



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

A review analyzing the industrial biodiesel production practice starting from vegetable oil refining

Citation for published version:

Santori, G, Di Nicola, G, Moglie, M & Polonara, F 2012, 'A review analyzing the industrial biodiesel production practice starting from vegetable oil refining', *Applied Energy*, vol. 92, pp. 109-132.
<https://doi.org/10.1016/j.apenergy.2011.10.031>

Digital Object Identifier (DOI):

[10.1016/j.apenergy.2011.10.031](https://doi.org/10.1016/j.apenergy.2011.10.031)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Early version, also known as pre-print

Published In:

Applied Energy

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



2
3 **A review analyzing the industrial biodiesel production practice starting from**
4 **vegetable oil refining**

5 Giulio Santori^a, Giovanni Di Nicola^b, Matteo Moglie^b, Fabio Polonara^b

6 ^aThe University of Edinburgh, School of Engineering, Institute for Materials and Processes, Sanderson Building,
7 The King's Buildings, Mayfield Road, EH9 3JL, Edinburgh, Scotland, UK ^bUniversità Politecnica delle Marche,
8 Dipartimento di Energetica, via Breccie Bianche, Polo Montedago, 60131, Ancona, Italy, g.dinicola@univpm.it

9
10 **Abstract**

11 One of the most promising renewable fuels proposed as an alternative to fossil diesel is biodiesel. The
12 competitive potential of biodiesel is limited by the price of vegetable oils, which strongly influences
13 the final price of this biofuel. On the other hand, extensive use of vegetable oils may cause other
14 significant problems such as starvation in developing countries. Appropriately planning and designing
15 the whole production process, from the seed to the biodiesel end-product, is essential to contain the
16 influence of energy inefficiencies on the high price of the end-product. The present study reviews the
17 technologies currently used in the production of biodiesel. We first discuss the technologies for
18 extracting the vegetable oil from the seed, and its subsequent refining and conversion into biodiesel.
19 This study focuses on the characteristics of the production processes currently used in the sector,
20 illustrating the technological options and emphasizing the drawbacks of certain practices and the best
21 choices available. The vegetable oils tend to be processed using procedures that are well established,
22 but oriented more towards obtaining products suitable for the foodstuffs industry, and that
23 consequently use technologies that are sometimes excessive for energetic purposes. The processes for
24 extracting the vegetable oil from the seed generally include a set of steps, the complexity of which
25 depends on the raw material. Basically, the two extraction technologies involved rely on the use of
26 pressure or solvents. In practice, the two systems are often combined. Using the vegetable oils as a
27 source of energy makes some of these steps superfluous and enables technologies to be used that
28 would be unsuitable for foodstuffs production. This study focuses on feasible technological
29 improvements that would give rise to oil that is still suitable for use as a source of energy, but at a
30 lower cost. The refined vegetable oil can subsequently be converted into biodiesel by means of a great
31 variety of technologies, many of which are still not suitable for applications on an industrial scale.
32 The solution that has met with the greatest favor is homogeneous alkaline transesterification with
33 KOH and methanol. Even when dealing with this type of conversion alone, it is impossible to
34 establish a universal schema to describe the conversion or purification stages because there are
35 numerous possible different solutions. When we then look more closely at the state of the art in
36 industrial biodiesel production plants, we encounter the potential problems introduced by the type and
37 characteristics of the original raw material. Comparing some of the reference solutions that have
38 inspired numerous installations, a sensitivity analysis is conducted on the main elements involved in
39 the process, focusing on their behavior in different working conditions to obtain products with the
40 characteristics required by the international standards (EN 14214:2008, ASTM D 6751 07b).

41
42 **Keywords:** biodiesel, production process, industrial practice, vegetable oil refining, biodiesel
43 refining, transesterification

51	Contents
52	1. Introduction
53	2. Characteristics of vegetable oils
54	3. Industrial scale production of vegetable oils
55	3.1. Common vegetable oil refining processes
56	3.2. Processing cost and market of refined vegetable oil
57	3.3. Special refining processes for biodiesel production
58	3.3.1. Esterification
59	4. Transesterification
60	5. Guidelines on the biodiesel production process
61	5.1. The pumping in biodiesel plants
62	5.2. Transesterification reactors
63	5.2.1. Stirred batch reactors
64	5.2.2. Continuous stirred tank reactors and other reactors
65	5.3. Separation of the BD phase from the GL phase
66	5.4. Recovering excess alcohol from biodiesel
67	5.5. Ester washing
68	5.6. Ester drying
69	5.7. Adding oxidation inhibitors
70	5.8. GL phase acidification
71	5.9. Separation of the alcohol from the GL phase
72	5.10. Alcohol purification
73	6. Three basic plant process flow diagrams
74	6.1. Set-up of common components
75	6.2. Process flow diagram 1
76	6.2.1. Washing column L1-WASH analysis
77	6.2.2. Dryer L1-DRYER analysis
78	6.2.3. GL phase flash evaporator L1-FLASH-02 analysis
79	6.3. Process flow diagram 2
80	6.3.1. Flash evaporator L2-FLASH-01 analysis
81	6.3.2. Washing column L2-WASH analysis
82	6.4. Process flow diagram 3
83	6.4.1. GL phase flash evaporator L3-FLASH-02 analysis
84	6.4.2. Glycerin drying L3-DRYER analysis
85	7. Standardization of biodiesel
86	8. Conclusions
87	Acknowledgements
88	References
89	
90	

91 **1. Introduction**

92 Crude oil is a non-renewable resource that will eventually run out. In the meantime, the steady
93 increase in its consumption, the depletion of the reserves and the uncertain political situation in some
94 oil-producing countries are leading to a rapid increase in the cost of crude oil.

95 Alternatives to oil are renewable energy sources and, among these, vegetable oils and their energy
96 derivatives [1, 2] and biodiesel, in particular are regarded as the most promising. Biodiesel has the
97 advantage of not being responsible for any emission of CO₂ connected with its use. As a matter of

98 fact, the CO₂ released into the atmosphere by biofuel combustion is the same CO₂ that was absorbed
 99 by photosynthesis by the growing plant. In addition, the CO emissions are more limited than from
 100 fossil diesel, while a slightly higher level of NO_x emissions can be expected [3].
 101 However renewable fuels cannot replace fossil fuels for the time being, they can only contribute to
 102 reduce the latter's consumption [4]. Even if all the animal and vegetable fats currently available on
 103 the market were to be converted into biofuel, this would still only cover a limited part of the demand
 104 for fuel [5]. Moreover, the chances of the price of biodiesel being able to compete with fossil diesel
 105 are limited by the price of vegetable oil, which accounts for about 80% [6-8] of the final price of the
 106 biofuel. Although day-to-day variations in the commodities market can naturally change these
 107 considerations, Fig. 1 shows that the price of crude oil is still lower than that of refined vegetable oil
 108 [9-11] primarily due to the link between crude petroleum oil, vegetable oil refining process and
 109 speculation [12]. Actually the cost-effectiveness of using biodiesel relies entirely on its exemption
 110 from taxation [13]. An even more pressing problem, however, concerns the debate on the morality of
 111 using fertile land to grow biomass for conversion into energy instead of food crops, while so many
 112 people around the world go hungry [14].

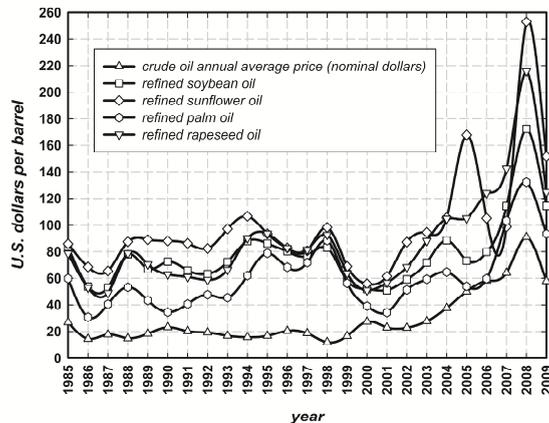


Fig. 1: Prices of some refined vegetable oil varieties.

113 Most of the vegetable oil currently used as biodiesel feedstock could also be used as edible oil, and
 114 this introduces a new variable in the food commodities market (which is already under strain),
 115 preventing any proper control over the prices of basic commodities intended for human nutrition. The
 116 most likely way to escape this dangerous contradiction is to completely separate the agro-energy
 117 business from the agro-food business [15, 16]. This can feasibly be done by intensive microalgae
 118 farming schemes: although this is still in the experimental phase as a biodiesel feedstock source, it has
 119 revealed far better features than land crops in terms of yield per cultivated area [17, 18].
 120
 121
 122

123 Microalgae are an excellent alternative to land crops for a number of reasons: i) they grow year-
124 round; ii) their yield in terms of oil per unit of cultivated area is significantly higher; iii) they can be
125 grown on land unsuitable for food crops;

126 While we wait for the microalgae to reveal their full potential due to several technical problems [19,
127 20], we must get by with the biodiesel produced entirely from land crops. A proper production
128 process planning and design (from seed to vegetable oil, to biodiesel) are consequently the
129 fundamental to reduce the energy inefficiencies that strongly influence the final price of this product.

130 To seek ways to reduce these production costs, this paper analyses the whole chain leading from seed
131 to biodiesel from a technical standpoint, starting with the following technological issues:

- 132 • considering the plant process flow diagram currently used in industrial applications, a proper set-
133 up of the process parameters can ensure effective energy savings with no negative fallout on
134 product quality;
- 135 • current industrial practice often relies on procedures designed to obtain food-grade quality, which
136 is too high for energy purposes;
- 137 • even if the production process can be said to be sufficiently standardized, different biodiesel
138 producers use their own parameters and solutions to optimize the yield, costs and quality of their
139 end-product.

140 The present paper describes the main techniques and technologies on the industrial landscape and
141 characterizes the main procedures in the process for obtaining biodiesel from vegetable oil, with a
142 view to establishing the optimal process parameters and showing how the quality change with
143 different operating conditions.

144

145 2. Characteristics of vegetable oils

146 On Earth there are over 4000 vegetable species from which vegetable oil can be extracted. Some of
147 the most common crops are listed in table 1 [21] in ascending order of their yield per hectare.

Table 1:

Annual oil yield per cultivated hectare [kg ha⁻¹]

Crop	Crop	Crop	Crop	Crop	Crop
Maize	145	Pumpkin	449	Opium	978
Lupine	195	Mustard	481	Rape	1000
Hibiscus	230	Camelina	490	Olive	1019
Calendula	256	Sesame	585	Ricin	1188
Cotton	273	Safflower	655	Jojoba	1528
Hemp	305	Rice	696	Jatropha	1590
Soy	375	Walnut	790	Avocado	2217
Coffee	386	Sunflower	800	Coconut	2260
Flax	402	Cocoa	863	Palm	5000
Hazelnut	405	Peanuts	890		

148
 149 Oil from these crops contains 90-98% acylglycerols [22], a class of saponifiable and neutral lipids.
 150 The acylglycerols are characterized by the acyl group and are divided into monoacylglycerols,
 151 diacylglycerols and triacylglycerols, according to the three functions of alcoholic glycerol, which are
 152 esterified respectively with one, two or three fatty acids. The acyl chain represents 85-88% of the total
 153 weight of a triacylglycerol, depending on the type of fat, and they can be divided into saturated and
 154 unsaturated fatty acids [23]. Table 2 shows the most common fatty acids found in fats, oils and
 155 biological membranes.

Table 2:
 Most common fatty acids in vegetable oil and biological membranes

Trivial name	Systematic name	CN:DB*	Structure
Unsaturated fatty acids			
Capronic acid	Hexanoic acid	6:0	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$
Caprylic acid	Octanoic acid	8:0	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$
Lauric acid	Dodecanoic acid	12:0	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
Myristic acid	Tetradecanoic acid	14:0	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$
Palmitic acid	Hexadecanoic acid	16:0	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
Stearic acid	Octadecanoic acid	18:0	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
Arachidic acid	Eicosanoic acid	20:0	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$
Saturated fatty acids			
Caproic acid	9-Decenoic acid	10:1	$\text{CH}_2=\text{CH}(\text{CH}_2)_7\text{COOH}$
Palmitoleic acid	9-Hexadecenoic acid	16:1	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Oleic acid	cis-9-Octadecenoic	18:1	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Linoleic acid	9,12-Octadecadienoic acid	18:2	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_2(\text{CH}_2)_6\text{COOH}$
Linolenic acid	6,9,12-Octadecatrienoic acid	18:3	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_6\text{COOH}$
Arachidonic acid	5,8,11,14-Eicosatetraenoic acid	20:4	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_4(\text{CH}_2)_2\text{COOH}$

*CN is the number of carbon atoms in molecule, DB is the number of double bond between carbon atoms.

156
 157 The thermophysical properties of triacylglycerols at temperatures between 20°C and 70°C, and at
 158 ambient pressure, are of interest in the study of the biodiesel production process but not readily
 159 available because interest has always focused on the properties of triacylglycerols at high
 160 temperatures and pressures [24], mainly deriving from studies on hydrogenation [25]. So little reliable
 161 information is available on the feedstock side of the biodiesel process, i.e. the triacylglycerols [26].
 162 The thermodynamic data needed for a sufficient characterization of the acylglycerols are requested by
 163 the process simulation tools. In fact, often these simulation tools use correlation derived by a limited
 164 number of experimental data, giving results affected by not negligible errors. The experimental data
 165 present in literature are still few and especially on the compounds with oleic acid (tri-olein, di-olein,
 166 mono-olein) taken as “model compounds”. Conversely, there is an abundance of data available on the
 167 output side of the biodiesel production process. In table 3 are listed some thermodynamic
 168 experimental data measured on tri-olein, di-olein, mono-olein. Many values are still lacking.
 169

Table 3:

Some experimental thermodynamic data of tri-olein, di-olein and mono-olein

		Tri-olein	Ref	Note	dev	Di-olein	Ref	Note	dev	Mono-olein	Ref	Note
kg/kmol	Molecular Weight	885.43	[27]			620.99	[27]			356.54	[27]	
K	Critical Temperature	--	--	--	--	--	--	--	--	--	--	--
Pa	Critical Pressure	--	--	--	--	--	--	--	--	--	--	--
m ³ /kmol	Critical Volume	--	--	--	--	--	--	--	--	--	--	--
	Critical Compressibility Factor	--	--	--	--	--	--	--	--	--	--	--
K	Melting Point	278.15 ^A	[28]		<3%	294.65 ^B	[29]		<1%	305.15 ^C	[30]	
K	Triple Point Temperature	--	--	--	--	--	--	--	--	--	--	--
Pa	Triple Point Pressure	--	--	--	--	--	--	--	--	--	--	--
K	Normal Boiling Point	--	--	--	--	--	--	--	--	--	--	--
m ³ /kmol	Liquid Molar Volume (298.15K)	0.974	[31]	--	<5%	0.677	[31]	--	<5%	0.378	[31]	at triple point
J/kmol	Std Heat of Formation	--	--	--	--	--	--	--	--	--	--	--
J/kmol	Std Gibbs Energy of Formation	--	--	--	--	--	--	--	--	--	--	--
J/kmol·K	Std Absolute Entropy	--	--	--	--	--	--	--	--	--	--	--
J/kmol	Heat of Fusion at MP	9.41E+07	[32]		<3%							
J/kmol	Heat of Combustion	--	--	--	--	--	--	--	--	--	--	--
	Acentric Factor	--	--	--	--	--	--	--	--	--	--	--
C·m	Dipole Moment	1.05E-29	[33]	in benzene at 303 K.	N.D.							
m ² /kmol	Van der Waals Area	--	--	--	--	--	--	--	--	--	--	--
m ³ /kmol	Van der Waals Volume	--	--	--	--	--	--	--	--	--	--	--
	Refractive Index	1.467	[34]	--	<0.2%	1.4663	[35]	at 295 K	<0.2%	1.463	[36]	at 293 K
K	Flash Point	--	--	--	--	--	--	--	--	427	[37]	
	Dielectric Constant	3.109	[38]	at 293.15 K.	N.D.							
J/kmol·K	Heat Capacity, Solid (298.15K)	--	--	--	--	--	--	--	--	--	--	--
N/m	Surface Tension (298.15K)	0.0343	[31]	Error<5%	0.3(min)-0.7(max)							
W/m·K	Thermal Conductivity, Liquid (298.15K)	0.1713	[31]	Error<5%	0							
Pa	Vapor Pressure, Liquid (298.15K)	34.3673	[31]	Error<50%	0.2(min)-0.3(max)							
Pa·s	Viscosity, Liquid (298.15K)	0.06896	[31]	Error<10%	0							

N.D.:Not Declared

A: For the beta or triclinic form. For the beta prime or orthorhombic form use 261.15 K. For the alpha or hexagonal form use 239.15 K.

B: For the beta form

C: For the stable form I. Form II melts at 298.15 K . Form III (vitreous form) melts at 285.65 K.

170 On average, biodiesel produced from vegetable oils consists of a mixture of esters of fatty acids with
171 a number of carbon atoms from 14 to 22 and various levels of unsaturation. The unsaturation gives
172 the biodiesel variable thermophysical properties, which have been increasingly investigated in
173 experimental studies[39-42].
174

175 **3. Industrial scale production of vegetable oils**

176 Vegetable oils are produced on an industrial scale using processes that depend on both the physical
177 and the chemical characteristics of the feedstock. All seeds contain fat, but few of them contain fat in
178 quantities large enough to make its extraction convenient.

179 The purpose of extraction techniques is to separate the fats from the proteins (which are mutually
180 immiscible) with the greatest degree of purity at the lowest cost, avoiding any side reactions. The
181 vegetable oils emerging from the refining process mainly comprise acylglycerols, free fatty acids,
182 phospholipids, steroids, water and other compounds [43]. Storing the seeds is the first step in the
183 extraction process, since any raw material decay phenomena (mould formation, lipolytic enzyme
184 activation, etc.) need to be carefully avoided. To do so, the seeds' water content is maintained at 5-7%
185 wt by means of drying in hot-air furnaces [44]. Then the seeds are cleaned to remove any coarse
186 impurities in order to achieve a good product quality and protect the equipment in the plant. Before
187 oil extraction starts, most of the seeds are treated to remove their ligno-cellulosic outer protective
188 layer. To make the oil spill smoother, it is important to maintain the low humidity level achieved
189 during the initial drying phase. The extraction technologies are generally characterized by a series of
190 operations whose complexity depends on the morphology of the raw material, but there are
191 substantially two extraction techniques [45]:

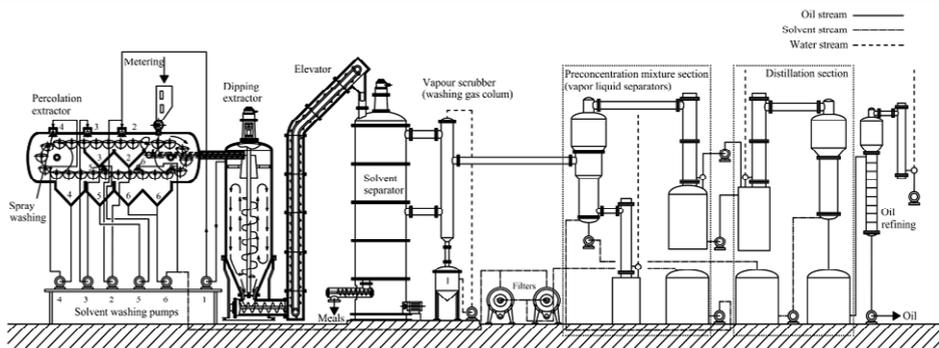
- 192 • mechanical, i.e. driven by pressure: it preserves the special characteristics of the foodstuff and
193 residual product. The seeds are fed into an extruder that compresses the seeds, warming them in
194 the process. A preliminary crushing action is often used before reaching the extruder in the case
195 of oilseeds with high oil content. Discontinuous or continuous presses are used. In the first case,
196 now applied just to olive seeds [46] or to other seeds but just in developing countries [47], the
197 pressure applied is around 30-40 bar and the temperatures close to 95°C. In the second case,
198 pressures as high as 400 bar can be reached in combination with temperatures up to 120-155°C
199 [48, 49]. The press type depends on the raw material. Seeds with a high oil content are usually
200 fully or partially treated by mechanical means. Full extraction leaves a minimum oil content in
201 the press cake of 5-12% wt, while partial mechanical extraction leaves an oil content of about
202 20% wt in the cake [50].The by-product from extraction is usually cooled and used as animal
203 feed.

204 • chemical, i.e. involving a solvent. The oil within the cells is difficult to extract, demanding a
 205 very slow diffusion process. Careful pre-treatment (lamination, crushing, conditioning, etc) of
 206 the raw material is of paramount importance for the diffusion process, which is also influenced
 207 by the type of solvent used [51]. Commonly used solvents include n-hexane [52], white spirit,
 208 trichloroethylene, carbon sulfide and biosolvents [53, 54]. Plants usually operate continuously
 209 and the systems can be classified as immersion, percolation or mixed immersion-percolation
 210 (Fig. 2). In immersion plants, the raw material is immersed directly in a counter-current flow of
 211 solvent. In this system is the materials can be used without any pretreatment. In percolation
 212 plants, the flow of solvent moves rapidly over the surface of the raw material. This procedure
 213 can produce oil-rich mixtures (up to 35% wt). Mixed immersion-percolation plants were
 214 developed to treat seeds with high oil content. They consist of two parts, the first removes the
 215 majority of the vegetable oil by percolation, and then the second extracts the remaining oil by
 216 immersion. There are also discontinuous plants consisting of sets of extractors with various
 217 capacities where the oil is extracted by immersion. The mixture being treated passes from one
 218 extractor to the next, gradually becoming richer in oil.

219 The mechanical method produces better-quality oil while the chemical one ensures greater yields.

220 In practice, the two systems are often combined. Mechanical extraction is generally used for seeds
 221 containing lipids in quantities exceeding 20% wt and residual in the waste product around 10-15%.

222 Chemical extraction is used if the lipids content is below 20% wt and residual lower than 2%.



223 Fig. 2: Mixed immersion-percolation plant process flow diagram with solvent extraction method.
 224
 225

226 3.1 Common vegetable oil refining processes

227 After extraction, the oil-rich mixture goes through units to remove unwanted compounds (proteins,
 228 gums, resins, phosphates, ketones, aldehydes). The impurities are generally large particles in
 229 suspension (pieces of plant tissue, mucilages, resinous products), fine colloidal particles (invisible in

230 transparent oil), free fatty acids produced by acylglycerols hydrolysis and colored and semi-volatile
231 substances dissolved in the oil. The unwanted compounds are removed by means of the treatments of
232 purification, mucilage removal, de-acidification, bleaching, deodorization. Purification involves
233 removing any water and impurities in suspension. This can be achieved by low-temperature
234 sedimentation or filtering with press filters or centrifugation.

235 The purpose of removing mucilage (degumming) is to eliminate the phosphates and other compounds
236 without reducing the oil acidity. Mucilage can be removed by treatment with: (a) H_2SO_4 at various
237 concentrations; (b) water (hydration) or aqueous solutions of electrolytes; (c) adsorbent materials. In
238 the case of hydration, the oil is mixed with very hot water, which hydrates the phospholipids, yielding
239 an insoluble solid sediment that precipitates and can be separated with a centrifugation. The
240 degummed vegetable oil must then be dried to remove the residual water.

241 Deacidification (neutralization) is used to obtain a pH-neutral oil. Various technologies are used for
242 this purpose, i.e.

- 243 • neutralization with alkali;
- 244 • deacidification with selective solvents;
- 245 • neutralizing distillation;
- 246 • esterification of free fatty acids with glycerine.

247 Neutralization with alkali is the most often-used method for neutralizing oils. The process is typically
248 discontinuous and the vegetable oil is mixed with an aqueous NaOH solution in excess of 10% wt at
249 60-80°C. The mass is slowly shaken to promote the reaction that converts the free fatty acids into
250 soaps, while preventing any formation of oil-soap emulsions. In the discontinuous process the
251 alkaline treatment takes place in reactors with a conical base to promote the separation of the neutral
252 soap phase. The continuous process is faster and less oil is lost, but it is more complex and the plant-
253 related costs are higher. There are several continuous neutralization methods (Sharples, Short Mix,
254 Long Mix), but the main common steps are:

- 255 • hydration of the mucilage, with or without separation;
- 256 • a preliminary coarse neutralization and soap separation;
- 257 • a refined neutralization and soap separation;
- 258 • rinsing with water and separation of the water;
- 259 • vacuum drying.

260 Any oils are bleached to remove most of their pigments. Final deodorization and winterization
261 remove any odoriferous substances (Fig. 3) and acylglycerols with high melting point [55].

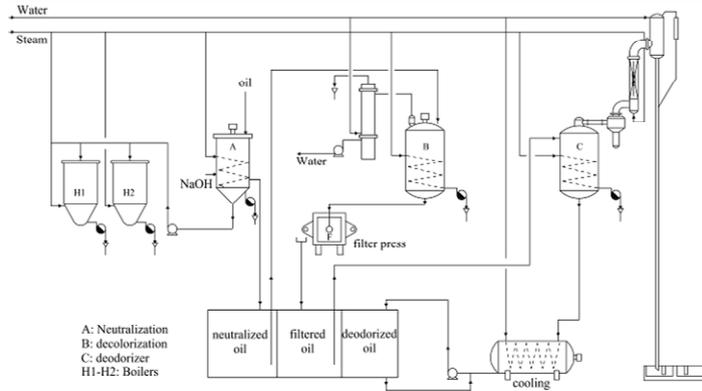


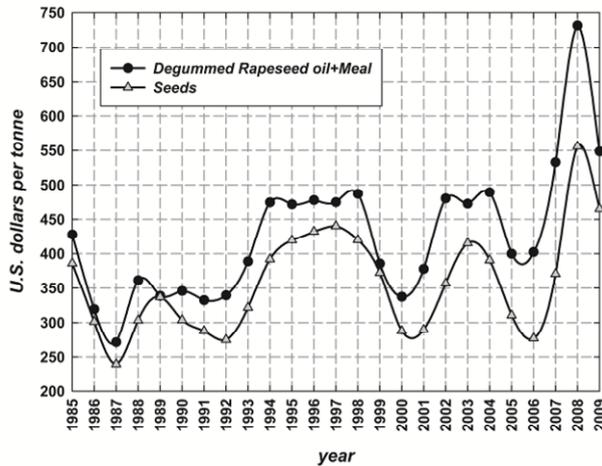
Fig. 3: Process flow diagram of a conventional vegetable oil refining plant.

262
 263
 264

3.2 Processing cost and market of refined vegetable oil

265
 266
 267

In Fig. 4 the rapeseed oil is taken as reference to compare the price of the seeds with the price of the vegetable oil (degummed) and meal to understand the value added by the refining process.



268
 269
 270

Fig. 4: comparison between input and outputs prices of a refinery producing Rapeseed oil

The Fig. 4 considers 1 tonne of seeds as input, 0.48 tons (oil content in the seeds) of degummed rapeseed oil and 0.52 tons of meal as outputs and it offers some upper limits to estimate the costs and the margins of the process to obtain rapeseed oil.

273

274 Table 4 presents a summary of some vegetable oil processing costs. Such data show that the cost to
 275 process the vegetable oil represents about the 7-9% of the market price for the rapeseed oil, 6-10% for
 276 the sunflower oil and 18-28% for the soybean oil.

Table 4:
 processing costs for some vegetable oil variety production with prepress/solvent
 technology with 24h/day, 300days/year of operation taken from [56]

Rapeseed	tons/day	44	66		
	\$/liter	0.16	0.14		
Sunflower	tons/day	500	1000	1500	2000
	\$/liter	0.24	0.18	0.16	0.15
Soybean	tons/day	650	1250	1850	2450
	\$/liter	0.41	0.33	0.29	0.27

Note: the processing costs are referred to 2008. They have been re-estimated using inflation data [56]

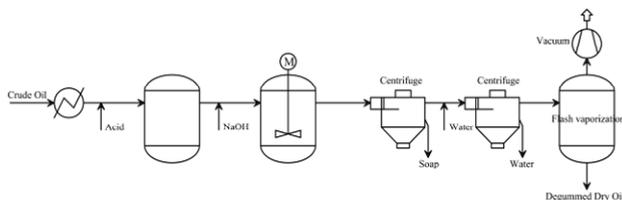
277
 278 For decades, the technology for obtaining refined vegetable oil remains unchanged, but the final price
 279 of vegetable oil undergoes considerable oscillations. For some varieties of vegetable oil the oscillation
 280 in the price is linked to oscillation in the price of fossil crude oil. The strength of this dependence
 281 depends on the variety of vegetable oil. In fact, the market price of rapeseed oil has a link stronger
 282 than the other varieties of vegetable oil with the price of crude oil. Other varieties of vegetable oil are
 283 less affected by fluctuations of crude oil because their main use is in food [58]. An increase in the
 284 price of vegetable oil also has an impact on biodiesel. However these increases are mitigated by the
 285 reduction of the margin for the biodiesel manufacturers. Manufacturers are encouraged to reduce the
 286 margin because the price of biodiesel would be intolerable for the customers. Sometimes, to handle
 287 short periods of rising prices biodiesel manufacturers uses the credit aging. Thus the biodiesel
 288 facilities are stressed by the searching of feedstocks at lower price.

289 290 **3.3 Special refining processes for biodiesel production**

291 Vegetable oils for biodiesel production must be suitably pre-treated before entering the
 292 transesterification process (Fig. 5) [59] whenever feedstock quality and refinement cannot otherwise
 293 be adequately guaranteed. This means that the oil sometimes undergoes treatments already
 294 implemented in a previous step. The first step is to heat the oil to about 90°C, followed by mixing
 295 with a strong mineral acid, which acts as a flocculant clarifying the oil. The acid treatment is used to
 296 remove any hydrophobic gums still contained in the vegetable oil. This conditioning step is
 297 completed with the mixture stationing in a tank for about 10 minutes.

298 In the next step the vegetable oil is mixed with NaOH (usually 0.1-0.2% wt) for neutralization. The
 299 NaOH enables the removal of free fatty acids that would give problems in subsequent biodiesel

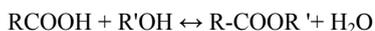
300 production. Then centrifugation follows to separate the soap of the previous step. Successively water
 301 is added and the solution is centrifuged to remove traces of impurities. The washing water is then
 302 separated from the vegetable oil by means of a vacuum flash-vaporization process conducted with the
 303 oil at 116°C and 0.8-0.9 bar absolute. This makes it possible to reduce the water content to less than
 304 0.1% wt [60]. The oil is often sent to the process plant at temperatures between 40°C and 50°C. It is
 305 also best for the oil to be filtered to ensure that no solid particles enter the biodiesel production
 306 section [61]. Then, providing its fatty acid content is appropriate (<2.5% wt) [62], the oil can be sent
 307 to the transesterification stage.



308
 309 Fig. 5: Vegetable oils neutralization process for biodiesel production.
 310

311 3.3.1 Esterification

312 To avoid completely soap formation in the transesterification reactor, the maximum amount of free
 313 fatty acids allowable for a system with an alkaline catalyst must be <0.5% wt (acid value<1) [63-65].
 314 If this is not the case, a preliminary esterification treatment is required. In the esterification reaction,
 315 alcohols and carboxylic acids convert to give rise to esters [66]. Esterification follows the pattern:



318
 319 The vegetable oil is dried (to water content of 0.4% wt) and filtered before it is loaded into the acid
 320 esterification tank, where it is mixed with methanol (molar ratio alcohol to free fatty acids between
 321 20:1 and 40:1) and large quantities of H₂SO₄ (10% wt of the total fatty acids content [67]). The
 322 reactor is stirred at about 600 rpm at a temperature of 60°C for 1.5 to 2 hours [68].

323 The reaction produces water, so the reacting mixture is pumped into a settling tank where the
 324 methanol, water and H₂SO₄ separate from esters and fatty acids. The methanol/acid/water mixture
 325 being treated can be re-used later to neutralize and acidify the glycerine. The oily phase leaves the
 326 settling tank with low free fatty acid content and can be sent to the transesterification reactor. If the
 327 free fatty acid content is still too high, a second acid esterification stage is performed. If a two-stage
 328 acid treatment is needed, mixing is suspended until after the methanol has been separated and
 329 removed. Then fresh methanol and some acid are added once again and the mixing process resumes.

330 As soon as the reaction has reached equilibrium, the methanol/acid/water mixture is removed by
331 settling or centrifugation.

332

333 **4. Transesterification**

334 Transesterification is a chemical reaction between an ester and an alcohol that produces a new ester in
335 which reacting alcohol replaces the original alcoholic group. The transesterification process takes
336 place as follows:

337



339

340 Alkyl esters of fatty acids and glycerol are produced when the reaction involves the triacylglycerols in
341 vegetable oils or animal fats. The transesterification reaction of triacylglycerols proceeds as follows:

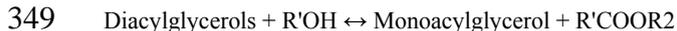
342



344

345 This reaction actually takes place in three steps, during which unwanted compounds, such as
346 diacylglycerols and monoacylglycerols, also make an appearance [69, 70].

347



351

352 The three reactions occur in series for the oil and in parallel for the alcohol. When the oil and alcohol
353 are immiscible, or only partially miscible, the parallel character of the three reactions is evident in the
354 first few minutes, when mass transfer is an important factor in the reaction [71]. To avoid any
355 transport phenomena affecting the reaction times, the reaction is completed under high-speed stirring.
356 After the first few minutes, the serial character of the reaction prevails [72]. As the triglycerides are
357 converted to diglycerides, at the same moment diglycerides are converted to monoglycerides. In the
358 three reactions, the esters increase the miscibility between the compounds of the reaction mixture,
359 acting as solvents for alcohol and glycerides. In this sense the transesterification is a reaction with
360 solvent, in which the solvent is one among the products of the reaction. So the reaction between
361 vegetable oil and reacting alcohol (the rate determining step) is helped by the esters presence and
362 vegetable oil reacts gradually in higher quantities.

363 Transesterification is an equilibrium reaction so both reagents and products will be present
364 simultaneously when it comes to an end. Since the main products of interest are the esters, the
365 reaction is run with alcohol in excess to increase the proportion of esters at equilibrium [73]. At
366 equilibrium two partially miscible phases are obtained, a glycerol rich phase (bottom) and a esters
367 rich phase (upper). Each phase has a different content of the other compounds present in the reacting
368 mixture [74]. An increase in temperature increases the reaction rate and yield, providing it is
369 consistent with the evaporation temperature of the alcohol adopted. The enthalpy of transesterification
370 reaction is [75] at 40°C -9.8 ± 0.9 kJ/mol for biodiesel formed from rapeseed oil and methanol and -
371 9.3 ± 0.7 kJ/mol when rapeseed oil and ethanol is used. For these kinds of vegetable oil and alcohols
372 the transesterification is a slight exothermic reaction. The reaction is catalyzed by various
373 compounds. The catalyst may be alkaline [76] or acid [77], using biochemical compounds (enzymatic
374 catalysis) [78, 79], or even acid or alkaline compounds that form a heterogeneous solutions with
375 reagents and products [80, 81]. The alkaline catalysts most commonly used in the experimental
376 investigation are: NaOH, KOH, carbonates [82, 83], sodium methoxide and potassium methoxide,
377 while typical acid catalysts include: H_2SO_4 , HCl, H_3PO_4 and sulfonic acids [84]. Many of these
378 catalysts are unsuitable for industrial applications [85], which mainly rely on an alkaline catalyst
379 homogeneous with methanol [86]. The reasons why industrial processes use alkaline catalysts are:

- 380 • high reaction rate,
- 381 • low capital costs [87],
- 382 • a high yield,
- 383 • a low temperature,
- 384 • a low excess alcohol,
- 385 • a low corrosive power of intermediate products (which is a major drawback of acid catalysis)
- 386 • a quite fast reaction (about 2hours for equilibrium)

387 In most cases, the alkaline catalyst used is KOH at concentration from 0.1 to 1.5% of vegetable oil
388 mass, and the alcohol involved is in a molar ratio alcohol:vegetable oil of 6:1.

389 When methanol and KOH are used in a stoichiometric ratio, the transesterification reaction can be
390 rewritten as:

391



393

394 The product of this reaction is a mixture of fatty acid methyl esters, known as biodiesel; the by-
395 product of the reaction is glycerol, which can be recovered, purified and placed on the market or
396 further processed to produce hydrogen by steam reforming [88, 89] or many other compounds with a

397 high added value by anaerobic fermentation [90] or by algal metabolism [91]. The kinetic model
 398 describing the reactions involved in transesterification follows a second order scheme [92]:

$$\frac{d[TG]}{dt} = -k_1[TG][MeOH] + k_2[FAME][DG]$$

399 $\frac{d[DG]}{dt} = k_1[TG][MeOH] - k_2[FAME][DG] - k_3[DG][MeOH] + k_4[FAME][MG]$

$$\frac{d[MG]}{dt} = k_3[DG][MeOH] - k_4[FAME][MG] - k_5[MG][MeOH] + k_6[FAME][G]$$

$$\frac{d[G]}{dt} = k_5[MG][MeOH] - k_6[FAME][G]$$

$$\frac{d[FAME]}{dt} = k_1[TG][MeOH] - k_2[FAME][DG] + k_3[DG][MeOH] - k_4[FAME][MG] + k_5[MG][MeOH] - k_6[FAME][G]$$

$$\frac{d[MeOH]}{dt} = -k_1[TG][MeOH] + k_2[FAME][DG] - k_3[DG][MeOH] + k_4[FAME][MG] - k_5[MG][MeOH] + k_6[FAME][G]$$

400
 401 Where TG, DG, MG, MeOH, FAME, G are respectively triacylglycerol, diacylglycerol,
 402 monoacylglycerol, methanol and glycerol. Tables 5a, 5b and 6 show some of the most important
 403 results for industrial applications obtained from the transesterification of commonly-available
 404 vegetable oils with methanol or ethanol and an alkaline catalyst.

405
 406
 407

Table 5a: Results of alkaline homogeneous alkaline transesterification of sunflower oil with methanol

Reagents		Catalyst	Reaction conditions				Kinetics constants (l/mol*min)						Equilibrium	Ref.		
Oil	Acohol		Impeller Speed [rpm]	Alcohol/Oil molar Ratio	Temp. [°C]	Cat. conc. (% wt oil)	Res. time [min]	k1	k2	k3	k4	k5	k6	biodiesel yield (% wt) in res. time		
Sunflower Oil	MeOH	KOH	600	6:1	25	0.5	120	0.1	0.3	0.2	0.1	0.2	0.0160		[92]	
		[76] [92] [93] [94] [95]	600	6:1	35	0.5	120	0.2	1	1.7	2.2	0.3	0.0110		[92]	
		Free fatty acid content in oil (% weight)	600	6:1	45	0.5	120	0.4	1.9	3.8	4.4	0.3	0.0077		[92]	
		0.02;saponification value of oil (mg KOH/g)	600	6:1	55	0.5	120	0.8	6	11	16	0.3	0.0035		[92]	
		193.7; iodine value of oil (mg of I2/g) 130.2;	600	6:1	65	0.5	120	1.5	14	23	41	0.4	0.0026		[92]	
		peroxide value of oil (mequiv/kg) 17.1;	600	6:1	25	1	120	0.1	0.4	0.3	0.2	0.3	0.0130		[92]	
		homogeneous mixture with the specified	600	6:1	35	1	120	0.3	1.5	2.5	3.1	0.4	0.0077		[92]	
		impeller speed	600	6:1	45	1	120	0.5	3.1	7	10	0.5	0.0030		[92]	
			600	6:1	55	1	120	1.6	8.5	21	23	0.6	0.0012		[92]	
			600	6:1	65	1	120	3.1	24	33	58	0.5	0.0009		[92]	
			600	6:1	25	1.5	120	0.2	0.7	0.4	0.4	0.5	0.0040		[92]	
			600	6:1	35	1.5	120	0.4	2	4.3	4.7	0.6	0.0005		[92]	
			600	6:1	45	1.5	120	0.7	5	12	13	0.7	0.0006		[92]	
			600	6:1	55	1.5	120	2.1	11	30	30	0.8	0.0001		[92]	
			600	6:1	65	1.5	120	4	27	55	66	0.9	0.0001		[92]	
			N.R.	7.5:1	65	1.5	60								89.15-89.42	[93] [94]
			N.R.	4.5:1	65	1.5	60								90.7-90.43	[93] [94]
			N.R.	7.5:1	25	0.5	60								99.88-99.28	[93] [94]
			N.R.	4.5:1	25	1.5	60								97.77-97.17	[93] [94]
			N.R.	7.5:1	65	0.5	60								98.32	[93] [94]
			N.R.	7.5:1	25	1.5	60								96.58-96.88	[93] [94]
			N.R.	4.5:1	65	0.5	60								98.7	[93] [94]
			N.R.	4.5:1	25	0.5	60								96.37-96.96	[93] [94]
			N.R.	6:1	45	1	60								98.11	[93] [94]
			N.R.	6:1	78.63	1	60								93.33-94.28	[93] [94]
			N.R.	6:1	11.36	1	60								96.39-97.37	[93] [94]
			N.R.	6:1	45	1.84	60								92.07-92.45	[93] [94]
			N.R.	6:1	45	0.16	60								97.69-97.94	[93] [94]
			N.R.	8.52:1	45	1	60								97.66-97.77	[93] [94]
			N.R.	3.47:1	45	1	60								96.04-83.82	[93] [94]
			600	6:1	65	1	240								91.67±0.27	[76]
			600	6:1	60	1	120								86.7±0.9	[95]
			NaOH		600	6:1	25	0.5	4						86	[97]
	[76] [96] [95] [97] [98] [99] [100]		600	6:1	65	0.5	4						98.1	[97]		
			600	6:1	25	1.5	4						99.7	[97]		
	Homogeneous mixture with		600	6:1	65	1.5	4						100	[97]		
	600 rpm impeller speed		600	6:1	45	1.71	4						100	[97]		
			600	6:1	73.3	1	4						99.7	[97]		
			600	6:1	16.7	1	4						96.6	[97]		
			600	6:1	45	0.29	11						89	[97]		
			600	6:1	30	1	120						90.9±0.8	[95]		
			600	6:1	45	1	120						92.8±1.0-97.77	[95] [97]		
			600	6:1	60	1	120						97.1±0.9	[95]		
			600	3:1	60	1	120						61.5±0.7	[95]		
			600	9:1	60	1	120						93.0±1.2	[95]		
			600	12:1	60	1	120						86.0±1.5	[95]		
			600	15:1	60	1	120						83.8±1.2	[95]		
			600	18:1	60	1	120						81.0±0.8	[95]		
			600	6:1	60	0.25	120						51.6±1.0	[95]		
			600	6:1	60	0.5	120						65.0±0.8-98	[95] [98]		
			600	6:1	60	0.75	120						92.9±0.9	[95]		
			600	6:1	60	1.25	120						82.7±1.5	[95]		
			600	6:1	60	1.5	120						78.1±1.2	[95]		

N.R. =Not Reported

Table 5b:
Results of alkaline homogeneous alkaline transesterification of sunflower oil with ethanol

Reagents		Catalyst	Reaction conditions					Kinetics constants (l/mol*min)						Equilibrium	Ref.		
Oil	Acohol		Impeller Speed [rpm]	Alcohol/oil molar Ratio	Temp. [°C]	Cat. conc. (% wt oil)	Res. time [min]	k1	k2	k3	k4	k5	k6	biodiesel yield (% wt) in res. time			
Sunflower Oil	EtOH	KOH	600	5:1	20	0.5	60							76.66	[101]		
		[98] [101]	600	5:1	32	0.5	60							84.45	[101]		
		Free fatty acid in oil (% weight) 0.45; viscosity (40°C-mm*mm/s)	600	5:1	20	1.5	60								97.53	[101]	
		46.61;saponification value of oil (mg of KOH/g)	600	5:1	32	1.5	60								95.57	[101]	
		193.7; Iodine value of oil (mg of I2/g) 89.1; peroxide value of Oil (mequiv/kg)	600	7:1	20	0.5	60								88.76	[101]	
		10.1; homogeneous mixture with 600 rpm impeller speed.	600	7:1	32	0.5	60								92.65	[101]	
			600	7:1	20	1.5	60								89.38	[101]	
			600	7:1	32	1.5	60								93.59	[101]	
			600	6:1	26	1	60								91.35	[101]	
			600	6:1	26	1	60								88.12	[101]	
			600	6:1	26	1	60								89.12	[101]	
			600	6:1	26	1	60								86.31	[101]	
			600	3:1	75	0.5	60								81	[98]	
			NaOH	600	6:1	25	0.75		1.742	0.119	5.74*10 ⁻³						[102]
			[102]	600	6:1	25	1		3.254	0.240	9.03*10 ⁻³						[102]
			Any information about vegetable oil quality	600	6:1	25	1.25		4.145	0.371	11.04*10 ⁻³						[102]
				600	9:1	25	0.75		1.003	0.091	1.89*10 ⁻³						[102]
				600	9:1	25	1		4.643	0.215	4.52*10 ⁻³						[102]
				600	9:1	25	1.25		7.736	0.405	6.06*10 ⁻³						[102]
				600	12:1	25	0.75		3.170	0.140	11.10*10 ⁻³						[102]
				600	12:1	25	1		6.93	0.327	45.0*10 ⁻³						[102]
				600	12:1	25	1.25		11.82	0.497	111.3*10 ⁻³						[102]
				600	6:1	50	0.75		5.18	0.486	8.16*10 ⁻³						[102]
				600	6:1	50	1		6.04	0.698	11.1*10 ⁻³						[102]
				600	6:1	50	1.25		6.52	0.938	12.8*10 ⁻³						[102]
				600	9:1	50	0.75		4.95	0.498	3.64*10 ⁻³						[102]
				600	9:1	50	1		8.17	0.941	5.65*10 ⁻³						[102]
				600	9:1	50	1.25		9.26	1.163	7.03*10 ⁻³						[102]
				600	12:1	50	0.75		10.8	0.524	34.5*10 ⁻³						[102]
				600	12:1	50	1		13.5	0.741	74.4*10 ⁻³						[102]
		600	12:1	50	1.25		17	1.337	135.4*10 ⁻³						[102]		
		600	6:1	75	0.75		6.24	0.891	12.3*10 ⁻³						[102]		
		600	6:1	75	1		7.84	1.165	14.2*10 ⁻³						[102]		
		600	6:1	75	1.25		8.8	1.335	14.9*10 ⁻³						[102]		
		600	9:1	75	0.75		7.5	1.423	5.72*10 ⁻³						[102]		
		600	9:1	75	1		9.57	1.68	6.43*10 ⁻³						[102]		
		600	9:1	75	1.25		12.6	1.921	7.35*10 ⁻³						[102]		
		600	12:1	75	0.75		10.9	1.795	82.5*10 ⁻³						[102]		
		600	12:1	75	1		16.1	2.31	135.3*10 ⁻³						[102]		
		600	12:1	75	1.25		20.8	2.956	201.4*10 ⁻³						[102]		

Kinetics model: pseudo second-order type

N.R.=Not Reported

Table 6:
Results of homogeneous alkaline transesterification of some vegetable oil varieties with methanol and ethanol

Reagents		Catalyst	Reaction conditions					Kinetics constants (1/mol*min)						Equilibrium	Ref.			
Oil	Acohol		Impeller speed [rpm]	Alcohol/oil molar ratio	Temp. [°C]	Catalyst conc. (% wt oil)	Res. time [min]	k1	k2	k3	k4	k5	k6	Global rate constant	biodiesel yield (% wt) in specified res. time			
Rapeseed Oil	MeOH	KOH [103] [62]	600	6:1	65	1	120								96	[103]		
			600	3:1	65	1	120								57	[103]		
			600	6:1	35	1	120									90.6	[103]	
			600	6:1	50	1	120									93.2	[103]	
			180	6:1	65	1	120									81.5	[103]	
	EtOH	KOH [104]	360	6:1	65	1	120									96	[103]	
			N.R.	6:1	65	1	120									95-96	[62]	
			Low	6 (pure):1	30	1	120									91.7	[104]	
			High	6 (5% w of water):1	30	1	120									29	[104]	
			Low	6 (5% w of water):1	75	1	120									77.8	[104]	
Soybean Oil	MeOH	KOH [100]	N.R.	6:1	40	0.8	60								100	[104]		
			NaOH [105] [106]	300	6:1	50	0.2	90	0.049	0.102	0.218	1.28	0.239	0.007		95	[105] [106]	
Palm Oil	MeOH	KOH [107]	N.R.	6:1	50	1	100	0.018		0.036		0.112		Kinetics model: hydrolysis type		[107]		
			N.R.	6:1	55	1	100	0.024		0.051		0.158			[107]			
			N.R.	6:1	60	1	100	0.036		0.07		0.141			[107]			
			N.R.	6:1	65	1	100	0.048		0.098		0.191			[107]			
			NaOH [108] [109] [100]	350	10:1	60	0.5	25								0.163	98	[108]
			350	10:1	60	0.75	25									0.313	98	[108]
	EtOH	KOH [110]	350	10:1	60	1	25								0.526	98	[108]	
			350	6:1	60	0.5	25								0.097	98	[108]	
			350	8:1	60	0.5	25								0.147	98	[108]	
			350	10:1	70	0.5	25								0.309	99	[108]	
			N.R.	6:1	60	1	30									95	[100]	
			N.R.	6:1	60	1			0.634	0.000	7.104	4.912	7.860	0.121			95	[109]
N.R.=Not Reported														92	[110]			

411

412

413
414
415
416
417
418
419
420
421
422

5. Guidelines on the biodiesel production process

It is impossible to describe the processing or purification stages used in biodiesel production because there are many possible solutions that make one facility different from another. However we can compare some reference solutions from which many installations have drawn inspiration referring to the block diagram shown in Fig. 6. About the reaction, the alkaline transesterification of vegetable oil and methanol is the most commonly adopted solution. For the separation units the components involved are mainly centrifugal separators and distillation units. The components and process stages are briefly described in the following paragraphs, according to their specific application in a biodiesel plant.

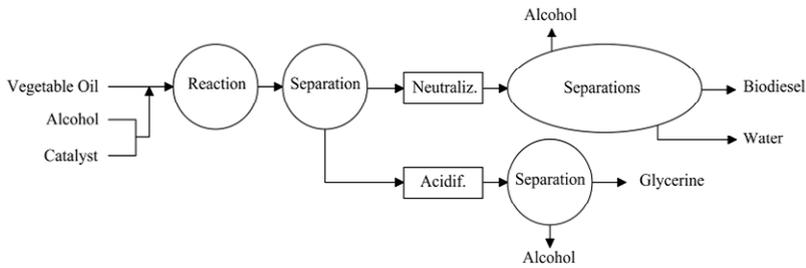


Fig. 6: Block diagram of the biodiesel production process.

423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441

5.1 The pumping in biodiesel plants

Centrifugal and volumetric rotary pumps are generally used in plants producing biodiesel: the former are used when no emulsion occurs among the compounds [111]; the latter especially for the transfer of viscous fluids and when a careful flow control is needed to ensure a consistent, low-speed and uniform flow over a wide range of heads, with no pulsing. As usual volumetric pumps are used to deliver the reagents in the reactors. In addition mechanical vacuum pumps or diffusion vacuum pumps are also needed in biodiesel production. Rotary types, mechanical vacuum pumps are present exclusively for the flash distillation units. The type of rotary vacuum pumps most often used are the liquid ring vacuum pumps [112] because in a biodiesel plant the vacuum level is not too low. In fact, in general the minimum vacuum levels generated by liquid ring vacuum pumps (depending on the nature and temperature of the liquid they contain) are higher than 0.08-0.06bar at the vapor pressure of the liquid they contain. Such pressure level is sufficiently below the operational level requested for a biodiesel plant.

442 **5.2 Transesterification reactors**

443 From a chemical and physical viewpoint, knowing the reaction time and how it relates to diffusion
444 mechanisms and transport by convection enables a thoughtful design of the reaction stage [113]. The
445 most important parameters to consider in a reactor are the conversion degree of an interesting reagent
446 and the selectivity of the reaction to the interesting products. The main variables governing the
447 conversion degree and selectivity in the transesterification are temperature, residence time and mixing
448 rate, although for the transesterification the temperature is limited by the evaporation of the alcohol
449 used as reagent and the residence time is limited due to the conversion rate no longer changes
450 significantly after the first few minutes [114]. Indeed the mixing rate is an unconstrained factor which
451 is to maximize. The turbulence by stirring inside the reactor contrasts the immiscibility between the
452 reagents and helps the reaction rate [115, 116]. Obviously also the catalyst influences the yield.
453 Actually the catalysts appeared in the industrial practice are a limited variety of strong homogeneous
454 bases, but in general the transesterification is catalyzed by alkaline- or alkaline-earth-hydroxides like
455 NaOH, KOH, CsOH or RbOH with a little difference in triglyceride's conversion [82]. In the
456 industrial sector just KOH and NaOH are practically used as catalysts and also the plants born using
457 KOH [117] had used successively NaOH. Nowadays NaOH and KOH are replaced by sodium
458 methoxide (CH_3ONa) due to the absence of water when it is mixed with the alcoholic reagent. The
459 KOH has been dismissed because it produces water when mixed with methanol but especially due to
460 the need to manage the dust in the plant area. So currently the majority of biodiesel plants use
461 CH_3ONa [118].

462 The two main chemical reactor types, used in the large scale plants, are the stirred batch reactors
463 (BRs) and the continuous stirred tank reactors (CSTRs). Experimentally also the continuous tubular
464 reactors (PFRs), mini and micro-reactors have been successfully tested.

465

466 **5.2.1 Stirred batch reactors**

467 In a plant with batch reaction the alcohol and catalyst are premixed in a preliminary unit, then the
468 vegetable oil, alcohol and catalyst are sent to the reactor, where they are stirred for about 1h at about
469 60°C with maximum temperatures around 65°C . Some systems use a two-stages reaction. Nowadays
470 most manufacturers adopt a single stage reaction, with reaction conditions optimized internally to
471 ensure higher yield with shorter reaction times [119]. In some cases, where a two stages reaction is
472 adopted, the glycerine being removed between the two stages, in order to increase the conversion
473 degree of the reaction to around 98-99% and minimizing the reaction-inhibiting effect of the products.
474 In such systems, 80-90% wt of alcohol and catalyst entering the process are added to the oil before
475 loading the first reactor. The reaction products are subsequently taken from the first reactor by

476 flooding or maintaining a constant level inside the reactor. Before it goes into the second reactor, the
477 outflow of products from the first reactor is sent to the stage for separating the glycerol-rich phase
478 (GL) from the phase rich in esters (BD). The remaining 10-20% wt of alcohol and catalyst are added
479 to the second reactor [120]. Discontinuous reaction systems in current practice use molar ratios of
480 alcohol:vegetable oil ranging from 4:1 to 20:1 [121] with residence times of 30min, although the use
481 of lower molar ratios leads to high enough yields. In fact performing the reaction in two stages with
482 molar ratios respectively 1:4.5 (1% wt KOH respect to the wt of the vegetable oil) and 1:1 (0.2% wt
483 KOH respect to the wt of the vegetable oil) and residence times of 30min, the yield of 98.5% could be
484 obtained [122]. However the trend of the facilities is to decrease the amount of methanol and catalyst
485 for the reaction, increasing the reaction temperature and the stirring. To decrease the methanol
486 amount helps to decrease the energy for the purification of the excess in the distillation column. After
487 the single stage reaction section, the process is continuous thanks to the presence of buffer tanks
488 capable of containing the product coming from 3-4 batch reaction cycles or containing the amount of
489 the products from several alternatively-operated single batch reactions. In fact batch reactors are
490 generally not used for large production rates, for which the separation and purification steps that
491 follow the reaction are much more efficiently operated on a continuous basis. The most used alkaline
492 catalysts are in amounts ranging from 0.1% to 2% wt of alcohol used. At the start of the reaction,
493 thorough mixing is needed to bring oil, alcohol and catalyst into intimate contact. Towards the end of
494 the reaction, a lower stirring speed can increase the conversion degree and facilitate the separation of
495 the GL phase (an inhibitor product of the reaction) from the BD phase [123]. Several studies have
496 been performed on the stirring of the batch reactors because this is one among the most important
497 aspects to maximize the reaction yield. The turbulence induced by a mixer depends on the geometry
498 of the mixer and reaction vessel. Therefore it is difficult to derive just one value of intensity of mixing
499 in terms of rpm able to perform an optimal mixing between methanol and vegetable oil. Some
500 information are reported by [92, 105]. Performing the reaction in simple reactor vessels, mixing the
501 reacting mixture with mechanical stirrers between 300rpm and 600rpm (corresponding respectively to
502 impeller Reynolds numbers 6200 and 12400) the yield increases at higher intensities. For Reynolds
503 numbers higher then 12400 (600rpm), the mixing do not affect the tryglicerides conversion and so the
504 reactor can be considered perfectly mixed. Deeper investigations are in [124] where the flow regime
505 and the drop size are aspects studied in case of the unreacting binary system methanol/vegetable oil
506 and in case of multicomponent and time-dependent reacting mixture. This work states that the
507 behavior of the transesterification can be explained by the increasing of the interfacial area, due to
508 intensive drop breakage process during the stirring. After few minutes the transesterification becomes

509 slower approaching the state of equilibrium due to the decrease of methanol concentration and the
510 increase of the products.

511

512 **5.2.2 Continuous stirred tank reactors and other reactors**

513 The CSTRs are used where large production rates are required. The reaction is often conducted using
514 few (2 or 3) CSTRs in a cascade pattern [125, 126]. The first reactor may be of larger volume so that
515 the mixture spends more time in it, thus achieving a higher conversion degree. Then the initial GL
516 phase is separated from the BD phase and carried to a second reactor, where the reaction is fairly
517 rapid and the yield can be as high as 98% [127]. Mixing ensures that the composition inside the
518 reactor is homogeneous, as well as having the effect of increasing the dispersion of glycerine
519 produced in BD, allowing a longer time for the next phase separation. In [128] and experimental
520 activity on a 6-stage continuous reactor (2.272 l) was evaluated. Effects of residence time (3-12 min),
521 stirrer speed (0-800 rpm), and NaOH concentration (0.25-1.0% wt of oil) on yields were investigated
522 at molar ratio of methanol to oil of 6:1 and temperature of 60°C. Higher stirrer speed increased the
523 reaction rate but excessive stirrer speed decreased the reaction rate probably due to the GL phase
524 dispersion. At NaOH of 1.0 wt% of oil, the reactor could produce biodiesel at purities ranging from
525 97.5% to 99.2 wt% within residence times of 6-12 min. Other continuous reactors which improve the
526 surface contact between reagents have been tested with good results. Atomizing the oil and in contact
527 with methanol vapours at 70°C-90°C it is possible obtain the 96% of triglycerides conversion with a
528 residence time of few seconds [129].

529 The PFRs is another type of continuous reactor where the mass flow through each area of the reactor
530 is always the same [130, 131]. Industrial applications of the PFRs reactor have been proposed [132]
531 but effective installation are not existing. Various kind of tubular reactors was experimented. With
532 fixed-bed plug flow reactors [133] a yield of 91.7% can be obtained within 19min of residence time,
533 65°C, 1.2%wt of KOH and molar ratio methanol:rapeseed oil 6:1.

534 Using the micromixing effects gives high reaction yields. In [134] corrugated plates heat exchanger as
535 a reactor was adopted. Reynolds numbers between 9 and 17 was realized in a very compact tubular
536 reactor.

537

538 **5.3 Separation of the BD phase from the GL phase**

539 The products emerging from a transesterification reactor can easily form an emulsion, especially if
540 they come into contact with water [111]. These problems are reduced by using volumetric gear
541 pumps. The presence of significant quantities of mono-, di- and triacylglycerols in the final mixture
542 can lead to a layer of emulsion forming at the interface between the BD and GL phase. This layer is

543 bound to mean a loss of product if it is not recovered and separated. In the worst cases, the resulting
544 biodiesel fails to comply with the specific legislation and has to be processed again. If this problem
545 crops up, the whole reaction needs to be redesigned to improve the triacylglycerols conversion
546 degree. After the reaction, the GL phase is removed from the BD phase. The closer the pH of the
547 reaction mixture to neutral, the faster the coalescence of the GL phase will be: this is one of the
548 reasons for reducing the total quantity of catalyst in the reaction. Given the low solubility of glycerol
549 in esters, separation does not usually take long and it can be done directly in the reactor, or in a
550 settling tank at small plants, or through a centrifuge in case of continuous installations. The presence
551 of methanol in both phases increases the solubility of ester and glycerol [135]. The BD phase is
552 quickly separated from the GL phase, effectively exploiting the difference in density between the two
553 phases (about 880 kg/m³ for the BD phase and 1050 kg/m³ for the GL phase). The centrifuge
554 completes this operation on a mixture with a temperature of 50°C-60°C and can also separate the
555 solids that accumulate on the outer edge of the centrifuge drum. The excess methanol tends to act as a
556 solvent, slowing down the separation process, but the excess methanol is typically not removed from
557 the product flow before the GL and BD are separated to avoid reversing of the transesterification
558 reaction. After it has been separated from the GL, the BD goes to a neutralization stage, where H₃PO₄
559 is used because the resulting K₃PO₄ can be used as a fertilizer. In case of NaOH or CH₃ONa catalysts
560 there is not formation of fertilizer and the salts are considered waste, so in these cases, the
561 neutralization is performed with citric acid powder. However in some discontinuous systems, the
562 reaction mixture is neutralized before the BD and GL phases are separated.

563 Immiscible or only partially miscible compounds with different densities in solid and liquid phase are
564 separated by means of centrifugal units. The compounds fed into the separators are submitted to a
565 centrifugal forces field at a speed represented by the Stokes law [136]. In the case of a liquid-liquid
566 system, the mechanism is no different from that of a solid-liquid system, except for the fact that
567 droplets of liquid are moving instead of solid particles. These droplets move throughout a liquid phase
568 and give rise to another phase by coalescence.

569 The disk centrifuge handles larger flow rates and turns at lower speeds, developing centrifugal forces
570 up to 7000 times the force of gravity. It can manage up to 20m³h⁻¹ of input containing moderate
571 amounts of solid matter, which is downloaded continuously in the form of mud. Such centrifuges are
572 designed mainly for liquid-liquid systems, but they can also be used in liquid-liquid-solid or liquid-
573 solid systems if the end product to obtain is a clarified liquid. Disk centrifuge is the type most often
574 used in biodiesel production plants [137].

575
576

577 **5.4 Recovering excess alcohol from biodiesel**

578 After separating the GL and neutralization, the BD enters the methanol separation stage, which is
579 usually a stripping process or vacuum flash vaporization, in the classic version or in a falling film
580 evaporator. The molar fraction of methanol in equilibrium with the biodiesel is very low for lower
581 than atmospheric pressures. The alcohol recovery process may be preceded by a process of
582 acidification to remove any soap in the biodiesel. The free fatty acids remaining in the BD phase and
583 the salts will be removed afterwards by washing with neutral water. If the amount of soap is limited,
584 this stage may not be necessary, but if it is considerable (>1000ppm), then the soap would risk
585 causing "foaming" inside the flash separation tank. Removing the methanol in the flash separation
586 tank might also make the soap remaining in the BD phase solution precipitate, clogging the filters and
587 sieves.

588
589 **5.5 Ester washing**

590 The water used in the ester washing process is at 50-60°C and has a slightly acidified pH (3-6% wt of
591 H₂SO₄ or HCl) to remove any soap that might form during the reaction and to neutralize any
592 contaminants. e.g. calcium and magnesium, the catalyst, the salts and free fatty acids. The salts will
593 be removed by the water, and the free fatty acids will remain in the BD. This rinsing with water also
594 enables any residual methanol and free glycerine to be extracted from the BD, although this methanol
595 will need to be removed from the water before the washing stage to prevent it from getting into the
596 wastewater. The neutralizing process adopted before the washing cycle reduces the washing water
597 consumption and minimizes any formation of emulsions in subsequent purification stages. The BD
598 phase then undergoes water separation, which is often done by a centrifuge operating at a temperature
599 of >40°C and capable of separating any solids accumulating on the outer edge of the drum as well.
600 Then the BD, consisting by now almost entirely of esters, can come into contact with clean water
601 again (which must still be separated). Later in the washing process, any remaining water (usually
602 <3500ppm) is eliminated from the BD by drying [138], thus obtaining biodiesel. The methanol is
603 recovered from the washing water using a distillation column.

604
605 **5.6 Ester drying**

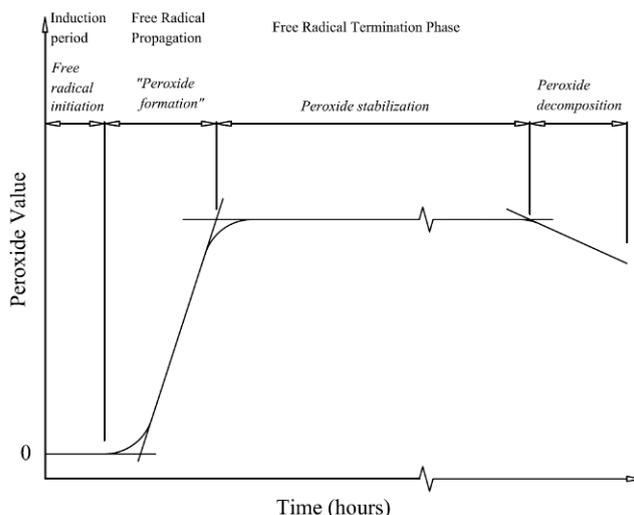
606 The simplest approach to drying BD is to use an isotherm flash evaporation unit. Vacuum evaporators
607 are commonly used for high-capacity operations. These systems operate at lower pressures to allow
608 for the water to evaporate at temperatures below 100°C. An alternative to heating and evaporation is
609 to use a thin-film evaporator under vacuum conditions. When the BD (now mainly consisting of ester)
610 is poured into the evaporator, its direct contact with the walls makes its ~~heated~~ water content

611 evaporate rapidly. Since the total amount of water remaining in the biodiesel after the separation is
612 low, adsorbent materials can also be used to remove these traces of water.

613

614 5.7 Adding oxidation inhibitors

615 Biodiesel contains a large number of molecules with double bonds, so it is susceptible to oxidation
616 [139]. This effect is increased particularly when the esters are exposed to light and air [140] or still
617 contain traces of free fatty acids [141]. Fig. 7 shows the typical oxidation behaviour of vegetable oils
618 and animal fats [142]. Biodiesel follows the same degrading path. The oxidation process is monitored
619 by measuring the peroxide level, or the fraction of oil or biodiesel converted into peroxide molecules
620 (H_2O_2), the first step in the oxidation process. Vegetable oils, animal fats and biodiesels have a so-
621 called induction period, in which no conversion occurs, after which oxidation rapidly sets in. Once
622 peroxide appear, then they decompose in aldehydes. Some of the oxidation inhibitors typically used
623 with lipids in the food industry are butylated hydroxyanisole (BHA), butyl hydroxytoluene (BHT),
624 propylgallate (PG), the tertiary butyl hydroquinone (TBHQ), pyrogallol (PY) [143], Tinuvin P and
625 benzotriazol [144]. It is possible also to adopt natural oxidation inhibitors like the tocopherols [145],
626 but they deteriorate quickly increasing temperature and pressure. The most effective additive for use
627 in foodstuffs is TBHQ [146]. The same additives have been used for biodiesel antioxidation too [147-
628 149]. However effectiveness of the antioxidants is $TBHQ > PY > PG$ [150].



629
630 Fig. 7: Effect of time on peroxide formation and decomposition.
631
632

633 **5.8 GL phase acidification**

634 At the end of the reaction, the alcohol content in GL phase is much higher than in BD phase. The GL
635 phase leaving the separator is only 50%-60% glycerol and contains some of the excess methanol and
636 most of the catalyst and soap [151]. These features make its value limited and its disposal difficult.
637 The first GL phase refining stage usually involves adding acid to convert the soap into free fatty acids
638 and salts. These free fatty acids are insoluble in GL phase, so they can be separated, removed and
639 recycled. The fraction rich in free fatty acids collects on the surface of the GL phase and can be
640 removed and recycled in the esterification process [152]. These free fatty acids should be less than
641 1% of the obtained biodiesel.

642

643 **5.9 Separation of the alcohol from the GL phase**

644 After acidification and free fatty acids separation, the methanol can be removed from the GL phase. It
645 is better to do this after acidification, because removing the methanol while the GL phase still
646 contains soap leads to the solidifying. First, the liquid mixture is heated up to 90°C-120°C, then the
647 heated liquid is sent through a pressure-reducing valve into a tank. The drop in pressure induced by
648 the valve makes the more volatile part of the liquid evaporate. This takes place in a vacuum. At this
649 point, the GL phase would consist of glycerine with a purity nearing 85%, which can be sold as crude
650 glycerine. The glycerine refining process can be taken further, aiming for a purity of more than
651 95.5%-97.7%, by means of a vacuum distillation or an ion-exchange process, but it is only worth
652 reaching such levels of purity if the glycerine is to be used by the pharmaceutical industry. If such an
653 option is of interest, this would demand purifying the glycerine to at least 99.5%, as required by the
654 European Pharmacopoeia. The methanol removed from the flows of BD phase and GL phase tends to
655 collect all the water that may have entered the process. This water has to be removed in a continuous
656 distillation column before the methanol is recycled in the process. The methanol recovered must have
657 a water content <0.1% wt, so that the water in the reagent mixture is minimal during
658 transesterification [153, 154]. This phase is much more complex if ethanol has been used as the
659 alcohol, because it forms an azeotrope with water. In such case a pressure swing adsorption system is
660 used to remove the water [155, 156].

661

662 **5.10 Alcohol purification**

663 In case of methanol continuous distillation is the separation technique used for the purification before
664 the reaction. This is the component with higher thermal power requirement [157] and also the bulkier.
665 In fact to separate methanol and water sufficiently need from 15 to 30 trays, a reflux ratio ranging
666 between 0.8 and 5, temperature from 110°C to 130°C depending on the pressure in the column

667 (commonly atmospheric). Such conditions are needed to decrease the chemical oxygen demand
668 (COD) load in the wastewater and so to decrease also the remediation treatments of the wastewater.
669 Typically the residual methanol content in water is below the 5% wt. This flow rate of wastewater can
670 be mixed with the glycerine final stream to adjust the purity at some levels. To adopt this solution
671 allow an high saving on disposal costs. Kettle reboilers are most often used in the distillation columns
672 in the biodiesel industry. Boiling occurs on the shell side, thus enabling any suspended matter to be
673 deposited on the bottom without influencing the heat exchange. The liquid to be vaporized flows just
674 once through the heat exchanger, making kettle reboilers suitable for thermo-unstable fluids such as
675 those derived from vegetable oils [158, 159].

676

677 **6. Three basic plant process flow diagrams**

678 The ASPENPLUS software was used to simulate the three most widely adopted continuous biodiesel
679 production processes, conducting a sensitivity analysis on these three processes to quantify the
680 response of their various units in different operating conditions. This analysis is useful in enabling a
681 more efficient planning of the production process. ASPENPLUS enables us to define in detail all the
682 necessary components, the thermodynamic models behind the operation of the system components
683 chosen, and all the chemical and physical properties of the compounds involved in the process. Plant
684 design starts with a description of its process flow diagram, i.e. the position and type of the units
685 needed for the production process. Then the behavior of some of these units can be analyzed to see
686 how certain parameters involved in the process respond to change. The compounds chosen from the
687 ASPENPLUS database were methanol, KOH, glycerol, biodiesel, K_3PO_4 , H_3PO_4 and vegetable oil.
688 Special attention was paid to define the vegetable oil and the biodiesel. We chose to define the
689 vegetable oil as a set of compounds derived from oleic acid because thermodynamically-reliable
690 experimental data are available, while this is not the case of varieties of compounds derived from
691 other fatty acids. Triolein has also been partially defined in the ASPENPLUS database. The same
692 approach was applied to the biodiesel as for the vegetable oil. We considered a mixture of esters
693 derived from different fatty acids coming from a vegetable oil: assuming that triolein was the only
694 compound in vegetable oil, the biodiesel would consist of methyloleate alone. The proper functioning
695 of each component relies on the choice of thermodynamic model used to describe the chemical and
696 physical conversion of the mixtures. The choice of thermodynamic model depends on the nature of
697 the compounds and the thermodynamic system's working conditions. In the literature there are few
698 experimental data on the phase balance involved in the systems considered [160, 161]. The A-
699 UNIFAC (UNIFAC with the Association activity coefficient model) and GCA-EOS (Group
700 Contribution Association Equation Of State) models have a good predictive capacity for the

701 compounds and the thermodynamic conditions considered [162], but the A-UNIFAC model is not
702 available in ASPENPLUS. The most suitable model in ASPENPLUS is the UNIFAC-Dortmund
703 [163], the use of which can overcome the limits of the original UNIFAC-VLE [164] and UNIFAC-
704 LLE [165] and predict the phase equilibria of heterogeneous multi-component systems at the working
705 temperatures involved in the installations and for the compounds considered here.

706

707 **6.1 Set-up of common components**

708 The plants analyzed refer to a mass flow rate of the vegetable oil of 2 tons h⁻¹ and assuming a
709 continuous operation. We chose to have transesterification take place in two heated reactors. The
710 refined vegetable oil is sent at 20°C by a positive-displacement pump to the first reactor. The MeOH
711 is conducted with a centrifugal pump inside 2 mixers, adding 30kg of KOH (in solid flakes) or
712 catalyst in a proportion of 1.5% wt of the oil to each mixer through a hopper. The solution required
713 for the first reaction is delivered by a positive-displacement pump to the first reactor, already mixed
714 in a static mixer with vegetable oil in molar ratio of 6:1. The reactor is stirred at 1000 rpm. Before
715 entering the reactor, the mixture passes through a heat exchanger that warms it to 60°C. The triolein
716 conversion degree in the first reactor (REAC-01) is about 86% and the residence time approximately
717 30 minutes. The products of the reaction are transferred by a positive-displacement pump to a first
718 centrifugal separator (SEP-01), where the BD and GL phases are separated. En route, the BD is mixed
719 in a static mixer with a new alcohol-catalyst solution (adding another 30 kg of KOH to the MeOH
720 delivered by a positive displacement pump that mix the vegetable oil and methanol in a molar ratio of
721 20:1. The reaction mixture passes through a heat exchanger that warms the fluid up to 60°C. In this
722 second reactor, a triglyceride conversion degree of 96% is reached with a residence time of 30
723 minutes [166]. After this stage, there is another centrifugal unit for separating the GL phase from the
724 BD phase. This separation can also be done by gravity, which would reduce the energy consumption
725 of the process, but increase its operating times. Considering the dependence of the first separation
726 (SEP-01), performed at 1bar, on temperature (Fig. 8), it is evident that a lower temperature does not
727 significantly affect the amount of glycerol obtained, but it does affect the methanol content in the GL
728 phase.

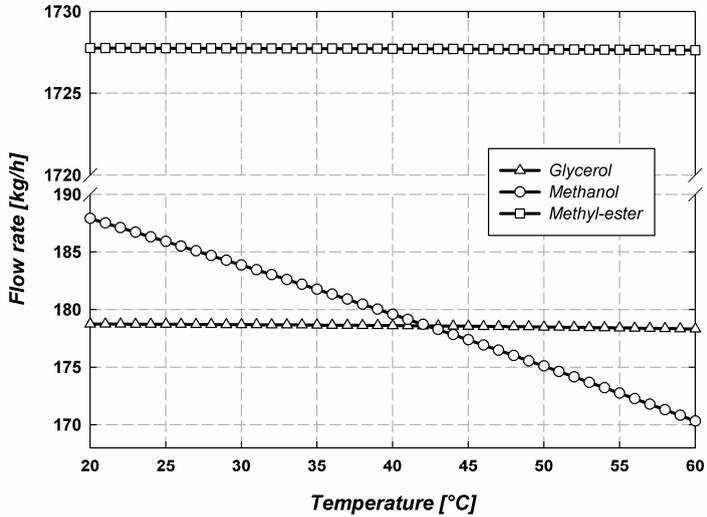


Fig. 8: Temperature dependence of separation SEP-01.

In the second separator, which also operates at 1bar (SEP-02), as shown in Fig. 9, the separation temperature affects the ester content in the BD phase and this affects all subsequent purification stages.

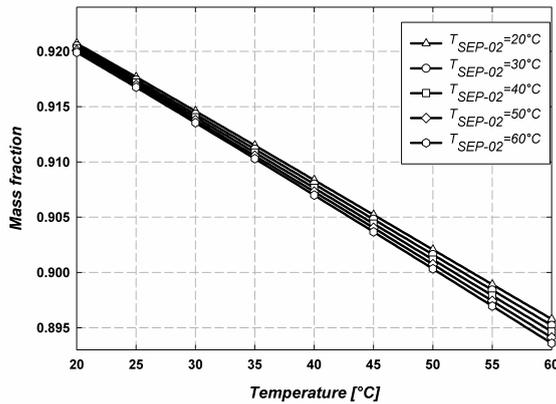
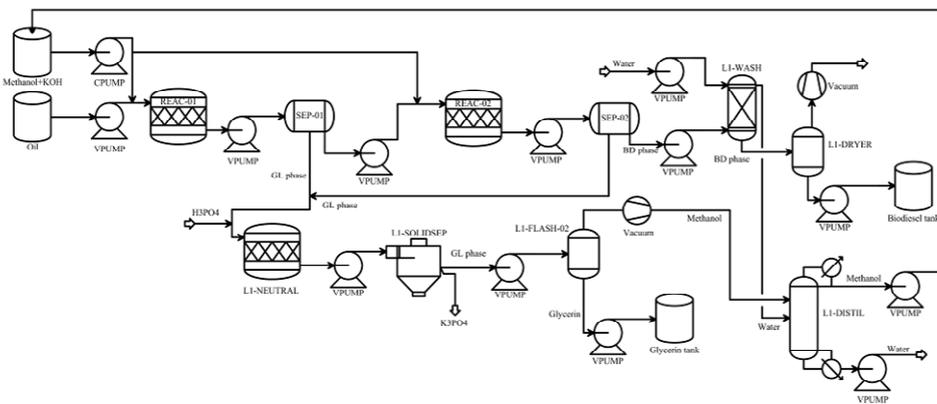


Fig. 9: Effect of temperature change on ester mass fraction separation out from SEP-02.

6.2 Process flow diagram 1

Once separated, the BD and GL phases undergo a series of different treatments (Fig. 10). The main stream produces biodiesel from the BD phase. The BD phase is rinsed with water (L1-WASH) to

741 remove all residual methanol, catalyst, glycerol and soaps. So first additives are added to the obtained
 742 biodiesel, and then it is dried at 120°C and 200mbar (L1-DRYER) to remove all traces of the washing
 743 water, and it is finally filtered. The secondary stream from the process involves treating the GL phase
 744 adding 50% wt of an aqueous solution of H₂SO₄. This acidification process is carried out in a tank,
 745 stirring the mixture, at a temperature close to the reaction temperature and at atmospheric pressure
 746 (L1-NEUTRAL). Three different phases can be obtained: a lower GL phase, an upper free fatty acids
 747 phase, and a solid precipitated salt phase (K₃PO₄). The mixture undergoes centrifugation to separate
 748 the solid precipitate. The GL phase is then sent for flash distillation (L1-FLASH-02) to recover the
 749 methanol. If the vegetable oil has a high content of free fatty acids, the GL phase is heated to 110°C
 750 and 0.4bar after this distillation process, thereby achieving two distinct phases, one of fatty acids and
 751 the other of glycerine (with a purity of about 85%) for further separation. The methanol-rich flow in
 752 the vapour phase leaving the flash distiller is mixed with washing water from the stream involved in
 753 the BD phase, which has been neutralized with H₂SO₄ to eliminate any traces of catalyst and convert
 754 the traces of soap into free fatty acids. Then, the whole water and methanol mixture is treated in a
 755 distillation column to recover methanol with a purity >99.99%.



756
 757 Fig. 10: Process flow diagram 1.
 758
 759

760 6.2.1 Washing column L1-WASH analysis

761 The washing column extracts the methanol and any impurities from the BD phase. As seen in Fig. 11
 762 and Fig. 12, increasing the temperature of the process negatively affects the washing conditions, so
 763 this should be done using water and BD phase at low temperatures to achieve the maximum content
 of methyl-esters and the minimum content of water and methanol in the BD phase.

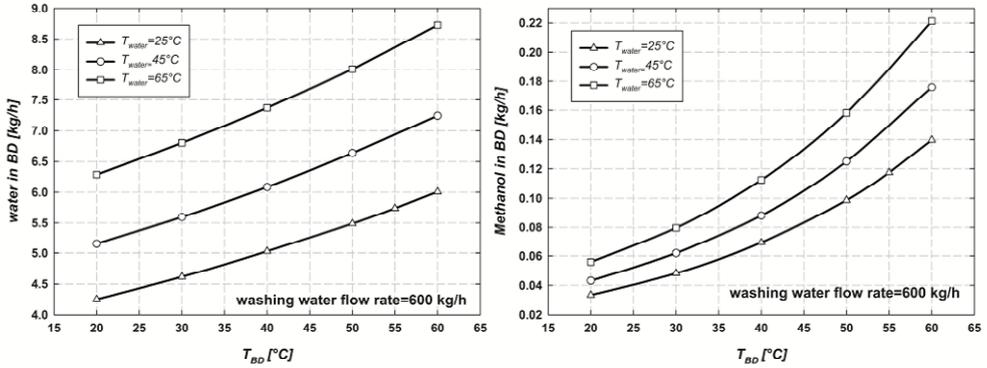


Fig. 11: Mass flow rate of water (left) and mass flow rate of methanol (right) in BD phase after washing with 600 kg/h of water for various inlet temperature of BD phase and washing water.

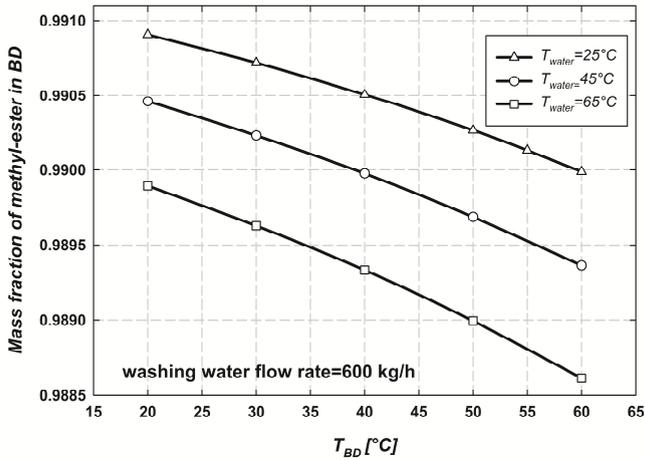


Fig. 12: Mass fraction of methyl-ester in BD phase with 600 kg/h of washing water for various inlet temperature of BD and washing water.

Considering a temperature at 25°C, Fig. 13 shows that increasing the washing water flow gives a better product, rich in esters and almost all the methanol can be extracted. The results confirm the validity of the current practice of using water in quantities equating to one third by mass of the phase being washed.

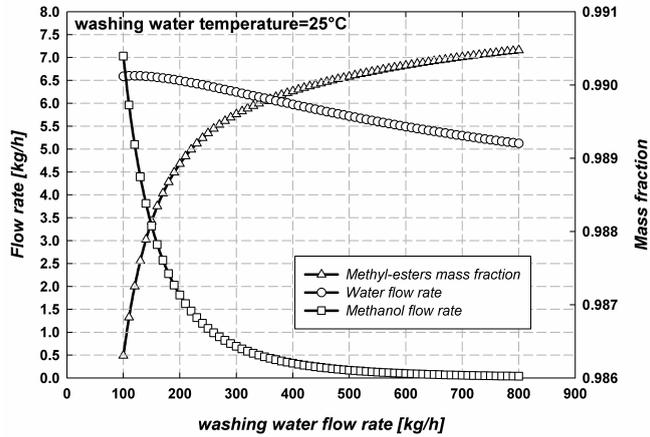


Fig. 13: Mass fraction of methyl-ester, mass flow rate of methanol and water in BD phase for various mass flow rate of washing water.

6.2.2 Dryer L1-DRYER analysis

The flash evaporator named L1-DRYER in process flow diagram 1 separates water from the ester to comply with the standards, i.e. a specific content <500mg/l. For a given washing water flow rate, Fig. 14 and Fig. 15 show the variations of the water content in the BD phase after the dryer, evaporating at 150°C and various pressures, and considering the BD phase at 40°C and 60°C, respectively.

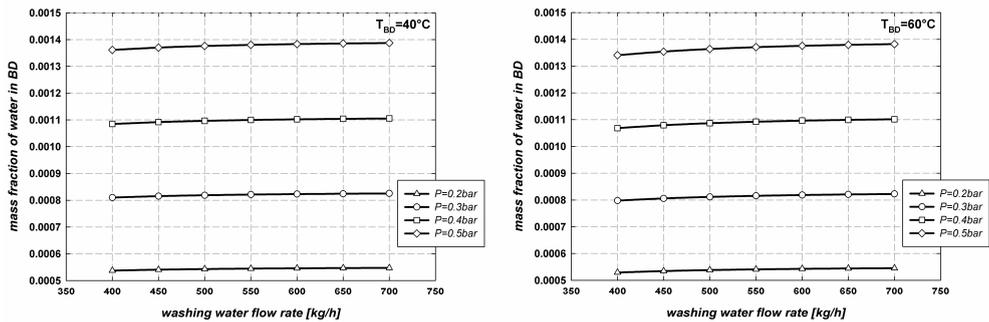


Fig. 14: Water mass fraction in BD phase in relation to water flow rate and drying pressure with BD phase at 40°C (left) and 60°C (right).

As shown in Fig. 15, completing this operation at 115°C and 0.1bar avoids the risk of methyl-ester deterioration due to temperatures above 150°C-250°C being reached [167]. By washing the previous stage with 600 kg/h of water at 25°C and evaporating under a vacuum with an input temperature of

791 the BD phase set at 60°C, the water content in the BD leaving the evaporator can be controlled by
 792 adjusting the pressure and drying temperature.

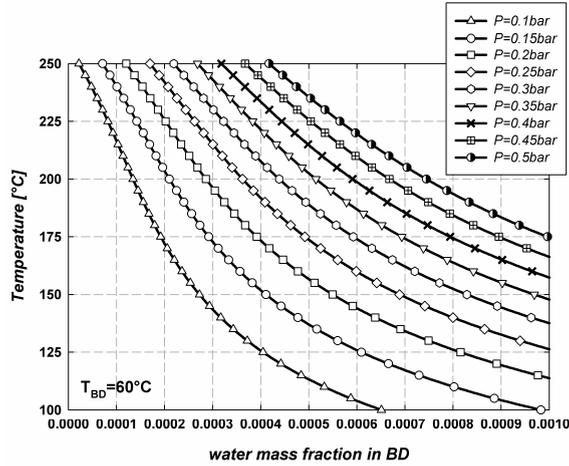


Fig. 15: Water mass fraction in BD phase at various temperatures and pressures.

793
 794
 795
 796 **6.2.3 GL phase flash evaporator L1-FLASH-02 analysis**

797 The flash evaporator for separating the glycerine from the methanol must be able to obtain a glycerine
 798 containing glycerol in quantities higher than 85% wt, which is suitable for industrial purposes. Fig. 16
 799 shows how temperature and pressure affect the glycerol content in the GL phase.

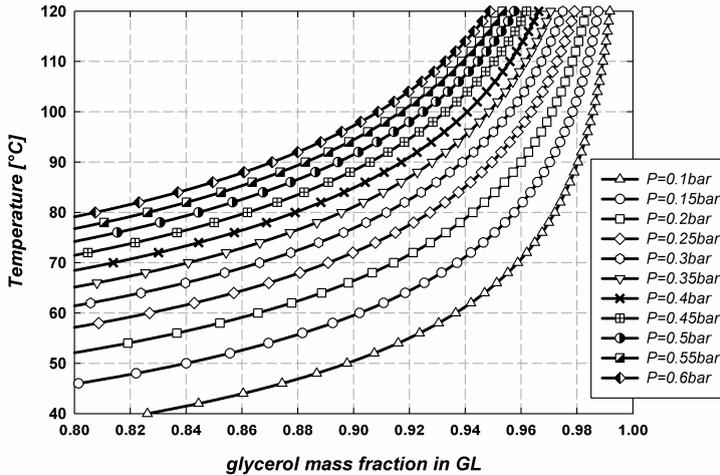


Fig. 16: Glycerol mass fraction in GL phase at various distillation temperatures and pressures.

800 Design decisions usually go for a pressure of 0.5bar. Fig. 17 shows that the mass fraction of glycerol
 801 is more sensitive to pressure changes at low pressures. At 0.1 bar, a 0.05bar variation produces a 2%
 802
 803
 804

805 change in the mass fraction of glycerol, while at 0.5bar the same pressure change produces a 0.4%
 806 change in said fraction of glycerol.
 807 Additional operations, such as filtration and/or bleaching, are needed to obtain a glycerine with a
 808 purity higher than 85% (i.e. to reach the >99.5% grade required in the pharmaceutical field).

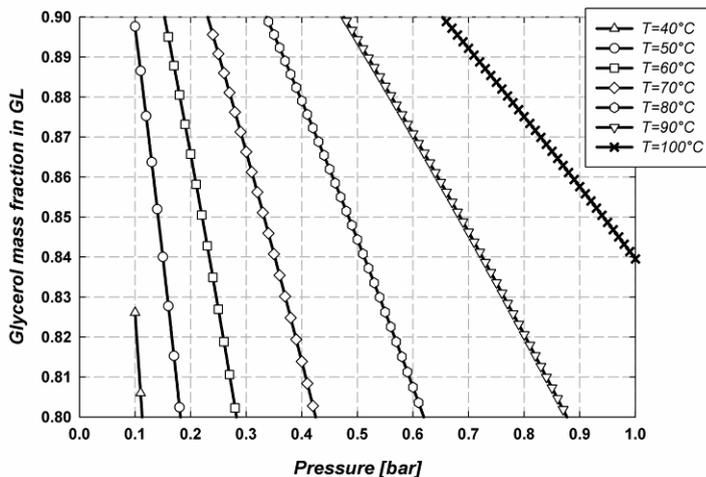


Fig. 17: Glycerol mass fraction in GL phase at various pressure changes.

6.3 Process flow diagram 2

813 Process flow diagram 2 (Fig. 18) was studied assuming the same initial conditions as in the previous
 814 case, and the part concerning the transesterification reaction and the GL phase refining line remained
 815 the same. The BD phase leaving the second separator is sent, in this case, to a flash evaporator (L2-
 816 FLASH-01), where methanol is separated from the BD before the latter is rinsed with water (L2-
 817 WASH) to remove any remaining impurities. The resulting biodiesel is then dried (L2-DRYER).

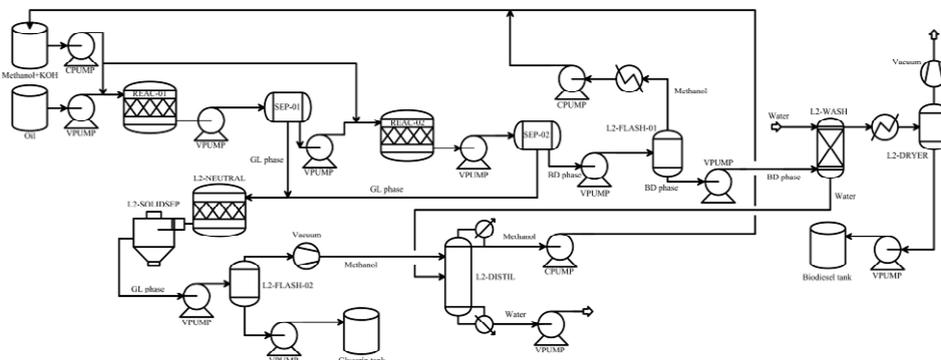
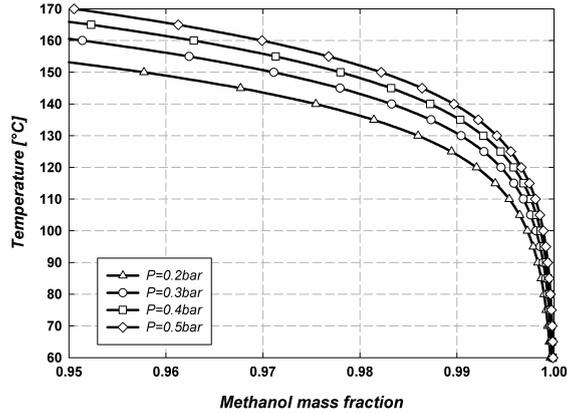


Fig. 18. Process flow diagram 2.

818
 819
 820

821 **6.3.1 Flash evaporator L2-FLASH-01 analysis**

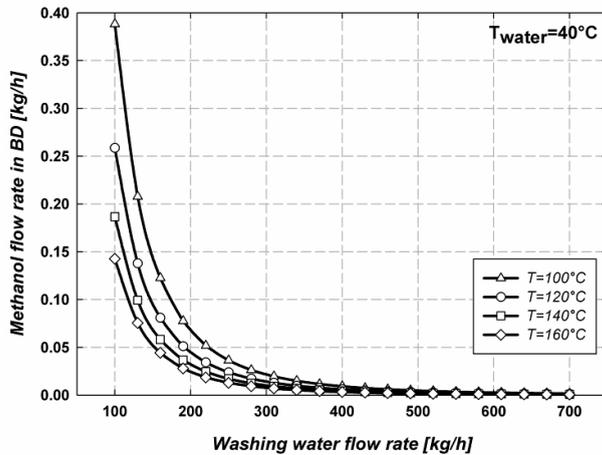
822 The methanol in the BD phase is recovered by flash evaporation after the separator SEP-02. Fig. 19
823 shows that changes in the pressure and temperature conditions influence the purity of the methanol
824 sent to the reactor.



825
826 Fig. 19. Methanol mass fraction in vapour phase from L2-FLASH-01 at various temperatures and
827 pressures
828

829 **6.3.2 Washing column L2-WASH analysis**

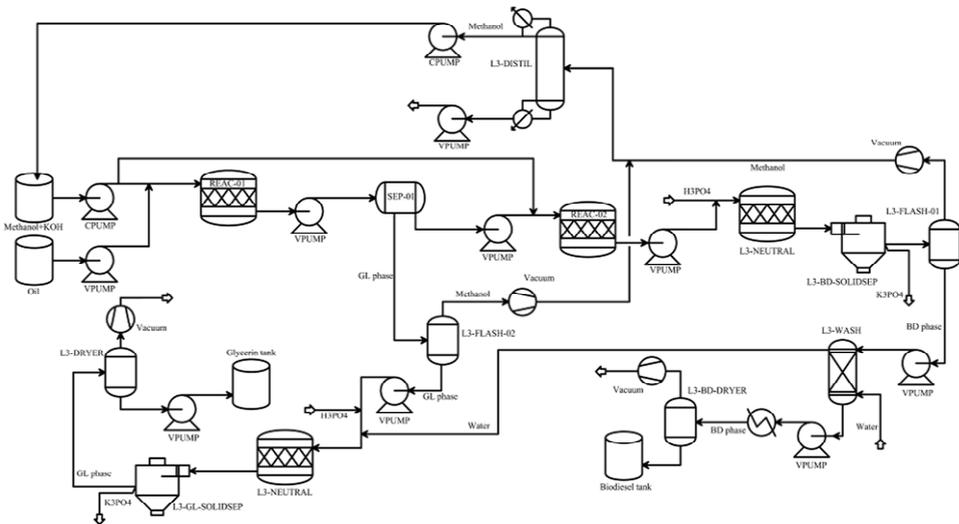
830 Any methanol and glycerol still contained in the BD phase is extracted in the washing column. As
831 shown in Fig. 20, using more water ensures a lower methanol content in the BD phase. In addition, a
832 lower temperature of the BD phase at the inlet of the washing column allows less water to be used.



833
834 Fig. 20. Methanol mass flow rate in BD phase from extraction column in relation to the water flow
835 rate and the inlet temperature of BD phase considering a water temperature of 40°C

836 **6.4 Process flow diagram 3**

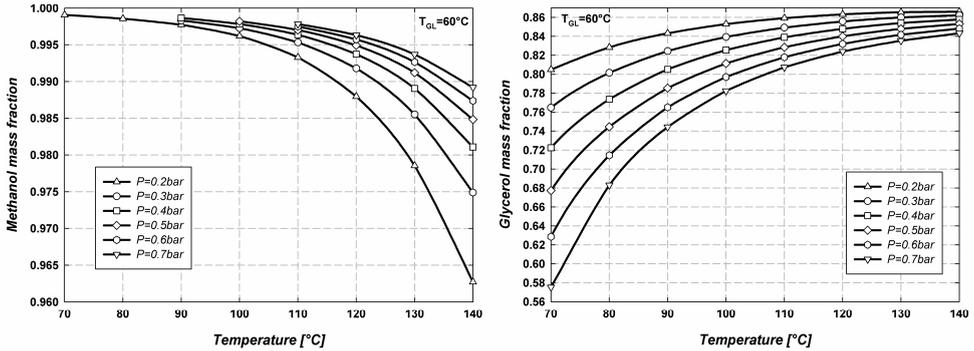
837 In process flow diagram 3 (Fig. 21), after the second separator (SEP-02), the reaction products are
 838 sent by a positive-displacement pump to a neutralizing reactor, where a strong mineral acid (H_3PO_4)
 839 is added (0.2-0.3% wt) to remove soaps and create an acidic pH to inhibit foam formation. The
 840 subsequent vaporization (L3-FLASH-01) is implemented in a range of temperatures between 80°C
 841 and 90°C and enables all the methyl alcohol in excess to be removed. The unit operates in a vacuum
 842 at 0.1bar. The condensed methanol is collected in a tank at a temperature of 25°C. After adding a dose
 843 of water around 10% wt, the BD phase is sent by the positive-displacement pump to a centrifugal
 844 separator or washing column (L3-WASH). These treatments clean the BD phase from the glycerol in
 845 solution. Since some water remains in the BD phase (mainly esters) the product needs to be dried.
 846 A positive-displacement pump is used to pump the mixture of esters and water now comprising the BD
 847 phase to a dryer at 115°C, heating the mixture to 95°C through a heat exchanger en route. The dryer
 848 operates in a vacuum at 0.01bar, obtained with a liquid ring pump. The GL phase, on the other hand,
 849 is sent to a flash evaporator (L3-FLASH-02) at 90°C to separate the methanol and, after condensing,
 850 it returns to the service tank. The biodiesel obtained using this system has a purity >99% and a free
 851 glycerol content <30ppm.



852
 853 Fig. 21. Process flow diagram 3.
 854
 855
 856
 857

858 **6.4.1 GL phase flash evaporator L3-FLASH-02 analysis**

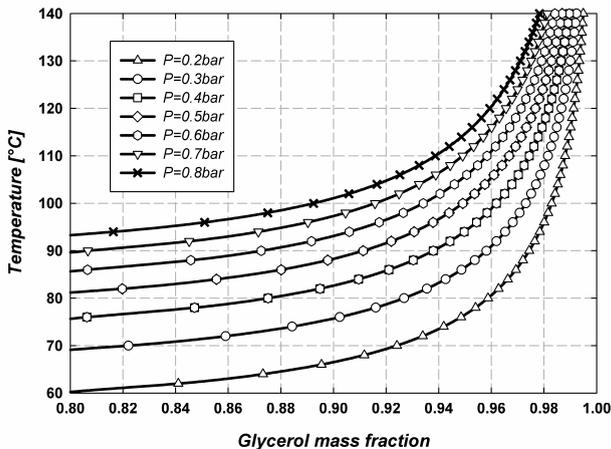
859 This separator is for evaporating the methanol from the glycerine by flash evaporation to obtain
 860 99.9% of pure methanol in the vapour phase and glycerine with a purity of 80-88% in the liquid
 861 phase. Fig. 22 shows how increasing the working temperature improves the purity of the glycerine.



862 Fig. 22. Methanol mass fraction (left) and glycerol (right) in the liquid phase at various temperatures
 863 and pressures with GL phase at 60°C.
 864
 865
 866

867 **6.4.2 Glycerine drying L3-DRYER analysis**

867 Using an acidification unit enables K_3PO_4 to be obtained from the catalyst in the GL phase [168,
 868 169]. This stage involves adding water to dilute the H_2PO_4 . It is consequently necessary to include
 869 another flash evaporator for the drying of the glycerine. Fig. 23 shows that this process can be run
 870 under conditions of moderate vacuum and temperature.



871 Fig. 23. Glycerol mass fraction in GL phase at various drying temperatures and pressures.
 872
 873
 874

875 **7. Standardization of biodiesel**

876 The standards EN 14214:2008 e ASTM 6751 07b show clearly the correct composition of biodiesel.

877 The biodiesel facilities are stressed customers on the production of biodiesel with quality levels

878 higher then the quality suggested by the standards. Some details about the quality levels for a

879 marketable biodiesel, are reported in table 7. Here the standards levels are compared with the market

880 limits.

Table 7:
Quality of biodiesel reported in the standards and required by market

		EN 14214:2008	ASTM 6751 07b	Market limits	
Density (15°C)	g/cm ³	0.86-0.90			
Viscosity (40°C)	mm ² /s	3.5-5	1.9-6		
Distillation	% (°C)		90% (360°C)		
Flash point	°C	>101min	>93min	>120min or >130min for marine	
Sulphur	mg/kg	≤ 10	≤ 15	≤ 5	Required by few customers for high quality product
CCR 100%	% m/m		≤ 0.05		
Carbon residue (10% dist.residue)	% m/m	≤ 0.3		≤ 0.15	Required by rare customers for high quality product
Sulphated ash	% m/m	≤ 0.02	≤ 0.02		
Water	mg/kg	≤ 500	≤ 500	≤ 300	
Total contamination	mg/kg	≤ 24		≤ 10	Required rarely
Cu corrosion max	3h (50°C)	1	3		
Oxidation stability	h (110°C)	≥ 6	≥ 3	≥ 10	Required by few customers for high quality product
Cetane number		51 min	47 min		
Acid value	mg KOH/g	≤ 0.5	≤ 0.5	≤ 0.30	
Methanol	% m/m	≤ 0.2	≤ 0.2		
Ester content	% m/m	≥ 96.5			
Monoglyceride	% m/m	≤ 0.8		≤ 0.40	
Diglyceride	% m/m	≤ 0.2			
Triglyceride	% m/m	≤ 0.2			
Free glycerol	% m/m	≤ 0.02	≤ 0.02		
Total glycerol	% m/m	≤ 0.25	≤ 0.24		
Iodine value	g I ₂ /100 g	≤ 120		≤ 115	Required by rare customers for high quality product
Linoleic acid methyl ester	% m/m	≤ 12			
C(x:4) & greater unsaturated esters	% m/m	≤ 1			
Phosphorus	mg/kg	≤ 4		≤ 10	
Gp I metals (Na, K)	mg/kg	≤ 5	≤ 5	≤ 2	
Gp II metals (Ca, Mg)	mg/kg	≤ 5	≤ 5	≤ 2	

881 **8. Conclusions**

882 Alternative fuels are gaining in importance due to unstable crude oil prices and the consequences of
883 emissions deriving from crude oil compounds. Many studies have shown that triacylglycerols are
884 promising sources for the production of alternative fuels. One possibility involves the
885 transesterification of vegetable oils with alcohol catalyzed by basic homogeneous compounds to
886 obtain esters of fatty acid. This method of catalysis is preferable to others because of its high yield
887 and relatively low installation costs [170]. Designing large-scale biodiesel production plants of this
888 type requires a preliminary design effort based on data that are currently incomplete in the technical
889 and scientific literature. This difficulty is compounded by the need to know the chemical and physical
890 characteristics, composition and purity of the vegetable oil used, which also depends on how the oil is
891 extracted and refined. The above-mentioned issues affect how the raw material is converted and
892 purified to produce biodiesel, which can be done in various ways. Sometimes these plants are not
893 optimized, however, giving rise to an end-product that only complies with the specifications dictated
894 by the standards EN 14214:2008 and ASTM D 6751 07b if a great deal of energy goes into the
895 process, and that carries the risk of creating conditions leading to the product's deterioration. An
896 analysis of the main elements involved in such systems emphasizes how they react to changes in
897 operating conditions to obtain a product with the necessary characteristics. Starting from the results
898 discussed, the operation of a given plant can be optimized to achieve the best possible purity of the
899 end-product with the minimal energy expenditure [171, 172].

900
901 **Acknowledgment**

902 This work was supported by Fondazione CARIVERONA within the framework of the project
903 "BIOMASSE DI OGGI E DI DOMANI: dai reflui zootecnici e dalle microalghe un contributo
904 all'agricoltura sostenibile e all'energia rinnovabile".

905
906 **References**

- 907 [1] Demirbas A. Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical
908 methanol transesterification methods. *Progr Energy Combust Sci* 2005;31:466-87.
- 909 [2] Demirbas A. Importance of biodiesel as transportation fuel. *Energy Policy* 2007;35:4661-70.
- 910 [3] Monyem A, Van Gerpen JH. The effect of biodiesel oxidation on engine performance and
911 emissions. *Biomass Bioenergy* 2001;20:317-25.
- 912 [4] Thamsiroj T, Murphy JD. A critical review of the applicability of biodiesel and grass
913 biomethane as biofuels to satisfy both biofuel targets and sustainability criteria. *Appl Energy* 2011;88:
914 1008-19. doi: 10.1016/j.apenergy.2010.10.026.

915 [5] Chisti Y. Biodiesel from microalgae beats bioethanol. *Trends Biotechnol* 2008;26:126-31.
916 doi:10.1016/j.tibtech.2007.12.002

917 [6] Bozbas K. Biodiesel as an alternative motor fuel: Production and policies in the European Union.
918 *Renewable Sust Energy Rev* 2008;12 542-52.

919 [7] Apostolakou AA, Kookos LK, Marazioti C, Angelopolous KC. Techno-economic analysis of a
920 biodiesel production process from vegetable oils. *Fuel Proc Technol* 2009;90:1023-1031.

921 [8] Hasheminejad M, Tabatabaei M, Mansourpanah Y, Khatami far M, Javani A. Upstream and
922 downstream strategies to economize biodiesel production. *Bioresour Technol* 2011;102:461-468.

923 [9] www.InflationData.com. All rights reserved. InflationData.com is affiliated with Financial Trend
924 Forecaster, a publication of Capital Professional Services.

925 [10] www.ismea.it. All rights reserved. Ismea (Istituto di Servizi per il mercato agricolo e alimentare).

926 [11] www.imf.org. Data collected by the International Monetary Fund.

927 [12] Ajanovic A. Biofuels versus food production: Does biofuels production increase food prices?.
928 *Energy* 2011;36:2070-76.

929 [13] Lin L, Cunshan Z, Vittayapadung S, Xiangqian S, Mingdong D. Opportunities and challenges for
930 biodiesel fuel. *Appl Energy* 2011;88:1020-31.

931 [14] Sunderasan S. The food vs. fuel debate: A nuanced view of incentive structures. *Renewable*
932 *Energy* 2009;34:950-54.

933 [15] Buyx A, Tait J. Ethical Framework for Biofuels. *Science* 2011;332:540-41.
934 doi:10.1126/science.1206064.

935 [16] Lin L, Cunshan Z, Vittayapadung S, Xiangqian S, Mingdong D, Opportunities and challenges for
936 biodiesel fuel. *Appl Energy* 2011;88:1020-31. doi: 10.1016/j.apenergy.2010.09.029.

937 [17] Lal R. World crop residues production and implications of its use as a biofuel. *Environ Int*
938 2005;31:575-84.

939 [18] Schenk PM, Thomas-Hall SR, Stephens E, Marx UC, Mussgnug JH, Posten C, Kruse O,
940 Hankamer B. Second Generation Biofuels: High-Efficiency Microalgae for Biodiesel Production.
941 *Bioenergy Resour* 2008;1:20-43. doi:10.1007/s12155-008-9008-8.

942 [19] Pleanjai S, Gheewala SH. Full chain energy analysis of biodiesel production from palm oil in
943 Thailand. *Appl Energy* 2009;86:S209-S214. doi: 10.1016/j.apenergy.2009.05.013.

944 [20] Li YG, Xu L, Huang YM, Wang F, Guo C, Liu CZ. Microalgal biodiesel in China: Opportunities
945 and challenges. *Appl Energy* 2011;88:3432-7. doi: 10.1016/j.apenergy.2010.12.067.

946 [21] Pahl G. Biodiesel, coltivare una nuova energia. Roma:Franco Muzzio Editore; 2006.

947 [22] Srivastava A, Prasad R. Triacylglycerols-based diesel fuels. *Renewable Sust Energy Rev*
948 2000;4:111-33.

949 [23] Lisa M, Holcapek M. Triacylglycerols profiling in plant oils important in food industry, dietetics
950 and cosmetics using high-performance liquid chromatography-atmospheric pressure chemical
951 ionization mass spectrometry. *J Chromatogr A* 2008;1198-1199:115-30.

952 [24] Christov M, Dohrn R. High-pressure fluid phase equilibria-Experimental methods and systems
953 investigated (1994–1999). *Fluid Phase Equilib* 2002;202:153-218.

954 [25] Pereda S, Bottini SB, Brignole EA. Gas-liquid reactions under supercritical conditions-phase
955 equilibria and thermodynamic modelling. *Fluid Phase Equilib* 2002;194-197:493-99.

956 [26] Coupland JN, McClements DJ. Physical Properties of Liquid Edible Oils. *JAOCS* 1997;74:1559-
957 64.

958 [27] IUPAC. Atomic Weights of the Elements 1999. *J Phys Chem Ref Data* 2001;30:701-12.

959 [28] Hagemann JW, Tallent WH. Differential Scanning Calorimetry of Single Acid Triglycerides:
960 Effect of Chain Length and Unsaturation. *JAOCS* 1972;49:118-23. doi: 10.1007/BF02612641

961 [29] Daubert BF, Lutton ES. X-Ray Diffraction Analyses of Synthetic Unsaturated Monacid
962 Diglycerides, *J Am Chem Soc* 1947;69:1449-51. doi: 10.1021/ja01198a055.

963 [30] Gros AT, Feuge RO. Physical Properties of Aceto- and Butyro-Oleins, Mono-Olein, and Diolein.
964 *JAOCS* 1957;34:239-44. doi: 10.1007/BF02640258.

965 [31] Design Institute for Physical Properties, Sponsored by AIChE [2005, 2008, 2009,2010], DIPPR
966 Project 801-Full Version, Design Institute for Physical Property Research/AIChE.

967 [32] Hagemann JW, Tallent WH, Barve JA, Ismail IA, Gunstone FD. Polymorphism in Single-Acid
968 Triglycerides of Positional and Geometric Isomers of Octadecenoic Acid. *JAOCS* 1975;52:204-7.

969 [33] Paranjpe GR, Davar DJ. Dielectric Properties of Some Organic Substances. *Indian J Phys*
970 1938;12:283-8.

971 [34] Privett OS, Blank ML. A Method for the Structural Analysis of Triglycerides and Lecithins.
972 *JAOCS* 1963;40:70-5. doi: 10.1007/BF02654747.

973 [35] Serebrennikova GA, Sarycheva IK, Preobrazhensky NA. Investigation of Lipids. XI.Synthesis of
974 Triglycerides of Soybean Oil. *J Gen Chem USSR* 1962;32:2174-208.

975 [36] Weast RC, Astle MJ. Handbook of Data on Organic Compounds. CRC Press;Boca Raton; 1985.

976 [37] Chemika Biochemika, Fluka Chemical Corporation, Ronkonkoma, NY (1990); Fluka Catalog.

977 [38] Lide DR. Handbook of Chemistry and Physics. 85th ed. Boca Ranton: CRC Press; 2005.

978 [39] Knothe G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel*
979 *Process Technol* 2005;86:1059-70.

980 [40] Demirbas A. Relationships derived from physical properties of vegetable oil and biodiesel fuels.
981 *Fuel* 2008;87:1743-48.

982 [41] Kafuku G, Mbarawa M. Alkaline catalyzed biodiesel production from moringa oleifera oil with
983 optimized production parameters. *Appl Energy* 2010;87:2561-5. doi: 10.1016/j.apenergy.2010.02.026.
984 [42] Wang R, Song B, Zhou W, Zhang Y, Hu D, Bhadury PS, Yang S. A facile and feasible method
985 to evaluate and control the quality of *Jatropha curcus* L. seed oil for biodiesel feedstock: Gas
986 chromatographic fingerprint, *Appl Energy* 2011;88:2064-70. doi: 10.1016/j.apenergy.2010.12.078.
987 [43] Official Methods and Recommended Practices of the AOCS. 5th Edition, 2nd Printing. S.
988 Boulder, Urbana, IL:AOCS Press; 2007.
989 [44] Pirova M. *Industrie agrarie alimentari*. 2nd Edition. Udine:Del Bianco; 1971.
990 [45] Demirbas A. *Biodiesel: A Realistic Fuel Alternative for Diesel Engines*. 1st ed.
991 London:Springer; 2008.
992 [46] Ranalli A, Cabras P, Iannucci E, Contento S. Lipochromes, vitamins, aromas and other
993 components of virgine olive oil are affected by processing technology. *Food Chem* 2001;73:445-51
994 [47] Owolarafe OK, Osunleke AS, Odejebi OA, Ajadi SO, Faborode MO. Mathematical modelling
995 and simulation of the hydraulic expression of oil from oil palm fruit. *Biosyst Eng* 2008;101: 331-40.
996 [48] Kartika IA, Pontalier PY, Rigal L. Extraction of sunflower oil by twin screw extruder: Screw
997 configuration and operating condition effects. *Bioresour Technol* 2006;97:2302-10.
998 [49] Willems P, Kuipers NJM, De Haan AB. Hydraulic processing of oilseeds: Experimental
999 determination and modelling of yield and pressing rates. *J Food Eng* 2008;89:8-16
1000 [50] Kartika IA, Pontalier PY, Rigal L. Oil extraction of oleic sunflower seeds by twin screw
1001 extruder: influence of screw configuration and operating conditions. *Ind Crops Products* 2005;22:207-
1002 22.
1003 [51] Harrington KJ, D'Arcy-Evans C. Transesterification in Situ of Sunflower Seed Oil. *Ind Eng*
1004 *Chem Prod Res Dev* 1985;24:314-18.
1005 [52] Nash AM, Frankel EN., Limited Extraction of Soybeans with Hexane. *JAOCS* 1986;63:244-246.
1006 [53] Virost M, Tomao V, Ginies C, Visinoni F, Chemat F. Green procedure with a green solvent for
1007 fats and oils' determination Microwave-integrated Soxhlet using limonene followed by microwave
1008 Clevenger distillation. *J Chromatogr A* 2008;1196-1197:147-52.
1009 [54] Monick JA, Treybal RE. Separation of Monoacylglycerols, Diacylglycerols and Triacylglycerols
1010 by Liquid-Liquid Extraction. *JAOCS* 1956;33:193-7.
1011 [55] Bockisch M. *Fats and oils Handbook*. 1st Edition. S. Boulder, Urbana:AOCS Press; 1998.
1012 [56] Scheithauer R, Dripchak K. Economics of vegetable oil processing. Technical Report for U.S.
1013 Department of Energy. ORNL/Sub/87-SA185/1, Oak Ridge National Laboratory, Tennessee:Oak
1014 Ridge, 1988.

1015 [57] OECD Factbook 2010: Economic, Environmental and Social Statistics. ISBN 92-64-08356-1.
1016 OECD; 2010.

1017 [58] Peri M, Baldi L. Vegetable oil market and biofuel policy: An asymmetric cointegration
1018 approach. *Energy Economics* 2010;32:687-93.

1019 [59] Pre-Treatment of Oils and Fats for Biodiesel Production. Westfalia Separator Food Tec.

1020 [60] Ma F, Hanna MA. Biodiesel production: a review. *Bioresour Technol* 1999;70:1-15.

1021 [61] Russel Finnex. Biodiesel production: Going green to improve productivity. *Filtration Sep*
1022 2008;45:24-25.

1023 [62] Leung DYC, Xuan Wu, Leung MKH. A review on biodiesel production using catalyzed
1024 transesterification. *Appl Energy* 2010;87:1083-95.

1025 [63] Marchetti JM, Errazu AF. Technoeconomic study of supercritical biodiesel production plant.
1026 *Energy Conversion Manage* 2008;49:2160-64.

1027 [64] Montefrio MJ, Xinwen T, Obbard JP. Recovery and pre-treatment of fats, oil and grease from
1028 grease interceptors for biodiesel production. *Appl Energy* 2010;87:3155-61. doi:
1029 10.1016/j.apenergy.2010.04.011.

1030 [65] Lin L, Ying D, Chaitep S, Vittayapadung S. Biodiesel production from crude rice bran oil and
1031 properties as fuel. *Appl Energy* 2009;86:681-8. doi: 10.1016/j.apenergy.2008.06.002.

1032 [66] Tesser R, Di Serio M, Guida M, Nastasi M, Santacesaria E. Kinetics of Oleic Acid Esterification
1033 with Methanol in the Presence of Triacylglycerols. *Ind Eng Chem Res* 2005;44:7978-82.

1034 [67] Official Method 3d-63 (99) in Section C, Commercial Fats and Oils, Official Methods and
1035 Recommended Practices of the AOCS, 5th Edition, 2nd Printing. S. Boulder, Urbana:AOCS Press;
1036 2007.

1037 [68] Berrios M, Siles J, Martin MA, Martin A. A kinetic study of the esterification of free fatty acids
1038 (FFA) in sunflower oil. *Fuel* 2007;86:2383-88.

1039 [69] Di Nicola G, Pacetti M, Polonara F, Santori G, Stryjek R. Development and optimization of a
1040 method for analyzing biodiesel mixtures with non-aqueous reversed phase liquid chromatography. *J*
1041 *Chromatogr A* 2008;1190:120-6.

1042 [70] Holcapek M, Jandera P, Fischer J, Prokes B. Analytical monitoring of the production of biodiesel
1043 by high performance liquid chromatography with various detection methods. *J Chromatogr A*
1044 1999;858:13-31.

1045 [71] Ataya F, Dube MA, Ternan M. Single-Phase and Two-Phase Base-Catalyzed Transesterification
1046 of Canola Oil to Fatty Acid Methyl Esters at Ambient Conditions. *Ind Eng Chem Res* 2006;45:5411-
1047 17.

1048 [72] Meher LC, Vidya Sagar D, Naik SN. Technical aspects of biodiesel production by
1049 transesterification-a review. *Renewable Sust Energy Rev* 2006;10:248-68.

1050 [73] Sharma YC, Singh B, Upadhyay SN. Advancements in development and characterization of
1051 biodiesel: A review. *Fuel* 2008;87:2355-73.

1052 [74] Santori G, Arteconi A, Di Nicola G, Moglie M, Stryjek R. Quantitation of Compounds in
1053 Biodiesel Mixtures with Reversed-Phase Liquid Chromatography. *Energy & Fuels* 2009;23:3783-9.
1054 doi: 10.1021/ef900140r.

1055 [75] Sotoft LF, Westh P, Christensen KV, Norddahl B. Novel investigation of enzymatic biodiesel
1056 reaction by isothermal calorimetry. *Thermochim Acta* 2010;501:84-90. doi:
1057 10.1016/j.tca.2010.01.014.

1058 [76] Vicente G, Martinez M, Aracil J. Integrated biodiesel production: a comparison of different
1059 homogeneous catalysts systems. *Bioresour Technol* 2004;92:297-305.

1060 [77] Ataya F, Dube MA, Ternan M. Acid-Catalyzed Transesterification of Canola Oil to Biodiesel
1061 under Single- and Two-Phase Reaction Conditions. *Energy & Fuels* 2007;21:2450-59.

1062 [78] Yesiloglu Y. Immobilized Lipase-Catalyzed Ethanolysis of Sunflower Oil. *JAACS* 2004;81:157-
1063 60.

1064 [79] Chattopadhyay S, Karemore A, Das S, Deysarkar A, Sen R. Biocatalytic production of biodiesel
1065 from cottonseed oil: Standardization of process parameters and comparison of fuel characteristics,
1066 *Appl Energy* 2011;88:1251-56.

1067 [80] MacLeod CS, Harvey AP, Lee AF, Wilson K. Evaluation of the activity and stability of alkali-
1068 doped metal oxide catalysts for application to an intensified method of biodiesel production. *Chem*
1069 *Eng J* 2008; 135:63-70.

1070 [81] Di Serio M, Tesser R, Pengmei L, Santacesaria E. Heterogeneous Catalysts for Biodiesel
1071 Production. *Energy & Fuels* 2008;22:207-17.

1072 [82] Arzamendi G, Arguinarena E, Campo I, Zabala S, Gandia LM. Alkaline and alkaline-earth
1073 metals compounds as catalysts for the methanolysis of sunflower oil. *Catal Today* 2008;133-135: 305-
1074 13.

1075 [83] Baroi C, Yanful EK; Bergougnou MA. (2009) Biodiesel Production from *Jatropha curcas* Oil
1076 Using Potassium Carbonate as an Unsupported Catalyst. *Int J Chem Reactor Eng* 2009;7:A72.
1077 Available at: <http://www.bepress.com/ijcre/vol7/A72>.

1078 [84] Fukuda H, Kondo A, Noda H. Biodiesel Fuel Production by Transesterification of Oils. *J Biosci*
1079 *Bioeng* 2001;92:405-416.

1080 [85] Marchetti JM, Miguel VU, Errazu AF. Possible methods for biodiesel production. *Renewable*
1081 *Sust Energy Rev* 2007; 11:1300-11.

- 1082 [86] Demirbas A. Progress and recent trends in biofuels. *Progr Energy Combust Sci* 2007;33:1–18.
- 1083 [87] West AH, Posarac D, Ellis N. Assessment of four biodiesel production processes using HYSYS
- 1084 Plant. *Bioresour Technol* 2008;99:6587-601.
- 1085 [88] Adhikari S, Fernando SD, Haryanto A. Hydrogen production from glycerin by steam reforming
- 1086 over nickel catalysts. *Ren Energy* 2008;33:1097-100.
- 1087 [89] Slinn M, Kendall K, Mallon C, Andrews J. Steam reforming of biodiesel by-product to make
- 1088 renewable hydrogen. *Bioresour Technol* 2008;99:5851-58.
- 1089 [90] Shams SY, Gonzalez R. Anaerobic fermentation of glycerol: a path to economic viability for the
- 1090 biofuels industry. *Curr Opin Biotechnol* 2007;18:213-19. doi:10.1016/j.copbio.2007.05.002.
- 1091 [91] Cerón Garcia MC, Sánchez Mirón A, Fernández Sevilla JM, Molina Grima E, Garcia Camacho
- 1092 F. Mixotrophic growth of the microalga *Phaeodactylum tricornutum* Influence of different nitrogen
- 1093 and organic carbon sources on productivity and biomass composition. *Process Biochem* 2005;40:297-
- 1094 305.
- 1095 [92] Vicente G, Martinez M, Aracil J, Esteban A. Kinetics of sunflower oil methanolysis. *Ind Eng*
- 1096 *Chem Res* 2005;44:5447-54.
- 1097 [93] Vicente G, Martinez M, Aracil J. Optimisation of integrated biodiesel production. Part II. A
- 1098 study of the material balance. *Bioresour Technol* 2007;98:1754-61.
- 1099 [94] Vicente G, Martinez M, Aracil J. Optimisation of integrated biodiesel production. Part I. A study
- 1100 of the biodiesel purity and yield. *Bioresour Technol* 2007;98:1724-33.
- 1101 [95] Rashid U, Anwar F, Moser BR, Ashraf S. Production of sunflower oil methyl esters by optimized
- 1102 alkali-catalyzed methanolysis. *Biomass Bioenergy* 2008;32:1-4. doi:10.1016/j.biombioe.2008.03.001
- 1103 [96] Arzamendi G, Campo I, Arguinarena E, Sanchez M, Montes M, Gandia LM. Synthesis of
- 1104 biodiesel with heterogeneous NaOH/alumina catalysts: comparison with homogeneous NaOH. *Chem*
- 1105 *Eng J* 2007;134:123-30.
- 1106 [97] Vicente G, Coteron A, Martinez M, Aracil J. Application of the factorial design of experiments
- 1107 and response surface methodology to optimize biodiesel production. *Ind Crops Products* 1998;8:29-
- 1108 35.
- 1109 [98] Freedman B, Pryde EH. Variables Affecting the Yields of Fatty Esters from Transesterified
- 1110 Vegetable Oils. *JAOCS* 1984;61:1638-43. doi:10.1007/BF02541649
- 1111 [99] Bambase ME Jr, Nakamura N, Tanaka J, Matsamura M. Kinetics of Hydroxide-Catalyzed
- 1112 Methanolysis of Crude Sunflower Oil for the production of Fuel-Grade Methyl Esters. *J Chem*
- 1113 *Technol Biotechnol* 2007;82:273-80
- 1114 [100] Balat M, Balat H, Progress in biodiesel processing, *Appl Energy* 2010;87:1815-35.

- 1115 [101] Bouaid A, Martinez M, Aracil J. A comparative study of the production of ethyl esters from
1116 vegetable oils as a biodiesel fuel optimization by factorial design. *Chem Eng J* 2007;134:93-9.
- 1117 [102] Marjanovic Ana V, Olivera S Stamenkovic, Zoran B Todorovic, Miodrag L Lazic, Vlada B
1118 Veljkovic. Kinetics of base-catalyzed sunflower oil ethanolsis. *Fuel* 2010;89:665-71.
- 1119 [103] Rashid U, Anwar F. Production of biodiesel through optimized alkaline-catalyzed
1120 transesterification of rapeseed oil. *Fuel* 2008;87 265-73.
- 1121 [104] Korus R, Hoffman D, Bam N, Peterson C, Drown D. Transesterification process to manufacture
1122 ethyl ester of rape oil. *Proceedings of 1st Biomass Conference of the Americas Burlington, VT*
1123 1993;815-26.
- 1124 [105] Nouredini H, Zhu D. Kinetics of transesterification of soybean oil. *JAOCS* 1997;74:1457-63.
- 1125 [106] Freedman B, Butterfield RO, Pryde EH. Transesterification Kinetics of Soybean Oil. *JAOCS*
1126 1986;63:1375-80. doi:10.1007/BF02679606
- 1127 [107] Darnoko D, Cheryan M. Kinetics of palm oil transesterification in a batch reactor. *JAOCS*
1128 2000;77:1263-66.
- 1129 [108] Sit Foon C, Yuen May C, Ah Ngan M, Cheng Hock C. Kinetics study on transesterification of
1130 palm oil. *J Oil Palm Res* 2004;16 19-29.
- 1131 [109] Leevijit T, Wisutmethangoon W, Prateepchaikul G, Tongurai C, Allen M. A second order
1132 Kinetics of Palm Oil Transesterification. *The Joint International Conference on Sustainable Energy*
1133 *and Enviroment, Hua Hin, Thailand, 2004;277-81.*
- 1134 [110] Alamu OJ, Waheed MA, Jekayinfa SO. Alkali-catalyzed laboratory production and testing of
1135 biodiesel fuel from nigerian palm kernel oil. *CIGR J* 2007;9:1-11.
- 1136 [111] Lin CY, Lin SA, Effects of emulsification variables on fuel properties of two- and three-phase
1137 biodiesel emulsions. *Fuel* 2007;86:210-7.
- 1138 [112] Travaini C. Temperature Rising. *Pumps & Systems* 2006;June:60-1.
- 1139 [113] Westerterp KR, Van Swaaij WPM, Beenackers AACM. *Chemical Reactor Design and*
1140 *Operation, 2nd Edition. Stretford, Manchester:Wiley; 1988.*
- 1141 [114] Pilar Dorado M, Ballesteros E, Mittelbach M, Lopez FJ. Kinetic Parameters Affecting the
1142 Alkali-Catalyzed Transesterification Process of Used Olive Oil. *Energy & Fuels* 2004;18:1457-62.
- 1143 [115] Xuereb C, Bertrand J. 3-D Hydrodynamics in a tank stirred by a double propeller system and
1144 filled with a liquid having evolving rheological properties. *Chem Eng Sci* 1996;51:1725-34.
- 1145 [116] Gunvachai K, Hassan MG, Shama G, Hellgardt K. A new solubility model to describe biodiesel
1146 formation kinetics. *Process Saf Environ Prot.* 2007;85:383-9.
- 1147 [117] Ferella F, Mazzotti Di Celso G, De Michelis I, Stanisci V, Vegliò F. Optimization of the
1148 transesterification reaction in biodiesel production. *Fuel* 2010;89:36-42.

- 1149 [118] Demirbas A. Competitive liquid biofuels from biomass. *Appl Energy* 2011;88:17-28.
- 1150 [119] Operational Handbook of the NovaOl plants in Leghorn, Italy. Leghorn, 2009.
- 1151 [120] Van Gerpen J. Biodiesel processing and production. *Fuel Process Technol* 2005; 86:1097-107.
- 1152 [121] Tanaka Y, Okabe A, Ando S. Method for the preparation of a lower alkyl ester of fatty acids.
- 1153 US Patent 4303590. 1981.
- 1154 [122] Jeong GT, Park DH. Batch (One- and Two-Stage) Production of Biodiesel Fuel From Rapeseed
- 1155 Oil. *Appl Biochem Biotechnol* 2006;129-132:668-79.
- 1156 [123] Bouaid A, Diaz Y, Martinez M, Aracil J. Pilot plant studies of biodiesel production using
- 1157 *Brassica carinata* as raw material. *Catal Today* 2005;106:193-6.
- 1158 [124] Olivera S, Stamenkovic, Lazic ML, Todorovic ZB, Veljkovic VB, Skala DU. The effect of
- 1159 agitation intensity on alkali-catalyzed methanolysis of sunflower oil, *Bioresour Technol*
- 1160 2007;98:2688-99.
- 1161 [125] Danckwerts PV. Continuous flow systems. Distribution of residence times. *Chem Eng Sci*
- 1162 1953;2:1-13.
- 1163 [126] Bacovsky D, Körbitz W, Mittelbach M, Wörgetter M. (2007). Biodiesel Production:
- 1164 Technologies and European Providers. IEA Task 39 2007;Report T39-B6.
- 1165 [127] Muniyappa PR, Brammer SC, Noureddini H. Improved conversion of plant oils and animal fats
- 1166 into biodiesel and co-product. *Bioresour Technol* 1996;56:19-24.
- 1167 [128] Leevijit T, Tongurai C, Prateepchaikul G, Wisutmethangoon W. Performance test of a 6-stage
- 1168 continuous reactor for palm methyl ester production, *Bioresour Technol* 2008;99:214-21.
- 1169 [129] Behzadi S, Farid MM. Production of biodiesel using a continuous gas-liquid reactor. *Bioresour*
- 1170 *Technol* 2009;100:683-689.
- 1171 [130] Busto M, D'Ippolito SA, Yori JC, Iturria ME, Pieck CL, Grau JM, C. R. Vera CR. Influence of
- 1172 the Axial Dispersion on the Performance of Tubular Reactors during the Noncatalytic Supercritical
- 1173 Transesterification of Triacylglycerols. *Energy & Fuels* 2006;20:2642-2647.
- 1174 [131] Zheng M, Skelton RL, Mackley MR. Biodiesel reaction screening using oscillatory flow meso
- 1175 reactors. *Process Saf Environ Prot* 2007;85:365-371.
- 1176 [132] Assmann G, Blasey G, Gutsche B, Lutz J, Rigal J, Armengaud R, Cormary B. Continuous
- 1177 process for producing lower alkyl esters. Patent WO9105034. 1991.
- 1178 [133] Lu P, Yuan Z, Li L, Wang Z, Luo W, Biodiesel from different oil using fixed-bed and plug flow
- 1179 reactors. *Renewable Energy* 2010;35:283-7.
- 1180 [134] Santacesaria E, Di Serio M, Tesser R, Casale L, Verde D, Turco R, Bertola A. Use of a
- 1181 Corrugated Plates Heat Exchanger Reactor for Obtaining Biodiesel with Very High Productivity.
- 1182 *Energy & Fuels* 2009;23:5206-12.

1183 [135] Knothe G, Van Gerpen J, Krahl J. The Biodiesel Handbook. 1st Edition. Champaign,
1184 Illinois:AOCS Press. 2005.

1185 [136] Tseitlin OA, Vishnyakova IV. Flow Patterns for Liquid-Liquid Dispersions in Force Fields of
1186 Various Intensities. *Theor Found Chem Eng* 2007;41:424-9.

1187 [137] Perry RH. Perry's chemical engineers' handbook. Seventh Edition. New York Mc Graw Hill;
1188 1999.

1189 [138] Marchetti JM, Miguel VU, Errazu AF. Techno-economic study of different alternatives for
1190 biodiesel production. *Fuel Process Technol* 2008;89:740-8. doi:10.1016/j.fuproc.2008.01.007

1191 [139] Paligova J, Jorikova L, Cvengros J. Study of FAME Stability. *Energy & Fuels* 2008;22:1991-6.

1192 [140] Ribeiro NM, Pinto AC, Quintella CM, da Rocha GO, Teixeira LSG, Guarieiro LLN, do Carmo
1193 Rangel M, Veloso MCC, Rezende MJC, Serpa da Cruz R, de Oliveira AM, Torres EA, de Andrade
1194 JB. The Role of Additives for Diesel and Diesel Blended (Ethanol or Biodiesel) Fuels: A Review.
1195 *Energy & Fuels* 2007;21:2433-45.

1196 [141] Miyashita K, Takagi T. Study of the oxidative rate and peroxidant activity of free fatty acids.
1197 *JAOCS* 1986;63(10):380-4.

1198 [142] St. Angelo AJ. *Lipid Oxidation in Food*. 1st Edition. Washington, DC:ACS Symposium Series
1199 500. 1992.

1200 [143] Knothe G, Some aspects of biodiesel oxidative stability. *Fuel Process Technol* 2007; 88:669-77.

1201 [144] Azeredo HMC, de Assis J, Faria F, da Silva MAAP, Minimization of peroxide formation rate in
1202 soybean oil by antioxidant combinations. *Food Resour Int* 2004;37:689-94.

1203 [145] Frohlich A, Schober S. The influence of tocopherols on the oxidation stability of methyl esters.
1204 *JAOCS* 2007;84(6):579-85.

1205 [146] Furia TE. *Handbook of Food Additives*. 2nd Edition. Cleveland, OH:CRC Press. 1972.

1206 [147] Mittelbach M, Schober S. The Influence of Antioxidants on the Oxidation Stability of
1207 Biodiesel. *JAOCS* 2003;80:817-23.

1208 [148] Dunn RO, Effect of antioxidants on the oxidative stability of methyl soyate (biodiesel). *Fuel*
1209 *Process Technol* 2005;86:1071-85.

1210 [149] Chen YH, Chen JH, Luo YM, Shang NC, Chang CH, Chang CY, Chiang PC, Shie JL. Property
1211 modification of jatropha oil biodiesel by blending with other biodiesels or adding antioxidants.
1212 *Energy* 2011;36:4415-21.

1213 [150] Jain S, Sharma MP. Stability of biodiesel and its blends: A review. *Renewable Sust Energy Rev*
1214 2010;14:667-78.

1215 [151] Hajek M, Skopal F. Treatment of glycerol phase formed by biodiesel production. *Bioresour*
1216 *Technol* 2010;101:3242-45.

1217 [152] Van Gerpen J, Pruzsko R, Clements D, Shanks B, Knothe G. Building a Successful Biodiesel
1218 Business: Technology Considerations, Developing the Business. Analytical Methodologies. 2nd
1219 Edition. Biodiesel Basics; 2006.

1220 [153] Wright HJ, Segur JB, Clark HV, Coburn SK, Langdon EE, DuPuis RN. A report on ester
1221 interchange. JAOCS 1944;21:145-8.

1222 [154] Feuge RO, Grose T. Modification of vegetable oils. VII. Alkali catalyzed interesterification of
1223 peanut oil with ethanol. JAOCS 1949;26:97-102.

1224 [155] Brown CJ, Hlavacek V, Simo M. Apparatus and method for the removal of water from ethanol.
1225 US Patent 2009216051 (A1)

1226 [156] Simo M, Brown CJ, Hlavacek V, Simulation of pressure swing adsorption in fuel ethanol
1227 production process. Comput Chem Eng 2008;32:1635-49. doi: 10.1016/j.compchemeng.2007.07.011.

1228 [157] Nguyen N, Demirel Y. Retrofit of distillation columns in biodiesel production plants. Energy
1229 2010;35:1625-32.

1230 [158] Kister HZ. Distillation Design. 1st Edition. New York:McGraw Hill Professional; 1992.

1231 [159] Luyben WL. Distillation Design and Control Using Aspen Simulation. 1st Edition. Hoboken,
1232 NJ:Wiley-Interscience. 2006.

1233 [160] Zhou H, Lu H, Liang B. Solubility of Multicomponent Systems in the Biodiesel Production by
1234 Transesterification of *Jatropha curcas* L. Oil with Methanol. J Chem Eng Data 2006;51:1130-5.

1235 [161] Cerce T, Peter S, Weidner E. Biodiesel-Transesterification of Biological Oils with Liquid
1236 Catalysts: Thermodynamic Properties of Oil-Methanol-Amine Mixtures. Ind Eng Chem Res
1237 2005;44:9535-41.

1238 [162] Andreatta AE, Casas LM, Hegel P, Bottini SB, Brignole EA. Phase Equilibria in Ternary
1239 Mixtures of Methyl Oleate, Glycerol and Methanol. Ind Eng Chem Res 2008;47:5157-64. doi:
1240 10.1021/ie0712885.

1241 [163] Negi DS, Sobotka F, Kimmel T, Wozny G, Schomacker R. Liquid-Liquid Phase Equilibrium in
1242 Glycerol-Methanol-Methyl Oleate and Glycerol-Monoolein-Methyl Oleate Ternary Systems. Ind Eng
1243 Chem Res 2006;45:3693-6.

1244 [164] Poling BE, Prausnitz JM, O'Connell JP. The Properties of Gases and Liquids. Fifth Edition.
1245 New York:McGraw-Hill. 2001.

1246 [165] Magnussen T, Rasmussen P, Fredenslund A. UNIFAC Parameter Table for Prediction of
1247 Liquid-Liquid Equilibria. Ind Eng Chem Process Des Dev 1981;20:331-339.
1248 doi:10.1021/i200013a024.

1249 [166] Simonetti N. (I.C.I.C. S.p.a.), Internal report about Fox-petroli plant design in Vasto, Italy.
1250 Ancona, 1991.

- 1251 [167] Zhang Y, Dube MA, McLean DD, Kates M. Biodiesel production from waste cooking oil: 1.
1252 Process design and technological assessment. *Bioresour Technol* 2003;89:1-16.
- 1253 [168] Wei Chiu C, Goff MJ, Suppes GJ. Distribution of methanol and catalysts between biodiesel and
1254 glycerin phases. *AIChE J* 2005;51:1274-78. doi:10.1002/aic.10385.
- 1255 [169] Zhou W, Boocock DGB. Phase Distributions of Alcohol, Glycerol and Catalyst in the
1256 Transesterification of Soybean Oil. *JAACS* 2006;83:1047-52.
- 1257 [170] Haas MJ, McAloon AJ, Yee WC, Foglia TA. A process model to estimate biodiesel production
1258 costs. *Bioresour Technol* 2006;97:671-8.
- 1259 [171] Di Nicola G, Moglie M, Santori G. Analisi del processo industriale di produzione del biodiesel.
1260 *LA TERMOTECNICA* 2009;May:50-7.
- 1261 [172] Di Nicola G, Moglie M, Pacetti M, Santori G. Bioenergy II: Modeling and Multiobjective
1262 Optimization of Different Biodiesel Production Processes. *Int J Chem React Eng* 2010;8:A16.
1263 Available at: <http://www.bepress.com/ijcre/vol8/A16>