**APPENDIX - III**

**Experimental Conditions for Preparing Castor Oil - Hydrocellulose Based Polyols and Calculations of Their Hydroxyl Numbers:**

**Experimental Conditions:**

- Wt. ratio of CO to BC used: 10 : 1 (for polyol no.1) | 20 : 1 (for polyol no.2)
- Catalyst (NaOH): 2% (w/w) of the reactants.
- Temperature: 155-165°C
- Time: 4 hours
- Pressure: 10 mm of Hg.

**Calculations of Hydroxyl Numbers:**

Transesterification of castor oil with hydrocellulose results in a mixture of different types of partial esters, glycerol, unreacted hydrocellulose and unreacted castor oil. The structural formulae of the different types of possible products have been shown in Fig. A.1, and their characteristic values are presented in Table III-1.

**Table III-1: Characteristic Values of the Different Components.**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Component</th>
<th>Molecular Weight</th>
<th>Hydroxyl Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Unreacted BC</td>
<td>162*</td>
<td>1038.88</td>
</tr>
<tr>
<td>2</td>
<td>Mono ester</td>
<td>442</td>
<td>380.76</td>
</tr>
<tr>
<td>3</td>
<td>Diester</td>
<td>722</td>
<td>233.10</td>
</tr>
<tr>
<td>4</td>
<td>Triester</td>
<td>1002</td>
<td>167.96</td>
</tr>
<tr>
<td>5</td>
<td>Unreacted CO</td>
<td>932</td>
<td>180.57</td>
</tr>
<tr>
<td>6</td>
<td>Diglyceride</td>
<td>652</td>
<td>258.12</td>
</tr>
<tr>
<td>7</td>
<td>Monoglyceride</td>
<td>372</td>
<td>452.41</td>
</tr>
<tr>
<td>8</td>
<td>Glycerol</td>
<td>92</td>
<td>1829.34</td>
</tr>
</tbody>
</table>

* On the basis of anhydroglucose unit.
Fig. A.1 Structural formulae of the different expected products resulting from transesterification reaction between castor oil and hydrocellulose.
Now, two types of events are taking place in this transesterification reaction: products based on hydrocellulose residue (type-I) and products based on oil residue (type-II).

Probability of the type-I events

\[
\frac{\text{total no. of possibilities of the type-I species}}{\text{total no. of all possibilities of products in the equilibrium transesterfied mixture}}
\]

For the case when trifunctional hydrocellulose is transesterified with trifunctional castor oil, the total number of possibilities of both types of events can be calculated as below:

**Events of type - I:**

- **all 3 A's**: \(3c_0 = 1\)
- **2 A's; 1 B**: \(3c_1 = 3\)
- **1 A; 2 B's**: \(3c_2 = 3\)
- **all 3 B's**: \(3c_3 = 1\)

**Total possibilities = 8**

**Events of type - II**

- **all 3 B's**: \(3c_3 = 1\)
- **1 A; 2 B's**: \(3c_2 = 3\)
- **2 A's; 1 B**: \(3c_1 = 3\)
- **all 3 A's**: \(3c_0 = 1\)

**Total = 8**

Probability of the type-I events = \(8\) / \(8+8\) = 1/2

and probability of the type-II events = 1 - 1/2 = 1/2
Thus, the probabilities or in other words, the mole fractions of the different components existing in the equilibrium transesterified mixture, as calculated by Bianchini's formula (187), are to be multiplied by these two factors 1/2 and 1/2, respectively, for the cases of type - I and type - II species.

**Polyol No. 1**

Weight of reactants taken:

- **Castor oil** = 20.2134g.
- **Hydrocellulose** = 2.0214g
- **Sodium hydroxide** = 0.4446g.

Weight of castor oil consumed for saponification with sodium hydroxide = \( \frac{932}{120} \times 0.4446 = 3.4531 \) g.

Weight of castor oil left for transesterification = 20.2134 - 3.4531 = 16.7603 g = 0.0179831 mole

Hydrocellulose taken for reaction = 2.0214 g = 0.0124777 mole

Now according to Bianchini's method,

\[
\bar{g} = \frac{3 \times 0.0179831}{0.0179831 + 0.0124777} = 1.7711
\]

and \( f_p = 3 \)

The mole fractions of the different components are then given by:

- \( Y_{oa} \) (for unreacted HC) = \( 3c_o \times \left( \frac{1.7711}{3} \right)^0 \times (1 - \frac{1.7711}{3}) \)^3 \times 1/2 = 0.0344

Similarly,

- \( Y_{1a} \) (for mono ester) = 0.1486
- \( Y_{2a} \) (for diester) = 0.2142
- \( Y_{3a} \) (for triester) = 0.1029
- \( Y_{ob} \) (for unreacted CO) = 0.1029
Y₁b (for diglyceride) = 0.2142
Y₂b (for monoglyceride) = 0.1486
and Y₃b (for glycerol) = 0.0344

Additional suffixes a and b have been used to distinguish the products based on hydrocellulose residue and oil residue, respectively.

Weight per cent of the different components can then be calculated on the basis of mole fractions as in table III-2.

Table III-2: Calculation of Weight Per Cent for Different Components

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
<th>Mol.wt.</th>
<th>Amount, g.</th>
<th>Weight, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y₁a</td>
<td>0.0344</td>
<td>162</td>
<td>5.5728</td>
<td>0.8945</td>
</tr>
<tr>
<td>Y₁b</td>
<td>0.1486</td>
<td>442</td>
<td>65.6812</td>
<td>10.5424</td>
</tr>
<tr>
<td>Y₂a</td>
<td>0.2142</td>
<td>722</td>
<td>154.6524</td>
<td>24.8231</td>
</tr>
<tr>
<td>Y₃a</td>
<td>0.1029</td>
<td>1002</td>
<td>103.1058</td>
<td>16.5494</td>
</tr>
<tr>
<td>Y₁b</td>
<td>0.1029</td>
<td>932</td>
<td>95.9028</td>
<td>15.3933</td>
</tr>
<tr>
<td>Y₂b</td>
<td>0.2142</td>
<td>652</td>
<td>139.6584</td>
<td>22.4165</td>
</tr>
<tr>
<td>Y₃b</td>
<td>0.1486</td>
<td>372</td>
<td>55.2792</td>
<td>8.8728</td>
</tr>
</tbody>
</table>

The hydroxyl number of the mixture is thus calculated as,

\[
(1038.88 \times 0.0089) + (380.76 \times 0.1054) + (233.1 \times 0.2482) \\
+ (167.96 \times 0.1655) + (180.57 \times 0.1539) + (258.12 \times 0.2242) \\
+ (152.44 \times 0.0887) + (1829.34 \times 0.0051) \\
= 9.25 + 40.13 + 57.86 + 27.6 + 27.79 + 57.87 + 40.13 + 9.33 \\
= 270.16
\]
Polyol No. 2

Quantities of reactants taken:

- Castor oil = 23.5576g.
- Hydrocellulose = 1.1778g.
- Sodium hydroxide = 0.4948g.

For saponification, weight of castor oil consumed

\[ \frac{232 \times 0.4948}{120} = 3.8429 \text{g.} \]

Moles of reactants taken for transesterification reaction:

- Castor oil = 19.7147g. i.e., 0.0211531 mole
- Hydrocellulose = 1.1778g. i.e., 0.0072703 mole.

Hence

\[ \tilde{a} = \frac{3 \times 0.0211531}{0.0211531 + 0.0072703} = 2.2326 \]

and \( f_p = 3 \)

Therefore, the mole fractions of different components are given by,

\[ Y_{oa} \text{(for unreacted EC)} = 3C_0 \left( \frac{2.2326}{3} \right)^3 \left( 1 - \frac{2.2326}{3} \right)^{3/2} \approx 0.0084 \]

\[ Y_{1a} \text{(for monoester)} = 0.073 \]

\[ Y_{2a} \text{(for diester)} = 0.2125 \]

\[ Y_{3a} \text{(for triester)} = 0.2061 \]

\[ Y_{ob} \text{(for unreacted CO)} = 0.2061 \]

\[ Y_{1b} \text{(for diglyceride)} = 0.2125 \]

\[ Y_{2b} \text{(for monoglyceride)} = 0.073 \]

\[ Y_{3b} \text{(for glycerol)} = 0.0084 \]
Mass calculations for the different components are presented in Table III-3.

**Table III-3: Mass Calculations**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
<th>Mole wt.</th>
<th>Wt. g.</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y_{oa}</td>
<td>0.0084</td>
<td>162</td>
<td>1.3608</td>
<td>0.1809</td>
</tr>
<tr>
<td>Y_{1a}</td>
<td>0.073</td>
<td>442</td>
<td>32.266</td>
<td>4.29</td>
</tr>
<tr>
<td>Y_{2a}</td>
<td>0.2125</td>
<td>722</td>
<td>153.425</td>
<td>20.3988</td>
</tr>
<tr>
<td>Y_{3a}</td>
<td>0.2061</td>
<td>1002</td>
<td>206.522</td>
<td>27.4571</td>
</tr>
<tr>
<td>Y_{ob}</td>
<td>0.2061</td>
<td>932</td>
<td>192.0852</td>
<td>25.5389</td>
</tr>
<tr>
<td>Y_{1b}</td>
<td>0.2125</td>
<td>652</td>
<td>138.55</td>
<td>18.4211</td>
</tr>
<tr>
<td>Y_{2b}</td>
<td>0.073</td>
<td>372</td>
<td>27.156</td>
<td>3.6106</td>
</tr>
<tr>
<td>Y_{3b}</td>
<td>0.0084</td>
<td>92</td>
<td>0.7728</td>
<td>0.1027</td>
</tr>
</tbody>
</table>

**Hydroxyl number of the mixture**

\[
- (1038.88 \times 0.0018) + (380.76 \times 0.0429) + (233.1 \times 0.204)
+ (167.96 \times 0.2746) + (180.57 \times 0.2554) + (258.12 \times 0.1842)
+ (452.41 \times 0.0361) + (1829.34 \times 0.0010)
\]

\[= 1.87 + 16.33 + 47.55 + 46.12 + 46.12 + 47.55 + 16.33 + 1.83\]

\[= 223.76\]