REFERENCES


[40] Caparella T. Biodiesel plants open in Germany. *Render Mag* 2002;37:16


[77] [Anonim]. Use of palm oil as fuel for diesel engines. www.codeart.org/en/technique/energie/huile_de_palme_combustible_moteur/M%E9moire_moteurhuile%20_palme_en.htm [19 Feb 2008]


## Appendix 1  Biodiesel development roadmap [5]

<table>
<thead>
<tr>
<th>Year</th>
<th>2006-2010</th>
<th>2011-2015</th>
<th>2016-2025</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Market</strong></td>
<td>Biodiesel Supply 1.5 Million kL 10% of ADO</td>
<td>Biodiesel Supply 3 Million kL 15% of ADO</td>
<td>Biodiesel Supply 6.4 Million kL 20% of ADO</td>
</tr>
<tr>
<td><strong>Product</strong></td>
<td>Palm / Jatropha Biodiesel</td>
<td>Biodiesel Low Production Cost</td>
<td>High Quality Biodiesel</td>
</tr>
<tr>
<td><strong>Technology</strong></td>
<td>Commercial Plant (5000 – 20,000 Tons/year)</td>
<td>Commercial Plant (20,000 – 100,000 Tons/year)</td>
<td>Commercial Plant of High Quality Biodiesel</td>
</tr>
<tr>
<td><strong>Research And Development</strong></td>
<td>Biodiesel Process Intensification</td>
<td>Design &amp; Engineering Plant</td>
<td>Performance Test</td>
</tr>
<tr>
<td></td>
<td>Blending Technology</td>
<td>Updating of Standard &amp; Performance Test</td>
<td>Optimization &amp; Modification of Plant</td>
</tr>
<tr>
<td></td>
<td>Fuel Additive Technology</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### National Biodiesel Standard
- Optimization & Modification of Plant
- Performance Test
- Design & Engineering Plant
- Updating of Standard & Performance Test
- Blending Technology
- Biodiesel Process Intensification
### Appendix 2  Characteristic comparisons of fossil diesel fuel and biodiesel [72]

<table>
<thead>
<tr>
<th>No</th>
<th>Parameter</th>
<th>Unit</th>
<th>FDF (1)</th>
<th>Biodiesel (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Density</td>
<td>kg/m³</td>
<td>820 - 870 (15°C)</td>
<td>850 – 890 (40°C)</td>
</tr>
<tr>
<td>2</td>
<td>Kinematic viscosity (40 °C)</td>
<td>Mm²/s (cSt)</td>
<td>1.6 - 5.8</td>
<td>2.3 – 6.0</td>
</tr>
<tr>
<td>3</td>
<td>Cetane number</td>
<td>min.</td>
<td>45</td>
<td>min. 51</td>
</tr>
<tr>
<td>4</td>
<td>Flash point</td>
<td>°C</td>
<td>min. 60</td>
<td>min. 100</td>
</tr>
<tr>
<td>5</td>
<td>Cloud point</td>
<td>°C</td>
<td>max. 18</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Pour point</td>
<td>°C</td>
<td>max. 18</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Copper strip corrosion</td>
<td>Rating</td>
<td>max. no 1</td>
<td>max. no 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Carbon residue</td>
<td>% (m/m)</td>
<td>-</td>
<td>max 0.05</td>
</tr>
<tr>
<td>9</td>
<td>Water and sediment</td>
<td>% -vol.</td>
<td>max. 0.1</td>
<td>max. 0.30</td>
</tr>
<tr>
<td>10</td>
<td>90% (v/v) recovered at distillation temperature</td>
<td>°C</td>
<td>-</td>
<td>max. 360</td>
</tr>
<tr>
<td>11</td>
<td>95% (v/v) recovered at distillation temperature</td>
<td>°C</td>
<td>max. 370</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>Ash content (sulfated ash)</td>
<td>% (m/m)</td>
<td>max. 0.01</td>
<td>max. 0.02</td>
</tr>
<tr>
<td>13</td>
<td>Sulfur content</td>
<td>ppm-m (mg/kg)</td>
<td>max. 5000</td>
<td>max. 100</td>
</tr>
<tr>
<td>14</td>
<td>Phosphorous content</td>
<td>ppm-m (mg/kg)</td>
<td>-</td>
<td>max. 10</td>
</tr>
<tr>
<td>15</td>
<td>Acid number</td>
<td>mg-KOH/g</td>
<td>max.0.6</td>
<td>max.0.8</td>
</tr>
<tr>
<td>16</td>
<td>Free glycerol</td>
<td>% (m/m)</td>
<td>-</td>
<td>max. 0.02</td>
</tr>
<tr>
<td>17</td>
<td>Total glycerol</td>
<td>% (m/m)</td>
<td>-</td>
<td>max. 0.24</td>
</tr>
<tr>
<td>18</td>
<td>Ester content</td>
<td>% (m/m)</td>
<td>-</td>
<td>min. 96.5</td>
</tr>
<tr>
<td>19</td>
<td>Iodine number</td>
<td>% (m/m)</td>
<td>-</td>
<td>max. 115</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Halphen test</td>
<td></td>
<td>-</td>
<td>Negative</td>
</tr>
</tbody>
</table>

Note: can be separately tested as long as sediment content maximum 0.01 %-vol

1. FDF = Fossil Diesel Fuel, automotive Diesel Oil, [www.pertamina.com](http://www.pertamina.com)
   (accessed 19 June 2006)

2. SNI Biodiesel No. 04-7182-2006, based on ASTM D 6751 & EN 14214
Appendix 3  The Photograph of the equipment for transesterification and esterification by semi-batch process
Appendix 4 The photograph of GC analyzer

(a) A GC-2010AF (SPL/FID) Series Gas Chromatograph System

(b) A LabSolution GSsolution software from SHIMADZU CO. Japan
Appendix 5  The photograph of HPLC analyzer

(a) An HPLC equipped with a model 880-PU pump, a degasser DG-2080-53, and a column oven CO-965

(b) An intelligent sampler 855-AS
Appendix 6  The photograph of TLC/FID analyzer

(a) An Iatroscan MK-5 Analyzer

(b) Iatrocorder TC-11

(c) Type SIII Chromarods were used as thin layer
Appendix 7  The photograph of equipment for continuous transesterification process

(a) All of the equipment

(b) Inside of BCR with inner tube

(c) Inner tube
Appendix 8 Prediction of the bubble diameter and interfacial area

The standard form of a bubble column is shown in figure (a). As a rule, the height-to-diameter ratio is greater than 1 (3 to 10). Gas is introduced through perforated tubes, perforated trays, and, in rare cases, through sintered plates. The superficial velocities of the gas are normally spread between 1 and 30 cm/s. The superficial velocity is the ratio of the volumetric flow rate to the empty cross-sectional area of the column [71].

Various types of bubble column [71]

Internal arrangements are sometimes made (Fig. b). The installation of a guide cylinder transforms the column into a gas-lift (inner tube). While offering good transfer properties, this unit helps to achieve greater liquid homogeneity due to the methodical circulation, and this may be important. The introduction of perforated plate partitions (Fig. c) helps to improve the transfer properties, but mainly offers the advantage of restricting the backmixing of the gas phase. This effect is more pronounced with fewer perforations, so that effective partitioning is achieved when a gas cap develops below each perforated plate (Fig. d). In all these processes, gas holdup ($\varepsilon_G$) and bubble size diameter ($d_b$) are important design
parameters, since the gas-liquid interfacial area available for mass transfer ($A_v$) is defined by equation:

$$A_v = \frac{6 \varepsilon_G}{d_b}$$  \hspace{1cm} (15)

Bubble size distribution and gas holdup in gas-liquid dispersions depend extensively on column geometry, operating conditions, physico-chemical properties of the two phases and type of gas sparger. The design of bubble column has primarily been carried out by means of empirical or semi-empirical correlations based mainly on experimental data. The scale up of bubble columns is still poorly understood due to the complexity of flow patterns and their unknown behavior under different sets of design parameters such as diameter, height to diameter ratio, physical properties of the liquid and gas, etc. The gas holdup in bubble columns has been measured by Van Dierendonck [73], who obtained the following correlation:

$$\varepsilon_G = 1.2 \left( \frac{\mu_L u_{SG}}{\sigma_L} \right)^{1/4} \left( \frac{u_{SG}}{\sigma_L g} \frac{\rho_L}{\sigma_L g} \right)^{1/4}$$  \hspace{1cm} (16)

According to Van Dierendonck, the bubble diameter is given by the following equation:

$$d_b \rho_L g = c \left[ \frac{u_{SG}}{\sigma_L g} \left( \frac{\rho_L}{\sigma_L g} \right)^{1/4} \right]^{-(1/2)} M^{-1/8}$$  \hspace{1cm} (17)

c = 6.25 for pure liquids and 2.1 for electrolytes, and $M = \sigma_L^3 \rho_L / \mu_L^4 g$. The interfacial area is then obtained from following equation:
From which it can be seen that \( A_v \) is independent of viscosity but varies linearly with the superficial gas velocity.

The mass transfer coefficient for the liquid phase is given by Calderbank [73]:

\[
k_L = 0.42 \sqrt{\frac{\mu_L g}{\rho_L}} \sqrt{\frac{\rho_L D_{NL}}{\mu_L}} \text{ for } d_b \geq 2 \text{ mm}
\]

so that \( k_L \) is independent of bubble size and velocity and depends only on the physical properties of the system. When \( d_b < 2 \text{ mm} \), Van Dierendonck recommends:

\[
k_L = k_L (2 \text{ mm}) \times 500 d_b \text{ (in m/s)}
\]

1. **Estimations of physical properties of liquid (palm oil)**

*Estimation of liquid density of palm oil (\( \rho_L \)):* The density – temperature relation is represented by a linear equation [74]:

\[
\rho_L = a + bT
\]

Where \( a \) and \( b \) are constants and \( T \) is temperature in K. Using the two density data at two temperatures, the constants \( (a \text{ and } b) \) were determined. The density values of palm oil at 15.6 and 38 °C are 920 [75] and 918 kg/m³ [16], respectively. The following correlation was obtained for the density of palm oil:

\[
\rho_L = 945.679 - 0.089T
\]

*Estimation of liquid viscosity of palm oil (\( \mu_L \)):* Reid et al.[76] proposed the following expression for the viscosity calculation for a temperature range from freezing to the normal boiling point:
\[ \ln \mu_L = c + \frac{d}{T} \]  \hspace{1cm} (23)

Where \( c \) and \( d \) are constants and \( T \) is temperature in K. Using the two viscosity data at two temperatures, the constants \( (c \) and \( d \)\) were determined. The viscosity values of palm oil at 20 and 38 °C are 70 [77] and 39.6 mm\(^2\)/s [16], respectively. The following correlation was obtained for the viscosity of palm oil:

\[ \ln \mu_L = -5.5941 + \frac{2883.87}{T} \]  \hspace{1cm} (24)

**Estimation of the surface tension of palm oil (\( \sigma_L \))**:

For values of reduced temperature \( (T_r) \) between 0.4 and 0.7, the surface tension-temperature relation is represented by a linear equation [77]:

\[ \sigma_L = e + fT \]  \hspace{1cm} (25)

Where \( e \) and \( f \) are constants and \( T \) is temperature in K. Using the two surface tension data at two temperatures, the constants \( (e \) and \( d \)\) were determined. The surface tension values of palm oil at 30 and 60 °C are 30 [78] and 30.9 mN/m [79], respectively. The following correlation was obtained for the surface tension of palm oil:

\[ \sigma_L = 20.1 + 0.03T \]  \hspace{1cm} (26)

The density, viscosity and surface tension of palm oil at 250, 270 and 290 °C were calculated with using eqs. (22), (24) and (26) and the result of calculation is presented in the following table:

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>Density (kg/m(^3))</th>
<th>Viscosity (mm(^2)/s)</th>
<th>Viscosity (kg m(^{-3}) s(^{-1}))</th>
<th>Surface tension (mN/m)</th>
<th>Surface tension (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>523</td>
<td>899.132</td>
<td>0.9231</td>
<td>0.0008</td>
<td>36.6</td>
<td>0.0366</td>
</tr>
<tr>
<td>543</td>
<td>897.352</td>
<td>0.7535</td>
<td>0.0007</td>
<td>37.2</td>
<td>0.0372</td>
</tr>
<tr>
<td>563</td>
<td>895.572</td>
<td>0.6239</td>
<td>0.0006</td>
<td>37.8</td>
<td>0.0378</td>
</tr>
</tbody>
</table>
Estimation of gas-liquid diffusivity

The diffusivity of MeOH in palm oil was obtained using the Wilke and Chang Correlation [80] as shown below:

\[ D_{AL} = 1.173 \times 10^{-16} \left( \frac{\lambda M_L}{\mu_L} \right)^{0.5} T \left( \frac{\mu}{\rho} \right)^{0.6} \]  

(27)

Where the value of \( \lambda \) is 1 and \( M_L \) is the molecular weight of the liquid (palm oil = 858) and \( \rho_L \) is the molar volume of solute (MeOH gas) calculated using the ideal gas equation:

\[ \rho \rho = V / \rho = RT / P \]  

(28)

The molar volume of MeOH, diffusivity of MeOH in palm oil, and the mass transfer coefficient for the liquid phase (\( d_b \geq 2 \text{ mm} \)) at 250, 270 and 290 °C were calculated with using eqs. (27), (28), (19) and the result of calculation is presented in the following table:

<table>
<thead>
<tr>
<th>( T (K) )</th>
<th>( \rho_A (\text{m}^3/\text{kmol}) )</th>
<th>( D_{AL} (\text{m}^2/\text{s}) )</th>
<th>( k_f ) for ( d_b \geq 2 \text{ mm} (\text{m/s}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>523</td>
<td>42.886</td>
<td>2.27E-10</td>
<td>0.000137</td>
</tr>
<tr>
<td>543</td>
<td>44.526</td>
<td>2.83E-10</td>
<td>0.000158</td>
</tr>
<tr>
<td>563</td>
<td>46.166</td>
<td>3.47E-10</td>
<td>0.000181</td>
</tr>
</tbody>
</table>

2. Calculations for the transesterification reaction by semi-batch process.

Estimation of the superficial gas velocity (\( u_{SG} \)):

For the reaction temperature 290 °C = 563 K

Mass flow rate of MeOH liquid = 4 g/min  
Molar flow rate of MeOH liquid = 4 g/min x 32 g/gmol = 0.125 gmol/min  
Volumetric rate of MeOH gas = \( (n RT)/P \) (assumption as an ideal gas)  
\[ = (0.125)(0.082)(563)/1 = 5.77 \text{ L/min} \]  
\[ = 9.618 \times 10^{-5} \text{ m}^3/\text{s} \]  
Diameter of the reactor \( D \) = 9.85 cm = 0.0985 m  
The cross-sectional area of the reactor = 0.0076 m$^2$
Superficial gas velocity \((u_{SG}) = (9.618 \times 10^{-5}) / 0.0076 = 0.0126\) m/s

Superficial gas velocities at the reaction temperatures 250 and 270 \(^\circ\)C are 0.0117 and 0.0122 m/s, respectively.

The gas holdup, the bubble diameter the gas-liquid interfacial area were calculated by using eq. (16), (17), and (18) respectively and the results of calculation are shown in the following table.

<table>
<thead>
<tr>
<th>(T) (K)</th>
<th>(\varepsilon_G) (m(^3)/m(^3))</th>
<th>(d_b) (m)</th>
<th>(A_v) (m(^2)/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>523</td>
<td>0.0442</td>
<td>0.0023</td>
<td>117.297</td>
</tr>
<tr>
<td>543</td>
<td>0.0429</td>
<td>0.0021</td>
<td>120.128</td>
</tr>
<tr>
<td>563</td>
<td>0.0417</td>
<td>0.0020</td>
<td>122.884</td>
</tr>
</tbody>
</table>

### 3. Calculations for the transesterification reaction by continuous process

*Estimation of the superficial gas velocity \((u_{SG}) :*

For the reaction temperature 290 \(^\circ\)C = 563 K

Volumetric rate of MeOH liquid = 2.5 ml/min = 1.5x10\(^{-4}\) m\(^3\)/h

Density of MeOH = 790 kg/m\(^3\)

Mass flow rate of MeOH = 1.5x10\(^{-4}\) m\(^3\)/h x 790 kg/m\(^3\) = 0.1185 kg/h

Molar flow rate of MeOH = 0.1185/32 = 3.7 x 10\(^{-3}\) kmol/h = 3.7 gmol/h

Volumetric rate of MeOH gas = \((n R T)/P\) (assumption as an ideal gas)

\[
= (3.7)(0.082)(563)/1 = 170.9585 \text{ L/h}
\]

\[
= 0.171 \text{ m}^3/\text{h}
\]

Diameter of the reactor = 5.5 cm = 0.055 m

The cross-sectional area of the reactor = 0.00237 m\(^2\)

Superficial gas velocity \((u_{SG}) = 0.171 / 0.00237 = 72 \text{ m/h} = 0.020 \text{ m/s}

The superficial gas velocities for the others operating condition were calculated with the same method. Then the gas holdup, the bubble diameter, the gas-liquid interfacial area, and the mass transfer coefficient for the liquid phase were calculated by using eq. (16), (17), (18), and (20) respectively and the results of calculation are shown in the following table.
4. Correlations for bubble column reactor

(a) Mean bubble diameter, $d_b$, proposed by Yoshida [71]:

$$
\frac{d_b}{D} = a \left( \frac{g D^2 \rho_L}{\sigma_L} \right)^b \left( \frac{g D^3 \rho_L}{\mu_L^2} \right)^c \left( \frac{V_{SG}}{\sqrt{gD}} \right)^d
$$

(29)

$$
\left( \frac{g D^2 \rho_L}{\sigma_L} \right) = \text{Bond number (Bo)}
$$

$$
\left( \frac{g D^3 \rho_L}{\mu_L^2} \right) = \text{Galileo number (Ga)}
$$

$$
\left( \frac{V_{SG}}{\sqrt{gD}} \right) = \text{Froude number (Fr)}
$$

For the continuous process experiment, the values of Bond number, Galileo number and Froude number are given in the following table:
T (K) | MeOH flow Rate, ml/min | \( \frac{d_b}{D} \) | Bo | Ga | Fr
---|---|---|---|---|---
523 | 3 | 0.035 | 9509.091 | 1913284055 | 0.02997
543 | 3 | 0.033 | 9872.727 | 2872021040 | 0.03133
563 | 1.5 | 0.038 | 10236.364 | 4188536867 | 0.01635
563 | 2.5 | 0.033 | 10236.364 | 4188536867 | 0.02724
563 | 3 | 0.031 | 10236.364 | 4188536867 | 0.03269
563 | 4 | 0.029 | 10236.364 | 4188536867 | 0.04359
563 | 6 | 0.027 | 10236.364 | 4188536867 | 0.06538

Constants \( a, b, c \) and \( d \) in Eq. (29) can be calculated with linear regression using MINITAB. There following results were obtained:

\[
a = 10^{36.8} \\
b = 11.51 \\
c = -1.170 \\
d = -0.244456 \\
R^2 = 0.978
\]

(b) Transfer coefficient \( (k_L) \) proposed by Yoshida [71]:

\[
k_L d_b = a \left( \frac{\mu_L}{\rho_L D_{L}} \right)^b \left( \frac{g d_b \rho_L^2}{\mu_L^3} \right)^c \left( \frac{g d_b \rho_L}{\sigma_L} \right)^d
\]

(30)

With using the similar method, constants \( a, b, c \) and \( d \) in the Eq.(30) are:

\[
a = 10^{-5.31} \\
b = 1.07 \\
c = 0.911 \\
d = -0.366 \\
R^2 = 1
\]
(c) Productivity of ME was proposed:

\[
\left( \frac{P_{ME} L}{\rho_{ME} U_{SG}} \right) = a \left( \frac{d_b}{D} \right)^b
\]  

(31)

Where \( P_{ME} \) = Productivity of ME, \( \text{kg/m}^3/\text{s} \)

\( \rho_{ME} \) = Density of palm methyl ester, 880 kg/m^3

\( L \) = Height of the reactor, 0.21 m

\( D \) = Diameter of the reactor, 0.055 m

The constants \( a \) and \( b \) can be obtained by using two experiment data at 290 °C with the MeOH feed flow rate at 2.5 and 3.0 mL/min, the data are shown in the following table:

<table>
<thead>
<tr>
<th>( \frac{d_b}{D} )</th>
<th>( \log \frac{d_b}{D} )</th>
<th>( u_{SG}, \text{m/s} )</th>
<th>( P_{ME}, \text{kg/L/h} )</th>
<th>( P_{ME}, \text{kg/m}^3/\text{s} )</th>
<th>( \frac{P_{ME} L}{\rho_{ME} U_{SG}} )</th>
<th>( \log \left( \frac{P_{ME} L}{\rho_{ME} U_{SG}} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.033</td>
<td>-1.48509</td>
<td>0.020</td>
<td>0.058</td>
<td>0.01611</td>
<td>0.000192</td>
<td>-3.7162</td>
</tr>
<tr>
<td>0.031</td>
<td>-1.50991</td>
<td>0.024</td>
<td>0.128</td>
<td>0.03556</td>
<td>0.000354</td>
<td>-3.4516</td>
</tr>
</tbody>
</table>

Two equations used to determine the value of \( a \) and \( b \) are:

(i) : -3.716 = \( \log a + b \) (-1.48509)

(ii) : -3.4516 = \( \log a + b \) (-1.50991)

Equation (i) and (ii) can be solved by the elimination and substitution method, constants \( a \) and \( b \) in the Eq.(31) are:

\( a = 10^{-19.546} \) and \( b = -10.659 \), so Eq. (31) becomes:

\[
\left( \frac{P_{ME} L}{\rho_{ME} U_{SG}} \right) = 10^{-19.546} \left( \frac{d_b}{D} \right)^{-10.659}
\]
Appendix 9  Material and Heat Balance Calculation

Material Balance for the 3.0 mL/min MeOH Feed Flow Rate

Reaction temperature = 290 °C
Volume of oil in the reactor = 200 mL
Molecular weight (MW) of MeOH = 32 g/gmol
Density of MeOH = 0.79 g/cm³
Flow rate of MeOH = 3.0 mL/min = 142.2 g/h : 32 g/gmol = 4.44 gmol/h
Production rate of biodiesel = 25.59 g/h
Productivity of biodiesel = (25.59/1000) kg/0.2 L/h = 0.128 kg/L/h
ME content in the product = 95.1% w/w
ME in the product = 0.951 x 25.59 = 24.34 g/h
(MW of ME is 287) = 24.34/287 = 0.085 gmol/h
The overall reaction is: (for one hour)

\[ TG + 3\text{MeOH} \rightarrow \text{GL} + 3\text{ME} \]

0.085 gmol

Glycerol production (MW of GL is 92) = 1/3 x 0.085 gmol x 92 g/gmol = 2.607 g. In the experiment result, production rate of GL was 2.736 g/h, so the purity of GL is about (2.607/2.736) x 100% = 95.29% w/w.

Oil (as uME) in the GL phase = 2.736 – 2.607 = 0.129 g
Oil (as uME) in the ME phase = 25.59 – 24.34 = 1.25 g
Oil (TG) reacts = 1/3 x 0.085 gmol = 0.028 gmol = 24.31 g
(MW of TG is 858)

Flow rate of oil feed = 0.129 + 1.25 + 24.31 = 25.69 g/h = 0.03 gmol/h
Conversion of TG = (0.028/0.03) x 100% = 94.77% mol/mol
Yield of FAME = (mass of FAME/ mass of oil) x 100%
= (24.34/25.69) x 100% = 94.75% w/w
MeOH reacts = 0.085 gmol = 2.72 g
Unreacted MeOH = 142.2 – 2.72 = 139.48 g
The molar ratio of MeOH to oil = 4.44/0.03 = 148 (mol/mol)
Summary of material balance in the reactor is:

<table>
<thead>
<tr>
<th>Components</th>
<th>Rate of mass input (g/h)</th>
<th>Rate of mass output (g/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil (TG)</td>
<td>25.69</td>
<td>139.48</td>
</tr>
<tr>
<td>MeOH</td>
<td>142.20</td>
<td>25.59</td>
</tr>
<tr>
<td>Biodiesel Product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure ME</td>
<td></td>
<td>24.34</td>
</tr>
<tr>
<td>uME</td>
<td></td>
<td>1.25</td>
</tr>
<tr>
<td>Glycerol product:</td>
<td></td>
<td>2.736</td>
</tr>
<tr>
<td>Pure GL</td>
<td></td>
<td>2.607</td>
</tr>
<tr>
<td>uME</td>
<td></td>
<td>0.129</td>
</tr>
<tr>
<td>Total</td>
<td>167.89</td>
<td>167.81</td>
</tr>
</tbody>
</table>

For 1000 kg/h biodiesel product, the mass balance is:

<table>
<thead>
<tr>
<th>Components</th>
<th>Rate of mass input (kg/h)</th>
<th>Rate of mass output (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil (TG)</td>
<td>1000</td>
<td>5450</td>
</tr>
<tr>
<td>MeOH</td>
<td>5557</td>
<td>1000</td>
</tr>
<tr>
<td>Biodiesel Product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure ME</td>
<td></td>
<td>951</td>
</tr>
<tr>
<td>uME</td>
<td></td>
<td>49</td>
</tr>
<tr>
<td>Glycerol product:</td>
<td></td>
<td>107</td>
</tr>
<tr>
<td>Pure GL</td>
<td></td>
<td>102</td>
</tr>
<tr>
<td>uME</td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>Total</td>
<td>6557</td>
<td>6557</td>
</tr>
</tbody>
</table>
Material Balance for the 2.5 mL/min MeOH Feed Flow Rate

Reaction temperature = 290 °C
Volume of oil in the reactor = 200 mL
Flow rate of MeOH = 2.5 mL/min = 118.5 g/h ; 32 g/gmol = 3.703 g mol/h
Production rate of biodiesel = 11.68 g/h
Productivity of biodiesel = (11.68/1000) kg/0.2 L/h = 0.058 kg/L/h
ME content in the product = 96.7% w/w
ME in the product = 0.967 x 11.68 = 11.29 g/h = 11.29/287 = 0.039 g mol/h

The overall reaction is: (for one hour)

TG + 3MeOH → GL + 3ME

0.039 g mol

Glycerol production = 1/3 x 0.039 g mol x 92 g/gmol = 1.196 g

In experiment result, production rate of GL was 1.248 g/h, so the purity of GL is about (1.196/1.248) x 100% = 95.83% w/w.

Oil (as uME) in the GL phase = 1.248 – 1.196 = 0.052 g
Oil (as uME) in the ME phase = 11.68 – 11.29 = 0.39 g
Oil (TG) reacts = 1/3 x 0.039 g mol = 0.013 g mol = 11.154 g
Flow rate of oil feed = 0.052 + 0.39 + 11.154 = 11.60 g/h = 0.014 g mol/h
Conversion of TG = (0.013/0.014) x 100% = 96.32% mol/mol
Yield of FAME = (mass of FAME/ mass of oil) x 100%
= 11.29/11.60 x 100% = 97.33%
MeOH reacts = 0.039 g mol = 1.25 g
Unreacted MeOH = 118.5 - 1.25 = 117.25 g

The molar ratio of MeOH to oil = 3.703/0.014 = 272
Summary of material balance in the reactor is:

<table>
<thead>
<tr>
<th>Components</th>
<th>Rate of mass input (g/h)</th>
<th>Rate of mass output (g/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil (TG)</td>
<td>11.60</td>
<td>117.25</td>
</tr>
<tr>
<td>MeOH</td>
<td>118.50</td>
<td>11.68</td>
</tr>
<tr>
<td>Biodiesel Product:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure ME</td>
<td></td>
<td>11.29</td>
</tr>
<tr>
<td>uME</td>
<td></td>
<td>0.39</td>
</tr>
<tr>
<td>Glycerol product:</td>
<td></td>
<td>1.248</td>
</tr>
<tr>
<td>Pure GL</td>
<td></td>
<td>1.196</td>
</tr>
<tr>
<td>uME</td>
<td></td>
<td>0.052</td>
</tr>
<tr>
<td>Total</td>
<td>130.10</td>
<td>130.18</td>
</tr>
</tbody>
</table>

Note: (*) The difference of the value of total input and output is very small, this is caused by rounding off of figures. For 1000 kg/h biodiesel product, the mass balance is:

<table>
<thead>
<tr>
<th>Components</th>
<th>Rate of mass input (kg/h)</th>
<th>Rate of mass output (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil (TG)</td>
<td>1000</td>
<td>10038</td>
</tr>
<tr>
<td>MeOH</td>
<td>10145</td>
<td>1000</td>
</tr>
<tr>
<td>Biodiesel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure ME</td>
<td>967</td>
<td></td>
</tr>
<tr>
<td>uME</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Glycerol</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>Pure GL</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>uME</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11145</td>
<td>11145</td>
</tr>
</tbody>
</table>
Heat Balance for the 3.0 mL/min MeOH Feed Flow Rate

To calculate the heat balance, some of data are needed:

1. Heat capacity \((C_p)\) of MeOH (liquid and gas), palm oil (TG), ME and GL
2. Heat of formation of TG, MeOH, ME and GL
3. Heat of vaporization of MeOH, ME and GL

Data:

Heat capacity of MeOH liquid and gas are obtained from Appendix 6 and 3:

\[ C_p = A + B T + C T^2 + D T^3 + E T^4 \quad \text{kJ/kmol K} \]

<table>
<thead>
<tr>
<th>Materials</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol (cair)</td>
<td>-2.5825E+02</td>
<td>3.3582E+00</td>
<td>-1.1639E-02</td>
<td>1.4052E-05</td>
<td>0</td>
</tr>
<tr>
<td>methanol (gas)</td>
<td>3.4493E+01</td>
<td>-2.9189E-02</td>
<td>2.8684E-04</td>
<td>-3.1250E-07</td>
<td>1.10E-10</td>
</tr>
</tbody>
</table>

Heat of vaporization at normal boiling point of MeOH is obtained from Appendix 2: Reklaitis GV. *Introduction to Material and Energy Balances*. New York: John Wiley & Sons, 1983 [81].

Heat of vaporization of MeOH \((\Delta H_{\text{nb}})^{\text{MeOH}}\) = 35270.4 kJ/kmol

Normal boiling point of MeOH \((T_{\text{nb}})^{\text{MeOH}}\) = 64.5 °C


\[
\frac{\Delta H_{\text{nb}}}{T_{\text{nb}} R} = \frac{1.092(\ln P_C - 1.013)}{0.930 - T_m}
\]

Where \(P_C\) = critical Pressure, bar
\(T_m\) = reduced temperature at \(T_{\text{nb}} = T_{\text{nb}} / T_C\)
\(T_C\) = critical temperature, K
Estimates of the latent heat of vaporization of a pure liquid at any temperature from the known value at a single temperature may be based on a known experimental value or on a value estimated by Riedel equation. The method proposed by Watson has found wide acceptance [82]:

$$\Delta H_T = \left( \frac{1 - T_r}{1 - T_1} \right)^{0.38}$$

Where:

- $n_A$ = the number of atoms in the molecule.
- $\Delta = \text{the quatities are evaluated by summing contributions for various atoms or groups of atoms as shown in Table 2-2 (page 15) of Reid RC, Prausnitz JM, Poling BE, The Properties of Gases and Liquids. 4th ed. USA: McGraw-Hill Book Co., 1987.[76].}

For methyl esters:

- $T_{nb} = 678.95 \text{ K}$, based on the fatty acid composition $T_{nb} = 620 \text{ K}$
- $T_C = 847.38 \text{ K}$
- $P_C = 11.61 \text{ bar}$

Heat of vaporization for ME:

- $\Delta H_{nb} = 40925 \text{ kJ/kmol} = 142.6 \text{ kJ/kg}$
- $\Delta H_{80^\circ C} = 55003.37 \text{ kJ/kmol} = 191.65 \text{ kJ/kg}$
  (result from HYSYS = 190.2 kJ/kg)
- $\Delta H_{112^\circ C} = 53622.33 \text{ kJ/kmol} = 186.84 \text{ kJ/kg}$
- $\Delta H_{290^\circ C} = 49938.44 \text{ kJ/kmol} = 174.0 \text{ kJ/kg}$

Heat of vaporization of GL was calculated use HYSYS = 842.5 kJ/kg
Heat capacity of TG, ME and GL are estimated by **Kopp’s rule**: Cp for a molecular compound is the sum of contributions for each atomic elements in the compound. Atomic heat capacities of Kopp’s Rule for element C, H and O are 12, 18 and 25, respectively (Source: Himmelblau DM. Basic Principles and Calculations in Chemical Engineering. 3rd ed. Prentice-Hall, Englewood Cliffs, NJ, 1974, p.270.) [83].

- Cp for TG = 2578.91 kJ/kmol = 3.01 kJ/kg K
- Cp for ME = 906.47 kJ/kmol = 3.16 kJ/kg K
- Cp for GL = 255 kJ/kmol = 2.77 kJ/kg K

Standard heat of formation ($\Delta H^\circ_f$) at 25°C (298 K) for TG, ME, GL and MeOH are estimated use the **Joback method**:

$$\Delta H^\circ_f (298 K) = 68.29 + \sum n_j \Delta H$$

where $n_j$ the number of groups of the $j$th type and the $\Delta$ contributions are for the $j$th atomic or molecular group (Source: Reid RC, Prausnitz JM, Poling BE. *The Properties of Gases and Liquids*. 4th ed. USA: McGraw-Hill Book Co., 1987. pp 154-155) [76].

- $\Delta H^\circ_f (298 K)$ for TG = -1986374 kJ/kmol
- $\Delta H^\circ_f (298 K)$ for ME = -734905 kJ/kmol
- $\Delta H^\circ_f (298 K)$ for GL = -567220 kJ/kmol
- $\Delta H^\circ_f (298 K)$ for MeOH = -216200 kJ/kmol

**Calculation of Heat Balance.**

The heat balance of the biodiesel production process was determined by trial and error and use a HYSYS software. The products (FAME and glycerol) in the liquid phase was separated from unreacted methanol in the vapour phase by flash distillation process (one step distillation) in a flash drum (FD). The operating condition of FD is 1 atm (101.3 kPa) and 112 °C. The temperature of each flow process was determined by energy balance equation. The flow process diagram of biodiesel production is shown as follow:
The flow process diagram of biodiesel production

**Basis : 1 hour (h) of operating time**

Assumption: Heat loss is 30% (The efficiency of heat exchanger is 70%)

Heat transfer in HE-1 which is given by hot fluid:

\[
Q_1 = \sum m \cdot C_p (r_1 - r_2) = 1000 [(3.16)(5) + 186.84] + 107[2.77(5) + 842.5] + 5450 (1.58)(5) = 337314.279 \text{ kJ}
\]

\[
Q_1 = 337314.279 (0.7) = 236120 \text{ kJ}
\]

The cold fluid in HE-1 is feed palm oil, temperature of oil exit from HE-1:

\[
T_2 = 108^\circ C
\]

Heat transfer in HE-2 which is required by cold fluid (oil):

\[
Q_2 = m \cdot C_p (280 -108) = 1000(3.01)(172) = 516985
\]

\[
Q_2 = 516985/0.7 = 738550 \text{ kJ}
\]

The hot fluid of HE-2 is gas product exit from the BCR, the temperature of gas product exit from HE-2 :

\[
T_2 = (m \cdot C_p + m \cdot C_p + m \cdot C_p)(290-T_2)
\]
\[ T_2 = 237 \, ^\circ C \]

Heat transfer in HE-3 which is required by cold fluid (MeOH fresh feed):

\[ Q_3 = 1000(3.16) + 107(2.77) + 5557(1.94)(290- T_2) \]

\[ T_2 = 223 \, ^\circ C \]

Heat transfer in HE-4 which is required by cold fluid (MeOH feed to BCR):

\[ Q_4 = 1000(3.16) + 107(2.77) + 5557(1.72)(223- T_2) \]

\[ T_2 = 117 \, ^\circ C \]

Note:

- \( C_p \) of MeOH liquid between 27-65 °C = 2.66 kJ/kg °C
- \( C_p \) of MeOH gas between 65-112 °C = 1.52 kJ/kg °C
- \( C_p \) of MeOH gas between 112 -117°C = 1.58 kJ/kg °C
- \( C_p \) of MeOH gas between 117-223 °C = 1.72 kJ/kg °C
- \( C_p \) of MeOH gas between 223-237 °C = 1.70 kJ/kg °C
- \( C_p \) of MeOH gas between 237-290 °C = 1.94 kJ/kg °C
- \( C_p \) of MeOH gas between 25-213 °C = 1.59 kJ/kg °C
- \( C_p \) of MeOH gas between 25-290°C = 1.69 kJ/kg °C
Heat transfer in the BCR ($Q_R$):

Heat of the reaction ($\Delta H^\circ_R$) = $(3 \Delta H^\circ_{f\ ME} + \Delta H^\circ_{f\ GL}) - (\Delta H^\circ_{f\ TG} + \Delta H^\circ_{f\ MeOH})$

= -136601.796 kJ/kmol TG x 1.1655 kmol TG

= -159210 kJ. (exothermic reaction)

Enthalpy of the reactant ($H_R$): $T_{ref} = 298$ K

$H_{TG} = n_{TG} \cdot C_{p\ TG} \cdot (T_R - T_{ref}) = 1000 \cdot (3) \cdot (280-25) = 766460$ kJ

$H_{MeOH} = n_{MeOH} \cdot C_{p\ gas} \cdot (213-25) = 5557 \cdot (1.59) \cdot (188) = 1661098$ kJ

$(H_R) = 766460 + 1661098 = 2427558$ kJ

Enthalpy of the products ($H_P$)

$H_{MeOH} = n_{MeOH} \cdot C_{p\ gas} \cdot (290-25) = 5450 \cdot (1.69) \cdot (265) = 2440782.5$ kJ

$H_{ME} = n_{ME} \cdot C_{p\ ME} \cdot (290 - 25) + n_{ME} \cdot \Delta H_{290^oC}$

= $836949.92 + 174001.52 = 1010951.44$ kJ

$H_{GL} = n_{GL} \cdot C_{p\ GL} \cdot (290-25) + n_{GL} \cdot \Delta H_{290^oC}$

= $78592.66 + 90147.5 = 168740.16$ kJ

$H_P = 2440782.50 + 1010951.44 + 168740.16 = 3620474$ kJ

Energy balance: Input = Output

$H_R + \Delta H^\circ_R + Q_R = H_P$

$2427558 + 159210 + Q_R = 3620474$

$Q_R = 1033706$ kJ

If the thermal efficiency 70% so $Q_R = 1476723$ kJ = 1.5 GJ

Heating value of palm methyl esters = 39.7 MJ/kg (prediction value based on the fatty acid composition). For 1000 kg/h FAME, heating value of palm methyl esters = 39700 MJ/h = 39.7 GJ/h. Heating value of refined palm oil is 39.3 MJ/kg [75].

Ratio of output energy to input energy = $39.7/1.5 = 26.5$ (without electricity and heating value of palm oil).
The specific energy consumption is 1.5 MJ/kg biodiesel.

The Lurgi Process used alkaline catalyst required 350 kg steam for 1000 kg biodiesel product (Source from an unpublished article). If the steam was assumed as saturated steam at 110 °C with the specific enthalpy value 2691.3 kJ/kg and the boiler efficiency was 80%, so input of energy to boiler is:
The enthalpy of boiler feed water $= C_p (30-0) = 4.17 \text{ J/g } ^\circ\text{C} \times 30 = 125.1 \text{ J/g} = 125.1 \text{ kJ/kg}$. The ratio of output energy to input energy $= 39.7/1.123 = 35.35$. The specific energy consumption is $1.123 \text{ MJ/kg biodiesel}$. 

\[
= [350 \text{ kg} \times (2691.3 - 125.1)] \text{ kJ/kg} / 0.8 \\
= 1122.71 \text{ MJ} = 1.123 \text{ GJ}
\]