14

Biodiesel Manufacturing

14.1

Introduction to Biofuels

Biofuels are valuable sources of sustainable energy. Interest in them will rise tremendously in the coming years due to the perspective of a dramatic shortage of oil and gas reserves, simultaneously with an accelerated worldwide demand in fuels, namely in the large emergent economies. Biofuels have at least five merits. They:

1. reduce the energetic dependence of nations with respect to fossil resources acting as stabilizing factors in a global market environment;
2. reduce the global pollution by less CO₂ emissions on a lifecycle basis;
3. reduce the local pollution in terms of CO, CO₂, sulfur and fines particles;
4. enable recycling various potentially energetic industrial and domestic wastes, as cooking oil and fats, as well as agricultural residues;
5. ensure a better balance between industry and agriculture, creating new jobs in rural areas and sustainable economic growth.

The biofuels also raise concerns with respect to a possible shortage of agricultural resources needed for food. In return, it could be said that the biofuels aim to valorize primarily nonfood raw materials and nonused land resources. In addition, the biofuels should be considered as only a component, an important one, of the diversity of renewable energetic resources.

14.1.1

Types of Alternative Fuels

Table 14.1 presents a classification of alternative transportation fuels in terms of origin and ecological efficiency with respect to classical gasoline and petroleum diesel. Some features are briefly commented.

Natural gas for vehicles (NGV) is a methane-based fuel that presents superior combustion efficiency, reduced CO and NOₓ emissions, and no sulfur. The proven natural-gas reserves are superior to those of oil. NGV usage is widespread in countries possessing large resources, such as Argentina, Columbia and Venezuela, but is very limited in Europe and the USA.
LPG is a blend of propane and butane obtained as secondary products of natural-gas exploration or during crude oil processing. For this reason LPG is included usually in alternative fuels. Although the combustion properties of LPG are excellent, its wider usage is prevented by supply limitations and safety problems.

Synfuels are synthetic hydrocarbons obtained from syngas, a mixture of CO and H₂. The composition of synfuels is comparable to either gasoline or diesel, depending on the manufacturing conditions. The technology, based on the well-known Fischer–Tropsch synthesis, is in practice very demanding. Syngas can be obtained from gas, coal and biomass, the liquid products being named accordingly GTL, CTL and BTL. The technology of GTL was developed by Shell in Malaysia in the decade 1980–90. Today, new large-scale plants are being erected in the Persian Gulf region. The liquefaction of coal (CTL) has been running at large scale for decades at Sasol in South Africa. New CTL plants are in construction in China and the USA. Despite progress in technology, the CTL has a low ecologic efficiency. The valorization of biomass as a renewable resource is much more advantageous and generates significant interest today, namely in Europe. The efficiency of synfuels production depends largely on the gas-reforming technology. From this viewpoint the use of a methane-rich feedstock has a definite advantage over coal.

Bioethanol is experiencing a fast growth on the global scale, particularly in Brazil and the USA. Ethanol is already one of the largest chemical commodities. A major advantage of bioethanol is its blending capacity with normal gasoline, between 5 and 85%. Up to 5% bioethanol may be tolerated without particular problems, but higher concentrations require an adaptive motor engine known as “flex technology”. Another interesting valorization of bioethanol is as ETBE (ethanol-
tert-butyl-ether), a gasoline additive for better combustion. Unlike MTBE (methyl-tert-butyl-ether) banned today because of the pollution threat to ground water, the ETBE has a low solubility in water and is consequently environmental acceptable. Older MTBE plants are revamped today to ETBE processes.

Biodiesel consists of a mixture of fatty-acid esters. Fatty-acid methyl esters (FAME) are the most involved because methanol is the cheapest alcohol, but other alcohols, namely ethanol, may be employed as well. The manufacturing process is based on the transesterification of triglycerides by alcohols to fatty esters, with glycerol as a byproduct. In this way, highly viscous triglycerides are converted in long-chain monoesters presenting much lower viscosity and better combustion properties. Homogeneous or heterogeneous catalysis are used to enhance the reaction rate. Raw materials are vegetable oils, preferably nonedible, but also different wastes, such as used frying oils or animal fats (tallow).

The biodiesel can be used alone or blended, as B20 in 20 wt% with petrodiesel. As shown in Table 14.2, the biodiesel has remarkable combustion properties reflected in a drastic reduction of all emissions, excepting for a small increase in NO\textsubscript{x}. Over a life cycle the CO\textsubscript{2} reduction is about 65% [13].

Intensive research is devoted to fuel-cell vehicles (FCVs). Hydrogen-powered engines can be viable if a cost-effective hydrogen process can be found. At the present time the main hydrogen source is methane reforming, including from biogas. Another possibility is coal gasification, but with a substantial CO\textsubscript{2} penalty. Water electrolysis might be interesting if the price of nonfossil electricity becomes competitive. Methanol fuel cells are in rapid progress.

### 14.1.2 Economic Aspects

Economic incentives and private interest in new opportunities are boosting the biofuels market at exceptionally high rates. The European Union gives a strong example. By 2010 the share of alternative fuels should rise to 5.75% by energy value and 6% by volume [14, 15]. Biodiesel is the preferred option in Europe. In contrast, in the USA and Brazil bioethanol is leading, but biodiesel has good
prospects too [9, 15, 35]. As Figure 14.1 shows, the growth of biodiesel capacity in Europe is impressive: 6.1 Mt in 2006 or 65% increase compared with 2005, by a ratio of six with respect to 2001. Germany is the leading country (2.7 Mt in 2006), followed by France and Italy. In recent years large-scale production capacities emerged in the UK, Spain, Poland and the Czech Republic. In 2006 there were biodiesel plants in 21 of the 25 European countries involving around 3 million hectares of arable land. The use of biodiesel as a transport fuel does not require any changes in the distribution system, therefore avoiding expensive infrastructure changes. Biodiesel is also used as an efficient heating oil.

14.2
Fundamentals of Biodiesel Manufacturing

14.2.1
Chemistry

Fatty esters are currently manufactured by the transesterification of triglycerides with light alcohols. The triglycerides are found in vegetable oils and animal fats, more generally known as lipids. The transesterification reaction takes place in the presence of a suitable catalyst, acid or base. The fatty ester is released simultaneously with the reformation of the OH group in glycerol. The overall reaction occurs in three stages is controlled by chemical equilibrium, as expressed by the reactions below:

\[
\begin{align*}
\text{Triglyceride} & : & \text{Diglyceride} \\
\text{Diglyceride} & : & \text{Monoglyceride} \\
\text{Monoglyceride} & : & \text{Glycerol} & \text{Methyl esters}
\end{align*}
\]
At full conversion of intermediates the overall reaction is:

\[
\begin{align*}
\text{Triglyceride} & \quad + \quad 3 \text{CH}_3\text{OH} & \quad \text{Glycerol} & \quad + \quad 3 \text{R}_1\text{COO-C}_3\text{H}_3 \\
\text{H}_2\text{C}-\text{OOC-CH}_2\text{-R}_1 & \quad + \quad 3 \text{CH}_3\text{OH} & \quad \text{H}_2\text{C}-\text{OH} & \quad + \quad 3 \text{R}_1\text{COO-C}_3\text{H}_3 \\
\text{H}_2\text{C}-\text{OOC-CH}_2\text{-R}_1 & \quad + \quad 3 \text{CH}_3\text{OH} & \quad \text{H}_2\text{C}-\text{OH} & \quad + \quad 3 \text{R}_1\text{COO-C}_3\text{H}_3 \\
\end{align*}
\]

Thus, three molecules of fatty esters are produced for each molecule of triglyceride that needs three molecules of alcohol. The yield in biodiesel is about 90%. Full profit could be taken by converting glycerol to fuel by an appropriate chemistry.

The maximum achievable composition depends on the equilibrium constants of the individual steps. As an order of magnitude, they are of the order of about 10, 3 and 10 at 60°C. In consequence, a substantial excess of alcohol is necessary to achieve higher ester yield close to 99%, as well as lower content in di- and monoglycerides.

Since the reaction rate is not fast enough at low temperature the transesterification makes use of catalysts. In fact, they make the difference between technologies. The catalysts can have acid or base character, and be homogeneous or heterogeneous. Base catalysts are preferred since they are faster. Homogeneous catalysts manifest higher activity, but need expensive postprocessing stages. Therefore, technologies based on continuous operation and solid catalyst would be preferable.

The lipid feedstock may contain variable proportions of free fatty acids (FFA), which should be converted in esters before transesterification. Otherwise, the formation of soaps occurs by reaction with the hydroxide catalyst, as follows:

\[
\text{R}_1\text{COO-CH} + \text{NaOH} \rightarrow \text{R}_1\text{COONa} + \text{H}_2\text{O}
\]
Another source of soaps is the saponification of ester dissolved in the glycerol phase:

\[
R_1\text{-COO-CH}_3 + \text{NaOH} \rightarrow R_1\text{-COONa} + \text{CH}_3\text{OH}
\]

The soaps can be reconverted to FFA by treatment with mineral acid:

\[
R_1\text{-COO-CNa} + \text{acid} \rightarrow R_1\text{-COOH} + \text{salt}
\]

The above simple reactions involve, in practice, costly operations, such as neutralization, washing, liquid phase and solid separations. These can be substantially reduced or even suppressed if superactive heterogeneous catalysts are employed.

For the esterification of FFA, superacid solid catalysts can be applied, such as ion-exchange resins (Amberlist, Naion) or sulfated zirconia [22–24]. The preferred environment is a reactive-distillation column.

Regarding the transesterification, the research of heterogeneous catalysts is less advanced because of the difficulty of finding superbase catalysts. This issue will be presented later in this chapter. To date the most interesting innovation comes from the French Petroleum Institute where a heterogeneous catalyst based on zinc and aluminum oxides was developed and is currently being applied in commercial plants [2].

### 14.2.2 Raw Materials

A remarkable feature of lipids, either vegetal or animal, is that they share the same fatty acids in triglycerides in the range C12–C20 (Table 14.3). However, there are significant differences in composition. Thus, soybean, sunflower and rapeseed oils are all based on C18 acids, the first two being richer in unsaturated linoleic acid, which could introduce a problem of stability with respect to oxidation. The palm oil has an important amount of C16 acid. Coconut oil is given as an example of C12–C14 rich oil. As in palm oil the composition of tallow spreads over C16–C18 acids.

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Soybean</th>
<th>Rapeseed</th>
<th>Sunflower</th>
<th>Palm</th>
<th>Coconut</th>
<th>Tallow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric</td>
<td>12:0</td>
<td>0.1</td>
<td></td>
<td>0.1</td>
<td>46.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Myristic</td>
<td>14:0</td>
<td>0.1</td>
<td></td>
<td>1.0</td>
<td>19.2</td>
<td>2.8</td>
</tr>
<tr>
<td>Palmitic</td>
<td>16:0</td>
<td>10.2</td>
<td>3.49</td>
<td>6.08</td>
<td>23.6</td>
<td>9.8</td>
</tr>
<tr>
<td>Stearic</td>
<td>18:0</td>
<td>3.7</td>
<td>0.85</td>
<td>3.26</td>
<td>14.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Oleic</td>
<td>18:1</td>
<td>22.8</td>
<td>64.4</td>
<td>16.93</td>
<td>44.2</td>
<td>6.9</td>
</tr>
<tr>
<td>Linoleic</td>
<td>18:2</td>
<td>53.7</td>
<td>22.3</td>
<td>73.73</td>
<td>10.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Linolenic</td>
<td>18:3</td>
<td>8.6</td>
<td>8.23</td>
<td>0.4</td>
<td>0</td>
<td>0.9</td>
</tr>
</tbody>
</table>
14.2.3 Biodiesel Specifications

As engine fuel, the long-chain unbranched fatty esters of biodiesel behave similarly to higher n-alkanes from petrodiesel. The biodiesel exhibits cleaner burning because of its oxygenated components, although the heat of combustion is only 90% from petrodiesel. Table 14.4 presents the quality specifications of biodiesel following the German norm 14214, which is typical of European standards. The most important combustion characteristic is the cetane number (CN), around 49. The CN number increases with the chain length, but decreases with the unsaturation of the fatty ester, and as a result depends on the raw-material composition. For example, CN is approximately 54 for methyl rapeseed ester, 50 for methyl palm ester, but only 46 for methyl soybean and sunflower esters.

The flash point indicates the temperature above which the fuel will ignite when exposed to a spark. This value, of about 110 °C, lower than for petrodiesel, is safer for transport purposes.

With respect to viscosity, which controls the fuel injection, the biodiesel shows somewhat higher values compared with petrodiesel, but this can be kept under 5 mm²/s by controlling the feedstock composition or by blending.

The cold filter plugging point (CFPP) indicates the possibility of using the fuel in low-temperature conditions. Similar information is given by the “pour point”, as well as by the “cloud point”. Biodiesel shows higher CFPP values, namely at larger content in saturated esters. The rapeseed methyl ester (pour point at −9 °C) exhibits good behavior compared with the palm methyl ester (pour point at 10 °C).

Carbon residue is a measure of deposit formation in the long run. Biodiesel manifests a more pronounced coke formation than conventional diesel. For this reason the content of mono-, di-, and triglycerides, should each be kept below 0.4 wt%. The total bounded and free glycerol should be below 1.5%.

### Table 14.4 Specification of biodiesel following the german norm DIN EN 14214.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Units</th>
<th>Min.</th>
<th>Max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>g/ml</td>
<td>0.875</td>
<td>0.900</td>
</tr>
<tr>
<td>Cetane number (CN)</td>
<td></td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>Viscosity (15 °C)</td>
<td>mm²/s</td>
<td>3.5</td>
<td>5.0</td>
</tr>
<tr>
<td>CFPP (cold filter plugging point)</td>
<td>°C</td>
<td>−10</td>
<td>−20</td>
</tr>
<tr>
<td>Water</td>
<td>ppm</td>
<td>–</td>
<td>300</td>
</tr>
<tr>
<td>Acidity number</td>
<td>mg KOH/g</td>
<td>–</td>
<td>0.5</td>
</tr>
<tr>
<td>Mono-/Di-/Triglycerides</td>
<td>wt%</td>
<td>–</td>
<td>0.4/0.4/0.4</td>
</tr>
<tr>
<td>Glycerol</td>
<td>wt%</td>
<td>–</td>
<td>0.25</td>
</tr>
<tr>
<td>Oxidation stability (110 °C)</td>
<td>h</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>
Higher alcohol content may cause the degradation of rubber gaskets and should be limited to under 1%. The acidity number reflects the presence of free fatty acids, which can contribute to accelerated engine aging. For the same reasons, the water content should be kept quite low, at max. 300 ppm. Finally, in order to ensure proper storage, the oxidation stability of the fuel should be at least 5 h at 110 °C.

The above-described specifications are supported by suitable analytical methods, based on chromatography and spectroscopy [30].

### 14.2.4 Physical Properties

Saturated fatty acids are solids characterized by melting points well above room temperature, as well as by high boiling points (Table 14.5). These properties show monotonic evolution with the carbon number. If a double bond appears, an abrupt change in properties takes place. Higher free energy is reflected in lower melting and boiling points. For example, there is a significant difference in the melting points of stearic acid (70 °C), oleic acid (16 °C) and linoleic acid (−5 °C), which are saturated, with one and two double bounds, respectively. The same trend is exhibited by the methyl fatty esters, which in general have much lower melting and boiling points than the corresponding fatty acids.

Group contribution methods can be applied for property prediction of fatty-acid systems. For vapor-pressure prediction the following equation has been recently proposed and tested successfully against experimental data [6, 40]:

\[
\ln P_{v, \alpha} = \sum_k N_k \left( A_{1k} + \frac{B_{1k}}{T^{1.5}} - C_{1k} \ln T - D_{1k} \right) + \\
\left[ M_i \sum_k N_k \left( A_{2k} + \frac{B_{2k}}{T^{1.5}} - C_{2k} \ln T - D_{2k} \right) \right] + Q \tag{14.1}
\]

<table>
<thead>
<tr>
<th>Acid</th>
<th>Carbon</th>
<th>Melting point (°C)</th>
<th>Nbp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acid</td>
<td>Methyl ester</td>
<td>MG</td>
</tr>
<tr>
<td>Lauric</td>
<td>12:0</td>
<td>44</td>
<td>44</td>
</tr>
<tr>
<td>Myristic</td>
<td>14:0</td>
<td>54</td>
<td>18.8</td>
</tr>
<tr>
<td>Palmitic</td>
<td>16:0</td>
<td>63</td>
<td>30.6</td>
</tr>
<tr>
<td>Stearic</td>
<td>18:0</td>
<td>70</td>
<td>39.1</td>
</tr>
<tr>
<td>Oleic</td>
<td>18:1</td>
<td>16</td>
<td>−19.8</td>
</tr>
<tr>
<td>Linoleic</td>
<td>18:2</td>
<td>−5</td>
<td>−35</td>
</tr>
</tbody>
</table>

a) From Aspen Plus database
with $T$ in Kelvin and $P_v$ in Pascal. $N_k$ is the number of group $k$ in the molecule and $M_i$ the molecular weight. $A$, $B$, $C$, and $D$ are group parameters obtained by regression of experimental data, as shown in Table 14.6. The correction term $Q$ is given by:

$$Q = \xi_1 q + \xi_2$$  \hspace{1cm} (14.2)

The factor $q$ is calculated by:

$$q = \alpha + \beta T^{1.5} - \gamma \ln(T) - \delta T$$  \hspace{1cm} (14.3)

Table 14.6 Parameters for predicting the vapor pressure of long-chain fatty acid and derived oxygenated components.

<table>
<thead>
<tr>
<th>Group</th>
<th>$A_{1k}$</th>
<th>$B_{1k}$</th>
<th>$C_{1k}$</th>
<th>$D_{1k}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_1$</td>
<td>-117.5</td>
<td>7232.3</td>
<td>-22.7939</td>
<td>0.0361</td>
</tr>
<tr>
<td>CH$_2$</td>
<td>8.4816</td>
<td>-10987.8</td>
<td>1.4067</td>
<td>-0.00167</td>
</tr>
<tr>
<td>COOH</td>
<td>8.0734</td>
<td>49152.6</td>
<td>0.0359</td>
<td>-0.00207</td>
</tr>
<tr>
<td>CH = cis</td>
<td>2.4317</td>
<td>1410.3</td>
<td>0.7868</td>
<td>-0.004</td>
</tr>
<tr>
<td>CH = trans</td>
<td>1.843</td>
<td>526.5</td>
<td>0.6584</td>
<td>-0.00368</td>
</tr>
<tr>
<td>COO</td>
<td>7.116</td>
<td>49152.6</td>
<td>2.337</td>
<td>-0.00848</td>
</tr>
<tr>
<td>OH</td>
<td>28.4723</td>
<td>-16694</td>
<td>3.257</td>
<td>0</td>
</tr>
<tr>
<td>CH$_2$--CH$_3$--CH$_2$</td>
<td>688.3</td>
<td>-349293</td>
<td>122.5</td>
<td>-0.1814</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>$f_0$</th>
<th>$f_1$</th>
<th>$s_0$</th>
<th>$s_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esters</td>
<td>0.2773</td>
<td>-0.00444</td>
<td>-0.4476</td>
<td>0.0751</td>
</tr>
<tr>
<td>Acylglycerols</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>0.001</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Alcohols</td>
<td>0.7522</td>
<td>-0.0203</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Calculation $q$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.4443</td>
<td>-499.3</td>
<td>0.6136</td>
<td>-0.00517</td>
</tr>
</tbody>
</table>
The parameters \( \alpha, \beta, \gamma \) and \( \delta \) have been obtained by the regression of the databank as a whole. Note that the term \( Q \) takes into account the effect of functional groups by means of two parameters \( \xi_1 \) and \( \xi_2 \), in turn given by the following expressions:

\[
\begin{align*}
\xi_1 &= f_0 + N_c f_1 \\
\xi_2 &= s_0 + N_{cs} s_1
\end{align*}
\] (14.4)

\( N_c \) is the number of carbon in the molecule, while \( N_{cs} \) is the number of carbon in the alcoholic part. Table 14.6 shows the values of the parameters involved in the above correlations.

As an example, let us consider propyl laurate ester. The groups are \( \text{CH}_3 \) (2), \( \text{CH}_2 \) (12) and COO (1). In addition \( N_c = 15, N_{cs} = 3 \) and \( M_i = 242 \). The vapor pressure (Pa) is:

\[
\ln P_v = \left\{ \left[ 2(-117.5) + 12(8.4816) + 1(7.116) + 242(2(0.00338) + 12(0.00091) + 1(0.00279)) \right] + \left[ 2(7232.3) + 12(-10987.8) + 1(49152.6) + 242(2(-63.3963) + 12(6.7157) + 1(10.0396)) \right] \right\} / T^{1.5} - \left\{ 2(-22.7939) + 12(1.4067) + 1(2.337) + 242(2(-0.00106) + 12(0.000041) + 1(-0.00034)) \right\} \ln T
\]

By consequence, the following dependence vapor pressure/temperature is generated:

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>396.85</th>
<th>423.15</th>
<th>453.15</th>
<th>473.15</th>
<th>523.15</th>
<th>593.34</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_v ) (Pa)</td>
<td>261.4</td>
<td>1034.4</td>
<td>3749</td>
<td>7680</td>
<td>18798</td>
<td>100000</td>
</tr>
</tbody>
</table>

The method can be applied for saturated fatty acids, unsaturated fatty acids, fatty esters, fatty alcohols and acyl-glycerols. The regression is based on 1200 data points. The absolute deviation in predicting vapor pressure is 6.82%. Another advantage of Eq. (14.1) is the capability of predicting the VLE of mixtures of fatty acids and esters by using the UNIFAC model for liquid activity. The comparison with experimental data shows good accuracy not achieved by other methods [40].

As mentioned above, the viscosity is an important physical parameter. Table 14.7 presents comparatively the values recommended by the standards for diesel fuels in the USA and Europe. It can be observed that they are in a small range, but the upper limit is somewhat higher for biodiesel with respect to petrodiesel. Actually, the fatty esters exhibit larger variation of viscosity due to their chemical nature compared with hydrocarbon molecules. Influencing factors are chain length, position, number, and nature of double bonds, as well as the nature of the
oxygenated groups [26]. As illustrated by Table 14.8, the introduction of a double bond contributes significantly to lowering the kinematic viscosity of all concerned species. The effect of oxygenated moieties is approximately $\text{COOH} \approx \text{C} = \text{O} > \text{COOCH}_3 \approx \text{C} = \text{O} > \text{C} = \text{O} > \text{C} > \text{no oxygen}$. It is interesting to note that the introduction of a second $-\text{OH}$ group in the C18:1 chain, as in methyl ricinoleic issued from ricinoleic acid (C18:1–12$-\text{OH}$), has a dramatic impact on viscosity, which rises by an order of magnitude. For example, the unblended biodiesel from castor oil exceeds the viscosity specification.

### 14.3 Manufacturing Processes

#### 14.3.1 Batch Processes

Older biodiesel processes are essentially batchwise. The oil is submitted to transesterification in a stirred-tank reactor in the presence of a large amount of methanol, and base catalyst, mostly NaOH or KOH. An excess of methanol is necessary chiefly to ensure full solubility of triglyceride and keep the viscosity of the reaction mixture low, but also for shifting the chemical equilibrium. A minimum molar ratio methanol:triglyceride of 6:1 is generally accepted [16, 17, 29]. The reaction
Biodiesel manufacturing takes place at temperatures from 60 to 80°C, slightly below the mixture boiling point at the operating pressure. Previously, the oil should be neutralized by treatment with aqueous sodium hydroxide for the removal of free fatty acids. These can be found between 0.5 and 5% in the vegetable oils, somewhat more in animal fats, but can rise to up to 30% in used cooking oil. High FFA content needs special pretreatment by esterification. The transesterification reaction may be considered finished when the conversion reaches 98.5%. However, the mixture composition should respect the quality biodiesel specifications. The excess methanol is recovered for the next batch. The remaining mixture is submitted to the separation of esters from glycerol. This can take place either by decantation or by centrifugation. Water may be added to improve the phase split. The oil phase containing fatty esters is sent to finishing by neutralization with acid, followed by washing and drying. Phosphoric acid is frequently for neutralization used since Na₃PO₄ or K₃PO₄ can be recovered and sold as fertilizers. The water phase from washing is returned to glycerol separation.

After mixing of glycerol streams the result is about 50% glycerol–water solution with some methanol, residual base catalyst and soaps. Firstly, the methanol recovery takes place by flash distillation or film evaporation. Then, by adding acid the soaps are transformed in free fatty acids, which separate from glycerol as a top oily phase. Next, the FFA can be recovered and valorized by esterification with methanol. Finally the glycerol should have a purity of about 85% and be sold to specialized refiners. Purity of 99.5–99.7% can be achieved by applying vacuum distillation or ion-exchange process.
The batch process allows high flexibility with respect to the composition of the feedstock. In turn, the economic indices are on the lower side because of lower equipment productivity and higher operation costs, such as manpower and automation. The use of a large excess of methanol is reflected in higher energy consumption if no heat-integration measures are taken. Large amounts of wastewater formed by acid-base neutralization need costly treatment.

The productivity can be greatly improved by the implementation of continuous operations and the use of process-intensification techniques, such as reactive distillation. The replacement of a homogeneous catalyst by a heterogeneous one is highly desirable. These aspects will be discussed in greater detail in the next section.

14.3.2 Catalytic Continuous Processes

Figure 14.3 depicts the conceptual scheme of a continuous process working at low pressure that is capable of processing a feedstock with a larger amount of free fatty acids, such as unrefined nonedible vegetable oils, tallow fat and used cooking oil. For this reason in the first reactor R-1 the esterification of free fatty acids with methanol is carried out, preferably in a reactive-distillation device with solid catalyst. The amount of FFA should be reduced to below 1%, but preferably under 0.5%. Then the transesterification reaction follows in the unit R-2. A homogeneous catalyst is currently used, either as alkaline hydroxide or alkaline methoxide. The conversion should be high enough, in general over 98.5%. To ensure high yield in monoester and minimum amounts of mono-/di-/triglycerides minimum two reactors in series with glycerol intermediate separation should be employed.

![Figure 14.3 Process flow diagram for biodiesel manufacturing by a continuous process.](image-url)
reaction mixture is then submitted to phase separation in crude ester and glycerol in the unit S-1. The separation can take place by decanting or by centrifugation. The glycerol phase is treated with acid for soap removal and recovery as FFA. Then, the methanol is recovered by evaporation and recycled. The crude ester follows the route of methanol separation in the unit S-4, the neutralization of the entrained catalyst, as well as the conditioning of biodiesel by washing and drying. The material balance loop is closed by the recovery of excess methanol from water solution by distillation.

The scheme in Figure 14.3 shows a modern method of ester/glycerol separation, namely by the technique known as “coalescence separator” [21]. This is applied in Figure 14.3 to the unit D-1. Such equipment avoids the use of water for phase separation. In this way, much more concentrated glycerol can be obtained with water only from the neutralization operation of low salt content. Another advantage is low energy consumption for methanol recovery. Such technology is applied by Henkel in Germany by the production of fatty-acid methyl esters [7].

Using a solid catalyst in the transesterification phase allows a substantial simplification of the process flowsheet. Figure 14.4 illustrates the process ESTERFIP-H™ developed by the French Petroleum Institute [2]. Two reactors are employed with intermediate glycerol separation. Excess methanol is recovered by multistage flash evaporation represented by the units S-1, S-2, S-3 and S-4. Phase separation of ester and glycerol are carried out in the units D-1, D-2 and D-3 by coalescence separation or centrifugation. It can be seen that the neutralization and washing steps are absent. Methanol can be recycled as vapor, with the result of low energy consumption.

![Simplified flowsheet of a transesterification process using a solid base catalyst](image.png)

**Figure 14.4** Simplified flowsheet of a transesterification process using a solid base catalyst [2].
14.3.3

Supercritical Processes

Performing the esterification in supercritical conditions has been studied initially as a method to solve the problem of miscibility of oil and methanol that hinders the kinetics in normal conditions. Since the critical coordinates of methanol are $T_c = 239^\circ C$ and $P_c = 80$ bar, raising the temperature and pressures at sufficiently high values is necessary. Studies conducted in Japan demonstrated the feasibility of producing biodiesel by the esterification of rapeseed with methanol without a catalyst working around $350^\circ C$ and 200 bar at molar ratio methanol:oil of 42:1 for reaction times below 4 min [10, 27, 28, 38]. The advantage of avoiding a catalyst is obvious. However, the conditions of pressure and temperature are severe and need special equipment. Recent research showed the real yield can be reduced by thermal degradation of biodiesel, namely of unsaturated fatty esters [20]. For this reason, lowering the reaction temperature and pressure is highly desirable.

The assessment of the critical region of a mixture triglyceride/methanol can be made by applying the approach explained next. The critical properties of individual triglycerides components can be estimated by a suitable group-contribution method, and then using mixing rules for averaging the parameters function of composition. As an example, let us consider coconut oil, based on lauric and myristic acids (see Table 14.3). The critical properties of the oil calculated by Lydersen’s method [34] are $T_c = 606.8^\circ C$ and $P_c = 6.2$ atm. Table 14.9 presents the critical values obtained for different molar ratio methanol/oil starting with 6, corresponding to a low solubility limit, and ending with 42, the highest practical value tested in laboratory experiments [3]. It can be seen that the critical temperature drops rapidly with increased methanol/oil ratio to about $280^\circ C$, while the critical pressure rises up to about 70 atm, close to methanol. In practice, operating parameters of $350^\circ C$ and 190 bar were employed at a residence time of 400 s.

The addition of cosolvent in combination with supercritical conditions seems to be an efficient means to reduce significantly the operating temperature [4]. For example, soybean oil could be converted with methanol into biodiesel with 98% yield by using propane, at least in 0.05 molar ratio to methanol, at $280^\circ C$ and 12.8 MPa. Similar results have been reported with CO$_2$ in a molar ratio of 0.1 with respect to methanol. In both cases the optimal ratio methanol/oil was 24 and residence time of 10 min [5].

Table 14.9 Critical properties of mixtures oil/methanol at different molar ratios $R$ [3].

<table>
<thead>
<tr>
<th>Properties</th>
<th>MeOH</th>
<th>Coconut oil</th>
<th>$R = 6$</th>
<th>$R = 12$</th>
<th>$R = 24$</th>
<th>$R = 42$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$, $^\circ C$</td>
<td>239.5</td>
<td>606.8</td>
<td>395.9</td>
<td>345.9</td>
<td>305.8</td>
<td>282.2</td>
</tr>
<tr>
<td>$P_c$, atm</td>
<td>79.9</td>
<td>6.2</td>
<td>37.2</td>
<td>50.3</td>
<td>61.7</td>
<td>68.4</td>
</tr>
<tr>
<td>$V_c$, l/mol</td>
<td>118</td>
<td>2.366</td>
<td>0.33</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
</tr>
</tbody>
</table>
Due to the absence of the catalyst the process flowsheet employing the supercritical technology should be much simpler, but in exchange the manufacture of hardware is much more demanding. Effective energy integration is also necessary. Despite these advantages the industrial implementation of supercritical esterification has not been reported.

14.3.4 Hydrolysis and Esterification

A simpler manufacturing procedure would consist in first performing the hydrolysis of triglycerides and isolating the fatty acids followed by esterification employing the robust technology of a solid heterogeneous catalyst. Significant advantages would be the possibility of extracting high value fatty acids from the lipid material, as well as obtaining high-purity glycerol. The hydrolysis reaction can be carried out without a catalyst working in milder conditions compared to full esterification. A temperature close to 270°C and pressures from 70 to 200 bar have been found applicable [31]. Another advantage is that the overall yield can be increased by suppressing the back reaction of glycerol with the methyl ester. The reaction exhibits an autocatalytic effect due to the fatty acid produced, from which a small recycle can be provided.

Figure 14.5 presents a conceptual flowsheet. Oil and water are brought at high pressure, homogenized in a static mixer and heated. A volumetric ratio water/oil 1:1 is appropriate. The hydrolysis takes place in the reactor R-1 in slightly subcritical conditions at 270°C and 100 bar. The yield in fatty acids is around 90% for a residence time about 40 to 60 min [28]. Therefore, a simple long coil can be used as the chemical reactor. After cooling and pressure reduction, the reaction mixture is separated into two phases in S-1. The oily phase containing a large majority of fatty acids is sent directly to esterification, or optionally to fatty-acid separation in the unit S-2 by vacuum distillation. The esterification reactor R-2 is preferably a reactive distillation using a solid acid catalyst on structured packing. The heavies

![Figure 14.5 Process for biodiesel by supercritical hydrolysis and esterification.](image-url)
from S-2 containing glycerides can be recycled to R-1, or disposed of as combustible waste. The unit R-2 delivers in bottom fatty-acid methyl esters diluted with methanol, from which biodiesel with fuel specifications is obtained from the evaporator Ev-1. The top stream from R-2 is sent to the distillation column S-3, from which water and methanol are recovered and recycled to R-1 and R-2, respectively. The glycerol phase from S-1 goes to the unit S-4 from which high-purity glycerol is obtained.

Summing up, the process based on the hydrolysis of triglycerides seems very attractive, despite the fact that supercritical operation raises a technical challenge. By making use of recycles the process can be designed to achieve material consumption close to stoichiometric requirements. Pumping liquids at high pressures requires moderate energy. By heat integration the utility consumption could be kept at low level.

### 14.3.5 Enzymatic Processes

The transesterification reaction can be catalyzed by enzymes, the most common being the lipase. The reaction takes place at normal pressure and temperatures 50 to 55°C with low energy consumption. The yield of methanolysis depends on several factors as temperature, pH, type of micro-organism producing the enzyme, the use of cosolvents, etc. However, low yields in methyl esters and very long reaction times make the enzymatic processes not competitive enough at this time [9, 11, 17].

### 14.3.6 Hydropyrolysis of Triglycerides

A fundamentally different chemical way of converting biotriglycerides to fuels is hydrogenation followed by pyrolysis in the presence of a suitable catalyst. The process invented by the Finnish company Neste Oy [www.nesteoil.com] is known as NExBTL (biomass to liquid). Figure 14.6 shows a simplified reaction scheme. The fuel produced is essentially a mixture of long-chain hydrocarbons instead of long-chain esters. In addition, the whole feedstock is valorized, including glycerol converted to propane. It is claimed that the resulting fuel has superior combustion

![Figure 14.6 Reaction scheme describing the NExBTL process.](image-url)
properties compared to ester biodiesel, such as for example higher cetane number (84 to 99), cloud point down to \(-30^\circ C\) and better storage stability. For this reason NExBTL is occasionally called “second-generation” biodiesel. However, this process implies the availability of a low-cost hydrogen source, as well as more complex and expensive equipment.

14.3.7
Valorization of Glycerol

Glycerol is a high added value byproduct when it can be isolated of high purity. This is the case when solid catalyst or supercritical hydrolysis is employed. Because of biodiesel large amounts of low-quality glycerol become available and the price is pushed down. For example, 10 million tons per year biodiesel supplies glycerol of 1 million tons per year. Converting the glycerol to chemicals and/or fuels becomes imperative. One alternative is etherification with alcohols (e.g. methanol or ethanol) or alkenes (e.g. isobutene) to produce branched oxygenated components. Various catalysts can be employed such as zeolites, ion-exchange resins and acidic homogeneous catalysts. Tert-butyl ethers of glycerol can be used as ingredients in biodiesel and gasoline, offering an alternative to oxygenates additives such as ETBE.

14.4
Kinetics and Catalysis

14.4.1
Homogeneous Catalysis

Homogeneous catalysis remains largely employed today because ensuring simple and robust technology, as well as high reaction rates, despite some important economical and environmental disadvantages [7–9, 11, 16, 17, 37]. For the production of biodiesel by transesterification both acid and base catalysis can be applied, but the latter is much more efficient. The difference can be explained by the reaction mechanism, as explained by Figures 14.7 and 14.8. The glycerol part of the triglyceride is designated by R1 and the fatty acid by R2. In homogeneous acid catalysis (Figure 14.7) the first step consists of triglyceride activation by protonation (1) at the CO group where the oxygen is more active, followed by the formation of a carbocation complex (2). By nucleophilic attack with methanol (3) a tetrahedral carbon complex forms, which by losing the proton decomposes further (4) in a new methyl fatty ester and diglycerides. The methanolysis proceeds similarly with diglyceride and monoglyceride. It can be seen that if water is present it will produce fatty acid by hydrolysis in the step (3) and as a consequence it will decrease the yield of fatty ester. For this reason the water amount in the triglycerides should be reduced below 0.5%.

Base catalysis involves a completely different mechanism, as explained by Figure 14.8. The active species this time is an alkoxide, namely the methoxide \(^n\text{O–CH}_3\).
This can be produced \textit{in-situ} by the reaction of methanol with hydroxide liberating water:

\[
\text{NaOH} + \text{CH}_3\text{OH} \leftrightarrow \text{Na}^+\text{OCH}_3 + \text{H}_2\text{O}
\]

The methoxide can be introduced as preprepared from alcohol and an alkali metal. In this case, the absence of water favors the reaction rate, as well as easier post-processing. The first step consists of the nucleophilic attack of the methoxide to the carbonyl group, which leads to the formation of a tetrahedral carboanionic complex. Next, the transition complex decomposes into a fatty ester and a diglycerol anion, which reacts with an alcohol molecule, reforming the catalytic species. The other transesterification stages take place similarly. The whole reaction process is controlled by chemical equilibrium.

As mentioned above, the reaction rate by base catalysis is much faster than by acid catalysis by three orders of magnitude. The above presentation of the reaction mechanism can deliver an explanation: the formation of carboanionic tetrahedral intermediate results directly by the nucleophilic attack of the substitution species, while the carbocationic complex needs an intramolecular arrangement.

The transesterification of triglycerides with methanol to fatty methyl esters and glycerol implies three reaction stages passing through the formation of diglyceride and monoglyceride intermediates. For each stage the equilibrium constant can be expressed as the ratio of forward and backward reactions:
Kinetic experiments have been reported in literature for the treatment of different
types of lipidic feedstock with methanol, such as for soybean [16, 33], rapeseed
[25] and sunflower oil [1, 36]. The aim is to optimize the reaction conditions,
namely the amount of catalyst, the excess of methanol and the reaction tempera-
ture. The results depend largely on the composition of the raw materials, but some
trends can be distinguished:

1. Optimal amount of base catalyst is 0.5 to 1.5% w/w. Methoxides are more active
than alkali hydroxides. More catalyst than needed favors soap formation and makes phase separation difficult.

2. The optimal molar ratio of methanol/triglyceride is between 6 and 9. Adding
small amounts of cosolvents, such as propane and tetrahydrofuran, can reduce
the excess of methanol.

3. The optimal reaction temperature is rather low, between 60 and 80 °C.

Since the reaction network consists of three-step series-parallel reactions, an
important aspect in the kinetic modeling is the relation to the end-product speci-
fications, more precisely the content in tri-, di- and monoglycerides. Table 14.10
presents the results of a recent study regarding the methanolysis of sunflower oil
by using NaOH catalyst [1] and second-order kinetics based on the stoichiometric
coefficients. The standard run measurements were done at a molar reactant ratio
of 6, 0.5% catalyst, 60 °C and mixing speed of 400 rpm. The results draw attention
to a complex reaction mechanism in the sense that the kinetic constants depend
on the operation conditions. The first reaction leading to diglyceride is the slowest
step. The equilibrium constants of the first and last stage are close to 10, but about
3 for the intermediate step. As a consequence, even if the triglyceride conversion
can reach high values over 97.5% the amount of monoglyceride will remain sub-
stantial, around 2%, well above the maximum of 0.4% tolerated by quality specifi-
cations. In contrast, the amount of di- and tri-glycerides may drop below 0.5%.
Using an excess of methanol does not help to reduce the concentration of mono-
glyceride. Another strategy is needed, as shown later in this chapter.

| Table 14.10 Kinetic constants for the methanolysis of sunflower oil [1]. |
|-----------------|-------|------|-------|-------|-------|-------|
|                 | \(k_1\) | \(k_2\) | \(k_3\) | \(k_4\) | \(k_5\) | \(k_6\) |
| Standard run    | 0.0895 | 0.0094 | 0.3480 | 0.1285 | 0.4884 | 0.0380 |
| Mixing at 600 rpm| 0.1316 | 0.0195 | 0.3227 | 0.2470 | 0.8611 | 0.0606 |
| Reaction at 40 °C| 0.0218 | 0.0029 | 0.0651 | 0.0319 | 0.2280 | 0.0128 |
| 1.0% catalyst   | 0.2314 | 0.0166 | 0.4488 | 0.1068 | 0.8770 | 0.0632 |
| 10:1 mole ratio | 0.0738 | 0.0067 | 0.0811 | 0.0798 | 0.3472 | 0.0537 |
| Activation energy | 14.040 | 10739 | 16049 | 13907 | 7173 | 10997 |

a) \(1/\text{mol/min}\)

b) \(\text{cal/mol}\)
14.4.2 Heterogeneous Catalysis

The replacement of homogeneous catalysis by solid catalysts brings obvious economical and technological advantages. For this reason, a considerable research effort is being devoted in this area.

A first application regards the esterification reaction. Here, solid catalysts with acidic character can be used, such as zeolites, ion-exchange resins, sulfated metal oxides, sulfated carbon fibers, etc. However, only few are suitable for handling long-chain complex molecules. Figure 14.9 presents a comparison of acidic heterogeneous catalysts that can be used in biodiesel manufacturing [23]. Some can achieve super acidity comparable with sulfuric acid. Ion-exchange resins, such as Nafion and Amberlyst are capable of achieving high reaction rate at moderate temperatures below 130°C, but their chemical stability at longer operation seems to raise concerns. On the contrary, sulfated zirconia and tin oxides can be used at higher temperatures, 140 to 180°C, and ensure high reaction rates, but are sensitive to deactivation by sulfur-group leaching if free water is present. Since the water produced by esterification limits also achieving high conversion because of the chemical equilibrium, a good solution for solving both problems is employing reactive distillation.

The second area of heterogeneous catalysis in biodiesel manufacturing is the transesterification reaction. Here again, the base catalysts exhibit typically much higher activity than the acidic ones, but finding effective catalysts is still an open problem. Some solid metal oxides, such as those of tin, magnesium, and zinc could be used directly, but they actually act by a homogeneous mechanism.

Figure 14.9 Esterification of dodecanoic acid with 2-ethylhexanol: comparison of homogeneous and heterogeneous acid catalysts at 130°C (left); comparison of Amberlyst, Nafion and sulfated zirconia (SZ) at 150°C (right). The amount of solid catalyst, 3 wt%, refers to the total mass of reactants [23, 24].
producing a significant amount of soaps or glycerates. A variety of synthetic catalysts based on alkaline-earth metal oxides (Ca, Mg, Sn, Zn), as well as alkali metals (Na, K) hydroxides or salts impregnated on alumina have been studied to date, but their activity and robustness remains insufficient [11–13, 39]. As mentioned, a successful industrial application of base heterogeneous catalysis has been reported [2], but not confirmed by other studies so far.

14.5 Reaction-Engineering Issues

In older processes based on a batch reactor the research from the laboratory can be scaled up without much difficulty. However, the overall productivity is seriously diminished by the time of additional operations, such as charge loading, heating, cooling and discharging. Switching on continuous reactors offers a number of alternatives, as will be presented in this section. As a modeling basis we consider the kinetics of sunflower oil catalyzed by NaOH, as described by the data in Table 14.11. The simulation is done in Aspen Plus™, the chemical species being assimilated to those corresponding to oleic acid. The target is to obtain the biodiesel quality as close as possible to the specifications presented in Table 14.5.

Firstly, the relation composition–time in a batch operation is computed (Figure 14.10). The profile corresponds to series-parallel equilibrium reactions. At 60°C the reaction rate catalyzed by NaOH is fast: conversion over 98.5% can be reached in 20 min and chemical equilibrium at 99.8% in about 30 min. However, the content in mono- and diglycerides remains relatively high at 6.5 and 2.2% mol, or 2.6 and 1.6 wt%, much higher than the required specifications. Lowering the
temperature to 50 °C can slightly shift the equilibrium to lower DGLY and MGLY, still above specifications, but the reaction time becomes longer. Another possibility is raising the amount of methanol with the disadvantage of supplementary costs. Therefore, an effective method is performing the reaction in minimum two steps, with intermediate removal of glycerol so as to limit the backward reactions as much as possible.

Figure 14.11 presents alternative continuous plug-flow reactors (PFR) for the transesterification reaction. An isothermal plug-flow reactor has identical performance with a batch reactor in terms of conversion and product distribution. A PFR can be built either as a tubular reactor, or as series of a sufficient number of perfectly stirred zones hosted in the same shell. Considering homogeneous or heterogeneous catalysis generates subsequent alternatives. A packed-bed column (Figure 14.11a) is suitable when a superactive heterogeneous catalyst is available. PFR as long reaction tube (Figure 14.11b) can be used with homogeneous or heterogeneous catalyst, at least as a prereactor. Static mixing elements can be inserted to ensure homogeneous phase reaction.

An interesting possibility for performing the transesterification reaction is offered by reactive distillation (RD). This has been applied at the laboratory scale with a homogeneous catalyst demonstrating superior productivity [19]. Solid catalyst imbedded in structured packing can be used if its activity is high enough to cope with the constraints set by the hydraulics. A key advantage of reactive distillation is the possibility of ensuring much higher local ratio methanol/glycerides than in a PFR by means of the internal reflux, while the initial feed can be close to stoichiometric requirements. The energy consumption can be kept reasonable low by appropriate heat-integration measures, namely operating the column at higher pressure and temperatures.

Continuous stirred-tank reactors (CSTR) are currently used for biodiesel manufacturing. Obviously, a single CSTR would require a huge volume to achieve the performance of a batch or PFR-like reactor, but the use of several CSTRs in series can improve the productivity considerably (Figure 14.12a). Intermediate
separation of glycerol will help achieving lower monoglycerides content. Another possibility for increasing the productivity is a multiagitated reaction column (Figure 14.12b), applicable for both homogeneous and heterogeneous catalysts. In addition, PFR and CSTR-like reactors can be combined, the first being more productive at higher conversions.

Summing up, from the reaction-engineering viewpoint there are a considerable number of alternatives. The most critical factor in design is the availability of an active catalyst and its performance with respect to the raw materials.

### 14.6 Phase-Separation Issues

A key operation in biodiesel manufacturing is the separation of glycerol and FAME from the reaction mixture by liquid–liquid decanting. Thermodynamic studies on this subject are scarce despite the industrial interest. Table 14.11 presents data for...
the system methanol/methyl oleate/glycerol that could be seen as representative [32]. It can be observed that the reciprocal solubility of glycerol and methyl ester at 60 °C is very low, the ester being practically insoluble in glycerol. Methanol is distributed between the phases but preferentially in glycerol. The same remains valid at higher temperature. The mono-olein has a low solubility in the glycerol phase. Note that the LLE prediction by UNIFAC or UNIFAC-Dortmund for the system methanol-glycerol-methyl ester is in satisfactory agreement with the experimental data, but deviates considerably for the mixture involving mono-olein. The data from Table 14.12 can serve for identifying the binary interaction parameters of a convenient thermodynamic model, such as NRTL.

14.7 Application

As a simulation example we treat the production of biodiesel from rapeseed in a plant capacity of 200 ktonne per year. The feedstock has a high content of oleic acid triglyceride, around 65%, such that the kinetic data from Section 14.6 can be used for sketching the design of the reaction section. For simplification, we consider that the oil was pretreated for removing impurities and gums, as well as FFA by esterification over solid catalyst. The free fatty acids and water content in oil feed should be less than 0.5%w. NaOH and KOH in 0.5 to 1.5% w/w are used as catalysts.

It is useful to examine a simple material balance in terms of the stoichiometric requirements, as presented in Table 14.12. It can be seen that the amount of lipid largely dominates the manufacturing rate. The glycerol obtained as a byproduct is approximately equal to the amount of methanol introduced in the reaction. The same large imbalance is also valid for the volumetric feeds.

Figure 14.13 presents a process flow diagram built up with the conceptual elements examined so far in this chapter. The flowsheet aims to illustrate different reaction and separation techniques. Note that the heat-integration elements are not presented in order to keep the flowsheet simple. The feed of oil and methanol, including recycle, ensures a molar ratio methanol:oil of 6:1. Good mixing of reactants is necessary to ensure a homogeneous reaction phase, otherwise an induction period will affect the conversion. The mixing of reactants can be done preferably in a static device.
Figure 14.13 Process flow diagram for biodiesel manufacturing.
After heating at about 65 °C the esterification starts in the reactor R-1, which can be a CSTR, but preferably a PFR or a combination PFR/CSTR. The first reactor should ensure a conversion slightly above 90%. Intermediate removal of glycerol takes place to shift the equilibrium and get lower content of monoglyceride. A simple phase split by decanting can be applied at temperatures of 40 to 60 °C. The decanting time could be very variable, between a few minutes and 1h. The presence of soaps and monoglycerides hinders the phase separation, while more neutral pH and lower methanol content helps. Modern coalescence separators can ensure a relatively smooth separation if the amount of soap is not excessive.

After makeup in methanol and catalyst the oil phase is submitted to a second transesterification step in the reactor R-2. The conversion should rise to a minimum of 98.5%. The phase separation is done this time by means of the centrifuge K-1. It is worth noting that centrifugal phase separation is becoming a state-of-the-art method in biodiesel technology. Centrifugation can be applied in all separation steps, including neutralization, washing and soap removal. Centrifuges of various capacities are available, such as from 60 to 1600 tonne/day supplied by the German company GEA.

After neutralization with acid, H₃PO₄, the resulting mixture is submitted to methanol stripping. In this way, about 90% from the excess methanol can be recycled directly to reaction section. The next stage is a wash with hot water at 50 °C for deep purification from methanol, glycerol, soaps and salt. This operation can be done in a countercurrent column, or directly in a centrifugal separator. Because of the presence of double bounds and ester groups the oil phase will contain a significant amount of water, well above the threshold of 300 ppm set by the specification norm (see Table 14.5). The removal of water and residual solids from the biodiesel is done by centrifugation in the unit K-2, and the final polishing before shipping by a vacuum flash evaporator.

The glycerol recovered in the previous stages is treated with acid for catalyst neutralization. The soaps are converted to fatty acids that precipitate at the top of the glycerol phase, and are sent back to the esterification stage.

After pH adjustment the crude glycerol is submitted to methanol recovery by vacuum distillation. The bottom product is usually a glycerol–water solution of about 50%. Its concentration can be increased up to 85% by vacuum evaporation. The water is recycled to the washing step. Normally, the glycerol is shipped to a specialized refiner, where the purity can be increased further to 99.5 and 99.7% by ion-exchange techniques and vacuum distillation.

The above flowsheet can be simulated by means of an appropriate simulation package. In the absence of a comprehensive kinetic model and of fundamental thermodynamic data the results will be only approximate, namely with respect to satisfying the quality specifications. However, the simulation allows the designer to obtain an overall view of streams, utilities and equipment, needed for an economic assessment.

Haas et al. [18] developed a computer model to estimate the capital and operating costs of a moderately sized industrial biodiesel production facility with a capacity of 33.5 ktonne (10 million gallons) using degummed soybean oil as
feedstock. The major process operations were continuous transesterification, as well as ester and glycerol recovery, the process flow diagram being close to those presented in Figure 14.13. The investment costs inside battery limits were calculated to be 11.3 million US$. The largest contributors, accounting for nearly one third of the expenditures, were storage tanks of feedstock and products, sized for 25-day period. At a value of US$ 0.52/kg for feedstock soybean oil, a biodiesel production cost of US $0.53/l was predicted. The oil feedstock accounted for 88% of total estimated production costs. These are linearly dependent on the cost of oil. The sale of glycerol 80% could reduce the production costs by 6%.

14.8 Conclusions

Biodiesel is an alternative renewable fuel that has seen rapid development in recent years, namely in Europe. It can be manufactured from vegetable or animal fats by reaction with light alcohols, namely with methanol and ethanol. In most cases, the biodiesel is a mixture of fatty-acid methyl esters (FAME). From the chemistry viewpoint the raw materials for biodiesel are quite homogeneous, being based on triglycerides. These are esters of glycerol with fatty acids involving both saturated and unsaturated long carbon chains from C14 to C20. Another possibility is converting the triglycerides with hydrogen to hydrocarbons. The fuel obtained has superior combustion features and good CO₂ balance being sometimes called “second-generation” biodiesel.

The key merit of converting triglycerides into fatty esters is a drastic reduction in viscosity, about one order of magnitude, at a level compatible with the fuel-injection devices. The biodiesel is environmental friendly. Better combustion allows the level of greenhouses gases to be reduced, while sulfur is practically absent.

The quality of biodiesel is regulated by standards. The most important regards the content of free and bound glycerol. This cannot be modified by effective separation techniques. Therefore, the major element in design should be to obtain a composition of the mixture leaving the reaction system capable of matching the biodiesel specifications. This is difficult to achieve in view of the variety of raw materials.

Several technologies can be employed. The most widespread today makes use of homogeneous catalysts, in batch or in continuous-flow environments. Both reaction and separation steps can create bottlenecks. The availability of heterogeneous catalysis allows the suppression of neutralization and washing steps, leading to a simpler and more efficient process. However, the research of super active and robust catalysts is still an open problem. Supercritical hydrolysis and transesterification can be conducted without a catalyst, but in extreme conditions of pressure and temperature.

The design of the reaction section offers several alternatives. Plug-flow-like reactor type gives the best productivity with resonable reaction times from 10 to
20 min. Two-stage reactions with intermediate glycerol removal is necessary for pushing the equilibrium composition to low mono- and di-glycerides content. A reactive distillation environment is particularly efficient for both esterification and transesterification when a superactive and robust solid catalyst is available.

Evaluating the profitability of biodiesel manufacturing reveals that this is dominated by the cost of the raw materials by more than 80%. The storage tanks account for more than one third of the equipment costs. Therefore, further progress can be achieved in simplifying the process by adopting heterogeneous catalysis or supercritical processing.

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