T-103

Base Case (T-103) Case 01	Modified Case (T-103) by PRO/II Case 02
Diameter = 0.8 m	Diameter = 1.6 m
Temperature at bottom = 260°C	Temperature at bottom = 275°C
Reflux = 2	Reflux = 2
% Recovery = 70%	% Recovery = 85%
Q_H = 2.15MMBTU/hr Q_C = 0.42MMBTU/hr	Q_H = 2.2MMBTU/hr Q_C = 3.8MMBTU/hr
Total utility costs = 37.15 USD/hr	Total utility costs = 54.86 USD/hr

The result shows that the existing column could not get the optimal product recovery is its diameter too small. The modified case suggested that the diameter should be increased. However, the utilities in this design (Case 02) are not optimum. So the second necessary step is to optimize the utility cost supply for the column. In this step, feed position and reflux ratio will be varied to get the minimum utilities cost by Optimizer in PRO/II.

The Objective function is:

Minimize $\{Q_h, (MMBTU/hr) = F(feed\ position;\ reflux\ ratio)\}$

The design data comparison of distillation column T-103 between the PRO/II simulated result (Case 02) and the optimized result (Case 03) is shown in Table 4.20.

Table 4.20 Data comparison between real plant and result from PRO/II (Alternative 1) of T-103

Modified Case (T-103) by PRO/II	Modified Case (T03) by PRO/II
Case 02	*Case 03*
Diameter = 1.6 m	Diameter = 1.4 m
Temperature at bottom = 275°C	Temperature at bottom = 275°C
Reflux = 2	Reflux = 0.5
% Recovery = 85%	% Recovery = 85%
Q_H = 2.2MMBTU/hr Q_C = 3.8MMBTU/hr	Q_H = 0.56MMBTU/hr Q_C = 2.30MMBTU/hr
Total utility costs = 54.86 USD/hr	Total utility costs = 20.63 USD/hr

In this process, water is used to cooling the hot streams. So the cost for this utility is very cheap. This is the reason why although the total utilities of modified case higher than base, the utilities cost of modified case lower than base case because of 1.59 MMBTU/hr of hot utility can be reduced or 16.6 USD/hr (100,000 USD/year equivalent).

The simulation results from PRO/II of the existing distillation column T-103 are listed in Table 4.21.

Table 4.21 The specification sheet for distillation column T-103

SPECIFICATION SHEET FOR COLUMN T-103					
DISTILLATION COLUMN					
Identification: Item Distillation Column Item No. T-103 No. require 1					
Function: Separate Methyl Esters from the mixture of Glycerol, Methanol, Triglyceride, Monoglyceride, Diglyceride					
Operation: Continuous					
Materials handled:	Feed	Liquid Dist.	Bottoms	Side Draw	Vapor Dist.
Rate (kmol/hr):	24.50	2.00	3.50	19.00	0.00
(liters/hr)	7998.00	556.30	1450.90	5990.80	0.00
Composition:					
Glycerol	0.003	0.010	0.000	0.001	
Methanol	0.008	0.090	0.000	0.000	
Triglyceride	0.012	0.000	0.110	0.000	
Methyl Esters	0.960	0.900	0.820	0.999	
Monoglyceride	0.004	0.000	0.035	0.000	
Diglyceride	0.004	0.000	0.035	0.000	
Temperature (°C)	270	180	275	250	
Pressure (atm)	0.130	0.112	0.139	0.122	
Design Data: Number of trays: 10 Pressure: 0.112 atm (Top) Pressure drop: 0.005 atm/100 cm Function height: 700 cm For packed column: HETP = 3.5 ft, so function height = 1200 cm Material of construction: Carbon-steel Recommended inside diameter: 140 cm Tray efficiency: 0.7 Feed stage: 7 Side stream stage: 5			Molar reflux ratio: 16.5 kmol/h Tray spacing: 60.96 cm		
Utilities: Condenser duty Qc = -2.38 MM BTU/hr; Reboiler duty Qh = 0.56 MM BTU/hr					

As illustrated in Figure 4.16, the most common type of packed distillation column consists of a cylindrical shell containing an inert packing material. In this present study, pall ring (size 2") packing type was used.
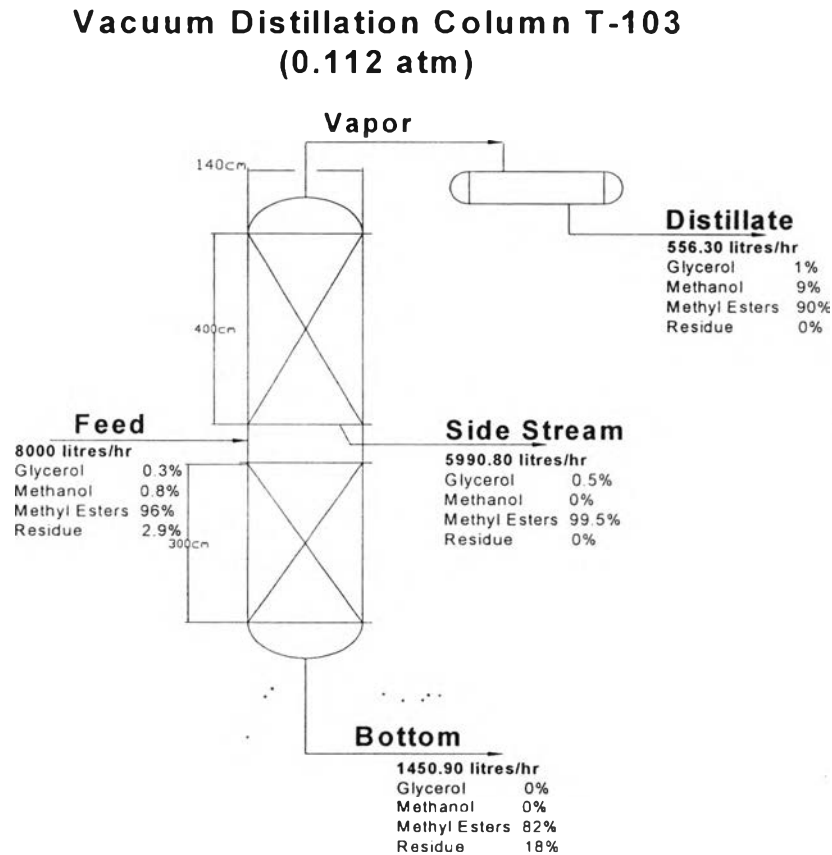

Figure 4.16 The principal performance of modified distillation column T-103.

The design data comparison of distillation column T-103 between the PRO/II simulated result (Case 02) and the real plant is shown in Table 4.22.

Table 4.22 Data comparison between real plant and result from PRO/II (Alternative 1) of T-103

	Real Plant (Base case) T-103	Altenative Design 1 (Modified case) T-103	Remark
Functional height	1200 cm	1200 cm	
Inside diameter	80 cm	140cm	modification
Material	Carbon-Steel	Carbon-Steel	Non-corrosion environmental
Liquid distillate (liters/hr)	834.45	556.30	modification
Bottom (liters/hr)	2300	1450.9	modification
Side stream	4860	5990.8	modification
Top Temp. (°C)	160	80	
Bottom Temp. (°C)	270-280	275	
Top pressure (atm)	0.112	0.112	
Bottom pressure (atm)	0.150	0.139	
Feed location	6m from Top	8m from Top	
Side stream location	4m from Top	6.5m from Top	
Condenser Heat duty (Qc)	- 0.42 MMBTU /hr - About 4,070 liters water/hr	- 2.38 MM BTU/hr - About 23,000 liters water/hr	Vapor phase at top tray of base case is not sufficient to reflux back into the column, so the side stream flow rate does not meet specification.
Reboiler Heat duty (Qh)	- Add 2.15 MMBTU/hr - About 15 Gal FO/hr	- Add 0.56 MMBTU /hr - About 4 Gal FO/hr	Fuel oil supply for reboiler in real plant is three times higher than the result obtained from PRO/II due to the higher reflux ratio in the real plant. By optimizing the column, 5% of total energy supply for plant can be saved.

Comments and discussions for the above results are as follows:

1. The key components in this distillation column are Methyl Stearate and Monoglyceride. The difference in relative volatility between the two components is high, so the reflux ratio is not very important in this case. But the fixed side stream flowrate is high so that the reflux ratio has to be calculated to matches this specification.

2. Top temperatures are very different because the recoveries on the top of the column of the two cases are different.

3. Due to the limitation of the hot oil and the material of the column, the temperature at the bottom should be below 285°C. In this case, the optimum temperature is 275°C. In this condition, the recovery of methyl esters (main product) is 85%. (See appendix C for detail calculation).

The recovery of the real plant, however, is approximately 60-70% methyl esters. In my opinion, the reasons are as follows:

> The difference of boiling temperature among the predicted data (ICAS) and the real data of some components at the bottom, such as Triglyceride, Monoglyceride, Diglyceride.

> The packed structure inside the real column is different from the column in PRO/II; as a result, the pressure drop is different.

> The inside diameter of the existing column is too small as compared with the recommended inside diameter from PRO/II (40% smaller); therefore, vapor flowrate is not enough to obtain the recovery specification.

4. Finally, the most important thing gained from this design is that 5% of the total energy supply for the plant was saved, or 330 liters of fuel oil a day equivalent, could be reduced and 15% recovery of B100, or 30,000 liters of B100 a day equivalent, could be increased. The benefit earned from the improved design is 400,000 USD a year equivalent

The detailed design of improved column by PRO/II compared to the existing one is shown in Figure 4.17 and the process flowsheet is given in Figure 4.18.
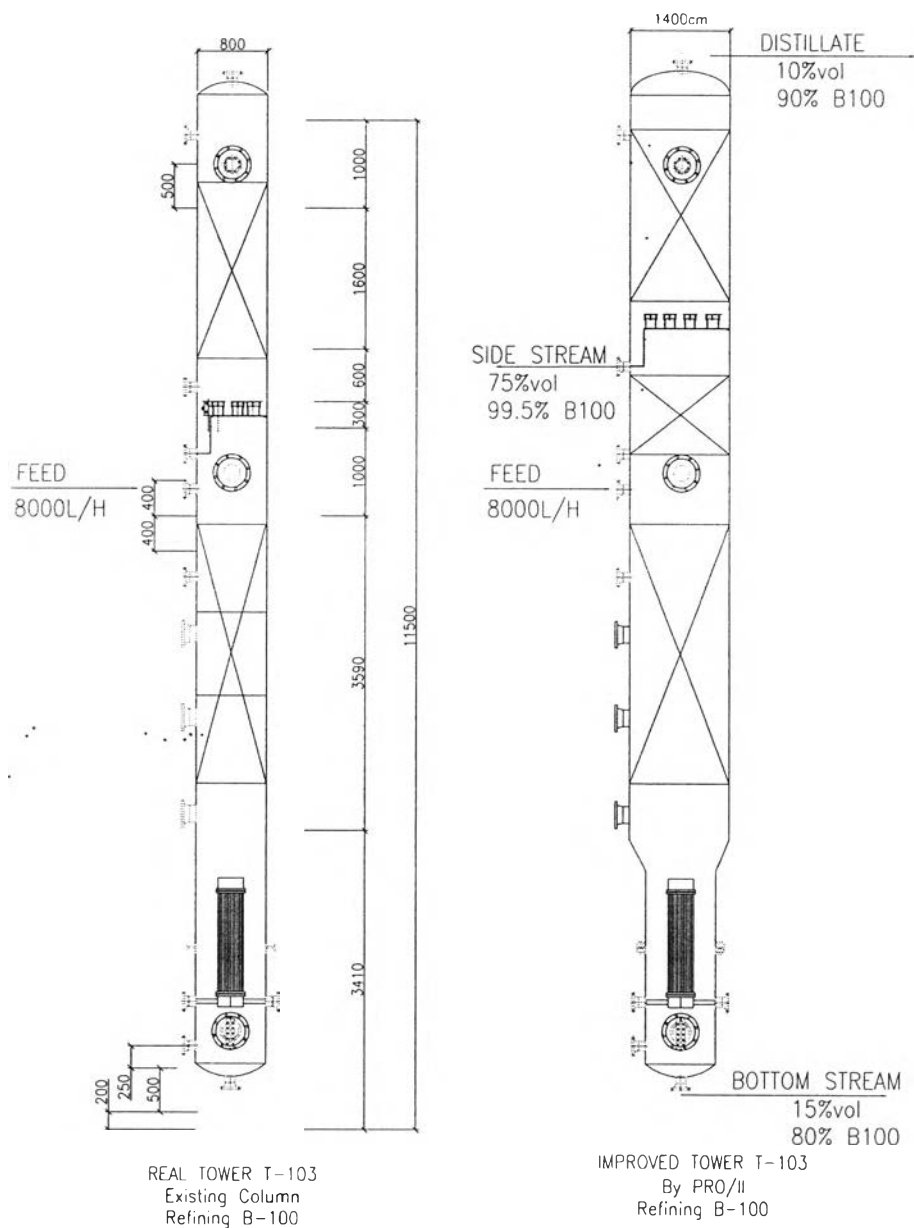

Figure 4.17 The design details of the existing column is compared with the improved one (by PRO/II).
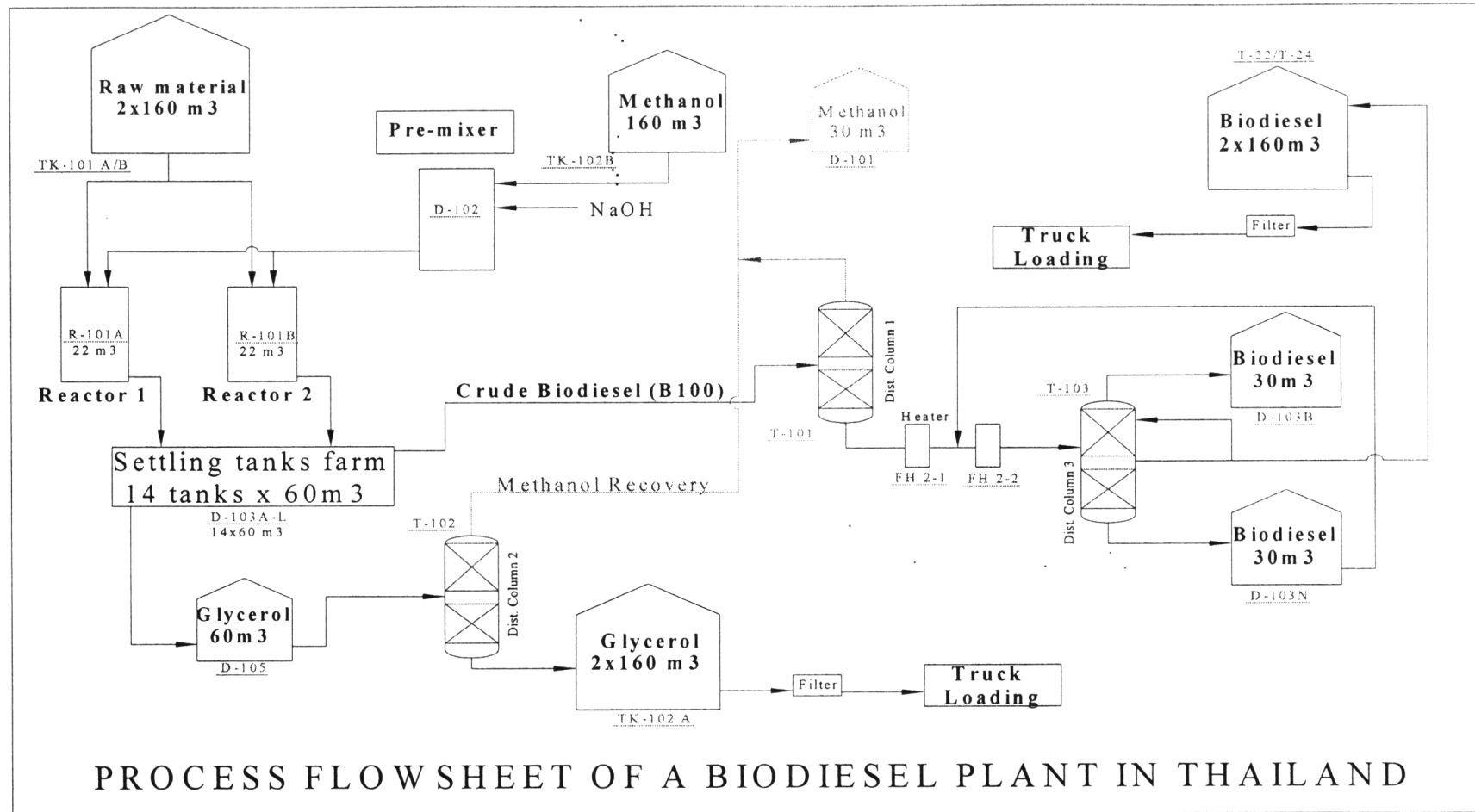
Figure 4.18 Alternative design 1 is suggested by this research work.

4.5.2 Distillation Column T-101

The results collected from PRO/II are shown in Table 4.23 below.

Table 4.23 The specification sheet for distillation column T-101

SPECIFICATION SHEET FOR COLUMN T-101					
DISTILLATION COLUMN					
Identification: Item Distillation Column Item No. T-101 No. required 1 Vacuum pressure at the top = 0.210 atm					
Function: Separate Methanol (recovery 99%) from the mixture of Methanol, Glycerol, Methyl Esters, Triglyceride, Monoglyceride, Diglyceride					
Operation: Continuous					
Materials handled:	Feed	Liquid Dist.	Bottoms	Side Draw	Vapor Dist.
Rate (kmol/hr):	37.9	13.4	24.5	0.0	0.0
(liters/hr)	8542.9	544.9	7998.0	0.0	0.0
Phase	Mixed	Liquid	Liquid		
Composition:					
Glycerol	0.002	0.000	0.003		
Methanol	0.359	0.998	0.008		
Triglyceride	0.008	0.000	0.019		
Methyl Esters	0.627	0.200	0.960		
Monoglyceride	0.002	0.000	0.005		
Diglyceride	0.002	0.000	0.005		
Temperature (°C)	117	64.5	180		
Pressure (atm)	1	1	0.230		
Design Data: Number of trays: 6 Pressure: 0.210 atm (top) Function height: 300 cm For packed column: HETP = 3.5 ft, so function height = 700 cm Material of construction: Carbon-steel Recommended inside diameter: 61 cm Tray efficiency: 0.7 Feed stage: 4				Molar reflux ratio: 7.9 kmol/h Tray spacing: 60.96 cm	
Utilities: Condenser duty Qc = -0.40 MM BTU/hr; Reboiler duty Qh = 1.41 MM BTU/hr					

The principle operation of column T-101 is illustrated in Figure 4.19, and comparison between the simulated result (PRO/II) and the design data of real plant is shown in Table 4.24
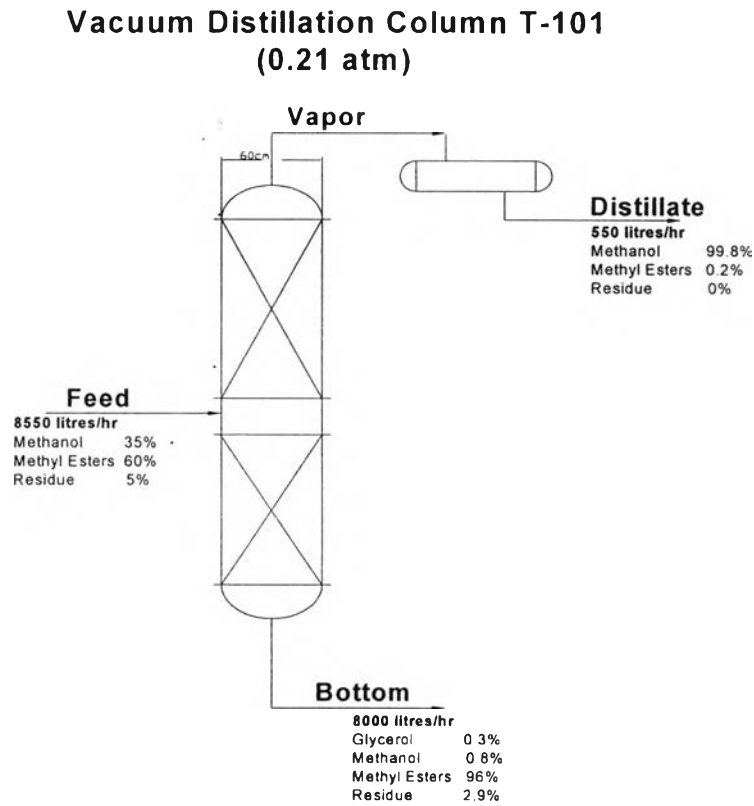

Figure 4.19 The principal functioning of the designed distillation column T-101.

Table 4.24 Comparison between the real plant data and the results collected from PRO/II (T-101)

	Real Plant Base case T-101	Data from PRO/II Modified case T-101	Remark
Functional height	350 cm	300 cm	
Inside diameter	50 cm	61 cm	Need modification
Material	Carbon-Steel	Carbon-Steel	Non-corrosion environmental
Liquid dist. liters/hr	500	544.9	
Bottom (liters/hr)	8000	7998	
Top Temp.(°C)	70	65	The temperature of real plant should be reduced to save energy supply
Bottom Temp.(°C)	170-180	180	The bottom temperature of real plant is enough to get 99% methanol recovery at top
Top pressure (atm)	0.210	0.210	
Bottom pressure (atm)	0.25	0.23	
Feed location	3.5 m from Top	3.5 m from Top	
Side stream location			
Condenser Heat duty	- -0.40 MMBTU/hr - About 3,000 liters water/hr	- -0.45 MMBTU/hr - About 3,500 liters water/hr	The cooling water flow rate of the real plant is close to the simulation result obtained from PRO/II.
Reboiler Heat duty	- Add 2.13 MM/hr - Add about 15 gallons FO/hr	- Add 1.41 MM/hr - About 10 gallons FO/hr	The difference is due to the efficiency of the heat transfer.

Comments and discussions:

1. The key components in this distillation column are methanol and glycerol.

2. The difference in relative volatility between the two components is high, so the reflux ratio is not very important in this case.

3. The Bottom temperature of the real plant is 170-180°C: PRO/II shows that it is good enough to get 99% methanol recovery.

Note: Because methanol is toxic agent, this experiment must be handled with care.

The data collected from the simulation and the real plant are the same. The operating condition of the real distillation column (T-101) is stable. Therefore, the design of this column in the process should not be modified.

4.6 Heat Integration

Target: Optimal matching between hot and cold streams to minimize utility consumption, minimum number of heat exchangers needed

4.6.1 Current Heat Exchanger Network Survey

A. The conditions and properties of the hot and cold streams are as follows (Tables 4.25 and 4.26).

Table 4.25 The conditions and properties of hot streams

Stream No.	H1	H2	H3
PROII process	S24	S36	S30
Condition	Hot	Hot	Hot
Fcp (BTU/hr°C)	5.60	16.43	3.70
Tin	65.20	233.10	275.00
Tout	35.00	70.00	60.00
Q available 10³BTU/hr	169.00	2683.30	3.73

Table 4.26 The conditions and properties of cold streams

Stream No.	C1	C2	C3
Stream No. in PROII process	R01-02	S14	S40
Condition	Cold	Cold	Cold
Fcp (10^3BTU/hr^{0}C)	8.80	25.79	32.56
Tin	30.00	60.00	180.00
Tout	64.00	117.00	274.00
Q available 10^3BTU/hr	300.00	1470.00	3061.00

B. Heat Utilities Supplied for Current Process

> Hot Utilities $Q_H = 2601.65 \times 10^3$ BTU/hr

> Cold Utilities $Q_C = 1620.24 \times 10^3$ BTU/hr

C. The Composite Curves and the "Pinch point" or $\Delta T_{minimum}$

In Figure 4.20, both the hot and cold temperature scales on the right ordinate are plot. The hot cascaded data versus the hot temperature is plot to get the hot composite curve (above curve) and the cold cascaded data versus the cold temperature to get the cold composite curve (below curve).
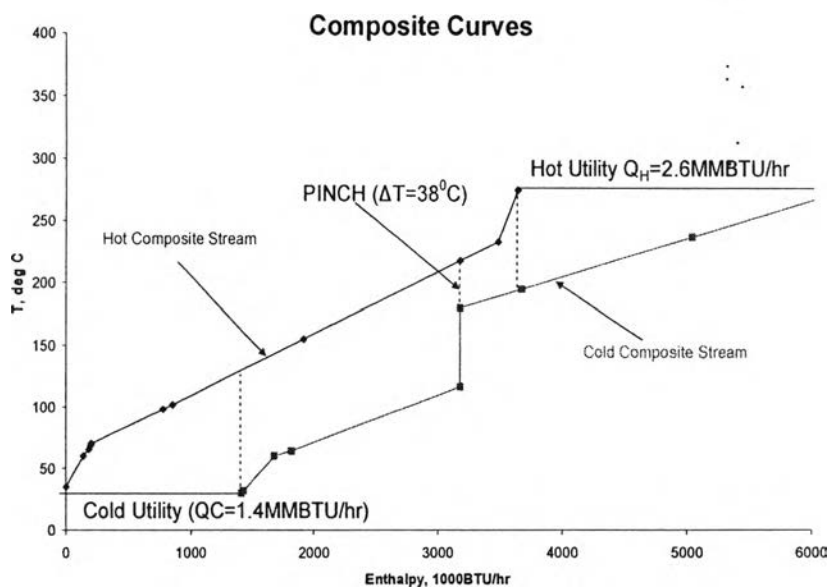

Figure 4.20 Composite Curves

From this diagram, $\Delta T_{min} = 38°C$

The heat exchanger network at this ΔT_{min} can be modified to reduce the utility usages by adding more exchanger area.

4.6.2 Optimum Approach Temperature, ΔT_{min}

The minimum approach temperature, ΔT_{min}, can be obtained by optimizing MER (maximum energy recovery) versus HEX (Heat Exchanger Network). Clearly, as $\Delta T_{min} \rightarrow 0$, the exchanger area for heat transfer approaches is infinity, while the utility requirements are reduced to the absolute minimum. At the other extreme, as $\Delta T_{min} \rightarrow \infty$, the heat transfer area approaches zero and the utility requirements are increased to maximum, without heat exchanger between the hot and cold streams.

To find the optimum approach temperature, six cases of ΔT_{min} will be surveyed (i.e. $\Delta T_{min}= 38°C$, $30°C$, $25°C$, $20°C$, $15°C$ and $10°C$). After that, the cost of required surface area of the heat exchanger (Table 4.28) and utilities are calculated (Table 4.39). Plot these two curves as the function of ΔT_{min}, the optimum point can be found easily.

Case 01: $\Delta T_{min} = 38°C$

Table 4.27 The Pinch analysis at $\Delta T_{min} = 38°C$

Minimum Utility 10^3BTU/hr		Pinch (^{0}C)	from	to
Hot	2601.65			
Cold	1416.13	199	180	218

Once the minimum utilities have been calculated above (Table 4.27), the heat exchanger network can be designed (Figure 4.21) as follows.
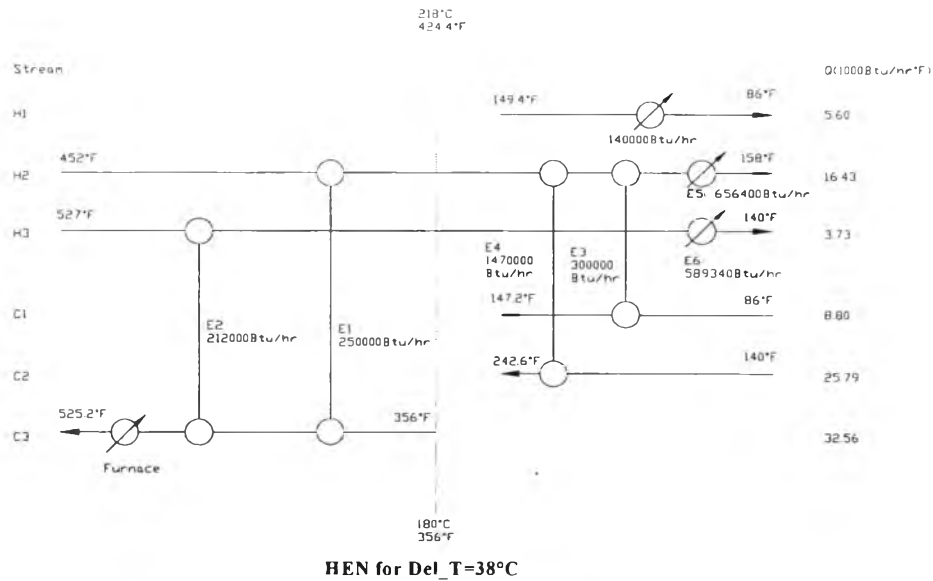
Figure 4.21 Heat exchanger network of the process when $\Delta T_{min} = 38°C$

Sizing for Heat Transfer Equipment:

Considering the countercurrent, shell, and tube heat exchanger, sizing equations for these heat exchangers can be found from the following equation:

$$A=Q/U(\Delta T_{lm}) \qquad (4.8)$$

where

Q is the heat duty of each heat exchanger;

A is required area.

The log mean temperature (ΔT_{lm}) is given by the following:

$$\Delta T_{lm} = ((T1\text{-}t2)\text{-}(T2\text{-}t1))/\ln((T1\text{-}t2)/(T2\text{-}t1)) \qquad (4.9)$$

The overall heat transfer coefficients can be estimated from Perry's Chemical Engineers' Handbook-Section 11 (11-5); we have U=15 $BTU/ft^2\text{-}hr\text{-}°F$. The calculation can then be performed in the Table 2.28.

Table 4.28 The capital cost of heat exchanger

Unit	T1(^{0}F)	T2(^{0}F)	t1(^{0}F)	t2(^{0}F)	Del_T	Q(BTU/hr)	A(ft^2)	Cost (USD)
E1	452.0	424.4	356.0	370.0	75.0	250000.0	222.2	
E2	527.0	424.4	370.0	382.0	92.4	212600.0	153.4	
E3	424.4	392.0	86.0	147.0	291.5	300000.0	68.6	
E4	392.0	230.0	140.0	242.6	117.2	1470000.0	836.2	
E5	230.0	158.0	86.0	104.0	96.5	656400.0	453.5	
E6	424.4	140.0	86.0	104.0	149.6	590000.0	262.9	
Total							1996.8	

Case 02: ΔT_{min} = 30°C

Similar to the calculation in Case 01; the final results in this case are shown in Tables 29 and 30 below.

Table 4.29 The Pinch analysis at ΔT_{min} = 30°C

Minimum Utility (10^{3}MMBTU/hr)	
Hot	2440.607
Cold	1255.09

Pinch ^{0}C	from	to
195	180	210

Table 4.30 The capital cost of heat exchanger

Unit	T1(^{0}F)	T2(^{0}F)	t1(^{0}F)	t2(^{0}F)	Del_T	Q(BTU/hr)	A(ft^2)	Cost (USD)
E1	452.0	410.0	356.0	365.0	69.2	383000.0	369.0	
E2	527.0	410.0	365.0	378.0	86.9	242000.0	185.7	
E3	410.0	377.0	86.0	147.0	276.8	300000.0	72.3	
E4	377.0	216.0	140.0	242.6	102.4	1470000.0	956.7	
E5	216.0	158.0	86.0	104.0	90.5	530000.0	390.3	
E6	401.0	140.0	86.0	104.0	142.5	559000.0	261.4	
Total							2235.4	

Case 03: ΔT_{min} = 25°C

Similar to the calculation in Case 01; the final results in this case are shown in Tables below.

Table 4.31 The Pinch analysis at $\Delta T_{min} = 25°C$

Minimum Utility (10^3MMBTU/hr)	
Hot	2339.957
Cold	1154.44

Pinch °C	from	to
192.5	180	205

Table 4.32 The capital cost of heat exchanger

Unit	T1(°F)	T2(°F)	t1(°F)	t2(°F)	Del_T	Q(BTU/hr)	A(ft²)	Cost (USD)
E1	452.0	401.0	356.0	365.0	63.7	466000.0	487.6	
E2	527.0	401.0	365.0	378.0	79.6	261000.0	218.7	
E3	401.0	368.0	86.0	147.0	267.8	300000.0	74.7	
E4	368.0	204.0	140.0	242.6	91.3	1470000.0	1073.6	
E5	204.0	158.0	86.0	104.0	85.2	448000.0	350.4	
E6	401.0	140.0	86.0	104.0	142.5	540000.0	252.6	
Total							2457.6	▮▮▮▮

Case 04: $\Delta T_{min} = 20°C$

Similar to the calculation in Case 01; the final results in this case are shown in Tables below.

Table 4.33 The Pinch analysis at $\Delta T_{min} = 20°C$

Minimum Utility 10^3BTU/hr	
Hot	2239.31
Cold	1053.79

Pinch (°C)	from	to
190	180	200

Table 4.34 The capital cost of heat exchanger

Unit	T1(°F)	T2(°F)	t1(°F)	t2(°F)	Del_T	Q(BTU/hr)	A(ft²)	Cost (USD)
E1	452.0	392.0	356.0	386.0	49.5	540000.0	727.4	
E2	527.0	392.0	386.0	401.0	39.4	280000.0	473.6	
E3	392.0	359.0	86.0	147.0	258.7	300000.0	77.3	
E4	359.0	198.0	140.0	242.6	83.8	1470000.0	1168.9	
E5	198.0	158.0	86.0	104.0	82.5	362000.0	292.5	
E6	392.0	140.0	86.0	104.0	139.8	522000.0	249.0	
Total							2988.6	▮▮▮▮

Case 05: ΔT_{min} = 15°C

Similar to the calculation in Case 01; the final results in this case are shown in Tables below.

Table 4.35 The Pinch analysis at ΔT_{min} = 15°C

Minimum Utility (10^3MMBTU/hr)	
Hot	2138.657
Cold	953.14

Pinch °C	from	to
187.5	180	195

Table 4.36 The capital cost of heat exchanger

Unit	T1(°F)	T2(°F)	t1(°F)	t2(°F)	Del_T	Q(BTU/hr)	A(ft²)	Cost (USD)
E1	452.0	383.0	356.0	390.0	42.1	630000.0	997.6	
E2	527.0	383.0	382.0	450.0	17.5	298000.0	1135.5	
E3	383.0	350.0	86.0	147.0	249.7	300000.0	80.1	
E4	350.0	189.0	140.0	242.6	74.4	1470000.0	1316.9	
E5	189.0	158.0	86.0	104.0	78.3	284000.0	241.7	
E6	383.0	140.0	86.0	104.0	137.0	503000.0	244.8	
Total							4016.5	

Case 06: ΔT_{min} = 10°C

Similar to the calculation in Case 01; the final results in this case are shown in Tables below.

Table 4.37 The Pinch analysis at ΔT_{min} = 10°C

Minimum Utility 10^3BTU/hr	
Hot	2038.01
Cold	852.49

Pinch (°C)	from	to
185	180	190

Table 4.38 The capital cost of heat exchanger

Unit	T1(^{0}F)	T2(^{0}F)	t1(^{0}F)	t2(^{0}F)	Del_T	Q(BTU/hr)	A(ft^2)	Cost (USD)
E1	452.0	374.0	356.0	395.0	33.8	710000.0	1399.0	
E2	527.0	374.0	373.0	413.0	23.9	317000.0	885.8	
E3	374.0	340.0	86.0	147.0	240.2	300000.0	83.2	
E4	340.0	179.0	140.0	242.6	63.8	1470000.0	1535.9	
E5	179.0	158.0	86.0	104.0	73.5	200000.0	181.4	
E6	392.0	140.0	86.0	104.0	139.8	485000.0	231.3	
Total							4316.6	

Table 4.39 The utilities cost

	Δtmin(^{0}C)	10^3BTU/hr	gallon/day	USD/gallon	Utility USD/day	Utility USD/year
Case01	38	2600	449	2.08	934.6026	280380.8
Case02	30	2440	422	2.08	877.0886	263126.6
Case03	25	2340	404	2.08	841.1423	252342.7
Case04	20	2237	386	2.08	804.1177	241235.3
Case05	15	2140	370	2.08	769.2498	230774.9
Case06	10	2035	351	2.08	731.5063	219451.9

The variations in heat transfer area and utilities requirements with ΔT_{min} translate into variations in capital and utilities costs, shown schematically in Figure 4.22
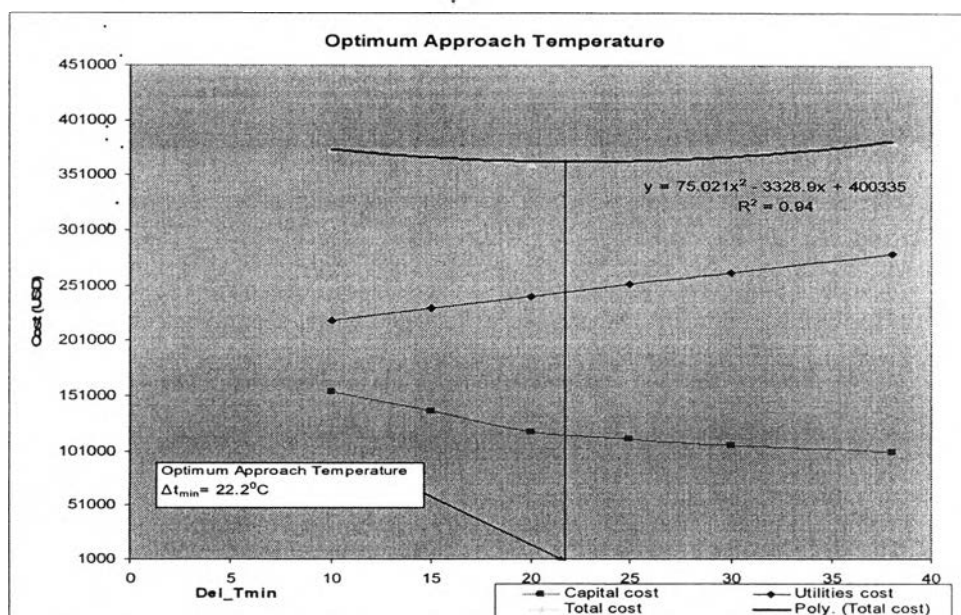
Figure 4.22 Trade-off between surface area of heat exchanger and utilities as a function of ΔT_{min}.

From the above diagram it is shown that the equation for total cost curve is:

$$y = 75.021x^2 - 3328.9x + 400335$$

To find the minimum point for this curve, the equation $y' = 0$ have to solve. After solve this equation, the optimum approach temperature is $\Delta T_{min} = 22.2°C$.

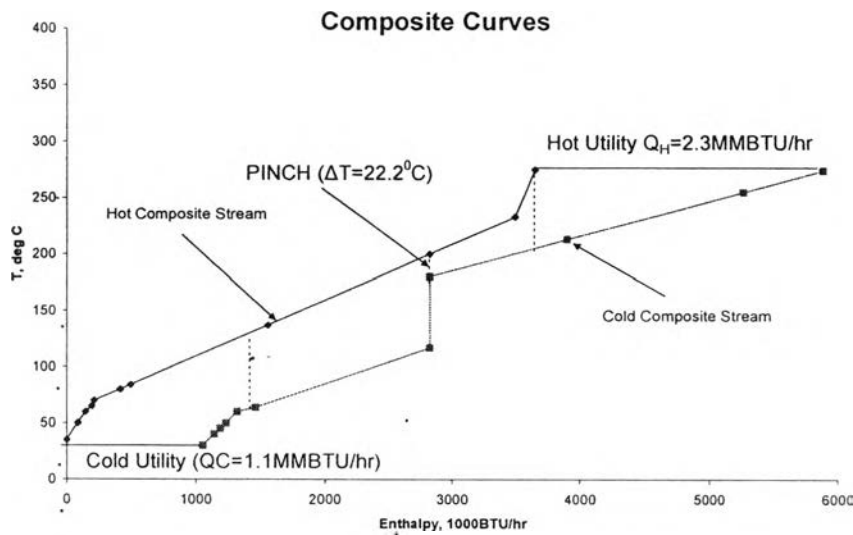**Figure 4.23** Composite Curves, $\Delta T_{min} = 22.2°C$.

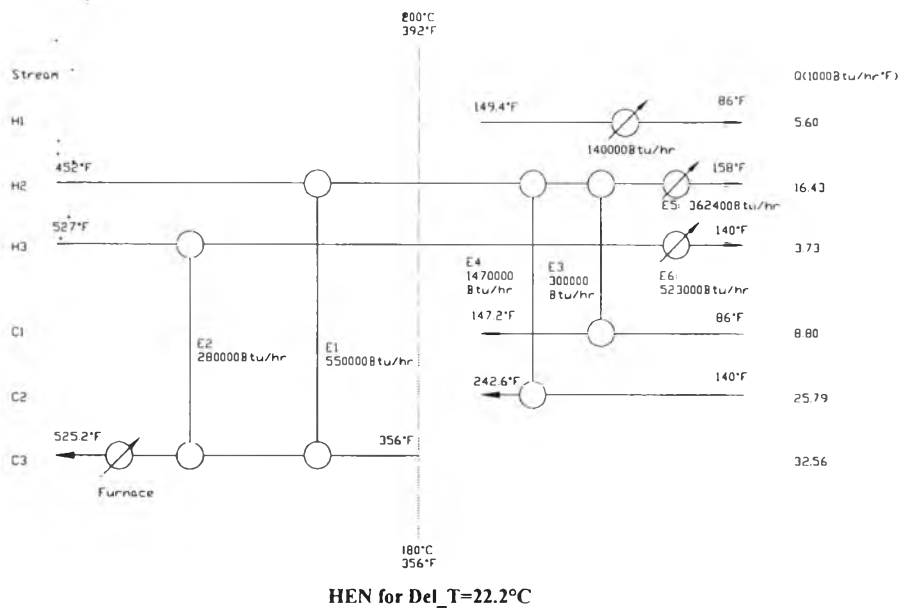**Figure 4.24** Heat exchanger network of the process when $\Delta T_{min} = 22.2°C$

4.7 Environmental Impact

4.7.1 Defining a Carbon Footprint

A carbon footprint is defined as the total amount of carbon dioxide (CO_2) and other greenhouse gases emitted over the full life cycle of a product or service. It functions as a CO_2 equivalent (in kg or tons), which accounts for the same global warming effects of different greenhouse gases. Carbon footprints can be calculated using a Life Cycle Assessment (LCA) method, or it can be restricted to the immediately attributable emissions from energy use of fossil fuels.

In this study, the second method, carbon calculation from energy use of fossil fuel, is applied.

Biodiesel is a biodegradable fuel and typically produces about 60% less carbon dioxide emissions than those from petroleum-based diesel, as it is itself produced from atmospheric carbon dioxide via photosynthesis in plants.

4.7.2 Among Carbon Offsetting Calculations

A. From the optimum operation condition of the distillation column, 5% total energy supply can be saved:

$$5\% \times 6400 \text{ liters fuel oil/day} = 320 \text{ liters/day}$$

Carbon offsetting by optimization:

$$320 \text{ liters/day} \times 3 \text{ kg } CO_2/\text{liters} = 960 \text{kg } CO_2/\text{day}$$

$$1 \text{kg of fuel oil produces } 3 \text{ kg } CO_2$$

B. From the plant:

1 kg of diesel produces 2.6 kg CO_2

The capacity of the biodiesel plant is 200,000 liters/day

If we assume that the carbon dioxide emission of biodiesel is about 60% less than petroleum-based diesel, the carbon offsetting is:

$$2.6 \times 200,000 \times 60\% = 312,000 \text{ kg/day}$$

Total carbon offsetting: 960 + 312,000 = 313,000 kg CO_2/day.