1 Chapter 24: Economic Assessment for Biodiesel Production

- 2 Authors
- 3 *Jorge M. Marchetti (jorge.mario.marchetti@nmbu.no)
- 4 Mangesh R. Avhad (avhad.mangesh@ymail.com)

5 Affiliation: Department of Mathematical Sciences and Technology, Norwegian University of Life

- 6 Sciences, Drøbakveien 31, Ås 1432, Norway.
- 7 Abstract

8 Biodiesel production as well as consumption in the European nations are augmenting, taking into 9 account the uncertainties connected to fossil fuel reserves and the related natural effects of their use. This biofuel can be generated from numerous oil-rich feedstocks and by using different 10 11 processing technologies. Therefore, the techno-economic assessment for biodiesel production 12 becomes of high relevance to make critical decisions under uncertainties that are essential for the successful implementation of the process on an industrial scale. The economic aspects of using 13 different triglycerides and non-triglycerides based lipid biomass as well as the processing 14 technologies for biodiesel production are thoroughly discussed and compared in this chapter. 15

17 24.1 Introduction

18 Energy is a basic requirement for human existence; and the demand for the same has been consistently gaining because of the increasing human population. According to the International 19 Energy Outlook 2016 set by the U.S. Energy Information Administration, the total world energy 20 21 consumption will grow by 48 % between 2012 and 2040. The energy consumption for the transportation sector increases at an annual rate of 1.4 %, tallying for 49 % growth from 2012 to 22 2040. Transportation energy demand growth occurs almost entirely in regions outside of the 23 Organization for Economic Cooperation and Development (OECD). The fastest growth in the 24 energy consumption per capita in the transportation sector occurs in China and India; however, 25 26 the total transportation energy use per capita remains lower than in the OCED regions. In 2012, 27 the OCED and non-OCED national accounted for 55 % and 45 % of the world's total transportation energy consumption, respectively. In 2020, the OECD and non-OECD shares of 28 29 world transportation energy use are projected to be equal. In the non-OECD regions, where 80% 30 of the world's population resides, transportation energy demand nearly doubles, with an average annual increase of 2.5 % (International Energy Outlook 2016). Among the different energy 31 32 resources, fossil fuels continue to supply most of world's energy; liquid fuels, natural gas, and coal account for 78 % of total world energy consumption. The use of fossil fuel resources for the 33 energy production has several hazardous impacts on the ecosystem, such as large greenhouse gas 34 emissions, acid rain, and global warming. Furthermore, a consistent fear of dwindling reserves of 35 crude oil and oscillating fuel prices have made todays necessity to find an alternative resources of 36 energy which are sustainable, renewable, environmentally friendly, economically reasonable, and 37 easily available (Avhad and Marchetti 2015). As part of the global response to the climate change, 38 policies in several nations around the world have been introduced. The policies are formed to 39

safeguard the sustainable use of renewable energy. The European Union (EU) has been taking the 40 41 initiative in establishing the renewable and sustainable energy prominence. The EU Renewable Energy Directive 2009/28/EC (RED) set a target of increasing the share of renewable energy use 42 43 in the EU from 8.5 % in 2005 to 20 % by 2020 with the motive to promote cleaner transport, to 44 limit the greenhouse gas emissions, and to stimulate innovation and the technological development. In addition to the overall target for renewables, all member states have to reach a 45 46 target of 10 % share of renewable energy for transport (EU Directive 2009/28/EC 2009). The 47 directive implemented in Norway, a country which is not a member of the EU, but part of the 48 European Economic Area (EEA), sets a goal of increasing the share of renewable energy from 49 60.1 % in 2005 to 67.5 % by 2020 (Rosenberg, Lind, and Espegren 2013). Lund and Mathiesen 50 (Lund and Mathiesen 2009) reported a study focused on the energy system analysis of Denmark. It was concluded that 50 % and 100 % renewable energy supply in Denmark by the year 2030 and 51 2050, respectively, from the domestic resources (biomass and combinations of wind, wave, and 52 solar power) is physically possible. However, the challenges for the design of 100 % renewable 53 energy systems in Denmark included the integration of high share of intermittent resources in the 54 energy system, the involvement of the transportation sector in the strategies, and the balance 55 between large consumption of biomass and large amounts of electricity for direct use, or for 56 production of synthetic fuels (Lund and Mathiesen 2009). The above-mentioned strict targets for 57 58 the utilization of renewable energy in transport has boosted the use of biofuels. The synthesis of 59 transportation fuel from biomass is expected to minimize the entire dependency on the utilization of petroleum-derived fuel (Huber, Iborra, and Corma 2006). The "Roadmap for Biomass 60 61 Technologies", set by the U.S. Department of Energy, has predicted that by 2030, 20% of transportation fuel would be produced from biomass (U.S. Department of Energy 2002). 62

Among different biofuels, biodiesel has been gaining substantial relevance as a potential 63 64 alternative or additive to current petroleum-derived diesel not only because this oxygenated fuel can be synthesized from oil-rich biomass but also for a reason that it offers minor environmental 65 66 toxicity and is biodegradable in nature (Avhad and Marchetti 2016). According to the American 67 Society for Testing and Materials (ASTM), biodiesel is defined as mono-alkyl esters derived from 68 lipid feedstocks, such as vegetable oils and animal fats. The combustion of biodiesel offers net 69 carbon dioxide emissions reduction of 78 % (based on lifecycle analysis), 48 % less carbon 70 monoxide, 47 % less particulate matters, and 67 % less hydrocarbons, when compared with 71 petroleum-based diesel (Poddar et al. 2016, Tsoutsos et al. 2016). Both biodiesel production and 72 consumption have augmented considerably in the past decade in the European market; possibly, 73 due to the previous mentioned benefits. The prime advantage of producing and utilizing biodiesel 74 involves the reduction of foreign oil imports. The European biodiesel market is one of the largest in the world, accounting for approximately 80 % of the total biofuel production in the EU 75 76 (Tsoutsos et al. 2016). The breakdown of total EU biofuel consumption, in energy content, in year 2014 for transport by biofuel type is shown in Figure 24.1. The share of biofuel types consumed 77 in several EU countries in 2014 for transport is shown in Figure 24.2. The major biodiesel 78 79 producers in Europe include Neste (Finland), Total, Avril (France), Marseglia Group, Eni (Italy), Petrotec, ADM Biodiesel, Verbio AG (Germany), Infinita (Spain), amongst others. The biodiesel 80 81 consumption in the EU transport was registered to increase by 7.8 % in the year 2014, when 82 compared to that of in 2013 (EurObserv'ER 2015). A graphical representation showing a comparison of biodiesel consumption in the EU countries between the year 2013 and 2014 is 83 84 presented in Figure 24.3. According to the Spanish Institute for Diversification and Saving of 85 Energy (IDAE), the biodiesel consumption in Spain raised from 825,026 tons in 2013 to 903,544

tons in 2014. Few southern European countries import high proportion of biodiesel from other 86 87 nations, such as Indonesia and Argentina. This is predicted due to low oil prices and economical crisis. However, the consumption of biofuel in Spain has started to accelerate as the country's 88 89 economic situation is recovering with the associated increase in road fuel consumption. The 90 statistics presented by the Department of Energy and Climate Change (DECC) suggested that the volume of biodiesel consumed in United Kingdom in 2014 was 1.24 times of that in 2013. While, 91 92 German biodiesel consumption increased slightly in 2014 than the previous year (EurObserv'ER 93 2015).

94 The available literature suggested that biodiesel presents high combustion efficiency, high cetane number, minimal sulfur content, low particulate matters, high flashpoint, and improved 95 lubrication (Avhad and Marchetti 2015). However, the final fuel properties are heavily dependent 96 on the fatty acid composition of the lipid feedstock. On other side, the type of lipid feedstock 97 98 utilized for biodiesel production has a significant influence on the cost of this biofuel since it has 99 been reported that the price of raw material accounts for 60-80 % of the total production cost of 100 biodiesel (Helwani et al. 2013, Avhad and Marchetti 2015, Zheng et al. 2013). Consequently, a 101 wide range of edible, non-edible, and waste lipid feedstocks have been tested for biodiesel production. The food-grade oils, such as rapeseed oil, sunflower oil, soybean oil, and palm oil are 102 utilized in a large-scale for biodiesel production in several countries, like the United States of 103 America, Argentina, Brazil, European nations, Malaysia, and Indonesia (Da Porto, Decorti, and 104 105 Tubaro 2012, Zheng et al. 2012). However, their application for biodiesel production resulted in the rise of food prices, deforestation, land use change, agriculture of monoculture plants, and 106 biodiversity threatening concerns in some developing nations around the world. The sustainable 107 biodiesel production could be possible by the generation of lipid feedstock from the perennial 108

plants grown on degraded farmland. Since the recent few years, consistent scientific efforts are 109 110 underway in finding a cost-effective and abundantly available non-edible oil-rich biomass for biodiesel production (Karmakar, Karmakar, and Mukherjee 2010, Balat 2011). As a next 111 112 generation lipid feedstock, *jatropha* oil, karanja oil, mahua oil, linseed oil, amongst others have 113 been employed for biodiesel production (Sánchez et al. 2015, Atabani 2013). India and Brazil have driven their attention towards the utilization of *jatropha*, castor bean, and karanja oil as a 114 115 feedstock for biodiesel production (Rincón, Jaramillo, and Cardona 2014). Jojoba oil, which 116 profoundly differs from other seed oils because of the absence of glycerol molecule in its chemical 117 structure, is another non-edible lipid biomass that was rarely utilized but is gaining high relevance these days for the synthesis of value-added jojobyl alcohols and biodiesel (Sánchez et al. 2015, 118 119 Avhad et al. 2016). The application of non-edible biomass for large-scale biodiesel production 120 might be advantageous because the agriculture of such plants could be both profitable and troublefree. These plants grows strong in soil even of marginal fertility, requires less water, needs less 121 122 maintenance, survive under hot regional weather, and have a long life span (Avhad et al. 2016, Al-Widyan and Al-Muhtaseb 2010, Al-Hamamre and Rawajfeh 2013). Moreover, algal lipids are 123 also considered as a promising alternative feedstock for biodiesel production. The available 124 125 reports suggests that algae are capable of producing 250 times the oil quantity per acre as soybean, and up to 31 times higher oil than palm (Hossain and Salleh 2008). Microalgae are described to 126 127 have higher oil content, when compared with macroalgae. The lipid content in microalgae can 128 exceed 70 % of the dry cell mass depending on certain conditions, such as light intensity, organic carbon and nitrogen sources, temperature, pH, salinity, and dissolved oxygen level. While, 129 130 microalgae can be cultivated using an open raceway, a photobioreactor, and a fermenter technology (Metting 1996, Sawangkeaw and Ngamprasertsith 2013). Despite the high lipid 131

productivity of microalgae, its usage on an industrial scale for biodiesel production faces serious 132 133 challenges, such as its high cost, and the need for sustainable outdoor cultivation microalgal strain and effective lipid extraction technology (Halim, Danquah, and Webley 2012). In a standpoint of 134 135 finding an additional low-cost feedstock, the capability of used cooking oil and waste animal fats 136 for their transformation to biodiesel was also investigated (Lam, Lee, and Mohamed 2010). The available reports indicated that the exploitation of used cooking oil for biodiesel production 137 138 resulted in 83-85 % carbon savings (Tsoutsos et al. 2016). The production of biodiesel from tallow 139 oil was stated to have high cetane number, good stability, and low price (Rincón, Jaramillo, and 140 Cardona 2014). The Finnish oil company, Neste, claimed to be world's largest biofuel producer from wastes and residues (frying oil, animal fats, fish oil, etc.) stating to produce 1.3 million tons 141 142 of biodiesel in the year 2014 (EurObserv'ER 2015). The utilization of used cooking oils for biodiesel production was reported to be advantageous because: (i) it is a residue, and therefore, 143 its generation requires no energy inputs, and (ii) its utilization for biodiesel production would 144 145 eliminate the disposal concerns (Talebian-Kiakalaieh, Amin, and Mazaheri 2013, Nair et al. 2012). However, the occurrence of oxidation, hydrolysis, and the polymerization reactions while 146 the frying process of vegetable oil results in the generation of impurities, free fatty acids (FFAs), 147 and water components in oils (Banerjee and Chakraborty 2009). This in return would demand the 148 additional treatment and purification steps for the used cooking oils before its application for 149 150 biodiesel production. Secondly, the shortage of used cooking oils in European countries may require its import, which in consequence, might increase the cost of the raw material for biodiesel 151 production (Tsoutsos et al. 2016). 152

Among different methodologies available for the transformation of lipid feedstock to biodiesel,the alcoholysis process has been extensively applied. The alcoholysis process is also known as

transesterification of triacylglycerols (TAGs) and esterification of FFAs. The stoichiometry of the 155 156 transesterification reaction between the TAGs based plant oils and alcohol requires a mole of TAGs and three moles of alcohol to produce three moles of biodiesel and a mole of glycerol. This 157 158 process consists of three sequential reversible reactions, where in a mole of biodiesel is released 159 in each step, and monoaclyglycerols and diacylglycerols are the intermediate products (Avhad and Marchetti 2016). The general reaction and a sequence for the transesterification process is 160 161 shown in Figure 24.4 and 24.5, respectively. In a stoichiometry of the alcoholysis reaction 162 between the non-TAGs based oil (jojoba oil) and alcohol, one molecule of oil reacts with a 163 molecule of alcohol to synthesize one molecule of biodiesel and a molecule of jojobyl alcohols (Avhad et al. 2016). The general schematic representation for the transesterification of non-TAGs 164 165 based plant oils (jojoba oil) can be seen in Figure 24.6. The esterification reaction between FFAs 166 and alcohol involves the formation of one mole of biodiesel and water after the reaction between one molecule of FFAs and a molecule of alcohol. A general esterification reaction is shown in 167 168 Figure 24.7. The alcoholysis reactions are the reversible process, and therefore an excess of alcohol are required to shift the reaction equilibrium towards the formation of products. The types 169 of alcohol that could be utilized for the alcoholysis reactions include short chain, long chain, and 170 cyclic alcohols; however, low molecular weight alcohols (methanol and ethanol) are widely used 171 for biodiesel production (Avhad and Marchetti 2015). Methanol is used because of its high 172 reactivity, polarity, easy phase-separation, and low price (Sánchez, et al. 2015), while, the 173 application of ethanol is advantageous from an ecological standpoint because it can be derived 174 from the reasonable cost and abundantly available lignocellulosic biomass and due to its low 175 176 toxicity (Limayem and Ricke 2012, Marchetti, Miguel, and Errazu 2007a).

The catalytic material is applied to the alcoholysis process to stimulate the reaction rate, modify 178 179 the reaction kinetics, reduce the process time, and increase the selectivity of the desired products. The available literature suggested that several studies have been focused on finding an appropriate 180 181 catalytic material for biodiesel production (Avhad and Marchetti 2015, 2016, Chouhan and Sarma 182 2011, Lee et al. 2014). The ideal catalyst for biodiesel production should not only present superior activity and selectivity towards the desired products but also be easily available, simple to prepare, 183 184 less expensive, and reusable. However, the selection of the type of catalytic material for biodiesel 185 production is heavily dependent on the nature of the feedstock. The base catalyzed-alcoholysis 186 reactions are faster than the acid ones; consequently, the synthesis of biodiesel is completed using relatively low reaction time. The most commonly utilized base catalysts for the industrial-scale 187 188 biodiesel production include sodium hydroxide, and potassium hydroxide. However, the applicability of homogeneous base catalysts is restricted to high quality lipid feedstocks 189 containing negligible amount of FFAs (less than 0.5 %) and moisture (Lukić et al. 2013, Jasen 190 191 and Marchetti 2012). The existence of high amount of FFAs in the lipid feedstocks directs the saponification reaction, in the presence of soluble base catalyst, leading towards the formation of 192 undesired soap. The soap formation minimizes the biodiesel yield because of the generation of 193 esters-glycerol emulsion. Whereas, moisture in the reaction mixture promotes the hydrolysis of 194 the esters; thus, reducing the biodiesel yield (Avhad and Marchetti 2015). The operation of the 195 acid-catalyzed alcoholysis reaction could eliminate the above-mentioned technical hurdles 196 197 because the performance of acid catalysts is not affected by the presence of high amount of FFAs and moisture in the lipid feedstock. Furthermore, the appliance of acid catalysts could be 198 199 advantageous because it can assist both transesterification and esterification reactions. The acid catalysts, therefore, can possibly be utilized for biodiesel production from waste oils, animal fats, 200

and the industrial by-products. The frequently used acid catalysts are sulfuric acid, and 201 202 hydrochloric acid. However, the acid-catalyzed alcoholysis reactions are extremely slow and could take around a day for the complete transformation of oil to biodiesel (Marchetti and Errazu 203 204 2008a, Soriano Jr, Venditti, and Argyropoulos 2009). The need of high reaction conditions have 205 been a major reason of concern for its upscaling on an industrial platform. Additionally, the appliance of non-green catalyst also creates worries related to human safety and corrosion of the 206 207 equipment (Lee et al. 2014). The possibility of catalyst reutilization could be ensured with the 208 replacement of homogeneous catalysts with the heterogeneous catalytic system. The 209 heterogenization of the alcoholysis process is possible if the catalyst is neither consumed nor dissolved in the reaction mixture. The heterogeneous catalytic materials can then be easily 210 211 separated from the post-reaction mixture through the physical methods, such as the filtration and 212 the centrifugation. The utilization of potential heterogeneous catalyst hold the capability of minimizing the separation and purification stages for biodiesel production, and decreasing the 213 214 post-reaction wastewater and other contaminant content. The process intensification enabled because of the heterogenization biodiesel production could not only allow recycling of the catalyst 215 but also increase the yield and the purity of biodiesel as well glycerol. The challenges associated 216 with the utilization of heterogeneous catalysis for biodiesel production includes: (i) limited 217 catalytic active sites in comparison to homogeneous catalysts, (ii) sometimes need of severe 218 219 reaction conditions, (iii) generally, tri-phasic reaction systemic (liquid/liquid/solid) leading 220 towards the occurrence of mass transfer resistance, (iv) complicated and time-consuming catalysts synthesis procedure, (v) poisoning of the catalyst because of the surrounding atmosphere, (vi) 221 222 need of characterization of solid materials to determine physical as well as chemical properties (Avhad and Marchetti 2016). A wide range of solid catalysts have been tested for biodiesel 223

production, such as metal oxides, mixed metal oxides, hydrotalcites, heteropoly acids, ionexchange resins, silica-, zirconia-based catalysts, amongst others. Among several options, calcium oxide catalysts has been gaining scientific as well as industrial relevance because of its low solubility in methanol, high basicity, high activity, low cost, and easy synthesis from natural resources (Avhad and Marchetti 2016).

229 The process parameters also play an important role in deciding the final cost of biodiesel. The process parameters, such as catalyst amount, alcohol-to-feedstock molar ratio, reaction 230 temperature, reaction time, and stirring intensity are most frequently studied for the alcoholysis 231 232 reactions performed in a conventional method to achieve maximum biodiesel yield using lowest possible energy input (Marchetti, Miguel, and Errazu 2007b). The change in reaction method has 233 234 been also carried out to reduce the processing cost and achieve maximum biodiesel yield using milder reaction conditions. For instance, the alcoholysis reaction performed under the 235 236 supercritical conditions possesses some advantages over the conventional process. The alcoholysis reactions performed under supercritical conditions results in the rapid transformation 237 of the lipid feedstock to biodiesel without even using a catalyst. The supercritical reaction 238 239 conditions enables a mutual solubility between the oil and the alcohol phase; thus, eliminating the concerns related to mass transfer. Furthermore, the non-requirement of catalysts for biodiesel 240 production helps straightforward post-reaction separation and purification stages. This reaction 241 method being unaffected by the presence of high content of FFAs and moisture in the reaction 242 mixture, the low-quality lipid feedstocks, such as waste cooking oils and animal fats can be 243 transformed to biodiesel using the supercritical reaction conditions. However, severe reaction 244 parameters (high temperatures and high pressures) and large alcohol-to-oil molar ratio are 245 required to perform the alcoholysis reaction under the supercritical conditions. The use of large 246

amount of alcohol would require supplementary energy for the pre-heating stages, and the 247 248 recycling process. The utilization of high reaction temperatures would not only increase the capital cost of biodiesel but also deteriorate the quality of biofuel. The use of high temperatures 249 250 initiate the thermal cracking phenomenon; thus, reducing the biodiesel yield (Olivares-Carrillo 251 and Quesada-Medina 2011). Additionally, high temperatures and pressure conditions demand both an expensive reactor and a safety management. The research studies focused on the reduction 252 253 of high reaction temperatures include the addition of liquid and gaseous co-solvents (Trentin et 254 al. 2011, Tsai, Lin, and Lee 2013), and the catalyst (Santana, Maçaira, and Larrayoz 2012, Shin 255 et al. 2013).

256 24.2 Economical aspect of biodiesel production technologies

As mentioned before, biodiesel can be produced by different technological approaches (Avhad 257 and Marchetti 2015, Marchetti, Miguel, and Errazu 2007b). However, this only shows the 258 259 potentiality of the technology to produce the desire fuel but has no comment on the liability of the 260 process to be actually commercialized. From a perspective to be able to establish a 261 commercialized process, the different economical aspects of different technologies will be 262 presented here and compared. There are several factors to be considered when comparing processes, especially when they are different technologies involved. In order to have the more 263 264 reliable comparison, several general conditions were establish such as the production rate, cost of the raw material, price of biodiesel, prices of the byproducts (this is based on their quality and 265 relevance), number of process equipment (this is related to the number of reactors used), among 266 267 others. We do know that these assumptions are arbitrarily, but are made by us to our processes in 268 order to compare each of them with other. Comparison with our technologies under other economical scenarios is not recommendable due to the different considered assumptions. 269

Several researchers have been working on the economic evaluation of different technological 270 271 solutions for biodiesel production from different sources. Among all of them, it can be found that the work reported by Nelson et al. (Nelson 1994) studied the production process of 100,000 ton 272 273 per year of biodiesel from beef tallow and methanol, in the presence of an alkali catalyst. In this 274 work, the comparison of the process and its evaluation was conducted using the total capital cost involved in the process. A similar work was carried out by Graboski and McCormick (Graboski 275 276 and McCormick 1998) who studied a 38.8 million liter per year process. The authors studied and 277 compared different raw materials and the process economic evaluation was done considering the 278 credits of biodiesel, the credits of glycerol, and the cost of equipment as the selection criteria. A 279 comparison among acid and base catalyst using waste cooking oil was done by (Zhang et al. 280 2003). Their process description was quite in detail, and the use of HYSYS was presented for a 281 complete process flow diagram. The difference with the previous works is that the plant capacity being only 8000 ton per year in this case. Based on the commercialized software, Hass et al. (Haas 282 283 et al. 2006) presented an economic analysis over an alkali catalyst for biodiesel production using soybean oil with a capacity of 37 million liter per year. The reported study presented a sensitivity 284 analysis over the price of oil and biodiesel. Similar investigations were conducted by Marchetti 285 et al. (Marchetti, Miguel, and Errazu 2008, Marchetti and Errazu 2008b), but using an acid oil as 286 a feedstock and with a plant capacity of 36000 ton/year. In these works four technologies were 287 288 compared: (i) pre-acid esterification followed by acid-catalyzed transesterification, (ii) acid catalytic process, (iii) heterogeneous solid ion-exchange resin catalyzed process, and (iv) 289 supercritical process. In those reported studies, the direct and indirect cost for each technology as 290 291 well as additional expenses involved in the process were taken into consideration. The performed comparison was based on the net present value (NPV) with an objective of investigating the 292

profitability of the technology and possibility for further study. The heterogeneous catalyzed 293 294 process appeared as a promising approach, while, the supercritical showed a negative NPV with 295 the period of the work. West et al. (West, Posarac, and Ellis 2008) studied a similar raw material 296 (acid oil) but compared the after tax return rate and for only 8000 ton per year plant capacity. van 297 Kasteren and Nisworo (van Kasteren and Nisworo 2007) compared the supercritical technology, 298 achieving different result, when compared with those reported in some cases by Marchetti et al. 299 (Marchetti and Errazu 2008b, Marchetti, Miguel, and Errazu 2008). This is because the main 300 difference was based on the scale of the process as well as in the quality of the raw material; while 301 Marchetti et al. (Marchetti and Errazu 2008b, Marchetti, Miguel, and Errazu 2008) used acid oil, van Kasteren and Niswoore (van Kasteren and Nisworo 2007) carried out their work with waste 302 303 cooking oil, where the amount of fatty acid was higher.

Over the last few years, novel technological evaluation of different process have been considered. 304 305 Even more life cycle analysis has been carried out and presented in order to have a broader picture 306 of the biodiesel production scenario. Moreover, different sources of raw material such as algae or second-generation raw materials and non-edible oil have been tested and evaluated. Among other 307 308 works, Seo et al. (Seo, Han, and Han 2014) have performed an evaluation of the production of algae oil while using algae residues as a food source for algae biomass. This oil-based biomass 309 could then be transformed into biodiesel via different technologies and procedures. Rincón et al. 310 (Rincón, Jaramillo, and Cardona 2014) have also studied the use of algae for biodiesel, in which 311 the authors have compared different feedstocks such as edible oil (palm oil) and non-edible oils 312 313 (*jatropha* oil, tallow oil, microalgae, and waste cooking oil). In their scenario, different reaction configurations for different raw materials was presented based on their need for purity and pre-314 and post-processing steps. Economic analysis was carried out in order to compare the future 315

prospective of each alternative. Based on their assumption and pricing, it was found out that the 316 317 total cost for producing biodiesel was the lowest when a basic catalyst is employed and *jatropha* oil having low content of free fatty acids is used as feedstock, follow by a process in which waste 318 319 cooking oil with an acid catalyst is used for biodiesel production. As it was expected, the use of 320 refined oil gives the highest cost for production due to the high price of the raw material. Researchers have also studied the use of waste cooking oil for the alcoholysis process, in the 321 322 presence of enzymatic catalyst. Lisboa et al. (Lisboa et al. 2014) presented a comparison of the 323 enzyme-catalyzed transesterification in the presence of supercritical carbon dioxide. To achieve 324 the latest mention scenario pressure is modify from atmospheric to 25 MPa. The authors presented four study cases when different down streaming purification stages were required and unrequired 325 326 to achieve the desire purity in the final product. Based on their direct and indirect costs, as well 327 as the investment and production cost, the total biodiesel costs per liter were compared. The best alternative is related to the scenario when the applied pressure and temperature for the separation 328 329 step are the lowest. Glisic and Orlovic (Glisic and Orlović 2014) also studied the effect of elevated pressure and temperature on the process for biodiesel production. In their work, the authors 330 present a good comparison of the effect of these two variables over the economics of a 331 supercritical plant and conventional plant. After their comparison, it was concluded that the 332 breaking even price of biodiesel with the supercritical technology was better than with the 333 334 conventional technology. However, the operating cost of the process especially those related to energy consumption and cost due to the high temperatures and pressure was not reported. The 335 item for utilities was considered, but there was no specification on what percentage of those 336 337 utilities is energy-based consumption. Moreover, with the purity of raw material having 5% FFAs 338 in within, the conventional technology with base catalyst is not recommended be for this quality

raw material (Freedman, Pryde, and Mounts 1984, Canakci, and van Gerpen 1999, Zheng et al. 339 340 2006, Marchetti 2010). Due to that the purification of the products gets more complicated or a pre-treatment step is required, making this technology more equipment dependent, and therefore, 341 342 with a higher investment. Another approach is followed by El-Galad et al. (El-Galad, El-Khatib, 343 and Zaher 2015), wherein the authors have performed an economic evaluation for the esterification of fatty acids into biodiesel. For their purpose, a technology to treat 2000 kg per 344 345 hour of oleic acid in the presence of methanol and sulfuric acid was proposed. The capital cost 346 were estimated based on market price in Egypt, making these values narrow to a one-market 347 perspectives well as market dependent. The economic evaluation has shown that the technology is suitable for an economically attractive biodiesel process. However, it is not clear how from the 348 349 soap and oil residues the authors purify this waste to produce 2000 kg per hour of oleic acid to be 350 used in their technology.

351 As it could be seen from the previous selected worked, some of them use refined oil while other used non-edible oil, cooking oils, acid oil, or waste oils. All these feedstocks not only have 352 different physico-chemical properties but also market and social value. As mentioned, refined oil 353 354 are edible oil, and therefore must not be consumed for fuel production. Therefore, more and more work are relating in the use of waste and non-edible oil for biodiesel production. Even more, the 355 general price for refine oil are so high that normally a process will not be economically attractive 356 for investment if there are no governmental incentives. However, price of the major variables 357 involve in the process, equipment, as well as market dependent such as the price of the oil and the 358 selling price of the biodiesel have a major role in the economic analysis of each process. Due to 359 that the prediction of price is not a simple, and the sensitivity studies are a crucial element in order 360 to understand the effect of different aspect and its consequences in the long run of a plant. Due to 361

that, some result from different sensitivities studies and their effects over the biodiesel production 362 process will be compared and presented in the following write-up. As mentioned before, one of 363 the major variable is the quality of the oil, and associate to it its cost. It is worth mentioning that 364 not all the oils can grow all over the world. O'Brien (O'Brien 2008) presented a list of the different 365 366 types of oil and where they are being produce; this list can be seen in Table 24.1. The authors have also included a column with the amount of oil that each seed can produce in each case. It is, 367 however, important to notice that the price range for one particular oil could vary considerable 368 369 from country to country.

Table 24.1: Major producer for several vegetable oils [Reprinted with permission from O'Brien et al. 2008]

Seed	Amount of oil (%)	Productive areas		
Canola	40-45	Canada, China, India, France, Austria, United Kingdom, Germany, Poland, Denmark, Check Republic		
Corn	3.1-5.7	USA, Mexico, Russia, Belgium, France, Italy, Germany, Spain, United Kingdom.		
Cotton	18-20	China, Russia, USA, India, Pakistan, Brazil, Egypt, Turkey.		
Peanut	45-50	China, India, Nigeria, USA, Senegal, South Africa, Argentina		
Crocus	30-35	China, USA, Spain, Portugal		
Soybean	18-20	USA, Brazil, Argentina, China, India, Paraguay, Bolivia		
Sunflower	35-45	Russia, Argentina, Austria, France, Italia, Germany, Spain, United Kingdom.		
Coconut	65-68	Filipinas, Indonesia, India, México Sri Lanka, Thailand, Malaysia, Vietnam, Mozambique, New Guinea, Republic of Côte d'Ivoire		
Olive	15-35	Spain, Italy, Italia, Greece, Tunes, Turkey, Morocco, Portugal, Syria, Algeria, Yugoslavia, Egypt, Israel, Libya, Jordan, Lebanon, Argentina, Chile, Mexico, Peru, USA, Australia.		
Palm	45-50	Malaysia, Indonesia, China, Filipinas, Pakistan, México, Bangladesh, Colombia, Nigeria, Republic of Côte d'Ivoire		
Palm kernel	44-53	Malaysia, Indonesia, China, Filipinas, Pakistan, México, Bangladesh, Colombia, Nigeria, Republic of Côte d'Ivoire		

In order to make a sensitivity study of the major variables involved, it is important to know the 372 373 process that is being considered because this has a great impact on the economic analysis. Marchetti (Marchetti 2013, Sánchez et al. 2015, Marchetti 2016) presented two sensitivities 374 375 studies for three technologies to produce biodiesel, i) conventional alkali technology, and ii) 376 supercritical technology. The two processes can be seen in Figure 24.8 and Figure 24.9. As it can be seen, the flow diagram is similar in both cases, allow us to make a better comparison. Sanchez 377 378 et al. (Sánchez et al. 2015) presented a similar work with a process based on the transformation 379 of jojoba oil into jojobyl alcohols and biodiesel. In this case, the main product is not the fuel, but 380 the biochemical. This non-edible oil based process is also presented for comparison in order to present the difference when the process technology presented are different. This flow diagram can 381 382 be seen in Figure 24.10. The major difference between these two technologies is based on the fact 383 that their production capacity are different as well as that the conventional technology is not suitable for high impurity based raw material. Figure 24.11 shows a comparison of the effect of 384 385 the oil price for both technologies. It can be seen that in Figure 24.11(a) the oil price affects linearly the internal return rate (IRR), this is because the supercritical technology not only 386 transesterified the oil but also can carry on the esterification reaction. In Figure 24.11(b), it can 387 be seen a very unusual tendency; this flatting tendency on the IRR values has a starting point for 388 an oil price of \$ 400 US per ton. Within these values, the amount of FFAs increase to a point 389 390 where the saponification reaction is taking place in a considerable speed and a large amount of 391 soap are being produce and therefore the biodiesel yield does not increase.

Both analysis presented in Figure 24.11 was done for the glycerol-based oil. However, a similar work was done by Sanchez et al. (Sánchez et al. 2015) where a biodiesel process was studied using a non-triglycerides based oil i.e. jojoba oil as raw material. In this case, as presented in Figure 24.12, a similar effect as obtained where the lowest the price of the raw material the higher the IRR it goes. In this case, it was considered that when the price goes down almost half price the IRR value increases almost 40 times.

The other major variable that could affect considerable the profitability of the process is the selling 398 399 price of the major product of the process. While in the cases studied by Marchetti (Marchetti 2013, 2011) the major product was biodiesel, in the work done by Sànchez et al. (Sánchez et al. 2015) 400 the main product was jojoba alcohols being produced. The latest have been considered of high 401 price due its difficulty of being produce with todays' technological possibilities. As it can be seen 402 from Figure 24.13(a), the effect of biodiesel price on the conventional process makes the 403 404 production technology more economically attractive, with a payback time of no more than 5 years 405 when the process has the lowest price for biodiesel. Within that worst scenario, the IRR is close to 10 %. In the case of the supercritical technology, as presented in Figure 24.13(b), the price for 406 407 biodiesel was slightly different, but the major tendency is that for the lowest price for the fuel, they payback time is over 16 years, making it less interest for investors. In Figure 24.13(c), it can 408 be seen a similar effect when the price of the jojobyl alcohols is varied. In this case, the lowest 409 410 cost estimated for selling the alcohols will produce a negative effect on the economics of the process given a payback time of 22 year, with a very low IRR. It was found in that work that the 411 price of \$ 513 US per kilograms of alcohols is the cutting price where the process became 412 economically attractive. 413

Other researchers have also done similar sensitivity studies over those or even over other variables involved in the process. In the case of the supercritical technology, the energy inputs could become crucial for the technology to be profitable, while in the case of a conventional technology the use of cleaning water and waste treatment of the effluents will have a relevant role. Even more, the price of glycerol is also a credit that could be beneficial for the process; however, its purity is
a strong conditional. Based on the purity and the amount being produce worldwide, this chemical
might become a new, promising, and cheap raw material for new chemicals (Marchetti 2012).
Based on the previous mentioned technical and economic aspects a comparison table is presented
in the Table 24.2.

Variable	Basic	Enzyme	Supercritical	Monolithic	Resin	Acid
		•				
Temp. [°C]	60-70	30-50	200-350	50-180	60-180	50-80
Products from FFA	Soaps	Esters	Esters	Esters	Esters	Esters
Effect of Water*	¥	↓			— ↓	
Yield to ester	Normal	High	High	Normal	Good	Normal
Purification of glycerol	Difficult	Simple	Simple	Simple	Simple	Difficult
Reaction time+	1-2 h	8-70 h	4-10 min	6 h	variable	4-70 h
Ester purification	Difficult	Simple	Simple	Simple	Simple	Difficult
Cost	Cheapest	Expensive	Expensive	Medium	Medium	Cheaper
Amount of equipment	High	Low	Low	Low	Low	High

423 Table 24.2. Comparison of different technologies for Biodiesel [Reprinted with permission from Marchetti 2012].

* in this case the down arrow mean that water is a draw back while the line means that the is not effect and the system will be able to treat a raw material with some amount of water. For the Enzyme case, a down arrow has been supply, in this case is important to say that is believe that some water is require for enzyme activation; however, a lot of water will produce a deactivation of the catalyst. In the case of the resin, it could be seen a down arrow as well as a line, this is because water has different effect over different solid catalyst. In the case of the monolithic scenario, a line has been selected because leaching it is not causing by water per se but for a non-stability of the catalyst.

+the reaction time set in this table is what it is most likely, however, it is important to point out that other times for
the same technology could be found in the open literature.

As it can be seen from Table 24.2, the technical variables varies from technology to technology.

434 Some of them are more different from the others with temperature and reaction time, however the

435 combination of all of them plus the economic aspects are the key elements to select the best option.

436 The base-catalyzed technology is cheap and relative fast, but there is a lot of down streaming

equipment and purification required making the process less attractive. In the case of acid-437 438 catalyzed technology, the reaction time is considerable bigger; however, this technology is capable of dealing with more impurities in the raw material. In the schedule, there are other lower 439 440 limits like the supercritical technology that could take care of the process in less than 5 minutes 441 but with a high-energy demand, and therefore, energy cost involved. As mentioned before this technology is also capable of treating waste raw material and produce a high quality by product 442 443 as well. In the case of the enzymatic technology, the process is simple as well as robust, and the 444 enzyme will work under mild conditions that result in inexpensive operating cost in energy 445 aspects. However, the price of the enzymes makes this technology less attractive for industrial scale. 446

As it has been presented from the technical and economic aspects, there are several points that needs to be considered in all the areas in order to establish a grading of priority for the technology to be used. This priority order is based on manmade decisions that are taken due to the market and social-political-economical situations of the location where the production plant will be built. Due to these external factors, is not possible to make a priority ranking that will be suitable for all possible scenarios at any possible location and a case-to-case study and evaluation is recommended.

454 **References**

- Al-Hamamre, Z., and K. M. Rawajfeh. 2013. Investigating the Energy Value of Jojoba as an Alternative Renewable Energy Source. *International Journal of Green Energy* 12 (4):398-404.
- Al-Widyan, M. I., and M. A. Al-Muhtaseb. 2010. Experimental investigation of jojoba as a
 renewable energy source. *Energy Conversion and Management* 51 (8):1702-1707.
- 459 Atabani, A. E., A. S. Silitonga, H. C. Ong, T. M. I. Mahlia, H. H. Masjuki, I. A. Badruddin, and
- 460 H. Fayaz. 2013. Non-edible vegetable oils: A critical evaluation of oil extraction, fatty acid
- 461 compositions, biodiesel production, characteristics, engine performance and emissions
- 462 production. *Renewable and Sustainable Energy Reviews* 18:211-245.
- Avhad, M. R., and J. M. Marchetti. 2015. A review on recent advancement in catalytic materials
 for biodiesel production. *Renewable and Sustainable Energy Reviews* 50:696-718.
- Avhad, M. R., and J. M. Marchetti. 2016. Innovation in solid heterogeneous catalysis for the
 generation of economically viable and ecofriendly biodiesel: A review. *Catalysis Reviews*:1-52.
- Avhad, M. R., M. Sánchez, E. Peña, A. Bouaid, M. Martínez, J. Aracil, and J. M. Marchetti. 2016.
 Renewable production of value-added jojobyl alcohols and biodiesel using a naturally-derived
 heterogeneous green catalyst. *Fuel* 179:332-338.
- Balat, M. 2011. Potential alternatives to edible oils for biodiesel production A review of current
 work. *Energy Conversion and Management* 52 (2):1479-1492.
- Banerjee, A., and R. Chakraborty. 2009. Parametric sensitivity in transesterification of waste
 cooking oil for biodiesel production—A review. *Resources, Conservation and Recycling* 53
 (9):490-497.
- 475 Canakci, J., and J. van Gerpen. 1999. Biodiesel production via acid catalysis. *Transactions of the*476 *American Society of Agricultural Engineers* 42: 1203-1210.
- Chouhan, A. P. S., and A. K. Sarma. 2011. Modern heterogeneous catalysts for biodiesel
 production: A comprehensive review. *Renewable and Sustainable Energy Reviews* 15 (9):43784399.
- 480 Da Porto, C., D. Decorti, and F. Tubaro. 2012. Fatty acid composition and oxidation stability of
 481 hemp (*Cannabis sativa L.*) seed oil extracted by supercritical carbon dioxide. *Industrial Crops*482 *and Products* 36 (1):401-404.
- 483 El-Galad, M. I., K. M. El-Khatib, and F. A. Zaher. 2015. Economic feasibility study of biodiesel
- 484 production by direct esterification of fatty acids from the oil and soap industrial sector. *Egyptian*
- 485 *Journal of Petroleum* 24 (4):455-460.

- EU Directive 2009/28/EC. 2009. Directive of the European Parliament and of the Council on theproduction of the use of energy from renewable resources.
- 488 EurObserv'ER. 2015. Biofuels Barometer. <u>http://www.eurobserv-er.org/biofuels-barometer-</u>
 489 <u>2015/</u> (accessed September 22, 2016).
- 490 Freedman, B., E. H. Pryde, and T. L. Mounts. 1984. Variables affecting the yields of fatty esters
- 491 from transesterified vegetable oils. Journal of the American Oil Chemists Society 61 (10):1638-
- 492 1643.
- Glisic, S. B., and A. M. Orlović. 2014. Review of biodiesel synthesis from waste oil under
 elevated pressure and temperature: Phase equilibrium, reaction kinetics, process design and
 techno-economic study. *Renewable and Sustainable Energy Reviews* 31:708-725.
- Graboski, M. S., and R. L. McCormick. 1998. Combustion of fat and vegetable oil derived fuels
 in diesel engines. *Progress in Energy and Combustion Science* 24 (2):125-164.
- Haas, M. J., A. J. McAloon, W. C. Yee, and T. A. Foglia. 2006. A process model to estimate
 biodiesel production costs. *Bioresource Technology* 97 (4):671-678.
- Halim, R., M. K. Danquah, and P. A. Webley. 2012. Extraction of oil from microalgae for
 biodiesel production: A review. *Biotechnology Advances* 30:709-732.
- Helwani, Z., N. Aziz, M. Z. A. Bakar, H. Mukhtar, J. Kim, and M. R. Othman. 2013. Conversion
- 503 of Jatropha curcas oil into biodiesel using re-crystallized hydrotalcite. Energy Conversion and
- 504 *Management* 73:128-134.
- Hossain, A. B. M. S, and A. Salleh. 2008. Biodiesel fuel production from algae as renewable
 energy. *American Journal of Biochemistry and Biotechnology* 4(3):250-254.
- Huber, G. W., S. Iborra, and A. Corma. 2006. Synthesis of Transportation Fuels from Biomass:
 Chemistry, Catalysts, and Engineering. *Chemical Reviews* 106 (9):4044-4098.
- Jasen, P., and J.M. Marchetti. 2012. Kinetic study of the esterification of free fatty acid and
- 510 ethanol in the presence of triglycerides using solid resins as catalyst. *International Journal of*
- 511 Low-Carbon Technologies 7 (4):325-330.
- Karmakar, A., S. Karmakar, and S. Mukherjee. 2010. Properties of various plants and animals
 feedstocks for biodiesel production. *Bioresource Technology* 101 (19):7201-7210.
- Lam, M. K., K. T. Lee, and A. R. Mohamed. 2010. Homogeneous, heterogeneous and enzymatic
- 515 catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A 516 review. Biotechnology Advances 28 (4):500 518
- 516 review. *Biotechnology Advances* 28 (4):500-518.
- 517 Lee, A. F., J. A. Bennett, J. C. Manayil, and K. Wilson. 2014. Heterogeneous catalysis for
- sustainable biodiesel production via esterification and transesterification. Chemical Society
- 519 *Reviews* 43 (22):7887-7916.

- 520 Limayem, A., and S. C. Ricke. 2012. Lignocellulosic biomass for bioethanol production: Current
- 521 perspectives, potential issues and future prospects. *Progress in Energy and Combustion Science*
- **522 38** (4):449-467.
- Lisboa, P., A. R. Rodrigues, J. L. Martín, P. Simões, S. Barreiros, and A. Paiva. 2014. Economic
 analysis of a plant for biodiesel production from waste cooking oil *via* enzymatic
 transesterification using supercritical carbon dioxide. *The Journal of Supercritical Fluids* 85:3140.
- Lukić, I., Ž. Kesić, S. Maksimović, M. Zdujić, H. Liu, J. Krstić, and D. Skala. 2013. Kinetics of
 sunflower and used vegetable oil methanolysis catalyzed by CaO·ZnO. *Fuel* 113:367-378.
- Lund, H., and B. V. Mathiesen. 2009. Energy system analysis of 100% renewable energy
 systems—The case of Denmark in years 2030 and 2050. *Energy* 34 (5):524-531.
- Marchetti J. M. 2010. Biodiesel production technologies. First edition. *New York: Nova Science Publisher, Inc.*
- Marchetti, J. M. 2011. The effect of economic variables over a biodiesel production plant. *Energy Conversion and Management* 52 (10):3227-3233.
- Marchetti, J. M. 2013. Influence of economical variables on a supercritical biodiesel production
 process. *Energy Conversion and Management* 75:658-663.
- Marchetti, J. M. 2016. Heterogeneous esterification of glycerol by using a gold catalyst. *Biomass Conversion and Biorefinery*:1-7.
- Marchetti, J. M., and A. F. Errazu. 2008a. Esterification of free fatty acids using sulfuric acid as
 catalyst in the presence of triglycerides. *Biomass and Bioenergy* 32 (9):892-895.
- Marchetti, J. M., and A. F. Errazu. 2008b. Technoeconomic study of supercritical biodiesel
 production plant. *Energy Conversion and Management* 49 (8):2160-2164.
- Marchetti, J. M., V. U. Miguel, and A. F. Errazu. 2007a. Heterogeneous esterification of oil with
 high amount of free fatty acids. *Fuel* 86 (5–6):906-910.
- Marchetti, J. M., V. U. Miguel, and A. F. Errazu. 2007b. Possible methods for biodiesel
 production. Renewable and Sustainable Energy Reviews 11 (6):1300-1311.
- Marchetti, J. M., V. U. Miguel, and A. F. Errazu. 2008. Techno-economic study of different
 alternatives for biodiesel production. Fuel Processing Technology 89 (8):740-748.
- 549 Marchetti, Jorge M. 2012. A summary of the available technologies for biodiesel production based
- on a comparison of different feedstock's properties. *Process Safety and Environmental Protection*
- **551 90** (3):157-163.

- 552 Metting, F. B. 1996. Biodiversity and application of microalgae. *Journal of Industrial* 553 *Microbiology* 17:477-489.
- Nair, P., B. Singh, S. N. Upadhyay, and Y. C. Sharma. 2012. Synthesis of biodiesel from low FFA
 waste frying oil using calcium oxide derived from Mereterix mereterix as a heterogeneous
 catalyst. *Journal of Cleaner Production* 29–30:82-90.
- 557 Nelson R. G., S. A. Howell, and J. A. Weber. 1994. Potential feedstock supply and costs for
- biodiesel production. In: '94 Proceedings of the Sixth National Bioenergy Conference. Western
- 559 *Regional Biomass Energy Program*, Renovo, NV (United States).
- 560 O'Brien R., W. Farr, P. Wan. 2008. Fats and Oils: Formulating and Processing for Applications.
 561 Third Edition. *CRC Press Taylor and Francis Group*.
- Olivares-Carrillo, P., and J. Quesada-Medina. 2011. Synthesis of biodiesel from soybean oil using
 supercritical methanol in a one-step catalyst-free process in batch reactor. *The Journal of Supercritical Fluids* 58 (3):378-384.
- Poddar, T., A. Jagannath, and A. Almansoori. 2016. Use of reactive distillation in biodiesel
 production: A simulation-based comparison of energy requirements and profitability indicators.
 Applied Energy http://dx.doi.org/10.1016/j.apenergy.2015.12.054.
- Rincón, L. E., J. J. Jaramillo, and C. A. Cardona. 2014. Comparison of feedstocks and
 technologies for biodiesel production: An environmental and techno-economic evaluation. *Renewable Energy* 69:479-487.
- Rosenberg, E., A. Lind, and K. A. Espegren. 2013. The impact of future energy demand on
 renewable energy production Case of Norway. *Energy* 61:419-431.
- Sánchez, M., F. Bergamin, E. Peña, M. Martínez, and J. Aracil. 2015. A comparative study of the
 production of esters from *Jatropha* oil using different short-chain alcohols: Optimization and
 characterization. *Fuel* 143:183-188.
- Sánchez, M., J. M. Marchetti, N. El Boulifi, M. Martínez, and J. Aracil. 2015. Jojoba oil
 biorefinery using a green catalyst. Part I: Simulation of the process. *Biofuels, Bioproducts and Biorefining* 9 (2):129-138.
- Sánchez, M., J. M. Marchetti, N. El Boulifi, J. Aracil, and M. Martínez. 2015. Kinetics of Jojoba
 oil methanolysis using a waste from fish industry as catalyst. *Chemical Engineering Journal*262:640-647.
- Sánchez, M., J. M. Marchetti, N. El Boulifi, M. Martínez, and J. Aracil. 2015. Jojoba oil
 biorefinery using a green catalyst. Part II: Feasibility study and economical assessment. *Biofuels*,
- 584 *Bioproducts and Biorefining* 9 (2):139-146.

- 585 Santana, A., J. Maçaira, and M. A. Larrayoz. 2012. Continuous production of biodiesel from
- vegetable oil using supercritical ethanol/carbon dioxide mixtures. *Fuel Processing Technology*
- 587 96:214-219.
- Sawangkeaw, R., and S. Ngamprasertsith. 2013. A review of lipid-based biomasses as feedstock
 for biofuels production. *Renewable and Sustainable Energy Reviews* 25:97-108.
- Seo, Y., S. Han, and J. Han. 2014. Economic biodiesel production using algal residue as substrate
 of lipid producing yeast Cryptococcus curvatus. *Renewable Energy* 69:473-478.
- Shin, H., J. Ryu, S. Bae, and Y. C. Kim. 2013. Biodiesel production from highly unsaturated
 feedstock via simultaneous transesterification and partial hydrogenation in supercritical methanol. *The Journal of Supercritical Fluids* 82:251-255.
- Soriano Jr, N. U., R. Venditti, and D. S. Argyropoulos. 2009. Biodiesel synthesis *via*homogeneous Lewis acid-catalyzed transesterification. *Fuel* 88 (3):560-565.
- Talebian-Kiakalaieh, A., N. A. S. Amin, and H. Mazaheri. 2013. A review on novel processes of
 biodiesel production from waste cooking oil. *Applied Energy* 104:683-710.
- Trentin, C. M., A. P. Lima, I. P. Alkimim, C. da Silva, F. de Castilhos, M. A. Mazutti, and J. V.
 Oliveira. 2011. Continuous production of soybean biodiesel with compressed ethanol in a
 microtube reactor using carbon dioxide as co-solvent. *Fuel* Processing Technology 92 (5):952958.
- Tsai, Y., H. Lin, and M. Lee. 2013. Biodiesel production with continuous supercritical process:
 Non-catalytic transesterification and esterification with or without carbon dioxide. *Bioresource Technology* 145:362-369.
- Tsoutsos, T. D., S. Tournaki, O. Paraíba, and S. D. Kaminaris. 2016. The Used Cooking Oil-tobiodiesel chain in Europe assessment of best practices and environmental performance. *Renewable and Sustainable Energy Reviews* 54:74-83.
- 609 U.S. Department of Energy. 2002. The Roadmap for Biomass Technologies in the U.S. Biomass610 R&D Technical Advisory Committee. Accession No. ADA 436527.
- U.S. Energy Information Administration. 2016. International Energy Outlook.
 http://www.eia.gov/forecasts/ieo/ (accessed June 27, 2016).
- van Kasteren, J. M. N., and A. P. Nisworo. 2007. A process model to estimate the cost of industrial
- scale biodiesel production from waste cooking oil by supercritical transesterification. *Resources*,
- 615 *Conservation and Recycling* 50 (4):442-458.
- West, A. H., D. Posarac, and N. Ellis. 2008. Assessment of four biodiesel production processes
 using HYSYS.Plant. *Bioresource Technology* 99 (14):6587-6601.

- Kie, W., and L. Zhao. 2013. Production of biodiesel by transesterification of soybean oil using
 calcium supported tin oxides as heterogeneous catalysts. *Energy Conversion and Management*76:55-62.
- Zhang, Y., M. A. Dubé, D. D. McLean, and M. Kates. 2003. Biodiesel production from waste
 cooking oil: 2. Economic assessment and sensitivity analysis. *Bioresource Technology* 90
 (3):229-240.
- Zheng, L., Y. H., W. Li, S. Yang, Q. Li, and Z. Yu. 2013. Exploring the potential of grease from
 yellow mealworm beetle (*Tenebrio molitor*) as a novel biodiesel feedstock. *Applied Energy*
- 626 101:618-621.
- 627 Zheng, L., Q. Li, J. Zhang, and Z. Yu. 2012. Double the biodiesel yield: Rearing black soldier fly
- 628 larvae, *Hermetia illucens*, on solid residual fraction of restaurant waste after grease extraction for
- 629 biodiesel production. *Renewable Energy* 41:75-79.
- Zheng, S., M. Kates, M. A. Dubé, and D. D. McLean. 2006. Acid-catalyzed production of
 biodiesel from waste frying oil. *Biomass and Bioenergy* 30 (3):267-272.

632 **Caption:**

Figure 24.1: Breakdown of total EU biofuel consumption in 2014 for transport by biofuel type[Modified with permission from EuroObserv'ER 2015].

635 Figure 24.2: Share of biofuel types consumed in the EU countries in 2014 for transport. --

636 Biodiesel, -Bioethanol, -Biogas, -Others (Pure used vegetable oil and unspecified biofuel)

637 [Reprinted with permission from EurObserv'ER 2015].

Figure 24.3: Biodiesel consumption for transport in the European Union. ■-2013, ■-2014 [Data source: EurObserv'ER 2015]. *For Denmark, biodiesel and bioethanol data is mixed due to*

640 confidentiality, so the figure contains both bioethanol and biodiesel. EU countries having no or

641 *insignificant consumption of biodiesel are not included in the figure.*

Figure 24.4: General transesterification reaction of TAGs based plant oils.

Figure 24.5: Stepwise transesterification reaction of TAGs based plant oils.

Figure 24.6: Stepwise transesterification reaction of non-TAGs based plant oils.

Figure 24.7: Generation esterification reaction of fatty acids.

Figure 24.8: Flow diagram for the conventional process [Reprinted with permission fromMarchetti 2011].

Figure 24.9: Flow diagram for the supercritical process [Reprinted with permission from Marchetti 2013].

Figure 24.10: Biorefinery process for the production of jojobyl alcohols and biodiesel [Reprintedwith permission from Sánchez et al. 2014].

Figure 24.11(a): Effect of the oil price over the supercritical process [Source Marchetti 2013].

Figure 24.11(b): Effect of the oil price over the conventional process [Source Marchetti 2011].

Figure 24.12: Effect of the oil price over jojoba oil based conventional process [Source Sánchez et al. 2015].

Figure 24.13(a): Effect of the biodiesel price in the process economy of conventional technology[Source Marchetti 2011].

Figure 24.13(b): Effect of the biodiesel price in the process economy of supercritical technology[Source Marchetti 2013].

Figure 24.13(c): Effect of the biodiesel price in the process economy of jojoba based conventional
technology [Source Sánchez et al. 2015].

Table 24.1: Major producer for several vegetable oils [Reprinted with permission from O'Brienet al. 2008]

Table 24.2: Comparison of different technologies for Biodiesel [Reprinted with permission fromMarchetti 2012].



Figure 24.1: Breakdown of total EU biofuel consumption in 2014 for transport by biofuel type [Modified with permission from EuroObserv'ER 2015].



Figure 24.2: Share of biofuel types consumed in the EU countries in 2014 for transport. ■-Biodiesel, ■-Bioethanol, ■-Biogas, ■-Others (Pure used vegetable oil and unspecified biofuel) [Reprinted with permission from EurObserv'ER 2015].



Figure 24.3: Biodiesel consumption for transport in the European Union. ■-2013, ■-2014 [Data source: EurObserv'ER 2015].

For Denmark, biodiesel and bioethanol data is mixed due to confidentiality, so the figure contains both bioethanol and biodiesel. EU countries having no or insignificant consumption of biodiesel are not included in the figure.



Triacylglycerols Alcohol Fatty acid alkyl esters

Figure 24.4: General transesterification reaction of TAGs based plant oils.



Figure 24.5: Stepwise transesterification reaction of TAGs based plant oils.



Figure 24.6: Stepwise transesterification reaction of non-TAGs based plant oils.



Figure 24.7: Generation esterification reaction of fatty acids.



Figure 24.8: Flow diagram for the conventional process [Reprinted with permission from Marchetti 2011].



Figure 24.9: Flow diagram for the supercritical process [Reprinted with permission from Marchetti 2013].



Figure 24.10: Biorefinery process for the production of jojobyl alcohols and biodiesel [Reprinted with permission from Sánchez et al. 2014].



Figure 24.11(a): Effect of the oil price over the supercritical process [Source: Marchetti 2013].



Figure 24.11(b): Effect of the oil price over the conventional process [Marchetti 2011].



Figure 24.12: Effect of the oil price over jojoba oil based conventional process [Sánchez et al. 2015].



Figure 24.13(a): Effect of the biodiesel price in the process economy of conventional technology [Marchetti 2011].



Figure 24.13(b): Effect of the biodiesel price in the process economy of supercritical technology [Marchetti 2013].



Figure 24.13(c): Effect of the biodiesel price in the process economy of jojoba based conventional technology [Sánchez et al. 2015].